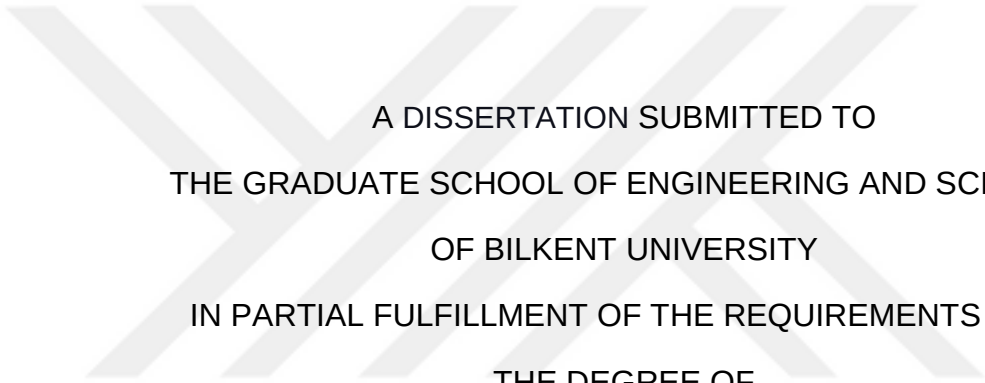


DESIGN OF MULTIFUNCTIONAL PRUSSIAN BLUE ANALOGUES FOR SOLAR DRIVEN WATER OXIDATION



A DISSERTATION SUBMITTED TO
THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
OF BILKENT UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
MATERIALS SCIENCE AND NANOTECHNOLOGY

By

Türkan Gamze Ulusoy Ghobadi

July 2021

DESIGN OF MULTIFUNCTIONAL PRUSSIAN BLUE ANALOGUES FOR
SOLAR DRIVEN WATER OXIDATION

By Turkan Gamze Ulusoy Ghobadi

July, 2021

We certify that we have read this dissertation and that in our opinion it is fully adequate,
in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

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ABSTRACT

DESIGN OF MULTIFUNCTIONAL PRUSSIAN BLUE ANALOGUES FOR SOLAR DRIVEN WATER OXIDATION

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Ph.D. in Materials Science and Nanotechnology

Advisor: Ferdi Karadaş,

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July 2021

The development of earth-abundant, robust, and low-cost photoanodes for water oxidation is one of the most critical steps in 'artificial leaf'. A promising approach in this field is to build dye-sensitized photoanodes by coupling a molecular photosensitizer (PS) with a water oxidation catalyst (WOC) on a proper semiconductor (SC) for efficient charge separation. All dye-sensitized photoanodes reported in the literature consist of either a ruthenium photosensitizer, a ruthenium water oxidation catalyst, or both. We aim to overcome this critical challenge by developing a new family of organic- or iron-based donor-acceptor chromophores incorporated in a Prussian blue (PB) structure, which are coated on proper semiconductors.

Our studies within this context could be divided into three sections:

(i) PB based photocatalytic water oxidation: In this work-package, an entirely precious metal-free chromophore-donor-water oxidation catalyst triad system is developed. The synthesis involves the coordination of a porphyrin derivative to a bridging $\text{Fe}(\text{CN})_5$ group, which is then reacted with cobalt ions to prepare a covalently linked chromophore-Prussian blue analogue ($\text{CoFe}(\text{CN})_5$ -Ligand) assembly. Light-driven water oxidation studies in the presence of an electron scavenger indicate that the triad is active and maintains a steady activity for at least 3 hours. Transient absorption experiments and computational studies reveal that the $\text{Fe}(\text{CN})_5$ group is more than just a linker.

It takes part in electron donation and co-operates with porphyrin in the charge separation process.

(ii) PB based photoelectrochemical water oxidation: Here, we move one step forward and design a ruthenium-free water oxidation photoanode by the sensitization of titanium dioxide (TiO_2) nanowires with a PB-organic chromophore structure. A phenazine-based organic group, Janus Green B (JG), is chosen as the chromophore since it has a broad absorption response in the visible and near-infrared ranges. The resulting multifunctional PB modified TiO_2 electrode demonstrates a low-cost and easy-to-construct photoanode, which exhibits a remarkable excited-state lifetime in the order of nanoseconds and an extended light absorption capacity of up to 500 nm. Moreover, the photoanode retains its structural integrity and photoelectrochemical activity for at least 2 hours. Despite all the above-mentioned improvements, the performance of the cell, $[\text{CoFe-JG}]/\text{TiO}_2$, is relatively poor due to improper band energy alignment between the chromophore and the semiconductor. In a follow-up study, we tune the chromophore and the semiconductor to achieve a proper band energy alignment, and thus, to improve the performance. Another phenazine-based molecule, Safranin O (SF), is utilized as the organic photosensitizer. Moreover, a visible-light absorbing semiconductor, WO_3 , is used to utilize the solar spectrum completely. $[\text{CoFe-SF}]/\text{WO}_3$ exhibits a record photocurrent density of 1.3 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$, demonstrating that proper modification of components in PB based dye-sensitized photoanodes could pave the way for the development of high-performance water splitting cells.

(iii) Iron chromophore based photoelectrochemical water oxidation: In this section, the iron site that has been previously utilized as a relay is promoted to an iron chromophore. Five cyanide ligands are coordinated to the iron site to destabilize the metal-centered states. At the same time, an electron-deficient cationic pyridinium group occupies the remaining coordination sphere of the octahedral iron site to facilitate the metal-to-ligand charge transfer (MLCT) process. This iron complex is coated initially on TiO_2 nanowires and then reacted with cobalt ions to produce a CoFe PB ($\text{CoFe}(\text{CN})_5\text{-L}$) layer on the electrode surface. In this photoanode, the excited-state lifetime of the iron chromophore exceeds 1 ns, which demonstrates the first example of an iron-sensitized water oxidation cell in the literature.

Overall, this thesis presents an alternative perspective to realize high performance, low-cost, stable, and robust dye-sensitized water oxidation systems. The impact of the acquired knowledge in this thesis is also discussed to define the current status, challenges, and future of PB based water oxidation systems.



Keywords: pentacyanoiron, cobalt-iron prussian blue, dye-sensitized photoelectrochemical cell, cyanide chemistry, artificial photosynthesis, iron chromophore, precious metal free dye and catalyst, water oxidation

ÖZET

GÜNEŞ IŞIĞINI KULLANARAK SUYU YÜKSELTGEYEBİLEN ÇOK İŞLEVİLİ PRUSYA MAVİSİ TÜREVLERİNİN TASARIMI

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Tez Eşdanışmanı: Ekmel Özbay
Temmuz 2021

Suyun yükseltgenmesi için doğada bol bulunan elementlerden ve maliyeti düşük bileşenlerden oluşan kararlı fotoanotların geliştirilmesi ‘yapay yaprak’ teknolojisinin en kritik adımlarından birisidir. Bu alanda umut verici bir yaklaşım, etkili yük ayrımı için uygun bir yarı iletken (SC) üzerinde, bir moleküler kromoforu (PS) suyu yükseltgeyen bir katalizör (WOC) ile birleştirerek boya duyarlı fotoanotlar geliştirmektir. Literatürde bilinen tüm ‘boya duyarlı fotoanotlar’da kromoforun veya suyu yükseltgeyen katalizörün yapısında veya her ikisinde rutenyum atomu bulunmaktadır. Uygun yarı iletkenler üzerine kaplanmış, Prusya mavisi (PB) yapısının içine entegre edilmiş organik veya demir temelli donör-akseptör kromofor ailesi geliştirerek bu kritik basamağı aşmayı hedefliyoruz.

Bu bağlamda çalışmalarımızı üç bölüme ayırabiliriz:

(i) PB temelli sistemlerle suyun fotokatalitik yükseltgenmesi: Bu çalışma paketinde, soy metal içermeyen kromofor-donör-suyu yükseltgen katalizör üçlü sistemi geliştirilmiştir. Sentez, bir porfirin türevinin pentasiyanodemir(II) kompleksine ($\text{Fe}(\text{CN})_5$) koordinasyonunu ve oluşan bu kompleksin kobalt iyonları ile tepkimeye sokularak kovalent olarak bağlı bir kromofor–PB analog ($\text{CoFe}(\text{CN})_5\text{–Ligand}$) yapısını oluşturmalarını içermektedir. Bir elektron çöpçüsü varlığında güneş ışığını kullanarak suyu yükseltgeyen çalışmalar, bu üçlü sistemin aktif olduğunu ve en az 3 saat boyunca aktivitesini koruduğunu

göstermektedir. Geçici absorpsiyon deneyleri ve teorik hesaplamalar, $\text{Fe}(\text{CN})_5$ grubunun bir bağlayıcıdan çok daha fazlası olduğunu ortaya koymaktadır. Bu grup, elektron donörü olarak ve yük ayırma işleminde porfirin ile birlikte çalışmaktadır.

(ii) PB temelli yapılarla suyun fotoelektrokatalitik yükseltgenmesi: Bu çalışma paketinde bir adım ileri giderek titanyum dioksit (TiO_2) nanotellerini PB-organik kromofor ile duyarlı hale getirerek rutenyum içermeyen suyu yükseltgeyen bir fotoanot tasarladık. Kromofor olarak; görünür ve yakın kızılötesi bölgesinde geniş soğurma bandına ve fenazin bazlı organik bir gruba sahip olduğu için Janus yeşili B (JG) seçilmiştir. Elde edilen çok işlevli PB ile modifiye edilmiş TiO_2 elektrodu; nanosaniyeler mertebesinde oldukça yüksek uyarılmış durum ömrü ve 500 nm'ye kadar uzatılmış bir ışık soğurma kapasitesini sergilemekte olup düşük maliyetli ve yapımı kolay bir fotoanot olduğunu da gösterir. Ayrıca, fotoanot yapısal bütünlüğünü ve fotoelektrokimyasal aktivitesini en az 2 saat süren fotoelektrokatalitik deney boyunca korumaktadır. Yukarıda bahsedilen tüm gelişmelere rağmen, hücrenin performansı, $[\text{CoFe-JG}]/\text{TiO}_2$, kromofor ve yarı iletken arasındaki uygun olmayan bant enerjisi seviyeleri nedeniyle nispeten zayıftır. Bunu takip eden bir çalışmada, uygun bir bant enerji seviyesi elde etmek ve böylece performansı iyileştirmek için kromoforu ve yarı iletkeni optimize etmeyi hedefledik. Bir başka fenazin bazlı molekül, Safranin O (SF), organik kromofor olarak kullanıldı. Ayrıca, güneş spektrumundan tamamen faydalanabilmek için görünür ışığı soğuran bir yarı iletken olan WO_3 kullanıldı. $[\text{CoFe-SF}]/\text{WO}_3$, 1,23 V_{RHE} ' de 1,3 mA/cm^2 ' lik rekor bir fotoakım yoğunluğu sergileyerek PB temelli boyaya duyarlı fotoanotlardaki bileşenlerin uygun şekilde modifiye edilmesinin, yüksek performansa sahip suyu ayrıştırma hücrelerinin geliştirilmesinin yolunu açabileceğini göstermektedir.

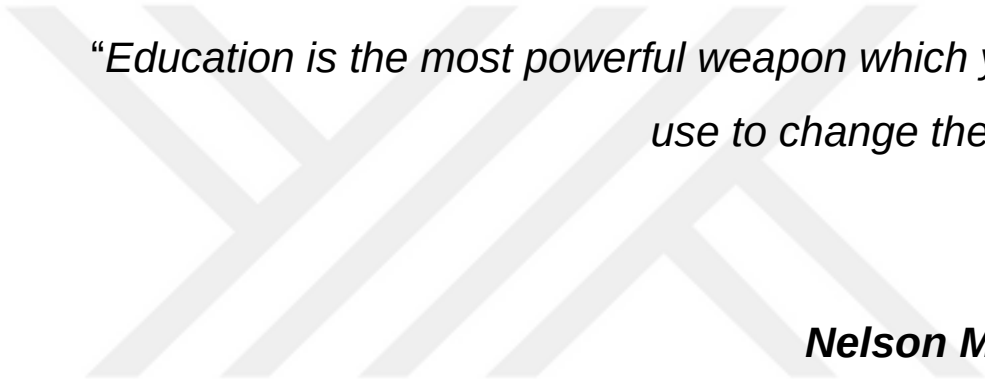
(iii) Demir kromofor temelli yapılarla fotoelektrokimyasal suyun yükseltgenmesi: Bu bölümde, daha önce bağlayıcı olarak kullanılan demir atomlarının demir kromofor olarak kullanılması hedeflenmiştir. Metal merkezli uyarılmış seviyeleri destabilize etmek için demir merkezine beş siyanür ligandı koordine edilir. Aynı zamanda, elektron eksikliği olan bir katyonik piridinyum grubu, metal-ligand yük transferi (MLCT) işlemini kolaylaştırmak amacıyla oktahedral demir bölgesinin kalan koordinasyon alanını doldurmak için kullanılır. Bu demir kompleksi, önce TiO_2 nanotelleri üzerine kaplanır, sonra elektrot yüzeyinde bir CoFe PB ($\text{CoFe}(\text{CN})_5\text{-L}$) tabakası oluşturmak için kobalt iyonları ile reaksiyona sokulur. Bu fotoanotta, demir kromoforun uyarılmış

durum ömrü 1 ns' yi aşmaktadır, bu da literatürde demirle duyarlı hale getirilmiş bir su yükseltgeme hücresinin ilk örneğini göstermektedir.

Genel olarak, bu tez, yüksek performanslı, düşük maliyetli, kararlı ve sağlam, boyaya duyarlı suyu yükseltgeme sistemlerini gerçekleştirmek için alternatif bir bakış açısı sunmaktadır. Bu tezde edinilen bilgiler PB-temelli yapıların suyu yükseltgemedeki kullanılan sistemlerinin mevcut durumunu, zorluklarını ve geleceğini tartışmak için de uygun bir zemin oluşturmaktadır.



Anahtar kelimeler: Pentasiyanür, kobalt-demir prusya mavisi, boya duyarlı fotoelektrokimyasal hücre, siyanür kimyası, yapay fotosentez, demir kromofor, soy-metal içermeyen boya ve katalizör, suyun yükseltgenmesi



*“Education is the most powerful weapon which you can
use to change the world.”*

Nelson Mandela

Acknowledgement

In the very first place I would like to give my thanks to the Bilkent University for offering me the precious opportunity to pursue a higher degree of education. I have met many people in contributing to my scientific and social life throughout my PhD thesis work. I want to thank all of them with all my heart. It has been a long journey for me, all made my PhD experience what it has been.

The present study was established in the Laboratory of Inorganic Chemistry (Department of Chemistry) and Institute of Materials Science and Nanotechnology (UNAM) at the Bilkent University under the supervision of Assist. Prof. Ferdi Karadas and Prof. Ekmel Ozbay.

A big and heartfelt thank goes to my supervisors, Prof. Ekmel Ozbay and Assist. Prof. Ferdi Karadas for giving me the opportunity to conduct a thesis in their research group. I highly appreciate the great amount of freedom I was granted during my works and the dedicated encouragement for new projects. I am really thankful for the discussions and extra supports that you gave me during past four years. It was a pleasure for me to work with you. I look forward to more fruitful years ahead and produce high quality scientific works.

I gratefully acknowledge financial support by Bilkent University Nanotechnology Research Center (NANOTAM).

I would like to thank our collaborators Engin Durgun, H. Gul Yaglioglu, Emre Erdem, and Eda Yilmaz for their support and the valuable collaboration we had. Thanks for the collaboration and/or the help that you provided along the way, so I owe the special thanks to your group members that my way crossed.

I would like to sincerely thank my jury members Yavuz Dede, Burak Ulgut, Emrah Ozensoy, and José Ramón Galán-Mascarós for their valuable comments and suggestions.

I would like to thank all of my present and past lab mates (who are too many to name but all friendly) and the technical staff in the department.

I also acknowledge Mete Duman (UNAM- National Nanotechnology Research Center) for his invaluable assistance with cover designs and frontispieces. I am

also grateful to K. Nur Ozvural for her art work in our published article. She was more than a collaborator for me with her modesty.

It is a great pleasure to acknowledge all the professors, instructors, engineers, and graduate students at UNAM Materials Science and Nanotechnology Department. From being UNAM family, all I have received not only warm atmosphere for making me always feel at home, but great experience too.

I would also like to thank colleagues and friends who I started with and I got some help from and for being good company throughout my PhD study. I spent so many years here, it is hard to say thank you for all of you. Especially with my Persian friends, I will never forget the great times that we had together.

Words can never be enough to express my sincerest thank to my family. I owe special thanks to my mom whose unwaivering support and incredible patience has kept me going. My sister Ipek, you deserve special thanks for your sistership, understanding, and sacrifice; thanks for your presence. I would like to thank my aunt for support in every aspect of my life. I would like to express my special gratitude to my parents-in-law for always supporting us and our decisions. You are always close to us despite the long distance we have, thank you. Thanks for all your great help with the caring my baby, Poyraz. You have all made my PhD experience what it has been.

Poyraz, thanks for your presence in our life. Thanks for being the best distraction I could ever wish for in the research years☺ and making every struggle worthwhile. Being a mom, is the toughest job in the world during a critical period of academic life.

Finally, there are no words to express my gratitude to my husband, Amir, for his constant courage, strength and perseverance to rise to this challenge. He is truly a source of inspiration. Thanks for always pushing me to become better, as a scientist and a person and continually reminded me of my potential. Glad to have you.

CONTENTS

CHAPTER 1. GENERAL INTRODUCTION.....	1
1.1. Thesis Goals.....	1
1.2. Thesis Outline.....	2
CHAPTER 2. SCIENTIFIC BACKGROUND.....	4
2.1. Preface.....	4
2.2. Water Splitting	5
2.2.1. Photoelectrochemical Water Splitting (PEC-WS)	5
2.2.1.1. <i>Electron Transfer Dynamics</i>	6
2.2.1.2. <i>Common Materials</i>	9
2.3. Prussian Blue Analogues (PBAs) for Water Oxidation.....	14
2.3.1. Basics.....	14
2.3.2. CoFe PBAs for Water Oxidation	15
2.3.3. PB Based Electrocatalytic Water Oxidation	18
2.3.4. PB Based Photocatalytic Water Oxidation.....	22
2.3.5. PB Based Photoelectrochemical Water Oxidation.....	24
CHAPTER 3. CHARACTERIZATION METHODS AND INSTRUMENTATION.....	29
3.1. Material Characterizations	29
3.2. Optical Characterizations.....	30
3.2.1. Steady-state Measurements	31
3.2.1.1. <i>Absorption spectroscopy</i>	31
3.2.1.2. <i>Photoluminescence spectroscopy</i>	32
3.2.2. Time-resolved Transient Methods	33
3.2.2.1. <i>Transient open circuit photovoltage decay measurement</i>	33
3.2.2.2. <i>Time resolved photoluminescence decay spectroscopy</i>	34
3.2.2.3. <i>Ultrafast femtosecond transient absorption spectroscopy</i>	34
3.3. Photoelectrochemical Measurements	35
3.3.1. Current-Voltage Measurement.....	37
3.3.2. Chronoamperometry	39
3.3.3. Electrochemical Impedance Spectroscopy	39
3.3.3.1. <i>Mott-Schottky Analysis</i>	39
3.3.4. Band Energy Diagrams.....	40
3.3.5. Efficiency Definitions	40
3.3.5.1. <i>The applied bias photon-to-current efficiency</i>	41
3.3.5.2. <i>Charge transfer efficiency: Hole (O₂) scavenger measurement</i>	41
3.3.5.3. <i>Faradaic efficiency: Oxygen evolution activity measurement</i>	42
3.3.5.4. <i>Incident photon to-current conversion efficiency</i>	43

3.4.	Electronic Structure Calculations.....	44
CHAPTER 4. PORPHYRIN INCORPORATED PB ASSEMBLY FOR PHOTOCATALYTIC WATER OXIDATION 47		
4.1.	Preface.....	47
4.2.	Introduction	48
4.3.	Experimental Procedures	49
4.3.1.	Materials.....	49
4.3.2.	Sample Preparation	49
4.4.	Results and Discussions.....	51
4.4.1.	Electrochemical Measurements.....	57
4.4.2.	Oxygen Evolution Activity Measurements	58
4.4.3.	Long-term Stability Analysis.....	60
4.4.4.	Quantum Chemical Calculations.....	62
4.4.5.	Steady State Absorption, Fluorescence and Femtosecond Transient Absorption Measurements	64
4.5.	Summary	70
CHAPTER 5. JANUS GREEN INCORPORATED PB FOR DYE-SENSITIZED WATER OXIDATION.....71		
5.1.	Preface.....	72
5.2.	Introduction	72
5.3.	Experimental Procedures	74
5.3.1.	Materials.....	74
5.3.2.	Sample Preparation	74
5.4.	Results and Discussions.....	77
5.4.1.	Design of the Photoelectrode.....	77
5.4.2.	Materials Characterization	79
5.4.3.	Photoelectrochemical Measurements.....	83
5.4.4.	Steady-State Absorption and Photoluminescence Measurements	86
5.4.5.	Incident Photon-to-current Conversion Efficiency.....	87
5.4.6.	Long-term Stability Analysis.....	88
5.4.7.	Oxygen Evolution Activity Measurements	89
5.4.8.	Femtosecond Transient Absorption Measurements	92
5.4.9.	Quantum Chemical Calculations and Mechanism	98
5.5.	Summary	100
CHAPTER 6. SAFRANIN INCORPORATED PB FOR DYE-SENSITIZED WATER OXIDATION.....102		
6.1.	Preface.....	102
6.2.	Introduction	103

6.3.	Experimental Procedures	104
6.3.1.	Materials.....	104
6.3.2.	Sample Preparation	105
6.4.	Results and Discussions.....	106
6.4.1.	Design of the photoelectrode	106
6.4.2.	Materials Characterization	108
6.4.3.	Photoelectrochemical Measurements.....	112
6.4.4.	Long-term Stability Analysis.....	116
6.4.5.	Oxygen Evolution Activity Measurements	121
6.4.6.	Steady-State and Transient Optical Measurements	122
6.4.7.	Computational Calculations and Mechanism.....	123
6.4.8.	Femtosecond Transient Absorption Measurements	124
6.5.	Summary	126
CHAPTER 7. IRON CHROMOPHORE INCORPORATED PB FOR DYE-SENSITIZED WATER OXIDATION		128
7.1.	Preface.....	129
7.2.	Introduction	129
7.3.	Experimental Procedures	131
7.3.1.	Materials.....	131
7.3.2.	Sample Preparation	131
7.4.	Results and Discussions.....	133
7.4.1.	Design of the photoelectrode	133
7.4.2.	Materials Characterization	134
7.4.3.	Photoelectrochemical Measurements.....	138
7.4.4.	Long-term Stability Analysis.....	139
7.4.5.	Oxygen Evolution Activity Measurements	140
7.4.6.	Steady-State Absorption Measurements	141
7.4.7.	Femtosecond Transient Absorption Measurements	144
7.4.8.	Computational Calculations and Mechanism.....	146
7.5.	Summary	148
CHAPTER 8. CONCLUSIONS.....		150
8.1.	Summary and Outlook	150
8.2.	Key Challenges and Recommendations	153
8.3.	Contributions.....	155
CHAPTER 9. BIBLIOGRAPHY.....		159

LIST OF FIGURES

Figure 2.1 Schematic of (a) a basic PEC-WS cell including an n-type SC photoanode and a metal cathode immersed in an electrolyte connected by an external electric wire, and (b) particulate form of the photocatalyst where the water splitting is achieved without external bias. (Reprinted with permission from Wiley Ref. [1]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 7

Figure 2.2 Comparison of different SCs, in contact with the aqueous electrolyte at pH = 0, according to their band gaps (in the units of nm) and band positions with respect to HER and OER half reactions. An additional overpotential of 200 and 400 mV was considered to define the optimum region. Since these overpotentials are merely estimated values (much less overpotentials are available in the literature)[47], [48] the highlighted region does not retain exact borders. (Reprinted with permission from Wiley Ref. [1]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 11

Figure 2.3 The steps involved in the operation of a DS-PEC. In this cell, the sensitizer photoactive material is a visible absorptive dye layer. (Reprinted with permission from Wiley Ref. [1]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 13

Figure 2.4 Synthesis and general structure of $A_nCo_x[Fe'(CN)_6].nH_2O$ ($A = H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}$): Here, nitrogen coordinated Co sites and carbon-coordinated Fe ones are bridged by cyanide (CN) groups to form an open framework. Catalytically active cobalt sites, which are surrounded by at least one water molecule, are highlighted with orange spheres. Alkali metal ion that resides in the tetrahedral positions of the cubic structure is omitted for clarity. Adapted (or “Reproduced in part”) with permission from John Wiley and Sons. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 15

Figure 2.5 Characteristic features of each constituent in a CoFe PBA. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 18

Figure 2.6 Schematic of (a) a general EC water oxidation setup including a WOC deposited on FTO coated glass, reference electrode (not shown in the

figure), and a metal cathode that is immersed in an electrolyte and connected by an external electric wire, and (b) the responsible PCET mechanism for EC water oxidation with CoFe PBAs. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) .. 21

Figure 2.7 Schematic of (a) a general PC water oxidation setup including a PS, WOC, and ES in an electrolyte, and (b) the responsible PCET mechanism for PC water oxidation with CoFe PBAs. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 23

Figure 2.8 Schematic of (a) a general PEC water oxidation setup, including a photoanode that consists of a SC and WOC immersed in an electrolyte, and (b) the responsible PCET mechanism for PEC water oxidation with CoFe PBAs. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 25

Figure 2.9 Schematic illustration of band energy levels for different CoFe PBA incorporated SC photoelectrodes under neutral conditions, pH 7: (a) PB/TiO₂, (b) PB/Fe₂O₃, (c) PB/Fe₂TiO₅, and (d) PB/BiVO₄. The ideal band alignment requires a condition in which ($\Delta_{\text{HOMO-VB}}$) should be smaller than ($\Delta_{\text{CB-HOMO}}$). Since both PB/Fe₂TiO₅ and PB/BiVO₄ do meet this condition, they have less probability of photoexcited carriers' recombination (shown as a red cross) at the HOMO level of PB compared to the other two systems. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 27

Figure 2.10 Schematic of (a) a general DS-PEC water oxidation setup, including a photoanode that consists of a dye-sensitized SC and WOC immersed in an electrolyte, and (b) the responsible PCET mechanism for PEC water oxidation with CoFe PBAs. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) .. 28

Figure 3.1 Experimental setup employed in this thesis studies. The PEC water oxidation measurements performed in an electrolyte solution under 1 sun illumination in a three-electrode cell (Dr. Bob's Cell) configuration. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 36

Figure 4.1 General synthetic scheme and molecular structures of [TPyP], [Fe-TPyP], and [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 52

Figure 4.2 ATR-FTIR spectra for [Fe-NH₃], [TPyP], [Fe-TPyP] and [CoFe-TPyP]. The broad peak at 3300 cm⁻¹ belongs to OH stretch while the one at around 1620 cm⁻¹ corresponds to H-OH bending of solvent water molecules. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 53

Figure 4.3 High resolution XPS spectra of N1s for (a) [Fe-NH₃], (b) [TPyP], (c) [Fe-TPyP] and (d) [CoFe-TPyP]. (b-d) The peaks indicate the presence of pyrrole NH, pyridyl N and pyrrole N. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 54

Figure 4.4 High resolution XPS spectra of Fe2p for (a) [Fe-NH₃], (b) [Fe-TPyP] and (c) [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 55

Figure 4.5 SEM images of the (a) [Fe-TPyP] and (b) [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 56

Figure 4.6 SEM images and related elemental mappings of Fe, N, Na, Co for (a) [Fe-TPyP] and (b) [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 56

Figure 4.7 The XRD pattern for [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 57

Figure 4.8 CV curves measured for the Blank FTO and [CoFe-TPyP] in N₂ saturated 50 mM PBS solution (pH 7) at a scan rate of 20 mV/s. Two redox couples belongs to [CoFe-TPyP], one at 0.27 V_{Ag/AgCl} (E_c - E_a = 60 mV) and another one at 0.47 V_{Ag/AgCl} (E_c - E_a = 80 mV) is obtained, which are assigned to Co²⁺/Co³⁺ redox couples of nonstoichiometric PB structures. Note that the CV curve for [ZnFe-TPyP] and that for the blank is similar suggesting that water

oxidation occurs at cobalt sites. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

..... 58

Figure 4.9 Photocatalytic oxygen evolution by [CoFe–TPyP] (10 mg) and $K_2S_2O_8$ (20 mM) in pH 7, 50 mM PBS. The same batch was used in each cycle. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 59

Figure 4.10 Photocatalytic oxygen evolution by i) [CoFe–TPyP] (10 mg) and $K_2S_2O_8$ (20 mM) (red curve), ii) CoFe PBA (10 mg), TPyP (5 mg) and $K_2S_2O_8$ (20 mM) (blue curve), and iii) [CoFe–TPyP] (10 mg) without any electron scavenger (green curve). All experiments were performed at pH 7 in a 20 mL, 50 mM PBS. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 59

Figure 4.11 ATR-FTIR spectra for pristine and post-catalytic (after a 3-hours photocatalytic experiment) [CoFe–TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 61

Figure 4.12 High resolution XPS spectra of Co2p, O1s, and Fe2p for (a, b, c) pristine and (d, e, f) post-catalytic [CoFe–TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 62

Figure 4.13 TD-DFT excitation behavior for [Fe–TPyP] at UB3LYP/def2-TZV level of theory. A hybrid Fe–d + porphyrin– $\pi \rightarrow$ porphyrin– π^* state is generated. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 64

Figure 4.14 Absorption spectra of [TPyP], [Fe–TPyP], and [CoFe–TPyP] in $CHCl_3$ solution (abs =1 at 417 nm). The absorption values of the studied [TPyP], [Fe–TPyP], and [CoFe–TPyP] compounds were adjusted to 1 absorbance. Inset is the enlarged form of Q band absorptions. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 65

Figure 4.15 Fluorescence spectra of [TPyP], [Fe–TPyP], and [CoFe–TPyP] in CHCl ₃ , at 417 nm excitation wavelength. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.).....	65
Figure 4.16 Fluorescence and absorption spectra of the 1.25x10 ⁻⁴ M [TPyP] and 1.25x10 ⁻⁴ M [Fe–TPyP] compounds in MeOH:DI. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)	66
Figure 4.17 TA spectra at zero-time delay and time evolution of the bleach signals at 424 nm wavelength for [TPyP], [Fe–TPyP], and [CoFe–TPyP] compounds. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)	67
Figure 4.18 Schematic illustration of the energy diagram for (a) [TPyP], (b) [Fe–TPyP], and (c) [CoFe–TPyP] compounds. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.).....	68
Figure 4.19 TA spectra of [TPyP] compound at 400 nm (pump) excitation. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)	68
Figure 4.20 TA spectra of [TPyP] compound at 400 nm (pump) excitation with different pump probe time delays. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)	69
Figure 4.21 TA spectra of [Fe–TPyP] compound at 400 nm (pump) excitation. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)	69
Figure 4.22 TA spectra of [Fe–TPyP] compound at 400 nm (pump) excitation with different pump probe time delays. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.).....	70

Figure 5.1 Synthesis route for [CoFe–JG]. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 75

Figure 5.2 Schematic illustration for the formation of CoFe PB modified dye-sensitized TiO₂ electrode as a photoanode (TiO₂/[CoFe–JG]) through a three-step process on FTO coated glass substrate: (i) hydrothermal growth for TiO₂ NWs, (ii) immersing them into Fe bonded Janus green dye ([Fe–JG]), and (iii) in-situ drop-casting of Co²⁺ ions containing solution. The electrode color change from blue to purplish. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 76

Figure 5.3 Structural and morphological properties: (a) LUMO plots and energies (eV) of the molecules (R) considered for the rational design of DS-PECs. The inclusion of a formal positive charge on the ligand by virtue of quaternized pyridyl salts resulted in a more electrophilic LUMO. (b) Chemical structure of [CoFe–JG] assembly. Arrows indicate the electron transfer pathway proceeding from the Co donor to Fe linker and then to JG acceptor group. (c) A rough schematic representation of in situ formation of an ultrathin PB complex on dye-sensitized TiO₂ photoanode yielding TiO₂/[CoFe–JG] electrode. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 78

Figure 5.4. (a) The photographs show (left to right) the WEs that are on the FTO samples; TiO₂ / [CoFe–JG], TiO₂ / [CoFe] and TiO₂. (b,c) Side-view of the SEM image of TiO₂ / [CoFe–JG] photoanode, scale bar: 3 μm. (c) The inset shows the top view of the NWs with the scale bar of 1 μm. (d) EDS line scan in HR-TEM from air to an individual PB coated TiO₂ NW with a high magnification of the interface, scale bar: 50 nm. (e) HR-TEM image of an individual PB coated TiO₂ NW ([TiO₂ / [CoFe]) with yellow contrasts indicating the existence of a <10nm-thick PB layer. (f) ATR-FTIR spectra for [Fe–NH₃], [JG], [Fe–JG], and [CoFe–JG]. The sharp peaks in the 2000–2100 cm⁻¹ range are attributed to CN stretch. (g) ATR-FTIR spectrum of TiO₂/[CoFe–JG] electrode, [CoFe–JG] bulk, and FTO. The dash circle shows the existence of CN band between 2000-2100 cm⁻¹. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 80

Figure 5.5 High resolution XPS spectra of N1s for (a) [Fe–NH₃], (b) [JG], (c) [Fe–JG], and (d) [CoFe–JG]. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 81

Figure 5.6 High resolution XPS spectra of (a, b) Fe2p for [Fe–NH₃], [Fe–JG], and (c) Co2p for [CoFe–JG] powders. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 82

Figure 5.7 High resolution XPS spectra of (a) Ti2p and (b) N1s for TiO₂/[CoFe–JG] electrode. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 83

Figure 5.8 (a) Illustrative representations of a 3D schematic of the PEC-WS system consisting of rutile TiO₂ NWs coated FTO electrode loaded with a sensitizer-catalyst dyad, TiO₂ /[CoFe–JG] (1.6 cm²), as a WE. (b) LSV measurements, *j*-*V* curves, of the WEs under light illumination, without using filter (solid symbols), and under dark (empty symbols) condition. Anodic scan rate: 50 mV/s, electrolyte: 0.1 M PBS (pH 7), light intensity: 100 mW/cm². (c) Calculated ABPE curves of TiO₂, TiO₂/[CoFe], TiO₂/[CoFe–JG] photoanodes. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 84

Figure 5.9 LSV measurements, *j*-*V* curves, of (a) the WEs under light illumination (solid symbols), under dark (empty symbols) with a white-light source coupled to a 420 nm long-pass filter, (b) the pristine TiO₂ NWs and 2, 4, and 6 times [CoFe] PB modified TiO₂ NW electrodes under light illumination, without filter (solid symbols), and under dark (empty symbols). Anodic scan rate: 50 mV/s, electrolyte: 0.1 M PBS (pH 7), and light intensity: 100 mW/cm². (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 85

Figure 5.10 Set of CV curves for the (a) TiO₂/[CoFe], (b) TiO₂/[CoFe–JG] in N₂-saturated 0.1 M PBS solution (pH 7) at different scan rates ranging from 5 to 200 mV/s. (c) The dependency of anodic and cathodic peak currents at 0.8 V_{RHE} as a function of scan rate. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 86

Figure 5.11 (a) Absorption spectra of the [JG], [Fe-JG], and [CoFe-JG] solutions. The PL spectra for [JG] and [Fe-JG] solutions with 650 nm excitation wavelength and [CoFe-JG] solution for an excitation wavelength of 575 nm. (10^{-3} M in EtOH solutions, 2 mm cuvette length). (b) The absorption spectra of TiO_2 /[Fe-JG], and TiO_2 /[CoFe-JG] electrodes. This data is obtained by taking the pristine TiO_2 NWs as the reference. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 87

Figure 5.12 (a) IPCE spectra of the PECs with a 1.23 V_{RHE} external bias. The wavelength was scanned from 300 to 500 nm with a step of 10 nm. (b) Schematic energy band diagram of TiO_2 /[CoFe-JG] showing the band alignments between different interfaces and the involved water oxidation electron transfer processes. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 88

Figure 5.13 (a) Chronoamperogram for 2 hours of illumination with a white-light source coupled to a 420 nm long-pass filter at 1.23 V_{RHE} bias with a light intensity of 100 mW/cm^2 . Different colors indicate the independent measurements of the same TiO_2 /[CoFe-JG] electrode at consecutive time slots. (b) The CA profile of TiO_2 /[JG] photoanode under a bias voltage of 1.23 V_{RHE} . (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 89

Figure 5.14 Faradic efficiency of TiO_2 /[CoFe-JG] measured by gas chromatography. Bulk electrolysis was performed at 1.23 V_{RHE} in a gas-tight electrochemical cell. The total amount of oxygen produced was calculated as the sum of the oxygen in the headspace detected by gas chromatography and oxygen dissolved in the solvent, as determined from Henry's Law (red line). The theoretical amount is extracted from the total amount of charge passed during chronocoulometry experiment (black line) yielding an 83% Faradaic efficiency. A buffer solution (pH 7) of 50 mL was used for experiments. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 90

Figure 5.15 After different PEC measurements, HR-TEM image of an individual photoanode (TiO_2 /[CoFe-JG]) and inset shows a post-photoelectrochemical TEM-EDS line scan of Co, Fe, Ti, O from air to a NW with high magnification

interface, indicating no deformation on the sample. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 91

Figure 5.16 High resolution XPS spectra of (a) Fe2p and (b) Co2p for pristine TiO₂/[CoFe–JG], and (c) Fe2p, and (d) Co2p for post TiO₂/[CoFe–JG] (after 2-hours CA experiment). (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 92

Figure 5.17 TA spectra of 10⁻³ M (a) [JG], (b) [Fe–JG] and (c) [CoFe–JG] compounds with different pump probe time delays and decay kinetics of (d) GSB, (e) ESA and (f) STE signals in EtOH solutions at 600 nm (pump) excitation. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 95

Figure 5.18 TA spectra of (a) TiO₂/[JG], (b) TiO₂/[Fe–JG], and (c) TiO₂/[CoFe–JG] compounds at 400 nm (pump) excitation with different pump probe time delays. Decay dynamics for (d) GSB and (e) ESA signals. The pump pulse intensity for all these measurements is 9.95 GW/cm². (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 97

Figure 5.19 Molecular orbitals and electronic states: (a) Critical DFT frontier orbitals for [Fe–JG] and [CoFe–JG] systems. Schematic representation of charge carrier dynamics for (b) TiO₂/[JG], TiO₂/[Fe–JG], and (c) TiO₂/[CoFe–JG]. (d) The summary of electron transfers in TiO₂/[CoFe–JG] (JG: PS, CoFe PBA: both donor (D) and WOC, and TiO₂: SC. PBA serves as (i) a strong electron D group, (ii) a WOC, and (iii) a tuner for the modification of the energetic levels of the chromophore. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 99

Figure 6.1 Illustration of (a) bare WO₃ nanoplates on FTO coated glass, and (b) the CoFe PB modified dye-sensitized WO₃ photoanode (WO₃/[CoFe–SF]). It is a three-step process: First WO₃ nanoplates are synthesized by hydrothermal technique. Then, WO₃ nanoplates are immersed into Fe bonded Safranin dye ([Fe–SF]) solution. Finally in-situ drop-casting a solution of Co²⁺ ions to form [CoFe–SF] bulk structure. The electrode color changes from green to reddish.

(c) The structure of $\text{WO}_3/[\text{CoFe-SF}]$: CoFe PB assembly forms an extended bulk network over WO_3 . (d) The role of each component in the dye-sensitized photoanode: in this molecular fragment, the $[\text{Fe-SF}]$ is the PS part, and Co site acts as the WOC. Moreover, CoFe PB component serves as a strongly electron donating group for SF. The cyanide bridge has a length of around 5 Å. Only a molecular fragment of the extended structure is displayed, and the coordination environment of the cobalt site is omitted for clarity. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 107

Figure 6.2 Top-view of SEM images of $\text{WO}_3/[\text{CoFe-SF}]$ photoanode. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 108

Figure 6.3 XRD pattern of the sample prepared WO_3 nanoplates at 120°C for 18 h and “♣” symbol refers to FTO pattern. The intense diffraction lines - like (020) and (200) - indicate the high crystallinity. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 109

Figure 6.4 ATR-FTIR spectra for $[\text{Fe-NH}_3]$, $[\text{SF}]$, $[\text{Fe-SF}]$, and $[\text{CoFe-SF}]$. The sharp peaks in the 2,000–2,100 cm^{-1} range are attributed to CN stretch. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 110

Figure 6.5 High resolution XPS spectra of Fe2p for (a) $[\text{Fe-SF}]$, (b) $[\text{CoFe-SF}]$, and (c) Co2p recorded for $[\text{CoFe-SF}]$. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 111

Figure 6.6 High resolution XPS spectra of (a) W4f, (b) Fe2p, and (c) Co2p recorded for $\text{WO}_3/[\text{CoFe-SF}]$. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 112

Figure 6.7 (a) 3D schematic diagram of the three-electrode cell used for PEC-WS measurements. (b) Pulsed LSV curves performed for WO_3 , $\text{WO}_3/[\text{CoFe}]$, and $\text{WO}_3/[\text{CoFe-SF}]$ electrodes under white-light illumination (top), and with 435 nm (middle) and 490 nm (bottom) cut-off filters. In all three conditions, the dye-sensitized photoanode has a much stronger response compared to bare and catalyst cases. For 490 nm cut-off case, the WO_3 , and $\text{WO}_3/[\text{CoFe}]$ photoanodes have no photoresponse while the $\text{WO}_3/[\text{CoFe-SF}]$ electrode shows photocurrent response. (c) IPCE spectra for the same photoanodes at

1.23 V_{RHE} . The inset shows a magnified image of the 400-600 nm range. The IPCE results in visible range originate from the [CoFe–SF]. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 113

Figure 6.8 (a) The EIS Nyquist plot of bare WO_3 , $WO_3/[CoFe]$, and $WO_3/[CoFe-SF]$ photoanodes. (b) The EIS Nyquist plot for $WO_3/[Fe-SF]$ photoanode. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 114

Figure 6.9 Chronoamperogram profile of $WO_3/[Fe-SF]$ photoanode for 15 min. solar irradiation time. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 115

Figure 6.10 Schematic band energy alignment and carrier dynamics for all three photoanodes between different interfaces and water oxidation levels. The energetic position of the PB layer in $WO_3/[CoFe]$ case has been significantly modified due to its connection to the dye molecule. This modification provides a proper band alignment for hole transport towards the water oxidation process. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 115

Figure 6.11 Chopped LSV measurements of PB modified WO_3 nanoplates. j - V curves, of the WO_3 electrode and 2, 4, and 6 times [CoFe] PB modified WO_3 electrodes under white-light illumination (no filter). (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 116

Figure 6.12 Chronoamperogram profiles of all three photoanodes during a 2-hours solar illumination at 1.23 V_{RHE} . This test confirms the stability of the photoanode upon solar irradiation. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 117

Figure 6.13 TEM and HR-TEM analysis of pristine and post catalytic $WO_3/[CoFe-SF]$. PBA region is shown by yellow color dashed lines. (a) Pristine $WO_3/[CoFe-SF]$ sample; (left) The HR-TEM image from the WO_3 -PBA interface, indicating the formation of an ultrathin PBA extended network on the WO_3 surface, (middle) TEM image of an individual pristine WO_3 nanoplate sensitized with [CoFe–SF] assembly, (right) HR-TEM of $WO_3/[CoFe-SF]$, showing the formation of island-like PBA shell layers on the WO_3 surface. Based on this HR-TEM image, the WO_3 semiconductor has a single crystalline

phase with an interplanar spacing of 0.37 nm, which is consistent with its monoclinic phase. (b) Post WO₃/[CoFe–SF] sample; (*left*) HR-TEM image from the WO₃-PBA interface, showing the formation of both continuous and island-like PBA layer, (*middle*) TEM image of an individual nanoplate after CA experiment, (*right*) HR-TEM image from the WO₃-PBA interface, showing the existence of a uniform PBA shell layer after CA experiment. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 118

Figure 6.14 Comparison of the TEM and HR-TEM analyses of pristine and post catalytic WO₃/[CoFe–SF] sample. (a) Pristine WO₃/[CoFe–SF] sample; (*left*) TEM-EDX line-scan in HR-TEM from air to an individual PB coated WO₃ nanoplate with a high magnification of the interface, scale bar: 100 nm, (*middle*) TEM image of the individual nanoplate, (*right*) The EDX spectrum from the defined area. (b) Post WO₃/[CoFe–SF] sample; (*left*) TEM-EDX line-scan analysis on the post-catalytic sample, proving the existence of PBA layer, (*middle*) TEM image of the individual nanoplate, (*right*) The EDX spectrum from the defined area. The Co:Fe ratio for the pristine sample is 2.46 while it is 1.06 for the post-catalytic one. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 119

Figure 6.15 High resolution XPS spectra of (a) W4f, (b) Fe2p, and (c) Co2p for pristine and post-catalytic WO₃/[CoFe–SF]. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 120

Figure 6.16 Photocatalytic degradation test, absorption profiles before and after 500 min solar light exposure of the (a) [SF] and (b) [CoFe–SF] aqueous solutions in the presence of the same amount of WO₃ powder. The optical image shows the related color change (c) before and (d) after the photocatalytic experiment for both solutions. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 120

Figure 6.17 Comparison of the measured oxygen evolution amount employing the same WO₃/[CoFe–SF] photoanode. The total amount of oxygen produced was calculated as the sum of the oxygen in the headspace detected by the O₂ probe in a gas-tight electrochemical cell. The theoretical amount is extracted from the total amount of charge passed during the CA experiment at 1.23 V_{RHE} yielding a 75% Faradaic efficiency. 0.1 M Na₂SO₄ solution (pH 3) of 15 mL was

used. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)..... 121

Figure 6.18 Steady State Measurements: (a) Absorption and fluorescence spectra (with an excitation of 520 nm) of the [SF], [Fe–SF], and [CoFe–SF] solutions (0.02 mM in MeCN solutions). The optical band gap of different complexes is defined by the intersection point of absorption and fluorescence spectra. Transient Optical Measurements: (b) [SF] and [CoFe–SF] solutions under dark, their fluorescence under white and green light illuminations. The TRF spectra of (c) the dye solutions and (d) photoanodes upon 495 nm excitation. The probe signal for each solution is shown in the legend. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 123

Figure 6.19 Theoretical First-Principle Calculations: HOMO and LUMO energy levels with the electron clouds for all 3 components of (a) [SF], (b) [Fe–SF], and (c) [CoFe–SF], calculated with PBC-DFT using hybrid functionals. Metal-to-Metal Charge Transfer (MMCT) Feature: (d) Changes observed in the UV-Vis spectrum of an aqueous solution of the [CoFe–SF] complex with the incremental addition of 1 M aqueous Na₂S₂O₈ solution. (e) The magnified image shows the presence of the MMCT state between the wavelength of 550 - 750 nm, which infers the effective depletion of the 3+ states in the same complex. Related color change in the solution (f) before and (g) after the experiment. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)..... 124

Figure 6.20 TA spectra of the electrodes upon 520 nm (pump) excitation at different pump-probe time delays for (a) WO₃/[SF], (b) WO₃/[Fe–SF], (c) WO₃/[CoFe–SF]. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 125

Figure 6.21 TA spectra for dye solutions: 0.02 mM (a) [SF], (b) [Fe–SF] and (c) [CoFe–SF] compounds in MeCN solutions at 420 nm (pump) excitation with different pump probe time delays. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)..... 125

Figure 6.22 Schematic representation of band alignments for (a) WO₃/[SF], (b) WO₃/[Fe–SF], (c) WO₃/[CoFe–SF] photoanodes. (d) Proposed molecular

mechanism of the PEC water oxidation for [CoFe–SF]. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.) 126

Figure 7.1 A molecular representation of synthesis route for [CoFe–PP]. Coordination of [Fe–PP] to the cobalt ions through the ambidentate cyanide ligands results in the appearance of a purplish color as shown in Figure 7.2b. Both [PP] and [Fe–PP] exhibit molecular structure while [CoFe–PP] has a bulk structure since cobalt ions are coordinated to the nitrogen atoms of the cyanide group. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 132

Figure 7.2 (a) A rough illustration of an iron-sensitized photoanode and the role of each component displayed in the molecular fragment of the bulk [CoFe–PP] layer: TiO₂ SC, [Fe–PP] is the PS, and cobalt site is the WOC. The grey arrow indicates the [CoFe–PP] extended framework on the TiO₂ surface. (b) Schematic illustration for the three-step preparation of TiO₂/[CoFe–PP] photoanode; (i) hydrothermal growth of TiO₂ NWs, (ii) coating TiO₂ NWs with [Fe–PP] to prepare TiO₂/[Fe–PP], and (iii) in-situ drop-casting of Co²⁺ ions to prepare TiO₂/[CoFe–PP]. The color of the electrode changes from purple to green. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 134

Figure 7.3 The ATR-FTIR of [Fe–NH₃], [PP], [Fe–PP], and [CoFe–PP] powders: The sharp peaks shown by dashed line in the 2,000–2,100 cm⁻¹ range are attributed to CN stretch. The CN stretching frequency has a sharp peak at 2,031 cm⁻¹ and the peak at around 567 cm⁻¹ is attributed to Fe–N coordination bond in [Fe–NH₃]. The CN/nitrile peak exhibits blue shifts for [Fe–PP] at ~2,050 cm⁻¹, which further shifts to ~2,071 cm⁻¹ for [CoFe–PP]. Therefore, it proves the coordination of iron sites to the PP ligand by σ -donation from the cyano nitrogen and then Fe–CN–Co coordination mode, which is direct evidence for the formation of a PB structure. FTIR of [PP] spectra show prominent bands between 1,600 and 1,330 cm⁻¹ attributed to C=C and C=N stretches of PP ligand, and there are signals observed at 500–1,660 cm⁻¹ confirming the presence of PP in the PB structure of the [CoFe–PP]. The sharp peak at around 1,264 cm⁻¹ is associated with N–H stretch; several peaks in the 1,000–1,330 cm⁻¹ and 2,850–2,900 cm⁻¹ range correspond to symmetric and asymmetric stretches of C–H bond. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 135

Figure 7.4 . (a) A side view SEM image of the $\text{TiO}_2/[\text{CoFe-PP}]$ photoanode and the inset displays the top view of the NWs, scale bars: 500 nm. (b) HR-TEM of $\text{TiO}_2/[\text{CoFe-PP}]$ shows its lattice fringes with interplanar spacings of 3.25 Å and 2.92 Å, which are consistent with the rutile phase. The down-right inset indicates the interface between the TiO_2 NW and a ~10 nm - thick PB layer, with a scale bar of 5 nm. The SAED pattern of a single NW, which is shown in the inset (top right), proves its single crystalline phase. (c) RAMAN spectrum of nanowires showing the formation of rutile phase TiO_2 . (d) EDS line scan in HR-TEM from air to an individual PB coated TiO_2 NW with a high magnification of the interface, scale bar: 20 nm. (e) Room temperature X-band EPR spectra of $[\text{Fe-NH}_3]$, $[\text{Fe-PP}]$, and $[\text{CoFe-PP}]$, revealing the nature of iron sites. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 137

Figure 7.5 High resolution XPS spectra of N1s spectra for [PP], [Fe-PP], and [CoFe-PP]. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 138

Figure 7.6 (a) Cross sectional illustration of $\text{TiO}_2/[\text{CoFe-PP}]$ electrode model; (b) Pulsed chronoamperograms performed at 1.23 V_{RHE} for 300 s for $\text{TiO}_2/[\text{CoFe-PP}]$ electrodes (dark-colored lines) and the bare TiO_2 electrode (light-colored lines) under white-light illumination and with cut-off filters: 420, 435, and 490 nm, sequentially. (c) IPCE spectra for $\text{TiO}_2/[\text{CoFe-PP}]$ and bare TiO_2 NWs with a 1.23 V_{RHE} external bias. The wavelength is scanned from 300 to 500 nm with a step of 10 nm. The inset shows a magnified image of IPCE in the 420–500 nm range. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 139

Figure 7.7 (a) Chronoamperogram profile of $\text{TiO}_2/[\text{CoFe-PP}]$ for 5-hours illumination at 1.23 V_{RHE} bias with 420 nm filter. The inset shows LSV profiles before and after the long-term stability test. (b) Faradic efficiency of $\text{TiO}_2/[\text{CoFe-PP}]$ measured by gas chromatography. Bulk electrolysis was performed at 1.23 V_{RHE} in a gas-tight electrochemical cell. The total amount of oxygen produced was calculated as the sum of the oxygen in the headspace detected by gas chromatography and oxygen dissolved in the solvent, as determined from Henry's Law (red line). The theoretical amount is extracted from the total amount of charge passed during CA experiment (black line) yielding an 80% Faradaic efficiency. A buffer solution (pH 7) of 50 mL was used

for experiments. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 140

Figure 7.8 The oxidation states of Co by XPS spectra were also compared for (a) pristine and (b) post-catalytic (after long-term CA) for $\text{TiO}_2/[\text{CoFe-PP}]$ electrode. As expected, the post-catalytic sample has an enhancement in Co^{3+} signal indicating that cobalt sites are partially oxidized during the water oxidation process. The fully oxidized form of cobalt (Co_3O_4) was, however, not observed, which indicates that the CoFe PB layer retains its structure under PEC conditions. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 140

Figure 7.9 Chronoamperogram profile for $\text{TiO}_2/[\text{Fe-PP}]$ showing that it degrades fast in time. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 141

Figure 7.10 Absorption spectra of the (a) $[\text{Fe-NH}_3]$, and (b) $[\text{PP}]$ in aqueous solutions. (c) Photograph of the $[\text{PP}]$ ligand and $[\text{Fe-PP}]$ in aqueous solutions: the transformation of a basic ligand into a chromophore. (d) Absorption spectra of the $[\text{PP}]$, $[\text{Fe-PP}]$, and $[\text{CoFe-PP}]$ in aqueous solutions. (10^{-3} M in distilled water, 2 mm cuvette length) and the inset shows the molar absorption coefficient spectrum (300 nm - 700 nm) of $[\text{Fe-PP}]$ dye in water. According to the $[\text{Fe-PP}]$ dye solution spectrum, molar absorption coefficients are $5723 \text{ M}^{-1} \text{ cm}^{-1}$ determined at max absorption wavelength of 486 nm. For obtaining calibration curve of $[\text{Fe-PP}]$ dye, 5 different concentrations (0.8791, 3.08, 13.3, 31.4, 80 μM in 3.5 mL) are prepared in distilled water. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 142

Figure 7.11 MLCT behavior of iron PS: (a) The absorption spectra for $\text{TiO}_2/[\text{Fe-PP}]$ and $\text{TiO}_2/[\text{CoFe-PP}]$ electrodes obtained by taking the bare TiO_2 electrode as reference. Inset shows the estimated optical band gaps of the same electrodes by extrapolating the line portion of the Tauc plot $(\alpha\omega)^{1/2}$ (α is the absorption coefficient and ω is the angular frequency) vs. $h\nu$. (b) Changes observed in the UV-Vis spectrum of an aqueous solution of the $[\text{CoFe-PP}]$ complex with the incremental addition of 1 M aqueous $\text{Na}_2\text{S}_2\text{O}_8$ solution. Inset: effectively depletion of the 2+ states visualized in the quartz cuvettes before and the final addition of $\text{Na}_2\text{S}_2\text{O}_8$. (c–d) The HOMO and LUMO levels with the

electron clouds for [Fe–PP] and [CoFe–PP] are calculated with PBC-DFT using hybrid functionals in their lowest energy electronic states ($S=0$ for [Fe–PP] and $S=3/2$ for [CoFe–PP]. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 143

Figure 7.12 TA spectra of (a) [Fe–PP] and (b) [CoFe–PP] in EtOH solution with 500 nm (pump) excitation with different pump-probe time delays and a range of probe signals spanning from 420 nm to 780 nm. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 144

Figure 7.13 (a–b) Femtosecond TA dynamics of TiO_2 /[Fe–PP] and TiO_2 /[CoFe–PP] photoanodes at 500 nm (pump) excitation with different pump-probe time delays. (c–d) Decay dynamics for ESA signals TiO_2 /[Fe–PP] and TiO_2 /[CoFe–PP]. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 145

Figure 7.14 (a) Comparison of the excitation characteristics of [Fe–PP] and [CoFe–PP] in their lowest energy electronic states ($S=0$ for the former and $S=3/2$ for the latter. MO labels are included according to the location of the majority of the electron density. [Fe–PP] shows a clear MLCT transition. All SOMOs are localized on Co in [CoFe–PP]. (b) The proposed PCET mechanism of the PEC water oxidation for TiO_2 /[CoFe–PP]: The $4e^-$ mechanism involves the oxidation and activation of the catalytic site by four PCET to yield a high-valent metal-oxo species.[113], [115] This active species is attacked by a nucleophilic water molecule to form a peroxo species, which is then released as an oxygen molecule. (c) Schematic energy band diagram and carrier dynamics for TiO_2 /[Fe–PP] and TiO_2 /[CoFe–PP] showing the band alignments between different interfaces and the involved water oxidation electron transfer process. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)..... 147

Figure 8.1 (a) The illustration of a PB based dye-sensitized water oxidation photoanode, in which a PB layer incorporating a PS-WOC assembly is coated over a SC. PB based PS-WOC assemblies: (b) PVP: poly 4-vinylpyridine, RuPS: Ruthenium photosensitizer, (c) TPyP: Tetrapyrrolylporphyrin, (d) JG: Janus green B, (e) SF: Safranin O, (f) PP: 4-(pyridyl)pyridinium cation.

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Figure 8.2 Road map for PB based water oxidation systems that shows the role of cyanometalate group in various water oxidation processes including EC, PC, and PEC. Studies highlighted here are as follows; CoFe,[92][99] CoM,[99] CoFe+Ru,[111] CoPt+Ru,[121] CoCo+Ru,[122] CaCo-Fe+Ru,[123] CuCo@CoCo+Ru,[105] CoFe/BiVO₄,[129] CoCo/BiVO₄,[130] CoFe/AuNPs/BiVO₄,[134] CoFe-L/BiVO₄,[133] CoFe/Fe₂O₃,[127] CoFe/Fe₂TiO₅,[128] CoFe-PVP,[112] CoFe-isn,[115] CoFe-Ru,[124] CoFe-TPyP,[125] CoFe-JG/TiO₂,[126] CoFe-SF/WO₃,[223] CoFe-PP/TiO₂,[138] (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.) 154

LIST OF TABLES

Table 2.1 EC water oxidation performances of PB based catalysts.....	20
Table 2.2 PC water oxidation performances of PB based photocatalysts.....	24
Table 2.3 PEC water oxidation performances of PB based photoelectrodes.....	28
Table 4.1 Summary of XPS results obtained from (a) [Fe–NH ₃], (b) [TPyP], (c) [Fe–TPyP], and (d) [CoFe–TPyP].	55
Table 4.2 Relative energies of [Fe–TPyP] for different spin states calculated with UCAM-B3LYP/Def2TZV//UB3LYP/LANL2DZ level of theory.....	63
Table 4.3 Spin densities on selected atoms for different spin states of [Fe–TPyP] using UB3LYP/LANL2DZ level of theory.	63
Table 4.4 Time components of the Soret energy states (S ₀ →S ₂) (at 424 nm probe wavelength) in the TA spectra of the studied compounds.	67
Table 5.1 Summary of N1s XPS results obtained from (a) [Fe–NH ₃], (b) [JG], (c) [Fe–JG], and (d) [CoFe–JG].....	82
Table 5.2 Time components of the GSB, ESA, and SE (pump at λ= 600 nm) in the TA spectra of the studied [JG]/EtOH fluid compound.	95
Table 5.3 Time components of the GSB, ESA, and SE (pump at λ= 600 nm) in the TA spectra of the studied [Fe–JG]/EtOH fluid compound.	95
Table 5.4 Time components of the GSB, ESA, and SE (pump at λ= 600 nm) in the TA spectra of the studied [CoFe–JG]/EtOH fluid compound.....	96
Table 5.5 Time components of the GSB, ESA, and SE (pump at λ= 400 nm) in the TA spectra of the compounds on TiO ₂ /[JG].	97
Table 5.6 Time components of the GSB, ESA, and SE (pump at λ= 400 nm) in the TA spectra of the compounds on TiO ₂ /[Fe–JG].	97
Table 5.7 Time components of the GSB, ESA, and SE (pump at λ= 400 nm) in the TA spectra of the compounds on TiO ₂ /[CoFe–JG].....	97

Table 6.1 XPS results of the Fe2p and Co2p regions obtained from [Fe–SF] and [CoFe–SF] samples.	111
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Chapter 1. General Introduction

Cyanide reacts rapidly with metal ions, which makes it a poisonous and potentially deadly molecule. The strong coordination bond between the cyanide group and metal ions, which is due to a combination of σ -donation and π -back donation, is considered as the origin of its potential danger. Herein this thesis, we aim to take advantage of high reactivity of the cyanide group to metal ions to address critical challenges in dye-sensitized photoelectrochemical (DS-PEC) water splitting including poor long-term stability and high-cost precious metal based synthetic pathway. A straightforward synthetic route for preparing a new family of photosensitizer (PS) and water oxidation catalyst (WOC) hybrid assemblies, which are low-cost, earth-abundant, and highly robust, is proposed. In these assemblies, the unique interaction between metal ions that are connected through a cyanide group ($M-CN-M'$) is utilized i) to build dye-sensitized water oxidation photoanodes, in which both the catalyst and the photosensitizer mutually support each other for efficient charge transfer and ii) to develop a series of water oxidation electrocatalysts, in which the high electron density can be delocalized via cyanide ligands. A series of experiments under bias and light are proposed to enlighten the charge transfer process in cyanide-based water oxidation and dye-sensitized electrodes. These studies enable a comprehensive view and a systematic analysis of cyanide-based earth-abundant DS-PEC systems, which provide an alternative pathway for sustainable photoconversion technologies and Prussian blue (PB) based devices.

1.1. Thesis Goals

My motivation in this Doctoral Thesis is to bridge our knowledge and current-to-future PB based applications. For this aim, in particular, I focus on the role of cobalt-iron Prussian blue (CoFe-PB) structure as a relay, catalyst, photosensitizer, and/or a combination of them. Then I emphasized the construction of PB based dye-sensitized photoanodes to achieve efficient and robust DS-PEC cells. Here in this thesis, four projects are presented to scrutinize the potential application of PB based assemblies for overall water splitting/water oxidation devices.

1.2. Thesis Outline

This thesis work is organized as follows:

Chapter 1 points out the motivation of the thesis. It gives general information on cyanide chemistry and our synthetic approach to achieve efficient DS-PEC design.

Chapter 2 is divided into two main parts. The first part provides basic information on photosynthesis, solar water splitting and its operation principle, key components and efficient architectures, and the impact of each component on photoelectrochemical performance. We also review the materials used to develop photoelectrochemical water splitting technologies. Later, in the second part, I present a comprehensive overview of cyanide-based PB design and their application as water oxidation catalytic assemblies to unveil the role of each structural unit in the water oxidation process. To better handle this task, we directed our primary attention to establishing a structure & activity relationship rather than a chronological literature review. The content of this chapter differs substantially from common reviews as we focused only on the PB-based systems (not the PB-derived ones) and gathered all the literature to elucidate the mechanism in these assemblies and describe the role of each component in the water oxidation process. This chapter, thus, provides brief information required for building efficient PB based water oxidation photoanodes and summarizes the general synthetic methodology employed throughout my PhD studies.

Chapter 3 gives detailed information about the characterization methods employed in this thesis, including standard characterization techniques, steady-state and transient optical characterizations, and photoelectrochemical measurements. A brief statement on theoretical calculations is also provided.

Chapter 4 presents our first study on connecting tetrakispyridyl porphyrin group to a pentacyanoferrate complex to prepare a noble-metal free chromophore-water oxidation catalyst dyad system, which is robust and efficient under photocatalytic working conditions. For the first time in literature, a porphyrin derivative is coordinated to a cobalt based PB analogue via a $\text{Fe}(\text{CN})_5$ linker. In this work, we demonstrate how PB analogue can dramatically tailor the optical properties and electron dynamics of an organic chromophore. The knowledge acquired in this step inspired us to put one step forward to extend

this photocatalytic platform into a photoelectrochemical water splitting photoanode device.

Chapter 5 introduces a cyanide pathway to develop robust and Ru-free dye-sensitized water oxidation photoanodes. We show that cyanide chemistry provides a viable alternative to Ru based systems in photoelectrochemical water splitting applications. Although this work is among the first studies that demonstrate a Ru-free photoanode for DS-PEC, the efficiency of this assembly is relatively poor. The obtained knowledge from this study is employed to design an ideal platform for an efficient DS-PEC water oxidation system.

Chapter 6 demonstrates an efficient, stable, and a Ru-free DS-PEC platform. We also move one step forward and show that this methodology could be employed for other proper semiconductors and organic photosensitizers to enhance the photocurrent activity. This work elucidates the linker's critical effect between the PS and the WOC unit and the band alignment between these two components on charge transfer dynamics in the photoelectrochemical water oxidation process.

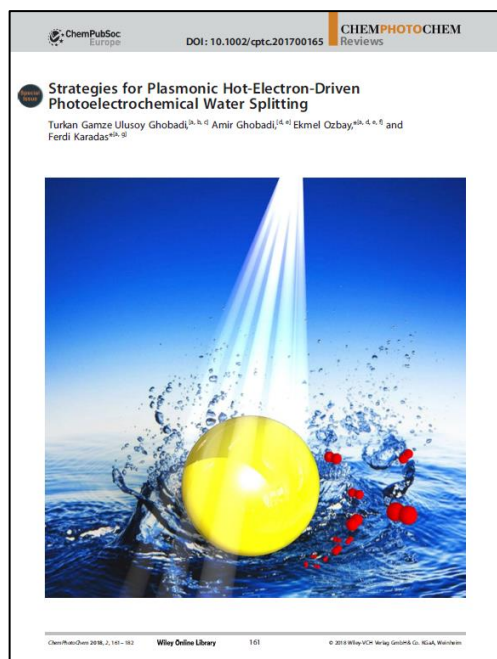
Chapter 7 opens up a new door for PB based assemblies. In the previous chapter, PB is connected to a photoactive organic PS, and the Fe site serves as a relay between WOC and PS units. In this chapter, we explore the potential of this iron site as a chromophore in a PB based assembly.

Chapter 8 emphasizes the current status of the PB based photoelectrochemical water oxidation devices. It also provides a possible route and a perspective on the possible future directions of this technology.

Chapter 2. Scientific Background

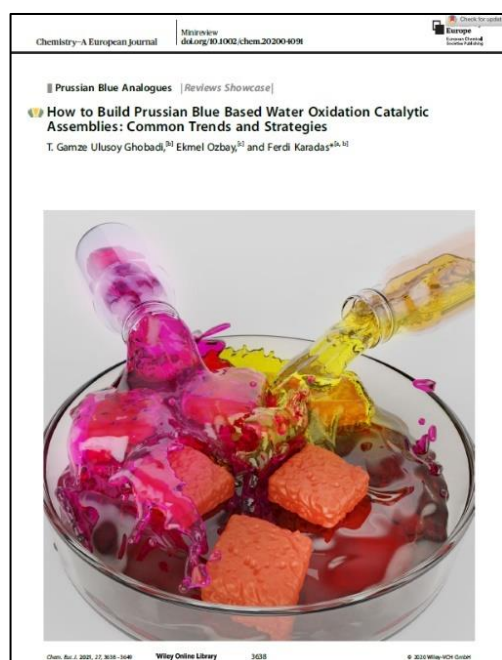
2.1. Preface

Part of this study was published as;



*“Review: Strategies for Plasmonic Hot-Electron Driven Photoelectrochemical Water Splitting”, T. G. Ulusoy Ghobadi, A. Ghobadi, E. Ozbay, F. Karadas, **ChemPhotoChem**, 2018, 2, 161 – 182 (Frontispiece).*

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*“Mini Review: How to Build Prussian Blue-Based Water Oxidation Catalytic Assemblies? Common Trends and Strategies”, T. G. Ulusoy Ghobadi, E. Ozbay, F. Karadas, **Chem. Eur. J.**, 2021, 27, 3638 – 3649 (Frontispiece).*

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2.2. Water Splitting

The biological systems that drive photosynthesis have been under vigorous research in recent years since it is considered the key process for the sustainability of life. Photosynthesis could simply be described as the conversion of sunlight to chemical energy, where water is activated by sunlight to produce high-energy chemicals. Although many enzymes with different functionalities are involved in this process, it is known to constitute three essential steps: (i) an antenna system for light harvesting; (ii) a donor-acceptor system for charge separation; and (iii) catalytic sites for water oxidation and water reduction. In natural photosynthesis, the water oxidation active sites are attached to protein chains in a specific configuration to release oxygen and protons in each catalytic cycle.[3] In this system, the sunlight is harvested by an “antenna” system made of molecular pigments (chlorophyll, carotenoids, phycobilins, etc.). The main function of the antenna system is to transfer the absorbed energy to their respective reaction centers through a transport layer (i.e., the donor-acceptor system). The acceptor part is connected to the active sites of water oxidation, which are bonded to protein chains. Four manganese atoms, which are surrounded by 2500 pigments, are required to produce oxygen from water. Therefore, the efficiency of natural photosynthesis is governed by the densities and portions of these pigments and catalytic sites.[4] The complex nature of this process also implies that challenging processes such as light-driven water oxidation can be achieved with a set of well-designed materials, which are equipped to handle specific parts of the process.

2.2.1. Photoelectrochemical Water Splitting (PEC-WS)

The concept of photoelectrochemical water splitting (PEC-WS) has emerged simply due to an effort to mimic photosynthesis by coupling solar energy and electrochemical water splitting in a single device.[5], [6] Although this approach provides a big step forward towards the conversion of solar energy to chemical energy by applying a small to no external bias, the necessity of using a combination of materials, as in the case of natural photosynthesis, makes the design of an ideal device rather challenging.[7] Nevertheless, the recently growing interest in PEC systems led to more than 3,000 scientific papers and several books in the last five years. While each of the previously studied systems mainly differs in the type of materials used, they adopt the same principle. It is then evident that the right combination of materials, serving as an

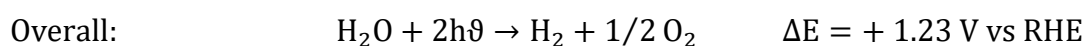
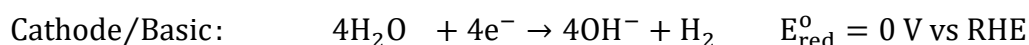
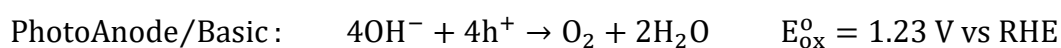
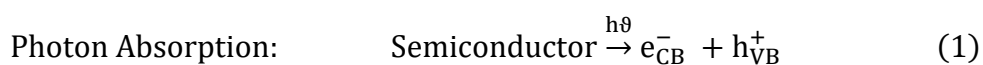
antenna, donor-acceptor, and catalyst, must be used in a proper fashion to construct a PEC-WS cell. Thus, the selection of an ideal material for a specific task should also be made based on the properties of the other material components of the device. Therefore, the understanding of the overall mechanism is of critical importance to introduce new materials and methodologies to the field.[6], [8]–[18]

Herein, a short introduction to the basic working principle of PEC-WS devices and common materials will be given.

2.2.1.1. Electron Transfer Dynamics

A simple design of a PEC-WS system, initially presented in 1972,[19] is shown in Figure 2.1. The basic cell is composed of at least one semiconductor (SC) as a photoactive material or photoelectrode and a metal counter electrode that are immersed in an electrolyte and connected by external electric wire. Overall, PEC-WS consists of two half reactions;[20], [21] i) oxidation of water to oxygen gas (O₂) and ii) reduction of protons to hydrogen gas (H₂), which take place at the (photo)anode and (photo)cathode, respectively. Generally, the photoanode is an n-type SC, and the photocathode is a p-type SC. Water splitting is thermodynamically an uphill reaction and requires relatively high energy (237 kJ/moles),[22] which corresponds to a band gap of 1.23 V per electron. In fact, oxygen evolution reaction (OER) requires multiple electron transfer during the formation of an O-O bond.[20], [23]

The redox reactions on each electrode occur by the following mechanisms and the standard redox potentials in an alkaline medium:



$$\Delta G = + 237 \text{ kJ/mol}$$

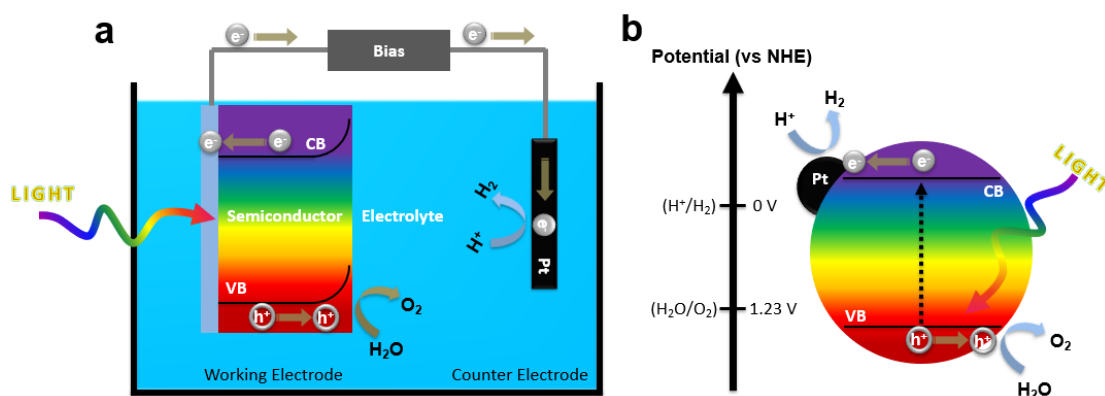


Figure 2.1 Schematic of (a) a basic PEC-WS cell including an n-type SC photoanode and a metal cathode immersed in an electrolyte connected by an external electric wire, and (b) particulate form of the photocatalyst where the water splitting is achieved without external bias. (Reprinted with permission from Wiley Ref. [1]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Before introducing the materials for PEC-WS, it is beneficial to give a brief on the conversion of solar energy to chemical energy through several kinetic-based processes inside the cell. In PEC-WS (Figure 2.1), the operation consists of four main steps;[24] (i) light absorption, (ii) charge separation, (iii) charge collection, and (iv) catalytic reactions. The first step is mainly dependent on the optical properties of the photoelectrode while the rest are strongly affected by the electronic properties of the photoactive components.

(i) Light absorption and charge carrier photoexcitation. A photoabsorber is mainly a SC with a suitable valence band (VB) and conduction band (CB), where the energy difference between these two levels is called the band gap (E_g) of the SC. While the lowest energetic level of the CB (LUMO) essentially defines the reducing potential of photoelectrons, the uppermost level of VB (HOMO) corresponds to the oxidizing potential of photoholes.[25] Upon light irradiation, a photon with energy higher than the band gap of the photoabsorber generates electron and hole pairs.[26] Since the main requirement of an ideal water splitting system (photoelectrolysis) is the use of only sunlight as a source of energy, a photoelectrode should have strong absorption across the solar spectrum and concurrently, its E_g should be higher than the electrochemical water splitting potential of 1.23 V to obtain a large amount of photo-excited carriers capable of performing the desired reactions.[27] Most of the materials, however, do not meet these energetic requirements.[6] Furthermore, the theoretical minimum E_g of the photoelectrode needs to be higher than the sum of this minimum required potential (1.23 V) and the cathodic and anodic

overpotentials (around 100 mV and 300 mV for a current density of 10 mA/cm² for catalytic reactions, respectively) which are due to catalyst activation, ohmic contact losses, and mass transport limitations.[28], [29] Therefore, the generally accepted minimum optical band gap of a semiconductor should be about 1.6 – 2.0 eV. Additionally, a certain amount of external bias is required for driving electron/hole transfer processes in an overall water splitting device. It should also be noted that recent studies have proven the operation of an unassisted efficient PEC-WS cell where the PEC system is monolithically integrated into a photovoltaic (PV) cell. The external bias is supplied with the PV cell to a device for water splitting process in such a system.[30], [31]

(ii) Separation of photogenerated charge carriers. When a PS is excited, electrons will be excited from VB to CB, and holes will be left free at the VB. A portion of these excited carriers will recombine on the SC surface or in the bulk within a few picoseconds (ps) and release their energy in the form of heat or phonons. Thus, rapid separation and collection of photo-induced carriers are desired to reduce the probability of e⁻-h⁺ recombination and to increase the overall yield of water splitting.[32] During photoelectrocatalysis, a space charge depletion layer occurs at the semiconductor-liquid electrolyte interface (also known as solid-liquid junction), which stimulates the upward band bending in a photoanode and downward band bending in a photocathode.[12], [33] This potential profile, which depends on the relative alignment of the SC work function and the reaction potential, enables the efficient separation of photoinduced charges and prevents the recombination of e⁻-h⁺ pairs.[34] Thus, it is favorable to use n-type and p-type SCs as photoanode and photocathode candidates, respectively.

(iii) Collection and Transportation of Charges to Electrode Surfaces. In this step, holes migrate to semiconductor-liquid junction at the n-type photoanode surface (they can also travel to the co-catalyst surface and then to its electrolyte interface), where the oxygen evolution reaction (OER) takes place. At the same time, electrons reach the counter electrode through an external wire to trigger the hydrogen evolution reaction (HER) at the surface.[35] In the case of a photocathode, which is a p-type SC, the photo-activated electrons are transferred to the SC surface. The HER takes place with the mediation of a co-catalyst. Consequently, the OER occurs in the counter electrode material while electrons travel to the photocathode with an external bias to recombine with the free holes in the photocathode.

(iv) Catalytic Reactions at the Surfaces. After the efficient separation of the carriers, these photogenerated electrons and holes are adsorbed on surface active sites to reduce and oxidize water to produce H_2 and O_2 gases, respectively. Holes have lower mobility and hence shorter diffusion lengths compared to electrons. Therefore, electrocatalysts can be employed as co-catalysts to enhance the kinetics of the water splitting process by reducing the activation energy for gas evolution.[36], [37] This method, however, can be applied at the expense of an additional charge transfer resistance due to an additional interface introduced to the system. The oxygen evolution step (photo-oxidation) is the rate-determining step due to its slow kinetics.

Comparing all reported systems in the literature is not an easy task because of the rapid growth of the field, substantially various PEC cell designs, and different efficiency parameters reported at different experimental conditions. Nevertheless, the studies indicate that the photoelectrode (both surface and its bulk) is vitally important since light absorption, charge separation and collection, and catalytic reactions occur in the same electrode. Thus, improving the optical and electrical characteristics of the photoelectrode material and its stability is of great importance in this field. This improvement can be attained with novel design architectures and/or the introduction of new materials.

2.2.1.2. Common Materials

Given that most of the solar irradiation energy is concentrated in visible (Vis) and near infrared (NIR) regimes, one of the most prominent features of an optimum light absorber is to have a low band gap ($E_g < 3$ eV). There are, however, a couple of bottlenecks that make this requirement difficult to satisfy, one of which, as noted hereinabove, is the difference between the energetic location of HER and OER processes that are located at 0 V_{RHE} and 1.23 V_{RHE} , respectively. Therefore, the realization of both reactions with a single SC ideally requires an optical band gap larger than 1.23 eV. This value rises to approx. 1.6 eV for practical applications, which corresponds to a wavelength of ~ 774 nm, due to ohmic losses in different parts of the system. In addition to this requirement, CB energy level of the photoanode should lie above the H^+/H_2 (0 V_{RHE}) and VB should be below O_2/H_2O (1.23 V_{RHE}) under standard conditions. In other words, both the reduction and oxidation potentials of water should be within the band gap of the SC.

Figure 2.2 shows how well the commonly studied SCs satisfy these requirements. The energy difference between the VB and the potential for water oxidation ($E_{VB}-E_{OER}$) is plotted with respect to the energy difference between the CB of the SC and the potential for hydrogen evolution ($E_{CB}-E_{HER}$). [25], [38], [39] Overpotentials of around 200 mV and 400 mV are also considered for HER and OER, respectively, to account for the losses during electrocatalytic processes. [40], [41] According to the figure, a SC that lies on the right side of the black dashed line has a suitable VB position for water oxidation. The same analogy can be made for water reduction as well. The diagram also displays the comparison of the band gaps of SCs in the units of wavelength to show whether the SC is suitable to harvest visible light or not. Therefore, an ideal SC, which can efficiently harvest visible light and derive both water oxidation and reduction, should lie in the highlighted triangular region. For example, TiO_2 , which is considered to be the first example of the photoelectrocatalytic splitting of water, has a suitable VB for water oxidation while it is a poor absorbing SC in the visible region. While TiO_2 remains to be the most studied SC in this field, [42] many other d^0 metal oxides, including ZrO_2 , NbO_2 , and WO_3 , [43] d^{10} metal oxides involving ZnO , [44] and even mixed oxides containing both d^0 and d^{10} metal ions such as $BiVO_4$ [45] have been widely studied. Some of these metal oxides have smaller band gaps than desired, and most of them exhibit poor optical and electrical performances. Moreover, as shown in Figure 2.2, their band positions are not suitable for performing the whole water splitting reaction. In the case of d^{10} metal oxides, they are generally more advantageous as photoactive materials in terms of the mobility of photogenerated electrons in the CB and photocatalytic activity due to hybridized empty sp orbitals of typical metals. [46] Besides these large band gap metal oxides, at the other end of the scale, there are several narrow band gap visible light responsive non-oxide SCs that can absorb most solar irradiation. These materials, however, have the chemical instability deficiency that mitigates their long-term sustainabilities under a high oxidative environment. [18] For example, metal chalcogenides, including CdS , appear to be one of the most suitable photocatalysts for overall water splitting, exhibiting band gap energies sufficiently small to allow for the absorption of visible light and having conduction and valence bands at potentials appropriate for water reduction and oxidation (see Figure 2.2).

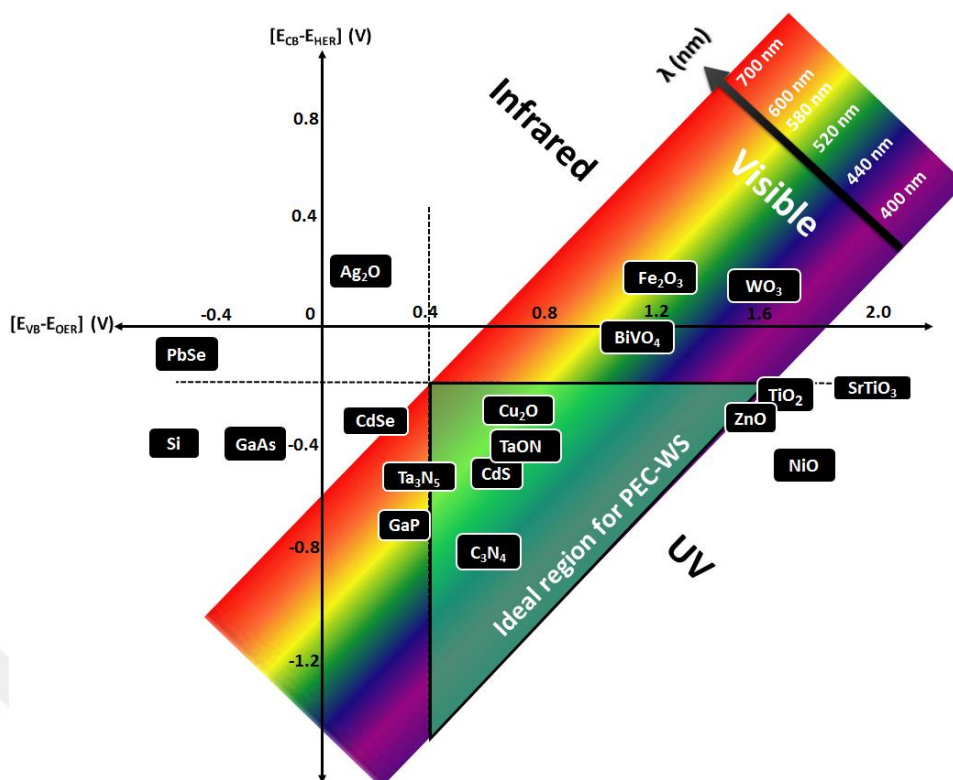


Figure 2.2 Comparison of different SCs, in contact with the aqueous electrolyte at pH = 0, according to their band gaps (in the units of nm) and band positions with respect to HER and OER half reactions. An additional overpotential of 200 and 400 mV was considered to define the optimum region. Since these overpotentials are merely estimated values (much less overpotentials are available in the literature)[47], [48] the highlighted region does not retain exact borders. (Reprinted with permission from Wiley Ref. [1]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

These metal chalcogenides, however, are not suitable for water oxidation since sulfide and selenide anions are more susceptible to oxidation than water, which causes CdS or CdSe catalysts themselves to be oxidized and degraded over time.[49] Therefore, the ideal approach would be to enhance optical properties and stabilities of oxide based SCs with novel strategies. In recent years, a significant part of the current research revolves around manipulating the band positions and band gaps of already studied SCs by doping. Doping could be performed with metal ions and/or non-metal elements since the position of valence and conduction bands are generally according to the type of metal and non-metal ions, respectively.[50] A well-known example to this approach is the gradual increase in the valence band energy of a d^0 metal oxide, such as Ta_2O_5 , with increasing the amount of N-doping. In contrast, the energy of the conduction band remains constant, leading to a decrease in the band gap. This method yields a SC, named TaON, which has ideal band positions for overall

water splitting (Figure 2.2).[51]–[53] Another viable method is the incorporation of alkali metal ions to the crystal structure of SCs, which has been employed particularly to enhance the stability of the crystal structure and even for the construction of new crystal structures. For example, a study performed on a series of alkali metal tantalates, MTaO_3 ($\text{M} = \text{Li}, \text{Na}, \text{and K}$), revealed that Ta-O-Ta angle in the crystal structure could be varied by changing the alkali metal ion, which has a direct effect on the band diagram.[54]

Since the seminal work in 1972, there is still no SC that simultaneously satisfies all of the requirements mentioned above despite decades of investigations since the seminal work. Therefore, it is common to combine multiple SCs (building junctions), which is essentially analogous to natural photosynthesis that uses a series of enzymes and molecules equipped with specific features. An efficient heterojunction system generally consists of two SCs, one of which has a VB suitable for water oxidation (higher than $1.23 \text{ V}_{\text{NHE}}$). In contrast, the other one has a CB suited properly for water reduction (lower than 0 V_{NHE}). Furthermore, they should have matched band positions with respect to each other to allow for efficient charge separation. For example, an enhancement in the photocurrent density has been achieved with $\text{BiVO}_4\text{-WO}_3$, [55], [56] $\text{TiO}_2\text{-WO}_3$, [57] $\text{TiO}_2\text{-SrTiO}_3$, [58] $\text{BaTiO}_3\text{-TiO}_2$, [59] ZnO-TiO_2 , [60] and $\text{BiVO}_4\text{-TiO}_2$ [61] compared to their single-component cases. This methodology has been used for non-oxide SCs as well. [62], [63] The efficiency of the visible absorption can also be improved by coupling the SC with a molecular chromophore (dye-sensitizing). These are known as dye-sensitized photoelectrochemical cells (DS-PECs), which consist of a metal oxide coupled to a molecular dye and catalyst assembly (dyad). [64], [65] As illustrated in the Figure 2.3, in the DS-PEC system, the absorption of the light is provided using a visible responsive dye. Although promising studies have been introduced by Sun et al. and others, these systems generally suffer from the high tendency of molecular dyads to decompose during the catalytic process. [66] Therefore, stability is still the main issue that limits the long-term operation and large scale compatibility of these systems.

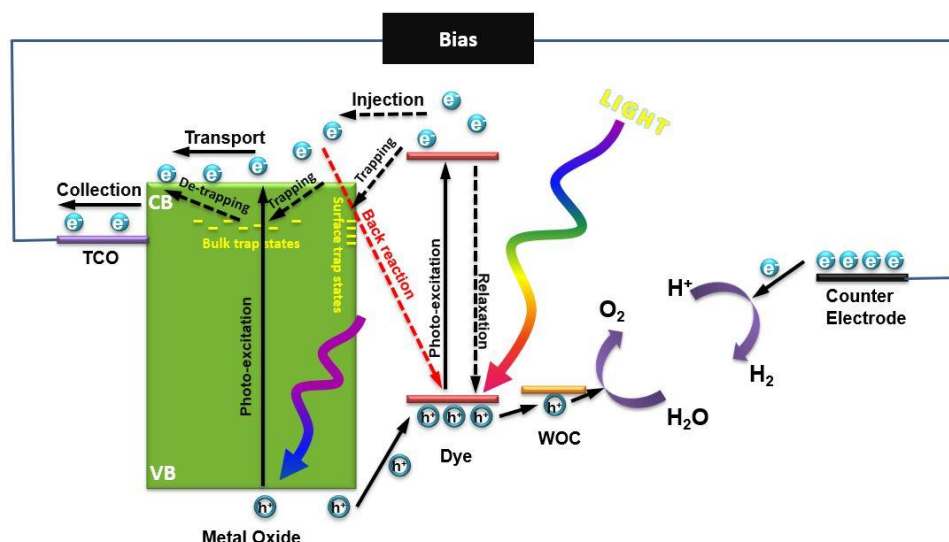


Figure 2.3 The steps involved in the operation of a DS-PEC. In this cell, the sensitizer photoactive material is a visible absorptive dye layer. (Reprinted with permission from Wiley Ref. [1]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

In summary, several different strategies[50] such as the doping of external elements to tune the band structure, construction of heterojunctions to suppress the recombination of electron–hole pairs, decreasing the particle sizes of the photocatalysts to reduce the migration distance of charge carriers, optimizing the crystal structure to expose more active facets,[24] using efficient electrocatalysts for HER and OER, and sensitizing the SC with molecular organic or inorganic molecular chromophores have been employed to improve the overall performance of PEC-WS. Thus, all in all, to bring the current water splitting cells into commercialization, we have to propose stable, high-performance, and low-cost architectures. Moreover, the proposed solution should be extendable to various semiconductor designs. In this thesis, the cyanide chemistry is adopted as a multifunction assembly to satisfy the above requirements. Next chapter will provide a detail information on the use of PB analogues in water oxidation process.

2.3. Prussian Blue Analogues (PBAs) for Water Oxidation

PB and its analogues (PBAs) have at least a three-century long history in coordination chemistry. Recently, cobalt-based PBAs have been acknowledged as efficient and robust water oxidation catalysts. Given the flexibility in their synthesis, the structure and morphology of cobalt-based PBAs have been modified for enhanced catalytic activity under electrochemical (EC), photocatalytic (PC), and photoelectrochemical (PEC) conditions. Here, in this chapter, the work on cobalt-based PBAs is presented in four sections: i) electrocatalytic water oxidation with bare PBAs, ii) photocatalytic process in the presence of a PS, iii) photoelectrochemical water oxidation by coupling PBAs to proper SCs, and iv) the utilization of PBA-PS assemblies coated on SCs for the DS-PEC water oxidation. This part will guide readers on the structure and catalytic activity relationship in cobalt-based PBAs by describing the role of each structural component. Furthermore, this aims to provide insight into common strategies to enhance the catalytic activity of PBAs.

2.3.1. Basics

As mentioned before, cyanide rapidly reacts with metal ions labeling itself a toxic and dangerous molecule. Despite its bad reputation, it can connect proper functional units to prepare low-cost and non-toxic multifunctional materials on a large scale.[67]–[72] The most well-known family of cyanide-based compounds is PB and PBAs, which can be facilely synthesized by mixing a hexacyanometalate complex with a 3d transition metal ion to afford mixed-metal cyanometallates. These materials, with a history dating back to the beginning of the 18th century, are known as microporous coordination polymers with a three-dimensional open framework structure. In a PB structure, metal cations are connected through cyanide bridging ligands forming a cubic coordination network with the general molecular formula $A_nM_x[M'(CN)_6]_n \cdot nH_2O$ (A = alkali-metal ions, M and M' = transition metal ions). Figure 2.4 shows the typical crystalline structure of a cobalt-based PBA, CoFe PBA, in which M = Co, M' = Fe. Given the diversity (adjustable metal active sites), high porosity, fast electron transfer, earth-abundance, and simple synthesis of PBAs, they have been investigated as promising materials in a wide range of applications including magnetism,[73] photomagnetism,[74] alkaline-ion batteries,[75]–[77] gas capture and storage,[78],[79] sensors,[80] H_2O_2 reduction,[81] electro-

chromic devices,[82], [83] and biomedicine.[68], [84] PBAs have recently received attention as potential robust and efficient WOCs for high performance and scalable water splitting devices. Several researchers have recently focused on PB derived multimetallic oxides, sulfides, and phosphides rather than cyanide-based coordination networks themselves.[85]–[89] This chapter, however, provides a comprehensive overview of cyanide-based water oxidation catalytic assemblies to exploit the role of each structural unit in a PB structure to the water oxidation process. Then, we unveil a new route for PB based assemblies which is the coordination of these components into a organic unit to bulid up a PS-WOC hybrid design.

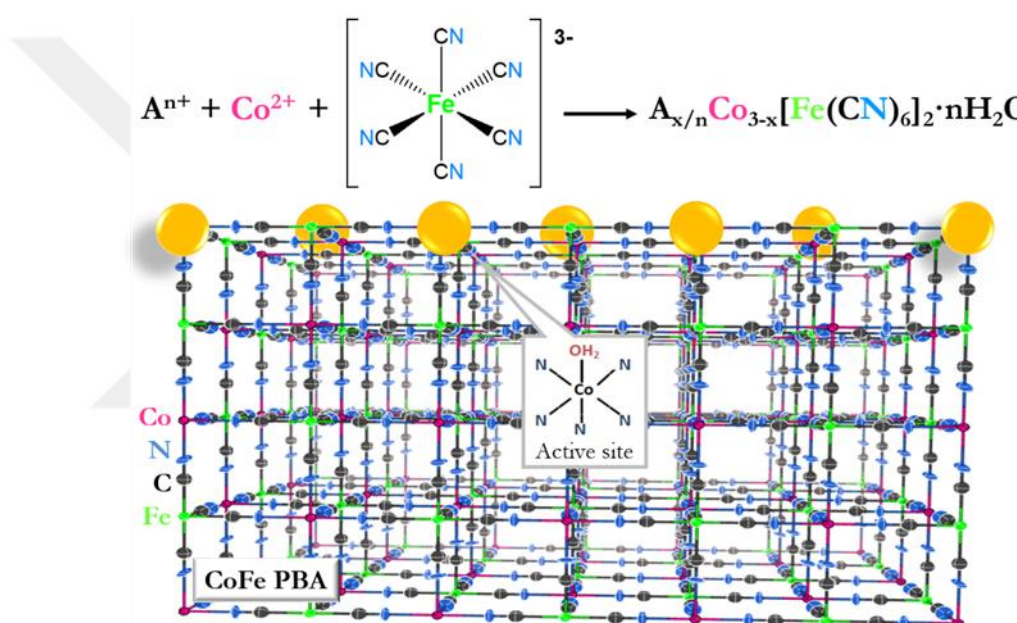


Figure 2.4 Synthesis and general structure of $A_nCo_x[Fe'(CN)_6].nH_2O$ ($A = H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}$): Here, nitrogen coordinated Co sites and carbon-coordinated Fe ones are bridged by cyanide (CN) groups to form an open framework. Catalytically active cobalt sites, which are surrounded by at least one water molecule, are highlighted with orange spheres. Alkali metal ion that resides in the tetrahedral positions of the cubic structure is omitted for clarity. Adapted (or “Reproduced in part”) with permission from John Wiley and Sons. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

2.3.2. CoFe PBAs for Water Oxidation

The use of cobalt-based catalysts in water oxidation has gained new momentum after the seminal work on the water oxidation catalytic activity of

cobalt oxides in the presence of a phosphate buffer (Co-Pi).[90], [91] This work has also accelerated the studies on heterogeneous catalysis with bulk systems. In 2013, a cobalt-based PBA also came into play as one of the first non-oxide heterogeneous WOCs.[92] The impact of that work was twofold: 1) It provided new insight into the water oxidation mechanism by demonstrating that an oxo-bridge is not essential for water oxidation catalysis, 2) a new family of heterogeneous catalysts is introduced to the field.

Following this work, significant studies were performed on the effectiveness of CoFe PBAs in the water oxidation process. Cobalt hexacyanoferrates can be regarded as non-stoichiometric coordination network compounds. The Co:Fe atomic ratio can vary between 1 to 2, depending on the synthesis, counter alkali metal cation, and the oxidation state of iron. The network consists of catalytically inactive iron sites surrounded by six cyanide groups, which serve as a bridging group between cobalt sites. A cobalt ion, on the other hand, is surrounded with a combination of nitrogen atoms of cyanide groups and water molecules forming a coordination sphere with a general formula, $\text{Co}^{\text{II}}(\text{NC})_x(\text{OH}_2)_{6-x}$. The cobalt site in a PB structure can easily be oxidized to its higher oxidation states, which makes it an ideal catalytic site for water oxidation. All the PB based WOCs studied up to date are, therefore, cobalt-based ones. Several key features that make cobalt-based PBAs ideal catalytic assemblies for water oxidation are listed below and schematically shown in Figure 2.5.

Simple Synthesis: Given the reactivity of both the carbon and nitrogen atoms of the cyanide group, a cyanide-based coordination polymer could be obtained by just mixing a cyanometalate complex with a transition metal ion resulting in a color change and a precipitate. The purification of the powder is generally performed by using aqueous or alcoholic solvents at room temperature under air with a high yield.

Diverse morphology: The flexible synthesis of PBAs could be modified to achieve a morphology that suits the needs of the desired application. Capping ligands and surfactants could easily be incorporated into the synthesis to control the surface chemistry, morphology, crystallinity, and the particle size of PBAs.[93]–[95]

Diversity: Given the straightforward synthesis, desired alkali (H, Li, Na, K, Rb, Cs), alkaline earth (Mg, Ca), and 3d transition metal ions (Cr, Mn, Fe, Co, Ni, Cu, Zn) could be incorporated into the PB structure, which enables a systematic investigation of the role of each component on a specific application.[96]–[98]

Earth abundance: Since all of the components in PBAs are earth abundant, non-toxic, and low-cost precursors, they can be utilized for building scalable and low-cost electrochemical devices and water splitting cells.

Robustness: Unlike most of the common oxide-based WOCs, PBAs exhibit exceptional stabilities even under harsh acidic conditions.[99] They can efficiently operate at almost all pH values (pH 1-13), which is highly desirable for water splitting devices. For example, a FeFe PB is an FDA approved drug for radiocesium, which is taken orally since it is stable even against gastric acid, pH 1.5.[100]–[103] The superior stability of PBAs under both neutral and acidic conditions could be attributed to strong σ -donation (mainly due negative charge of the ligand) and π -back donation (due to empty relatively low-energy π^* orbitals) between the metal ion and cyanide group, which yields a much lower solubility constant compared to metal oxides (K_{sp} for PB is 10^{-41} while it is approx. 10^{-15} for cobalt oxides). The superior pH endurance, therefore, makes PBAs strong candidates as robust WOCs. It is noteworthy that catalytic studies with PBAs above pH 13 should be performed with caution as they transform to metal hydroxides, which could also exhibit efficient water oxidation catalytic activities.

Porosity: PBAs are considered as one of the oldest coordination polymers and they exhibit a microporous nature since the cyanide bridging group creates microchannels with a size of $\sim 5 \text{ \AA}$, which enables the access of small molecules including water and oxygen, see Figure 2.5. Moreover, all PBAs exist in the same cubic structure regardless of the metal ions used and the metal-to-metal stoichiometric ratio. For example, the cobalt-to-iron ratio is generally greater than one to provide a charge balance.[104] Small voids occur in the structure due to the partial absence of cyanoferrate groups. Therefore, cobalt sites coordinated to at least one water molecule are present even in the subsurface of the structure. The catalytic activity of these interior defect sites is confirmed with a recent study, which suggests that a PB layer of around 7 nm thickness participates actively in the catalytic water oxidation process.[105]

Fast electron transfer: Short cyanide linker (M-CN-M' distance is $\sim 5 \text{ \AA}$) provides fast electronic communication between metal ions. Heteronuclear metal cyanide compounds generally fall into Class II based on Robin-Day classification revealing the partial localization of distinct valences.[106]–[110] Both metal sites in a CoFe PBA exhibit easily accessible $M^{2+/3+}$ redox processes. While $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ oxidation is one of the critical steps in a water

oxidation process, the $\text{Fe}^{2+/3+}$ redox process is utilized to increase the electron density of electron-deficient catalytic cobalt sites for enhanced water oxidation activity. Therefore, iron sites serve as bridging and donor groups in CoFe PBAs. The electronic effect of iron sites will be discussed in more detail in the next sections. This unique behavior could provide a fast electron transfer between metal ions to mediate the charge transfer during the water oxidation process.

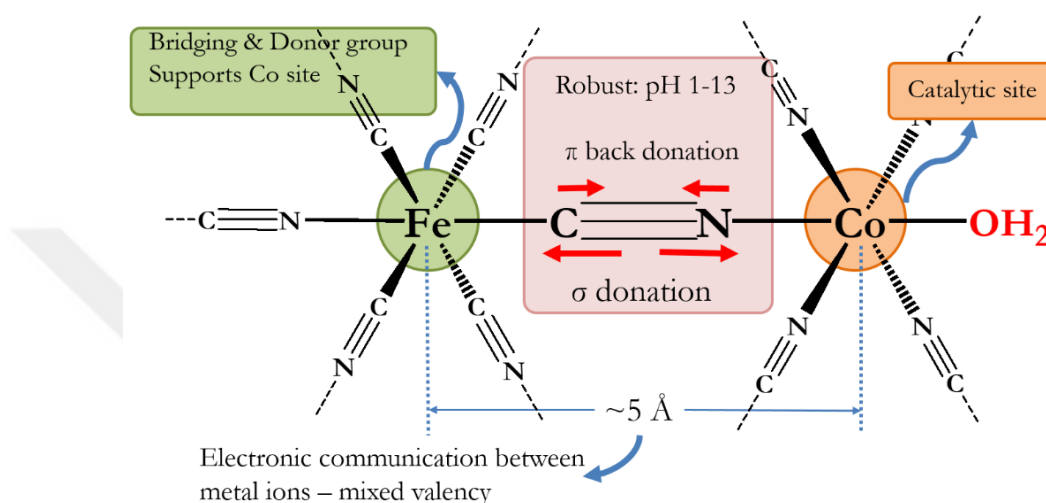


Figure 2.5 Characteristic features of each constituent in a CoFe PBA. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

All these advantages motivated the society to utilize CoFe PBAs in various platforms for water oxidation. The upcoming section will summarize the typical application of these units in water oxidation processes. In summary, PBAs are commonly utilized as a catalyst for SCs in the water oxidation process. However, in this thesis, we opened a new route for these assemblies. Rather than being a catalyst, their coordination with organic ligands will turn them into an active absorbing layer.

2.3.3. PB Based Electrocatalytic Water Oxidation

Electrocatalytic water splitting is mainly limited by the high overpotentials of both hydrogen evolution and oxygen evolution reactions. The complex multistep proton-coupled electron transfer ($4e^-$ process), water oxidation, is particularly considered as the most challenging half-reaction of the water splitting process. Here, CoFe PBAs advance as active electrocatalysts to

accelerate the sluggish oxygen evolution reaction kinetics by reducing the activation energy of the reaction. Catalytic studies performed on a series of metal hexacyanoferrates (M = Mn, Fe, Co, and Ni) indicate that cobalt is the most active catalytic site in PB structures.[111] In a classic three-electrode setup (Figure 2.6a), a typical CoFe PBA modified electrode, regardless of the synthetic method, exhibits two characteristic features in the anodic region: i) a quasi-reversible band at around 0.9 V_{Ag/AgCl} at pH 7, which is attributed to a Co^{2+/3+} redox process just before ii) an irreversible peak due to the catalytic water oxidation process.[92], [112] The electrode is extremely stable under neutral conditions as confirmed by long-term chronoamperometry and chronopotentiometry experiments. [99] The cobalt sites in a PB framework are more active than those in a bulk Co₃O₄ structure. Electrochemical studies reveal that a turnover frequency (TOF) of 2.6×10⁻³ s⁻¹ could be obtained at an overpotential (η) of 410 mV for Co₃O₄ while it is only 305 mV for a CoFe PBA modified electrode.[92] The cyanide linker, however, results in a lower surface concentration of catalyst in the order of 'nmol.cm⁻²' compared to bulk oxides (in the order of 'μmol.cm⁻²'), since the distance between the neighboring cobalt sites in a PB structure is approx. 10 Å (it is approx. 3 – 4 Å for oxides and sulfides). The majority of the earlier research conducted on electrocatalytic water oxidation with PBAs, therefore, revolved around increasing the surface concentration of active catalytic sites with either varying the cobalt precursor, or changing the cyanide precursor, or using support material, or a combination of these. These strategies are highlighted below with practical experimental methods:

i. Changing the cyanide precursor: The inspection of the effect of a structural parameter on the catalytic activity in bulk PBA systems can be quite challenging, as a slight change in the synthetic conditions or the precursors generally varies the morphological and electronic properties of the assembly. In the electrocatalytic water oxidation studies of CoFe PBAs, morphological changes have been monitored with the surface concentration of catalytic cobalt sites while electronic properties of the catalytic sites are compared based on TOF value. In 2013, Galán-Mascarós and co-workers employed a well-established potentiostat deposition method to prepare a CoFe PBA modified FTO coated glass with a surface concentration of approx. 1.4 nmol/cm². [92] A similar value is obtained when a CoFe PBA modified electrode is prepared with a drop-cast method.[113] In addition to a long distance between cobalt sites, the origin of relatively low surface concentration in CoFe PBAs is also due to their high crystallinities as depicted by sharp diffraction peaks in their powder

XRD patterns. Our group recently found that an amorphous CoFe coordination polymer could be obtained when the symmetric hexacyanoferrate complex is replaced with a polymer-bound pentacyanoferrate precursor.[112] The polymer herein serves as a capping group that limits the dimensionality of the cyanide-based network structure. The change of the morphology from a crystalline structure to an amorphous one leads to a sevenfold increase in the surface concentration. In other words, the amorphization of the reactive surface or decreasing the degree of crystallinity of the catalytic structure allows for better participation of the catalytic site to the water oxidation process and its easy transformation to the required intermediates.[114] Later, Bonacin and co-workers employed the $[\text{Fe}(\text{CN})_5(\text{isn})]$ complex (isn = isonicotinate) to prepare a CoFe PBA with a surface concentration of around 6.0 nmol.cm^{-2} . [115] Varying the number of cyanide groups coordinated to the cyanometalate group, therefore, provides a good opportunity to enhance the number of catalytic sites and/or defects on the surface for an oxygen evolution reaction.

A recent list of electrocatalytic water oxidation activities with important electrocatalytic parameters, including overpotentials, Tafel slopes, and TOF of PBAs, is provided in Table 2.1.

Table 2.1 EC water oxidation performances of PB based catalysts.

Catalyst ^[a]	Formula	η_{onset} , mV	$\eta_{1\text{mA}}^{\text{[b]}}$, mV	pH	TOF (s^{-1})	Tafel Slope, (mV/dec)	Ref
[Co-Fe]	$\text{K}_{2x}\text{Co}_{(2-x)}[\text{Fe}(\text{CN})_6]$ ($0.85 < x < 0.95$)	N/A	>600	7	2.6×10^{-3} at $\eta = 305 \text{ mV}$ 2×10^{-3} at $\eta = 300 \text{ mV}$ 0.5 at $\eta = 550 \text{ mV}$	85-95	[92]
[Co-Fe(CN) ₅ -P4VP]	$\text{Co}_{1.5}[\text{Fe}(\text{CN})_5\text{P4VP}]$	360	510	7	2.6×10^{-3} at $\eta = 284 \text{ mV}$	111	[112]
[Co-Fe] ^[c]	$\text{Co}_{1.5}[\text{Fe}(\text{CN})_6]$	N/A	500	7	N/A	91	[99]
[Co-Co ^{III}]	$\text{K}_{0.38}\text{Co}_{1.31}[\text{Co}(\text{CN})_6]$	283	565	7	5×10^{-2} at $\eta = 400 \text{ mV}$	99	[113]
[Co-Cr ^{III}]	$\text{K}_{0.41}\text{Co}_{1.29}[\text{Cr}^{\text{III}}(\text{CN})_6]$	303	598	7	5×10^{-3} at $\eta = 400 \text{ mV}$	96	[113]
[Co-Fe ^{III}]	$\text{K}_{0.31}\text{Co}_{1.35}[\text{Fe}^{\text{III}}(\text{CN})_6]$	323	717	7	4.4×10^{-3} at $\eta = 400 \text{ mV}$	127	[113]
[Co-Fe ^{II}]	$\text{K}_{0.70}\text{Co}_{1.65}[\text{Fe}^{\text{II}}(\text{CN})_6]$	343	1079	7	3×10^{-3} at $\eta = 400 \text{ mV}$	121	[113]
[Co-Fe]/Sb-SnO ₂	$\text{Co}_{1.5}[\text{Fe}(\text{CN})_6]$	520	N/A	1	N/A		[116]
[Co _{0.9} Fe _{0.1} -Co]	$\text{Co}_{1.34}\text{Fe}_{0.15}[\text{Co}(\text{CN})_6]$	303	569	7	2.6×10^{-3} at $\eta = 295 \text{ mV}$	104	[117]
[Co _{0.5} Fe _{0.5} -Co]	$\text{Co}_{0.75}\text{Fe}_{0.75}[\text{Co}(\text{CN})_6]$	323	591	7	2.6×10^{-3} at $\eta = 312 \text{ mV}$	104	[117]
[Fe-Co]	$\text{Fe}_{1.5}[\text{Co}(\text{CN})_6]$	475	730	7	N/A	112	[117]
[CoFe-isn]	$\text{Co}_2[\text{Fe}(\text{CN})_5\text{isn}]$	324	N/A	7	7.0×10^{-3} at $\eta = 400 \text{ mV}$	146	[115]

^[a] In a given abbreviation, the metal ions coordinated to nitrogen ends of the cyanide group are given before dash, and the ones after the dash symbol represent the cyanometalate precursors. For pentacyanometal-based PBAs, the ligand connected to the iron site is given after metal sites. In all PBAs, the oxidation state of Co^{II} ion is the precursor. ^[b] $\eta_{1\text{mA}}$ represents the overpotential (mV) at 1 mA/cm^2 . ^[c] Overpotential (mV) at 10 mA/cm^2 is 760 mV .

Coordinatively saturated iron ion is considered to be an inactive site in the catalytic process. In CoFe PBAs, the electron density on one metal site, however, affects the other one since PBAs fall in Class II mixed-metal compounds based on Robin-Day classification.[106]–[110] Electrochemical studies performed on CoFe PBAs indicate that the $\text{Fe}^{2+/3+}$ and $\text{Co}^{2+/3+}$ redox potentials are close to each other, which makes it difficult to differentiate from

each other.[104] A series of cobalt hexacyanometalates, $\text{Co}_x[\text{M}(\text{CN})_6]$, $\text{M} = \text{Fe}^{2+/3+}$, Co^{3+} , and Cr^{3+} , was studied to elucidate the effect of the hexacyanometalate group on the water oxidation activity of cobalt sites.[113] Although the morphology and surface concentration are similar, the TOF value of the cobalt site in CoM PBAs ranges dramatically from $3 \times 10^{-3} \text{ s}^{-1}$ for $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$ PBA to $5 \times 10^{-2} \text{ s}^{-1}$ for $\text{Co}^{\text{II}}\text{Fe}^{\text{II}}$ PBA. Therefore, the hexacyanometal group bears a clear electronic effect on the catalytic activity of cobalt sites. A catalytic mechanism is also proposed, which is supported by experimental studies and theoretical calculations (Figure 2.6b). The $4e^-$ mechanism, similar to the oxide-based mechanism, involves the oxidation and activation of the catalytic site by four proton-coupled electron transfer (PCET) to yield a high-valent metal-oxo species. This active species is attacked by a nucleophilic water molecule to form a peroxo species, which is then released as an oxygen molecule. Since the relatively long distance between two cobalt sites in a PB structure prevents the collaboration of active sites for catalysis, the $4e^-$ water oxidation process is considered to occur on just one cobalt site. Similar to the water oxidation mechanism in cobalt oxides, one of the two critical steps, the oxidation of Co^{3+} to a higher oxidation state or the nucleophilic attack of the water molecule to a cobalt-oxo species, should be the rate-determining step in PB systems. The nature of these two steps differs from each other since an increase in the electron density of catalytic cobalt sites decreases the rate of the former process and increases the latter one. The cyanide stretching frequency (ν_{CN}) by infrared spectroscopy is monitored to evaluate the electron density of cobalt sites since ν_{CN} provides a rough comparison of the electron densities of PBAs. The shift in the cyanide stretch to higher frequencies is well correlated with the enhancement in water oxidation activity in a series of CoM PBAs, which suggests that the nucleophilic attack of the water molecule should be the rate-determining step.

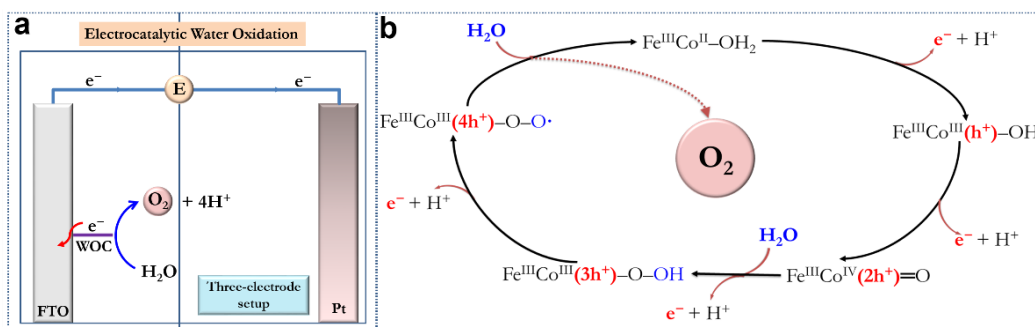


Figure 2.6 Schematic of (a) a general EC water oxidation setup including a WOC deposited on FTO coated glass, reference electrode (not shown in the figure), and a

metal cathode that is immersed in an electrolyte and connected by an external electric wire, and (b) the responsible PCET mechanism for EC water oxidation with CoFe PBAs. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

ii. Changing the cobalt precursor: Not only the cyanide precursor but also nature and coordination environment of cobalt ions play a critical role in the catalytic performance of PBAs. Since cyanometalates react rapidly with bare cobalt ions, the growth of PB structure can be controlled by employing a cobalt precursor with a relatively low solubility product in aqueous solutions. For this purpose, a Co(OH)_x coated FTO electrode was reacted with a hexacyanoferrate solution to afford CoFe PB cubic structures in the 50 nm to 1 μm range by Galán-Mascarós *et al.* [99] A surface concentration of above 100 nmol/cm^2 is obtained with these electrodes while it is only around 2 nmol/cm^2 for the previously reported CoFe PBA prepared with an electrodeposition method.[92] This method also allows strong interfacial matching with the FTO surface and PB structures, which leads to a significant enhancement in the electrocatalytic activity (Table 2.2). Electrocatalytic water oxidation studies were also performed on PBAs with the formula $\text{Co}_{3-x}\text{Fe}_x[\text{Fe(CN)}_6]_2$ to elucidate the role of iron doping in two different studies.[117], [118] While the partial substitution of cobalt sites with iron doping has no significant effect at relatively low current densities, an enhancement at high current densities (above 40 mA/cm^2) was obtained mainly due to faster charge transfer kinetics.

2.3.4. PB Based Photocatalytic Water Oxidation

An ideal WOC should not only be efficient and robust but also should have matching energy level alignment with a visible-light absorbing component such as a PS or a SC. The HOMO level of a CoFe PB structure is generally placed at a slightly lower energy level than the water oxidation half potential, making it an ideal catalyst for prospective water splitting cells.

A PS should have a lower HOMO level than CoFe PBA for the efficient charge transfer between the PS and the WOC. Once this is achieved, the hole created in the HOMO level of the PS upon excitation can be transferred to the HOMO level of PB to activate the catalytic site (Figure 2.7a). An electron scavenger (ES) in the electrolyte is necessary to consume the electrons in the LUMO level of the PS, which provides its charge balance by accepting electrons from the water oxidation process (Figure 2.7b).

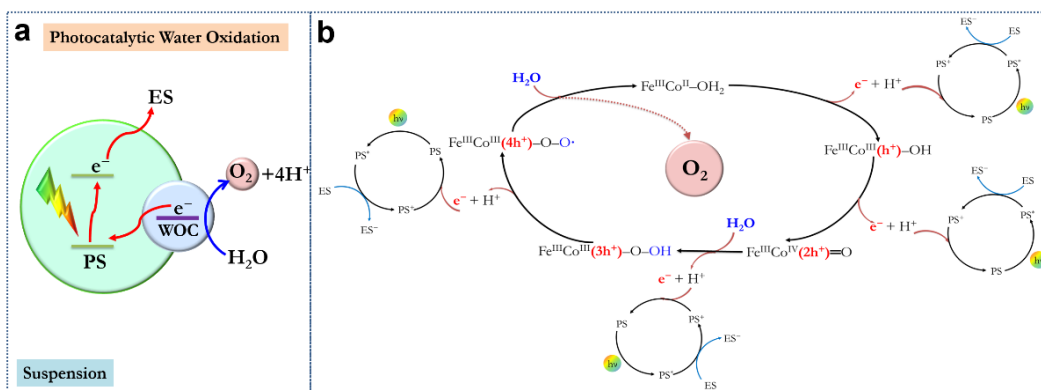


Figure 2.7 Schematic of (a) a general PC water oxidation setup including a PS, WOC, and ES in an electrolyte, and (b) the responsible PCET mechanism for PC water oxidation with CoFe PBAs. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

One of the well-known photosensitizer-electron scavenger (PS/ES) couples, $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$, has been commonly used in several studies to evaluate the photocatalytic performance of PBAs.[111] The activities are generally reported through a TOF value or a quantum yield (Table 2.2). It should be noted that, in earlier studies, FeFe PBAs have also been observed to be active under similar conditions but with relatively lower activities.[119], [120] Recent studies focus on understanding the photocatalytic process in CoFe PBAs and tuning the activity by changing the constituents of the cyanide network. For example, the substitution of $[\text{Fe}(\text{CN})_6]^{3-}$ component with $[\text{Co}(\text{CN})_6]^{3-}$ or $[\text{Pt}(\text{CN})_6]^{2-}$ groups enhances the catalytic activity of cobalt sites mainly due to the above-mentioned electronic effect through a short cyanide bridging group.[121], [122] Furthermore, the partial substitution of the hexacyanometal group with a tetracyanometalate one such as the $[\text{Pt}(\text{CN})_4]^{2-}$ complex also increases the number of active cobalt sites, which is also reflected on the quantum yield (50%). Unlike electrocatalytic studies, a significant increase in the photocatalytic activity was observed with the partial substitution of cobalt sites with iron. $(\text{Fe}_{0.75}\text{Co}_{0.25})_3[\text{Co}(\text{CN})_6]_2$ was observed to be around 50% more active than $\text{Co}_3[\text{Co}(\text{CN})_6]_2$, which is attributed to the stabilizing effect of iron sites on the higher oxidation states of active catalytic sites.[122] The role of counter cation, which is largely ignored in most studies, has been investigated by Fukuzumi and co-workers.[123] Interestingly, they observed a remarkable increase in the quantum yield up to 200% when a small quantity of calcium ions (Ca:Co atomic ratio is 0.042) is incorporated into the polymeric cyanide structure.

The Lewis acidity of calcium ions is assumed to play an important role similar to its effect in the natural photosynthetic process. Although the proper energy levels and a long excited-state lifetime of Ru(bpy)₃²⁺ complex makes it one of the most widely studied photosensitizers, it suffers from easy photodecomposition and thereby limiting its use for long-term photocatalytic studies and scalable applications. Our group has shown that the stability of a ruthenium pyridyl PS could be enhanced by immobilizing it within a PB structure by utilizing a polymer as a bridging platform.[124] A non-ruthenium analog, porphyrin PS/PB assembly was prepared later, which has a similar TOF (3.2×10⁻⁴ s⁻¹) and high stability similar to its ruthenium analogs.[125] It exhibits outstanding stability throughout a 3-hours photocatalytic test and has the potential to be implemented due to its facile synthetic pathway. This finding also paves the way for the development of robust and efficient heterogeneous PB based dye-sensitized photoelectrodes for water oxidation and this consequently built up our motivation to use PBAs in dye sensitized water splitting process.

Table 2.2 PC water oxidation performances of PB based photocatalysts

Photocatalysts	Formula	TOF (s ⁻¹)	Quantum Yield	O ₂ evolved (μmol/mgh)	Ref.
[Fe-Fe]	Fe ^{III} ₄ [Fe ^{II} (CN) ₆] ₃	N/A	2	N/A	[119]
[Co-Fe]	Co ₃ [Fe(CN) ₆] ₂	4.5×10 ⁻⁴	52	N/A	[111]
[Co-Co]	Co ₃ [Co(CN) ₆] ₂	8.1×10 ⁻⁴	88	N/A	[111]
[Co-CoPt]	[Co ^{II} (H ₂ O) ₂] _n [Co ^{III} (CN) ₆] _{0.63} [Pt ^{II} (CN) ₄] _{0.37}	N/A	50% 450 nm light	N/A	[121]
[Fe _{0.75} Co _{0.25} -Co]	(Fe _{0.75} Co _{0.25}) ₃ [Co(CN) ₆] ₂	N/A	6.9	N/A	[122]
[Co-Co]	Co ₃ [Co(CN) ₆] ₂	N/A	N/A	N/A	[122]
[CaCo-Co]	Ca _{0.06} Co ^{II} _{1.44} Co ^{III} (CN) ₆	N/A	200	N/A	[123]
[CoFe-TPyP]	Co ₆ [(Fe(CN) ₅) ₄ -porphyrin]	3.2×10 ⁻⁴	N/A	2.2	[125]
[CoFe-Ru]	Na _{0.96} Co _{2.86} [Fe(CN) ₅] _{2.13} -[P4VP] ₆ -[Ru(bpy) ₂] _{2.29} Cl _{2.29}	4.5×10 ⁻⁴	N/A	1.85	[124]
[CoFe]@[CoCo]	[Cu ^{II} _{1.5} [Fe ^{III} (CN) ₆] ₆]@[Co ^{II} _{1.5} Co ^{III} (CN) ₆]	N/A	N/A	2.05	[105]
[CuCo]@[CoCo]	[Cu ^{II} _{1.5} [Co ^{III} (CN) ₆] ₆]@[Co ^{II} _{1.5} Co ^{III} (CN) ₆]	N/A	N/A	1.5	[105]

2.3.5. PB Based Photoelectrochemical Water Oxidation

Photocatalytic studies encouraged scientists to couple PB based WOCs with proper SCs for the development of water oxidation photoanodes. One of the main criteria for preparing such a photoelectrode is the proper match between the energy levels of different components. The PEC process is initiated with the

excitation of the electrons in the SC from the VB to the CB. Then, once there is a proper energy match, the electrons from the PB catalyst are transferred to the SC VB, which leads to the oxidation of cobalt sites to become active catalysts for water oxidation. The common PEC mechanism is slightly different from the photocatalytic one. The electrons are transferred from PB to the SC rather than the chromophore, and then to the cathodic compartment, which is a standard Pt metallic electrode (

Figure 2.8a). The proposed mechanism is similar to the photocatalytic process, which is initiated by using photons by the SC to yield electrons in the CB and holes in the VB (

Figure 2.8b).

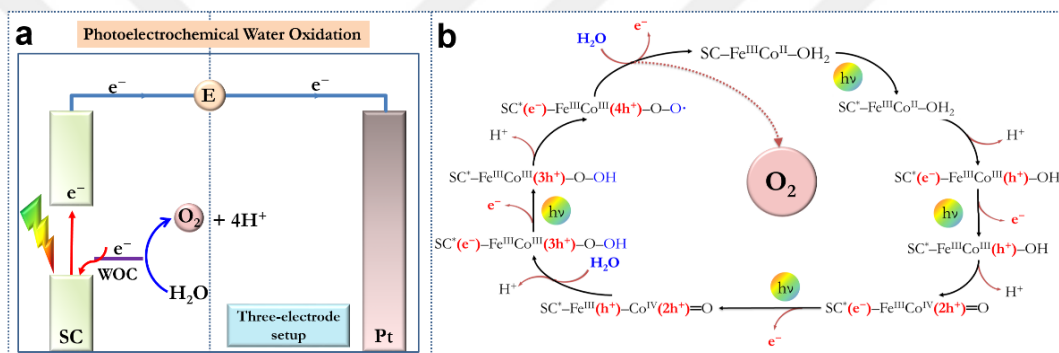


Figure 2.8 Schematic of (a) a general PEC water oxidation setup, including a photoanode that consists of a SC and WOC immersed in an electrolyte, and (b) the responsible PCET mechanism for PEC water oxidation with CoFe PBAs. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

The holes are then transferred to the cobalt sites to activate them for the water oxidation process. For an efficient charge transfer, the VB of the SC should be placed at a slightly lower energy level than the HOMO level PB. Furthermore, the relative energy difference between the VB of SC and the HOMO level of PB ($\Delta_{\text{HOMO-VB}}$) and between the CB of SC and the HOMO level of PB ($\Delta_{\text{CB-HOMO}}$) could be compared to evaluate their performances. The effect of the energy level alignment on the performance of PB coated SCs is shown in Figure 2.9. To date, various SCs have been coupled with PBAs to realize water oxidation photoanodes, as shown in Table 2.3. All of the SCs studied up to now have lower VB energy levels than the HOMO of CoFe PBA. In the case of PB/TiO₂, the CB is located at closer proximity compared to the VB, which results in poor PEC performance due to electron-hole recombination between the CB of SC

and HOMO level of PB.[126] In this case, the PB structure acts as a trapping center that mediates the electron-hole pair recombination. A similar scenario is also observed for PB/Fe₂O₃. [127] Galán-Mascarós and co-workers coated Fe₂O₃ nanowires with a thin layer of TiO₂ and upon annealing at high temperature a shell layer of Fe₂TiO₅ was formed. In this way, the energy levels (VB and CB) of Fe₂O₃ shift upwardly for a better energy level alignment.[128] This modification yields a photocurrent density of 1.25 mA/cm² at 1.23 V_{RHE}, which is almost one order of magnitude higher compared to the pristine Fe₂O₃ nanowires. BiVO₄, on the other hand, inherently has a proper band energy alignment among the recently employed SCs in this field. Both CoCo and CoFe PBAs enhance the photocurrent densities when they are coupled to BiVO₄. [129]–[131] Transient absorption measurements reveal that a PBA coating enhances performance by presenting a favorable interface for efficient hole transfer, thereby retarding recombination in the semiconductor, combined with the catalytic function necessary to drive water oxidation.[132]

Pires et al. also examined the use of cobalt pentacyanoferrate derivatives with different auxiliary ligands (CoFe-L; L = CN, NH₃, isn, and mpz) on PEC performances of BiVO₄ photoanodes and investigated the effect of the ligand on the relative alignments of the band edges.[133] They observed that the modification of Fe(CN)₅ precursors lead to less unfavorable loss of charge transport mobility and a favorable effect on the photocurrent generation compared to the hexacyanoferrate analog. PB coated BiVO₄ electrodes have also been coupled with Au plasmonic nanoparticles to further enhance the photocurrent performance under neutral conditions.[134] The resulting plasmonic-catalyst hybrid design exhibits a photocurrent density as high as 1.33 mA/cm² at 1.23 V_{RHE}. This study, in particular, shows that the diverse and facile cyanide chemistry allows the incorporation of proper units into cyanide-based photoelectrodes. As seen from the above-mentioned results, the PB based designs are essentially used as a catalyst that promotes the activity of a photoactive layer. However, in this thesis, we developed various designs in which PBA not only acts as a WOC but also as the active center that absorbs incoming photons. PB assemblies have been utilized to develop dye-sensitized water oxidation photoanodes. In this assembly, the dye acts as a molecular visible light absorbing material to generate electron-hole pairs, as shown in Figure 2.10a. The proposed mechanism involves the excitation of the PS with visible light to yield charge separation (Figure 2.10b). In an ideal scheme, the electrons in the excited state are then transferred to the CB of the SC, which is positioned at a lower energy level compared to the LUMO level of the PS. The

holes, which are required for the water oxidation process, are transferred first to iron sites and to catalytic cobalt sites due to their proper HOMO levels. Therefore, the mechanism implies that iron sites that connect the PS to the cobalt sites could participate also in the charge transfer process. Upcoming chapters will explain all the developed design architectures in which PBA is used to fabricate photoactive water oxidation components.

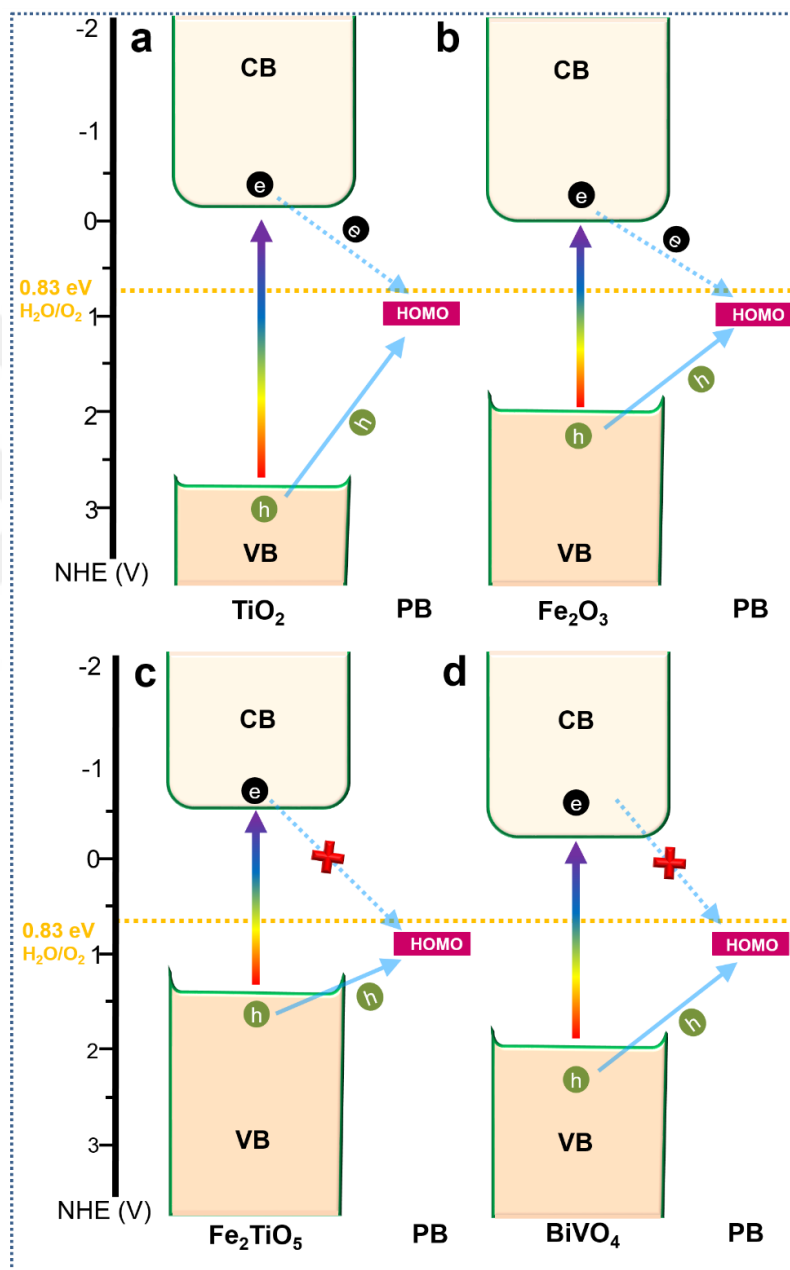


Figure 2.9 Schematic illustration of band energy levels for different CoFe PBA incorporated SC photoelectrodes under neutral conditions, pH 7: (a) PB/TiO₂, (b) PB/Fe₂O₃, (c) PB/Fe₂TiO₅, and (d) PB/BiVO₄. The ideal band alignment requires a condition in which ($\Delta_{\text{HOMO-VB}}$) should be smaller than ($\Delta_{\text{CB-HOMO}}$). Since both PB/Fe₂TiO₅ and PB/BiVO₄ do meet this condition, they have less probability of

photoexcited carriers' recombination (shown as a red cross) at the HOMO level of PB compared to the other two systems. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Table 2.3 PEC water oxidation performances of PB based photoelectrodes.

Photoanode*	$j @ 1.23 V_{RHE}$ (mA/cm ²)**	Illumination	Electrolyte	Ref.
[Co-Fe ^{III}]/BiVO ₄	~1.1	450W Xe lamp; AM1.5 solar filter; 1sun (100 mW/cm ²)	pH 7 (0.1 M KPi buffer)***	[132]
[Co-Fe ^{III}]/BiVO ₄	0.92	450W Xe lamp; AM1.5 solar filter; 1sun (100 mW/cm ²)	pH 7 (0.1 M KPi buffer)	[129]
[Co-Co ^{III}]/BiVO ₄	~0.25	AM1.5 solar filter; (100 mW/cm ²)	pH 7 (0.2 M K ₂ SO ₄)	[130]
[Co-Co ^{III}]/V ₂ O ₅ /BiVO ₄	~0.63	N/A; solar spectrum	N/A: aqueous solution	[131]
[Co-Fe ^{III}]/Fe ₂ O ₃	~0.23	450W Xe lamp; AM1.5 solar filter; 1sun (100 mW/cm ²)	pH 7 (0.1 M KPi buffer)	[127]
[Co-Fe ^{III}]/Fe ₂ TiO ₅ /Fe ₂ O ₃	1.25	150 W Xe lamp; AM1.5 solar filter; 1sun (100 mW/cm ²)	pH 1 (0.1 M NaNO ₃ + 0.1 M HNO ₃)	[128]
[Co-Fe ^{III}]/TiO ₂	~0.5	300W Xe lamp; AM1.5 solar filter; 1sun (100 mW/cm ²)	pH 7 (0.1 M KPi buffer)	[126]
[Co-Fe ^{III}]/BiVO ₄	1.33	300W Xe lamp; AM1.5 solar filter; 1sun (100 mW/cm ²)	pH 7 (0.1 M KPi buffer)	[134]

*Assemblies are deposited on FTO coated glass. ** For those, which do not report potentials versus RHE, the potentials are converted as follows; $1.23 V_{RHE} = 0.62 V_{Ag/AgCl}$ at pH 7. *** A 0.1 M solution of potassium phosphate (KH₂PO₄) buffer at pH = 7 (± 0.1).

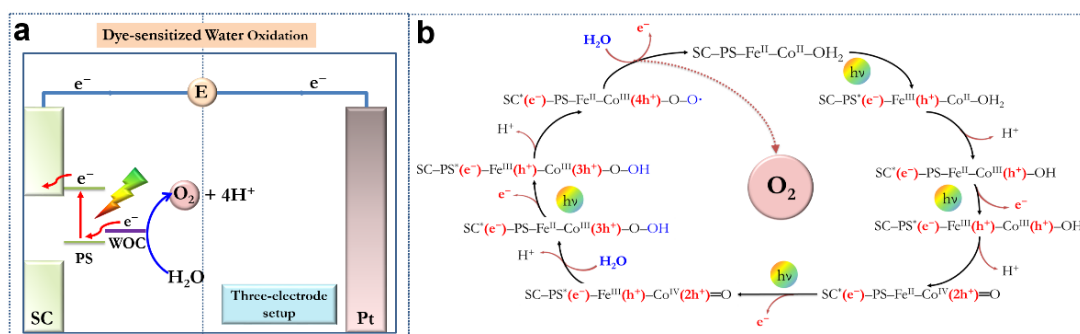


Figure 2.10 Schematic of (a) a general DS-PEC water oxidation setup, including a photoanode that consists of a dye-sensitized SC and WOC immersed in an electrolyte, and (b) the responsible PCET mechanism for PEC water oxidation with CoFe PBAs. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Chapter 3. Characterization Methods and Instrumentation

The experiments and characterization studies are conducted in Karadas Group Laboratories in the Chemistry Department and at UNAM, Bilkent University.

Transient absorption spectroscopy measurements are performed in Ankara University, Prof. Gul Yaglioglu's lab.

Computational studies are performed by Prof. Yavuz Dede (Gazi University) and Prof. Engin Durgun (Bilkent University).

Throughout this thesis, we have used several materials, optical and (photo)electrochemical characterization techniques. In the context of this chapter, we aim to provide an overview of these characterization methods along with the required theory to understand the performed measurements. In addition, we will briefly introduce related computational methods as well.

3.1. Material Characterizations

For the material synthesis and preparation, we employed various processes such as co-precipitation, sequential dip-coating, hydrothermal technique, spin-coating, immersing, electrodeposition, atomic layer deposition, and thermal evaporation. For structural characterizations in micro- and nano scales on both electrodes and the bulk materials, we have employed several tools:

- *Crystallinity, morphology, growth dimensions, imaging purposes, elemental composition*: Transmission Electron Microscopy (TEM, Tecnai G2-F30, FEI), High-resolution TEM (HR-TEM), Energy dispersive X-ray detector (EDX), Selected Area Electron Diffraction (SAED), and Scanning Electron Microscopy (SEM, FEI – Quanta 200 FEG), TEM Energy Dispersive X-ray Spectroscopy (TEM-EDS) line scan
- *Elemental composition, chemical bonding states, surface defects, oxygen vacancies, valence band maxima, oxidation states*: X-Ray Photoelectron Spectroscopy (XPS, ThermoScientific, Al K-Alpha radiation, $h\nu = 1486.6$ eV),
- *Crystallinity, crystal type, diffraction peaks*: X-ray Diffractometer (XRD, Panalytical X'pert Multi-Purpose),

- *Crystallinity, functional bonds formation (Cyanide, Metal-Carbon, Metal-Nitrogen stretches, etc.):* Raman Spectroscopy (WITecAlpha 300S scanning near-field optical microscope with Raman module),
- *Functional groups formation (Cyanide stretch, Fe-N coordination bond, N-H stretch, Fe-CN-Co coordination mode):* Fourier Transform Infrared Spectroscopy (ATR-FTIR, Bruker ALPHA Platinum-ATR spectrometer).
- *Spin orbital analysis:* X-band (9.86 GHz) EPR measurements were performed with Bruker EMXNano spectrometer (EPR spectroscopy). The magnetic field was determined using an NMR gaussmeter (ER 035M, Bruker). For magnetic-field calibration, polycrystalline DPPH with $g = 2.0036$ was used, which is already integrated to the spectrometer.

3.2. Optical Characterizations

Beyond electron-material interaction, the optical interactions (light-material interactions) can also provide further information about the material. For understanding the light-dependent processes which occur at the surface of electrodes and determining the below optical characterizations, we used the following instruments:

- *Absorbance, transmittance, reflectance, band gap, molar absorption coefficient, photocatalytic degradation testing:* Steady-State Absorption Spectroscopy (UV-Vis-NIR spectrophotometer, Cary 5000, Varian) in specular and diffuse reflection modes.
- *Fluorescence, photoluminescence, defect energetic location analysis, charge separation:* Steady-State Photoluminescence Spectroscopy (PL, Cary Eclipse).
- *Electron dynamics in energetic levels of the PS, excited state lifetime, electronic transitions in ultra-short time scales, recombination pathways related decay times:* Time-resolved Fluorescence (TRF) Spectroscopy also known as Time Resolved Photoluminescence Decay (TRPL) measurement
- *Charge transfer dynamics, excited state lifetime, injection dynamics, charge separation:* Femtosecond Transient Absorption Spectroscopy (TAS, Spectra Physics, Spitfire Pro XP, TOPAS).

3.2.1. Steady-state Measurements

3.2.1.1. Absorption spectroscopy

Solar irradiation is a broad electromagnetic wave spanning from UV to near-infrared range (approximately 300 nm to 2200 nm). All photoconversion systems convert this solar irradiation spectrum into usable electricity. The efficiency of these systems depends on the portion of the light that they absorb. Essentially for SC and dye materials, the photons with energies above the band gap can be absorbed. However, the spectral response of this absorption is an inherent property of any material. Therefore, it is crucial to understand the absorption spectral response of a material to understand its photoconversion capacity. For this aim, UV-VIS-NIR spectrophotometer is employed to explore the optical properties of the films and the dye solutions. In this measurement, a broadband light is illuminated on the sample and the transmitted signal is collected by a photodetector in other side. From this data, the absorption profile of the sample is also extracted. In the regions with stronger absorption, a larger portion of incoming photons are going to be absorbed. Besides the spectral response of the sample, this technique also provides information on the effective optical band gap of the material. The effective optical band gap is estimated using transmission/absorption data of UV-Vis-NIR spectrophotometer.

For this aim, first, the UV-Vis spectra of the films were collected via a spectrophotometer in diffuse reflection mode and the absorption value of the material is extracted considering no transmission from the sample ($A=1-R$). This absorption data is utilized to calculate the Kubelka–Munk function and resulting Tauc plot using below formula:

$$(F(R_{\infty}).h\nu)^n = B(h\nu - E_g) \quad (1)$$

In this formula, the n factor $(F(R_{\infty}).h\nu)^n$ depends on the nature of the electron transition and is equal to 1/2 or 2, for the indirect and direct transitions, respectively.[135] In this plot, the extrapolation of transition region with a linear function intersects with the x-axis in the point, which equates to the band gap, E_g , value. Briefly, using the Tauc plot, the linearity of the fitting against $h\nu$ using n are evaluated to assess the mode of transitions. For non-emissive powder and solid samples, this is the method commonly used to extract the E_g value. Specifically, the samples with large scattering cross-section, such as

nanowires, nanoparticles, nanotubes, have to be measured with diffuse reflectance mode to obtain reliable results. Because, in these architectures, the scattered light is the dominant portion of the light and their contribution should be distinguished from the absorbed part.

However, for the solutions with PL character, the band gap can be experimentally determined by the interception of normalized absorption and fluorescence/photoluminescence profiles (excitation wavelength at their main peak). In the next section fluorescence (or so-called PL spectroscopy) is studied.

3.2.1.2. Photoluminescence spectroscopy

Fluorescence or photoluminescence (PL) spectroscopy is a useful technique to investigate the material properties and dynamics taking place at a nano scale due to the high sensitivity of the photo-physical properties of the materials to even small changes in the molecular level. The main principle of operation of these tools relies on spectrally selective excitation of the samples. PL analysis is non-destructive. PL is the spontaneous emission of light from a material under optical excitation. When you excite a sample with a stream of photons having energies higher than the SC bandgap, as the consequence of this excitation, electrons will take apart from holes and will be excited to the CB. These excited electrons will be relaxed through the recombination with their counterparts at the VB. This relaxation can be radiative or non-radiative. If it becomes radiative, it shows itself as an emitted power. The spectral distribution of these PL data can be attributed to different data including the band gap, and the defect states energetic position. If the PL peak originates from CB to VB transition, it is called band-to-band emission. This peak position can be used to estimate the E_g of SCs. This transition may also occur through a trap state, which can be located anywhere inside the band gap of the SC. These photons have lower energy compared to band-to-band ones. Therefore, the emission from this trap-assisted recombination will lead to an emission at an energy lower than the E_g of the SC. The spectral position of these sub-peaks can be attributed to the energetic location of trap states.

Moreover, the intensity of this data can be used as a measure to estimate the electron-hole pair separation in a heterojunction design. Upon illumination, the excited electrons can be transferred from the CB of a material into that of other material, and via this separation, their radiative recombination probability

decreases. Thus, quenching in PL intensity can be interpreted into the electron-hole pair separation.

3.2.2. Time-resolved Transient Methods

Besides steady-state measurement that is a material property in steady-state condition, transient data can be used to probe the dynamics in time scales as small as femtosecond. In water splitting cells, the incoming light generates electron-hole pair carriers that have a probability to meet their conjugate carriers and recombine with each other. In general, recombination means a dissipation of the free energy provided by the photons to heat inside the cell and this reduces the efficiency of power conversion system and it is a must to keep its contribution as low as possible. To make this happen, we have to know carrier dynamics in transient scenarios. To scrutinize all of these kinetic processes, a proper time-resolved characterization can provide valuable information about these few micro/nano/femto seconds processes.

3.2.2.1. Transient open circuit photovoltage decay measurement

In water splitting cells, injection of electrons from the LUMO level of the dye molecules into the CB of the SC can be followed with a back reaction and in this way, a portion of excited pairs will recombine before they contribute in the water oxidation reaction. Thus, it is crucial to probe this phenomenon in ultrasmall time scales. One of the best ways to explore this phenomenon is probing the open circuit photovoltage (V_{OC}) decay (OCVD) temporal profile. The OCVD measurement is a relatively simple method firstly introduced at ([136]) for exploration of the recombination kinetics in dye-sensitized solar cells. Upon cutting off the light illumination on the device at V_{OC} , the excess electrons in the CB of SC will be removed through the recombination with the holes, and the rate of photovoltage decay is proportional to lifetime of the electrons by below expression:

$$\tau_n = -\frac{k_B T}{e} \left(\frac{dV_{OC}}{dt} \right)^{-1} \quad (2)$$

Slower recombination rate means longer electron lifetime, which in turn shows an induced retardation in recombination of the carriers, which is desired for photoconversion systems.

3.2.2.2. Time resolved photoluminescence decay spectroscopy

The above-mentioned OCVD measurement is generally used to probe the electron dynamics in microsecond scales. Moreover, it is the response of the electrons in a real device. In other words, to be able to measure OCVD, we have to make a photoconversion design. However, some processes need to be studied in nanosecond scales and at a single layer level. For this aim, another transient technique is used in this thesis studies, which is time resolved photoluminescence decay (TRPL). This technique is a useful tool to investigate lifetime decay kinetics of fluorescent materials. Using this technique, which was first explored by [137], the kinetics of electron injection from dye states to the CB of SC can be addressed. Since excited state decay kinetics are quite sensitive to molecular level interactions and their attributed dynamics, many different phenomena (e.g. rotation, diffusion, molecular conformations, molecular binding, energy transfer, charge transfer, etc.) can be directly observed through fluorescence decay curves. Simply, in a photoconversion system, we need to have long excited-state lifetimes to promote the water oxidation reaction of excited holes.

In our laboratory, we use a time-correlated single photon counting (TCSPC) system having a time resolution down to 4 ps (PicoHarp 300) integrated with a picosecond pulsed laser with an output central photon energy of 3.37 eV driven by a driver module (PDL-800 series) capable of delivering laser pulses with 80 MHz repetition rate. The system utilizes a fast photo multiplier tube (PMT) (Hamamatsu H5783 series) to resolve lifetimes on the order of tens of picoseconds. In our case, we excited the samples with a wavelength having an energy above the material band gap, and then we count the excited state electrons throughout the time to track their decay time. To probe this signal, we choose a specific probing wavelength which is within the PL spectra of the sample. The reduction in the number of these electrons show itself as a single/multiple exponential decay profile.

3.2.2.3. Ultrafast femtosecond transient absorption spectroscopy

Both techniques mentioned above are utilized to understand the carrier dynamics in micro and nanoseconds. Considering the fact that electrons transfer from one material to another junction, or thermalization of electrons to

the ground state are not ultrafast processes, these techniques are quite useful. However, the interband transitions (transitions within the CB or VB), which is a crucial factor in dye designs, cannot be probed with these materials due to the fact that these phenomena are in the femtosecond scales. These interactions can be studied with femtosecond transient absorption spectroscopy (TAS). In this technique, the material is pumped with a signal having photon energy above the band gap. After a delay in the range of fs-ns, a probe signal is sent toward the sample. In the output, the difference between pump-probe transmission is recorded for a broad probe signal range. The obtained spectra have mainly two regions; a positive region which is called excited state absorption (ESA) signal, a negative part which is called ground state bleaching (GSB). In ESA signal, pump beam excites electrons to the CB energetic levels, and afterward, if these electrons still stay in excited levels, the probe signal will be absorbed by them to jump to higher levels. Generally speaking, long lifetime ESA means a good carrier dynamics for water oxidation process. The other signal is GSB. GSB appears when the ground state is depleted with the pump photons and therefore, probe signals cannot be absorbed by the material. To perform TAS measurements, a Ti: Sapphire laser amplifier optical parametric amplifier system with 52 fs pulse duration and 1 kHz repetition rate (Spectra Physics, Spitfire Pro XP, TOPAS) and a commercial pump probe experimental setup (Spectra Physics, Helios) with a white light continuum probe was used for the experiments. Pulse duration was measured as 120 fs by cross-correlation inside the pump probe setup. The wavelength of the pump beam was chosen according to the steady state absorption spectra of studied compounds. Experimental data were analyzed by using Surface Xplorer software that is supported by ultrafast systems. In this thesis, the TAS measurement is performed to understand the carrier dynamics in dye and the electron transfer in heterojunction designs.

3.3. Photoelectrochemical Measurements

An electronic instrument that measures and controls the potential (or voltage) difference between two electrodes in an electrochemical cell is called a potentiostat. Photoelectrochemical measurements were performed using a Gamry Instruments Interface 1000 Potentiostat/Galvanostat in a conventional three-electrode electrochemical cell configuration (Bob's cell). Potentiostat cell cable connector on one end and the working electrode (WE), a reference electrode (RE), and a counter electrode (CE) on the other end.

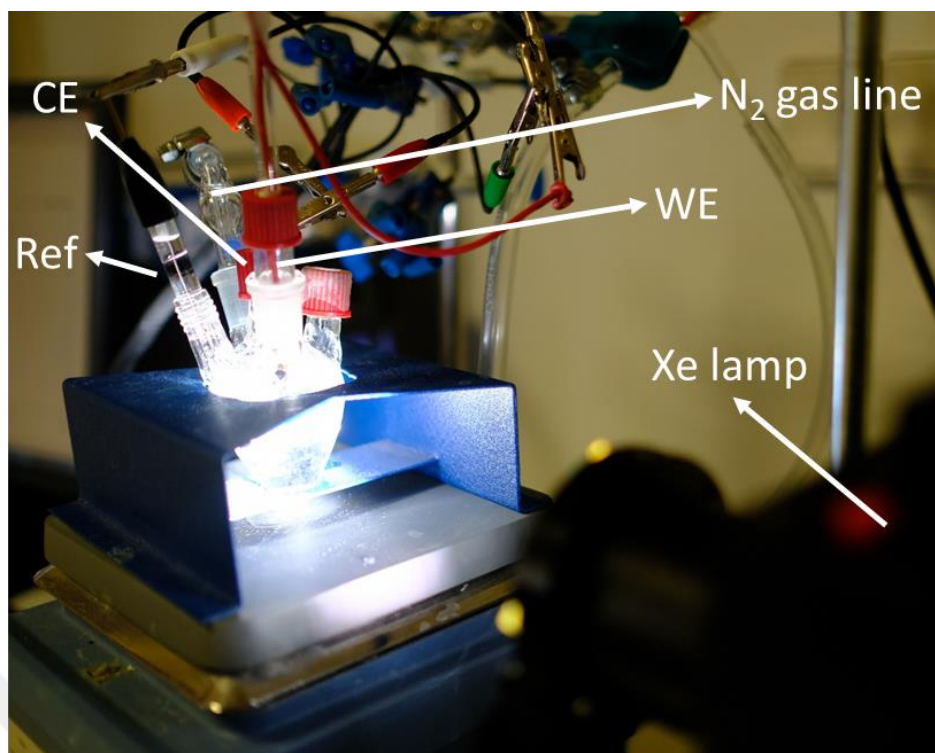


Figure 3.1 Experimental setup employed in this thesis studies. The PEC water oxidation measurements performed in an electrolyte solution under 1 sun illumination in a three-electrode cell (Dr. Bob's Cell) configuration. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

A potential controlled experiment is performed in this cell configuration; the potential of WE is held with respect to RE and current flows between the WE and CE. In the thesis studies, catalyst, dye, and/or both loaded electrodes as WE, Ag|AgCl|KCl_(sat.) as RE, and Pt mesh/wire as CE are used. These electrodes are placed in an electrically conductive solution at 25°C, which is generally a phosphate buffer neutral solution (pH=7) in our case to resemble the actual pH of the water. Before each measurement, the electrolyte was saturated with N₂ gas for 30 min to remove the dissolved O₂ gas. The experimental setup used throughout my PhD studies is shown in Figure 3.1.

Light dependent measurements were carried out using a solar simulator (Sciencetech, Model SLB-300B, 300 W Xe lamp, AM 1.5 global filter) was calibrated to 1 sun (100 mW/cm²) with a thermopile optical detector (Newport, Model 818P-010-12). Also, different cutoff filters depending on the photoanode transport host absorption profile were performed. Also, light impinges on the sample from the backside (glass side), where we have lower refractive index and lower reflectance from the surface.

For the convenience of comparison, in some cases, the potentials measured vs. Ag|AgCl|KCl_(sat.) (also denoted as V_{Ag/AgCl}) were converted to the pH independent reversible hydrogen electrode (RHE) scale using below Nernst equation:

$$E_{RHE} = E_{Ag|AgCl|KCl(sat.)} + 0.059 \text{ pH} + E^o_{Ag|AgCl|KCl(sat.)} \quad (3)$$

where E_{RHE} is potential estimated vs. RHE, $E_{Ag|AgCl|KCl(sat.)}$ is measured potential vs. Ag|AgCl|KCl_(sat.) electrode and $E^o_{Ag|AgCl|KCl(sat.)}$ is the standard electrochemical potential of the Ag|AgCl|KCl_(sat.) electrode i.e. 0.197 V.

In this thesis, the effectiveness of the catalysts and dye after surface treatment has been mainly determined utilizing the below measurements:

- *Photo and dark current characteristics, Photocurrent stability:* Linear Sweep Voltammetry (LSV), Chopped Linear Sweep Voltammetry (Chopped LSV)
- *Energy band alignment, redox potentials, half potentials, estimated chemical surface area (ESCA), HOMO&LUMO levels:* Cyclic Voltammetry (CV)
- *Short term&long terms stability, theoretical (expected) amount of O₂:* Chronoamperometry (CA)
- *Interfacial Charge transfer resistance:* Electrochemical Impedance Spectroscopy (EIS)
- *Conduction Band position, flat band potential, carrier density:* Mott-Schottky (MS)

The following section will touch on the techniques used to characterize the PEC water splitting performance and the methods for evaluating efficiencies.

3.3.1. Current-Voltage Measurement

Measurement of current-potential (I - E) or current density-potential (j - E) curves under dark and light conditions is a standard analysis to measure the PEC performance of the solar water splitting device. " j " is preferred usually which defines the ratio of photogenerated current to geometrical active area of the electrode. j - E measurements were performed in both standard three-electrode configuration and two-electrode systems.

For the j – E measurement, LSV is employed in a defined potential range. In this technique, an external voltage is applied at a specific scan rate (in V/s) (mostly 50 mV/s in our studies) in one direction (either anodic or cathodic scan) and the output current is recorded as a function of applied bias. This measurement is performed in the dark and under 1-sun irradiation, and the difference between these two profiles gives the amount of current produced using light irradiation, also called photocurrent. Moreover, chopped LSV offers a powerful method to simultaneously measure light and dark currents, under switch on/off conditions. In this thesis, chopped LSV has been widely used to evaluate the performance of devices.

CV is a very similar technique to LSV. This time, when applied voltage at a fixed rate reaches V_2 , then scan is reversed, and voltage is swept back to V_1 . This technique shows the characteristic oxidation and reduction peaks of different materials and their reversibility which defines their long-term stability. For example, PBAs have characteristic voltammetric peaks in well-defined potential ranges and scan rates depending on the pH. CV is a standard method for determining HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels of the organic compounds by measuring the redox potentials. E_{HOMO} represents the energy required to extract an electron from a molecule, which is an oxidation process and refers to E_{ox} . E_{LUMO} is the energy necessary to inject an electron to a molecule, thus implying a reduction process and refer to E_{red} . By using both LSV and CV under light and dark conditions, it can be clear that whether the material is oxygen evolving photoanodes, where the locally generated holes cause oxidation of water or not.

Finally, the electrochemically active surface area (ECSA) can also be estimated by measuring the electrochemical capacitance of the electrode–electrolyte interface in the double-layer regime (non-faradaic region) of the cyclic voltammograms. The anodic and cathodic capacitive currents were estimated from the non-faradaic region in which charge transfer is directly stemming from the scan rate (charge accumulation) rather than a chemical reaction. The plot of capacitive currents with respect to scan rates gives a straight line, and the slope is equal to double layer capacitance (C_{DL}). Thus, ESCA is linearly proportional to C_{DL} and can be calculated as:

$$ECSA = C_{\text{DL}}/C_s \quad (4)$$

C_s stands for the specific capacitance of standard electrode materials on a unit surface area.

3.3.2. Chronoamperometry

This technique is generally performed to evaluate the system stability under a fixed bias potential under dark and light conditions. In chronoamperometry (CA) measurement, $i-t$, a fixed potential (typically 1.23 V_{RHE} for O₂ evolution) is applied, and the resulting current is recorded as a function of time. If the current is steady under light and dark conditions, then the system is called stable in terms of charge transfer kinetics. This experiment is performed under constant bias voltage and for a duration from seconds to hours.

3.3.3. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) under light and dark conditions were conducted in the three-electrode setup. EIS spectra were recorded in the frequency range from 100 kHz to 0.1 Hz at a bias of 1.23 V_{RHE} with an alternating current (AC) voltage of 10 mV. From this measurement, a Nyquist plot is achieved that sketches the real part of impedance vs the imaginary part. This plot is commonly a semi-circle design in which the radius of the circle shows charge transfer resistance. A smaller radius means lower charge resistance and so favorable electron dynamics along with the photoanode-electrolyte interface. Since PB has an insulating nature, it exhibits a quite large resistance once it is formed as a thick bulk on SC.

3.3.3.1. Mott-Schottky Analysis

As a part of EIS experiment, Mott–Schottky (MS) relation was investigated and analyzed by performing EIS measurements in a three-electrode cell. The measurements were performed at potentials varying between -1 and 0.4 V_{Ag/AgCl} (depending on the material), where the frequency is set at a fixed value ranging in 1-5 KHz. This is a classical method of determining the flat band -potential (V_{fb}) of the semiconductor. From C^{-2} vs. E dependence, the V_{fb} can be determined by fitting theoretically MS equation:

$$\frac{1}{C_{sc}^2} = \frac{2}{(\epsilon_r \epsilon_o A^2 e N_d)} \times \left(V_{Applied} - V_{fb} - \frac{k_B T}{e} \right) \quad (5)$$

where C_{SC} is the space charge layer capacitance, e is the charge of an electron, ϵ is the relative permittivity of the semiconductor, ϵ_0 is the vacuum permittivity, A is the surface area, N_d is the majority carrier density, $V_{Applied}$ is the applied voltage (vs. Ag/AgCl), V_{fb} is the flat band potential, k_B is Boltzmann constant, and T is the absolute temperature.

V_{fb} can be found by interpolating the linear fitting of the transition region of MS plot with the x-axis. After determining this potential, from the previous studies, the CB position of the material can be estimated. Moreover, the slope of MS plot shows the conductivity of the sample. Smaller slope means higher carrier density and electron conductivity.

3.3.4. Band Energy Diagrams

The energy band model is crucial to understand device dynamics because it is the place where charge generation, separation and transfer, take place under light illumination. To fulfill the energy requirements and to elucidate the PEC results, it is essential to predict the VB, CB, or HOMO, LUMO levels of the system components. The bandgap of a semiconductor could be estimated with different techniques such as UV-Vis-NIR spectroscopy which is explained above. There is, however, no straightforward experimental method for determining band energy levels. One can only estimate these parameters by coupling optical methods (UV-Vis-NIR spectroscopy and PL methods), electrochemical methods (CV, LSV), and/or X-Ray spectroscopy techniques. It should be noted that each method has its own limitations. Moreover, these band diagrams, especially for organic systems, can contain multiple partially-filled bands as well as multiple completely filled and completely empty bands. In this regard, computational methods could be utilized to investigate their electron densities. In this thesis, optical band gap values are discussed based on a variety of characterization techniques, most of which rely on CV and MS plots.

3.3.5. Efficiency Definitions

Several efficiency requirements should be considered to describe the efficiency of a water oxidation device. These terms are listed in this section.

3.3.5.1. The applied bias photon-to-current efficiency

Unfortunately, most of the photoelectrodes are not able to split water under short-circuit conditions without additional overpotential by applied external electrical bias. Thus, the j - E response measured by the potentiostat as an energy difference between the WE and CE, the applied bias photon-to-current efficiency (ABPE) can be deduced to characterize the performance of the interfaces or materials with the following formula:

$$ABPE(\%) = \left[\frac{|j_{ph}| \times (V_{th} - |V_b|)}{P_{total}} \right]_{AM\ 1.5} \times 100 \quad (6)$$

where j_{ph} is the photocurrent density at the specified applied potential (mA/cm²), V_{th} is the theoretical water-electrolysis voltage (1.23 V), V_b is the applied potential (V vs RHE, V_{RHE}), and P_{total} is the incident power density of the light (mW/cm²). The desired efficiency is a value near 100 and a peak voltage as low as possible.

For oxygen evolution experiments, voltage is swept from a lower limit to a higher one with a specific scanning rate. Although this critical parameter is a qualitative comparison with different water splitting devices, it is not commonly used. These efficiency values are quite low when the photon absorbing material exhibits low photoconversion values.

3.3.5.2. Charge transfer efficiency: Hole (O₂) scavenger measurement

Using sacrificial agents is a common method to investigate one of the reactions of the water splitting process to satisfy the kinetic and thermodynamic potentials. For example, when an O₂ scavenging electrolyte, also known as a hole scavenger (h_s), is used, photogenerated holes are remarkably consumed by the sacrificial reagents resulting in an enhancement in charge separation. Hence, a maximum charge-transfer efficiency (η_{CT}) obtained in a cell is acquired with the assumption that no back reaction or surface recombination occur. For this purpose, LSV measurements in O₂ scavenging electrolyte under light conditions are performed to model the ideal condition. To calculate η_{CT} , the below formula is used:

$$\eta_{CT} = \frac{j_{H2O}}{j_{hs}} \quad (7)$$

Charge transfer efficiency describes the efficiency of a material to separate the excited carriers and their contribution to water oxidation reaction. It is also used to predict the amount of defects in the SC/electrolyte interface. It should be noted that the concentration of the hole-scavenging electrolyte should be high enough to obtain the maximum (100% efficient) charge transfer. In this thesis, 1 M Na₂SO₃ solution is used as the h_s to elucidate this process.

3.3.5.3. Faradaic efficiency: Oxygen evolution activity measurement

Faradaic efficiency for a PEC cell describes the contribution of the water oxidation reaction to the photocurrent generated. To calculate the Faradaic efficiency, the amount of evolved O₂ measured by the O₂ probe or gas chromatograph is divided to the theoretical (expected) amount of O₂ extracted from the CA experiment in a gas-tight three-electrode electrochemical cell.

$$\text{Faradic efficiency (\%)} = \frac{n_{\text{evolvedO}_2}}{n_{\text{theoreticalO}_2}} \quad (8)$$

In this formula, the theoretical oxygen amount is calculated from CA measurement. The theoretical oxygen evolution amount was calculated from the total amount of charge Q (Coulomb) through the PEC cell by integrating the area underneath i - t characteristics obtained from the CA measurement. Assuming that four holes are needed to produce one O₂ molecule, the theoretical O₂ amount in a mole can be calculated as follows:

$$Q = n_{O_2} \times 4 \times F \rightarrow n_{\text{theoreticalO}_2} = \frac{(i \times t)}{4 \times 96485} = \frac{\frac{A.s}{A.s}}{\frac{A.s}{mol}} \quad (9)$$

The number of moles of O₂ in the headspace produced under chronoamperometric conditions (1.23 V_{RHE}) given by the oxygen-sensing probe (Ocean Optics NeoFOX oxygen-sensing system equipped with a FOXY probe) under 1 sun illumination is calculated from the ideal gas law as follows:

$$n_{\text{evolvedO}_2} = \frac{(P_{O_2} \times V_{gs})}{R \times T} \quad (10)$$

where n_{O_2} = number of moles of O_2 ; V_{gs} = oxygen gas-space volume (in L); R (gas constant) = 0.082 atm L/mol K; and $T = 298$ K.

As mentioned above, the amount of evolved oxygen could also be determined by gas chromatography. In this method, a Xe lamp (300 W) is used as a light source and oxygen evolution is monitored with an Agilent 7829A gas chromatograph (Agilent Technologies, Wilmington, Delaware, USA). The system is equipped with a thermal conductivity detector (TCD), one split/splitless inlet (2:1 split ratio), and an Agilent 19095P-MS0 column (30 m $\times$ 530 μ m $\times$ 25 μ m HP-PLOT MoleSieve 5A: 3915.56054). The oven temperature is 40 °C. The temperatures of both the injection port and the thermal conductivity detector are set to 100 °C. Argon gas is used as the carrier gas at a flow rate of 4 mL/min. 100 μ L of the gas mixture is injected into the gas chromatograph using Hamilton SampleLock syringe (1750SL, volume 0.5 mL, needle size 22 ga bevel tip, and needle L 51 mm). A lower-bound TOF is determined by assuming that all cobalt ions in the bulk sample are catalytically active. The total amount of O_2 produced is calculated as the sum of the O_2 in the headspace (determined by GC) and the O_2 gas dissolved in the solvent (calculated using Henry's Law, with a constant of 769 atm⁻¹).

3.3.5.4. Incident photon to-current conversion efficiency

Incident photon-to-current conversion efficiency (IPCE) is a measure of conversion efficiency of photons to electrons (current) at each wavelength. The IPCE term for a PEC water oxidation electrode involves the photon absorbance, the charge separation, and the charge transportation from semiconductor to the electrolyte.

A white incident lamp (150 W Xe) is supplied as an illumination source for the IPCE measurement. The light is entered into a specific monochromator (Oriel 1/8 m cornerstone, 1200 lines/mm diffraction grating) and focused on the photoelectrode surface in the same three-electrode setup as described above. The cell is biased at 1.23 V_{RHE} using a computer-controlled potentiostat (CH instrument), and the resulting dark and light currents with a specific wavelength (step: 10 nm/step) were recorded. To elucidate the origin of the photocurrent, these two current values are subtracted from each other at different incident light wavelengths. To generate the IPCE throughout the UV and visible spectra, the following formula is used:

$$IPCE (\%) = \frac{1240}{\lambda} \times \frac{j}{P_{light}} \times 100 \quad (11)$$

where j is the photocurrent density (mA/cm^2), λ is the incident light wavelength (nm) from monochromatic light, and P_{light} is the power density of monochromatic light at a specific wavelength (mW/cm^2). The standard silicon photodiode (Thorlabs) was used to calibrate and measure the incident power density. It is also used to measure the monochromatic light in every single wavelength during an IPCE experiment. Moreover, to suppress the existence of higher order harmonic modes stemming from the reflections off the diffraction grating, a 500 nm high-pass filter at (Newport FEL0500) is employed at measurements above 500 nm.

In general, IPCE is a technique that provides information on the spectral response of the material under different incoming photon energies. It shows how efficiently a SC can convert incoming photons into e-h pairs and collect them toward the output circuit.

3.4. Electronic Structure Calculations

During four different publications of this thesis, two types of electronic structure calculations were employed. The theoretical calculations were performed by Prof. Yavuz Dede (Gazi University) and Prof. Engin Durgun (Bilkent University) research groups. The details of these calculations can be found in the resultant four papers of this thesis.

In summary, first, quantum chemical calculations were employed, which is ideal for molecular systems/models and small fragments of the catalyst. Herein, single molecule approach was kept and couple it with electronic calculations performed on the extended network by employing periodic boundary conditions (PBC). The primary goal of the first principles PBC calculations is to work with a more complete/correct description of the catalyst assembly and to predict the HOMO-LUMO bandgap. Note that the exact atomistic details of the catalyst cannot be revealed since these structures consist of molecular structures with different sizes that are connected to each to form a non-stoichiometric extended structure. Thus, ab initio calculations of a bulk phase were also reported. This structural description is also confirmed by these calculations since the experimentally obtained energies fall in between a molecular and a calculated

crystalline structure. The molecular system is also required to study the excitations at the molecular level. Molecular calculations provide qualitative data on energies and excitations. Note that calculations on the extended system and molecular calculations agree in their deductions. They differ only in the magnitude of the energies. Since the molecular system uses a small truncated model we do not dwell on the energies calculated with the molecular model. On the other hand, despite the small size of the molecular model, we can successfully employ to draw qualitative conclusions on the electronic structure of the ground states and characteristics of the excitations.

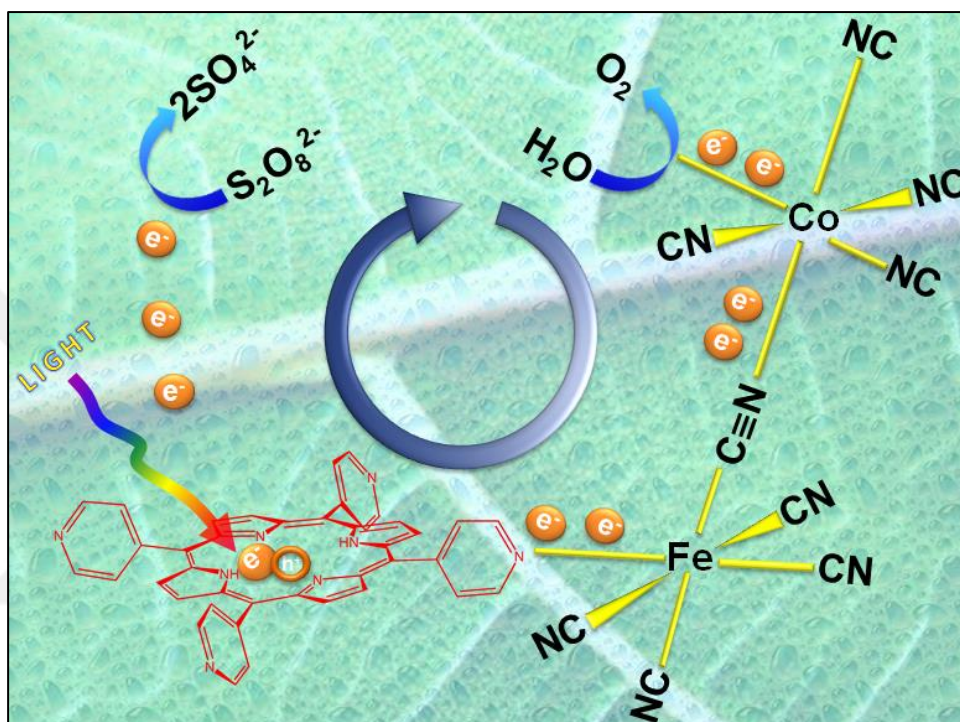
Overall, ***The first-principles electronic structure calculations*** based on density functional theory with periodic boundary conditions (PBC-DFT) were employed by using Vienna Ab initio Simulation Package (VASP).[139]–[142] The generalized gradient approximation (GGA-PBE) was chosen to describe the exchange-correlation functional.[143] The projected augmented wave (PAW) method[144] with a kinetic energy cutoff of 520 eV was used to define element potentials. All of the molecules were isolated in a cubic cell with a vacuum space of 15 Å to prevent a spurious interaction between periodic images. The structural relaxations were performed by using conjugate gradient optimization allowing 10^{-5} eV energy tolerance between two sequential steps and allowing a maximum of 0.01 eV/Å force on atoms. On top GGA-PBE, Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional approach, which is formed by mixing 25% of the Fock exchange with 75% of the PBE exchange and 100% of the PBE correlation energy was employed to elucidate molecular levels more accurately.[145] To treat the strong on-site Coulomb interaction of localized d-electrons, DFT+U method was also applied by using Dudarev approach, and apart from HOMO-LUMO gaps, similar electron localization features were obtained.[146]

Quantum chemical calculations were performed using the Density Functional Theory (DFT)[147]–[150] as implemented in the Gaussian 09 software suit.[151] Molecular fragments were employed in the chemical model. Geometries were fully optimized with B3LYP[149], [152] functional and effective core potential of Hay and Wadt, LANL2DZ,[153], [154] without any constraints on the symmetry. Vibrational frequency calculations on the optimized geometries ensured that the geometries correspond to the minima. Dunning's correlation consistent triple zeta basis set, cc-pVTZ,[155] was used in single point runs. This level of theory was found to be adequate for the description of electronic states and their relative energies in recent works.[113], [125], [126]

All possible spin states were evaluated to identify the ground electronic states for all structures. Discussions were based on the ground electronic states, i.e. $S=0$ for PP and [Fe-PP], and $S=3/2$ for [CoFe-PP].

Time Dependent Density Functional Theory (TD-DFT) was employed for calculating electronic absorption spectra in combination with the triple zeta, cc-pVTZ[155] basis set. Long range corrected functional of Yanai,[156] CAM-B3LYP, is used for the TD-DFT calculations. CAM-B3LYP was found to be successful for the correct evaluation of excitation behavior in similar systems.[125], [126] Solvent environment is modeled with the PCM approach[157]–[159] utilizing the parameters of ethanol and water as implemented in Gaussian 09. Excitations with small oscillator strengths ($f < 0.02$) were excluded from the discussions. Molecular orbitals were plotted with the Chemcraft Program[160] using a contour value of 0.03.

Chapter 4. Porphyrin Incorporated PB Assembly for Photocatalytic Water Oxidation



4.1. Preface

This chapter of the thesis is based on the publication "A Noble-Metal-Free Heterogeneous Photosensitizer-Relay Catalyst Triad Catalyzes Water Oxidation under Visible Light", T. G. Ulusoy Ghobadi, E. Akhuseyin Yildiz, M. Buyuktemiz, S. Sadigh Akbari, D. Topkaya, Ü. İşci, Y. Dede, H. G. Yaglioglu, F. Karadas, **Angew. Chem. Int. Ed.** 2018, 57, 17173 – 17177. Adapted (or "Reproduced in part") with permission from John Wiley and Sons, Ref. [125]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.2. Introduction

Artificial photosynthesis, which harnesses sunlight to split water, is a chemical transformation of utmost interest.[161] Several innovative photoelectrochemical cells for water splitting have been proposed since the pioneering work by Fujishima and Honda.[19], [162] Of these, DS-PECs utilize covalently coordinated chromophore-water oxidation catalyst (WOC) dyad assemblies [66], [163], [164] in an effort to mimic natural photosynthesis. This approach has further been expanded by integrating suitable donor and acceptor units to prepare molecular triads, tetrads, and pentads for efficient charge separation.[165]–[167] Molecular ruthenium complexes (as photosensitizers and/or WOCs) remain the most widely used despite their high cost and easy decomposition under photocatalytic conditions.[65], [168]–[176] Although the use of robust heterogeneous assemblies such as oxides could be a promising solution to improve stability, the lack of complete control on the coordination of metal ions in oxide chemistry does not allow the preparation of oxide-based dyads.[177] On the other hand, many cyanide-based assemblies have been prepared previously via a building block approach, similar to the preparation of dyads.[178]

Different perspectives of cobalt based PBAs as WOCs have recently been explored by us and other researchers.[99], [112], [121], [127], [129], [179], [180] PBAs consist of earth-abundant elements, perform at relatively low overpotentials (<500 mV for a current density of 1 mA/cm²), exhibit exceptional stabilities in a wide pH range (from 1 to 13), and can operate even with molecular chromophores for light-driven catalysis.[111] Recently, we employed a pentacyanoferrate complex rather than a hexacyanometal precursor to prepare an amorphous PBA with enhanced electrocatalytic activity.[112] The aforementioned study and many others reveal that the ammonia group of [Fe(CN)₅(NH₃)]³⁻ complex can be substituted with pyridyl containing organic moieties via a straightforward synthesis.[181], [182] Moreover, our results suggesting that [Fe(CN)₅] could facilitate the electron transfer between the chromophore and the catalyst encouraged us to use it for the development of a molecular sensitizer-heterogeneous catalyst system. For this purpose, a symmetrically substituted porphyrin derivative, 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphyrin, [TPyP], was selected as the chromophore since it can be produced in bulk scale, it has a high molar absorption coefficient in the visible region, and it contains available pyridyl groups for coordination to pentacyanoiron(II) group.

4.3. Experimental Procedures

4.3.1. Materials

Sodium nitroferricyanide or sodium nitroprusside ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), ammonium hydroxide solution (NH_4OH , 25% (v/v), Ethanol (EtOH), methanol (MeOH), Cobalt(II) acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Chloroform (CHCl_3) and Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$). Potassium phosphate buffer solutions were prepared by 0.1M KH_2PO_4 and 0.1M K_2HPO_4 . Deionized water (resistivity: 18 $\text{M}\Omega/\text{cm}$) is used in all experiments.

4.3.2. Sample Preparation

Synthesis of sodium aminopentacyanoferrate, $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$:

Briefly, 30 g of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ was dissolved in 120 mL of water, and 4 grams of NaOH was subsequently added to the solution under constant stirring in an ice bath. The temperature was kept below 10 °C during the whole experiment, and pH was always in the basic range. After mixing for approximately 30 min, a cold NH_4OH solution (~100 mL) was added dropwise until no precipitation and a color change from reddish to brownish was observed. Here, the presence of NaOH is critical to prevent the ammonia from forming side products such as a disodium salt, $\text{Na}_2(\text{NH}_4)[\text{Fe}(\text{CN})_5\text{NH}_3]$. Later, a sufficient amount of cold MeOH (~80 mL) was quickly added to the mixture until a yellow precipitate was acquired. To obtain a homogenous solution, the reaction mixture was stirred for 2 hours. The bright yellow precipitate is isolated from the unreacted reddish-yellow solution with vacuum filtration and rinsed with cold MeOH . The solid product was recrystallized three times in cold NH_4OH and MeOH solution for further purification to remove unreacted sodium nitroprusside or by-products. For recrystallization, the obtained yellow precipitate again dissolved in adequate amount of cold NH_4OH solution (~100 mL) and subsequently MeOH (~100 mL) under constant mild stirring. It was dried by keeping in vacuum oven at room temperature for overnight. The final yield was 50 %.

Synthesis of 5,10,15, 20-tetra(4-pyridyl)-21H,23H-porphyrin, $\text{C}_{40}\text{H}_{26}\text{N}_8$, [TPyP]: Briefly, 4-Pyridinecarboxaldehyde (25 mmol, 2.68 g) was added to

refluxing propionic acid (125 mL) and freshly distilled pyrrole (25 mmol, 1.75 mL) was added 5 min later. The reaction mixture was refluxed for 1.5 h, and then propionic acid was removed by distillation under reduced pressure. The remaining solid was washed by water, dried and the crude product was purified by column chromatography on silica gel eluted by a dichloromethane / ethanol mixture (25:1).

Synthesis of Pentacyanoferrate-Coordinated Porphyrin, $\text{Na}_{12}\text{Fe}_4\text{C}_{60}\text{H}_{26}\text{N}_{28}\cdot x\text{H}_2\text{O}$, [Fe–TPyP]: Compound [TPyP] (60 mg) was dissolved in ~10 mL of methanol at room temperature. Since $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ has limited solubility in methanol, excess amount of the sample (189 mg) was dissolved in a sufficient amount of MeOH. After mixing both solutions for about 30 minutes, solution containing $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ complex was added drop wise to the solution containing [TPyP] and the color of suspension changed from dark red to brownish. The reaction was allowed to continue mixing in a covered flask for 2 days. The unreacted $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ complex, which forms a precipitate, was removed by filtration and washed with ethanol. The solution was then concentrated with a rotary evaporator yielding a brown precipitate. The brown precipitate was isolated and dried under vacuum overnight at room temperature.

Synthesis of Cobalt Pentacyanoferrate-Coordinated Porphyrin, $\text{Co}_6\text{Fe}_4\text{C}_{60}\text{H}_{26}\text{N}_{28}\cdot x\text{H}_2\text{O}$, [CoFe–TPyP]: [Fe–TPyP] compound (40 mg, 24 μmoles) was dissolved in water and a 6 equiv. $\text{Co}(\text{NO}_3)_2$ aqueous solution was added dropwise to the [Fe–TPyP] solution. In order to collect the solid and remove soluble unreacted species, the suspension was centrifuged at 8000 rpm for 45 min with water and acetone, sequentially. The obtained product was dried in oven at 35 °C for one day.

Synthesis of [CoFe–TPyP] modified FTO electrode (in situ modified electrode): A 50 μL THF solution of [Fe–TPyP] (1 mM) was drop-casted on a FTO electrode (1cm $\times$ 1cm). Once the substrate is completely dried, the modified FTO electrode was dipped into an aqueous $\text{Co}(\text{CH}_3\text{COO})_2$ solution (0.16 M) horizontally for 15 min. Then, the slide was washed with distilled water to remove the excess Co^{2+} ions over the film. Finally, the FTO electrode was left for drying at room temperature.

Synthesis of Zinc Pentacyanoferrate-Coordinated Porphyrin, $\text{Zn}_6\text{Fe}_4\text{C}_{60}\text{H}_{26}\text{N}_{28}\cdot x\text{H}_2\text{O}$, [ZnFe–TPyP]: [Fe–TPyP] compound (40 mg, 24 μmoles) was dissolved in water and a 6 equiv. $\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution

was added dropwise to the [Fe-TPyP] solution. The suspension was centrifuged at 8000 rpm for 45 min with water and acetone, sequentially, to collect the solid and remove soluble unreacted species. The obtained product was dried in oven at 35 °C for one day.

[ZnFe-TPyP] modified FTO electrode (in situ modified electrode): A 50 μ L THF solution of [Fe-TPyP] (1 mM) was drop-casted on a FTO electrode (1 cm $\times$ 1 cm). Once the substrate is completely dried, the modified FTO electrode was dipped into an aqueous $\text{Zn}(\text{CH}_3\text{COO})_2$ solution (0.16 M) horizontally for 15 min. Then, the slide was washed with distilled water to remove the excess Zn^{2+} ions over the film. Finally, the FTO electrode was left for drying at room temperature.

4.4. Results and Discussions

The amminopentacyanoferrate complex, $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$, was first reacted with [TPyP] to prepare [Fe-TPyP], which was then reacted with Co^{2+} ions to prepare the triad, [CoFe-TPyP] (Figure 4.1). An assembly, in which a molecular chromophore is coordinated to a heterogeneous cyanide-based catalyst, was prepared with this synthetic route. The synthetic pathway adopts a molecular bottom-up approach similar to the ones previously reported for chromophore-catalyst assemblies, while it differs significantly from those by the formation of a heterogeneous assembly in the final step.

To confirm PBA formation, ATR-FTIR spectra for [Fe-NH₃], [TPyP], [Fe-TPyP] and [CoFe-TPyP] are measured. The characterization results are listed in Figure 4.2. The sharp peak in the 2000 - 2100 cm^{-1} range is attributed to CN stretch. The sharp peak at 2031 cm^{-1} obtained for $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ complex undergoes a blue shift for [Fe-TPyP] ($\sim$ 2043 cm^{-1}), which is followed by a further shift ($\sim$ 2079 cm^{-1}) in [CoFe-TPyP] indicating the presence of Fe-CN-Co coordination mode. The peaks that belong to porphyrin ring are observed for [TPyP], [Fe-TPyP], and [CoFe-TPyP] as expected. The peak at around 567 cm^{-1} is attributed to Fe-N coordination bonds. The peaks that belong to porphyrin ring are observed for [TPyP], [Fe-TPyP], and [CoFe-TPyP] as expected. The peak at around 567 cm^{-1} is attributed to Fe-N coordination bonds. Prominent bands between 1600 and 1330 cm^{-1} are attributed to C=C and C=N stretches of porphyrin ring. The sharp peak at around 1264 cm^{-1} belongs to N-H stretch, several peaks in the 1000-1330 cm^{-1} and 2850 - 2900 cm^{-1} range correspond to symmetric and asymmetric stretches of C-H bond.

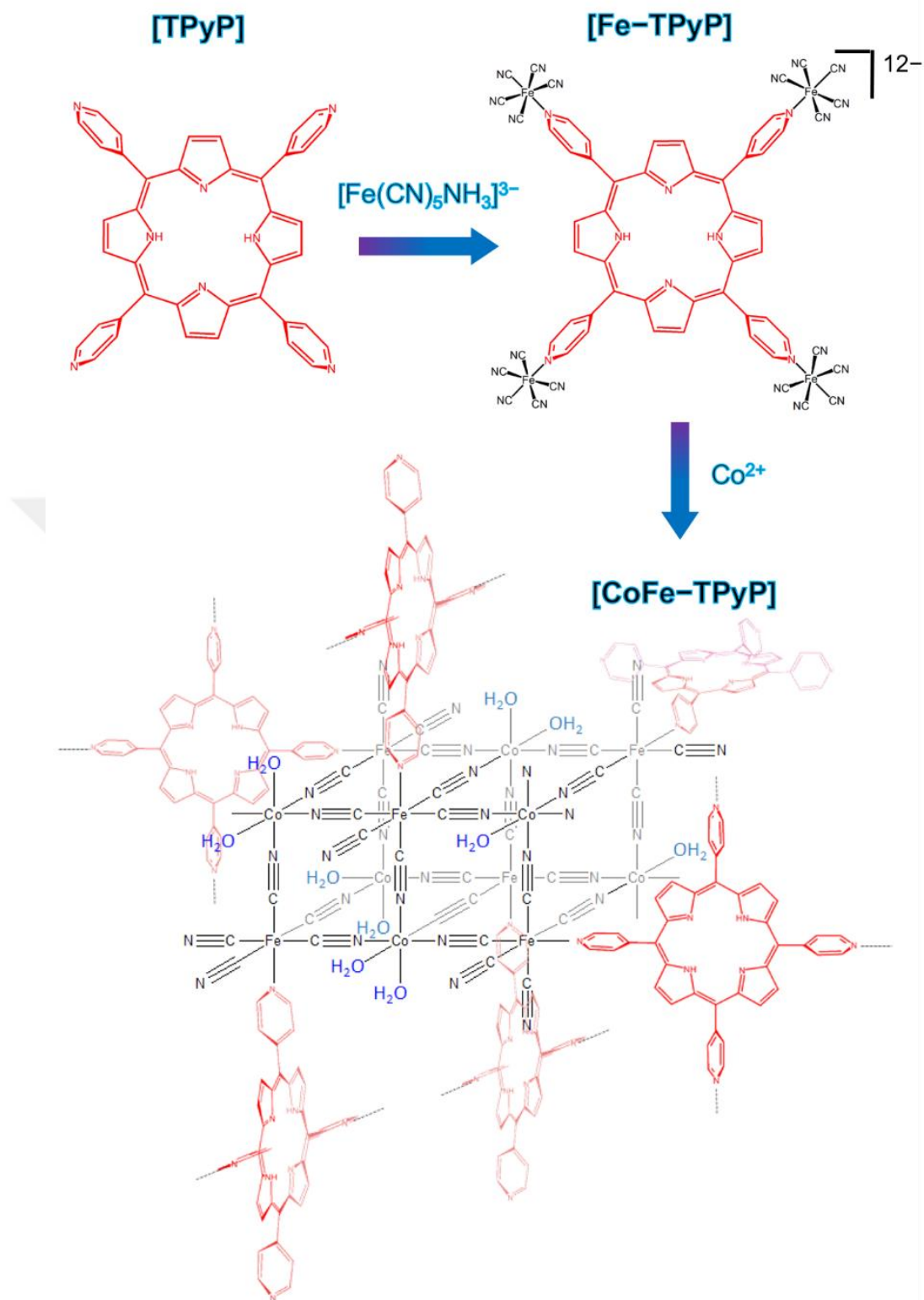


Figure 4.1 General synthetic scheme and molecular structures of [TPyP], [Fe-TPyP], and [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

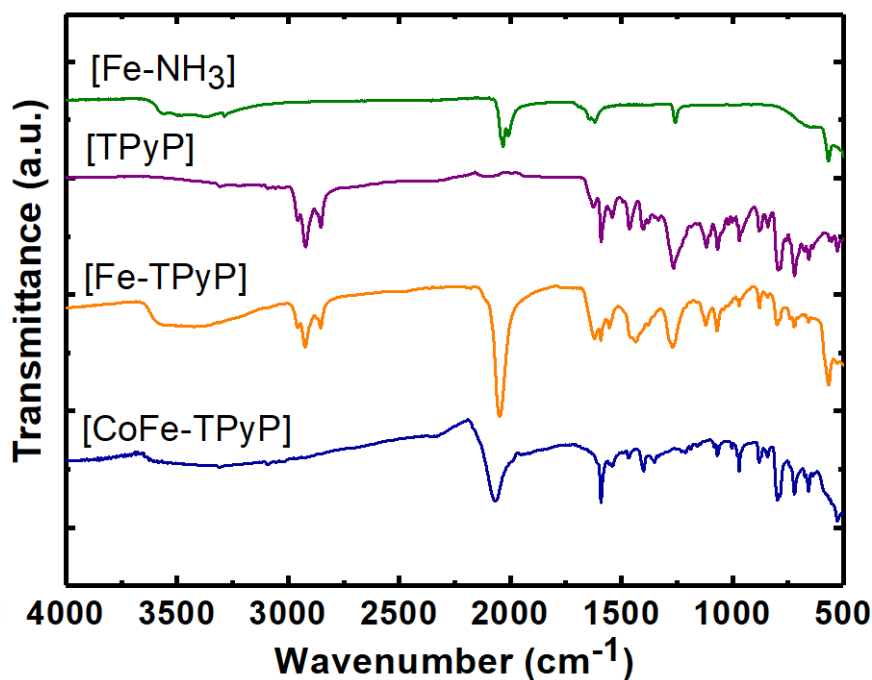


Figure 4.2 ATR-FTIR spectra for [Fe-NH₃], [TPyP], [Fe-TPyP] and [CoFe-TPyP]. The broad peak at 3300 cm⁻¹ belongs to OH stretch while the one at around 1620 cm⁻¹ corresponds to H-OH bending of solvent water molecules. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Thus, this characterization data confirms the formation of PBA in our triad samples. In the next step, XPS analysis is utilized to explore the chemical composition of the material. The XPS spectra of N1s and the Fe2p are shown in Figure 4.3a-d and Figure 4.4a-c and the results from deconvolutions are summarized in Table 4.1. N1s pattern of [Fe-NH₃] revealed peaks located at 397.74 and 399.04 eV, attributed to the nitrogen atoms of cyanide and NH₃, respectively. The N1s signal for [TPyP] can be deconvoluted into three peaks; nitrogen atoms in the pyridyl rings bound to the porphyrin meso carbons located at ~399.05 eV, unprotonated pyrrole N atoms located at ~398.14 eV, and protonated pyrrole NH atoms at ~399.9 eV, see Figure 4.3b.[183] N1s signals of [Fe-TPyP] and [CoFe-TPyP] can also be deconvoluted into three peaks similar to [TPyP] indicating the presence of porphyrin group in [Fe-TPyP] (Figure 4.3c,d). A slight decrease in each of the binding energies of N1s peaks is observed due to an increase in the electron density of the porphyrin ring because of π back bonding interaction between iron sites and pyridyl groups of the porphyrin ring. For [Fe-TPyP], the addition of Fe(CN)₅⁻ moieties to the porphyrin ring also leads to a relative increase in the intensity of the peak at 397.8 eV due to the overlap of the peaks that belong to unprotonated pyrrole N atoms and cyanide N atoms. In [CoFe-TPyP], the relative increase in the intensity shifts to the middle peak

at 398.65 eV since the nitrogen atoms binding energies of cyanide groups increase once they are coordinated to Co sites.

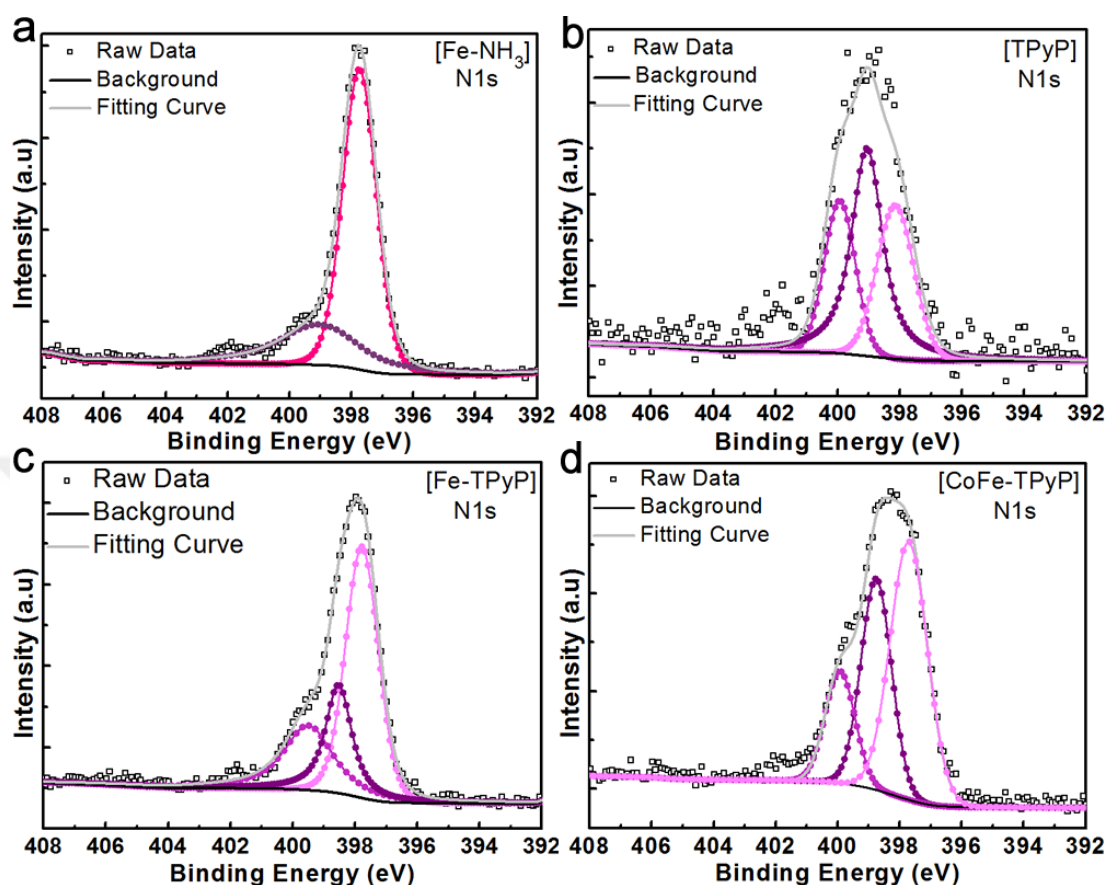


Figure 4.3 High resolution XPS spectra of N1s for (a) [Fe-NH₃], (b) [TPyP], (c) [Fe-TPyP] and (d) [CoFe-TPyP]. (b-d) The peaks indicate the presence of pyrrole NH, pyridyl N and pyrrole N. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

As shown in Figure 4.4b,c, Fe2p region exhibits a similar profile for [Fe-TPyP] and [CoFe-TPyP] with two major bands at around 708 and 721 eVs, which are assigned to 2p_{3/2} and 2p_{1/2} of Fe²⁺, respectively. Two small bands at ~710 eV and ~723 eV were also observed for both samples due to partial oxidation of Fe²⁺ to Fe³⁺ ions in Fe(CN)₅ fragments. Such an oxidation has been commonly observed in pentacyanoiron chemistry. It is also evidenced by IR spectra, which reveals a shoulder band in the cyanide region ~2105 cm⁻¹ for [Fe-TPyP] and ~2146 cm⁻¹ for [CoFe-TPyP]).

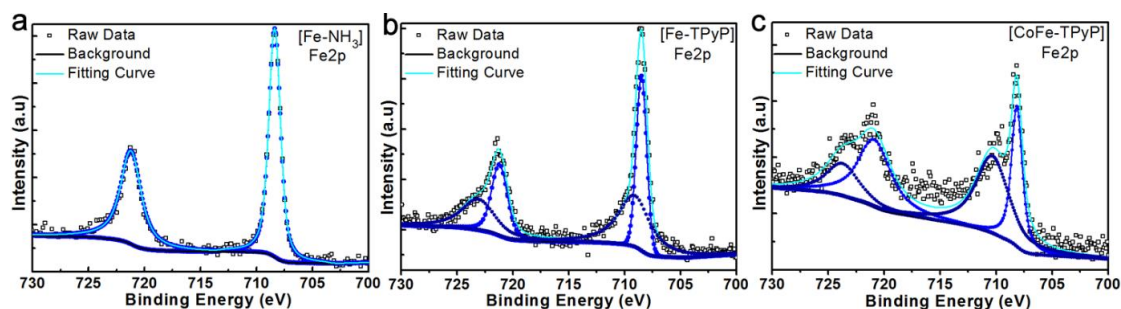


Figure 4.4 High resolution XPS spectra of Fe2p for (a) [Fe-NH₃], (b) [Fe-TPyP] and (c) [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Table 4.1 Summary of XPS results obtained from (a) [Fe-NH₃], (b) [TPyP], (c) [Fe-TPyP], and (d) [CoFe-TPyP].

Compounds	Fe2p, eV				N1s, eV				
	2p _{3/2} Fe ⁺²	2p _{1/2} Fe ⁺²	2p _{3/2} Fe ⁺³	2p _{1/2} Fe ⁺³	C≡N	N-Fe	pyridyl N	pyrrole N	pyrrole NH
[Fe-NH ₃]	708.37	721.21	-	-	397.74	399.04	-	-	-
[TPyP]	-	-	-	-	-	-	399.93	399.05	398.14
[Fe-TPyP]	708.49	721.21	709.09	723.10	-	-	399.5	398.52	397.78 ^[a]
[CoFe-TPyP]	708.15	720.88	710.33	723.7	-	-	399.56 ^[b]	398.65 ^[c]	397.72 ^[a]

[a]: pyrrole NH peak intensified with (C≡N) bond, both [b] (pyridyl N) and [c] (pyrrole N) peaks intensified with Co-NC-Fe.

Further investigation on crystallinity and chemical composition of the material is performed using SEM and SEM-EDX analysis methods. Figure 4.5a,b shows the SEM image of the dyad sample, which reveal a porous morphology for [CoFe-TPyP]. The corresponding SEM-EDX elemental mapping reveals the homogenous distribution of the elemental species (Figure 4.6a,b) in [Fe-TPyP] and [CoFe-TPyP]. Characterization studies and unique coordination mode of cyanide ligand suggest the presence of random sized PB structures with limited dimensionalities due to surrounding molecular porphyrin rings in [CoFe-TPyP] (Note that the compound has an amorphous nature, see Figure 4.7). The coordination of each Fe site to a porphyrin macrocycle reduces the dimensionality of PB structures significantly, which in return yields cobalt sites coordinated to at least one H₂O molecule that is essential for water oxidation.

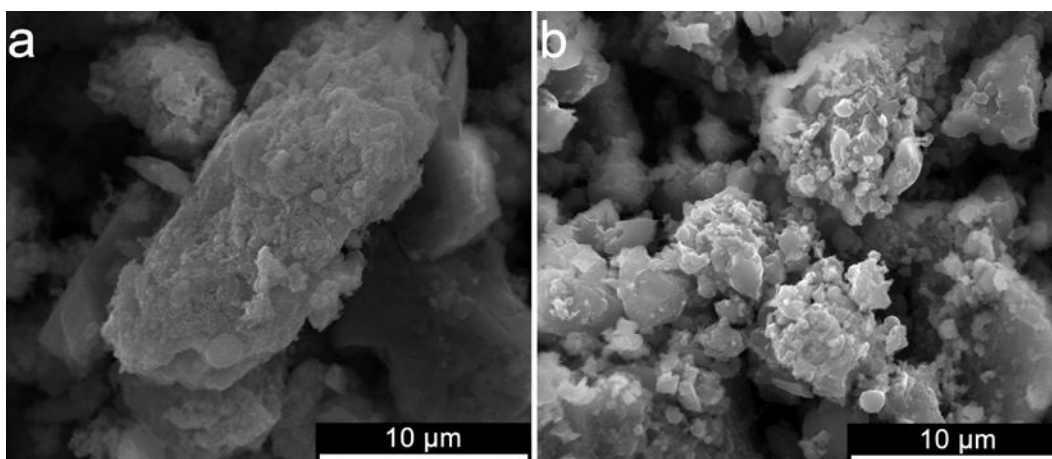


Figure 4.5 SEM images of the (a) [Fe-TPyP] and (b) [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

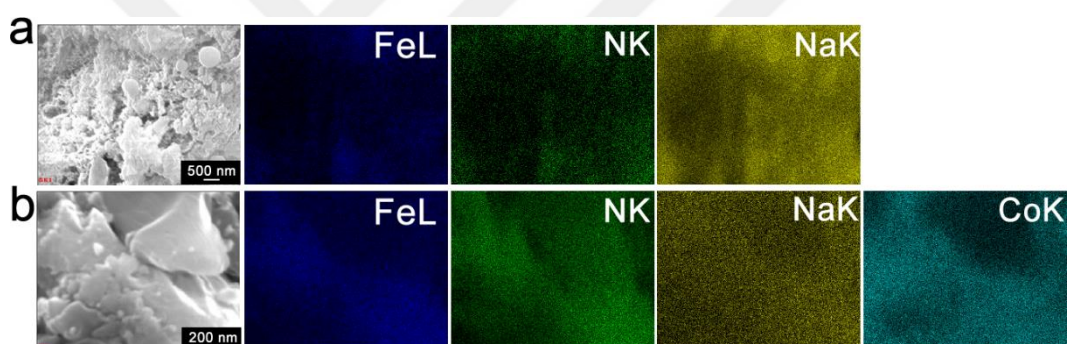


Figure 4.6 SEM images and related elemental mappings of Fe, N, Na, Co for (a) [Fe-TPyP] and (b) [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

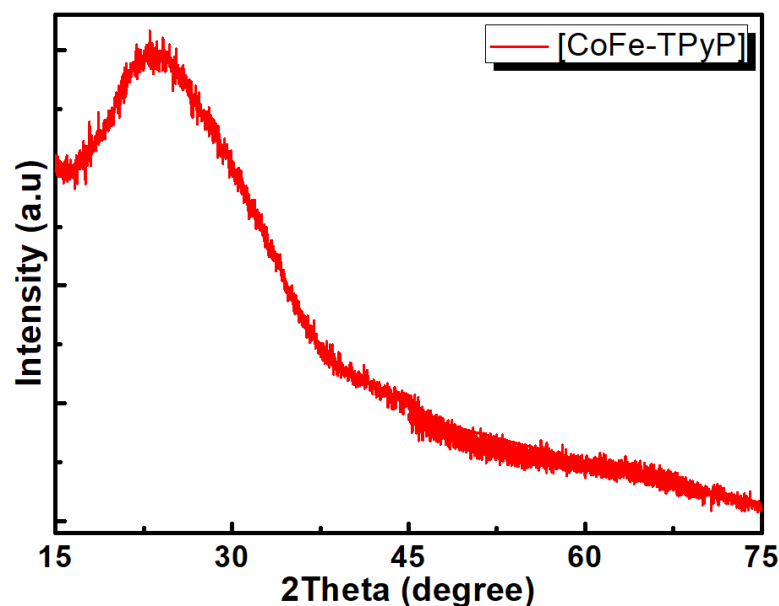


Figure 4.7 The XRD pattern for [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

4.4.1. Electrochemical Measurements

After completing structural analysis, the electrochemical measurements were performed in a phosphate buffer solution (1M KNO₃ in 50 mM PBS, pH 7.02) and the CVs were recorded in a range of 0 - 1.50 V_{Ag/AgCl} with a scan rate of 20 mV/s at room temperature. In the first step, the CV of [CoFe-TPyP] modified FTO electrode exhibits an irreversible peak at high anodic potentials corresponding to the catalytic water oxidation process. This feature is absent in the CV of [ZnFe-TPyP] modified FTO electrode, which indicates that water is oxidized only at cobalt sites (Figure 4.8).

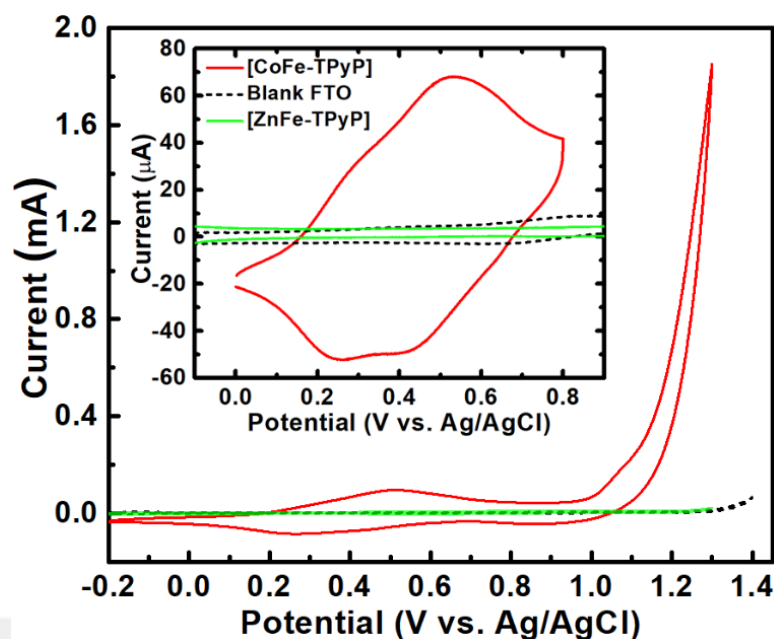


Figure 4.8 CV curves measured for the Blank FTO and [CoFe-TPyP] in N_2 saturated 50 mM PBS solution (pH 7) at a scan rate of 20 mV/s. Two redox couples belongs to [CoFe-TPyP], one at 0.27 $V_{Ag/AgCl}$ ($E_c - E_a = 60$ mV) and another one at 0.47 $V_{Ag/AgCl}$ ($E_c - E_a = 80$ mV) is obtained, which are assigned to Co^{2+}/Co^{3+} redox couples of nonstoichiometric PB structures. Note that the CV curve for [ZnFe-TPyP] and that for the blank is similar suggesting that water oxidation occurs at cobalt sites. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

4.4.2. Oxygen Evolution Activity Measurements

Photocatalytic studies on [CoFe-TPyP] have been performed using a suspension of powder sample with $K_2S_2O_8$ as a sacrificial electron acceptor in a 50 mM PBS, pH 7, at 25 °C. The reaction was performed with a solution of 25 mL placed in a round bottom flask. Photocatalytic O_2 evolution profile of [CoFe-TPyP] in the presence of a sacrificial electron acceptor ($K_2S_2O_8$) reveals a steady increase during a 1-hour experiment (Figure 4.9).

The curve yields a turnover frequency of $3.2 \times 10^{-4} \text{ sec}^{-1}$ (1.2 h^{-1}), which is similar to the one obtained with PBAs in the presence of a $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system and much higher than the one obtained when [TPyP] was mixed with a cobalthexacyanoferrate (Figure 4.10).[111] A similar profile was obtained for three cycles of the same batch, which indicates that [CoFe-TPyP] is stable during the photocatalytic water oxidation process. Overall, photocatalytic tests confirm that porphyrin and PB structures collaborate for light-assisted water

oxidation catalysis, which could be due to an efficient pathway for electron transfer between the chromophore and the catalytic cobalt sites.

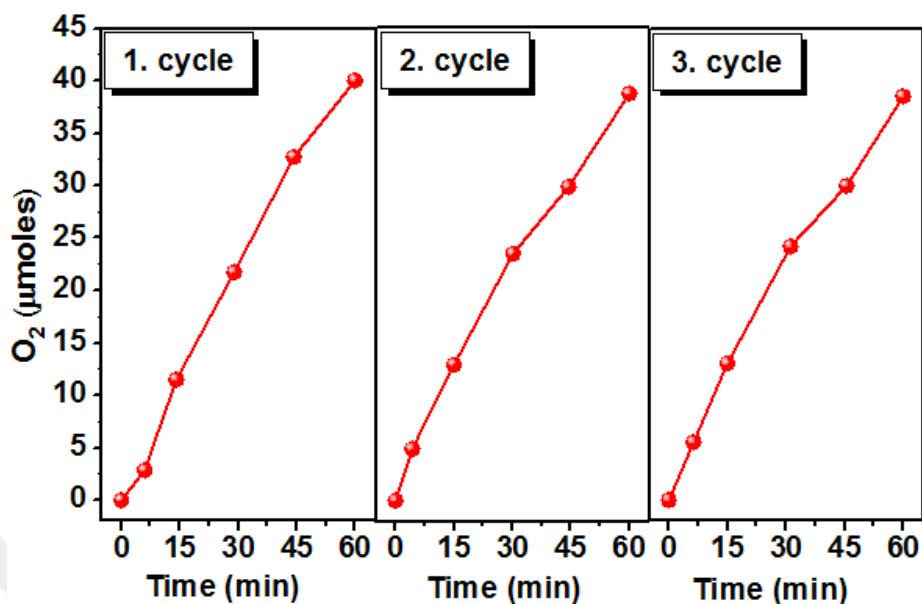


Figure 4.9 Photocatalytic oxygen evolution by [CoFe-TPyP] (10 mg) and $K_2S_2O_8$ (20 mM) in pH 7, 50 mM PBS. The same batch was used in each cycle. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

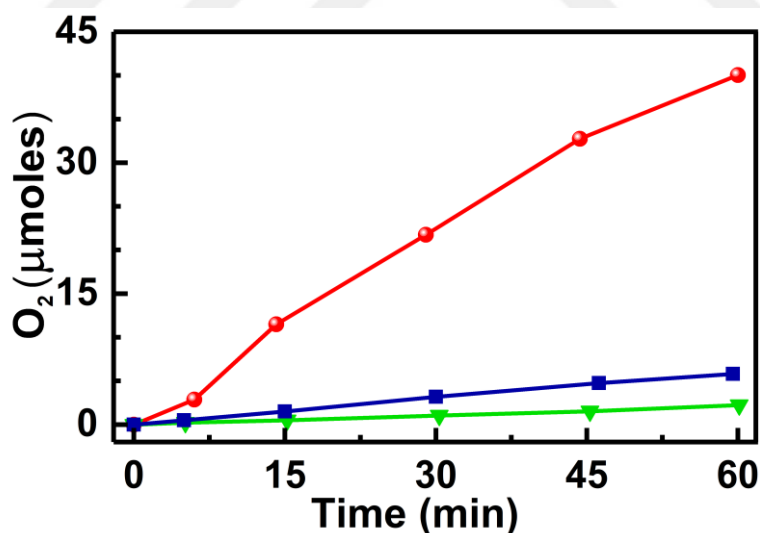


Figure 4.10 Photocatalytic oxygen evolution by i) [CoFe-TPyP] (10 mg) and $K_2S_2O_8$ (20 mM) (red curve), ii) CoFe PBA (10 mg), TPyP (5 mg) and $K_2S_2O_8$ (20 mM) (blue curve), and iii) [CoFe-TPyP] (10 mg) without any electron scavenger (green curve). All experiments were performed at pH 7 in a 20 mL, 50 mM PBS. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

4.4.3. Long-term Stability Analysis

Besides electrochemical stability of the samples, the structural integrity of the powder is also another issue that defines the stability of the sample. To explore this issue, ATR-FTIR characterizations were performed in pristine and post-catalytic samples, as shown in Figure 4.11. Post-catalytic powder sample was obtained by centrifugation and washing several times with water. Both spectra exhibit the characteristic peaks that belong to porphyrin ring. Similar to literature, a broadening and slight shift to higher frequencies is observed with the cyanide stretch, which is attributed to partial oxidation of Co^{2+} centers to Co^{3+} during catalytic water oxidation processes.

Additionally, XPS is utilized to evaluate the sample compositional stability. Figure 4.12a,d depicts the $\text{Co}2\text{p}$ spectra of the pristine sample and the one after the photocatalytic process (post-catalytic). Overall, similar spectra are recorded for both cases. The spectra are deconvoluted to a set of different Gaussian peaks. Two dominant peaks are located at 781.9 eV and 797.4 eV, which is in close accordance with that of $\text{Co } 2\text{p}_{1/2}$ and $\text{Co } 2\text{p}_{3/2}$ of +3 oxidation state of Co, i.e. Co^{3+} . [112] Another doublet with slightly higher binding energies is obtained, which corresponds to $\text{Co } 2\text{p}_{1/2}$ and $\text{Co } 2\text{p}_{3/2}$ doublet of Co^{2+} cation. In addition, 'shake-up' satellites have also been observed for these cases. High-spin Co^{2+} ions have intense or scalable satellite bands, whereas low-spin Co^{3+} ions have very weak or missing satellite bands and thus, these shake-up bands are generally attributed to Co^{2+} oxidation state. In the post catalytic sample, smaller (or negligible) satellite peaks were recorded compared to the pristine one, showing that Co^{3+} ions are in their low-spin states. This, in turn, proves the thermodynamically stable interconversion of $\text{Co}^{2+}/\text{Co}^{3+}$ states. [112]

Moreover, the existence of Co_3O_4 , which is the thermodynamically stable form of cobalt oxide, is distinguished by a dominant peak placed in energies below (or close to) 780 eV, [112], [184]–[186], which is not the case for our spectra. Thus, this confirms that our catalyst is stable and does not have any decomposition products such as CoO_x . This conclusion can also be confirmed by the $\text{O}1\text{s}$ region. As shown in Figure 4.12c,f, the $\text{O}1\text{s}$ spectra for both pristine and post catalytic ones exhibit similar profiles, which can be deconvoluted to one Gaussian peak located at ~ 532 eV. Based on previous references, the lattice and defect-related oxygen peaks appear in binding energies around 530 eV and 531 eV. [192]–[194] The oxygen peak located at 532 eV is attributed to chemisorbed oxygen molecules such as the water adsorbed on the surface of

the sample.[185], [187], [190] These results confirm that the compound retains its structure and maintains its stability throughout the photocatalytic process. Moreover, the Fe2p XPS spectrum has been extracted for the post-catalytic case. Similar to the pristine sample, two main peaks are observed in 708 and 721 eVs, which are assigned to $2p_{3/2}$ and $2p_{1/2}$ of Fe^{+2} , respectively (Figure 4.12b,e). Two small bands at ~ 710 eV and ~ 723 eV also correspond to Fe^{2+} to Fe^{3+} ions in $\text{Fe}(\text{CN})_5$ fragments. The similar XPS spectra in both cases further confirm the stability of PBA.

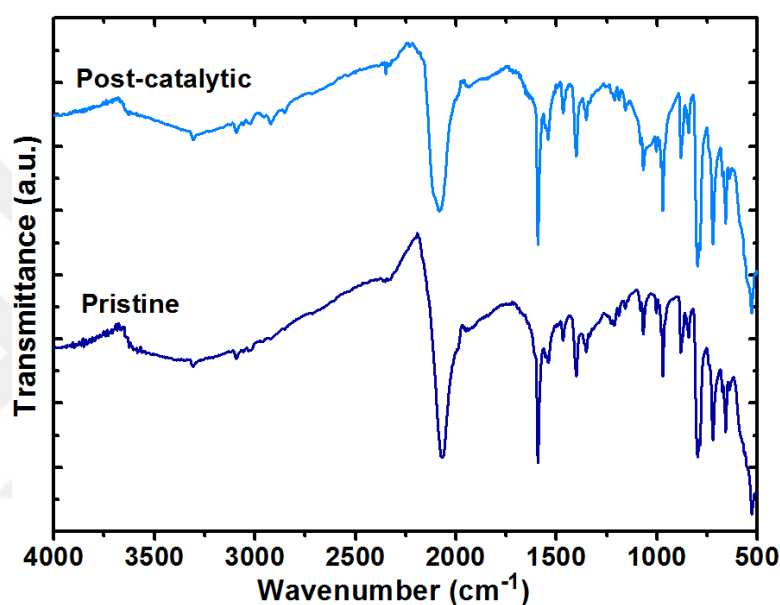


Figure 4.11 ATR-FTIR spectra for pristine and post-catalytic (after a 3-hours photocatalytic experiment) [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

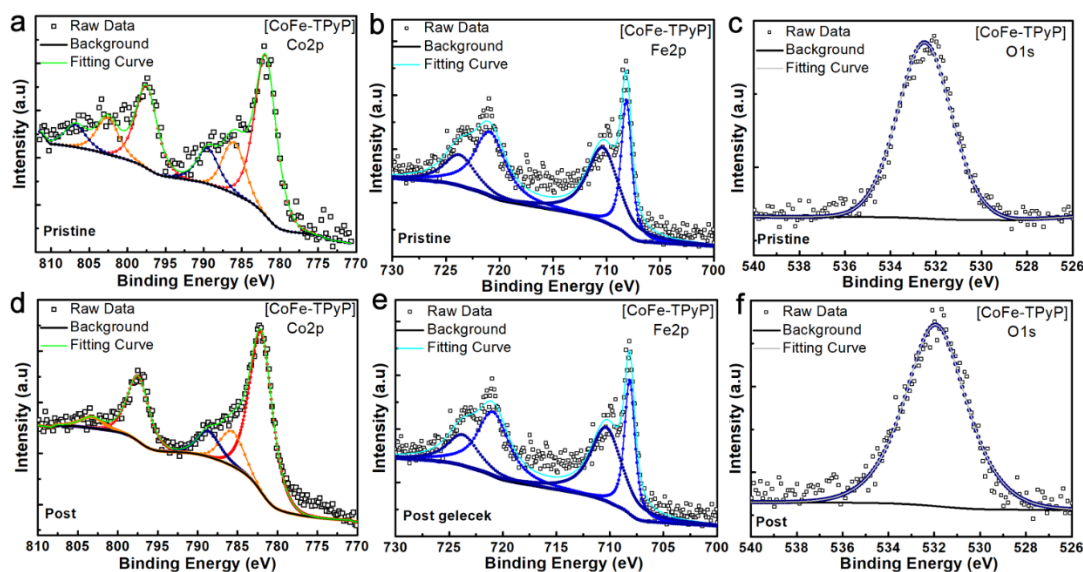


Figure 4.12 High resolution XPS spectra of Co2p, O1s, and Fe2p for (a, b, c) pristine and (d, e, f) post-catalytic [CoFe-TPyP]. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

4.4.4. Quantum Chemical Calculations

All the above characterization data proved the efficiency of the assembly in water oxidation. However, an in-depth understanding can be achieved using quantum chemical calculations. For this aim, Prof. Yavuz Dede group has performed quantum chemical calculations at the level of Density Functional Theory (DFT) with the Gaussian 09 software suit. Geometries were fully optimized using B3LYP functional without any constraints on symmetry. Effective core potentials of Hay and Wadt (LANL2DZ) were employed for the optimizations. Vibrational frequency calculations on the located stationary points were performed to ensure geometries correspond to true minima. Single point calculations were carried with the newer formulations of the basis sets by Ahlrichs and co-workers and long range corrected functional due to Yanai, CAM-B3LYP/Def2TZV. The energies were calculated with the solvent environment enabled using SMD approach as implemented in Gaussian. Methanol's dielectric constant was used in SMD calculations. Unrestricted spin formalism was utilized throughout all calculations. The ground state of [Fe-TPyP] is found to be a closed shell singlet (Table 4.2) with four electronically identical Fe centers having low spin configurations (Table 4.3) as expected for Fe in a strong ligand environment. From the frontier orbitals analysis, HOMO is comprised of Fe-*d* and porphyrin- π orbitals. Two other high lying occupied orbitals involved in the excitation are of porphyrin π and Fe-*d* + porphyrin- π in

character (Figure 4.13). These three molecular orbitals (MOs) delocalized on the porphyrin ring and Fe center are the domain for the excitation. The details of the calculations are provided in Ref [125].

Table 4.2 Relative energies of [Fe–TPyP] for different spin states calculated with UCAM-B3LYP/Def2TZV//UB3LYP/LANL2DZ level of theory.

Spin State	Energy (eV)
Closed Shell (Ground) Singlet	0.00
Open Shell (Excited) Singlet	0.51
Triplet	0.58
Quintet	1.68
Septet	3.90

Table 4.3 Spin densities on selected atoms for different spin states of [Fe–TPyP] using UB3LYP/LANL2DZ level of theory.

Spin State	Fe1	Fe2	Fe3	Fe4	TPyP
Singlet	0.00	0.00	0.00	0.00	0.00
Triplet	0.38	0.38	0.34	0.39	0.85
Quartet	0.56	0.63	0.62	0.58	1.83

In summary, quantum chemical calculations thus suggest that i) Fe-centers are involved in donating electrons and porphyrin is an electron acceptor, ii) this internal charge transfer repositions the electrons in two distinct fragments of the system and decreases the likelihood of charge recombination, thereby allowing the excited state to live long enough and to undergo other significant electronic changes, iii) the electron transfer yields an MLCT state, iv) the internally oxidized Fe-centers act as holes to further oxidize Co-sites – an essential feature for O–O bond formation at the Co-site as shown previously.[191].

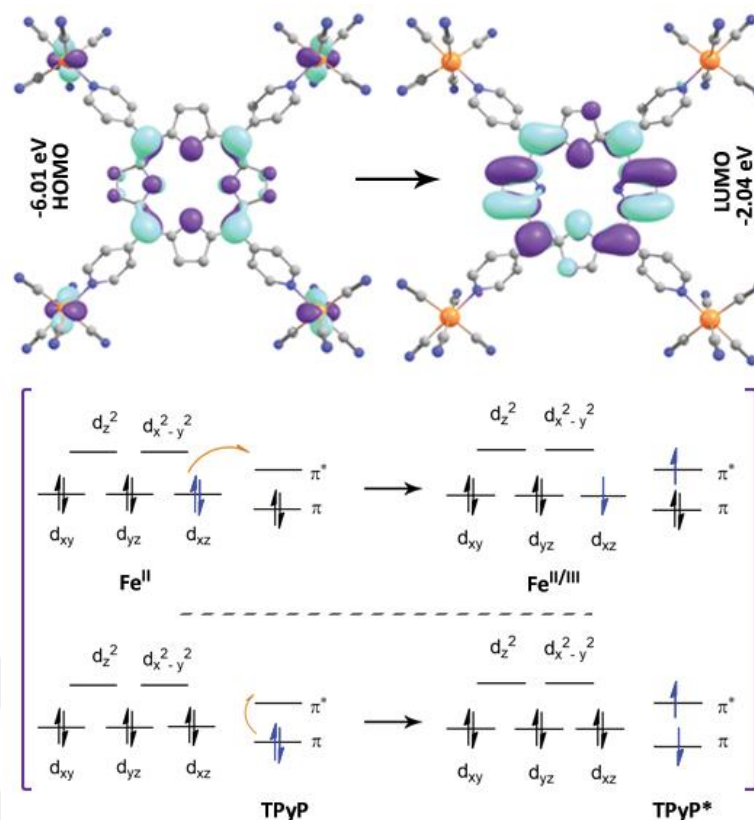


Figure 4.13 TD-DFT excitation behavior for [Fe-TPyP] at UB3LYP/def2-TZV level of theory. A hybrid Fe-d + porphyrin- $\pi \rightarrow$ porphyrin- π^* state is generated. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

4.4.5. Steady State Absorption, Fluorescence and Femtosecond Transient Absorption Measurements

Besides theoretical studies, these results are also verified by steady-state absorption, fluorescence (FL), and transient absorption (TA) measurements. Absorption graphs of the investigated compounds show typical characteristics of porphyrins as shown in Figure 4.14.[37] FL measurements are given in Figure 4.15 and Figure 4.16.

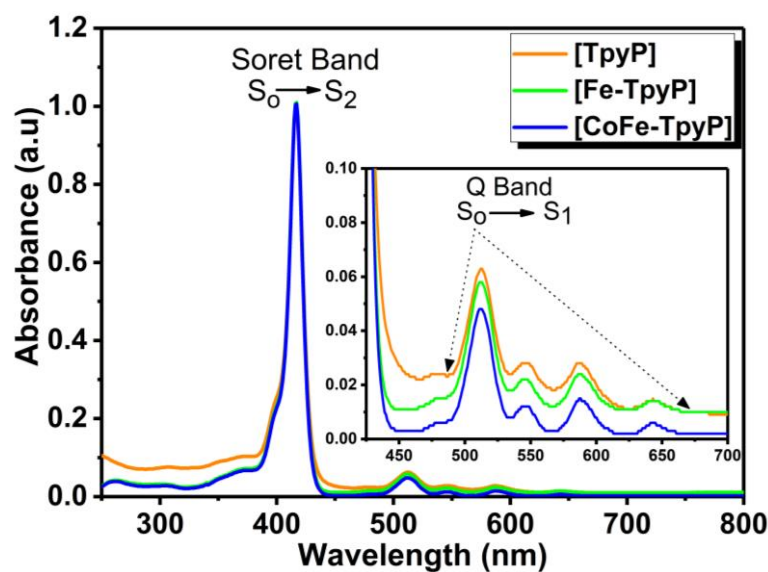


Figure 4.14 Absorption spectra of [TPyP], [Fe-TPyP], and [CoFe-TPyP] in CHCl_3 solution (abs = 1 at 417 nm). The absorption values of the studied [TPyP], [Fe-TPyP], and [CoFe-TPyP] compounds were adjusted to 1 absorbance. Inset is the enlarged form of Q band absorptions. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

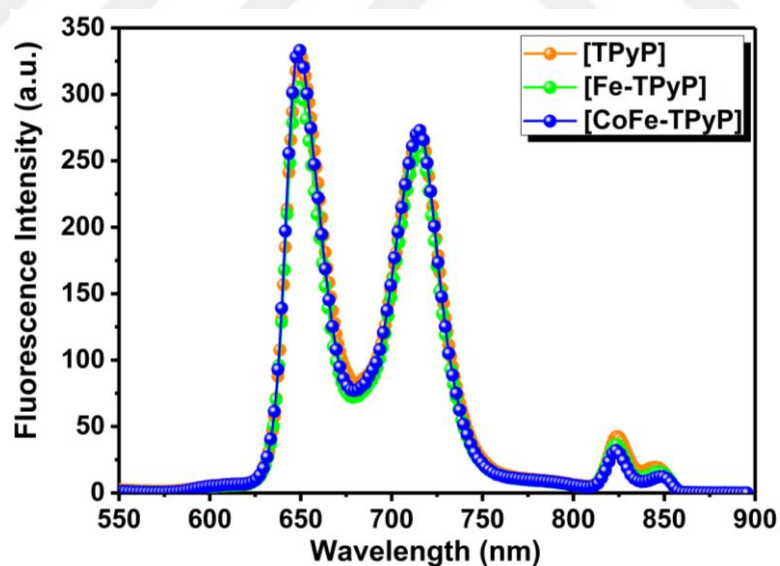


Figure 4.15 Fluorescence spectra of [TPyP], [Fe-TPyP], and [CoFe-TPyP] in CHCl_3 , at 417 nm excitation wavelength. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

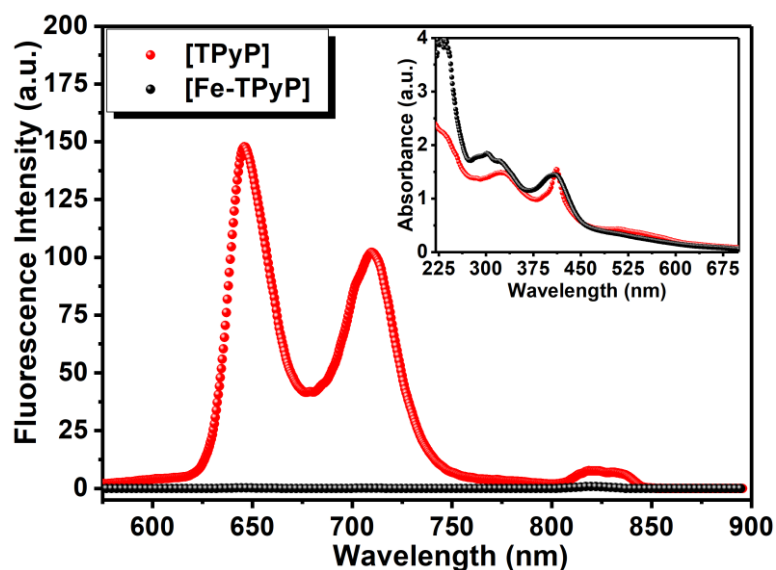


Figure 4.16 Fluorescence and absorption spectra of the 1.25×10^{-4} M [TPyP] and 1.25×10^{-4} M [Fe-TPyP] compounds in MeOH:DI. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

TA spectra for [TPyP], [Fe-TPyP], and [CoFe-TPyP] at zero time delay and decay traces of the bleach signals at 424 nm probe wavelength are given in Figure 4.17 along with the proposed electron transfer mechanism Figure 4.18. [TPyP] shows typical features including a characteristic ground state bleaching and a stimulated emission around 420 nm, Q bands bleaching around 520 and 650 nm, and T_1 – T_n absorption around 440 nm developing by intersystem crossing (ISC) process after 48 ps time delay (Figure 4.19 and Figure 4.20). Although TA measurement of [Fe-TPyP] is similar to that of [TPyP], it shows enhanced bleaching of Q bands as well as T_1 – T_n absorption band (Figure 4.21 and Figure 4.22).^[192] These data show the electron transfer from Fe-center to porphyrin. On the other hand, decay trace of 430 nm bleach signal for [Fe-TPyP] exhibits a longer lifetime (from pumped state to ground state) than that of [TPyP], which is required for the efficient photocatalytic process, Table 4.4. In the case of [CoFe-TPyP], excited-state absorption with a long lifetime around 430 nm appears at zero time delay suggesting that this is not a T_1 – T_n absorption.^[193] This profile also implies that the deactivation pathway of [Fe-TPyP] excited state is altered with the presence of Co-sites due to further electron transfer, which yields a longer living [CoFe-TPyP] state.

Table 4.4 Time components of the Soret energy states ($S_0 \rightarrow S_2$) (at 424 nm probe wavelength) in the TA spectra of the studied compounds.

Sample	$\tau_1(\text{ps})$	$\tau_2(\text{ps})$	$\tau_3(\text{ps})$
[TPyP]	30.56	1817.62	6582
[Fe-TPyP]	0.15	50.84	infinite
[CoFe-TPyP]	8.126	2636	4106

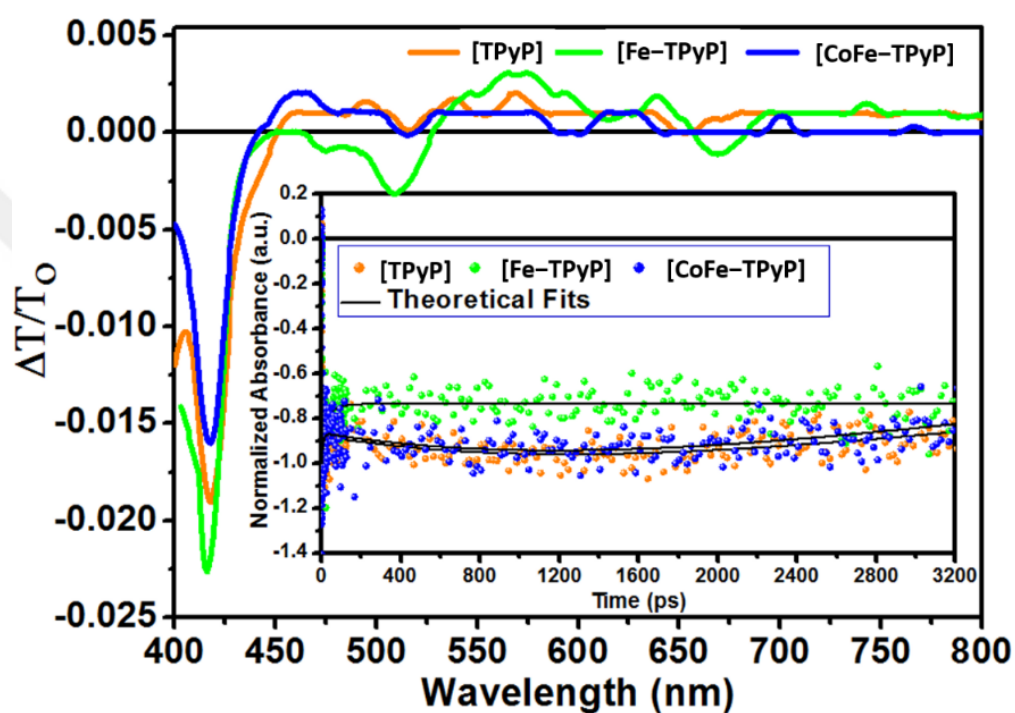


Figure 4.17 TA spectra at zero-time delay and time evolution of the bleach signals at 424 nm wavelength for [TPyP], [Fe-TPyP], and [CoFe-TPyP] compounds. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

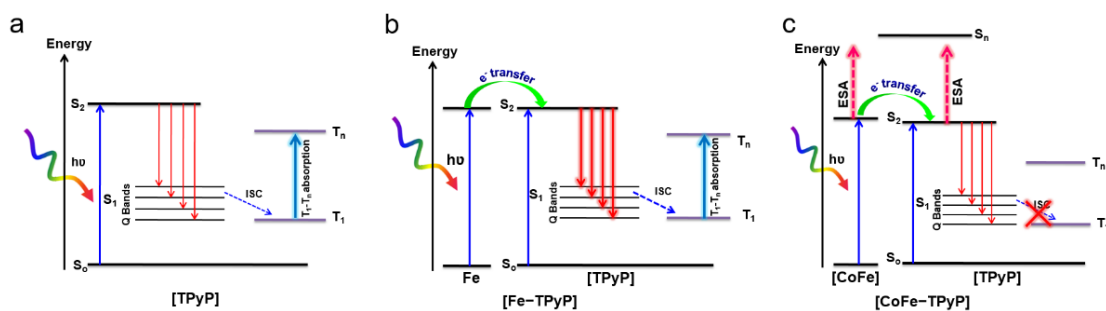


Figure 4.18 Schematic illustration of the energy diagram for (a) [TPyP], (b) [Fe-TPyP], and (c) [CoFe-TPyP] compounds. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

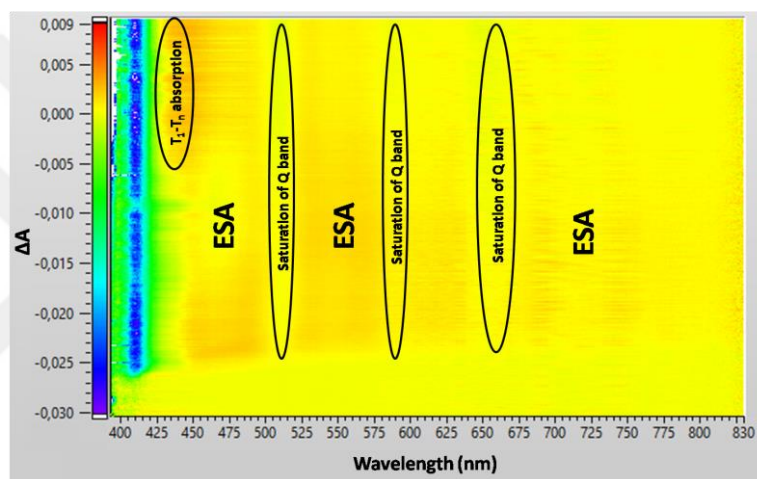


Figure 4.19 TA spectra of [TPyP] compound at 400 nm (pump) excitation. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

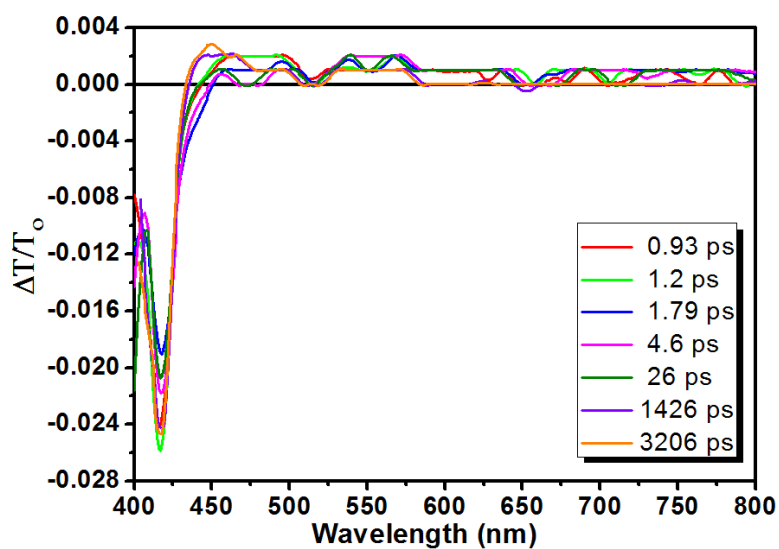


Figure 4.20 TA spectra of [TPyP] compound at 400 nm (pump) excitation with different pump probe time delays. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

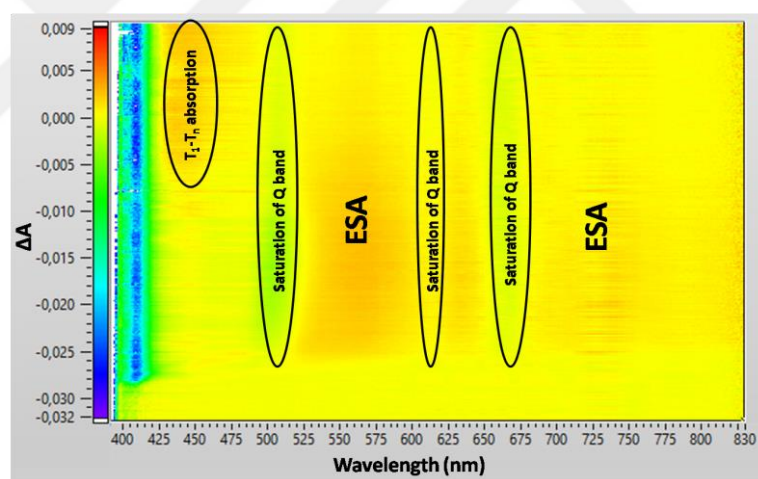


Figure 4.21 TA spectra of [Fe-TPyP] compound at 400 nm (pump) excitation. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

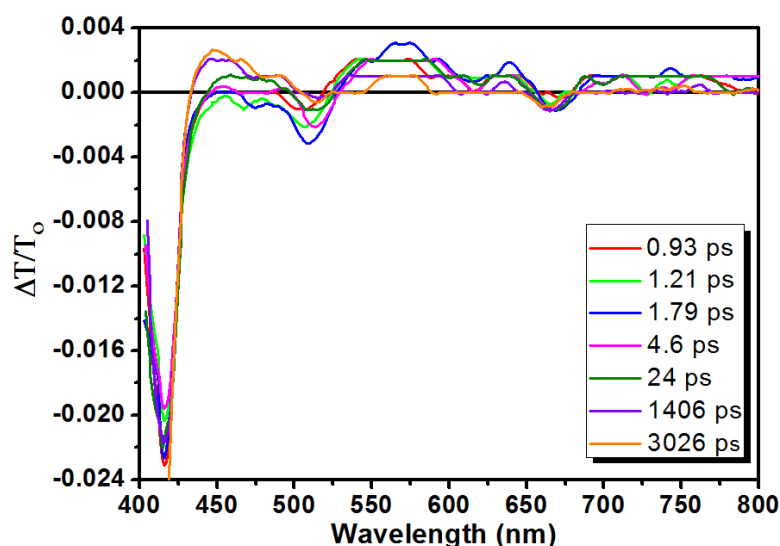
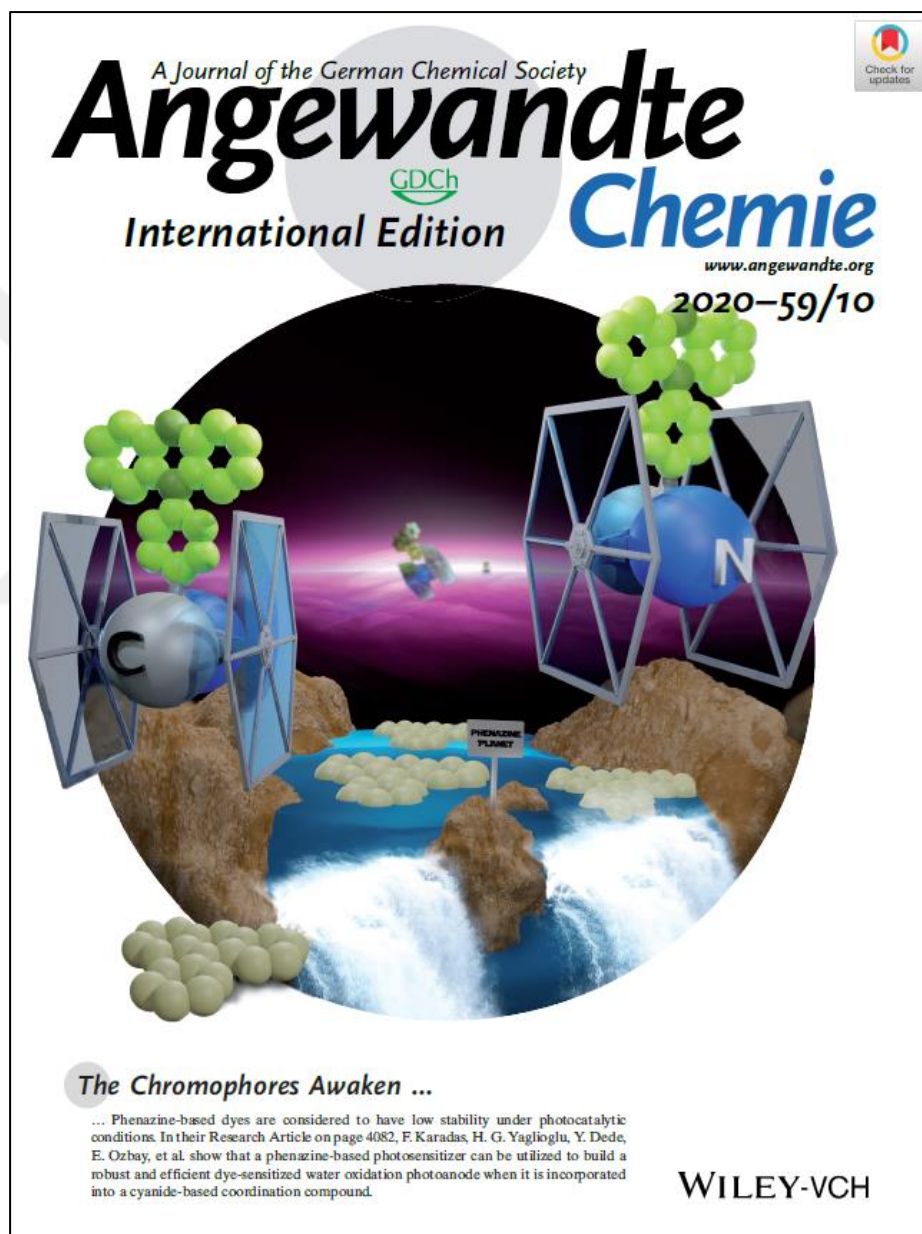


Figure 4.22 TA spectra of [Fe-TPyP] compound at 400 nm (pump) excitation with different pump probe time delays. (Reprinted with permission from Wiley Ref. [125]. Copyright © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

4.5. Summary

In summary, an entirely earth-abundant cyanide-based chromophore-relay-catalyst triad system for light driven water oxidation was reported for the first time by engaging cyanide chemistry with the dyad concept. The reported assembly is genuine due not only to the simplicity of its synthesis but also to the bifunctionality of each of its components. The porphyrin fragment is both a chromophore and a capping ligand for reducing the dimensionality of PB structures, thus, increasing the number of active catalytic sites. Transient absorption measurements and computational studies show that $[\text{Fe}(\text{CN})_5]$ moiety serves both as a robust linker and a donor group that facilitates the electron transfer from the catalyst to the chromophore. Co-sites are essential for catalytic water oxidation. They also play a critical role in the formation of a stable heterogeneous assembly. Overall, this proof-of-concept study indicates that cyanide-based systems could be the key element for the development of earth-abundant, robust, and efficient dye-sensitized photoanodes. The modular and versatile $\text{Fe}(\text{CN})_5$ chemistry is further explored in our labs by introducing other chromophores to generalize the concept of photocatalytic water oxidation with cyanide-based assemblies.

Chapter 5. Janus Green Incorporated PB for Dye-Sensitized Water Oxidation



5.1. Preface

This chapter of the thesis is based on the publication "*A Robust, Precious-Metal-Free Dye-Sensitized Photoanode for Water Oxidation: A Nanosecond-Long Excited-State Lifetime through a Prussian Blue Analogue*", T. G. Ulusoy Ghobadi, A. Ghobadi, M. Buyuktemiz, E. Akhuseyin Yildiz, D. Berna Yildiz, H. G. Yaglioglu, Y. Dede, E. Ozbay, F. Karadas., **Angew. Chem. Int. Ed.** 2020, 59, 4082 – 4090. (Inside Back Cover). Adapted (or "Reproduced in part") with permission from John Wiley and Sons, Ref. [126]. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

5.2. Introduction

Dye-sensitization is at the heart of several photochemical applications including solar cells, solar energy harvesting devices, and photoelectrochemical cells.[65], [194], [195] Recently, this concept has been ingeniously adapted to oxidize water, forming the foundation of DS-PECs.[163], [196]–[199] A DS-PEC architecture consists of a WOC coupled to a dye-sensitized metal oxide SC with a large band gap. Two main strategies have been employed so far to improve the rate of the catalytic four-electron water oxidation process and to reduce the back electron transfer in DS-PECs: i) connecting the chromophore and the catalyst with appropriate bridging groups forming a dyad,[64], [164], [200] and ii) introducing secondary electron donor and acceptor groups forming a triad,[201] tetrad,[166] and so on,[165] similar to natural photosynthesis. Recently, numerous molecular-based DS-PECs have been reported.[170], [171], [173], [174], [202] While molecular systems offer diversity and high performance, they are limited with precious Ru and Ir based WOCs and/or Ru chromophore units. Furthermore, the inherent poor stability (in the order of minutes) of molecular systems has been one of their bottlenecks.[203] Thus, in recent years, finding an earth-abundant alternative for Ru was pointed out as one of the primary perspectives for further implementing DS-PEC technology.[197] Along this path, the use of organic sensitizers has been found to be a promising design strategy for the replacement of Ru-based assemblies.[204] Aromatic macrocycles such as porphyrin and phthalocyanine derivatives have been the most commonly utilized sensitizers among organic based DS-PECs.[176], [205]–[207] The short excited state lifetime and short hole diffusion length of these dyes, however, generally limit their photocurrent to a value well below 100 $\mu\text{A}/\text{cm}^2$, which

decays rapidly with a nominal half-life of a couple-to-tens of minutes, limiting their long-term stability for practical usage.[176], [206] Moreover, in all of these organic systems, the catalytic site is made of Ir or Ru based metalated complexes, which violates the motivation for building an entirely earth-abundant DS-PEC system. In this respect, the use of bulk systems can be considered as a viable approach not only to introduce earth-abundant units to the field but also to improve the stability of such multi-component photoelectrodes. As the only example of an entirely precious metal-free water oxidizing dye-sensitized photoanode, Kirner *et al.* proposed an organic chromophore sensitized SnO₂ photoanode with a photocurrent, which decayed from ~40 to 20 $\mu\text{A}/\text{cm}^2$ over 5 min.[208] Later, this photoactive chromophore is coupled with a bulk cobalt oxide (CoO_x) WOC layer, in which the catalytic oxide layer also serves as a protective layer for the chromophore during the photoelectrocatalytic process.[177] The system, however, suffered from electron-hole recombination due to the inevitable growth of the CoO_x particles on the semiconductor surface in addition to the organic dye layer and, consequently, resulted in a dramatic decrease in the photocurrent. This deficiency can be mitigated via molecular dyad strategy where a covalent linkage will ensure close proximity between the chromophore and WOC and this, in turn, will promote fast and efficient carrier dynamics. It is, therefore, evident that a new chemistry toolbox is necessary for the proper coordination of chromophore and WOC in a three-dimensional bulk system. Besides metal oxide WOCs, cyanide-based extended networks, so-called PBAs have also attracted vigorous attention as potential non-oxide heterogeneous WOCs due to their diversity, entirely earth-abundant components, and exceptional stabilities in a wide pH range (from 1 to 13).[112], [127], [130], [179], [191], [209]–[212] In photoconversion applications, PBAs are essentially used as WOCs for efficient extraction of photogenerated holes of a SC photoanode. We have recently demonstrated that a pentacyanoferrate complex can be used as a bridging group to incorporate an organic chromophore to a PBA structure, thereby forming a robust three-dimensional triad assembly for the light-driven water oxidation process. [125]

Herein, we move a step forward and employ this synthetic methodology to build a robust precious-metal free dye-sensitized photoanode for water oxidation. The synthesis involves the straightforward coordination of pentacyanoferrate group to a pyridyl containing organic chromophore followed by reaction with cobalt ions to build a hetero trifunctional PBA in situ on a rutile TiO₂ nanowire (NW) electrode. The rutile phase has been preferred to anatase since the recombination kinetics for a rutile phase TiO₂ is an order of magnitude

slower compared to the latter.[213] Several different pyridyl containing organic ligands including positively charged nitrogen bearing ones were screened with quantum chemical calculations prior to synthesis. Guided by computational studies, the targeted organic chromophore, in this study, is Janus green B ([JG]) which has a broad absorption response with an upper edge in the near-infrared (NIR) regime. The sensitization ability of JG coordinated PB assembly and the role of each components in the electron transfer mechanism and charge separation is discussed based on photoelectrochemical measurements, transient absorption studies, and quantum chemical calculations.

5.3. Experimental Procedures

5.3.1. Materials

Janus Green B (denoted as JG), sodium sulfite (Na_2SO_3), sodium Sulfate (Na_2SO_4) sodium nitroferricyanide ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), ammonium hydroxide solution (NH_4OH , 25% (v/v), Ethanol (EtOH), methanol (MeOH), and Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Titanium (IV) butoxide ($\text{Ti}(\text{OBu})_4$, 97%, hydrochloric acid (HCl , 36%), and Millipore deionized water (resistivity: 18 $\text{M}\Omega/\text{cm}$), FTO coated glass (2 mm thick, 7 Ω/sq). Potassium phosphate buffer solution (PBS) was prepared by 0.1M KH_2PO_4 and 0.1M K_2HPO_4 .

5.3.2. Sample Preparation

Synthesis of Sodium aminopentacyanoferrate, $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$, [Fe–NH₃]: [Fe–NH₃] was synthesized according to our previous reported procedure with slight modifications.[112], [125].

Pentacyanoferrate-Coordinated JG, $\text{Na}_2\text{FeC}_{35}\text{H}_{31}\text{N}_{11} \cdot x\text{H}_2\text{O}$, [Fe–JG]: Compound [JG] (0.5 mmol) was dissolved in ~10 mL of ethanol at room temperature. Since [Fe–NH₃] has limited solubility in ethanol, an excess amount of the sample (0.5 mmol) was dissolved in a sufficient amount of EtOH. After mixing both solutions separately for about 30 minutes, a solution containing $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ complex was added dropwise to the solution containing [JG] and the color of suspension changed from blue to dark blue. The reaction was allowed to continue mixing in a covered flask for a day. The unreacted

$[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ complex, which forms a precipitate, was removed by filtration and washed with ethanol. The solution was then concentrated with a rotary evaporator yielding a blue precipitate. The blue precipitate was isolated and dried under vacuum overnight at room temperature.

Cobalt Pentacyanoferrate–Coordinated JG, $\text{NaCo}_3\text{FeC}_{35}\text{H}_{31}\text{N}_{11} \cdot x\text{H}_2\text{O}$, [CoFe–JG]: [Fe–JG] compound (20 mg, 28 μmoles) was dissolved in EtOH and 1 equiv. $\text{Co}(\text{NO}_3)_2$ in EtOH was added dropwise to the [Fe–JG] solution. In order to collect the solid and remove soluble unreacted species, the suspension was centrifuged at 6,000 rpm for 45 min with water and acetone, sequentially. The obtained product was dried in oven at 35°C for one day. The synthesis route is schematically summarized in Figure 5.1.

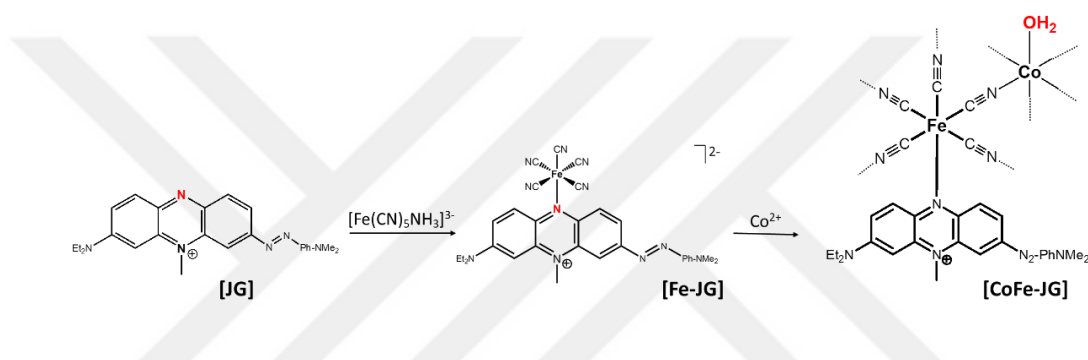


Figure 5.1 Synthesis route for [CoFe–JG]. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Synthesis of TiO_2 Nanowires (NWs), [TiO₂]: TiO_2 NW arrays were synthesized by modifying the hydrothermal technique as described in our previous study. [126] In detail, 1 mL of $\text{Ti}(\text{O}i\text{Bu})_4$ was added dropwise to the HCl solution, accompanied by intense stirring, which was prepared with the volume ratio of concentrated HCl to deionized (DI) water being 1:1. After being stirred for 30 min under ambient conditions, the precursor solution was transferred to a Teflon-lined stainless steel autoclave (capacity of 45 mL) with an FTO conducting side facing up at a 45° angle against the wall. In advance, FTO glasses (1 cm×2 cm) are cleaned sufficiently in sonication baths in DI water, acetone, and ethanol in sequence, each for 15 min and then dried by N_2 flow. The hydrothermal reaction was carried out at 180°C for 4 hours, and then it was allowed to cool down slowly at the room environment. Finally, the sample was rinsed with DI water to remove the residual solvent, and calcined at 450°C for 2 hours in a tube furnace under ambient air condition.

TiO_2 /[CoFe–JG] electrode (in situ PB modified dye-sensitized TiO_2 electrode): Here, an organic chromophore coordinated PB structure was

obtained with a straightforward two-step synthetic route. First, the ammino ligand of $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ $[\text{Fe}-\text{NH}_3]$ complex was substituted with a pyridyl containing molecular organic chromophore, [JG] in our case. Then, the [JG] coordinated pentacyanoiron(II) complex, $[\text{Fe}-\text{JG}]$, was reacted with Co^{2+} ions to afford a chromophore-PB ($[\text{CoFe}-\text{JG}]$) assembly (Figure 5.2). For the preparation of a $[\text{CoFe}-\text{JG}]$ modified TiO_2 electrode, an in situ procedure was adapted to maximize the interaction between the SC surface and $[\text{CoFe}-\text{JG}]$. TiO_2 NWs soaked in $[\text{Fe}-\text{JG}]$ (1.33 mM) in EtOH solution for 24 hours at room temperature. The samples were then rinsed with EtOH to remove any non-adsorbed dye molecules. Once the substrate was completely dried, $\sim 500 \mu\text{L}$ of $\text{Co}(\text{NO}_3)_3$ solution (0.16 M) was drop casted onto the $\text{TiO}_2/[\text{Fe}-\text{JG}]$ electrode. Then, the slide was washed with DI water to remove the excess Co^{2+} ions over the film. This process is repeated 2-3 times to complete the full coverage of PB analogue. Finally, the $\text{TiO}_2/[\text{CoFe}-\text{JG}]$ electrode was left for drying at room temperature.

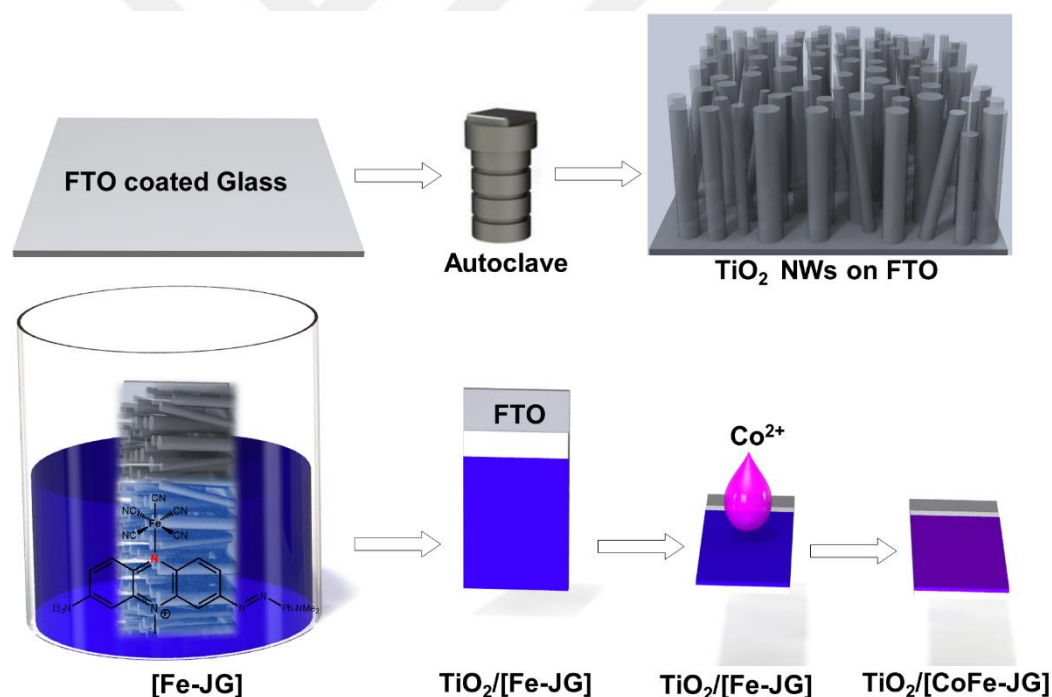


Figure 5.2 Schematic illustration for the formation of CoFe PB modified dye-sensitized TiO_2 electrode as a photoanode ($\text{TiO}_2/[\text{CoFe}-\text{JG}]$) through a three-step process on FTO coated glass substrate: (i) hydrothermal growth for TiO_2 NWs, (ii) immersing them into Fe bonded Janus green dye ($[\text{Fe}-\text{JG}]$), and (iii) in-situ drop-casting of Co^{2+} ions containing solution. The electrode color change from blue to purplish. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

5.4. Results and Discussions

5.4.1. Design of the Photoelectrode

The first step is to find a proper PS unit to achieve high performance water oxidation. Guided by our previous findings, we kept the $[\text{Fe}(\text{CN})_5]$ fragment and active Co site unchanged and screened various organic ligands (R) featuring a pyridyl group (Figure 5.3a). A combination of up-to-date quantum chemical calculations (performed by Prof. Dede's research group) showed that, in line with our previous results, [125], [191], [214] the critical LUMO is on the Co–O fragment (Figure 5.3a) for the active Co oxo/oxyl species.¹ Moreover, the inclusion of a formal positive charge on the ligand by virtue of quaternized pyridyl salts resulted in a more electrophilic LUMO. This was a hint to exploit ligands, possessing quaternized N atoms, on Fe in order to facilitate the nucleophilic attack of water at the Co–O center. The ground and excited state calculations on the model $\text{H}_2\text{O}-\text{Co}-\text{NC}-\text{Fe}-\text{R}$ system (not presented here) further suggest that LUMO is exclusively located on the chromophore unit. Therefore, the evolution of the presumed active form of the catalyst from $\text{H}_2\text{O}-\text{Co}-\text{NC}-\text{Fe}-\text{R}$ to $\text{O}-\text{Co}-\text{NC}-\text{Fe}-\text{R}$ can give rise to holes transferring to the catalytically active Co site. Given the aforementioned structural requirements, we further sought commercially available quaternized N dyes with available pyridyl groups. A phenazine-based dye, Janus green B, satisfies these conditions with its available pyridyl nitrogen site and quaternized nitrogen group. Moreover, it exhibits a superior optical response with several absorptions in the visible and NIR regions and possesses several amine groups that can be used to enhance the interaction between the chromophore and TiO_2 surface.

Here, an organic chromophore coordinated PB structure was obtained with a straightforward two-step synthetic route. First, the ammino ligand of $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ ($[\text{Fe}-\text{NH}_3]$) complex was substituted with a pyridyl containing molecular organic chromophore, [JG] in our case. Then, the [JG] coordinated pentacyanoiron(II) complex, $[\text{Fe}-\text{JG}]$, was reacted with Co^{2+} ions to afford a chromophore-PB ($[\text{CoFe}-\text{JG}]$) assembly. For the preparation of a $[\text{CoFe}-\text{JG}]$

¹Multi-reference calculations for model systems (not shown in here) also confirmed a local high spin center for the Co–O fragment, in line with our previous reports and as opposed to a recent report by Pires et al. where a closed shell configuration for the $_{27}\text{Co}(\text{III/IV})\text{ d}^6/\text{d}^5$ system in a low field ligand environment was proposed. [115]

modified TiO₂ electrode, an in-situ procedure was adapted to maximize the interaction between the SC surface and [CoFe–JG]. Hydrothermally grown rutile TiO₂ NWs on FTO coated glass was soaked in a solution containing [Fe–JG] overnight, forming the dye-sensitized TiO₂ electrode. This resulting electrode is reacted with Co²⁺ ions to obtain PB assembled dye-sensitized TiO₂ working electrode (TiO₂/[CoFe–JG]). Figure 5.3b,c shows the chemical structures of photosensitizer-catalyst assembly and the in situ construction on TiO₂ NWs. The Co sites are coordinated to single/multiple Fe linkers to form an interconnected bulky layer covering the photosensitizer organic molecules. A reference electrode was prepared by the sequential dip-coating of a regular CoFe PBA on TiO₂ NWs (TiO₂/[CoFe]). Three dip-coating steps are carried out for PBA layer.

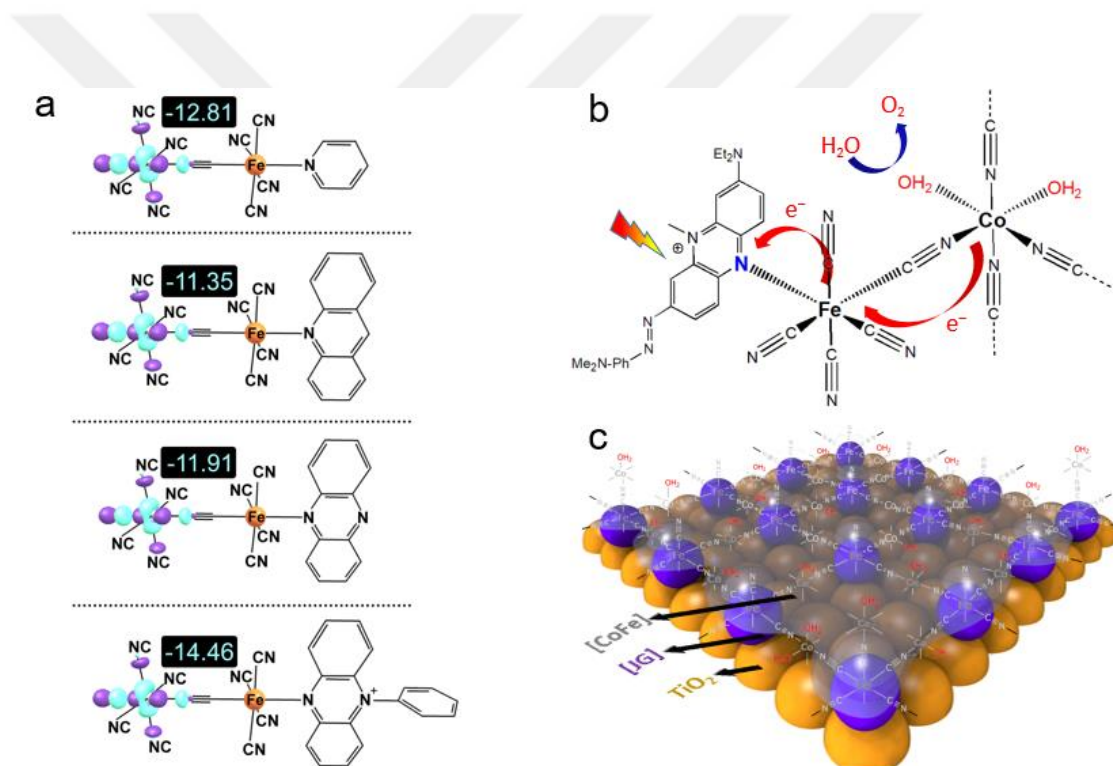


Figure 5.3 Structural and morphological properties: (a) LUMO plots and energies (eV) of the molecules (R) considered for the rational design of DS-PECs. The inclusion of a formal positive charge on the ligand by virtue of quaternized pyridyl salts resulted in a more electrophilic LUMO. (b) Chemical structure of [CoFe–JG] assembly. Arrows indicate the electron transfer pathway proceeding from the Co donor to Fe linker and then to JG acceptor group. (c) A rough schematic representation of in situ formation of an ultrathin PB complex on dye-sensitized TiO₂ photoanode yielding TiO₂/[CoFe–JG] electrode. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

5.4.2. Materials Characterization

Structural analysis is performed to elucidate the design morphology. The optical images of the bare TiO₂ NWs, TiO₂/[CoFe], and TiO₂/[CoFe–JG]) are displayed in Figure 5.4a. This figure shows the color change in the dye-sensitized photoanode. In addition to this, the top and cross-sectional scanning electron microscopy (SEM) images of the TiO₂/[CoFe–JG] photoanode indicate that TiO₂ NWs (with a ~1.5 μm length and a ~100 nm diameter) retain their morphology after [CoFe–JG] coating (Figure 5.4b,c). Transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDS) line scan analysis was performed in the vicinity of the NW surface to investigate the content of the coating (Figure 5.4d,e). The obtained TEM image and TEM-EDS analysis results confirm the formation of an ultrathin [CoFe] assembly with a thickness of around 10 nm on the surface of NW.

A further proof of successful formation of the assembly is achieved by the infrared (ATR-FTIR) spectroscopy of [JG], [Fe–JG], and [CoFe–JG] powders. These spectra exhibit similar features in the 1000-1600 cm^{-1} range confirming the presence of [JG] in the PB structure. [Fe–NH₃] exhibits a sharp CN peak at 2031 cm^{-1} , which shifts to a higher wavenumber for [Fe–JG] (~2058 cm^{-1}). [125] The blue shift is evidence for not only the coordination of [JG] to an iron complex but also the donor-acceptor interaction between the iron site and [JG], which plays a critical role in efficient electron transfer. The cyanide stretch exhibits a further shift (~2090 cm^{-1}) for [CoFe–JG] due to Fe–CN–Co coordination mode, and it is, in essence, a direct evidence for the formation of a PB structure (Figure 1f). A weak signal, observed at 2157 cm^{-1} , indicates the presence of partially oxidized Fe³⁺ and/or Co³⁺ sites. The peak at around 567 cm^{-1} is attributed to Fe–N coordination bonds. Prominent bands between 1600 and 1330 cm^{-1} are attributed to C=C and C=N stretches of the chromophore structure. The band with a maximum peak at 1384 cm^{-1} is from the stretching vibration of NO₃[–] ions in [CoFe–JG]. The sharp peak at around 1264 cm^{-1} belongs to N–H stretch; several peaks in the 1000 – 1330 cm^{-1} and 2850 – 2900 cm^{-1} range correspond to symmetric and asymmetric stretches of C–H bond. The broad peak at 3300 cm^{-1} belongs to OH stretch while the one at around 1620 cm^{-1} corresponds to the H–OH bending of solvent water molecules. A similar CN stretch feature is observed in the photoanodes, as well, see Figure 5.4g. Thus, all these results prove the successful formation of triad assembly on titania NWs.

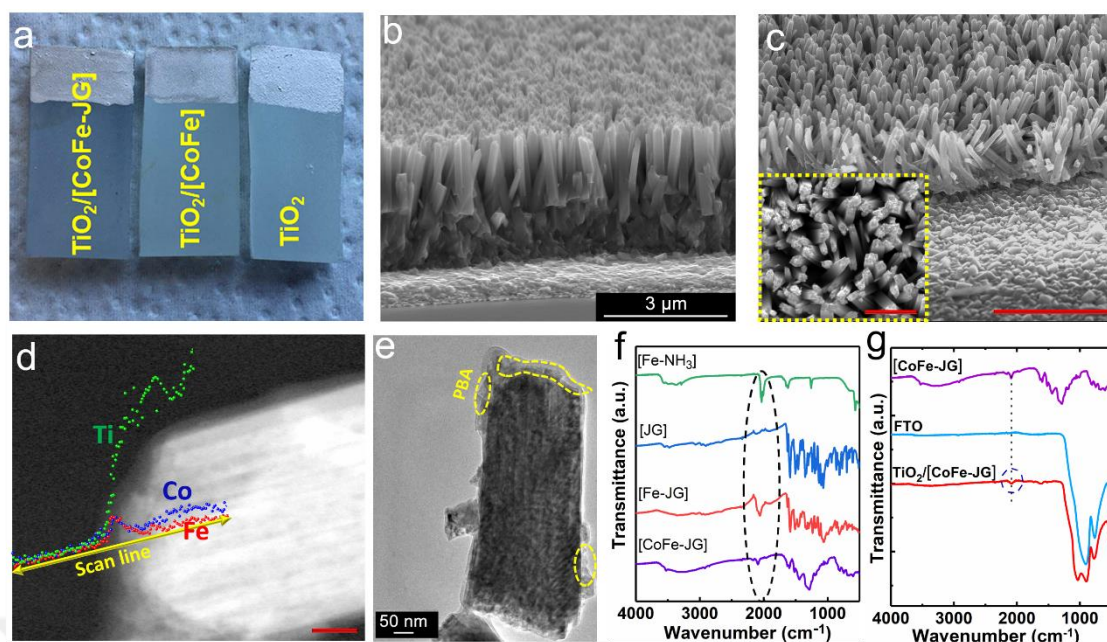


Figure 5.4. (a) The photographs show (left to right) the WEs that are on the FTO samples; TiO_2 / $[\text{CoFe-JG}]$, TiO_2 / $[\text{CoFe}]$ and TiO_2 . (b,c) Side-view of the SEM image of TiO_2 / $[\text{CoFe-JG}]$ photoanode, scale bar: 3 μm . (c) The inset shows the top view of the NWs with the scale bar of 1 μm . (d) EDS line scan in HR-TEM from air to an individual PB coated TiO_2 NW with a high magnification of the interface, scale bar: 50 nm. (e) HR-TEM image of an individual PB coated TiO_2 NW ($[\text{TiO}_2$ / $[\text{CoFe}]$) with yellow contrasts indicating the existence of a <10nm-thick PB layer. (f) ATR-FTIR spectra for $[\text{Fe-NH}_3]$, $[\text{JG}]$, $[\text{Fe-JG}]$, and $[\text{CoFe-JG}]$. The sharp peaks in the 2000–2100 cm^{-1} range are attributed to CN stretch. (g) ATR-FTIR spectrum of TiO_2 / $[\text{CoFe-JG}]$ electrode, $[\text{CoFe-JG}]$ bulk, and FTO. The dash circle shows the existence of CN band between 2000-2100 cm^{-1} . (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

After morphological analysis, the presence of the mixed oxidation states of metal ions in a PB structure is also confirmed by X-ray photoelectron spectroscopy (XPS) measurements conducted for both the powder ($[\text{CoFe-JG}]$) sample and the photoanode (TiO_2 / $[\text{CoFe-JG}]$) (Figure 5.5 - Figure 5.7 and Table 5.1). XPS spectra of N1s are shown in Figure 5.5a-d. N1s pattern of $[\text{Fe-NH}_3]$, revealed peaks located at 397.74 and 399.04 eV, which are attributed to the nitrogen atoms of cyanide and NH_3 , respectively (Figure 5.5a). The N1s region for $[\text{JG}]$ can be fitted by four components assigned to nitrogen in $-\text{N}=\text{N}-$ groups (~ 399.25), nitrogen atoms of nitride or N in aromatic ring/pyridine N, $=\text{N}-$, (~ 400 eV), tertiary amine in the side groups (~ 401 eV) and positively charged nitrogen atom ($-\text{N}^+$) in the ring ($\sim 403\text{--}404$ eV), [215] see Figure 5.5b. The nitrogen peaks were deconvoluted in a similar way for $[\text{Fe-JG}]$ and $[\text{CoFe-JG}]$ with cyanide N atoms, $\text{C}\equiv\text{N}$, (~ 397 eV) due to

the addition of $\text{Fe}(\text{CN})_5^-$ moieties to a carbon ring, see Figure 5.5c,d. In addition, in the [CoFe–JG] case, N atoms in the nitrate NO_3^- peaks stemming from the synthesis procedure, as expected, appeared ($\sim 406\text{--}407$ eV). In [CoFe–JG], the relative increase in the intensity shifts to 398.35 eV since the nitrogen atoms binding energies in the cyanide groups increase once they were coordinated to the Co sites. However, a slight decrease in other binding energies of N1s peaks was observed due to an increase in the electron density of the carbon ring because of π back bonding interaction between the iron sites and pyridyl groups of the carbon ring.

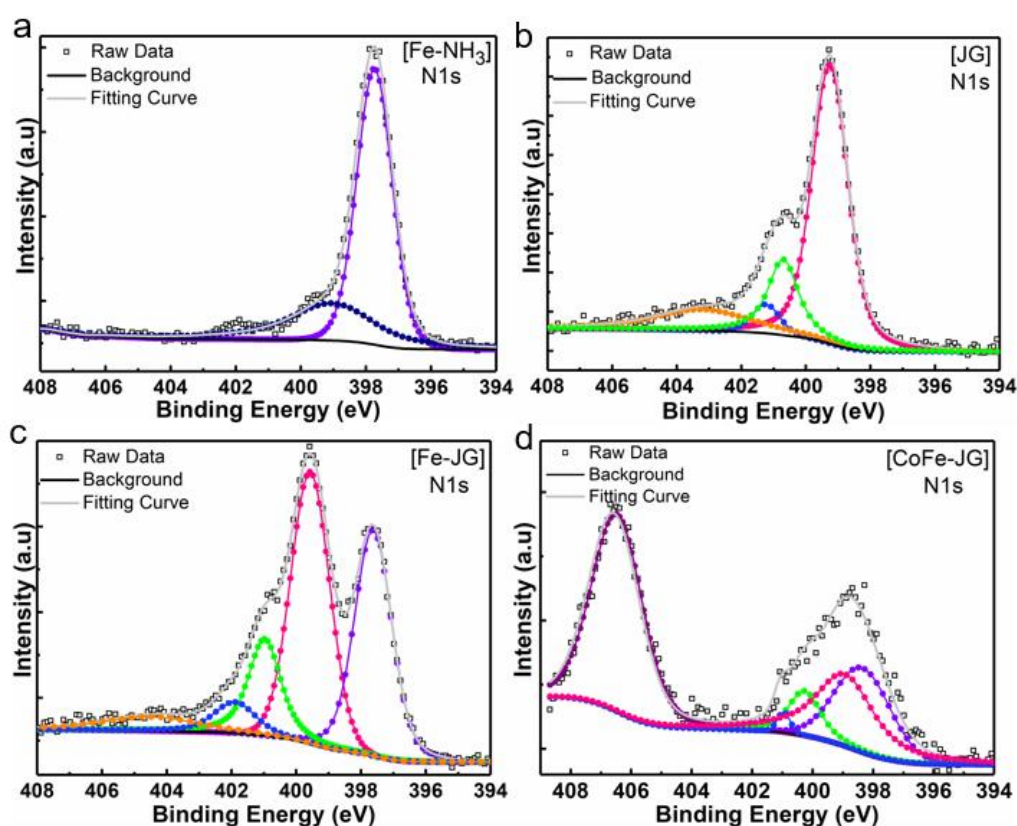


Figure 5.5 High resolution XPS spectra of N1s for (a) [Fe–NH₃], (b) [JG], (c) [Fe–JG], and (d) [CoFe–JG]. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Table 5.1 Summary of N1s XPS results obtained from (a) [Fe–NH₃], (b) [JG], (c) [Fe–JG], and (d) [CoFe–JG].

Compounds	N1s, eV						
	C≡N	N-Fe	-N=N-	=N-	NR ₃	N ⁺	NO ₃ ⁻
[Fe–NH ₃]	397.74	399.04	-	-	-	-	-
[JG]	-	-	399.25	400.7	401.23	403.18	-
[Fe–JG]	397.63	-	399.56	400.97	401.9	404.5	-
[CoFe–JG]	398.35	-	398.93	400.95	400.26	*-	406.47

*(not observed possibly due to donation from Fe(CN)₅ group)

The XPS profiles for the powders have been first analyzed. As shown in Figure 5.6a-b, Fe2p region exhibits in [Fe–NH₃] exhibits two dominant bands at around 708 and 721 eVs, which are assigned to 2p_{3/2} and 2p_{1/2} of Fe²⁺, respectively. Two small bands at ~710 eV and ~723 eV were also observed for [Fe–JG] due to the partial oxidation of Fe²⁺ to Fe³⁺ ions in Fe(CN)₅ fragments.[216]–[218] Such an oxidation, which has been commonly observed in pentacyanoiron chemistry, is also evidenced by IR spectra, which reveals a shoulder in the cyanide region ~2,159 cm⁻¹ for [Fe–JG] and ~2,129 cm⁻¹ for [CoFe–JG]. Figure 5.6c shows the high resolution Co2p spectrum for the [CoFe–JG] powder, which consists of two main broad peaks corresponding to 2p_{1/2} and 2p_{3/2} "spin-orbit" features, with a broad satellite.

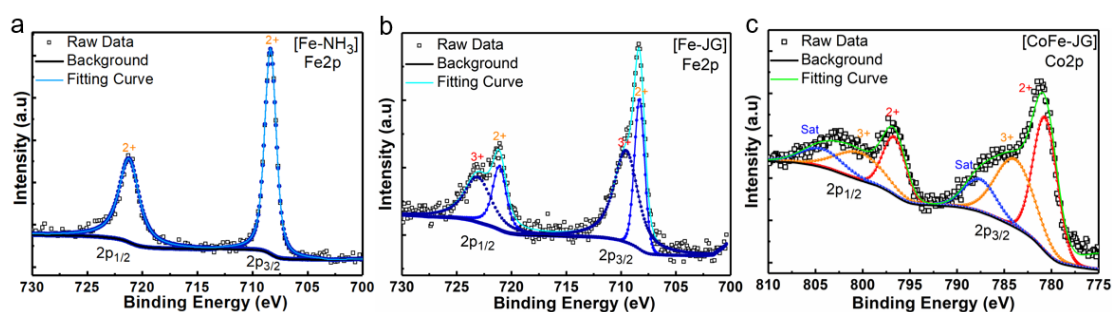


Figure 5.6 High resolution XPS spectra of (a, b) Fe2p for [Fe–NH₃], [Fe–JG], and (c) Co2p for [CoFe–JG] powders. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

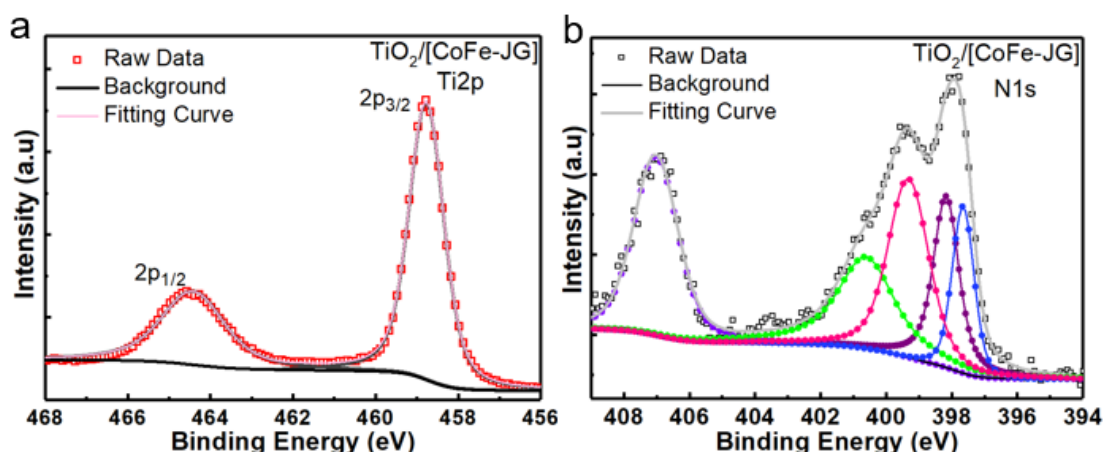


Figure 5.7 High resolution XPS spectra of (a) Ti2p and (b) N1s for TiO₂/[CoFe-JG] electrode. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

XPS analysis of Ti2p and N1s were also conducted for TiO₂/[CoFe-JG] photoanode. For pristine TiO₂ NWs, the core level binding energy of Ti2p_{3/2} and Ti2p_{1/2} were located at 458.77 eV and 464.42 eV, respectively (Figure 5.7a). The main peaks of the N1s core-spectra were fitted with 5 components at 406.93, 400.52, 399.2, 398.07, and 397.55 eV, signifying the existence of NO₃⁻, NR₃, =N-, -N=N-, and C≡N groups in the sample, respectively (Figure 5.7b).

5.4.3. Photoelectrochemical Measurements

The photoanodes were bare TiO₂ NWs “TiO₂”, PB coated TiO₂ NWs “TiO₂/[CoFe]”, JG modified PB coated TiO₂ NWs “TiO₂/[CoFe-JG]” with an exposed area of 1.6 cm². The PEC water oxidation measurements were performed with a three-electrode cell for TiO₂, TiO₂/[CoFe], and TiO₂/[CoFe-JG] as working electrodes (see cell configuration in Figure 5.8a). The linear sweep voltammograms (LSVs) exhibit no significant change in the current density in the absence of light (dark condition) at low overpotentials. At high potentials, above ~1.6 V_{RHE}, the current density of TiO₂/[CoFe] increases due to the electrocatalytic water oxidation process at the cobalt sites. This feature is, however, less prominent for TiO₂/[CoFe-JG] due to the presence of the insulating JG units, which indicates that TiO₂/[CoFe] serves as a better electrocatalyst than TiO₂/[CoFe-JG]. Interestingly, the trend is quite different under light irradiation condition. Under 1 sun solar light irradiation, without a filter case, the photocurrent performance for TiO₂/[CoFe-JG] is the highest reaching a photocurrent density of 551 μA/cm² at 1.23 V_{RHE} electrode (Figure 5.8b). A similar trend was observed with applied bias photon-to-current

efficiency (ABPE) plots (Figure 5.8c). At 0.65 V_{RHE} , $\text{TiO}_2/[\text{CoFe-JG}]$ electrode shows an ABPE of approximately 0.20%.

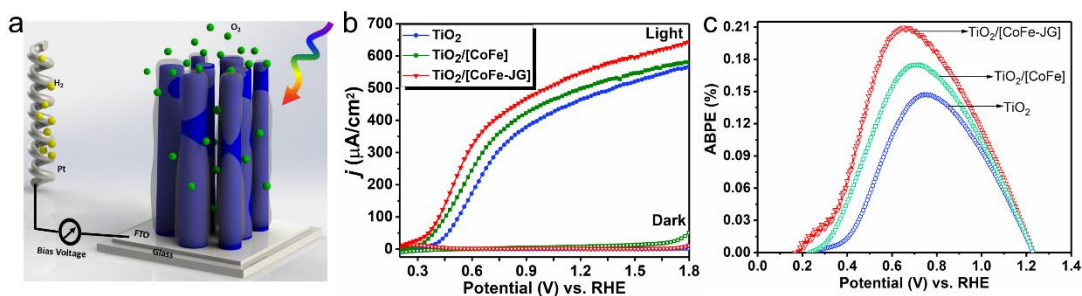


Figure 5.8 (a) Illustrative representations of a 3D schematic of the PEC-WS system consisting of rutile TiO_2 NWs coated FTO electrode loaded with a sensitizer-catalyst dyad, $\text{TiO}_2/[\text{CoFe-JG}]$ (1.6 cm^2), as a WE. (b) LSV measurements, j - V curves, of the WEs under light illumination, without using filter (solid symbols), and under dark (empty symbols) condition. Anodic scan rate: 50 mV/s, electrolyte: 0.1 M PBS (pH 7), light intensity: $100 \text{ mW}/\text{cm}^2$. (c) Calculated ABPE curves of TiO_2 , $\text{TiO}_2/[\text{CoFe}]$, $\text{TiO}_2/[\text{CoFe-JG}]$ photoanodes. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

To have a better qualitative comparison, the photoresponse raised from TiO_2 has been suppressed using a 420 nm cut-off filter. LSV profiles, under visible light illumination, demonstrate a current density of approx. $60 \mu\text{A}/\text{cm}^2$ at 1.23 V_{RHE} for $\text{TiO}_2/[\text{CoFe-JG}]$ electrode (Figure 5.9a). The bare TiO_2 reveals a photocurrent density of $27 \mu\text{A}/\text{cm}^2$ at the same voltage (originated from the tail absorption of the NW design). Since the filter has not completely suppressed the TiO_2 activity, it is essential to scrutinize whether this response arises from the dye absorber layer or from the catalyst-induced enhancement of the TiO_2 host. To answer this question, sequential dip-coating steps were carried out to maximize the PBA loading. As illustrated in Figure 5.9b, the highest light-dark current difference was achieved after four dipping steps. Larger steps do not significantly enhance the photocurrent but rather increase the dark activity. Moreover, $\text{TiO}_2/[\text{CoFe-JG}]$ electrode exhibits lower dark current densities and a higher onset overpotential compared to those of $\text{TiO}_2/[\text{CoFe}]$.

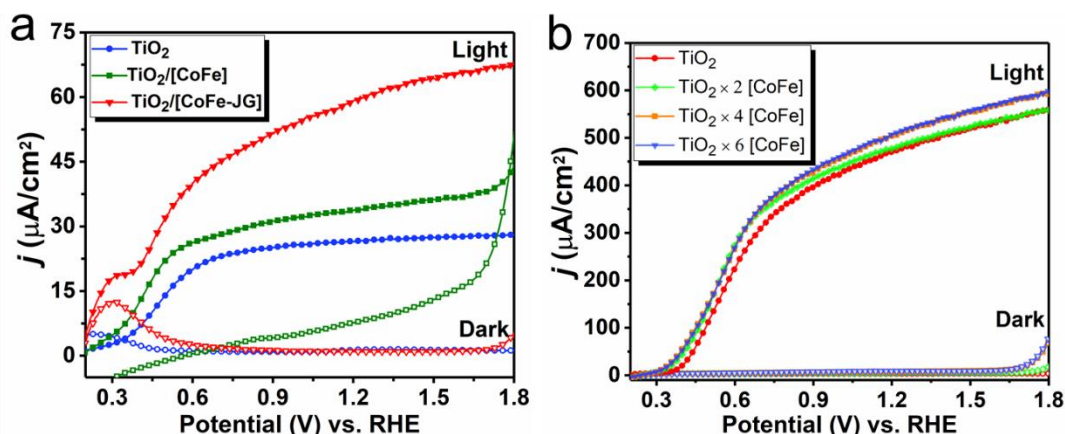


Figure 5.9 LSV measurements, j - V curves, of (a) the WEs under light illumination (solid symbols), under dark (empty symbols) with a white-light source coupled to a 420 nm long-pass filter, (b) the pristine TiO_2 NWs and 2, 4, and 6 times $[\text{CoFe}]$ PB modified TiO_2 NW electrodes under light illumination, without filter (solid symbols), and under dark (empty symbols). Anodic scan rate: 50 mV/s, electrolyte: 0.1 M PBS (pH 7), and light intensity: 100 mW/cm². (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Finally, the electrochemically active surface areas (ECSAs) for $\text{TiO}_2/[\text{CoFe}]$ and $\text{TiO}_2/[\text{CoFe-JG}]$ have been measured experimentally. Figure 5.10a,b shows the CV profiles of electrodes with different scanning rates ranging from 5 to 200 mV/s at 0.8 V_{RHE} in the N₂-saturated electrolyte (pH 7). The plot of capacitive currents with respect to scan rates shown in Figure 5.10c, gives a straight line and the slope is equal to double layer capacitance (C_{DL}). Thus, ESCA is linearly proportional to C_{DL} ($\text{ESCA} = C_{DL}/C_s$). When the electrodes are compared (by keeping the C_s same), The ESCA value of $\text{TiO}_2/[\text{CoFe}]$ is three times larger than that of the $\text{TiO}_2/[\text{CoFe-JG}]$ case. This data rules out the hypothesis that the interconnection of dye increases the Co numbers on the electrode surface. Thus, the integration of dye does not increase the surface concentration of Co sites on the electrode surface. This can be due to the fact that the surface of $\text{TiO}_2/[\text{CoFe}]$ have a larger amount of randomly oriented Co-Fe bonds, which enhances the adsorption of water, and so its catalytic performance is higher. This can be observed again by looking at the dark LSV in the Figure 5.9a.

These observations suggest that the relative photocurrent enhancement of $\text{TiO}_2/[\text{CoFe-JG}]$ cannot be explained by an increase in the surface concentration of catalytically active sites. Thus, the origin of this enhancement should be studied from the optical perspective.

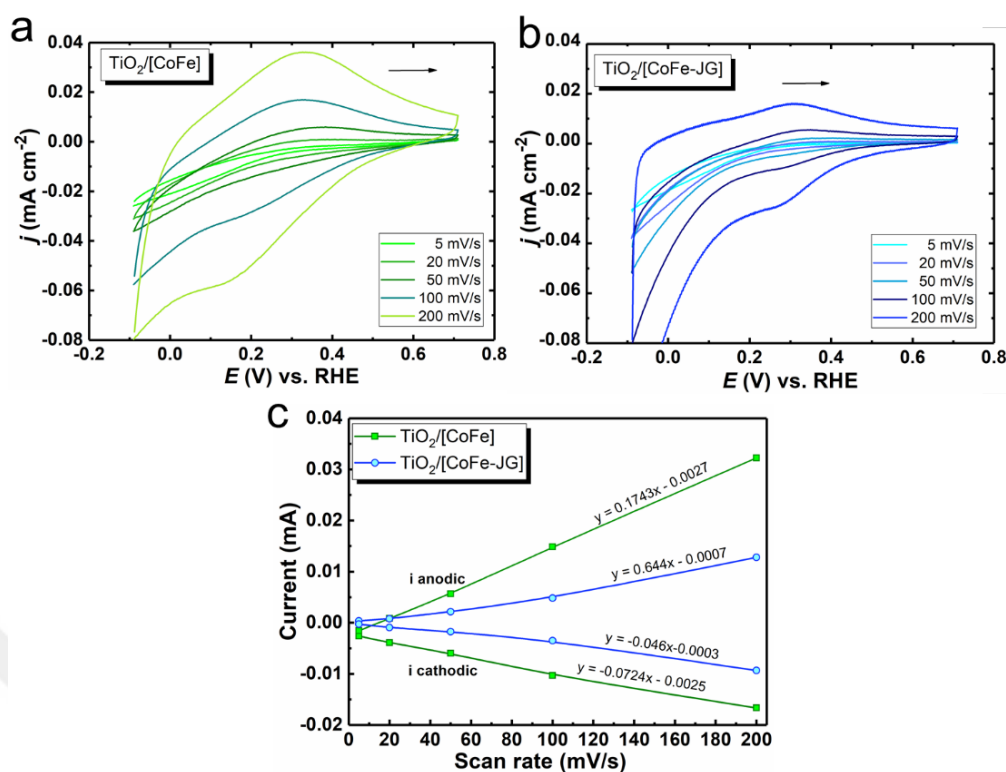


Figure 5.10 Set of CV curves for the (a) $\text{TiO}_2/[\text{CoFe}]$, (b) $\text{TiO}_2/[\text{CoFe-JG}]$ in N_2 -saturated 0.1 M PBS solution (pH 7) at different scan rates ranging from 5 to 200 mV/s . (c) The dependency of anodic and cathodic peak currents at 0.8 V_{RHE} as a function of scan rate. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

5.4.4. Steady-State Absorption and Photoluminescence Measurements

[JG] and [Fe-JG] reveal similar absorption trends with a peak at ~ 650 nm and a tail extending toward 800 nm, Figure 5.11a. The molar extinction coefficients for the dye were found to be in the order of $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Once the cyanide groups of [Fe-JG] are coordinated to Co^{2+} ions, a blue-shift in the absorption peak (575 nm) is observed. A similar trend is observed for TiO_2 based electrodes. The only difference is the blue shift in peak position (585 nm for $\text{TiO}_2/[\text{Fe-JG}]$, and ~ 540 nm for $\text{TiO}_2/[\text{CoFe-JG}]$), which is mainly due to higher refractive index of TiO_2 (compared to ethanol), see Figure 5.11b. The PL spectra of the samples have been explored by an excitation at their main peak wavelength. While the [JG] and [Fe-JG] reveal a weak PL in the ~ 700 –800 nm range, [CoFe-JG] represents a broad and strong response with a maximum at 615 nm. Therefore, it can be speculated that the PBA assembly tunes the energetic levels of the dye. While these absorption and PL results demonstrate

a broad spectral response (covering visible and NIR regimes) and efficient absorption dynamics for [CoFe-JG], the corresponding photocurrent LSV response is rather low, see Figure 5.9a.

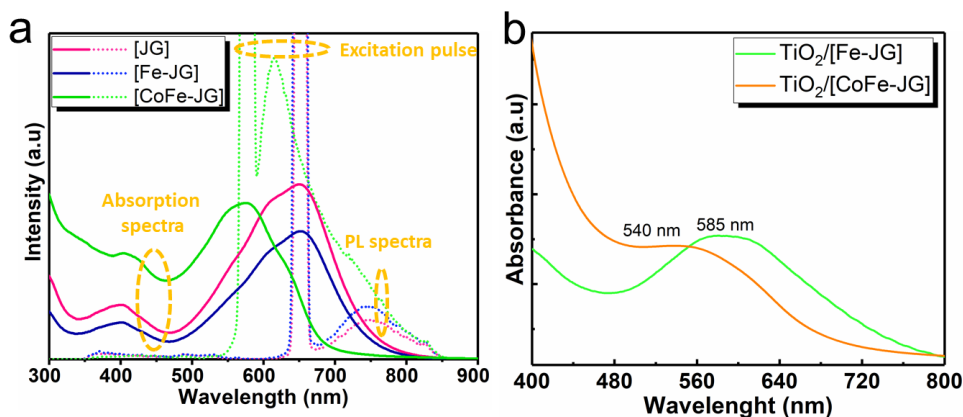


Figure 5.11 (a) Absorption spectra of the [JG], [Fe-JG], and [CoFe-JG] solutions. The PL spectra for [JG] and [Fe-JG] solutions with 650 nm excitation wavelength and [CoFe-JG] solution for an excitation wavelength of 575 nm. (10^{-3} M in EtOH solutions, 2 mm cuvette length). (b) The absorption spectra of TiO₂/[Fe-JG], and TiO₂/[CoFe-JG] electrodes. This data is obtained by taking the pristine TiO₂ NWs as the reference. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

5.4.5. Incident Photon-to-current Conversion Efficiency

Incident photon-to-current conversion efficiency (IPCE) is measured for all three photoanodes to interpret this unexpected low activity (Figure 5.12a). IPCE measurement were obtained by illumination the photoanodes in three-electrode setup with light of a specific wavelength (from 300 nm to 500 nm, step: 10 nm/step) and measuring the resulting short-circuit current keeping the voltage fixed at 1.23 V_{RHE}. The (j - V) curves were measured on photoanodes in 0.1 M PBS under dark and light conditions with a scanning rate of 50 mV/s between -0.4 V_{Ag/AgCl} and 1.2 V_{Ag/AgCl} by the LSV technique. IPCE spectra exhibit a strong UV response for all electrodes. The profiles for bare TiO₂ and TiO₂/[CoFe] samples are similar, with a peak at 370 nm and an edge at 440 nm (the absorption tail of TiO₂). Therefore, the PBA assembly does not tailor the effective optical band gap of TiO₂ and it only facilitates interfacial charge transfer dynamics. However, a broad yet weak visible light response is probed for TiO₂/[CoFe-JG] photoanode. It can be speculated that this weak response is derived from the [JG] chromophore. Nevertheless, this response shows an

exponential decline as we go toward longer wavelengths and it becomes near zero at 490 nm. Therefore, a clear mismatch appears between the absorption and IPCE spectra ranges, which requires further exploration. To understand the reason behind the aforementioned discrepancy, the band alignment is extracted for [CoFe–JG] assembly. According to the extracted energy diagram, proper alignment is achieved between the TiO_2 VB, HOMO of the dye, and water oxidation level. This matching, however, is not realized for the CB of TiO_2 and LUMO level of the PS, see Figure 5.12b, which limits the photoconversion efficiencies to wavelengths much smaller than the dye absorption edge. Another reason for the relatively low IPCE could be attributed to ultra-short excited state lifetime of the organic chromophore. This hypothesis is further interrogated by probing ultrafast carrier dynamics using femtosecond TA measurements, which will be explained in the next sections.

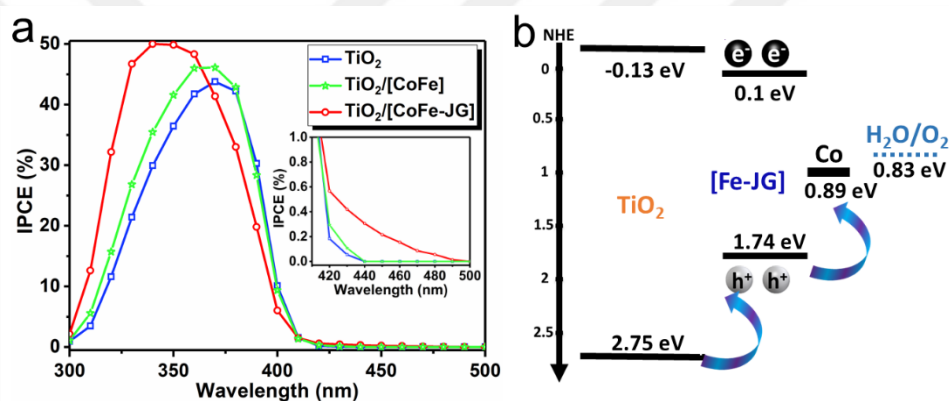


Figure 5.12 (a) IPCE spectra of the PECs with a 1.23 V_{RHE} external bias. The wavelength was scanned from 300 to 500 nm with a step of 10 nm. (b) Schematic energy band diagram of $\text{TiO}_2/[\text{CoFe-JG}]$ showing the band alignments between different interfaces and the involved water oxidation electron transfer processes. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

5.4.6. Long-term Stability Analysis

To test the long-term stability of the photoanode, transient photocurrent measurement by the chronoamperometry (CA) technique is conducted on $\text{TiO}_2/[\text{CoFe-JG}]$ over a total period of 2-hours (made of 4 independent time slots) at 1.23 V_{RHE} with regular time intervals while leaving the electrodes in the electrolyte solution. A gradual decrease in the photocurrent density is observed initially, followed by a consistent stable value (around 50 $\mu\text{A}/\text{cm}^2$) at each step (Figure 5.13a). This near constant photocurrent of $\text{TiO}_2/[\text{CoFe-JG}]$ (unlike

TiO₂/[JG] as depicted in Figure 5.13b) confirms the stability of [CoFe–JG] assembly. XPS studies, performed on TiO₂/[CoFe–JG] after long-term CA, also rules out the decomposition of PB structure to metal oxides. A similar electrolysis experiment at 1.23 V_{RHE} (at pH 7) was performed with a gas-tight cell and the amount of O₂ produced was recorded.

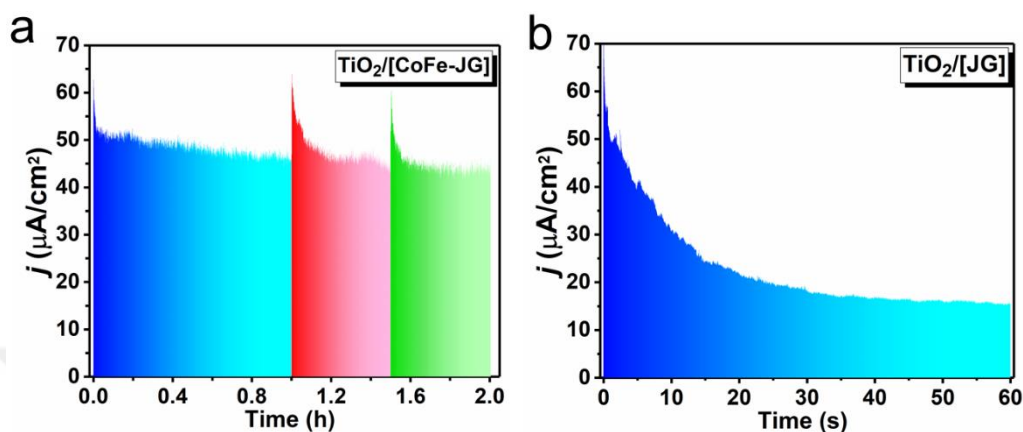


Figure 5.13 (a) Chronoamperogram for 2 hours of illumination with a white-light source coupled to a 420 nm long-pass filter at 1.23 V_{RHE} bias with a light intensity of 100 mW/cm². Different colors indicate the independent measurements of the same TiO₂/[CoFe–JG] electrode at consecutive time slots. (b) The CA profile of TiO₂/[JG] photoanode under a bias voltage of 1.23 V_{RHE}. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

5.4.7. Oxygen Evolution Activity Measurements

The total mole of O₂ generated under chronoamperometric conditions (1.23 V_{RHE}) during 2-hours and under 1 sun illumination was measured with gas chromatography in a gas-tight electrochemical cell. The theoretical oxygen evolution efficiency was calculated from the total amount of charge Q (C) passed through PEC cell. Assuming that 4 holes are needed to produce one O₂ molecule, the theoretical yield can be calculated as follows: $nO_2 = \frac{Q}{4F}$

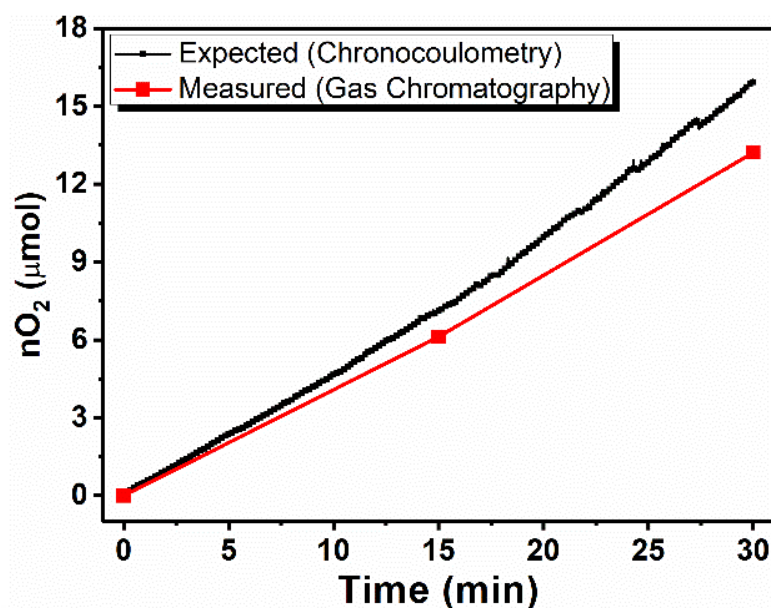


Figure 5.14 Faradaic efficiency of $\text{TiO}_2/[\text{CoFe-JG}]$ measured by gas chromatography. Bulk electrolysis was performed at $1.23 \text{ V}_{\text{RHE}}$ in a gas-tight electrochemical cell. The total amount of oxygen produced was calculated as the sum of the oxygen in the headspace detected by gas chromatography and oxygen dissolved in the solvent, as determined from Henry's Law (red line). The theoretical amount is extracted from the total amount of charge passed during chronocoulometry experiment (black line) yielding an 83% Faradaic efficiency. A buffer solution (pH 7) of 50 mL was used for experiments. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Based on these results, a Faradaic efficiency of approximately 83% is achieved (as explained in Figure 5.14), indicating that the photocurrent response is mainly originating from the water oxidation process. Moreover, TEM-EDS line scan analysis was performed on a single $\text{TiO}_2/[\text{CoFe-JG}]$ nanowire after CA measurements, shown in Figure 5.15. The elemental analysis in this figure confirms the existence of [CoFe] PB structure on the surface of TiO_2 NWs, which confirms the morphological stability of the photoanode. Also, the XPS spectra of the pre-stain electrodes (Figure 5.16a,b) and after 2-hours long CA (post catalysis) were also analyzed in order to probe changes in the oxidation states of Fe and Co (Figure 5.16c,d).

The post-catalytic electrode exhibits similar profile compared to pristine electrode while relative contributions of Co^{2+} and Co^{3+} differ (Figure 5.16b,d). The post-catalytic sample reveals an enhancement in Co^{3+} signal indicating that cobalt sites are partially oxidized during water oxidation process, as expected. All in all, we can conclude that PBA was successfully synthesized in-situ on the

TiO₂ NWs and the layer retains its structural integrity throughout the PEC water oxidation process. It is noteworthy that the lack of long-term stability is one of the main limiting factors in molecular Ru and organic based dyad systems. Moreover, [JG] belongs to a family of phenazine-based chromophores, which are known to easily decompose under photocatalytic conditions.[219] Therefore, the unprecedented stability of the photoelectrode implies that this methodology can be employed for a variety of organic chromophores even with low photostabilities. It can also be inferred that the PB network could play a crucial role in the stabilization of the organic chromophore, which is in good agreement with our previous study on a molecular Ru coordinated PBA.[124]

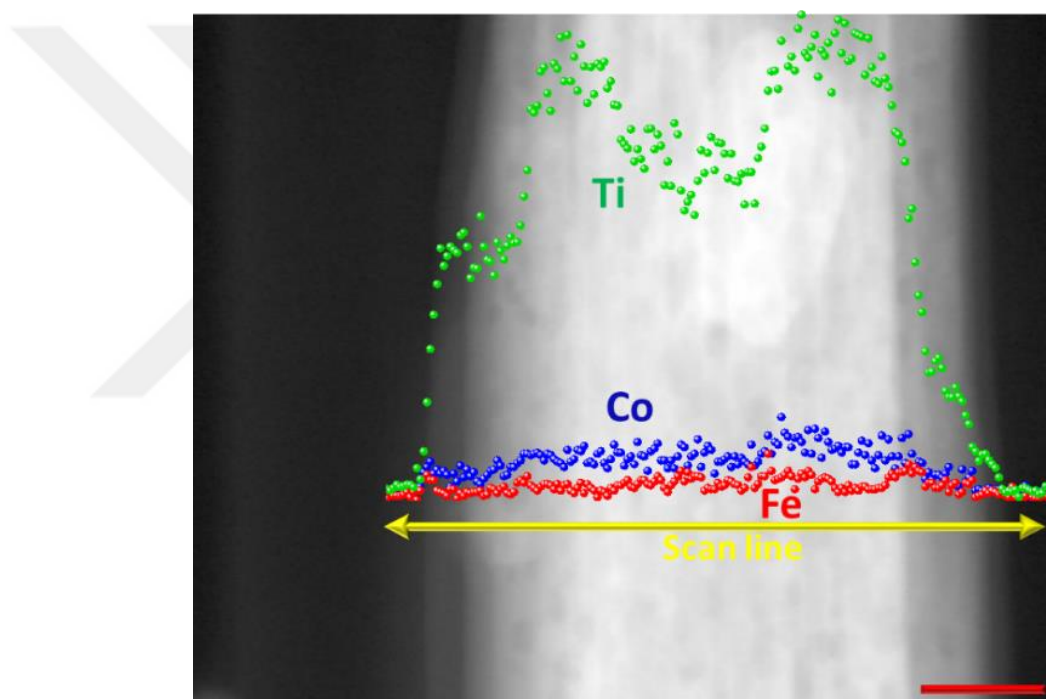


Figure 5.15 After different PEC measurements, HR-TEM image of an individual photoanode (TiO₂/[CoFe–JG]) and inset shows a post-photoelectrochemical TEM-EDS line scan of Co, Fe, Ti, O from air to a NW with high magnification interface, indicating no deformation on the sample. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

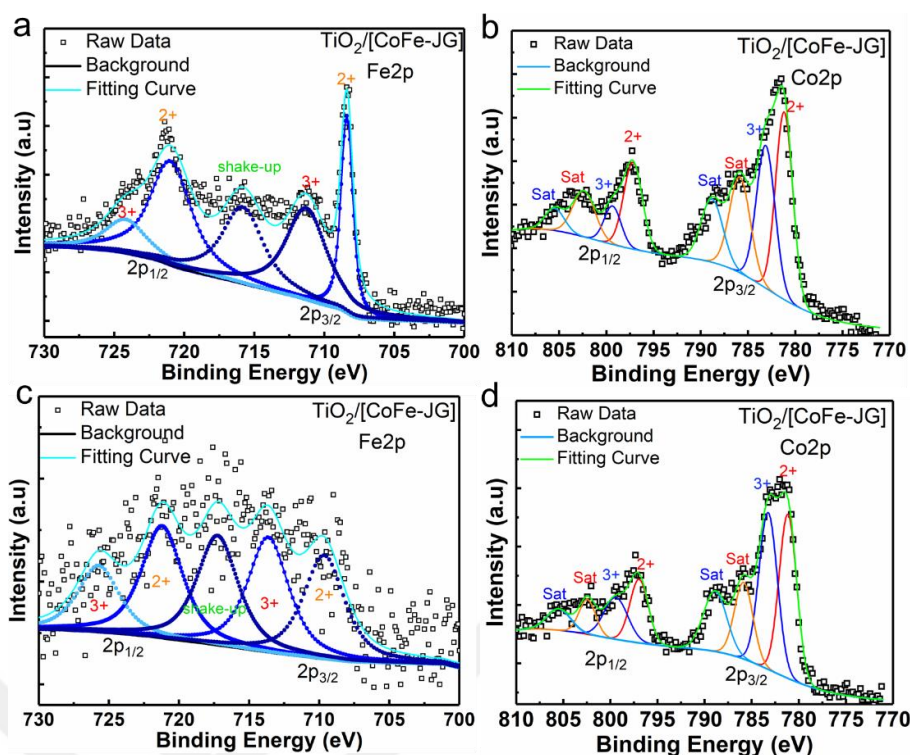


Figure 5.16 High resolution XPS spectra of (a) Fe2p and (b) Co2p for pristine TiO₂/[CoFe-JG], and (c) Fe2p, and (d) Co2p for post TiO₂/[CoFe-JG] (after 2-hours CA experiment). (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

5.4.8. Femtosecond Transient Absorption Measurements

TA measurements were performed for [JG], [Fe-JG], and [CoFe-JG] in EtOH to gain an insight into the ultrafast carrier dynamics of the photoanodes. In summary, the addition of Co WOC has significantly prolonged the ESA lifetime of [Fe-JG]. Therefore, it can be envisioned that electron injection probability from dye to the TiO₂ could be substantiated in the [CoFe-JG]. Samples are excited at a wavelength in the vicinity of their absorption peak. The initial observation shows that [JG] and [Fe-JG] have much shorter carrier dynamics compared to [CoFe-JG]. All three cases have a broad negative signal in the ~520–650 nm range, which is attributed to the depopulation of the ground state (GS) or so-called ground state bleaching (GSB). This signal comprises two coupled peaks at ~608 nm and ~648 nm for [JG] and [Fe-JG], Figure 5.17a,b. This behavior has also been observed in other organic dye molecules including methylene blue (MB).[220] It has been proven that the first excited state (S_1) splits into the upper excitonic state (S_1^+) and the lower state (S_1^-) in the MB dimer, due to the addition of the in-phase transition dipole moments of constituent

monomers[220]–[222]. The peak amplitude of the shorter wavelength (~608 nm) shows a gradual and continuous decline as the probe light delay increases (see Figure 5.17a,b). However, the second peak (~648 nm) with a global maximum at 200 fs delay, goes to its local maximum within the first 2.5 ps and then decays to the GS and vibrational state localized below the S_1 state. This implies that an ultrafast internal conversion (IC) takes place within the S_1 . In other words, the non-radiative decay from above states to the S_1^- state is faster than the one from S_1^- to GS. This behavior was not observed for the [CoFe–JG] sample, where a single GSB peak decays with a rather prolonged lifetime compared to [JG] and [Fe–JG]. The GSB peak locates at 575 nm, which shows a blue shift with respect to [JG] and [Fe–JG]. This data is in accordance with the steady-state absorption results, where the conjunction of Co sites widens the optical band gap of the chromophore. Moreover, in this sample, only a single peak is observed for the GSB signal rather than an S_1 state splitting. This presumably infers a drastic change in the energy levels of the chromophore, which will be scrutinized in upcoming sections. The second feature is a positive signal at $\lambda_{\text{probe}} < 540$ nm and $\lambda_{\text{probe}} > 650$ nm, which is originated from excited state absorption (ESA) signal. For [JG] and [Fe–JG] in EtOH, this ESA signal ($\lambda_{\text{probe}} > 650$ nm) increases gradually to its maximum at 2.5 ps time delay and then drops to zero within the first ~100 ps time delay, Figure 5.17b. This maximum at 2.5 ps time delay is in direct correlation with the peak time for the GSB population at 648 nm. This implies that the transition stems from S_1^- to the second excited state (S_2). This behavior, however, is not detected in the [CoFe–JG] case, at which ESA signal decays from a positive signal to a negative one and finally toward zero in the ns time delay scales. The third feature is the spectral change in the $\lambda > 750$ nm region. For [JG] and [Fe–JG], a negative signal is monitored at the first ps while longer delays impose a positive response that decays back to zero in the first ~100 ps delay. For [CoFe–JG] in EtOH, this negative signal is much broader, and it is effectively superposed with the GSB signal, Figure 5.17c.

To understand the origin of this spectral behavior, we need to look back at the PL of these three assemblies. As shown in Figure 5.17a, [JG] and [Fe–JG] exhibit a weak PL in the 700–800 nm range, while [CoFe–JG] has a broad and intense emission ranging from below 600 nm up to 850 nm. Therefore, the negative signal, in the long wavelength regime, may be attributed to the stimulated emission (STE) signal. For [JG] and [Fe–JG], this signal appears only in the 700–800 nm range while for [CoFe–JG], the STE occurs in a much broader bandwidth (from below 600 nm to 850 nm). This can be explained by

the fact that the recovery of GS population is achieved by both GSB and STE processes.

To gain a better qualitative comparison of the decay dynamics and the excited state lifetimes, the change in GSB, ESA, and STE signals have been recorded as a function of time delay, in Figure 5.17d-f, for all three solutions. Each of these data has been fitted to multi-exponential profiles, as summarized in Table 5.2 – Table 5.4. As shown in Figure 5.17d, for [JG] and [Fe–JG], GSB signals decay to the ground state within tens of ps while [CoFe–JG] shows a prolonged lifetime, in which the signal does not decay throughout our measurable scale. Therefore, a lifetime >3 ns, which is our measurable maximum delay range, is anticipated for [CoFe–JG]. Looking at the ESA signal decay profiles in Figure 5.17e, the signal increases to its maximum up to ~ 2.5 ps and then drops exponentially to zero with a rate similar to that of GSB, which suggests an ultrafast S_1 excited state decay rate for [JG] and [Fe–JG]. The behavior of [CoFe–JG] is rather more sophisticated. Within the first 40 ps, the response is positive and then it becomes negative. The positive signal arises from the $S_1 \rightarrow S_2$ excited state transition, while the negative signal is attributed to STE from the $S_1 \rightarrow$ GS transition. The decay trend in Figure 5.17e resembles the superposition of a positive and negative decaying exponential trend. At short probe light delay times ($\tau_{\text{delay}} < 40$ ps), the S_1 state undergoes in a dominant ESA transition. However, in longer delays, the S_1 state non-radiatively decay toward the S_1 band edge and then decay further to GS via STE ($S_1 \rightarrow$ GS transition). Therefore, the ESA is a dominant process in the short delay times while STE rules in the longer ones. As summarized in Table 5.4, for [CoFe–JG], the ESA spectra can be deconvoluted into three exponential functions with two positive decay rates of 5.4 ± 0.7 ps and 47 ± 4 ps. The former is probably due to some vibrational cooling while the latter is the decay rate of higher energy states to S_1 state edge.

Finally, at a probe wavelength of 810 nm, the time evolution of decay mechanism is plotted in Figure 5.17f. For [JG] and [Fe–JG], STE is the main decay mechanism in the first ps delays, while ESA becomes distinguished at larger probe light delays. Looking back into GSB signal fittings for [JG] and [Fe–JG], in Table 5.2 and Table 5.3, two dominant decay rates are 0.3 ± 0.1 ps (33%) and 14 ± 3 ps (66%). Therefore, within an ultrashort time, S_1 edge constitutes 33% of populated states and it decays to GS through STE, which is the origin of local maxima at sub-ps delays. However, the second component of GSB (with a 66% population) decays with a larger rate and, therefore, in this delay

period, the $S_1 \rightarrow S_2$ ESA transition takes over STE. The dominance of STE was recorded for all the time delays in the case of [CoFe-JG] in EtOH. Again, similar to the previous analysis, GSB decay for this compound has three components with short, moderate, and long rates of 0.6 ± 0.1 ps (36%), 11 ± 2 ps (39%), and 592 ± 25 ps (25%). Therefore, in all of the time delay scales, STE governs the decay process.

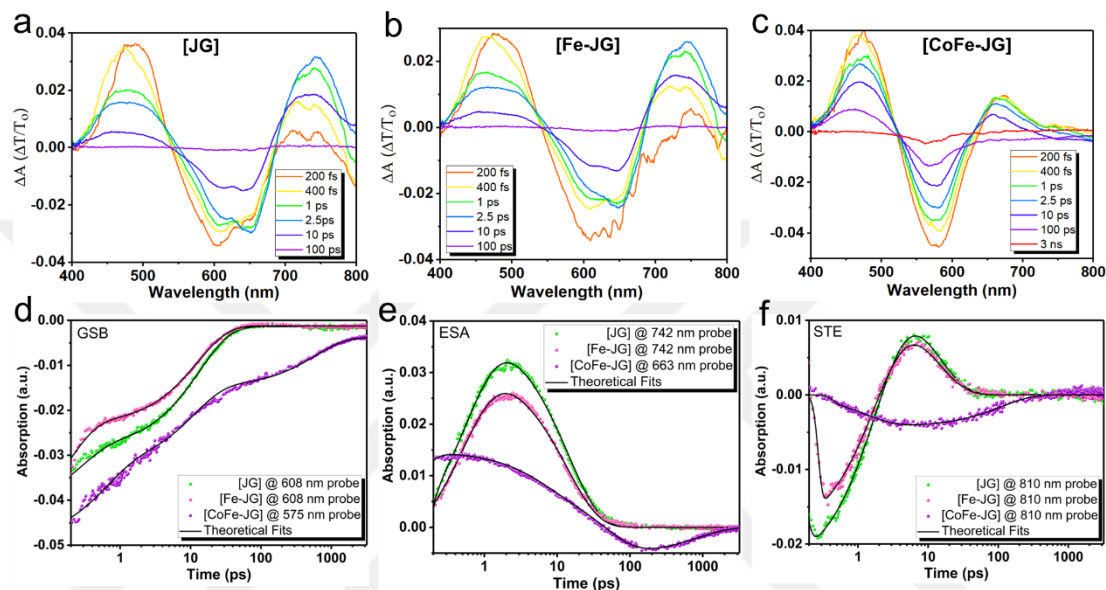


Figure 5.17 TA spectra of 10^{-3} M (a) [JG], (b) [Fe-JG] and (c) [CoFe-JG] compounds with different pump probe time delays and decay kinetics of (d) GSB, (e) ESA and (f) STE signals in EtOH solutions at 600 nm (pump) excitation. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Table 5.2 Time components of the GSB, ESA, and SE (pump at $\lambda = 600$ nm) in the TA spectra of the studied [JG]/EtOH fluid compound.

Sample	GSB (608 nm)		GSB (648 nm)		ESA (742 nm)		STE (810 nm)	
	A	τ (ps)	A	τ (ps)	A	τ (ps)	A	τ (ps)
[JG]/ EtOH	-0.013	0.26	-0.049	0.112	-0.0319	0.58	-0.036	2.012
	-0.0004	4.15	0.024	1.014	0.038	14.29	0.015	12.59
	-0.026	13.63	-0.039	9.025	-	-	-	-

Table 5.3 Time components of the GSB, ESA, and SE (pump at $\lambda = 600$ nm) in the TA spectra of the studied [Fe-JG]/EtOH fluid compound.

Sample	GSB (608 nm)		GSB (648 nm)		ESA (742 nm)		STE (810 nm)	
	A	τ (ps)	A	τ (ps)	A	τ (ps)	A	τ (ps)
[Fe-JG]/ EtOH	-0.016	0.16	-0.0435	0.112	-0.026	0.54	-0.027	1.96
	-0.0002	3.83	0.019	1.05	0.030	13.89	0.013	12.01
	-0.021	12.62	-0.032	8.96	-	-	-	-

Table 5.4 Time components of the GSB, ESA, and SE (pump at $\lambda = 600$ nm) in the TA spectra of the studied [CoFe–JG]/EtOH fluid compound.

Sample	GSB (575 nm)		ESA (663 nm)		STE (810 nm)	
	A	τ (ps)	A	τ (ps)	A	τ (ps)
[CoFe–JG]/ EtOH	-0.016	0.587	0.006	5.36	0.003	1.30
	-0.017	10.94	0.013	46.64	-0.004	110.8
	-0.011	592	-0.005	875	-	-

To gain insight on carrier dynamics in the ultimate photoanode, dye loaded TiO₂ NW samples were studied by TA analysis as well. The TA spectra have been collected for all three assemblies upon pumping at 400 nm. All spectra were fitted by multi-exponential functions and the data is summarized in Table 5.5 - Table 5.7. For [JG] and [Fe–JG] on TiO₂ NWs, two main features, ground state bleaching (GSB) and excited state absorption (ESA), are identified clearly, as in the case of ethanolic solutions of [JG] and [Fe–JG] discussed above, see Figure 5.18a,b. In addition, a weak stimulated emission (STE) signal at 800 nm was observed with long delay times. Therefore, it can be deduced that excited states undergo ultrafast deactivation into the S₁ edge. CV results reveal that energies of S₁ edge and TiO₂ CB are improperly aligned and, thus, the injection abilities in TiO₂/[JG] and TiO₂/[Fe–JG] are hampered and ultrashort excited state lifetimes are observed. However, for TiO₂/[CoFe–JG], which was probed at several probe wavelengths, neither GSB nor STE signals were observed (see Figure 5.18c). TiO₂/[CoFe–JG] exhibits a broadband ESA signal. The decay dynamics of GSB and ESA signals are displayed in Figure 5.18d,e. The ESA signals for TiO₂/[JG] and TiO₂/[Fe–JG] decay to zero within the first 10 ps, while it shows a much longer lifetime for TiO₂/[CoFe–JG]. The time evolution of the ESA signal for TiO₂/[CoFe–JG] is probed at three different probe wavelengths; 500 nm, 600 nm, and 700 nm. Two ultrafast decay times of <100 fs and ~2–3 ps are deduced from the fitting parameters. Besides these two fast components, a long lifetime decay (in the order of 200 ps with an amplitude below 10%), are also present for TiO₂/[CoFe–JG], see Table 5.7. Moreover, the extracted decay rates for three probe wavelengths (of 500 nm, 600 nm, and 700 nm) are quite similar to each other, Table 5.2 - Table 5.4. Lack of the GSB signal, together with the above results, suggests that an efficient injection into TiO₂ NWs occurs in TiO₂/[CoFe–JG]. Equivalently, the assembly of Co catalyst has suppressed the deactivation pathway of the excited states.

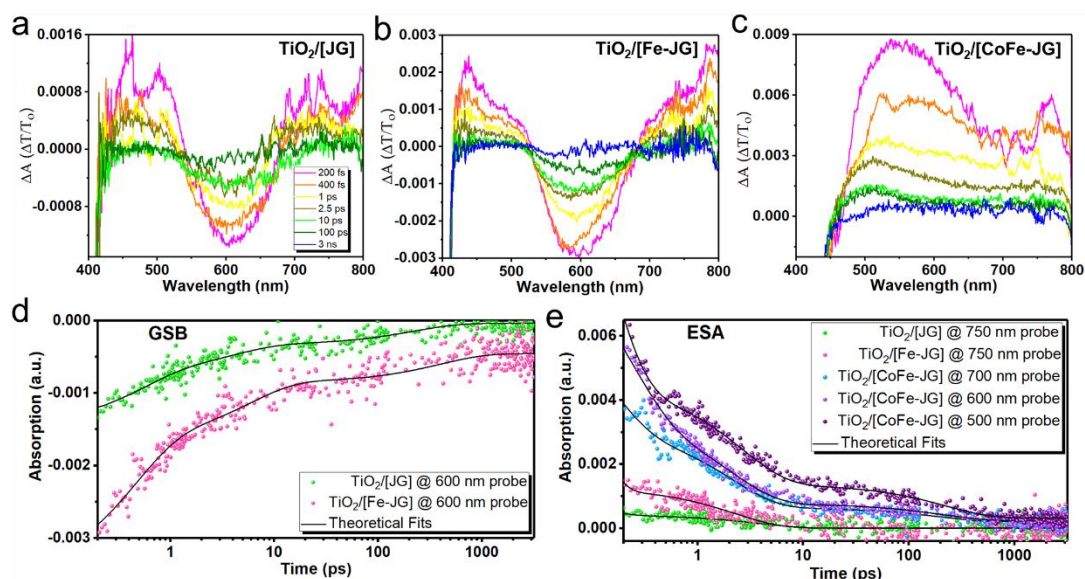


Figure 5.18 TA spectra of (a) TiO_2 /[JG], (b) TiO_2 /[Fe-JG], and (c) TiO_2 /[CoFe-JG] compounds at 400 nm (pump) excitation with different pump probe time delays. Decay dynamics for (d) GSB and (e) ESA signals. The pump pulse intensity for all these measurements is 9.95 GW/cm^2 . (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Table 5.5 Time components of the GSB, ESA, and SE (pump at $\lambda = 400 \text{ nm}$) in the TA spectra of the compounds on TiO_2 /[JG].

Samples	GSB (600 nm)		ESA (750 nm)	
	A	τ (ps)	A	τ (ps)
TiO_2 /[JG]	-0.0006	0.5	0.002	0.06
	-0.0004	4	0.0004	3.81
	-0.0003	219	-	-

Table 5.6 Time components of the GSB, ESA, and SE (pump at $\lambda = 400 \text{ nm}$) in the TA spectra of the compounds on TiO_2 /[Fe-JG].

Samples	GSB (600 nm)		ESA (750 nm)	
	A	τ (ps)	A	τ (ps)
TiO_2 /[Fe-JG]	-0.002	0.45	0.462	0.027
	-0.0008	5.73	0.0012	2.24
	-0.0004	400	-	-

Table 5.7 Time components of the GSB, ESA, and SE (pump at $\lambda = 400 \text{ nm}$) in the TA spectra of the compounds on TiO_2 /[CoFe-JG].

TiO_2 /[CoFe-JG]	ESA (500 nm)		ESA (600 nm)		ESA (700 nm)	
	A	τ (ps)	A	τ (ps)	A	τ (ps)
	0.009	0.1	0.005	0.22	0.004	0.13
	0.003	2.62	0.003	2.12	0.002	2.10
	0.001	221.6	0.0005	206.2	0.0004	186.6

5.4.9. Quantum Chemical Calculations and Mechanism

Further insight into the critical electron transfer events is provided by quantum chemical calculations on the ground and excited states. The calculations are performed by Prof. Dede's group. Although a quantitative treatment of the photoanode is unrealistic, model systems provide valuable qualitative insight into the observed differences of [Fe–JG] and [CoFe–JG] systems as shown in Figure 5.19a-c. The modulation of the orbital levels upon the inclusion of Co to the system suggests that; (i) Ligand centered (LC) $\pi \rightarrow \pi^*$ state is destabilized from 1.27 eV to 3.80 eV. Note also that the character of the excitation changes from phenazine $\rightarrow$ diazenylaniline to diazenylaniline $\rightarrow$ phenazine, (ii) the lowest metal to ligand charge transfer (MLCT) state changes character from Fe $\rightarrow$ JG to Co $\rightarrow$ JG, (iii) the energy of the lowest MLCT state shifts from 2.61 eV to 1.24 eV, and (iv) the Fe-based MLCT state of [Fe–JG] is also destabilized from 2.61 eV to 4.00 eV. Although we should not dwell on the calculated energies in the molecular orbital analysis the qualitative insight brought about is useful and suggests that, upon a mainly LC type of excitation, an electron transfer to the semi-conductor follows. Efficient charge separation is provided by the electron donating ability of Co sites given its properly aligned SOMO state with respect to the doubly occupied orbital on JG. The holes created on JG are transferred rapidly to the SOMO (singly occupied molecular orbital) of cobalt, which leads to the activation of cobalt site for catalytic water oxidation. Thus, cobalt site emerges as both an electron donor group taking part in electron flow and water oxidation catalytic site. All of these theoretical results are in line with our transient absorption studies and characterizations.

Overall, the addition of cobalt ions changes the optical and electronic properties of the electrode. The lowest transition energy of [Fe–JG] belongs to $\pi \rightarrow \pi^*$ LC state, which cannot inject its electrons to TiO₂ CB due to improper energy alignment.

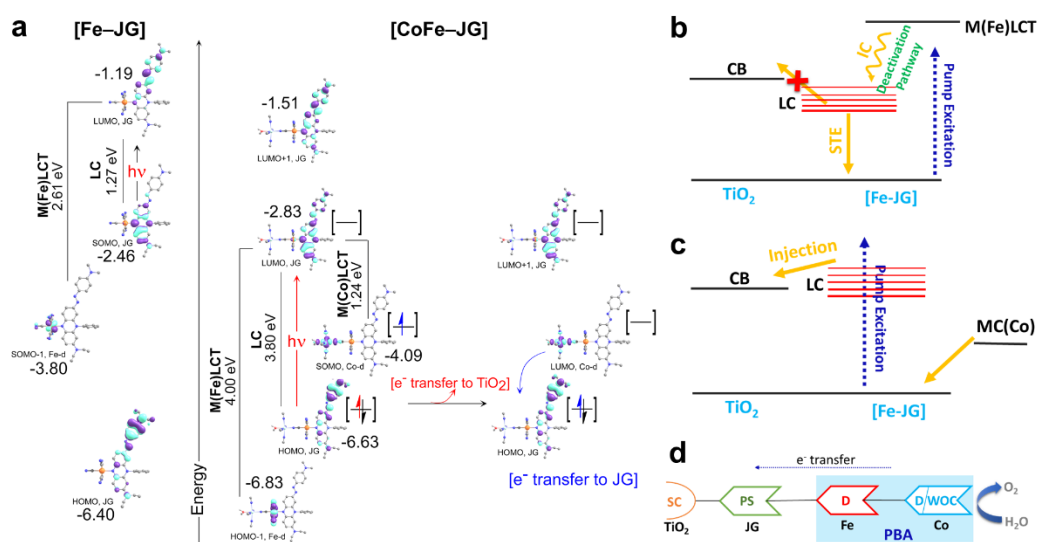


Figure 5.19 Molecular orbitals and electronic states: (a) Critical DFT frontier orbitals for [Fe-JG] and [CoFe-JG] systems. Schematic representation of charge carrier dynamics for (b) TiO₂/[JG], TiO₂/[Fe-JG], and (c) TiO₂/[CoFe-JG]. (d) The summary of electron transfers in TiO₂/[CoFe-JG] (JG: PS, CoFe PBA: both donor (D) and WOC, and TiO₂: SC. PBA serves as (i) a strong electron D group, (ii) a WOC, and (iii) a tuner for the modification of the energetic levels of the chromophore. (Reprinted with permission from Wiley Ref. [126]. Copyright © 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Furthermore, the excited electrons of [JG] are self-quenched in an ultrafast fashion (within tens of ps) due to the undesirable intermolecular aggregations similar to most of the metal-free organic dyes. Therefore, an ultrafast deactivation of excited electrons into the LC state significantly limits the photoresponse of the phenazine-based dye, see Figure 5.19b. To increase the excited state lifetime of [JG], the aforementioned deactivation pathway should be eliminated, which is achieved by its conjugation to a PB structure. An in-depth computational and ultrafast transient analysis reveals an unprecedented modification in the electronic and optical properties of [JG] upon its covalent bonding to PB structure. In TiO₂/[CoFe-JG], the energy of the LC state increases (relative to charge transfer states) due to strongly electron donating cobalt sites leading to a prolonged excited state lifetime (in the order of ns). The electron transfer depicted in Figure 5.19c also enhances the luminescence yield. The proposed PBA can, thus, be considered as a tri-functional assembly; i) a strong electron donating group, ii) a WOC, and iii) an assembly that modifies the energetic levels of the chromophore (its optical behavior), see Figure 5.19d.

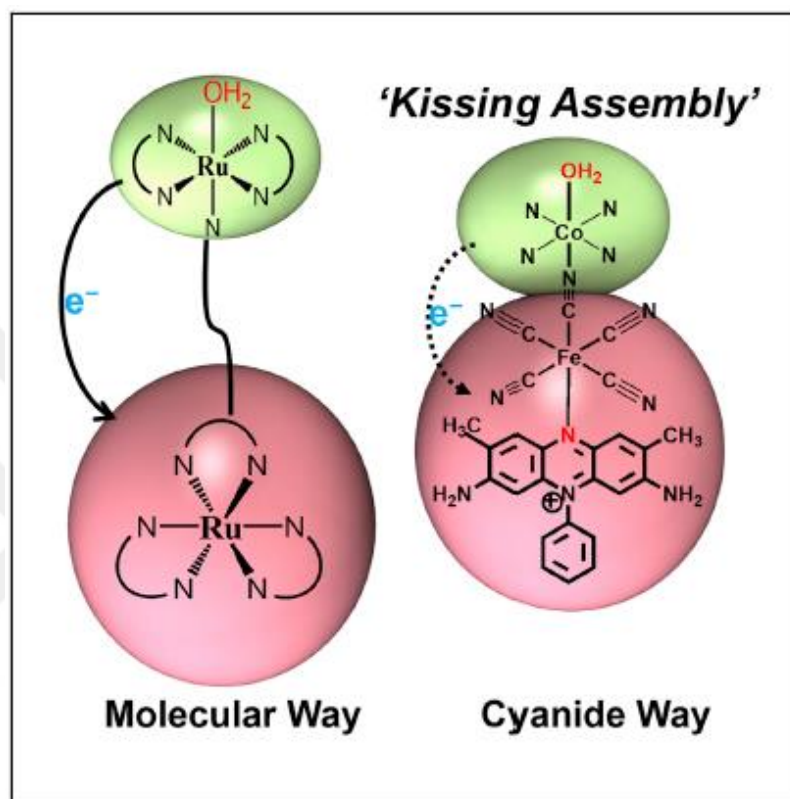
5.5. Summary

In this work, we demonstrate a strategy and construct, for the first time, an entirely earth-abundant long-term durable dye-sensitized photoanode for water oxidation by utilizing a hetero-multifunctional cyanide-based chromophore-catalyst assembly. While the heterogeneous oxide-based synthetic route yields robust photoelectrodes, the molecular-based approach provides the complete control of the final structure of the photoanode, and hence relatively higher performances. On the other hand, cyanide chemistry offers the engagement of strengths of both of the aforementioned approaches. A computational study guided screening was performed to include the key structural elements into the selected chromophore, i.e. quaternized nitrogen atom, prior to synthesis. The synthesis involves the coordination of molecular organic chromophore to a pentacyanoiron(II) group, which is completed by reacting with Co^{2+} ions in situ on TiO_2 to obtain a robust heterogeneous photoelectrode. Unlike its superior optical response with an absorption edge in the NIR range, the pristine [JG] chromophore shows poor carrier dynamics with a ps excited state lifetime. The conducted TA analysis and quantum chemical calculations demonstrated that excited electrons undergo an ultrafast quenching into the lowest LUMO state with an energetically inadequate position for electron injection. However, the covalent connection of PBA moiety drastically changes the story (Figure 5.19d). Besides their primary function as catalytic water oxidation sites, the cobalt ions in PB structure serve as donor groups to feed the HOMO level of the dye. Overall, the holes are first transferred to Fe center invoking the $\text{Fe}^{2+/3+}$ redox process and then to Co sites to activate them for the catalytic water oxidation process. The efficient charge transfer was achieved also as a result of desirable tuning of the LUMO level of the dye once it is connected to PB structure. Both iron and cobalt sites, hence the PB structure as a whole, serve as the electron donating group. The short cyanide bridging ligand (with a metal-to-metal distance of ca. 5 Å) plays a critical role in the electron donating ability of the catalytic cobalt sites since it provides fast electronic communication between metal ions and the organic chromophore. Thanks to this donation ability, a remarkably long excited state lifetime in the order of nanoseconds is recorded for the photoanode. Moreover, the DS-PEC cell design shows unprecedented stability for a phenazine-type chromophore, which is known to suffer from easy decomposition under photocatalytic conditions. The study marks the first successful attempt to utilizing a phenazine-type chromophore for a dye-sensitized photoanode. The most astonishing conclusion of this study is, thus,

the robustness and scalability of the proposed strategy. This work provides an easy-to-employ recipe for the utilization of a variety of pyridyl containing organic chromophores for various photo-conversion devices including dye-sensitized solar cells and DS-PECs. Therefore, the method proposed herein paves the way for a new family of dye-sensitized photoactive devices that can utilize a variety of organic chromophores even with ultrashort charge separation lifetimes and low photostabilities. Realization of water oxidation photoanodes incorporating a variety of organic dyes with proper electronic band positions (LUMO of dye and conduction band of TiO_2), which utilizes the design principles demonstrated in this work, are under way in our laboratories.



Chapter 6. Safranin Incorporated PB for Dye-Sensitized Water Oxidation



6.1. Preface

This chapter of the thesis is based on the publication "*Pushing the Limits in Photosensitizer-Catalyst Interaction via a Short Cyanide Bridge for Water Oxidation*", T. G. Ulusoy Ghobadi, A. Ghobadi, M. Demirtas, R. Phul, E. Akhuseyin Yildiz, H. G. Yaglioglu, E. Durgun, E. Ozbay, F. Karadas, **Cell Rep. Phy. Sci.**, 2021, 2, 100319. Adapted (or "Reproduced in part") with permission from Elsevier, Ref. [223]. Copyright © 2021 Elsevier.

6.2. Introduction

To date, precious metal-based complexes are the major ingredients of almost all photosensitizers (PSs), water oxidation catalysts (WOCs), and thus PS-WOC assemblies.[163] Besides their high cost, poor long-term stability of ruthenium-based assemblies limit their further upscaling for potential industrial usage. Despite intensive studies to improve the stability of these systems,[168], [224]–[226] their poor long-term performance is still a major challenge. Another pathway is to explore earth-abundant and stable alternatives for ruthenium. In this regard, 3D transition-metal complexes[227] and metal-free organic dyes[205] have been the subject of a decade-long investigation. Among 3D transition metals, “*iron hits the mark*”.[228], [229] Despite major breakthroughs on the iron chromophores, including 92% light-to-electron conversion yield,[230] nanosecond charge-transfer excited-state lifetime,[231] and room temperature photoluminescence,[232] there has been no successful attempt at developing an iron-sensitized water oxidation photoanode mainly due to the lack of a facile synthetic pathway. On the other hand, aromatic macrocycles including porphyrin and phthalocyanines have been the pioneer organic chromophores to replace ruthenium analogs.[205] Their poor carrier transport and sluggish interfacial dynamics, however, had to be compensated with Ir- or Ru-based complexes as WOCs.[168], [175], [233], [234] Even in this case, their photocurrents stayed below 100 $\mu\text{A}/\text{cm}^2$ with a nominal half-life of tens of minutes. Although precious metal-free water oxidizing dye-sensitized photoanodes were recently prepared by utilizing a perylene diimide derivative as the PS and CoO_x as the WOC, the assembly suffered from severe electron-hole recombination due to the undesired/uncontrolled growth of the catalyst on the semiconductor surface resulting in a dramatic decline in the photocurrent and a poor long-term stability.[208]

In previous chapters, we demonstrated stable and entirely earth-abundant PS-WOC assemblies via coordination of a pentacyanoferrate group to pyridyl-containing organic chromophores.[125], [126] Although the photoanode is stable with an excited-state lifetime in nanosecond scales, the performance falls behind the efficient Ru-based systems due to the unfavorable band alignment between the dye and the relatively wide bandgap TiO_2 . [126] The lack of an efficient component that can absorb light in the visible region, particularly above 500 nm, is also responsible for the relatively poor efficiency.

Herein, we move one step forward and build a cyanide-based water oxidation photoanode, which incorporates a visible light absorbing semiconductor and an organic photosensitizer that absorbs light above 500 nm. While common PS-WOC assemblies require the utilization of a relatively long organic group to connect a PS to a WOC, we employ a short cyanide ligand as the bridging group to mediate the charge transfer between these units. In the proposed architecture, an organic PS, safranin O (absorption bandwidth: $400\text{ nm} < \lambda < 550\text{ nm}$) is implemented to a CoFe PB structure [CoFe–SF] to improve its stability and tune its energy levels. It is then coated over the visible light-absorbing WO₃ nanoplates ($\lambda < 440\text{ nm}$) to build the dye-sensitized photoanode [CoFe–SF]/WO₃. Besides its narrow bandgap, the choice of WO₃ stems from the desirable energetic position of its conduction band (CB). The elegantly designed PS-WOC assembly offers highly efficient water oxidation through i) harvesting below bandgap photons and ii) acting as an energetically engineered WOC for the WO₃ host. At 1.23 V_{RHE} bias, 1.30 mA/cm² photocurrent is achieved by [CoFe–SF]/WO₃ while the maximum photo-dark current difference reaches to a remarkable value of 1.77 mA/cm² at 1.8 V_{RHE} and pH 3.

6.3. Experimental Procedures

6.3.1. Materials

Sodium tungstate dihydrate (Na₂WO₄·2H₂O), ammonium oxalate monohydrate (NH₄)₂C₂O₄·2H₂O, sodium nitroferricyanide (Na₂[Fe(CN)₅NO]·2H₂O), sodium hydroxide (NaOH), ammonium hydroxide solution (NH₄OH, 25% (v/v), ethanol (EtOH), acetonitrile (MeCN), methanol (MeOH), and Safranin O (or known Basic Red 2, C₂₀H₁₉ClN₄). Hydrochloric acid (HCl, 36%) and Millipore deionized water (resistivity: 18 MΩ/cm) were used for the WO₃ plate-like arrays on FTO coated glass (2 mm thick, 7 Ω/sq). Cobalt Hexacyanoferrate–PB in situ coatings were synthesized by Potassium hexacyanoferrate(III) (K₃Fe(CN)₆) and cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O). Na₂SO₄ (0.1 M) aqueous buffer solutions were prepared adjusted to the desired pH (pH 3) by titration with H₂SO₄.

6.3.2. Sample Preparation

Synthesis of Pentacyanoferrate-Coordinated Safranin, $\text{Na}_2\text{Fe}(\text{CN})_5(\text{C}_{20}\text{H}_{19}\text{N}_4) \cdot x\text{H}_2\text{O}$, [Fe–SF]: Sodium aminopentacyanoferrate, $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$, [Fe–NH₃] precursor was synthesized according to our previously reported procedure.[112], [125] The compounds [Fe–SF] and [CoFe–SF] were synthesized by adopting a similar synthetic approach according to our previous report.[126] $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ (0.5 mmol) was dissolved in a sufficient amount of water giving a bright yellow solution followed by the dropwise addition of ~10 mL ethanolic solution of [SF] (0.5 mmol). The color of the [SF] compound changed from pink to dark brown. The reaction mixture was left under constant stirring at room temperature overnight. The pink-brown concentrated solution was centrifuged at 6,000 rpm for 20 minutes in cold ethanol to get the purified product. Finally, the precipitate was collected and dried in an oven at 30-40°C overnight.

Synthesis of Cobalt Pentacyanoferrate-Coordinated Safranin, $\text{Co}_2\text{Fe}(\text{CN})_5(\text{C}_{20}\text{H}_{19}\text{N}_4)(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, [CoFe–SF]: [Fe–SF] compound (10 mg, 18 μmoles) was dissolved in MeCN and 1 equiv. $\text{Co}(\text{NO}_3)_2$ in EtOH was added dropwise to the [Fe–SF] solution. The resulting dark brown solution was left under stirring for 2-hours at room temperature. To get a purified product and remove soluble unreacted species, the suspension was centrifuged at 6,000 rpm for 20 min. The precipitate was washed with acetone until the desired *nanoplate arrays*, pure WO_3 was obtained. The final product was dried in an oven at 35°C for one day.

Synthesis of WO_3 : WO_3 nanoplate arrays, noted as WO_3 for short, were prepared by modifying the hydrothermal synthesis as previously described elsewhere.[235], [236] In detail, 231 mg of Na_2WO_4 as a tungsten resource dissolved in 30 mL distilled water. Then, 10 mL of 3 M HCl was added dropwise to the solution under constant stirring to form tungsten acid (H_2WO_4). After being stirred for 30 min. under ambient conditions, 0.2 g $(\text{NH}_4)_2\text{C}_2\text{O}_4$ was added as a structure-directing agent. To a 70 ml of solution, a total 30 mL DI water was added and stirred vigorously further for 30 minutes. The precursor solution was transferred to a Teflon-lined stainless-steel autoclave (capacity of 100 mL) with an FTO conducting side against the wall. In advance, FTO glasses (1 cm $\times$ 6 cm) are cleaned sufficiently in sonication baths in DI water, acetone, and ethanol in sequence, each for 15 min. and then dried by N_2 flow. The hydrothermal reaction was carried out at 120°C for 18 hours, and then it was

naturally cooled to room temperature. Finally, the sample was thoroughly rinsed with DI water to remove the residual solvent and calcined at 450°C for 2 hours in a ceramic furnace.

WO₃/[CoFe] electrode (in situ PB modified WO₃ electrode): The PB coatings were prepared according to the previously reported procedure with slight modifications.[134] In detail, WO₃ electrodes soaked in [K₃Fe(CN)₆] (0.02 M) in Milli-Q water solution for 1 minute at room temperature. The samples were then rinsed with water to remove the non-adsorbed Fe²⁺ ions. Once the substrate was completely dried, the electrode was immersed in Co(NO₃)₂·6H₂O solution (0.04 M) for a minute. Then, the electrode surface was washed with distilled water to remove the excess Co²⁺ ions over the film. This process is repeated at least two times to complete the full coverage of PBA. Finally, the WO₃/[CoFe] electrode was left to dry at room temperature.

WO₃/[CoFe–SF] electrode (in situ PB modified dye-sensitized WO₃ electrode): WO₃ electrodes soaked in [Fe–SF] (1.4 mM) in MeCN solution for 24 hours at room temperature. The samples were then rinsed with MeCN to remove any non-adsorbed dye molecules. Once the substrate was completely dried, ~500 µL of Co(NO₃)₃ solution (0.04 M) was drop cast onto the WO₃/[Fe–SF] electrode. Then, the slide was washed with distilled water to remove the excess Co²⁺ ions over the film. This process is repeated two times to complete the full coverage of PBA. Finally, the WO₃/[CoFe–SF] electrode was left to dry at room temperature.

6.4. Results and Discussions

6.4.1. Design of the photoelectrode

The surface texture of the metal oxide, as the electron extraction layer, is of great importance. Unlike nanoparticles, porous designs that impose a “random walk” direction for electron transfer, anisotropic one/two dimensional (1D/2D) structures promote the “direct transfer”.[237] Thus, single-crystalline WO₃ nanoplates are chosen to maximize the collection efficiency of the carriers. They are synthesized using a hydrothermal growth technique. An in-situ preparation of CoFe PB layer is chosen to improve physical interaction between WO₃ and [CoFe–SF] layer. WO₃ is first sensitized with a pentacyanoiron coordinated to safranin complex, [Fe–SF] complex, to afford a [Fe–SF]/WO₃ heterojunction, Figure 6.1a-b. Finally, in situ coordination of Co²⁺ ions leads to

forming a bulk PB layer on the semiconductor surface, [CoFe–SF]/WO₃ photoanode, Figure 6.1c. In the molecular perspective, [CoFe–SF] consists of organic chromophore groups ([SF]) connected to catalytic cobalt sites through Fe(CN)₅ groups, Figure 6.1d. The absence of diffraction peaks for a PB structure and the presence of characteristic peaks for the organic group and a Fe–CN–Co coordination mode in the Infrared spectrum suggest that [CoFe–SF] layer on WO₃ can be described as an amorphous non-periodic bulk structure as expected.[112]

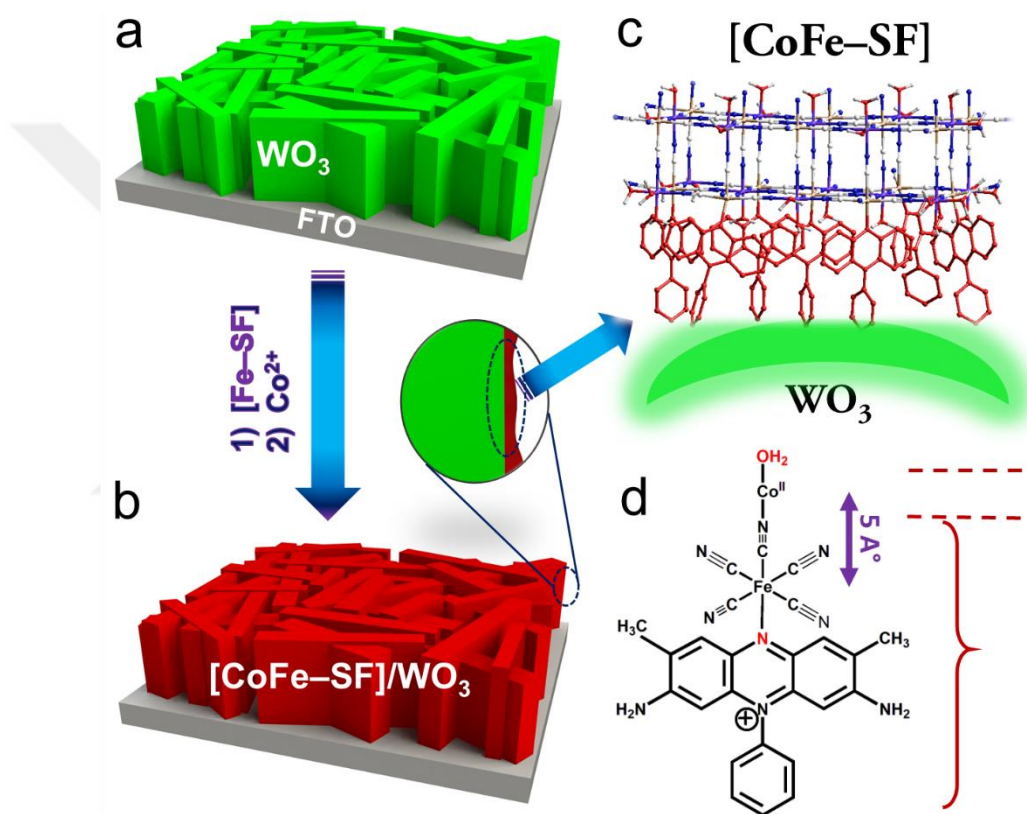


Figure 6.1 Illustration of (a) bare WO₃ nanoplates on FTO coated glass, and (b) the CoFe PB modified dye-sensitized WO₃ photoanode (WO₃/[CoFe–SF]). It is a three-step process: First WO₃ nanoplates are synthesized by hydrothermal technique. Then, WO₃ nanoplates are immersed into Fe bonded Safranin dye ([Fe–SF]) solution. Finally in-situ drop-casting a solution of Co²⁺ ions to form [CoFe–SF] bulk structure. The electrode color changes from green to reddish. (c) The structure of WO₃/[CoFe–SF]: CoFe PB assembly forms an extended bulk network over WO₃. (d) The role of each component in the dye-sensitized photoanode: in this molecular fragment, the [Fe–SF] is the PS part, and Co site acts as the WOC. Moreover, CoFe PB component serves as a strongly electron donating group for SF. The cyanide bridge has a length of around 5 Å. Only a molecular fragment of the extended structure is displayed, and the

coordination environment of the cobalt site is omitted for clarity. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

6.4.2. Materials Characterization

The SEM imaging of the sample is performed to understand the morphology of the WO_3 nanoplates. As we can see from Figure 6.2, the synthesized nanoplates have random and tightly packed morphology with a mean thickness of 50 - 150 nm and a length of $\sim 1 \mu\text{m}$.

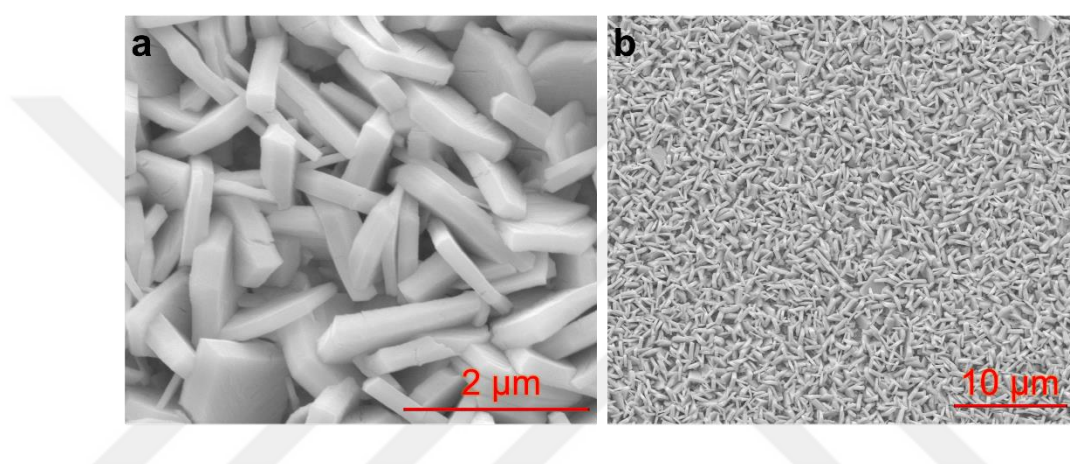


Figure 6.2 Top-view of SEM images of WO_3 /[CoFe-SF] photoanode. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

Powder X-ray diffraction (PXRD) has also been carried out, and the patterns have been collected in the range of $2\theta = 15 - 70^\circ$. The spectra (Figure 6.3) reveal that the diffraction peaks match well with the powder X-ray diffraction pattern for monoclinic phased tungsten oxide (JCPDS card no. 00-024-0747) with cell parameters $a = 7.2970 \text{ \AA}$ and $c = 7.6880 \text{ \AA}$. Thus, the prepared nanoplates exhibit single crystalline nature, which is highly desired for electronic transport processes in photoconversion systems.

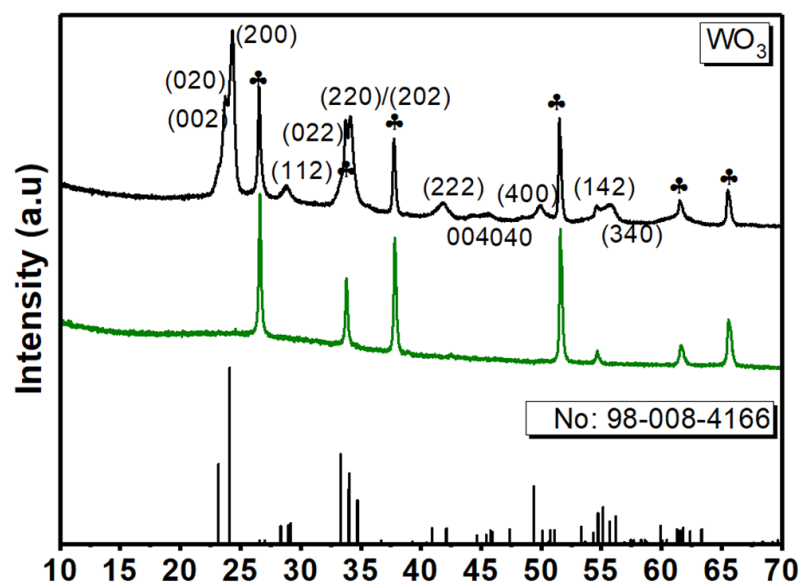


Figure 6.3 XRD pattern of the sample prepared WO_3 nanoplates at 120°C for 18 h and “♣” symbol refers to FTO pattern. The intense diffraction lines - like (020) and (200) - indicate the high crystallinity. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

After initial structural analysis on WO_3 nanoplates, the formation of PBA is examined. For this purpose, the infrared spectra (ATR-FTIR) of $[\text{Fe}-\text{NH}_3]$, $[\text{SF}]$, $[\text{Fe}-\text{SF}]$, and $[\text{CoFe}-\text{SF}]$ are measured and shown in

Figure 6.4. The cyanide stretching frequency has a sharp peak at $2,031\text{ cm}^{-1}$, and the peak at around 567 cm^{-1} is attributed to $\text{Fe}-\text{N}$ coordination bond and the one at $1,264\text{ cm}^{-1}$ is associated with $\text{N}-\text{H}$ stretch in $[\text{Fe}-\text{NH}_3]$. The CN/nitrile peak exhibits blueshifts for $[\text{Fe}-\text{SF}]$ at $\sim 2,100\text{ cm}^{-1}$ and $2,050\text{ cm}^{-1}$, which further shifts to $\sim 2,076\text{ cm}^{-1}$ for $[\text{CoFe}-\text{SF}]$. Therefore, it proves the coordination of iron sites (either Fe^{3+} or Fe^{2+}) to the SF dye by σ -donation from the cyano nitrogen and then $\text{Fe}-\text{CN}-\text{Co}$ coordination mode, which is direct evidence for the formation of a PB structure. FTIR spectrum of $[\text{SF}]$ shows prominent bands between $1,695$ and $1,330\text{ cm}^{-1}$ attributed to $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretches, and there are signals observed at 500 – $1,695\text{ cm}^{-1}$ confirming the presence of $[\text{SF}]$ in the PB structure of the $[\text{CoFe}-\text{SF}]$. The band with a maximum peak at around $1,300\text{ cm}^{-1}$ is from the stretching vibration of NO_3^- ions in $[\text{CoFe}-\text{SF}]$. Several peaks in the $1,000$ – $1,330\text{ cm}^{-1}$ range correspond to symmetric stretches of $\text{C}-\text{H}$ bond. The peak at around $1,620\text{ cm}^{-1}$ presents the $\text{H}-\text{OH}$ bending of absorbed water, and the broad one at $\sim 3,000$ – $3,600\text{ cm}^{-1}$ corresponds to OH stretch.

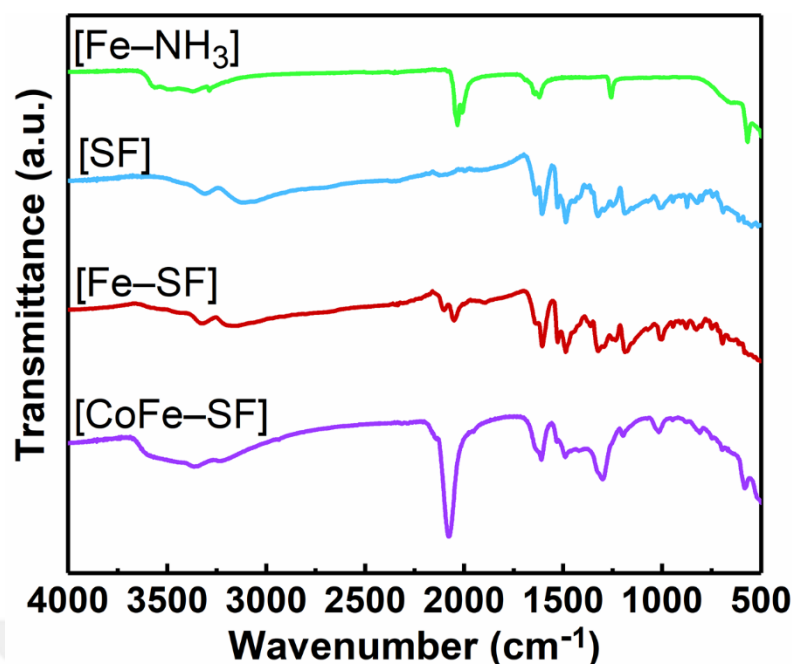


Figure 6.4 ATR-FTIR spectra for [Fe-NH₃], [SF], [Fe-SF], and [CoFe-SF]. The sharp peaks in the 2,000–2,100 cm⁻¹ range are attributed to CN stretch. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

To understand the chemical bonding states, the deconvolution of high-resolution XPS spectra over Fe2p, and Co2p were conducted for all of the samples and the results are summarized in Table 6.1. As shown previously, [125], [126] the Fe2p region exhibits in [Fe-NH₃] with two dominant bands at around 708 and 721 eVs, which are assigned to 2p_{3/2} and 2p_{1/2} of Fe⁺², respectively. The deconvolution of Fe2p peaks also gave additional information on the nature of surface oxidation commonly observed in pentacyanoiron chemistry, i.e. two small bands at 709.99 eV and 723.36 eV were observed for [Fe-SF] (Figure 6.5a), due to the partial oxidation of Fe²⁺ to Fe³⁺ ions in Fe(CN)₅ fragments. Such oxidation is also evidenced by IR spectra, which reveals a distinct band in the cyanide region ~2,100 cm⁻¹, for [Fe-SF] and ~2,150 cm⁻¹ for [CoFe-SF]. Similar to [Fe-SF] XPS results, the dominant peaks of Fe2p in the sample of [CoFe-SF] at the binding energies 708.37 and 720.99 eVs, which were assigned to 2p_{3/2} and 2p_{1/2} of Fe⁺², respectively, and binding energies of 710.48 eV and 722.5 eV also corresponded to 2p_{3/2} and 2p_{1/2} of Fe³⁺, respectively (Figure 6.5b). In the Co2p spectrum for the [CoFe-SF], peaks for Co2p_{3/2} and Co2p_{1/2} were observed at 784.13 and 800.49 eV, which indicated the formation of Co³⁺ in the PBA structure. Furthermore, the peaks that were at 781.69 and 797.57 eV were ascribed to Co2p_{3/2} and Co2p_{1/2} of Co²⁺ (Figure 6.5c). Moreover, ‘shake-up’ satellites (donated as Sat.) were also observed for

these cases, indicating the coexisting Co^{2+} and Co^{3+} cations in the PB structure of the sample.

Table 6.1 XPS results of the Fe2p and Co2p regions obtained from [Fe–SF] and [CoFe–SF] samples.

Compounds	Fe2p, eV				Co2p, eV			
	$2p_{3/2}$ Fe^{+2}	$2p_{1/2}$ Fe^{+2}	$2p_{3/2}$ Fe^{+3}	$2p_{1/2}$ Fe^{+3}	$2p_{3/2}$ Co^{+3}	$2p_{1/2}$ Co^{+3}	$2p_{3/2}$ Co^{+2}	$2p_{1/2}$ Co^{+2}
[Fe–SF]	708.8	721.61	709.99	723.36				
[CoFe–SF]	708.37	720.99	710.48	722.5	784.13	800.49	781.69	797.57

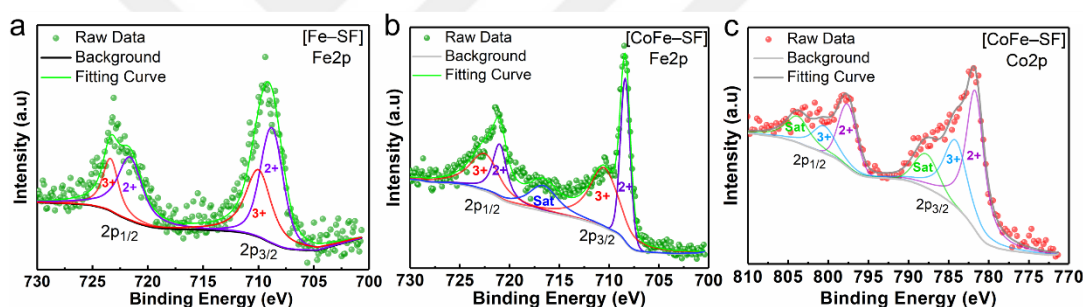


Figure 6.5 High resolution XPS spectra of Fe2p for (a) [Fe–SF], (b) [CoFe–SF], and (c) Co2p recorded for [CoFe–SF]. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

To achieve further evidences on the formation of PB on the WO_3 metal-oxide layer, XPS analysis of W4f, Fe2p, and Co2p was also conducted for WO_3 /[CoFe–SF] photoanode, see Figure 6.6a-c. Figure 6.6a shows the W4f spectra of the as-prepared sample that has a pair of $\text{W}4f_{5/2}$ (37.46 eV) and $\text{W}4f_{7/2}$ (35.31 eV) peaks assigned to the binding energies[238] of W^{6+} . Based on our previous XPS fittings,[126] the Co2p spectrum is deconvoluted into eight Gaussian profiles with fixed center binding energies (Figure 6.6c); two prominent peaks were located at 797.15 eV and 781.43 eV, which were in close accordance with that of $\text{Co}2p_{1/2}$ and $\text{Co}2p_{3/2}$ of Co^{2+} , respectively. Another doublet with slightly higher binding energies was obtained, which corresponds to the $\text{Co}2p_{1/2}$ (800.62 eV) and $\text{Co}2p_{3/2}$ (783.81 eV) doublet of the Co^{3+} cation.

In addition, 'shake-up' satellites were also observed at 805.42 eV and 802.75 eV, for $\text{Co}2p_{1/2}$, 788.71 eV, and 785.53 eV for $\text{Co}2p_{3/2}$.

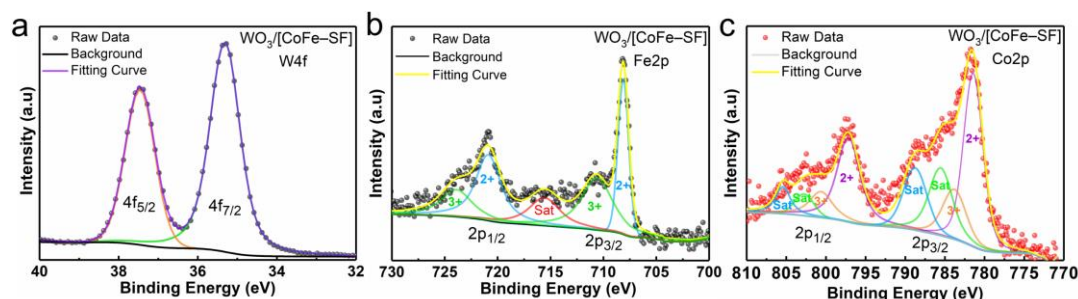


Figure 6.6 High resolution XPS spectra of (a) W4f, (b) Fe2p, and (c) Co2p recorded for $\text{WO}_3/[\text{CoFe-SF}]$. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

6.4.3. Photoelectrochemical Measurements

PEC studies are performed on bare WO_3 , $[\text{CoFe}]/\text{WO}_3$, and the $[\text{CoFe-SF}]/\text{WO}_3$ photoanode in a three-electrode setup to understand the role of each layer at pH 3 (Figure 6.7a). Pulsed LSV profiles are measured under AM1.5G illumination with 435 nm and 495 nm cut-off filters. Under solar irradiation, the maximum photo-dark current difference of 1.77 mA/cm^2 is achieved at $1.8 \text{ V}_{\text{RHE}}$ for $[\text{CoFe-SF}]/\text{WO}_3$, while it is only 1.14 mA/cm^2 and 0.9 mA/cm^2 for WO_3 and $[\text{CoFe}]/\text{WO}_3$ electrodes, respectively. When an excitation above $\lambda > 435 \text{ nm}$ is used to primarily suppress the photoresponse of WO_3 , all LSVs exhibit similar profiles. At the same time, that of $[\text{CoFe-SF}]/\text{WO}_3$ is more prominent than other electrodes. The use of a 495 nm cut-off filter, however, completely deactivates the photoresponse of WO_3 and $\text{WO}_3/[\text{CoFe}]$, while the $[\text{CoFe-SF}]/\text{WO}_3$ retained its photocurrent generation, see Figure 6.7b.

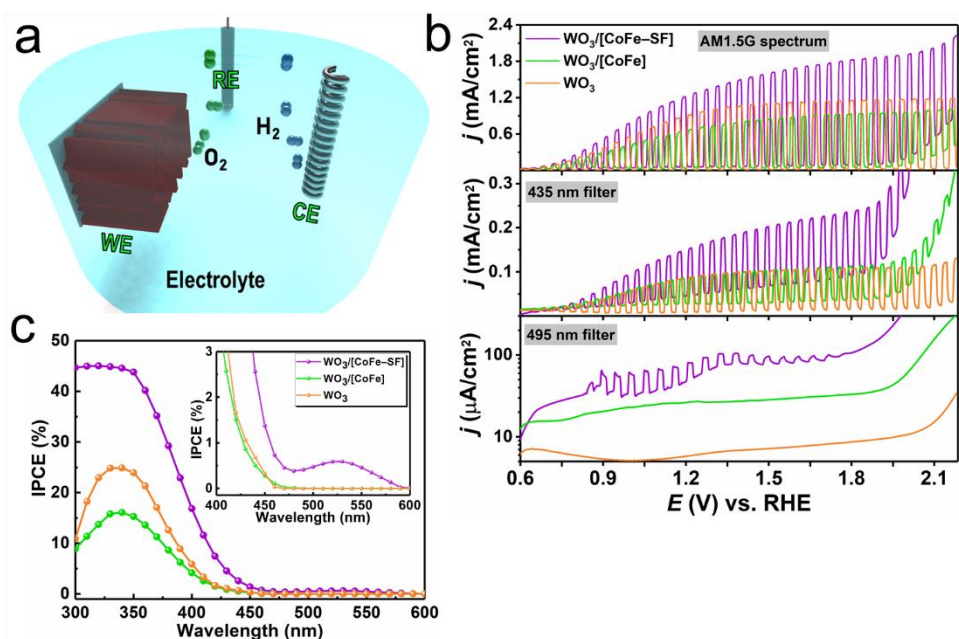


Figure 6.7 (a) 3D schematic diagram of the three-electrode cell used for PEC-WS measurements. (b) Pulsed LSV curves performed for WO_3 , $WO_3/[CoFe]$, and $WO_3/[CoFe-SF]$ electrodes under white-light illumination (top), and with 435 nm (middle) and 490 nm (bottom) cut-off filters. In all three conditions, the dye-sensitized photoanode has a much stronger response compared to bare and catalyst cases. For 490 nm cut-off case, the WO_3 and $WO_3/[CoFe]$ photoanodes have no photoresponse while the $WO_3/[CoFe-SF]$ electrode shows photocurrent response. (c) IPCE spectra for the same photoanodes at 1.23 V_{RHE} . The inset shows a magnified image of the 400-600 nm range. The IPCE results in visible range originate from the [CoFe-SF]. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

Indeed, a 495 nm cut-off filter was intentionally used to entirely deactivate the WO_3 photoresponse. The activity with this filter also rules out the possible decomposition of the PB assembly to an active catalytic system since a possible charge transfer mechanism involving the absorption of photons by WO_3 cannot operate under these conditions. A chromophore should, thus, be responsible for the photocurrent obtained. Based on Figure 6.7c, the IPCE for the bare sample is extended up to 460 nm, which is in line with the above-filtered LSV results. The same spectral response is observed for [CoFe]/ WO_3 , however, with lower efficiencies. The IPCE profile for [CoFe-SF]/ WO_3 differs. For above-bandgap photons, where both dye and semiconductor are responsive, the IPCEs are improved while in longer ranges (where only the dye is active), the photocurrent is extended up to 600 nm.

The catalytic behavior of [CoFe-SF] is proven by Nyquist plots obtained using electrochemical impedance spectroscopy (EIS) under solar irradiation at 1.23

V_{RHE} (Figure 6.8a). The semicircle radius, representing the charge transfer resistance, shrinks for $[\text{CoFe-SF}]/\text{WO}_3$, due to the alleviation of the interfacial charge dynamics. Similar behavior has previously been observed for PS-WOC assemblies.[239], [240] It is noteworthy that, without Co coordination, *i.e.* $[\text{Fe-SF}]/\text{WO}_3$, the charge resistance is much larger (Figure 6.8b), and consequently, the photocurrent is significantly lower with poor stability (Figure 6.9). Therefore, the formation of the CoFe PB structure is essential for an efficient water oxidation process. Band alignments were further extracted by combinational analysis of cyclic voltammetry (CV), Mott-Schottky, and absorption profiles. The band alignments are depicted in Figure 6.10. For $[\text{CoFe}]/\text{WO}_3$, the PB is positioned at almost equal energetic distances to the CB and valance band (VB) of WO_3 , mediating the electron/hole recombination (electrons from CB and holes from VB). Therefore, PB serves as a trapping center rather than a WOC, which reduces the photocurrents further as the PB loading increases Figure 6.11. On the other hand, for $[\text{CoFe-SF}]/\text{WO}_3$, both photo-currents are enhanced significantly and absorption capacity is extended to longer wavelengths since the energy levels are reorganized due to the close interaction between the safranin unit and PB structure.

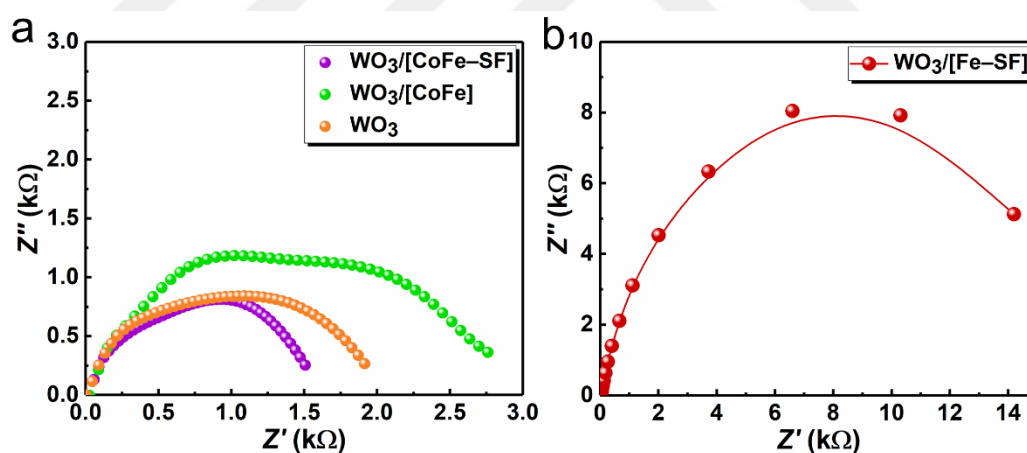


Figure 6.8 (a) The EIS Nyquist plot of bare WO_3 , $\text{WO}_3/[\text{CoFe}]$, and $\text{WO}_3/[\text{CoFe-SF}]$ photoanodes. (b) The EIS Nyquist plot for $\text{WO}_3/[\text{Fe-SF}]$ photoanode. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

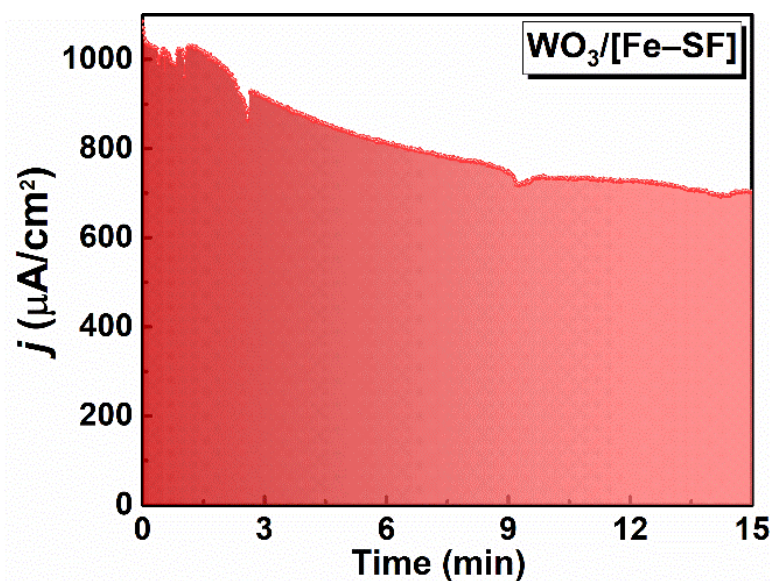


Figure 6.9 Chronoamperogram profile of $\text{WO}_3/[\text{Fe-SF}]$ photoanode for 15 min. solar irradiation time. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

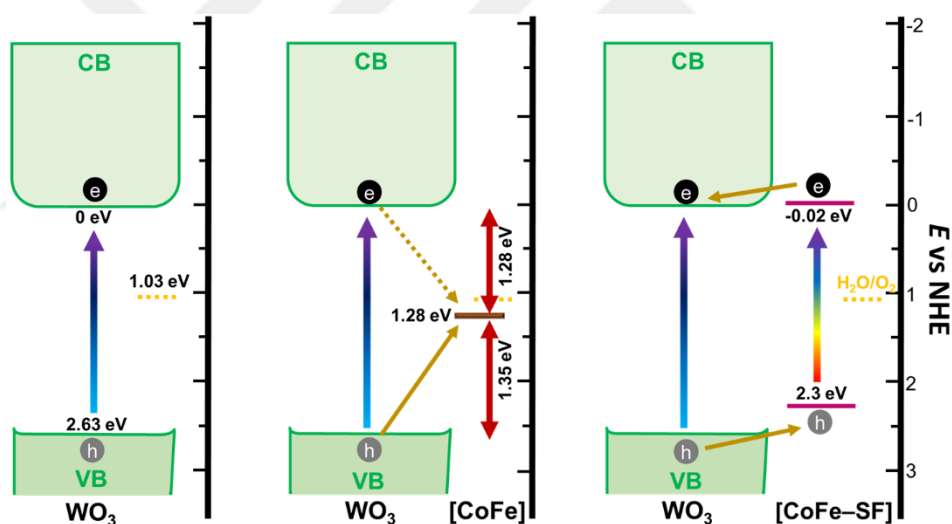


Figure 6.10 Schematic band energy alignment and carrier dynamics for all three photoanodes between different interfaces and water oxidation levels. The energetic position of the PB layer in $\text{WO}_3/[\text{CoFe}]$ case has been significantly modified due to its connection to the dye molecule. This modification provides a proper band alignment for hole transport towards the water oxidation process. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

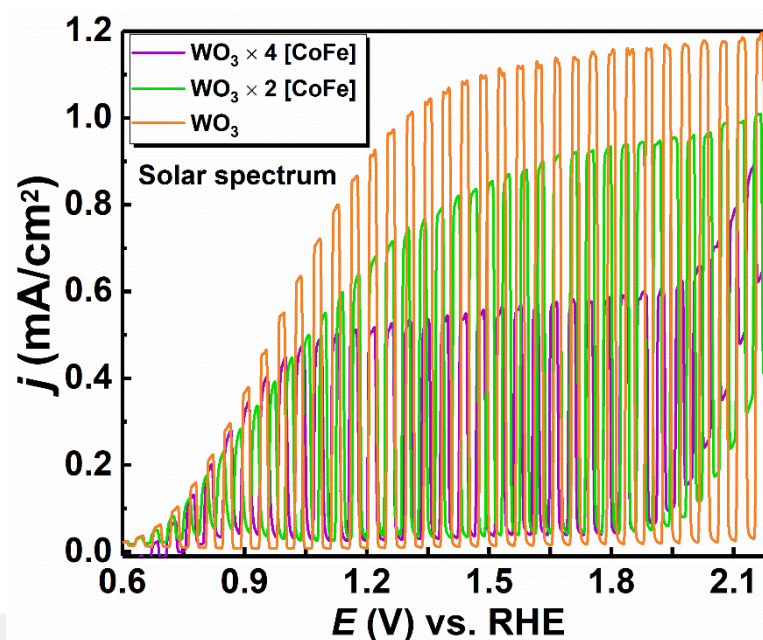


Figure 6.11 Chopped LSV measurements of PB modified WO_3 nanoplates. j - V curves, of the WO_3 electrode and 2, 4, and 6 times [CoFe] PB modified WO_3 electrodes under white-light illumination (no filter). (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

6.4.4. Long-term Stability Analysis

A system should have a high stability to be used in photoconversion applications. To have a better comparison, we start our analysis with the [Fe-SF] complex. [Fe-SF], just the chromophore itself, is molecular while [CoFe-SF] chromophore-catalyst assembly, is bulk. As shown above, a decline in the photocurrent response is observed for [Fe-SF] case as expected from a molecular chromophore, see Figure 6.9. WO_3 /[CoFe-SF] photoanode, however, maintains a relatively constant photocurrent response throughout a 2-hours experiment as shown in Figure 6.12. Thus, the formation of a bulk cyanide network is essential for a long term stability.

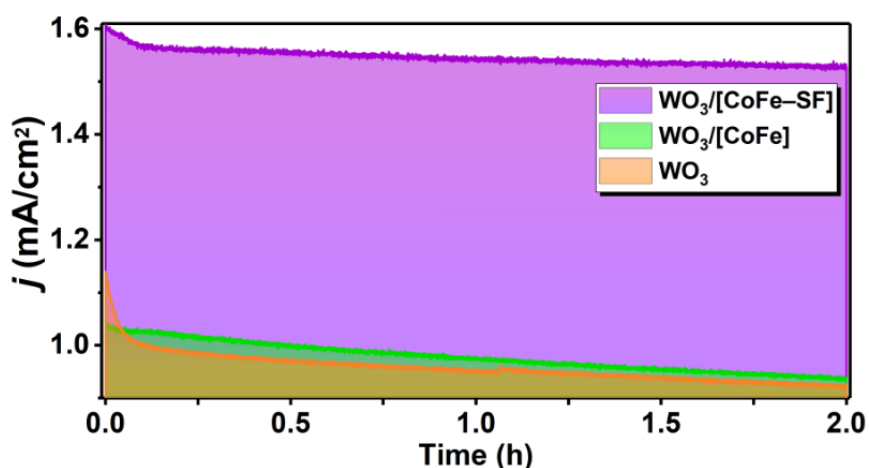


Figure 6.12 Chronoamperogram profiles of all three photoanodes during a 2-hours solar illumination at 1.23 V_{RHE} . This test confirms the stability of the photoanode upon solar irradiation. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

Besides PEC stability, structural integrity is of great importance since it governs the long-term stability of the design. To scrutinize this issue, we used transmission electron microscopy (TEM) and XPS analysis on both pristine and post-catalytic (after 2-hours long CA experiment) photoelectrodes. High-resolution TEM (HR-TEM) analysis suggests the presence of similar [CoFe-SF] layers (denoted as PBA) in both the pristine and post-catalytic photoelectrodes, confirming their long-term stability. These PBA shell layers are grown both as continuous and island-like regions on the surface of WO_3 nanoplates in pristine and post-catalytic $WO_3/[CoFe-SF]$ photoelectrodes (Figure 6.13a-b).

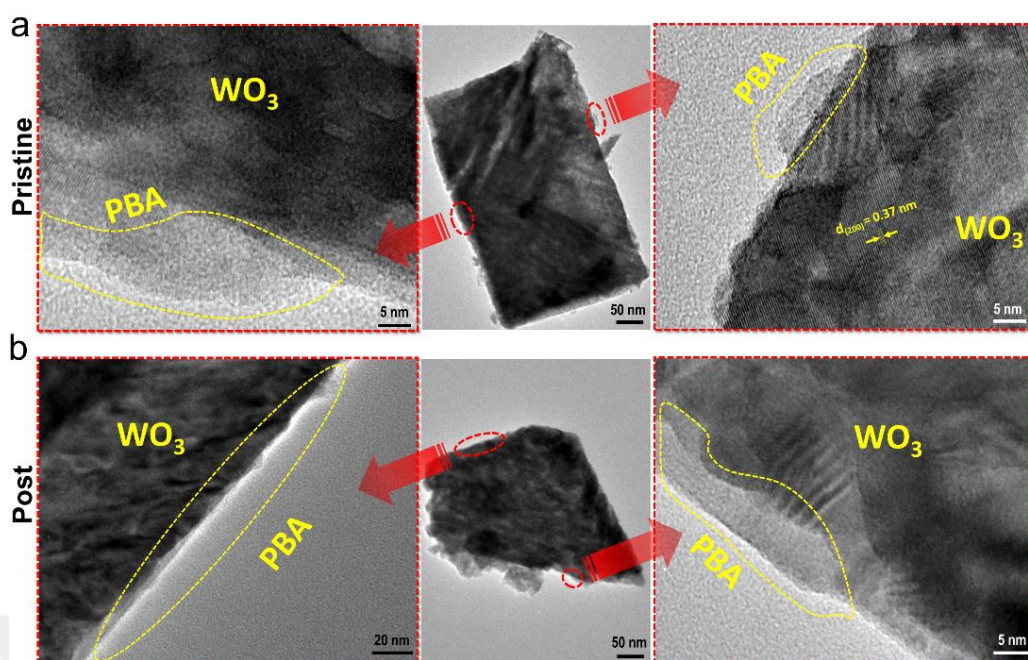


Figure 6.13 TEM and HR-TEM analysis of pristine and post catalytic $\text{WO}_3/[\text{CoFe-SF}]$. PBA region is shown by yellow color dashed lines. (a) Pristine $\text{WO}_3/[\text{CoFe-SF}]$ sample; (left) The HR-TEM image from the WO_3 -PBA interface, indicating the formation of an ultrathin PBA extended network on the WO_3 surface, (middle) TEM image of an individual pristine WO_3 nanoplate sensitized with $[\text{CoFe-SF}]$ assembly, (right) HR-TEM of $\text{WO}_3/[\text{CoFe-SF}]$, showing the formation of island-like PBA shell layers on the WO_3 surface. Based on this HR-TEM image, the WO_3 semiconductor has a single crystalline phase with an interplanar spacing of 0.37 nm, which is consistent with its monoclinic phase. (b) Post $\text{WO}_3/[\text{CoFe-SF}]$ sample; (left) HR-TEM image from the WO_3 -PBA interface, showing the formation of both continuous and island-like PBA layer, (middle) TEM image of an individual nanoplate after CA experiment, (right) HR-TEM image from the WO_3 -PBA interface, showing the existence of a uniform PBA shell layer after CA experiment. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

HR-TEM images also reveal that the WO_3 component exhibits a crystalline phase with interplanar spacing of 0.37 nm corresponding to (200) plane of the monoclinic phase of WO_3 structure, as shown in Figure 6.13a right panel. A further confirmation on the existence of a PB layer on the WO_3 surface, on a large scale, is achieved by using a TEM-EDX line scan and area EDX analysis. As shown in Figure 6.14a,b, both pristine and post-catalytic samples contain a PB layer on their surfaces.

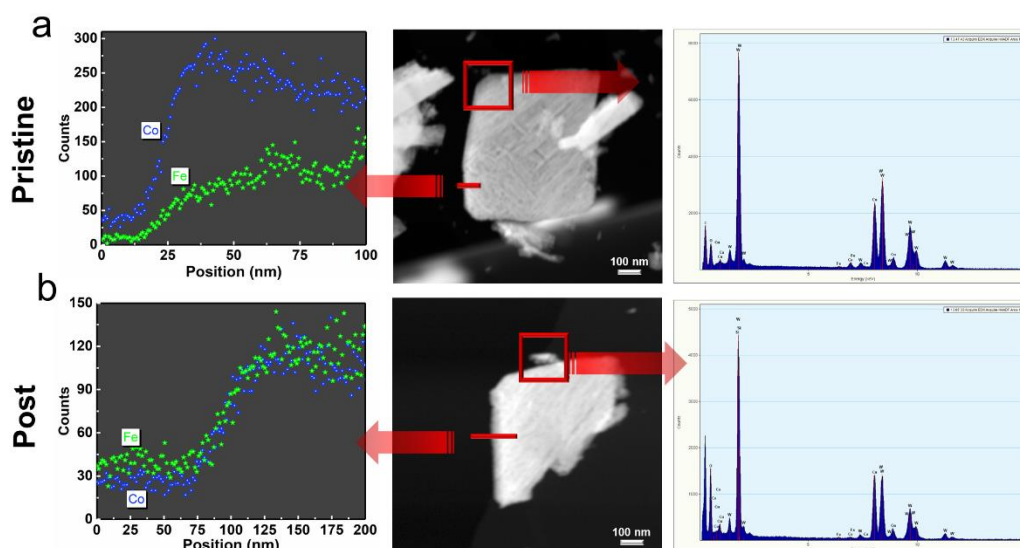


Figure 6.14 Comparison of the TEM and HR-TEM analyses of pristine and post catalytic $\text{WO}_3/[\text{CoFe-SF}]$ sample. (a) Pristine $\text{WO}_3/[\text{CoFe-SF}]$ sample; (left) TEM-EDX line-scan in HR-TEM from air to an individual PB coated WO_3 nanoplate with a high magnification of the interface, scale bar: 100 nm, (middle) TEM image of the individual nanoplate, (right) The EDX spectrum from the defined area. (b) Post $\text{WO}_3/[\text{CoFe-SF}]$ sample; (left) TEM-EDX line-scan analysis on the post-catalytic sample, proving the existence of PBA layer, (middle) TEM image of the individual nanoplate, (right) The EDX spectrum from the defined area. The Co:Fe ratio for the pristine sample is 2.46 while it is 1.06 for the post-catalytic one. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

Finally, XPS analysis is employed to examine the stability of the photoanode after the CA experiment. As expected, an enhancement in Co^{3+} and Fe^{3+} signals is observed in the post-catalytic sample, which indicates that cobalt and iron sites are partially oxidized during the water oxidation process, see Figure 6.15. However, the fully oxidized form of cobalt (Co_3O_4) was not observed, indicating that the CoFe PB layer retains its chemical stability under photoelectrochemical conditions.

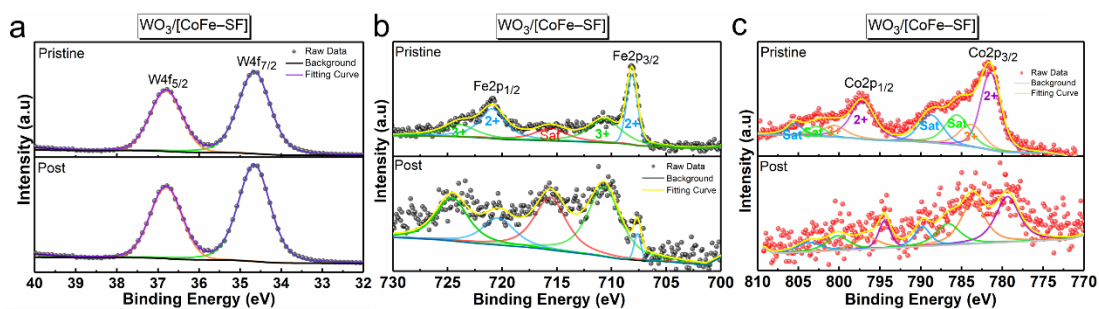


Figure 6.15 High resolution XPS spectra of (a) W4f, (b) Fe2p, and (c) Co2p for pristine and post-catalytic $\text{WO}_3/[\text{CoFe-SF}]$. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

A photocatalytic degradation experiment is performed further to prove the stability of $[\text{CoFe-SF}]$ bulk assembly. Here, both the $[\text{SF}]$ and $[\text{CoFe-SF}]$ are exposed to solar light (1 sun, 100 mW/cm^2) for 500 min in the presence of WO_3 powder ($\sim 2 \text{ mg}$). The change in the dye absorption peak as a function of exposure time to light was investigated, see Figure 6.16a-d. At the end of this experiment, the color of $[\text{SF}]$ solution fades. Its characteristic absorption bands disappear as expected.[241] On the other hand, $[\text{CoFe-SF}]$ exhibits a slight decrease in its spectral response even in the primitive design, in which the $[\text{CoFe-SF}]$ and WO_3 powder samples are mixed (Note that an in-situ synthesis is employed to improve the stability and physical interaction between WO_3 and $[\text{CoFe-SF}]$).

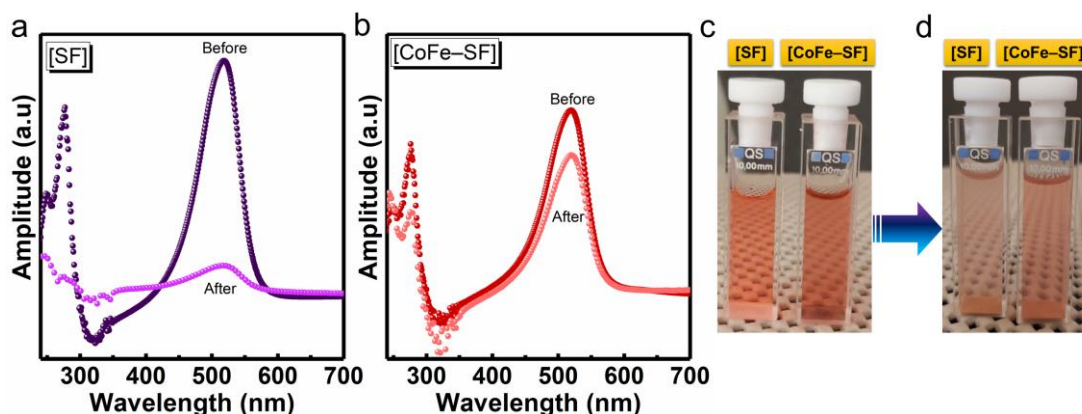


Figure 6.16 Photocatalytic degradation test, absorption profiles before and after 500 min solar light exposure of the (a) $[\text{SF}]$ and (b) $[\text{CoFe-SF}]$ aqueous solutions in the presence of the same amount of WO_3 powder. The optical image shows the related color change (c) before and (d) after the photocatalytic experiment for both solutions. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

A similar response in PS-semiconductor designs has previously been reported. The poor stability of the architecture is attributed to the unstable reduced state formed upon an electron transfer from the PS to the semiconductor.[242], [243] Therefore, the photocatalytic degradation experiment together with the aforementioned TEM, XPS, long term CA measurements, and IPCE response particularly in the 480-600 nm region indicate the critical role of the bulk PB structure on the stability and the performance of the photoanode.

6.4.5. Oxygen Evolution Activity Measurements

CA experiment at 1.23 V_{RHE} (at pH 3) was performed with a gas-tight cell and the amount of photogenerated O₂ was recorded by an O₂ probe. A Faradaic efficiency of approximately 75.3% (as explained in Figure 6.17) indicates that the photocurrent response is mainly originated from the water oxidation process.

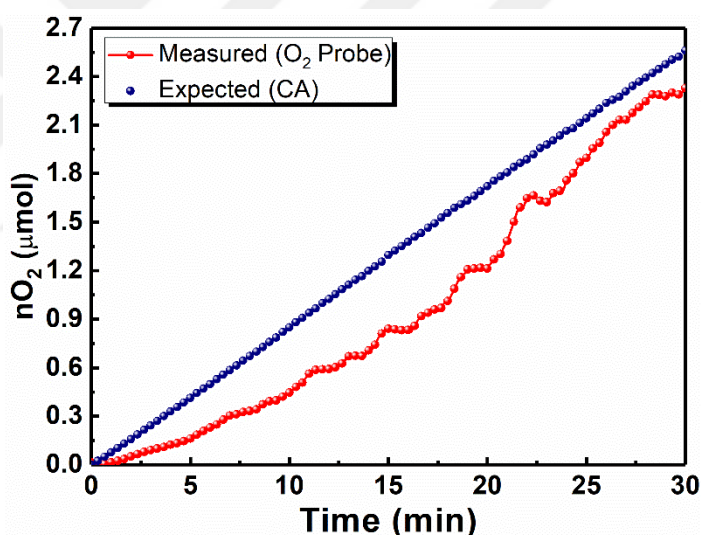


Figure 6.17 Comparison of the measured oxygen evolution amount employing the same WO₃/[CoFe–SF] photoanode. The total amount of oxygen produced was calculated as the sum of the oxygen in the headspace detected by the O₂ probe in a gas-tight electrochemical cell. The theoretical amount is extracted from the total amount of charge passed during the CA experiment at 1.23 V_{RHE} yielding a 75% Faradaic efficiency. 0.1 M Na₂SO₄ solution (pH 3) of 15 mL was used. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

6.4.6. Steady-State and Transient Optical Measurements

In the next step, optical studies are performed to understand the effect of PB structure on the energy levels of the PSs. While all dye complexes have similar absorption and fluorescence profiles (Figure 6.18a), a gradual blue shift occurs from [SF] to [Fe–SF] and to [CoFe–SF], which is also evident on their fluorescence colors, upon white and green light excitation, (Figure 6.18b). [SF] and [CoFe–SF] exhibit different profiles upon broadband illumination, where a wide range of optical excitations are possible. This indicates that they exhibit different excited state energetic levels, which is the origin of the fluorescence color difference between the two complexes. Electronic transitions in ultra-short time scales are tracked to elucidate this difference. Time-resolved fluorescence (TRF) spectroscopic studies are performed on both solutions and photoanodes with a 495 nm excitation. The decay dynamics in photoanodes are much faster than those in solutions due to new recombination pathways induced by WO₃ (Figure 6.18c). That is why solutions exhibit a single decay rate (LUMO→HOMO transition), while photoanodes have multiple exponential rates (multiple relaxation routes).

Moreover, the faster decays in [Fe–SF]/WO₃ and [CoFe–SF]/WO₃ are a sign of efficient injection dynamics (Figure 6.18d). The excited electrons are transferred into WO₃ CB and back-recombine with holes in the HOMO level. It is, thus, clear that energy levels are reconstructed with the incorporation of a PB layer.

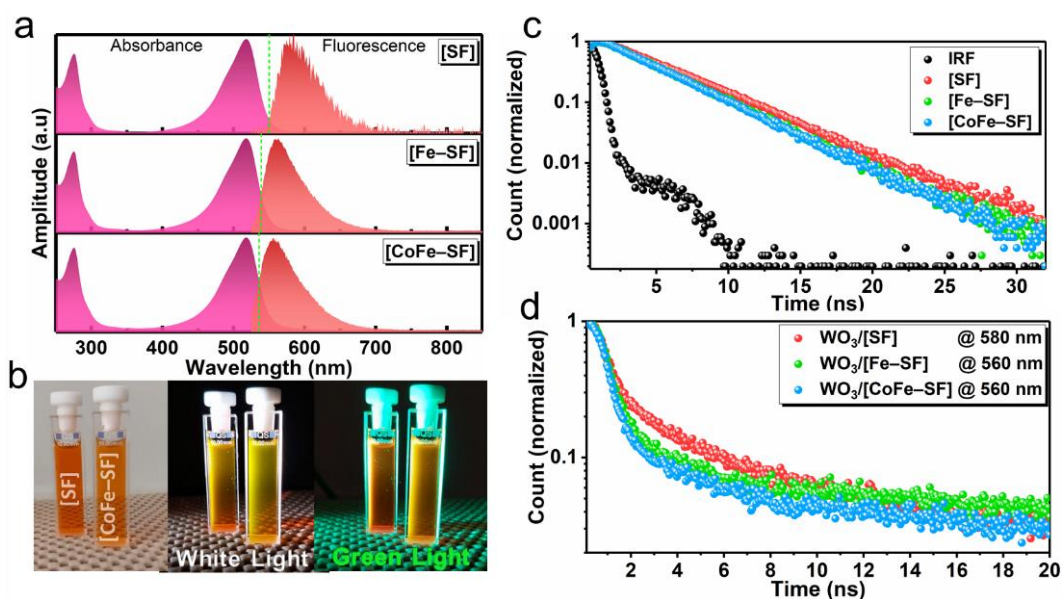


Figure 6.18 Steady State Measurements: (a) Absorption and fluorescence spectra (with an excitation of 520 nm) of the [SF], [Fe-SF], and [CoFe-SF] solutions (0.02 mM in MeCN solutions). The optical band gap of different complexes is defined by the intersection point of absorption and fluorescence spectra. Transient Optical Measurements: (b) [SF] and [CoFe-SF] solutions under dark, their fluorescence under white and green light illuminations. The TRF spectra of (c) the dye solutions and (d) photoanodes upon 495 nm excitation. The probe signal for each solution is shown in the legend. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

6.4.7. Computational Calculations and Mechanism

Ab initio electronic structure calculations based on density functional theory with periodic boundary conditions were employed to explore this modification at the molecular level (Figure 6.19a-c). All these theoretical studies are performed by Prof. Durgun's group. In line with the experimental findings (Figure 6.19a) ab initio calculations suggest that the integration of the [SF] group to the PB structure gradually widens the HOMO - LUMO gap. The nature of electronic states is also altered with the coordination of cobalt ions. The HOMO of [CoFe-SF] is distributed over the iron site and organic ligand while that of [Fe-SF] is fully localized only on the iron site. On the other hand, all of the excited states in [Fe-SF] are mostly ligand-centered (LC) in character, which mediates efficient metal-to-ligand charge transfer (MLCT). For [CoFe-SF], the LUMO is localized on the cobalt site (metal-to-metal charge transfer, MMCT) and LUMO- i ($i \geq 1$) are LC (ideal for MLCT process). The weak band at ~630 nm is assigned to the MMCT process ($\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II}} \rightleftharpoons \text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III}}$) as it is depleted

with the gradual addition of an oxidizing agent (1M aqueous $\text{Na}_2\text{S}_2\text{O}_8$) to oxidize metal ions to their +3 oxidation states (Figure 6.19d-g). The MMCT band is much weaker than the MLCT one, which suggests that MLCT dominates over the MMCT during the charge transfer process.

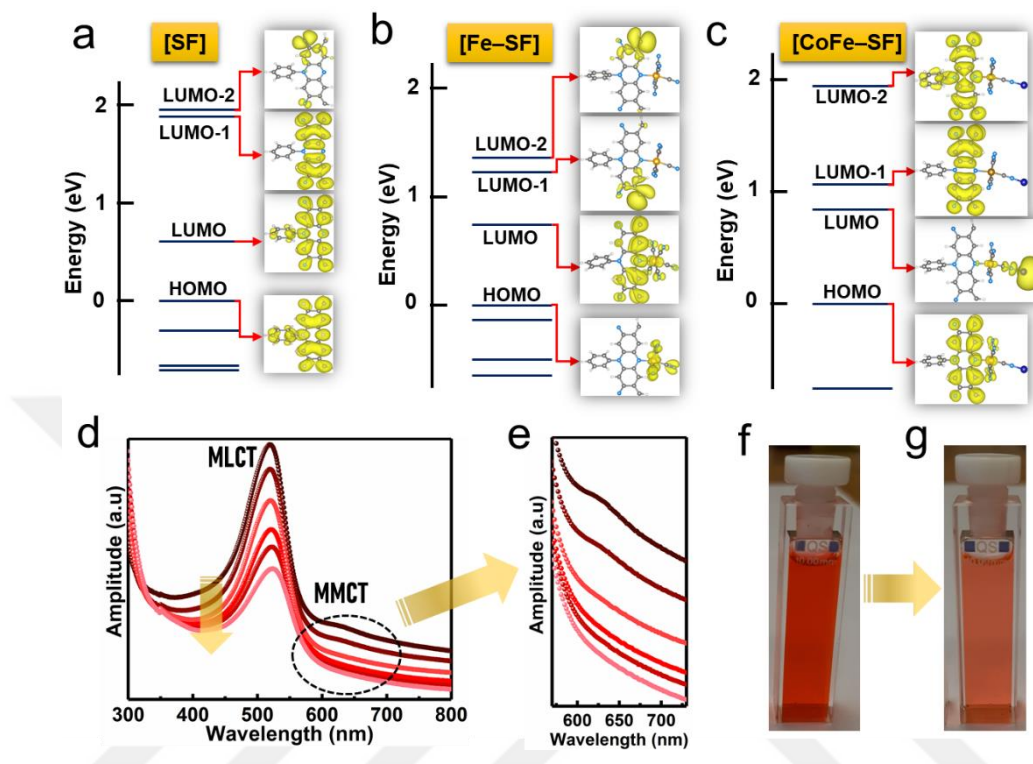


Figure 6.19 Theoretical First-Principle Calculations: HOMO and LUMO energy levels with the electron clouds for all 3 components of (a) [SF], (b) [Fe-SF], and (c) [CoFe-SF], calculated with PBC-DFT using hybrid functionals. Metal-to-Metal Charge Transfer (MMCT) Feature: (d) Changes observed in the UV-Vis spectrum of an aqueous solution of the [CoFe-SF] complex with the incremental addition of 1 M aqueous $\text{Na}_2\text{S}_2\text{O}_8$ solution. (e) The magnified image shows the presence of the MMCT state between the wavelength of 550 - 750 nm, which infers the effective depletion of the 3+ states in the same complex. Related color change in the solution (f) before and (g) after the experiment. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

6.4.8. Femtosecond Transient Absorption Measurements

Transient absorption (TA) spectroscopy is used to probe the electronic transitions in femtosecond transient scales. The TA spectra of WO_3 /[SF] and WO_3 /[Fe-SF], in different time delays, resembles that of their solutions with two main features: a negative signal attributed to ground state bleaching (GSB), and a positive response raised from excited-state absorption (ESA) (Figure 6.20a-c and Figure 6.21). The ESA signal followed with a sluggish GSB for

$\text{WO}_3/[\text{Fe-SF}]$ decays much faster (within the first 100 ps delay) than $\text{WO}_3/[\text{SF}]$. However, the ESA peak vanishes in the first 200 fs time delays for $\text{WO}_3/[\text{CoFe-SF}]$, and here the decay of the ESA feature without the loss of GSB amplitude is a signature of electron injection, Figure 6.20c, as explained in previous studies.[244]–[246]

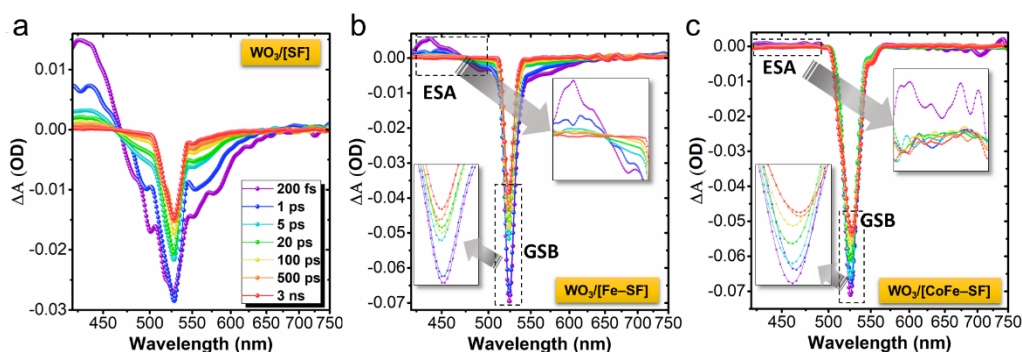


Figure 6.20 TA spectra of the electrodes upon 520 nm (pump) excitation at different pump-probe time delays for (a) $\text{WO}_3/[\text{SF}]$, (b) $\text{WO}_3/[\text{Fe-SF}]$, (c) $\text{WO}_3/[\text{CoFe-SF}]$. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

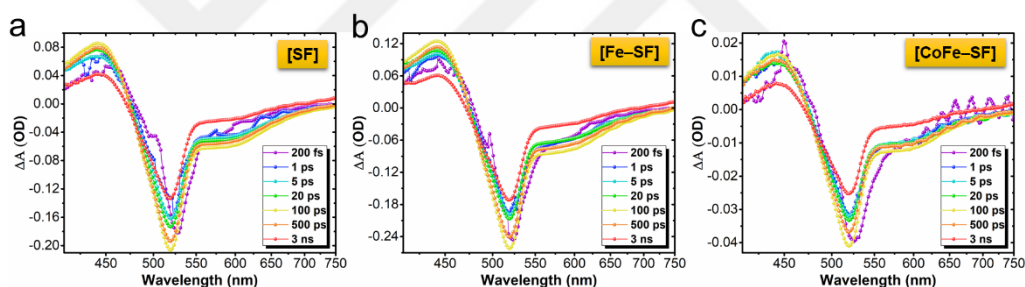


Figure 6.21 TA spectra for dye solutions: 0.02 mM (a) [SF], (b) [Fe-SF] and (c) [CoFe-SF] compounds in MeCN solutions at 420 nm (pump) excitation with different pump-probe time delays. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

This profile could be further proven by evaluating the band alignments between WO_3 and different dye complexes of [SF], [Fe-SF], and [CoFe-SF], as shown in Figure 6.22a-c. A more favorable band alignment for $\text{WO}_3/[\text{CoFe-SF}]$ is the reason for the efficient injection dynamics. Therefore, the PB extended network not only acts as a WOC, but also modifies the electronic level alignment between semiconductor host and dye absorber. Due to proper band alignment, the selective isolation of photoexcited electrons and holes is provided, leading to a high-water oxidation activity. Figure 6.22d schematically summarizes the responsible steps for PEC water oxidation using the proposed dye-sensitized photoanode.

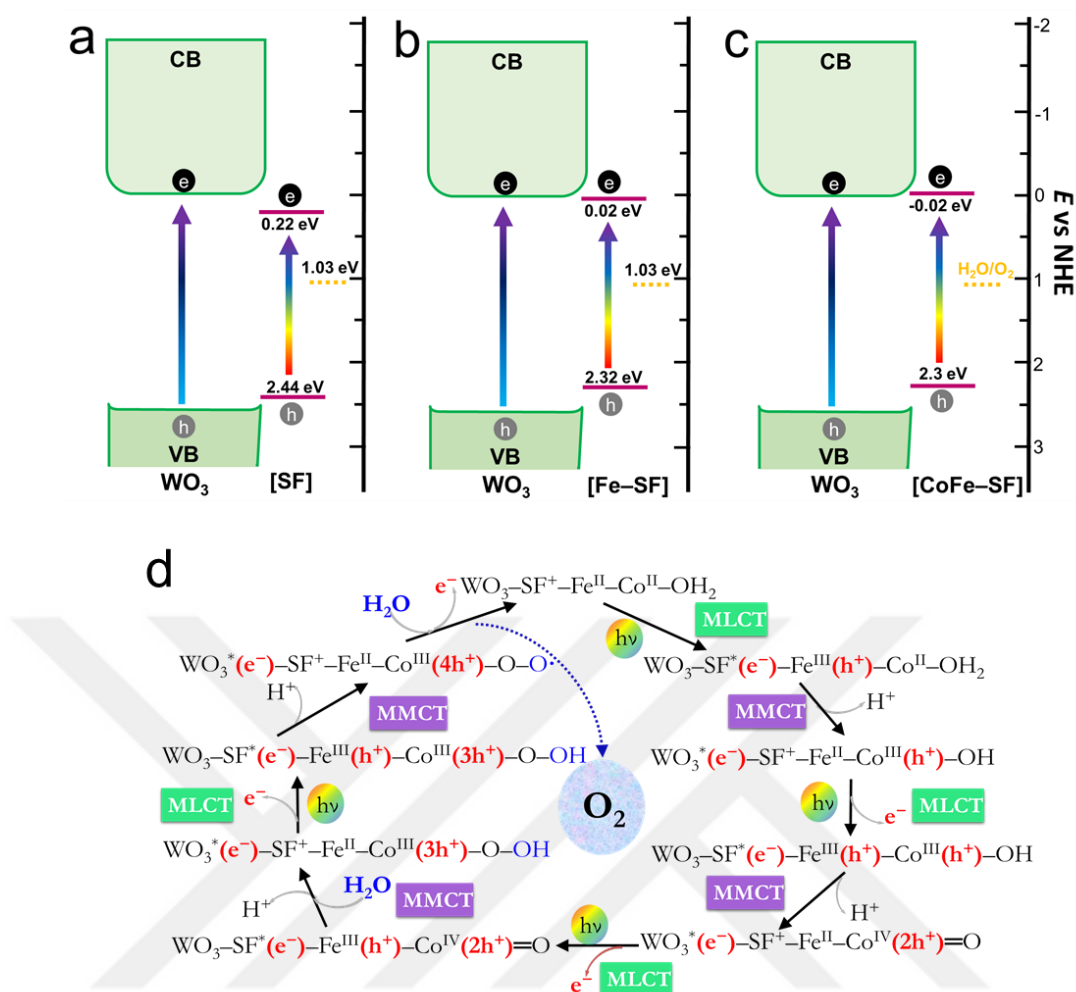


Figure 6.22 Schematic representation of band alignments for (a) WO₃/[SF], (b) WO₃/[Fe-SF], (c) WO₃/[CoFe-SF] photoanodes. (d) Proposed molecular mechanism of the PEC water oxidation for [CoFe-SF]. (Reprinted with permission from Elsevier Ref. [223]. Copyright © 2021 Elsevier.)

6.5. Summary

In this work, we present a strategy to push the limits of the interaction between the PS and the WOC for the development of a high-performance, precious-metal-free, dye-sensitized water oxidation photoanode. In this architecture, an organic photosensitizer that absorbs visible light above 500 nm, an iron relay group, and a cobalt water oxidation catalytic site were connected through short cyanide groups, which promotes electronic interaction between these components. Ultrafast TA and computational studies suggest the mixing of electronic states of organic PS, iron, and cobalt groups to reorganize the excited states for enhanced electron transfer during the PEC process. This strong interaction is reflected also in the stability and activity of the dye-

sensitized photoanode, which is built by the Ru-free PS-WOC assembly coated over a visible light-absorbing semiconductor, WO_3 . A photocurrent density of 1.3 mA/cm^2 can be achieved at $1.23 \text{ V}_{\text{RHE}}$ with an efficient photon-to-electron conversion up to 600 nm for at least 2-hours of illumination. In conclusion, we provide an easy-to-assemble pathway to develop earth-abundant, efficient, and robust dye-sensitized photoelectrodes through a cyanide-based synthetic approach. Given the diversity and simplicity of the approach, more examples will clearly follow to further explore cyanide-based dye sensitization



Chapter 7. Iron Chromophore Incorporated PB for Dye-Sensitized Water Oxidation



7.1. Preface

This chapter of the thesis is based on the publication "*Building an Iron Chromophore Incorporating Prussian Blue Analogue for Photoelectrochemical Water Oxidation*", T. G. Ulusoy Ghobadi, A. Ghobadi, M. Demirtas, M. Buyuktemiz, K. N. Ozvural, E. Akhuseyin Yildiz, E. Erdem, H. G. Yaglioglu, E. Durgun, Y. Dede, E. Ozbay, F. Karadas, **Chem. Eur. J.**, 2021, 27, 1 – 12 (Front Cover). Adapted (or "Reproduced in part") with permission from John Wiley and Sons, Ref. [138]. Copyright 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

7.2. Introduction

Earth-abundant photoactive complexes have become one of the central themes in light-harvesting applications, including dye-sensitized solar cells, artificial photosynthesis, photocatalysis, light-emitting diodes, and photodynamic therapy.[247] The main focus is centered on Fe(II) complexes owing to their earth-abundancy, low toxicity, and isovalency with the well-known precious, scarce, and expensive heavy metal (e.g. Ru(II), Os (II), Re(I), and Ir(III)) based photosensitizers.[248] The photoactivity of these complexes is governed by the metal-to-ligand charge transfer (MLCT) process, which is highly dependent on the electronic nature (donating & accepting ability) of the ligand and the interaction between the metal and the ligand. Since the relatively weak metal-ligand interactions in iron-bipyridyl complexes retard the MLCT process due to the readily accessible metal-centered (MC^*) states, so-called deactivation pathways, positioned energetically below the MLCT states.[228], [229] Common iron chromophores feature femtosecond range light-activated excited state lifetimes, making them unfeasible for solar to energy conversion devices. For example, the lifetime of MLCT excited state in the trisbipyridyl iron complex (below 100 fs) is much shorter than its ruthenium analog (approx. 100 ps).[227] The commonly employed strategy to enhance the lifetime of the MLCT state is to decorate the coordination sphere of the octahedral Fe(II) site with a combination of σ -donor and π -acceptor ligands. In this respect, the earlier studies revolve around the utilization of cyanoferrate(II) complexes, including $Fe(bpy)_2(CN)_2$ and $[Fe(bpy)(CN)_4]^{2-}$. [249]–[251] Despite the presence of strongly σ -donating cyanide ligands, they still exhibit accessible low-lying MC^* states relative to MLCT states. Some encouraging developments have been achieved recently, particularly with iron complexes coordinated to strongly σ -

donating cyclometalated ligands, which were found to effectively block deactivation pathways by destabilizing MC^* states.[248] Recent MLCT lifetimes of 9 ps and 528 ps were achieved by Fe(II) carbene complexes surrounded with CNC and CC-type ligands, respectively.[252], [253] A substantially longer excited-state lifetime of 37 ps was reported when an iron(II) carbene complex is immobilized on Al_2O_3 . [230] The increasing number of potential iron chromophores suggests that '*iron can be the new ruthenium*'. [231] This breakthrough, however, is bound to the incorporation of an iron chromophore into a dye-sensitized device, which is awaiting realization.

Recently, numerous ruthenium-based PS-WOC assemblies have been highlighted in PEC cells.[65], [199] Ruthenium-based assemblies have also been developed within a cyanide framework.[124], [179], [180] Unfortunately, the implementation of an iron chromophore into an earth-abundant dye-sensitized (water oxidation) photoanode so far has not been nearly as successful as their heavy counterparts, since it presents a threefold problem: i) The MLCT excited-state lifetimes of iron complexes are not sufficient to drive interfacial charge transfer at the SC surface, ii) they have relatively poor stabilities, and iii) the design of a bridging ligand that connects the iron chromophore to a catalyst, is a synthetic challenge. Along this line, a precious-metal free WOC that is stable and that can be bridged to the iron chromophore is another major challenge that has not been explored yet. Most of the WOCs, utilized for the dye-sensitized water oxidation process, are molecular ruthenium-based ones. So far, the replacement of molecular ruthenium with bulk oxides catalysts has only been possible with the expense of poor activity due to relatively high electron-hole recombination pathways.[177] In previous chapters, we utilized a cyanide-based synthetic pathway to take advantage of the strengths of both the molecular and bulk approaches. The synthetic protocol is much simpler than that of molecular ruthenium ones due to the high reactivity of both atoms of the cyanide groups towards 3d transition metal ions. PS and WOC units could be connected through a pentacyanoiron unit in a one-step reaction, which affords a rigid extended framework. Note that, metal pentacyanometalates exhibit amorphous nature due to the bulky organic ligand coordinated to the $Fe(CN)_5$ group.[112], [124] The organic ligand limits the dimensionality of the framework, thereby leads to the formation of a non-periodic bulk structure with random defect sites, which is desired for enhanced catalytic activity. In contrary to molecular chromophore-catalyst assemblies, the functional units form a rigid bulk structure once they are connected. These assemblies could, thus, be described as non-periodic bulk structures, which

consist of molecular PS and catalyst units. They were also observed to exhibit superior stability under photocatalytic and photoelectrochemical conditions due to relatively fast electron transfer between the components and the rigidity of the bulk structure.[125], [126], [223]

Herein, we move one step forward and transform the $\text{Fe}(\text{CN})_5$ group from an electronic relay to a chromophore unit. While a maximum of four cyanide ligands was coordinated to an iron site in previously studied cyanoiron chromophores,[249]–[251] in our design, five cyanide ligands are coordinated to the iron site to destabilize the MC^* states further. Moreover, the remaining coordination sphere of the octahedral iron site is occupied by an electron-deficient cationic pyridinium group rather than a common bipyridyl ligand to facilitate the MLCT process.[254], [255] The molecular donor-acceptor chromophore is then reacted with Co^{2+} ions to obtain an amorphous metal pentacyanometalate structure, which incorporates a photosensitizer coupled to a WOC unit through cyanide groups.

7.3. Experimental Procedures

7.3.1. Materials

1-(4-pyridyl) pyridinium chloride hydrochloride ($\text{C}_{10}\text{H}_9\text{ClN}_2\cdot\text{HCl}$) denoted as [PP], sodium nitroferricyanide ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), ammonium hydroxide solution (NH_4OH , 25% (v/v), ethanol (EtOH), methanol (MeOH), and cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$). Titanium (IV) butoxide ($\text{Ti}(\text{OBu})_4$, 97%, hydrochloric acid (HCl, 36%), and Millipore deionized water (resistivity: 18 $\text{M}\Omega/\text{cm}$) was used for the hydrothermal growth of TiO_2 NWs on FTO coated glass (2 mm thick, 7 Ω/sq). PBS was prepared by 0.1 M KH_2PO_4 and 0.1 M K_2HPO_4 .

7.3.2. Sample Preparation

Synthesis of Pentacyanoferrate-Coordinated 1-(4-Pyridyl) Pyridinium Chloride Hydrochloride, $\text{Na}_2\text{Fe}(\text{CN})_5(\text{C}_{10}\text{H}_9\text{N}_2)\cdot x\text{H}_2\text{O}$, [Fe-PP]: Sodium aminopentacyanoferrate, $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$ denoted as [Fe-NH₃] was synthesized according to our previously reported procedures.[112], [125] For the synthesis of the iron chromophore, [Fe-PP], [PP] (1.23 mmol) was dissolved in ~1 mL of distilled water at room temperature. At that point, a colorless

solution was observed. 1.23 mmol of $[\text{Fe}-\text{NH}_3]$ was added into that solution with the addition of 1 mL more distilled water, and the color changed suddenly from transparent to dark red. The reaction was allowed to continue mixing in a covered flask for 6 hours in the dark at room temperature. Since the solubility of the compound in ethanol is less than those of the precursors, 30 mL cold EtOH was added to the solution and stored at 4°C in a refrigerator overnight. The unreacted $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ complex and possible by-products were removed by filtration and washed with 50 mL cold ethanol. The dark purple precipitate was isolated and dried under vacuum overnight at room temperature. The yield was around 65%.

Synthesis of Cobalt Pentacyanoferrate-Coordinated 1-(4-Pyridyl) Pyridinium, $\text{CoFe}(\text{CN})_5(\text{C}_{10}\text{H}_9\text{N}_2) \cdot x\text{H}_2\text{O}$, $[\text{CoFe}-\text{PP}]$: First, 1 equiv. $\text{Co}(\text{NO}_3)_2$ in distilled water was added dropwise into an aqueous solution of $[\text{Fe}-\text{PP}]$ compound (113.75 mg, 23 mmol). To collect the solid and remove soluble unreacted species, the suspension was centrifuged three times at 6,500 rpm for 20 min. with water. The obtained olive green-colored product was dried in an oven at 65 °C for a day, see Figure 7.1 for the final chemical structure.

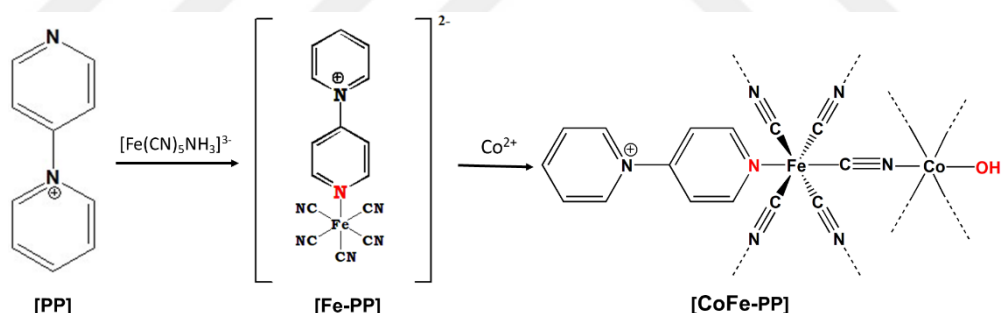


Figure 7.1 A molecular representation of synthesis route for $[\text{CoFe}-\text{PP}]$. Coordination of $[\text{Fe}-\text{PP}]$ to the cobalt ions through the ambidentate cyanide ligands results in the appearance of a purplish color as shown in Figure 7.2b. Both $[\text{PP}]$ and $[\text{Fe}-\text{PP}]$ exhibit molecular structure while $[\text{CoFe}-\text{PP}]$ has a bulk structure since cobalt ions are coordinated to the nitrogen atoms of the cyanide group. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Synthesis of photoanodes: Pristine TiO_2 NWs “ TiO_2 ”, and in situ PB modified dye-sensitized TiO_2 electrode (Co WOC and iron chromophore loaded TiO_2 NWs) “ $\text{TiO}_2/[\text{CoFe}-\text{PP}]$ ” were coated on FTO electrodes with an exposed area of 2 cm². TiO_2 NW arrays were synthesized by modifying the hydrothermal

technique as described in our previous study. [126] For the preparation of $\text{TiO}_2/[\text{CoFe-PP}]$ photoanode, bare NWs are first immersed into an EtOH solution containing $[\text{Fe-PP}]$ (1.33 mM) for about a day at room temperature. Afterward, weakly absorbed dye molecules are removed by rinsing with copious amount of ethanol and the electrode is dried for 15 min. Then, 400 - 500 μL of 0.04 M $\text{Co}(\text{NO}_3)_3$ in EtOH solution is drop-casted on the electrode surface. The sample is washed after 15 min. to remove unreacted Co^{2+} ions. This procedure is repeated 2 - 3 times to ensure a uniform PB layer on TiO_2 . Finally, the $\text{TiO}_2/[\text{CoFe-PP}]$ electrode is left for drying at room temperature.

7.4. Results and Discussions

7.4.1. Design of the photoelectrode

The iron chromophore was obtained by mixing a transparent solution of 1-(4-pyridyl)pyridinium chloride (PP^+Cl^-) with a pale yellow solution of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$, $[\text{Fe-NH}_3]$, to afford $\text{Na}_2[\text{Fe}(\text{CN})_5\text{PP}]$, $[\text{Fe-PP}]$, with a dark red solution due to the MLCT process between the iron site and PP^+ group. It is then coated on the rutile TiO_2 nanowires (NWs) modified FTO electrode to obtain $\text{TiO}_2/[\text{Fe-PP}]$, and reacted with Co^{2+} ions to obtain a CoFe-PP layer, $[\text{CoFe-PP}]$, on the SC surface, yielding $\text{TiO}_2/[\text{CoFe-PP}]$ (Figure 7.2a,b). The proposed photoanode, thus, contains a cyanide-based extended framework coated over a SC surface. Since both cyanide groups and pyridyl groups are known to interact with the TiO_2 surface, the Fe-PP group is believed to be randomly oriented on the TiO_2 surface to afford a non-periodic coordination network.[256] For the preparation of the target photoanode, an in situ synthetic procedure is adopted, in which the iron chromophore-catalyst assembly is prepared on the SC surface. [134] First, the TiO_2 electrode was sensitized with the iron chromophore, $[\text{Fe-PP}]$, and then reacted with Co^{2+} ions to enforce a catalyst-chromophore-semiconductor order (Co-Fe-PP-TiO_2) and to improve the physical interaction between layers. The coating process on TiO_2 is repeated two times to extend the molecular structure to a bulk one via the coordination of dangling cyanide groups to Co^{2+} ions. The previous studies on PB based photoelectrodes indicate that the number of repetitions in the coating process should be optimized carefully since the thickness of the PB layer plays a critical role in the stability and the activity of photoelectrode. A thin layer below around 10 nm thickness of bulk structure should be optimized since a thin layer decomposes quickly due to the lack of a rigid bulk structure, while at

thicknesses above 20 nm insulating nature of the PB layer results in a decrease in the photocurrent density.[126]

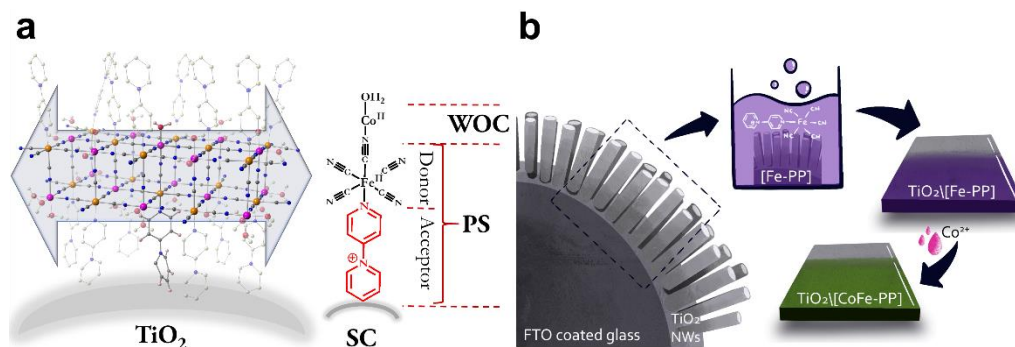


Figure 7.2 (a) A rough illustration of an iron-sensitized photoanode and the role of each component displayed in the molecular fragment of the bulk $[\text{CoFe-PP}]$ layer: TiO_2 SC, $[\text{Fe-PP}]$ is the PS, and cobalt site is the WOC. The grey arrow indicates the $[\text{CoFe-PP}]$ extended framework on the TiO_2 surface. (b) Schematic illustration for the three-step preparation of $\text{TiO}_2/[\text{CoFe-PP}]$ photoanode; (i) hydrothermal growth of TiO_2 NWs, (ii) coating TiO_2 NWs with $[\text{Fe-PP}]$ to prepare $\text{TiO}_2/[\text{Fe-PP}]$, and (iii) in-situ drop-casting of Co^{2+} ions to prepare $\text{TiO}_2/[\text{CoFe-PP}]$. The color of the electrode changes from purple to green. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

7.4.2. Materials Characterization

ATR-FTIR spectroscopy is utilized to enlighten the coordination modes in cyanide-based compounds, $[\text{Fe-NH}_3]$, $[\text{Fe-PP}]$, and $[\text{CoFe-PP}]$. Both reactions of the PP^+ group with $[\text{Fe-NH}_3]$ and that of Co^{2+} ions with $[\text{Fe-PP}]$ to obtain $[\text{Fe-PP}]$ and $[\text{CoFe-PP}]$, respectively, shift the cyanide stretch (ν_{CN}) slightly to higher wavenumbers (Figure 7.3). The shift in $[\text{Fe-NH}_3] \rightarrow [\text{Fe-PP}]$ reactions is attributed to the electron-accepting behavior of $[\text{PP}]$ group while the one in $[\text{Fe-PP}] \rightarrow [\text{CoFe-PP}]$ confirms the formation of a Fe-CN-Co coordination mode.[112] ν_{CN} for $[\text{CoFe-PP}]$ is much broader than that for $[\text{Fe-PP}]$ and also the ones for previously studied crystalline PBAs,[111], [113] due to the formation of a non-periodic bulk structure.

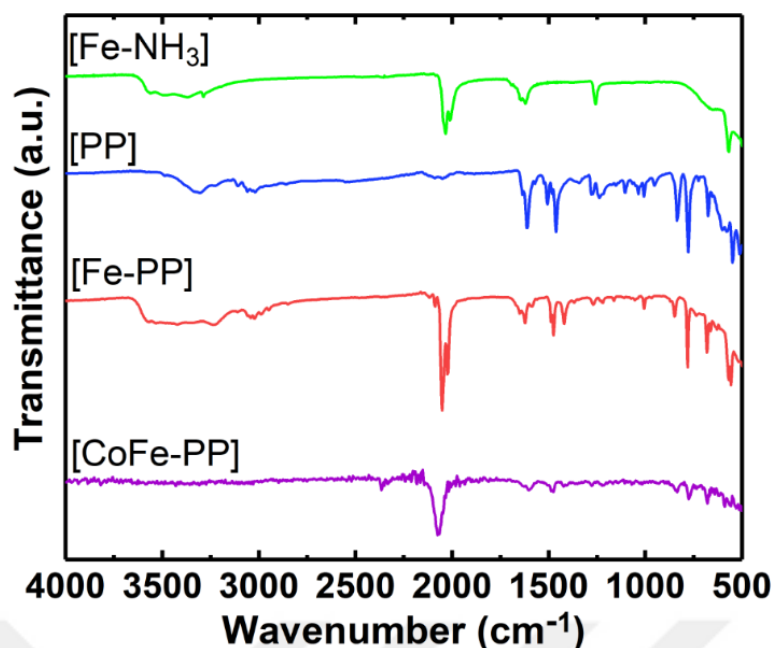


Figure 7.3 The ATR-FTIR of [Fe-NH₃], [PP], [Fe-PP], and [CoFe-PP] powders: The sharp peaks shown by dashed line in the 2,000–2,100 cm⁻¹ range are attributed to CN stretch. The CN stretching frequency has a sharp peak at 2,031 cm⁻¹ and the peak at around 567 cm⁻¹ is attributed to Fe–N coordination bond in [Fe-NH₃]. The CN/nitrile peak exhibits blue shifts for [Fe-PP] at ~2,050 cm⁻¹, which further shifts to ~2,071 cm⁻¹ for [CoFe-PP]. Therefore, it proves the coordination of iron sites to the PP ligand by σ -donation from the cyano nitrogen and then Fe–CN–Co coordination mode, which is direct evidence for the formation of a PB structure. FTIR of [PP] spectra show prominent bands between 1,600 and 1,330 cm⁻¹ attributed to C=C and C=N stretches of PP ligand, and there are signals observed at 500–1,660 cm⁻¹ confirming the presence of PP in the PB structure of the [CoFe-PP]. The sharp peak at around 1,264 cm⁻¹ is associated with N–H stretch; several peaks in the 1,000–1,330 cm⁻¹ and 2,850–2,900 cm⁻¹ range correspond to symmetric and asymmetric stretches of C–H bond. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Top and cross-sectional SEM images and HR-TEM analysis of the TiO₂/[CoFe-PP] photoanode confirms the formation of a non-periodic thin [CoFe-PP] layer with a thickness of around 10 nm, corresponding to roughly 5 Co–Fe–PP layers on the surface of TiO₂ NWs (with a 0.8–1.2 μ m mean length and a ~70–140 nm diameter) (Figure 7.4a). The sharp selected area electron diffraction (SAED) pattern (Figure 7.4b) and the RAMAN profile (Figure 7.4c) prove the growth of a single crystalline rutile phase of TiO₂ NWs.

The energy dispersive X-Ray spectroscopy line scan in TEM (TEM-EDS) is also performed in the vicinity of the NW surface to investigate the content of the elements on the NW surface (Figure 7.4d). The line scan confirms the presence

of Fe and Co atoms on the surface of the photoanode. Furthermore, EPR spectroscopy was performed on powder samples to elucidate the nature of iron ions in the PS-WOC assembly. It is known that diamagnetic Fe^{2+} cannot be detected solely via EPR measurements. Nevertheless, a broad EPR signal at around $g \sim 2.2 - 2.3$ could be observed for a high amount of magnetically interacting iron ions regardless of their oxidation states suggesting that the Fe-Fe (spin-spin) interactions dominate the EPR spectra.[257] The X-band EPR spectra measured at room temperature reveal a similar profile for $[\text{Fe}-\text{NH}_3]$ and $[\text{Fe}-\text{PP}]$ (Figure 7.4e). The broad line can be safely attributed to the dipolar interactions between low-spin Fe(III) sites with a coordination environment that reveals an EPR signal. On the other hand, $[\text{CoFe}-\text{PP}]$ exhibits an additional distinct sharp signal at around $g \sim 2.00$, which is assigned to magnetically isolated Fe^{3+} ions.[258], [259] Therefore, the EPR results suggest that cobalt ions favor the $\text{Fe}^{\text{II}}-\text{PP}^+ \rightarrow \text{Fe}^{\text{III}}-\text{PP}$ MLCT process due to the donating ability of cobalt sites. The Gaussian signal broadening, compared to $[\text{Fe}-\text{NH}_3]$ and $[\text{Fe}-\text{PP}]$, is also enhanced due to the increase in the number of spin-spin exchange interactions (dipolar coupling) in the extended framework as expected. XPS measurements performed on the $[\text{CoFe}-\text{PP}]$ powder sample and the $\text{TiO}_2/[\text{CoFe}-\text{PP}]$ electrode reveal three distinct peaks in N1s region (Figure 7.6) and traditional peaks in Co2p and Fe2p regions, suggesting that a mixed-valent CoFe PB layer incorporating PP groups is formed (not shown in here).

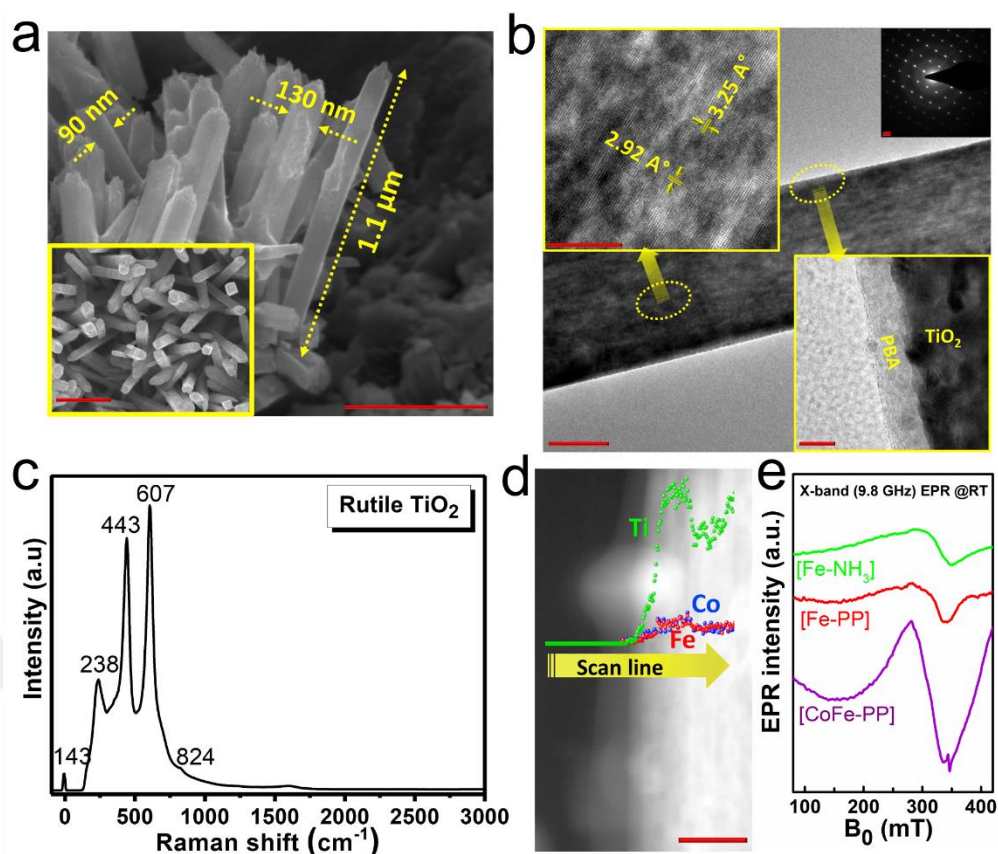


Figure 7.4 . (a) A side view SEM image of the TiO_2 /[CoFe-PP] photoanode and the inset displays the top view of the NWs, scale bars: 500 nm. (b) HR-TEM of TiO_2 /[CoFe-PP] shows its lattice fringes with interplanar spacings of 3.25 Å and 2.92 Å, which are consistent with the rutile phase. The down-right inset indicates the interface between the TiO_2 NW and a ~ 10 nm - thick PB layer, with a scale bar of 5 nm. The SAED pattern of a single NW, which is shown in the inset (top right), proves its single crystalline phase. (c) RAMAN spectrum of nanowires showing the formation of rutile phase TiO_2 . (d) EDS line scan in HR-TEM from air to an individual PB coated TiO_2 NW with a high magnification of the interface, scale bar: 20 nm. (e) Room temperature X-band EPR spectra of [Fe- NH_3], [Fe-PP], and [CoFe-PP], revealing the nature of iron sites. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

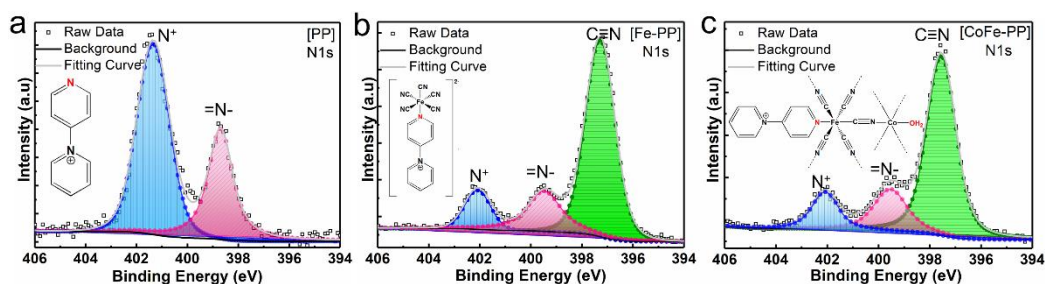


Figure 7.5 High resolution XPS spectra of N1s spectra for [PP], [Fe-PP], and [CoFe-PP]. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

7.4.3. Photoelectrochemical Measurements

The characterization techniques presented herein reveal that our *in situ* synthetic method leads to the formation of a unique non-periodic bulk CoFe-PP layer on TiO₂ as desired. After the initial structural analysis, light induced photocurrent measurements in a three-electrode cell was conducted to elucidate the role of each component in a TiO₂/[CoFe-PP] photoanode at pH 7 under a 1 sun irradiation (Figure 7.6a). Since there are two photoactive materials, TiO₂ and [CoFe-PP], the transient current responses of the electrode under on-off cycles of illumination were monitored with different cut-off filters and compared to the bare TiO₂ electrode (Figure 7.6b).

While TiO₂ significantly contributes to the photocurrent density either in the absence of a filter and with the 420 nm-filter due to its absorption tail, the effect of iron chromophore becomes more dominant as longer wavelength cut-off filters are used. TiO₂/[CoFe-PP] demonstrates a photo and dark current difference of approx. 5 $\mu\text{A}/\text{cm}^2$ at 435 nm filtered case, while it is only 1 $\mu\text{A}/\text{cm}^2$ for the bare one. For the 490 nm filtered case, TiO₂ is photo-irresponsive while TiO₂/[CoFe-PP] electrode is still active. In agreement with these findings, the IPCE response for TiO₂/[CoFe-PP] is extended up to 500 nm with an exponential decline while the one for bare TiO₂ decays to zero just below 420 nm (Figure 7.6c). Note that IPCE results confirm the photosensitizing ability of [Fe-PP] chromophore.

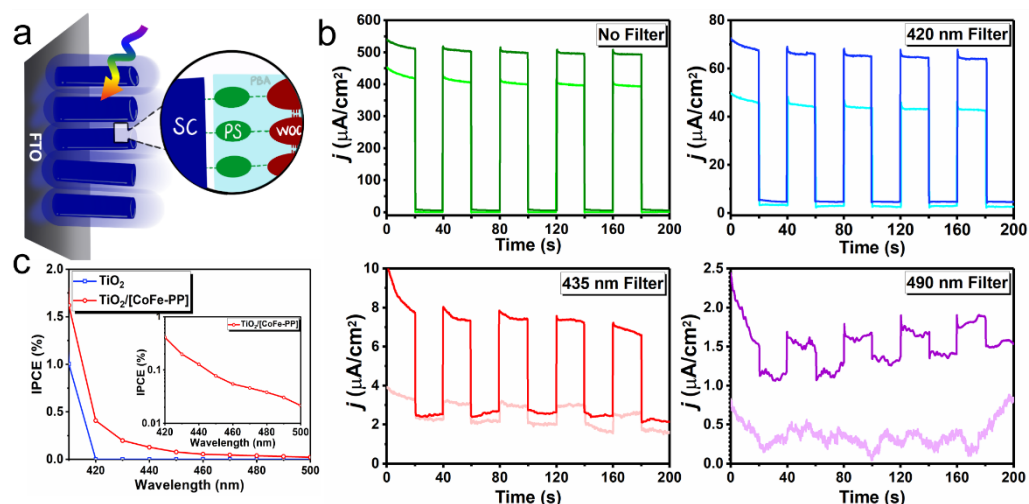


Figure 7.6 (a) Cross sectional illustration of $\text{TiO}_2/[\text{CoFe-PP}]$ electrode model; (b) Pulsed chronoamperograms performed at $1.23 \text{ V}_{\text{RHE}}$ for 300 s for $\text{TiO}_2/[\text{CoFe-PP}]$ electrodes (dark-colored lines) and the bare TiO_2 electrode (light-colored lines) under white-light illumination and with cut-off filters: 420, 435, and 490 nm, sequentially. (c) IPCE spectra for $\text{TiO}_2/[\text{CoFe-PP}]$ and bare TiO_2 NWs with a $1.23 \text{ V}_{\text{RHE}}$ external bias. The wavelength is scanned from 300 to 500 nm with a step of 10 nm. The inset shows a magnified image of IPCE in the 420–500 nm range. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

7.4.4. Long-term Stability Analysis

Besides the promising optical response of $\text{TiO}_2/[\text{CoFe-PP}]$, the photoanode exhibits outstanding stability during a 5-hours CA experiment, at a bias voltage of $1.23 \text{ V}_{\text{RHE}}$ (Figure 7.7a). To evaluate the stability of the photoelectrode, LSV is performed after CA and compared with the pristine profile, shown in Figure 7.7a inset, which shows almost the same photocurrent spectra. A similar experiment at $1.23 \text{ V}_{\text{RHE}}$ (at pH 7), with 420 nm cut-off filter, was performed with a gas-tight cell and the amount of photogenerated O_2 was recorded by GC, yielding a Faradaic efficiency of approximately 80% (as explained in Figure 7.7b), indicating that the photocurrent response is mainly originating from the water oxidation process. Moreover, XPS analysis performed on the post-catalytic $\text{TiO}_2/[\text{CoFe-PP}]$ electrode also confirms that $\text{TiO}_2/[\text{CoFe-PP}]$ retains its morphology (Figure 7.8). $\text{TiO}_2/[\text{Fe-PP}]$ electrode, however, degrades under the same conditions, which indicates the molecular Fe-PP complex decomposes under the same photoelectrochemical condition due to the loose coordination of monodentate PP group to the iron site. The evident enhancement in the stability of $\text{TiO}_2/[\text{CoFe-PP}]$ compared to $\text{TiO}_2/[\text{Fe-PP}]$,

thus, demonstrates that the rigidity of the PB bulk structure plays a critical role in the long-term stability of the iron photosensitizer. (Figure 7.9).

7.4.5. Oxygen Evolution Activity Measurements

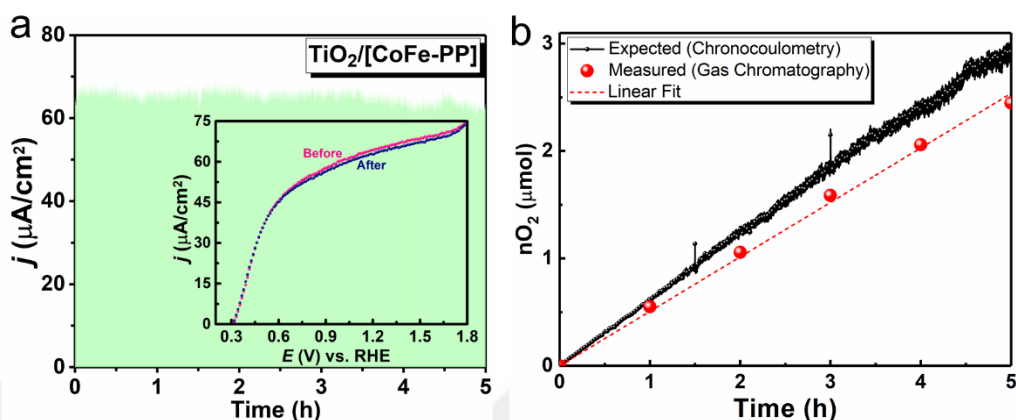


Figure 7.7 (a) Chronoamperogram profile of $\text{TiO}_2/[\text{CoFe-PP}]$ for 5-hours illumination at $1.23 \text{ V}_{\text{RHE}}$ bias with 420 nm filter. The inset shows LSV profiles before and after the long-term stability test. (b) Faradaic efficiency of $\text{TiO}_2/[\text{CoFe-PP}]$ measured by gas chromatography. Bulk electrolysis was performed at $1.23 \text{ V}_{\text{RHE}}$ in a gas-tight electrochemical cell. The total amount of oxygen produced was calculated as the sum of the oxygen in the headspace detected by gas chromatography and oxygen dissolved in the solvent, as determined from Henry's Law (red line). The theoretical amount is extracted from the total amount of charge passed during CA experiment (black line) yielding an 80% Faradaic efficiency. A buffer solution (pH 7) of 50 mL was used for experiments. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

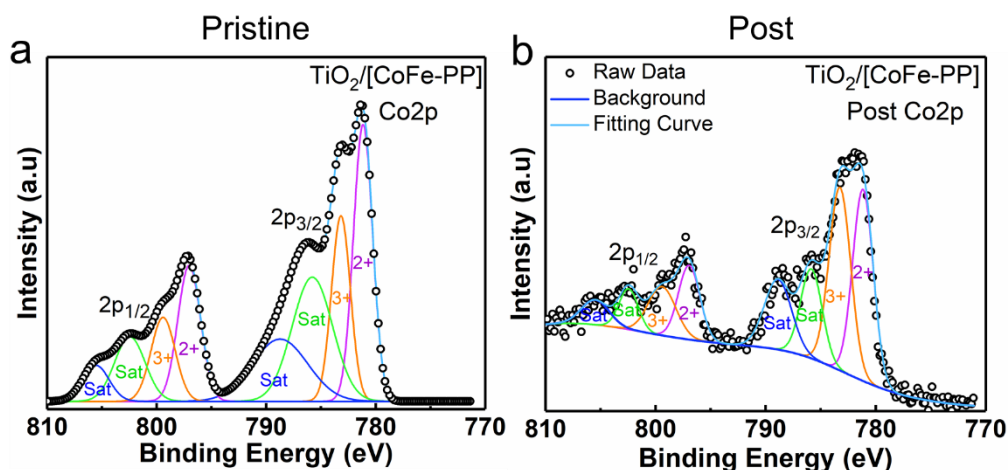


Figure 7.8 The oxidation states of Co by XPS spectra were also compared for (a) pristine and (b) post-catalytic (after long-term CA) for $\text{TiO}_2/[\text{CoFe-PP}]$ electrode. As expected, the post-catalytic sample has an enhancement in Co^{3+} signal indicating that cobalt sites are partially oxidized during the water oxidation process. The fully oxidized form of cobalt (Co_3O_4) was, however, not observed, which indicates that the CoFe PB

layer retains its structure under PEC conditions. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

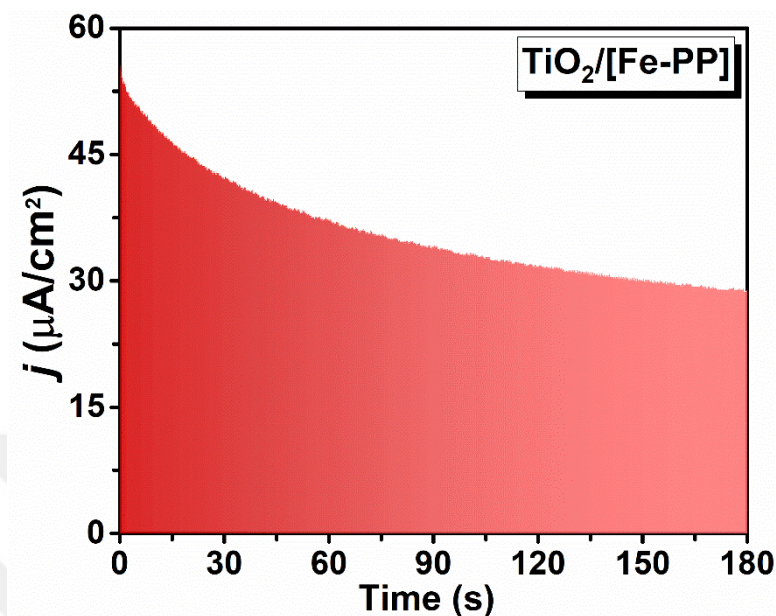


Figure 7.9 Chronoamperogram profile for $\text{TiO}_2/[\text{Fe-PP}]$ showing that it degrades fast in time. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

7.4.6. Steady-State Absorption Measurements

To gain an insight into the origin of the above promising results, the steady-state absorption measurements were conducted on solutions containing [PP], [Fe-PP] and [CoFe-PP] to understand the absorption behavior of the iron chromophore (Figure 7.10a-d). The molar extinction coefficient of [Fe-PP] is similar to those previously reported for potential iron chromophores.[260], [261]

The coordination of Co^{2+} ions shifts the MLCT band to shorter wavelengths (~ 430 nm) (Figure 7.11a). The weak band at ~ 615 nm is assigned to a MMCT transition ($\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II}} \rightarrow \text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III}}$) as it is depleted with the gradual addition of an oxidizing agent (1 M aqueous $\text{Na}_2\text{S}_2\text{O}_8$) to oxidize all of the metal ions to +3 oxidation states (Figure 7.11b).[74], [262]

The conservation of the MLCT band also confirms the stability of the iron chromophore under an oxidizing environment. Note that the MLCT absorption band and IPCE profile for [CoFe-PP] perfectly match.

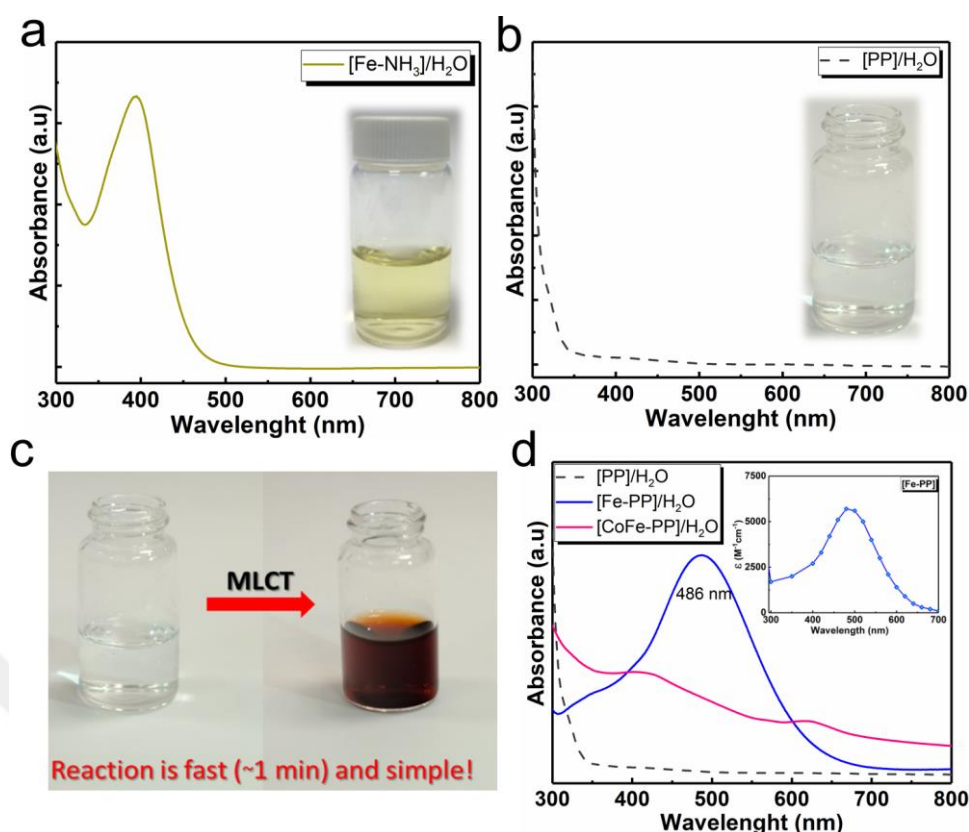


Figure 7.10 Absorption spectra of the (a) $[\text{Fe-NH}_3]$, and (b) $[\text{PP}]$ in aqueous solutions. (c) Photograph of the $[\text{PP}]$ ligand and $[\text{Fe-PP}]$ in aqueous solutions: the transformation of a basic ligand into a chromophore. (d) Absorption spectra of the $[\text{PP}]$, $[\text{Fe-PP}]$, and $[\text{CoFe-PP}]$ in aqueous solutions. (10^{-3} M in distilled water, 2 mm cuvette length) and the inset shows the molar absorption coefficient spectrum (300 nm - 700 nm) of $[\text{Fe-PP}]$ dye in water. According to the $[\text{Fe-PP}]$ dye solution spectrum, molar absorption coefficients are $5723 \text{ M}^{-1} \text{ cm}^{-1}$ determined at max absorption wavelength of 486 nm. For obtaining calibration curve of $[\text{Fe-PP}]$ dye, 5 different concentrations (0.8791, 3.08, 13.3, 31.4, 80 μM in 3.5 mL) are prepared in distilled water. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

To understand the absorption profiles of the molecular $[\text{Fe-PP}]$ complex and non-periodic bulk $[\text{CoFe-PP}]$ structure, different theoretical methods were employed. First-principles electronic structure calculations based on density functional theory with periodic boundary conditions (PBC-DFT) and hybrid functionals (HSE06) were chosen first, since this level of calculations can be applied both for molecular and periodic bulk systems (i.e. electronic levels and electronic band structure) and yield correct magnetic and electronic ground state.[146] The molecular configuration is reported as a prototype to better describe the MLCT mechanism and to enable comparisons with calculated excitation characteristics. In line with the experimental absorbance profile, PBC-DFT calculations performed on $[\text{PP}]$, $[\text{Fe-PP}]$, and $[\text{CoFe-PP}]$ suggest

that the HOMO-LUMO gap for [CoFe-PP] is larger compared to [Fe-PP] (Figure 7.11c,d). The nature of electronic states is also tuned with the coordination of Co^{2+} ions. The HOMO of [Fe-PP] is distributed over the Fe center as well as the PP ligand while that of [CoFe-PP] is fully localized on metal centers (both Co and Fe). Moreover, LUMO, LUMO+2, and LUMO+3 are dominantly located on the ligand center, which is an ideal molecular electronic level arrangement for an efficient MLCT process. The variation of the HOMO-LUMO gap (and/or electronic band gap) suggests that the structure of [CoFe-PP] fall within a molecular and an extended periodic configuration as expected. As correct magnetic state ordering can be obtained, the charge localization profile is not altered with the addition of on-site interaction energies (DFT+U) on transition metal centers.[146]

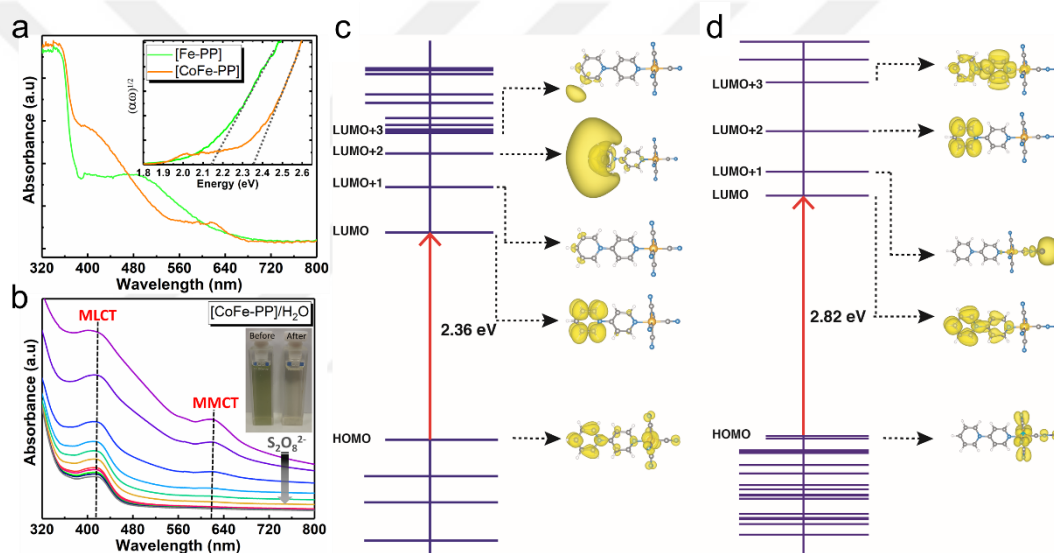


Figure 7.11 MLCT behavior of iron PS: (a) The absorption spectra for TiO_2 /[Fe-PP] and TiO_2 /[CoFe-PP] electrodes obtained by taking the bare TiO_2 electrode as reference. Inset shows the estimated optical band gaps of the same electrodes by extrapolating the line portion of the Tauc plot $(\alpha h\nu)^{1/2}$ (α is the absorption coefficient and ω is the angular frequency) vs. $h\nu$. (b) Changes observed in the UV-Vis spectrum of an aqueous solution of the [CoFe-PP] complex with the incremental addition of 1 M aqueous $\text{Na}_2\text{S}_2\text{O}_8$ solution. Inset: effectively depletion of the 2+ states visualized in the quartz cuvettes before and the final addition of $\text{Na}_2\text{S}_2\text{O}_8$. (c–d) The HOMO and LUMO levels with the electron clouds for [Fe-PP] and [CoFe-PP] are calculated with PBC-DFT using hybrid functionals in their lowest energy electronic states ($S=0$ for [Fe-PP] and $S=3/2$ for [CoFe-PP]). (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

7.4.7. Femtosecond Transient Absorption Measurements

Ultrafast transient absorption (TA) experiments were conducted to understand the excited state dynamics via charge transfer process at the femtosecond time scale. For both solution and photoanode designs, 400 nm pump excitation is utilized. The laser pulse energy is 1.5 μJ and to ensure the stability of the dyes, the absorption of the designs before and after experiment is measured. TA profiles of [Fe-PP] and [CoFe-PP] solutions provide clear evidence for the rapid population of the lowest excited state (Figure 7.12).

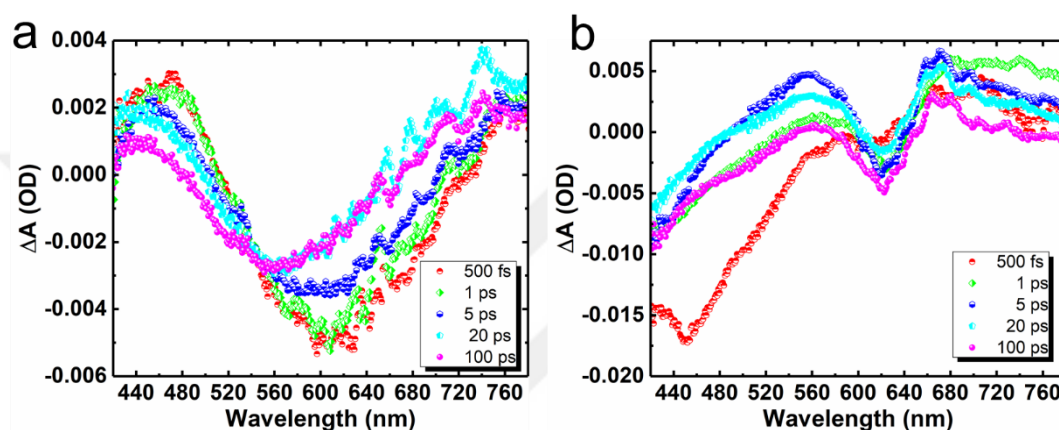


Figure 7.12 TA spectra of (a) [Fe-PP] and (b) [CoFe-PP] in EtOH solution with 500 nm (pump) excitation with different pump-probe time delays and a range of probe signals spanning from 420 nm to 780 nm. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

The TA spectra of [Fe-PP] in EtOH show two main features; a broadband GSB and a short-lived ESA signal, which indicate that the excited states are quenched into the lowest-lying state on the order of picoseconds. The short-lived ESA is, therefore, followed with a broadband GSB. However, the ultrafast carrier dynamics of the iron complex differ when it is coated on the semiconductor, TiO_2 . Upon excitation with a 500 nm pump wavelength, the TA spectra of TiO_2 /[Fe-PP] and TiO_2 /[CoFe-PP] are recorded for a broad probe range (430–780 nm) (Figure 7.13a,b). The absorption difference in various pump-probe delay times indicates a broadband ESA signal, which suggests that excited electrons are injected into TiO_2 CB with a high yield in an ultra-short time scale. The decay traces that are fitted into multiple exponential profiles reveal that TiO_2 /[Fe-PP] shows dual lifetimes of 105.7 ps (11%) and 108.2 fs (89%) at 600 nm probe wavelength (Figure 7.13c). The lifetimes recorded for TiO_2 /[CoFe-PP] are an order of magnitude longer with decay rates of 2.4 ns (3%), 7.8 ps (6%), and 71.7 fs (91%) (Figure 7.13d), which could be associated

with the donating ability of cobalt ions due to the well-known MMCT ability between cobalt and iron sites in a CoFe PBA.[74] Cobalt sites, thus, serve as secondary donor groups to enhance the MLCT ESA lifetime of the iron chromophore by feeding its ground state. The small portion (3%) of long-lived (2.4 ns) excited states also explains the relatively low photocurrent efficiency and weak IPCE.

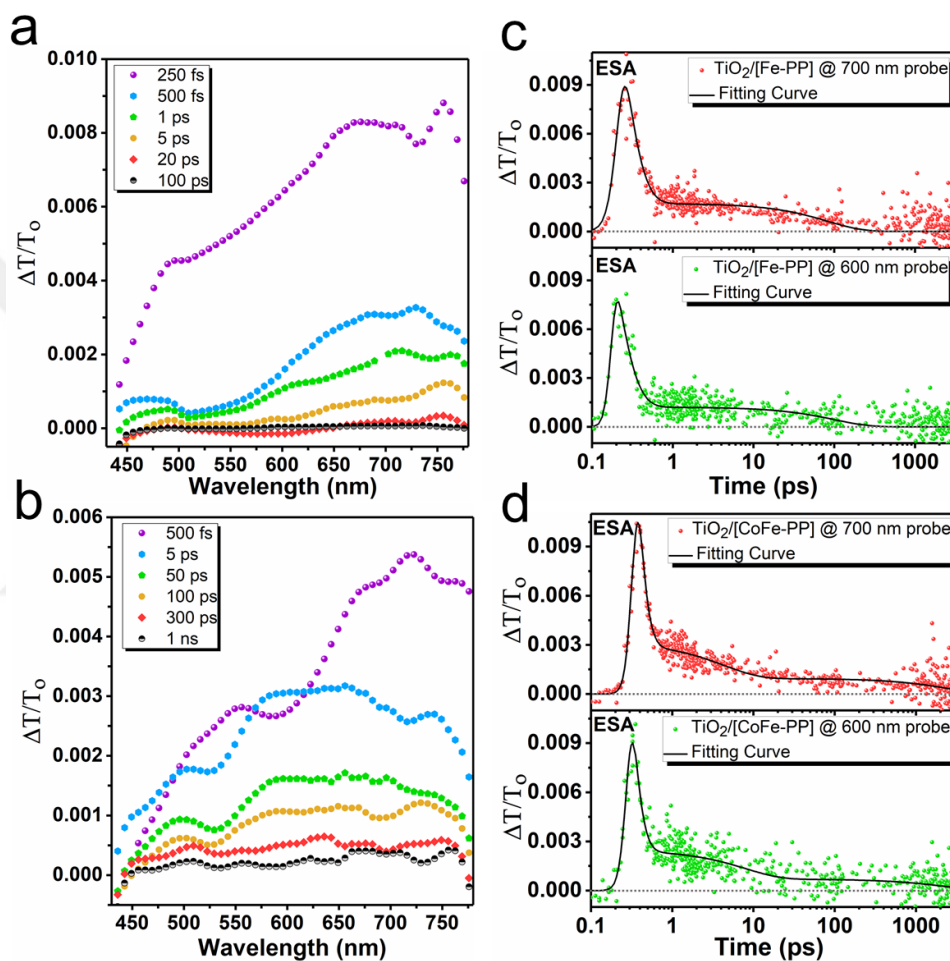


Figure 7.13 (a–b) Femtosecond TA dynamics of $\text{TiO}_2/[\text{Fe-PP}]$ and $\text{TiO}_2/[\text{CoFe-PP}]$ photoanodes at 500 nm (pump) excitation with different pump-probe time delays. (c–d) Decay dynamics for ESA signals $\text{TiO}_2/[\text{Fe-PP}]$ and $\text{TiO}_2/[\text{CoFe-PP}]$. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Nevertheless, the nanosecond scale ESA lifetime for the iron chromophore is a record feature compared to previously reported iron photosensitizers, which assisting iron chromophore with a secondary metal ion can be a viable strategy to enhance the lifetime of MLCT state.

7.4.8. Computational Calculations and Mechanism

The electronic structure calculations were further sought to investigate molecular orbitals. All the calculations were performed by Prof. Dede's research group. While PBC-DFT calculations were utilized to correlate HOMO-LUMO energy levels of both molecular and periodic model systems with experimental optical data and to investigate the origin of MLCT process, we herein performed quantum chemical calculations with DFT to elucidate the role of each component of the assembly on the charge transfer mechanism in the molecular level. Since the bulk structure could be considered as the non-periodic repetition of the bimetallic [CoFe-PP] molecular structure, organic [PP], monometallic [Fe-PP], and bimetallic [CoFe-PP] molecular structures were studied in this section. This level of calculations has previously been employed by our team to investigate the water oxidation mechanism and charge transfer in PB based systems.[113], [125], [126] The calculated molecular orbitals depicted in Figure 7.14a reveal that [PP] and [Fe-PP] are radically different in their excitation characteristics. The local excitation motif calculated for bare [PP] no longer survives in the case of [Fe-PP] and a clear MLCT excitation is observed. For [CoFe-PP], Co orbitals energetically lie between Fe-centered HOMO and PP-centered LUMO, which is appropriate for an efficient hole transfer from the iron to cobalt site.

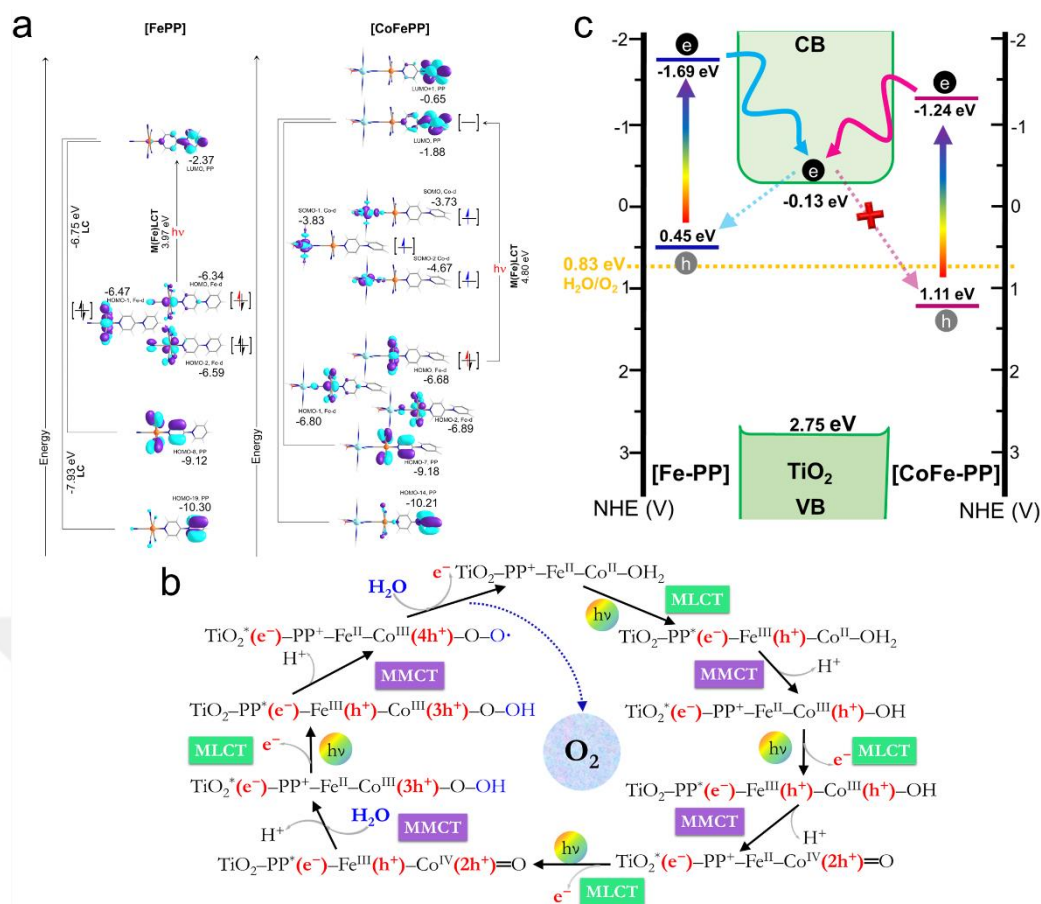


Figure 7.14 (a) Comparison of the excitation characteristics of [Fe-PP] and [CoFe-PP] in their lowest energy electronic states ($S=0$ for the former and $S=3/2$ for the latter). MO labels are included according to the location of the majority of the electron density. [Fe-PP] shows a clear MLCT transition. All SOMOs are localized on Co in [CoFe-PP]. (b) The proposed PCET mechanism of the PEC water oxidation for $\text{TiO}_2/[\text{CoFe-PP}]$: The $4e^-$ mechanism involves the oxidation and activation of the catalytic site by four PCET to yield a high-valent metal-oxo species.[113], [115] This active species is attacked by a nucleophilic water molecule to form a peroxo species, which is then released as an oxygen molecule. (c) Schematic energy band diagram and carrier dynamics for $\text{TiO}_2/[\text{Fe-PP}]$ and $\text{TiO}_2/[\text{CoFe-PP}]$ showing the band alignments between different interfaces and the involved water oxidation electron transfer process. (Reprinted with permission from Wiley Ref. [138]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Consequently, the overall process is initiated with a $\text{Fe} \rightarrow \text{PP}$ MLCT process followed by a fast electron transfer from the LUMO of PP to the CB of TiO_2 (Note that the LUMO designation refers to the electronic structure before the electron transfer). This MLCT process is followed by a hole transfer from the HOMO of Fe to a SOMO on Co (MMCT). The proposed mechanism for the photoelectrochemical water oxidation mechanism in Figure 7.14b indicates that MMCT and MLCT transitions play active roles in the charge separation process.

The electronic structure calculations, as well as experimental studies, suggest the presence of partial localization of distinct valences in [CoFe-PP], which is utilized for enhancing the ESA lifetime of the iron chromophore and, therefore, the charge separation process during the water oxidation process. The MMCT process is efficient thanks to the short bridging cyanide group promoting the cobalt sites to both a donor group that enhances the ESA lifetimes of the iron chromophore and a WOC that is activated once the holes are received from iron sites. We have reported a similar role for cobalt sites in previous works where Co is participating in the catalytic cycle after the electron transfer to TiO₂ takes place.[126] In this work, we show that cobalt sites can also be utilized to build an iron-sensitized water oxidation photoanode. Furthermore, the band alignment of the heterostructure, which is constructed with a combination of optical and PEC measurements, clearly shows the effect of electron-donating cobalt sites to the energy levels of [Fe-PP]. The improper large energy difference between LUMO of [Fe-PP] and the CB of TiO₂, see Figure 7.14c, which can lead to back-reaction and carrier's recombination,[232] is renovated with the coordination of Co ions to [Fe-PP]. In [CoFe-PP], proper alignment is achieved between the VB of TiO₂, the HOMO level of [CoFe-PP], and the water oxidation energy level. A larger energetic barrier is also created between TiO₂ CB and the HOMO of [CoFe-PP], which hampers the recombination pathways. Moreover, a more favorable band level promotes the participation of more photogenerated holes in the water oxidation process. Catalytic cobalt sites, therefore, transform the energetic levels of the iron chromophore in the desired fashion for enhanced charge separation and water oxidation activity.

7.5. Summary

In this work, we show that a donor-acceptor iron photosensitizer can be achieved by slightly tuning the regular PB synthesis through utilizing a pyridinium ligand coordinated pentacyanoferrate complex as the starting precursor. The straightforward synthetic methodology also allows the formation of a non-periodic bulk structure, which exhibits an efficient MLCT and MMCT process on the iron site. The working principle and the performance of the photoanode were elucidated with computational models (DFT, PBC-DFT, and TD-DFT), transient absorption, spectroscopic, and photoelectrochemical measurements. The MMCT process - a critical process in the water oxidation mechanism - reveals the active role of cobalt sites as donating groups in addition to their role as the WOC unit. Cyanide ligand, on the other hand, serves

as i) a short bridging group to facilitate the MMCT process, ii) a strong field ligand to deactivate the undesired MC* states, and iii) a strong electron-donating group to increase the donor ability of iron site toward the acceptor pyridinium group. Moreover, an electron-deficient cationic pyridinium ligand is preferred over the commonly employed bipyridyl groups to enhance the MLCT process.

PEC studies disclose the remarkable stability of the photoelectrode even during a 5-hours CA study. Moreover, iron chromophore extends the absorption capacity of the bare electrode up to approx. 500 nm, which is in good accordance with the absorption profile of [CoFe-PP]. ESA lifetime is prolonged from approx. 200 ps for TiO₂/[Fe-PP] to above 1 ns for TiO₂/[CoFe-PP], mainly due to the donating ability of cobalt sites toward iron centers, which is also described based on quantum chemical calculations.

This proof-of-concept study marks the first demonstration of an iron-sensitized water oxidation photoanode. Since the simple synthetic pathway allows for the easy tuning of components of the photoanode, including the semiconductor and the acceptor group, further studies will be conducted to expand the portfolio of iron sensitized water oxidation photoanodes for a better understanding of this new generation of dye-sensitized photoelectrodes.

Chapter 8. Conclusions

8.1. Summary and Outlook

Molecular and bulk synthetic approaches, both of which have critical drawbacks, have been adopted to develop dye-sensitized photoanodes. Throughout this thesis, we have proposed a cyanide-based synthetic pathway to take advantage of the strengths of both the molecular approach and the bulk one.[125] In this pathway, the molecular units are connected in a step-by-step fashion similar to the molecular approach, which forms a bulk assembly in the final step. The method enables easy control of the structure of the final product similar to the molecular-based approach. The synthetic protocol is much simpler than that of molecular ruthenium ones since the bridging group between the PS and WOC is a simple cyanide group, which can bind to water oxidation catalytic cobalt sites easily in a one-step reaction. The final bulk assembly exhibits superior stability and a rigid framework under PEC conditions. The PS and WOC units are connected through a $\text{Fe}(\text{CN})_5$ unit, which can easily coordinate to pyridyl containing organic molecules and polymers. A systematic study is performed to achieve this goal: First, a pyridyl containing porphyrin derivative, [TpyP] is incorporated into a CoFe PB structure, as explained in detail in chapter 4.[125] In this work, it was found that the iron site serves as an electron shuttle/relay between the PS and WOC units based on transient absorption and computational studies.

Second, the realization of this versatile pathway prompted us to prepare PB based dye-sensitized photoanodes as explained in chapter 5. As a proof of concept, a phenazine-based chromophore, JG, was implemented to a PB structure and then coupled to TiO_2 nanowires to develop the first entirely earth-abundant dye-sensitized photoanode ($[\text{CoFe-JG}]/\text{TiO}_2$).[126] In contrary to bare [JG], which decomposes quickly under photocatalytic conditions, JG in $[\text{CoFe-JG}]/\text{TiO}_2$ retains its structural integrity. Moreover, a photocurrent density of around $60 \mu\text{A}/\text{cm}^2$ was achieved at $1.23 V_{\text{RHE}}$ for 2-hours under white light coupled to a 420 nm filter. Although this was the first demonstration of a PB based water oxidation PEC cell while its performance is poor.

This result encouraged us to set our next target, which was development of a high performance PB based dye-sensitized photoanode. The third study was performed according to this motivation. Here, another phenazine incorporating

derivative, SF, was used as the organic PS. Moreover, to fully utilize the solar spectrum, a visible-light absorbing semiconductor, WO_3 , with proper band positions was chosen. $[\text{CoFe-SF}]/\text{WO}_3$ exhibits a record photocurrent density of 1.3 mA/cm^2 at just $1.23 \text{ V}_{\text{RHE}}$, which demonstrates that proper modification of components in PB based dye-sensitized photoanodes paves the way for the development of scalable and high-performance water splitting cells. The details have been provided in chapter 6.

An interesting feature that we observed in all the above-mentioned studies was the function of the metal site, particularly the iron site in the cyanometalate group. As explained in these three chapters, the cyanometalate group site was used merely as a bridging group (linker). Despite the easily accessible $\text{Fe}^{2+/3+}$ redox process in PBAs, the electronic effect of the iron site was overlooked, and the main attention was directed to the cobalt site. Nevertheless, both EC and PC studies, which indicate that CoCo PBAs exhibit relatively higher activities than CoFe PBAs, clearly point out the electronic effect of the cyanometalate group on the catalytic activity of the cobalt sites. The effect of the iron site is also evident when chromophore is directly coordinated to CoFe PBA structures. An organic PS could be implemented to the PB structure using an unconjugated bridging platform as in the case of CoFe-PVP-RuPS.[124] When it is connected directly to the iron site, as in the $[\text{CoFe-TPyP}]$ system, the ground states of the pentacyanoiron(II) and porphyrin groups, which are close in energy, are mixed to form a HOMO comprising Fe-d and porphyrin-p orbitals.[125] We observed a similar behavior when a phenazine-based chromophore, JG or SF, is connected to the iron site to build a water oxidation photoanode for water oxidation.[126] The electron transfer utilized in these systems constitutes a combination of ligand-to-ligand charge transfer (LLCT), the common feature observed in organic chromophores, and a MLCT), which is a characteristic feature for a metal PS. Thus, in these three works, the main function of Fe was to build up PBA WOC on PS unit. However, in an ideal platform, to maximize PS and WOC sites interaction, we need to turn Fe site into a photoactive center.

The fourth study was designed towards this goal. In this study, we utilized a transparent organic ligand to rule out the LLCT in the charge transfer process. When a pale yellow solution of $[\text{Fe}(\text{CN})_5(\text{NH}_3)]^{3-}$ is mixed with a colorless 4-

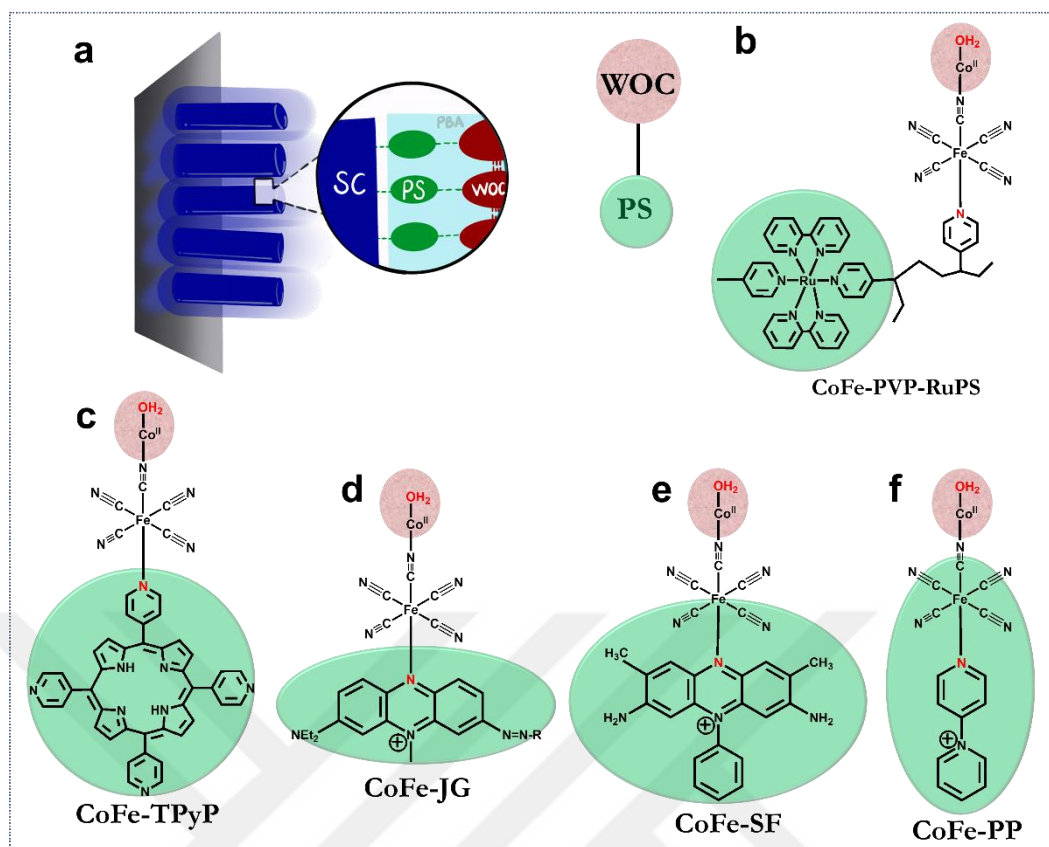


Figure 8.1 (a) The illustration of a PB based dye-sensitized water oxidation photoanode, in which a PB layer incorporating a PS-WOC assembly is coated over a SC. PB based PS-WOC assemblies: (b) PVP: poly 4-vinylpyridine, RuPS: Ruthenium photosensitizer, (c) TPyP: Tetrapyrroldiporphyrin, (d) JG: Janus green B, (e) SF: Safranin O, (f) PP: 4-(pyridyl)pyridinium cation. (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

(pyridyl)pyridinium solution (PP^+), the solution turns into an intense dark red color thereby indicating the formation of a push-pull iron chromophore, $[Fe-PP]$. The donating ability of $Fe(II)$ ion surrounded with a five electron-donating cyanide group and the electron ability of a cationic organic ligand form a donor-acceptor type iron chromophore.[263]–[267] The cyanide ligand plays an essential role in this assembly since the strong-field cyanide ligand increases the octahedral splitting and pushes the undesired MC orbitals to higher energy levels to avoid possible deactivation pathways that can compete with the MLCT transition.[256], [268]–[270] Upon coordination of the iron complex to cobalt ions, the deactivation of MC pathways enhances the excited state lifetime of the iron chromophore above an order of magnitude compared to the uncoordinated complex.[138] Furthermore, the short cyanide group mediates the electron transfer from the cobalt site to the iron site and then to the organic ligand. $TiO_2/[CoFe-PP]$, which marks the first example of an iron chromophore

utilized water oxidation photoanode, reveals that the iron site can also be promoted to a chromophore. Figure 8.1 schematically displays the chromophores implemented to PB structures up to now.

8.2. Key Challenges and Recommendations

Despite all the studies explained throughout this dissertation, there are still challenges yet to be addressed thoroughly, such as the efficiency and the cost. Although PB systems consist of non-precious elements, cobalt is one of the least abundant elements among 3d transition metals. The concentration of cobalt atoms in the structure could be diluted by the partial substitution of cobalt sites with relatively low-cost metal ions such as iron and copper to address this issue. The investigation of non-cobalt PBA coupled with proper SCs could also be an exciting venue to elucidate the effect of band energy alignment in semiconductor/catalyst photoelectrodes. Proper SCs could be investigated within this context to improve the performance of PB based photoanodes. Moreover, the counter cation in the Prussian blue structure could be tuned to enhance the surface concentration and increase the TOF of catalytic cobalt sites (synergistic effect). These strategies could be combined to develop efficient PB based photoanodes.

It should also be noted that the catalytic activity of PBAs is highly dependent on the synthetic approach, chemical composition, and crystallinity. Electrical conductivity decreases as the thickness of the PBA layer increases, thereby resulting in high overpotentials and low catalytic efficiency. Therefore, the optimum synthetic conditions for the ideal thickness and morphology of PBAs should be explored systematically using the strategies discussed throughout this review.

It is then clear that a lot is still awaiting to be discovered. Further research in these areas will accelerate the development of robust and efficient chromophores-catalyst assemblies (dyads, triads, etc.). Opportunities can come with challenges, but recent advances in the field indicate that PBAs hold the potential to play a significant role in developing scalable and efficient water splitting cells. In the end, to provide a clear picture of the current status of PB based PEC-WS designs, a schematic has been drawn, as shown in Figure 8.2.

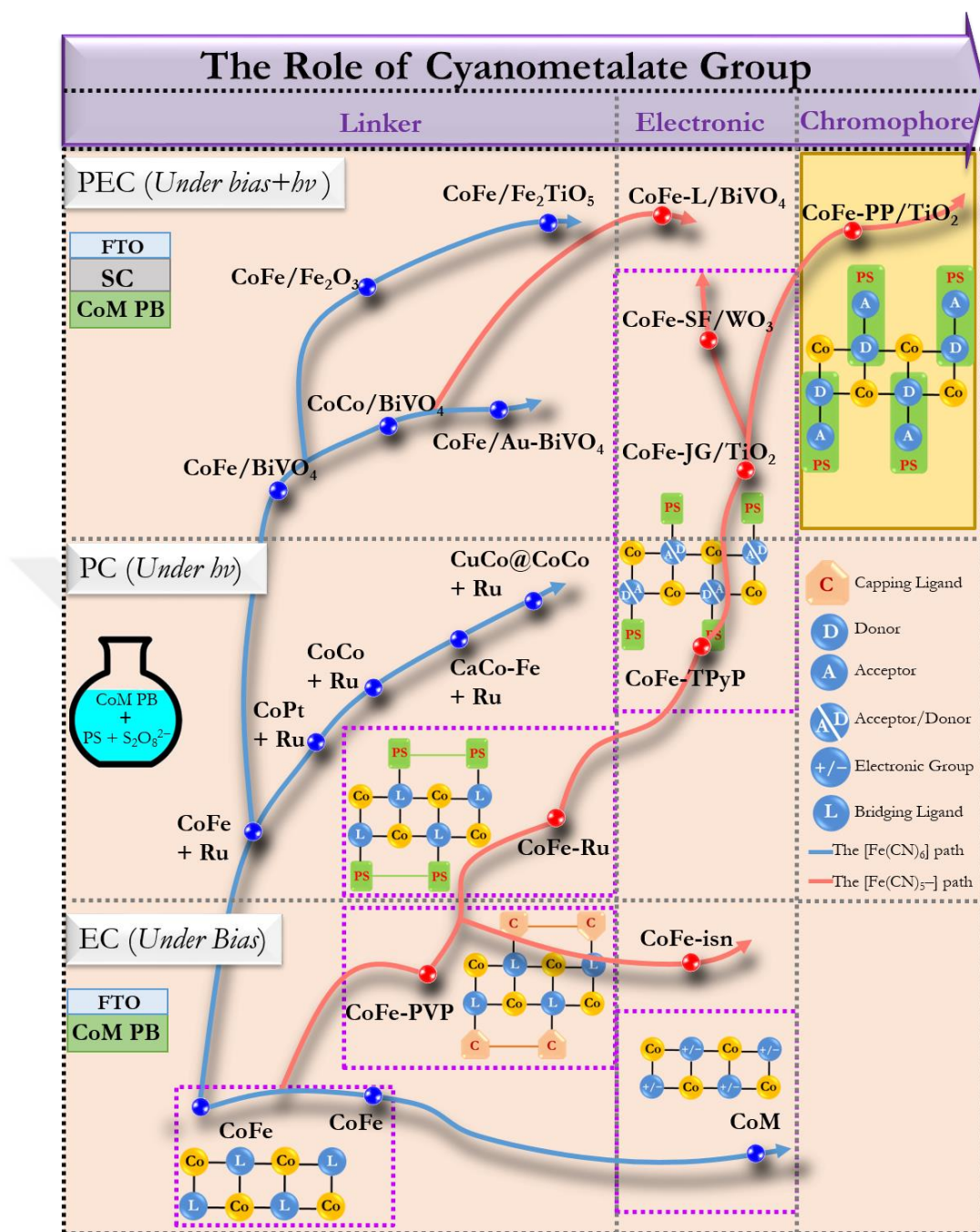


Figure 8.2 Road map for PB based water oxidation systems that shows the role of cyanometalate group in various water oxidation processes including EC, PC, and PEC. Studies highlighted here are as follows; CoFe,[92][99] CoM,[99] CoFe+Ru,[111] CoPt+Ru,[121] CoCo+Ru,[122] CaCo-Fe+Ru,[123] CuCo@CoCo+Ru,[105] CoFe/BiVO₄,[129] CoCo/BiVO₄,[130] CoFe/AuNPs/BiVO₄,[134] CoFe-L/BiVO₄,[133] CoFe/Fe₂O₃,[127] CoFe/Fe₂TiO₅,[128] CoFe-PVP,[112] CoFe-isn,[115] CoFe-Ru,[124] CoFe-TPyP,[125] CoFe-JG/TiO₂,[126] CoFe-SF/WO₃,[223] CoFe-PP/TiO₂,[138] (Reprinted with permission from Wiley Ref. [2]. Copyright © 2021 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

8.3. Contributions

Included in this Thesis

[29] T. G. Ulusoy Ghobadi, A. Ghobadi, M. Demirtas, M. Buyuktemiz, K. Nur Ozvural, E. Akhuseyin Yildiz, E. Erdem, H. G. Yaglioglu, E. Durgun, Y. Dede, E. Ozbay, F. Karadas, “*Building an Iron Chromophore Incorporating Prussian Blue Analogue for Photoelectrochemical Water Oxidation*”, **Chem. Eur. J.**, 2021, 27, 1 – 12. (Front Cover)

[28] T. G. Ulusoy Ghobadi, E. Ozbay, F. Karadas, “*Mini Review: How to Build Prussian Blue-Based Water Oxidation Catalytic Assemblies? Common Trends and Strategies*”, **Chem. Eur. J.**, 2021, 27, 3638 – 3649. (Frontispiece)

[27] T. G. Ulusoy Ghobadi, A. Ghobadi, E. Ozbay, F. Karadas, “*Review: Strategies for Plasmonic Hot-Electron Driven Photoelectrochemical Water Splitting*”, **ChemPhotoChem**, 2018, 2, 161 – 182. (Frontispiece)

[26] T. G. Ulusoy Ghobadi, A. Ghobadi, M. Buyuktemiz, E. Akhuseyin Yildiz, D. B. Yildiz, H. G. Yaglioglu, Y. Dede, E. Ozbay, F. Karadas, “*A Robust, Precious-Metal-Free Dye-Sensitized Photoanode for Water Oxidation: A Nanosecond-Long Excited-State Lifetime through a Prussian Blue Analogue*”, **Angew. Chem. Int. Ed.**, 2020, 59, 4082 – 4090. (Inside Back Cover)

[25] T.G. Ulusoy Ghobadi, E. Akhuseyin Yildiz, M. Buyuktemiz, S. Sadigh Akbari, D. Topkaya, Ü. İsci, Y. Dede, H. G. Yaglioglu, F. Karadas, “*A Noble-Metal-Free Heterogeneous Photosensitizer-Relay-Catalyst Triad Catalyzes Water Oxidation under Visible Light*”, **Angew. Chemie Int. Ed.**, 2018, 57, 17173 – 17177.

[24] T. G. Ulusoy Ghobadi, A. Ghobadi, M. Demirtas, R. Phul, E. Akhuseyin Yildiz, H. G. Yaglioglu, E. Durgun, E. Ozbay, F. Karadas, “*Pushing the limits in photosensitizer-catalyst interaction via a short cyanide bridge for water oxidation*”, **Cell Rep. Phy. Sci.**, 2021, 2, 100319.

Additional publications

[23] T. G. Ulusoy Ghobadi, S. Sadigh Akbari, E. Ozbay, F. Karadas, “*Photocatalytic water oxidation with a Prussian blue modified brown TiO₂*”, G. Gundogdu, **Chem. Commun.**, 2021, 57, 508-511.

- [22] T. G. Ulusoy Ghobadi, A. Ghobadi, F. Karadas, E. Ozbay, "Large scale compatible fabrication of gold capped titanium dioxide nanoantennas using a shadowing effect for photoelectrochemical water splitting", **Int. J. Hydrog. Energy**, 2020, 45, 1521-1531.
- [21] A. Ghobadi, T. G. Ulusoy Ghobadi, F. Karadas, E. Ozbay, "Highly Efficient Semiconductor-Based Metasurface for Photoelectrochemical Water Splitting: Broadband Light Perfect Absorption with Dimensions Smaller than the Diffusion Length", **Plasmonics**, 2020, 15, 829-839.
- [20] M. Ekin Gulseren, G. Kurt, T. G. Ulusoy Ghobadi, A. Ghobadi, G. Salkim, M. Ozturk, B. Butun, E. Ozbay, "Investigation of angstrom-thick aluminium oxide passivation layers to improve the gate lag performance of GaN HEMTs", **Mater. Res. Express**, 2019, 158, 22-27.
- [19] A. Ghobadi, T. G. Ulusoy Ghobadi, F. Karadas, E. Ozbay, "Review: Semiconductor Thin Film Based Metasurfaces and Metamaterials for Photovoltaic and Photoelectrochemical Water Splitting Applications", **Adv. Optical Mater.**, 2019, 1900028, 1-39.
- [18] G. Kurt, M.E. Gulseren, T.G. Ulusoy Ghobadi, S. Ural, O. A. Kayal, M. Ozturk, B. Butun, "Normally-Off AlGaIn/GaN MIS-HEMT with Low Gate Leakage Current Using a Hydrofluoric Acid Pre-Treatment", **Solid State Electron.**, 2019, 158, 22-27.
- [17] T. G. Ulusoy Ghobadi, A. Ghobadi, M. C. Soydan, M. B. Vishlaghi, S. Kaya, F. Karadas, E. Ozbay, "Strong Light–Matter Interactions in Au Plasmonic Nanoantennas Coupled with Prussian Blue Catalyst on BiVO₄ for Photoelectrochemical Water Splitting", **ChemSusChem**, 2020, 1 – 13, 2577–2588. (Front Cover)
- [16] A. Ghobadi, T. G. Ulusoy Ghobadi, E. Ozbay, F. Karadas, "Angstrom Thick ZnO Passivation Layer to Improve the Photoelectrochemical Water Splitting Performance of a TiO₂ Nanowire Photoanode", **Sci. Rep.**, 2018, 8, 16322.
- [15] A. Ghobadi, T. G. Ulusoy Ghobadi, Ali K. Okay, E. Ozbay, "Emerging Photoluminescence from Defective Vanadium Diselenide Nanosheets", **Photonics Res.**, 2018, 6, 244-253.
- [14] T. G. Ulusoy Ghobadi, B. Patil, F. Karadas, Ali K. Okay, E. Yilmaz, "Catalytic Properties of Vanadium Diselenide: A Comprehensive Study on Electrocatalytic Performance in Alkaline, Neutral and Acidic Media", **ACS Omega**, 2017, 2 (11), 8319-8329.

- [13] E. Yagmur, I. Gurten, I. Y. Gokce, T. G. Ulusoy Ghobadi, T. Aktar, Z. Aktas, "Examination of gas and solid products during the preparation of activated carbon using phosphoric acid", **J. Environ. Manage.**, 2018, 228, 328–335329.
- [12] M. Kunduraci, T. G. Ulusoy Ghobadi, E. Yilmaz, "Impact of Li₂O/Metal Mole Ratio on Lithium-ion Battery Anode Performance", **Int. J. Electrochem. Sci.**, 2018, 13, 5630-5644.
- [11] T. G. Ulusoy Ghobadi, M. Kunduraci, E. Yilmaz, "Improved lithium-ion battery anode performance via multiple element approach", **J. Alloys Compd.**, 2018, 730, 96-109.
- [10] N. El-Atab, T. G. Ulusoy Ghobadi, A. Ghobadi, J. Suh, Raisul Islam, A. K. Okyay, K. C Saraswat, Ammar Nayfeh, "Cubic-phase zirconia nano-islands growth using atomic layer deposition and application in low-power charge-trapping nonvolatile-memory devices" **Nanotechnology**, 2017, 28 (44), 445201.
- [9] H. R Rasouli, A. Ghobadi, T. G. Ulusoy Ghobadi, H. Ates, K. Topalli, A. K Okyay, "Nanosecond pulsed laser ablated sub-10nm Silicon Nanoparticles for improving photovoltaic conversion efficiency of commercial solar cells", **J. Opt.**, 2017, 19 (10), 105902.
- [8] E. Chubenko, V. Bondarenko, A. Ghobadi, T. G. Ulusoy, K. Topalli, A. K. Okyay, "Seed Layer Assisted Hydrothermal Deposition of Low-resistivity ZnO Thin Films", **MRS Advances**, 2017, 2 (14), 799-804.
- [7] T. G. Ulusoy Ghobadi, A. Ghobadi, T. Okyay, K. Topalli and A. K. Okyay, "Controlling luminescent silicon nanoparticle emission produced by nanosecond pulsed laser ablation: role of interface defect states and crystallinity phase", **RSC Adv.**, 2016, 6, 112520-112526.
- [6] N. El-Atab, F. Chowdhury, T. G. Ulusoy, A. Ghobadi, A. Nazirzadeh, A. K Okyay, A. Nayfeh, "~3-nm ZnO Nanoislands Deposition and Application in Charge Trapping Memory Grown by Single ALD Step", **Sci. Rep.**, 2016, 6, 38712.
- [5] T. G. Ulusoy, Amir Ghobadi, Ruslan Garifullin, Mustafa O Guler, Ali K Okyay, "A Heterojunction Design of Single Layer Hole Tunneling ZnO Passivation Wrapping around TiO₂ Nanowires for Superior Photocatalytic Performance", **Sci. Rep.**, 2016, 6, 30587.

[4] R. Garifullin, H. Eren, T. G. Ulusoy, Okyay, A. K., Biyikli, N. and Guler, M. O. “Self-assembled peptide nanofiber templated ALD growth of TiO₂ and ZnO semiconductor nanonetworks”, **Phys. Status Solidi A.**, 2016, 1-7.

[3] T. G. Ulusoy, B. Daglar, A. Yildirim, A. Ghobadi, M. Bayindir, and Ali K. Okyay, “Enhanced performance of dye-sensitized solar cells by omnidirectional antireflective coatings”, **J. of Photonics Energy**, 2015, 5, 053090.

[2] Amir Ghobadi, Halil I. Yavuz, T. G. Ulusoy, K. Cagatay Icli, Macit Ozenbas, Ali K. Okyay, “Enhanced Performance of Nanowire-Based All-TiO₂ Solar Cells using Subnanometer-Thick Atomic Layer Deposited ZnO Embedded Layer”, **Electrochim. acta**, 2015, 157, 23–30.

[1] T. G. Ulusoy, A. Ghobadi and A. K. Okyay, “Surface Engineered Angstrom Thick ZnO-sheathed TiO₂ Nanowires as Photoanode for Performance Enhanced Dye-sensitized Solar Cells”, **J. Mat. Chem. A**, 2014, 2, 16795–17188. (front inside cover).

Chapter 9. BIBLIOGRAPHY

- [1] T. G. Ulusoy Ghobadi, A. Ghobadi, E. Ozbay, and F. Karadas, "Strategies for Plasmonic Hot-Electron-Driven Photoelectrochemical Water Splitting," *ChemPhotoChem*, vol. 2, no. 3, pp. 161–182, 2018.
- [2] T. G. Ulusoy Ghobadi, E. Ozbay, and F. Karadas, "How to Build Prussian Blue Based Water Oxidation Catalytic Assemblies: Common Trends and Strategies," *Chem. - A Eur. J.*, vol. 27, no. 11, pp. 3638–3649, 2021.
- [3] C. N. R. Rao and S. R. Lingampalli, "Generation of Hydrogen by Visible Light-Induced Water Splitting with the Use of Semiconductors and Dyes," *Small*, vol. 12, no. 1, pp. 16–23, 2016.
- [4] L. Meda and L. Abbondanza, "Materials for Photo-Electrochemical Water Splitting," *Rev. Adv. Sci. Eng.*, vol. 2, pp. 200–207, 2013.
- [5] M. G. Kibria and Z. Mi, "Artificial photosynthesis using metal/nonmetal-nitride semiconductors: current status, prospects, and challenges," *J. Mater. Chem. A*, vol. 4, pp. 2801–2820, 2016.
- [6] R. Li, "Latest progress in hydrogen production from solar water splitting via photocatalysis, photoelectrochemical, and photovoltaic-photoelectrochemical solutions," *Chinese J. Catal.*, vol. 38, no. 1, pp. 5–12, 2017.
- [7] L. Hammarström, "Artificial photosynthesis: closing remarks," *Faraday Discuss.*, vol. 198, pp. 549–560, 2017.
- [8] J. Cen, Q. Wu, M. Liu, and A. Orlov, "Developing New Understanding of Photoelectrochemical Water Splitting via in-situ Techniques: A Review on Recent Progress," *Green Energy Environ.*, vol. 2, no. 2, pp. 100–111, 2017.
- [9] C. Xiang *et al.*, "Modeling, Simulation, and Implementation of Solar-Driven Water-Splitting Devices," *Angew. Chemie - Int. Ed.*, vol. 55, no. 42, pp. 12974–12988, 2016.
- [10] R. Sathre *et al.*, "Opportunities to improve the net energy performance of photoelectrochemical water-splitting technology," *Energy Environ. Sci.*, vol. 9, pp. 803–819, 2016.
- [11] D. Bae, B. Seger, P. C. K. Vesborg, O. Hansen, and I. Chorkendorff, "Strategies for stable water splitting via protected photoelectrodes," *Chem. Soc. Rev.*, vol. 46, no. 7, pp. 1933–1954, 2017.
- [12] C. Jiang, S. J. A. Moniz, A. Wang, T. Zhang, and J. Tang, "Photoelectrochemical devices for solar water splitting- materials and challenges," *Chem. Soc. Rev.*, vol. 46, pp. 4645–4660, 2017.
- [13] Y. Yang, S. Niu, D. Han, T. Liu, G. Wang, and Y. Li, "Progress in Developing Metal Oxide Nanomaterials for Photoelectrochemical Water Splitting," *Adv. Energy Mater.*, vol. 1700555, p. 26, 2017.
- [14] S. Bai, W. Yin, L. Wang, Z. Li, and Y. Xiong, "Surface and interface design in cocatalysts for photocatalytic water splitting and CO₂ reduction," *RSC Adv.*, vol. 6, no. 62, pp. 57446–57463, 2016.

- [15] J. Su and L. Vayssieres, "A Place in the Sun for Artificial Photosynthesis?," *ACS Energy Lett.*, vol. 1, pp. 121–135, 2016.
- [16] M. Crespo Quesada and E. Reisner, "Emerging Approaches to Stabilise Photocorroding Electrodes and Catalysts for Solar Fuel Applications," *Energy Environ. Sci.*, vol. 10, pp. 1116–1127, 2017.
- [17] W. T. Qiu, Y. C. Huang, Z. L. Wang, S. Xiao, H. B. Ji, and Y. X. Tong, "Effective strategies towards high-performance photoanodes for photoelectrochemical water splitting," *Acta Phys. - Chim. Sin.*, vol. 33, no. 1, pp. 80–102, 2017.
- [18] F. Nandjou and S. Haussener, "Degradation in photoelectrochemical devices: review with an illustrative case study," *J. Phys. D. Appl. Phys.*, vol. 50, no. 12, p. 124002, 2017.
- [19] Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode.," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [20] M. Barroso, C. a Mesa, S. R. Pendlebury, A. J. Cowan, T. Hisatomi, and K. Sivula, "Dynamics of photogenerated holes in surface modified α -Fe₂O₃ photoanodes for solar water splitting," *Pnas*, vol. 109, no. 39, pp. 15640–15645, 2012.
- [21] C. Xiaobo, S. Shaohua, G. Liejin, and M. Samuel S, "Semiconductor-based photocatalytic hydrogen generation.," *Chem. Rev.*, vol. 110, no. 11, pp. 6503–70, 2010.
- [22] X. Li, J. Yu, J. Low, Y. Fang, J. Xiao, and X. Chen, "Engineering heterogeneous semiconductors for solar water splitting," *J. Mater. Chem. A*, vol. 3, pp. 2485–2534, 2015.
- [23] K. J. Young *et al.*, "Light-driven water oxidation for solar fuels," *Coord. Chem. Rev.*, vol. 256, no. 21–22, pp. 2503–2520, 2012.
- [24] S. Bai, L. Wang, Z. Li, and Y. Xiong, "Facet-Engineered Surface and Interface Design of Photocatalytic Materials," *Adv. Sci.*, vol. 4, p. 26, 2017.
- [25] A. G. Tamirat, J. Rick, A. A. Dubale, W.-N. Su, and B.-J. Hwang, "Using hematite for photoelectrochemical water splitting: a review of current progress and challenges," *Nanoscale Horiz.*, vol. 1, no. 4, pp. 243–267, 2016.
- [26] M. D. Bhatt and J. S. Lee, "Recent theoretical progress in the development of photoanode materials for solar water splitting photoelectrochemical cells," *J. Mater. Chem. A*, vol. 3, no. 20, pp. 10632–10659, 2015.
- [27] T. Singh, T. Lehnert, T. Leuning, and S. Mathur, "Atomic layer deposition grown MOx thin films for solar water splitting: Prospects and challenges," *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 33, no. 1, p. 010801, 2015.
- [28] L. J. Minggu, W. R. Wan Daud, and M. B. Kassim, "An overview of photocells and photoreactors for photoelectrochemical water splitting," *Int. J. Hydrogen Energy*, vol. 35, no. 11, pp. 5233–5244, 2010.
- [29] X. Li, X. Hao, A. Abudula, and G. Guan, "Nanostructured catalysts for electrochemical water splitting: Current state and prospects," *J. Mater. Chem. A*, vol. 4, no. 31, pp. 11973–12000, 2016.
- [30] E. Verlage *et al.*, "A monolithically integrated, intrinsically safe, 10% efficient, solar-driven water-splitting system based on active, stable earth-abundant electrocatalysts in conjunction with tandem III–V light absorbers protected by amorphous TiO₂ films," *Energy Environ. Sci.*, vol. 8, no. 11, pp. 3166–3172, 2015.
- [31] J. L. Young, M. A. Steiner, H. Döschner, R. M. France, J. A. Turner, and T. G. Deutsch,

- "Direct solar-to-hydrogen conversion via inverted metamorphic multi-junction semiconductor architectures," *Nat. Energy*, vol. 2, no. 4, pp. 1–8, 2017.
- [32] A. Eftekhari, V. J. Babu, and S. Ramakrishna, "Photoelectrode nanomaterials for photoelectrochemical water splitting," *Int. J. Hydrogen Energy*, vol. 42, no. 16, pp. 11078–11109, 2017.
 - [33] S. Kumar, K. Ojha, and A. K. Ganguli, "Interfacial Charge Transfer in Photoelectrochemical Processes," *Adv. Mater. Interfaces*, vol. 4, no. 1600981, pp. 1–19, 2017.
 - [34] S. Bai, J. Jiang, Q. Zhang, and Y. Xiong, "Steering charge kinetics in photocatalysis: intersection of materials syntheses, characterization techniques and theoretical simulations," *Chem. Soc. Rev.*, vol. 44, no. 10, pp. 2893–2939, 2015.
 - [35] M. A. Modestino, S. M. H. Hashemi, and S. Haussener, "Mass transport aspects of electrochemical solar-hydrogen generation," *Energy Environ. Sci.*, vol. 9, no. 5, pp. 1533–1551, 2016.
 - [36] S. Pokrant, S. Dilger, S. Landsmann, and M. Trottman, "Size effects of cocatalysts in photoelectrochemical and photocatalytic water splitting," *Mater. Today Energy*, vol. 5, pp. 158–163, 2017.
 - [37] X. Yang, R. Liu, Y. He, J. Thorne, Z. Zheng, and D. Wang, "Enabling practical electrocatalyst-assisted photoelectron-chemical water splitting with earth abundant materials," *Nano Res.*, vol. 8, no. 1, pp. 56–81, 2014.
 - [38] M. S. Y. Xu, "The absolute energy positions of conduction and valence bands of selected semiconducting minerals," *Am. Mineral.*, vol. 85, pp. 543–556, 2000.
 - [39] J. Li and N. Wu, "Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: a review," *Catal. Sci. Technol.*, vol. 5, no. 3, pp. 1360–1384, 2015.
 - [40] M. F. Weber, "Efficiency of Splitting Water with Semiconducting Photoelectrodes," *J. Electrochem. Soc.*, vol. 131, no. 6, pp. 1258–1265, 1984.
 - [41] M. G. Walter *et al.*, "Solar Water Splitting Cells," *Chem. Rev. (ACS Publ.)*, vol. 110, no. 11, pp. 6446–6473, 2010.
 - [42] M. Ge *et al.*, "A review of TiO₂ nanostructured catalysts for sustainable H₂ generation," *Int. J. Hydrogen Energy*, vol. 42, no. 12, pp. 8418–8449, 2017.
 - [43] X. Liu, F. Wang, and Q. Wang, "Nanostructure-based WO₃ photoanodes for photoelectrochemical water splitting," *Phys. Chem. Chem. Phys.*, vol. 14, pp. 7894–7911, 2012.
 - [44] Z. Liu, Q. Cai, C. Ma, J. Zhang, and J. Liu, "Photoelectrochemical properties and growth mechanism of varied ZnO nanostructures," *New J. Chem.*, vol. 41, no. 16, pp. 7947–7952, 2017.
 - [45] K. Tolod, S. Hernández, and N. Russo, "Recent Advances in the BiVO₄ Photocatalyst for Sun-Driven Water Oxidation: Top-Performing Photoanodes and Scale-Up Challenges," *Catalysts*, vol. 7, no. 1, p. 13, 2017.
 - [46] S. Y. Tee *et al.*, "Recent Progress in Energy-Driven Water Splitting," *Adv. Sci.*, vol. 4, no. 1600337, p. 24, 2017.
 - [47] C. C. L. McCrory, S. H. Jung, J. C. Peters, and T. F. Jaramillo, "Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction," *J. Am. Chem.*

Soc., vol. 135, no. 45, pp. 16977–16987, 2013.

- [48] C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters, and T. F. Jaramillo, "Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices," *J. Am. Chem. Soc.*, vol. 137, no. 13, pp. 4347–4357, 2015.
- [49] K. Maeda and K. Domen, "New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light," *J. Phys. Chem. C*, vol. 18, pp. 7851–7861, 2007.
- [50] N. M. Gupta, "Factors affecting the efficiency of a water splitting photocatalyst: A perspective," *Renew. Sustain. Energy Rev.*, vol. 71, no. December 2016, pp. 585–601, 2017.
- [51] R. Abe, M. Higashi, and K. Domen, "Facile Fabrication of an Efficient Oxynitride TaON Photoanode for Overall Water Splitting into H₂ and O₂ under Visible Light Irradiation," *J. Am. Chem. Soc.*, vol. 132, no. 34, pp. 11828–11829, 2010.
- [52] M. Higashi, K. Domen, and R. Abe, "Highly stable water splitting on oxynitride TaON photoanode system under visible light irradiation," *J. Am. Chem. Soc.*, vol. 134, no. 16, pp. 6968–6971, 2012.
- [53] M. Higashi, K. Domen, and R. Abe, "Fabrication of efficient TaON and Ta₃N₅ photoanodes for water splitting under visible light irradiation," *Energy Environ. Sci.*, vol. 4, no. 10, p. 4138, 2011.
- [54] M. Wiegel, M. H. J. Emond, E. R. Stobbe, and G. Blasse, "Luminescence of alkali tantalates and niobates," *J. Phys. Chem. Solids*, vol. 55, no. 8, pp. 773–778, 1994.
- [55] J. Su, L. Guo, N. Bao, and C. A. Grimes, "Nanostructured WO₃/BiVO₄ heterojunction films for efficient photoelectrochemical water splitting," *Nano Lett.*, vol. 11, no. 5, pp. 1928–1933, 2011.
- [56] X. Shi *et al.*, "Efficient photoelectrochemical hydrogen production from bismuth vanadate-decorated tungsten trioxide helix nanostructures," *Nat. Commun.*, vol. 5, p. 4775, 2014.
- [57] W. Smith, A. Wolcott, R. C. Fitzmorris, J. Z. Zhang, and Y. Zhao, "Quasi-core-shell TiO₂/WO₃ and WO₃/TiO₂ nanorod arrays fabricated by glancing angle deposition for solar water splitting," *J. Mater. Chem.*, vol. 21, no. 29, p. 10792, 2011.
- [58] K. Sivula, F. Le Formal, and M. Grätzel, "WO₃-Fe₂O₃ photoanodes for water splitting: A host scaffold, guest absorber approach," *Chem. Mater.*, vol. 21, no. 13, pp. 2862–2867, 2009.
- [59] R. Li, Q. Li, L. Zong, X. Wang, and J. Yang, "BaTiO₃/TiO₂ heterostructure nanotube arrays for improved photoelectrochemical and photocatalytic activity," *Electrochim. Acta*, vol. 91, pp. 30–35, 2013.
- [60] S. Hernández *et al.*, "Optimization of 1D ZnO@TiO₂ core-shell nanostructures for enhanced photoelectrochemical water splitting under solar light illumination," *ACS Appl. Mater. Interfaces*, vol. 6, no. 15, pp. 12153–12167, 2014.
- [61] M. Xie, Y. Feng, X. Fu, P. Luan, and L. Jing, "Phosphate-bridged TiO₂-BiVO₄ nanocomposites with exceptional visible activities for photocatalytic water splitting," *J. Alloys Compd.*, vol. 631, pp. 120–124, 2015.
- [62] T. Takata and K. Domen, "Development of non-oxide semiconductors as light harvesting materials in photocatalytic and photoelectrochemical water splitting," *Dalt. Trans.*, vol. 46, pp. 10529–10544, 2017.

- [63] T. Wang and J. Gong, "Single-Crystal Semiconductors with Narrow Band Gaps for Solar Water Splitting," *Angew. Chemie - Int. Ed.*, vol. 54, no. 37, pp. 10718–10732, 2015.
- [64] J. R. Swierk and T. E. Mallouk, "Design and development of photoanodes for water-splitting dye-sensitized photoelectrochemical cells," *Chem. Soc. Rev.*, vol. 42, no. 6, pp. 2357–2387, 2013.
- [65] M. K. Brennaman *et al.*, "Finding the Way to Solar Fuels with Dye-Sensitized Photoelectrosynthesis Cells," *J. Am. Chem. Soc.*, vol. 138, no. 40, pp. 13085–13102, 2016.
- [66] Z. Yu, F. Li, and L. Sun, "Recent advances in dye-sensitized photoelectrochemical cells for solar hydrogen production based on molecular components," *Energy Environ. Sci.*, vol. 8, no. 3, pp. 760–775, 2015.
- [67] K. R. Dunbar and R. a Heintz, *Chemistry of Transition Metal Cyanide Compounds: Modern Perspectives*, vol. 45. 1997.
- [68] Z. Qin, Y. Li, and N. Gu, "Progress in Applications of Prussian Blue Nanoparticles in Biomedicine," *Adv. Healthc. Mater.*, vol. 7, no. 20, pp. 1–13, 2018.
- [69] S. Kitagawa, R. Kitaura, and S. Noro, "Functional Porous Coordination Polymers," *Angew. Chemie - Int. Ed.*, vol. 43, pp. 2334–2375, 2004.
- [70] Y. S. Meng, O. Sato, and T. Liu, "Manipulating Metal-to-Metal Charge Transfer for Materials with Switchable Functionality," *Angew. Chemie - Int. Ed.*, vol. 57, no. 38, pp. 12216–12226, 2018.
- [71] M. J. P. Muñoz and E. C. Martínez, *Prussian Blue Based Batteries*, vol. 3. 2018.
- [72] J. A. Hill, A. L. Thompson, and A. L. Goodwin, "Dicyanometallates as Model Extended Frameworks," *J. Am. Chem. Soc.*, vol. 138, no. 18, pp. 5886–5896, 2016.
- [73] J. M. Herrera *et al.*, "Mixed valency and magnetism in cyanometallates and Prussian blue analogues," *Phil. Trans. R. Soc. A*, vol. 366, no. 1862, pp. 127–138, 2008.
- [74] D. Aguilà, Y. Prado, E. S. Koumoussi, C. Mathonière, and R. Clérac, "Switchable Fe/Co Prussian blue networks and molecular analogues," *Chem. Soc. Rev.*, vol. 45, no. 1, pp. 203–224, 2016.
- [75] Y. Lu, L. Wang, J. Cheng, and J. B. Goodenough, "Prussian blue: a new framework of electrode materials for sodium batteries," *Chem. Commun.*, vol. 48, no. 52, pp. 6544–6546, 2012.
- [76] B. Wang *et al.*, "Prussian Blue Analogs for Rechargeable Batteries," *iScience*, vol. 3, pp. 110–133, 2018.
- [77] C. Deng and D. Wang, "Functional Electrocatalysts Derived from Prussian Blue and its Analogues for Metal-Air Batteries: Progress and Prospects," *Batter. Supercaps*, vol. 2, no. 4, pp. 290–310, 2019.
- [78] S. S. Kaye and J. R. Long, "Hydrogen storage in the dehydrated prussian blue analogues $M_3[Co(CN)_6]_2$ ($M = Mn, Fe, Co, Ni, Cu, Zn$)," *J. Am. Chem. Soc.*, vol. 127, no. 18, pp. 6506–6507, 2005.
- [79] F. Karadas, H. El-Faki, E. Deniz, C. T. Yavuz, S. Aparicio, and M. Atilhan, "CO₂ adsorption studies on Prussian blue analogues," *Microporous Mesoporous Mater.*, vol. 162, pp. 91–97, 2012.

- [80] A. A. Karyakin, "Prussian blue and its analogues: Electrochemistry and analytical applications," *Electroanalysis*, vol. 13, no. 10, pp. 813–819, 2001.
- [81] A. A. Karyakin, E. E. Karyakina, and L. Gorton, "On the mechanism of H₂O₂ reduction at Prussian Blue modified electrodes," *Electrochem. commun.*, vol. 1, no. 2, pp. 78–82, 1999.
- [82] L. M. N. Assis, R. Leones, J. Kanicki, A. Pawlicka, and M. M. Silva, "Prussian blue for electrochromic devices," *J. Electroanal. Chem.*, vol. 777, pp. 33–39, 2016.
- [83] L. Hedley, L. Porteous, D. Hutson, N. Robertson, and J. O. Johansson, "Electrochromic bilayers of Prussian blue and its Cr analogue," *J. Mater. Chem. C*, vol. 6, no. 3, pp. 512–517, 2018.
- [84] M. Shokouhimehr *et al.*, "Dual purpose Prussian blue nanoparticles for cellular imaging and drug delivery: A new generation of T1-weighted MRI contrast and small molecule delivery agents," *J. Mater. Chem.*, vol. 20, no. 25, pp. 5251–5259, 2010.
- [85] B. Singh and A. Indra, "Prussian blue- and Prussian blue analogue-derived materials: progress and prospects for electrochemical energy conversion," *Mater. Today Energy*, vol. 16, p. 100404, 2020.
- [86] L. M. Cao, D. Lu, D. C. Zhong, and T. B. Lu, "Prussian blue analogues and their derived nanomaterials for electrocatalytic water splitting," *Coord. Chem. Rev.*, vol. 407, p. 213156, 2020.
- [87] C. Xuan, J. Zhang, J. Wang, and D. Wang, "Rational Design and Engineering of Nanomaterials Derived from Prussian Blue and Its Analogs for Electrochemical Water Splitting," *Chem. - An Asian J.*, pp. 958–972, 2020.
- [88] J. Chen *et al.*, "Prussian blue, its analogues and their derived materials for electrochemical energy storage and conversion," *Energy Storage Mater.*, vol. 25, no. June 2019, pp. 585–612, 2020.
- [89] D. M. Dongni Zhao, Yuezhen Lu, "Effects of Structure and Constituent of Prussian Blue Analogs on Their Application in Oxygen Evolution Reaction," *Molecules*, vol. 25, no. 2304, pp. 1–26, 2020.
- [90] D. A. Lutterman, Y. Surendranath, and D. G. Nocera, "A self-healing oxygen-evolving catalyst," *J. Am. Chem. Soc.*, vol. 131, no. 11, pp. 3838–3839, 2009.
- [91] M. W. Kanan and D. G. Nocera, "In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co²⁺," *Science*, vol. 321, no. 5892, pp. 1072–1075, 2008.
- [92] S. Pintado, S. Goberna-Ferrón, E. C. Escudero-Adán, J. R. Galán-Mascarós, and J. R. G.-M. Sara Pintado, Sara Goberna-Ferrón, Eduardo C. Escudero-Adán, "Fast and persistent electrocatalytic water oxidation by Co-Fe Prussian blue coordination polymers," *J. Am. Chem. Soc.*, vol. 135, no. 36, pp. 13270–13273, 2013.
- [93] X. Liang *et al.*, "Prussian blue nanoparticles operate as a contrast agent for enhanced photoacoustic imaging," *Chem. Commun.*, vol. 49, no. 94, pp. 11029–11032, 2013.
- [94] G. Liang, J. Xu, and X. Wang, "Synthesis and characterization of organometallic coordination polymer nanoshells of Prussian blue using miniemulsion periphery polymerization (MEPP)," *J. Am. Chem. Soc.*, vol. 131, no. 15, pp. 5378–5379, 2009.
- [95] Y. Liu and X. Wang, "Synthesis, characterization, micellization and metal coordination polymerization of pentacyanoferrate-coordinated block copolymers for monodispersed soluble Prussian blue nanospheres," *Polym. Chem.*, vol. 3, no. 9, pp. 2632–2639, 2012.

- [96] S. S. Kaye and J. R. Long, "Hydrogen adsorption in dehydrated variants of the cyano-bridged framework compounds $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ ($A = H, Li, Na, K, Rb$)," *Chem. Commun.*, no. 43, pp. 4486–4488, 2007.
- [97] T. Li, F. He, and Y. D. Dai, "Prussian blue analog caged in chitosan surface-decorated carbon nanotubes for removal cesium and strontium," *J. Radioanal. Nucl. Chem.*, vol. 310, no. 3, pp. 1139–1145, 2016.
- [98] F. H. Köhler and O. Storcheva, "Paramagnetic Prussian Blue Analogues $Cs^{II}[M^{III}(CN)_6]$. The Quest for Spin on Cesium Ions by Use of ^{133}Cs MAS NMR Spectroscopy," *Inorg. Chem.*, vol. 54, no. 14, pp. 6801–6806, 2015.
- [99] L. Han *et al.*, "Enhanced activity and acid pH stability of Prussian blue-type oxygen evolution electrocatalysts processed by chemical etching," *J. Am. Chem. Soc.*, vol. 138, no. 49, pp. 16037–16045, 2016.
- [100] P. J. Faustino *et al.*, "Quantitative determination of cesium binding to ferric hexacyanoferrate: Prussian blue," *J. Pharm. Biomed. Anal.*, vol. 47, no. 1, pp. 114–125, 2008.
- [101] D. F. Thompson and C. O. Church, "Prussian Blue for Treatment of Radiocesium Poisoning," *Pharmacotherapy*, vol. 21, no. 11, pp. 1364–1367, 2001.
- [102] M. A. Miller, M. M. Patel, and T. Coon, "Prussian blue for treatment of thallium overdose in the US," *Hosp. Pharm.*, vol. 40, no. 9, pp. 796–797, 2005.
- [103] A. Mohammad, Y. Yang, M. A. Khan, and P. J. Faustino, "Long-term stability study of Prussian blue - A quality assessment of water content and cyanide release," *Clin. Toxicol.*, vol. 53, no. 2, pp. 102–107, 2015.
- [104] R. O. Lezna, R. Romagnoli, N. R. De Tacconi, K. Rajeshwar, N. R. De Tacconi, and K. Rajeshwar, "Cobalt Hexacyanoferrate: Compound Stoichiometry, Infrared Spectroelectrochemistry, and Photoinduced Electron Transfer," *J. Phys. Chem. B*, vol. 106, no. 14, pp. 3612–3621, 2002.
- [105] H. Tabe, A. Kitase, and Y. Yamada, "Utilization of core-shell nanoparticles to evaluate subsurface contribution to water oxidation catalysis of $[Co^{II}(H_2O)_2]^{1.5}[Co^{III}(CN)_6]$ nanoparticles," *Appl. Catal. B Environ.*, vol. 262, p. 118101, 2020.
- [106] C. Díaz and A. Arancibia, "The cyanide ligand as an efficient bridge in mixed-valence complexes," *Inorganica Chim. Acta*, vol. 269, no. 2, pp. 246–252, 1998.
- [107] L. T. Zhang *et al.*, "Influence of ligand substitution at the donor and acceptor center on MMCT in a cyanide-bridged mixed-valence system," *Dalt. Trans.*, vol. 48, no. 22, pp. 7809–7816, 2019.
- [108] W. M. Laidlaw, A. L. Thompson, and R. G. Denning, "Solvent and metal dependent ^1H NMR hyperfine shifts in paramagnetic pentaamminemetal cyanide-bridged mixed-valence complexes," *Dalt. Trans.*, vol. 42, no. 13, pp. 4695–4703, 2013.
- [109] E. J. Schelter, F. Karadas, C. Avendano, A. V. Prosvirin, W. Wernsdorfer, and K. R. Dunbar, "A family of mixed-metal cyanide cubes with alternating octahedral and tetrahedral corners exhibiting a variety of magnetic behaviors including single molecule magnetism," *J. Am. Chem. Soc.*, vol. 129, no. 26, pp. 8139–8149, 2007.
- [110] F. Karadas *et al.*, "A Family of Cyanide-Bridged Molecular Squares: Structural and Magnetic Properties of $[M]$," *Inorg. Chem.*, vol. 47, no. 2074–2082, pp. 1951–1959, 2008.
- [111] S. Goberna-Ferrón, W. Y. Hernández, B. Rodríguez-García, and J. R. Galán-Mascarós, "Light-driven water oxidation with metal hexacyanomethylate heterogeneous catalysts,"

ACS Catal., vol. 4, no. 6, pp. 1637–1641, 2014.

- [112] M. Aksoy, S. V. K. Nune, and F. Karadas, "A Novel Synthetic Route for the Preparation of an Amorphous Co/Fe Prussian Blue Coordination Compound with High Electrocatalytic Water Oxidation Activity," *Inorg. Chem.*, vol. 55, no. 9, pp. 4301–4307, 2016.
- [113] E. P. Alsaç, E. Ülker, S. V. K. Nune, Y. Dede, and F. Karadas, "Tuning Electronic Properties of Prussian Blue Analogues for Efficient Water Oxidation Electrocatalysis: Experimental and Computational Studies," *Chem. - A Eur. J.*, vol. 24, pp. 4856–4863, 2018.
- [114] A. Eftekhari, "Tuning the electrocatalysts for oxygen evolution reaction," *Mater. Today Energy*, vol. 5, pp. 37–57, 2017.
- [115] B. M. Pires *et al.*, "Electrochemical water oxidation by cobalt-Prussian blue coordination polymer and theoretical studies of the electronic structure of the active species," *Dalt. Trans.*, vol. 48, no. 15, pp. 4811–4822, 2019.
- [116] B. Rodríguez-García *et al.*, "Cobalt hexacyanoferrate supported on Sb-doped SnO₂ as a non-noble catalyst for oxygen evolution in acidic medium," *Sustain. Energy Fuels*, vol. 2, no. 3, pp. 589–597, 2018.
- [117] F. Karadas, "Investigation of the ideal composition of metal hexacyanocobaltates with high water oxidation catalytic activity," *Turkish J. Chem.*, vol. 43, no. 2, pp. 511–519, 2019.
- [118] L. Han and J. R. Galán-Mascarós, "The positive effect of iron doping in the electrocatalytic activity of cobalt hexacyanoferrate," *Catalysts*, vol. 10, no. 1, pp. 1–7, 2020.
- [119] M. Kaneko and A. Yamada, "Photoresponsive graphite electrode coated with bilayer membranes of prussian blue and polymer-pendant Ru(bpy)₂+₃," *Electrochim. Acta*, vol. 31, no. 2, pp. 273–275, 1986.
- [120] P. A. Christensen and A. Harriman, "Photo-oxidation of Water using Prussian Blue as Catalyst," *J. Chem. Soc., Faraday Trans.*, vol. 81, pp. 2461–2466, 1985.
- [121] Y. Yamada, K. Oyama, R. Gates, and S. Fukuzumi, "High catalytic activity of heteropolynuclear cyanide complexes containing cobalt and platinum ions: Visible-light driven water oxidation," *Angew. Chemie - Int. Ed.*, vol. 54, no. 19, pp. 5613–5617, 2015.
- [122] Y. Isaka, K. Oyama, Y. Yamada, T. Suenobu, and S. Fukuzumi, "Photocatalytic production of hydrogen peroxide from water and dioxygen using cyano-bridged polynuclear transition metal complexes as water oxidation catalysts," *Catal. Sci. Technol.*, vol. 6, no. 3, pp. 681–684, 2016.
- [123] Y. Yamada, K. Oyama, T. Suenobu, and S. Fukuzumi, "Photocatalytic water oxidation by persulphate with a Ca²⁺ ion-incorporated polymeric cobalt cyanide complex affording O₂ with 200% quantum efficiency," *Chem. Commun.*, vol. 14, pp. 224–232, 2017.
- [124] Z. Kap and F. Karadas, "Visible light-driven water oxidation with a ruthenium sensitizer and a cobalt-based catalyst connected with a polymeric platform," *Faraday Discuss.*, vol. 215, pp. 111–122, 2019.
- [125] T. G. Ulusoy Ghobadi *et al.*, "A Noble-Metal-Free Heterogeneous Photosensitizer-Relay-Catalyst Triad Catalyzes Water Oxidation under Visible Light," *Angew. Chemie Int. Ed.*, vol. 57, pp. 17173–17177, 2018.

- [126] T. G. Ulusoy Ghobadi *et al.*, "A Robust Precious Metal-free Dye-sensitized Photoanode for Water Oxidation: Nanosecond Long Excited State Lifetime via a Prussian Blue Analogue," *Angew. Chemie - Int. Ed.*, vol. 59, no. 10, pp. 4082–4090, 2020.
- [127] F. S. Hegner, D. Cardenas-Morcoso, S. Giménez, N. López, and J. R. Galán-Mascarós, "Level Alignment as Descriptor for Semiconductor/Catalyst Systems in Water Splitting: The Case of Hematite/Cobalt Hexacyanoferrate Photoanodes," *ChemSusChem*, vol. 10, no. 22, pp. 4552–4560, 2017.
- [128] P.-Y. Tang *et al.*, "Boosting Photoelectrochemical Water Oxidation of Hematite by Surface States Modification," *Adv. Energy Mater.*, vol. 1901836, pp. 1–11, 2019.
- [129] F. S. Hegner, I. Herraiz-Cardona, D. Cardenas-Morcoso, N. López, J. R. Galán-Mascarós, and S. Gimenez, "Cobalt Hexacyanoferrate on BiVO₄ Photoanodes for Robust Water Splitting," *ACS Appl. Mater. Interfaces*, vol. 9, no. 43, pp. 37671–37681, 2017.
- [130] K. Trzciński, M. Szkoda, K. Szulc, M. Sawczak, and A. Lisowska-Oleksiak, "The bismuth vanadate thin layers modified by cobalt hexacyanocobaltate as visible-light active photoanodes for photoelectrochemical water oxidation," *Electrochim. Acta*, vol. 295, pp. 410–417, 2019.
- [131] K. Trzciński, M. Szkoda, M. Sawczak, and A. Lisowska-Oleksiak, "Enhanced Photoelectrocatalytic Performance of Inorganic-Inorganic Hybrid Consisting BiVO₄, V₂O₅, and Cobalt Hexacyanocobaltate as a Perspective Photoanode for Water Splitting," *Electrocatalysis*, vol. 11, no. 2, pp. 180–187, 2020.
- [132] B. Moss *et al.*, "Unraveling Charge Transfer in CoFe Prussian Blue Modified BiVO₄ Photoanodes," *ACS Energy Lett.*, pp. 337–342, 2018.
- [133] B. Morandi Pires, F. S. Hegner, J. A. Bonacin, and J. R. Galan-Mascaros, "Ligand effects of Penta- and Hexacyanidoferrate-Derived Water Oxidation Catalysts on BiVO₄ Photoanodes," *ACS Appl. Energy Mater.*, 2020.
- [134] T. G. Ulusoy Ghobadi *et al.*, "Strong Light-matter Interaction in Au Plasmonic Nanoantennas Coupled with Prussian Blue Catalyst on BiVO₄ for Photoelectrochemical Water Splitting," *ChemSusChem*, pp. 1–13, 2020.
- [135] P. Makuła, M. Pacia, and W. Macyk, "How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV-Vis Spectra," *Journal of Physical Chemistry Letters*, vol. 9, no. 23. American Chemical Society, pp. 6814–6817, Dec-2018.
- [136] A. Zaban, M. Greenshtein, and J. Bisquert, "Determination of the electron lifetime in nanocrystalline dye solar cells by open-circuit voltage decay measurements," *ChemPhysChem*, vol. 4, no. 8, pp. 859–864, 2003.
- [137] S. E. Koops, B. C. O'Regan, P. R. F. Barnes, and J. R. Durrant, "Parameters influencing the efficiency of electron injection in dye-sensitized solar cells," *J. Am. Chem. Soc.*, vol. 131, no. 13, pp. 4808–18, Apr. 2009.
- [138] T. G. Ulusoy Ghobadi *et al.*, "Building an Iron Chromophore Incorporating Prussian Blue Analogue for Photoelectrochemical Water Oxidation," *Chem. - A Eur. J.*, vol. 27, no. 35, pp. 8966–8976, 2021.
- [139] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 54, no. 16, pp. 11169–11186, 1996.
- [140] G. Kresse and J. Hafner, "Ab initio molecular-dynamics simulation of the liquid-

- metamorphous- semiconductor transition in germanium,” *Phys. Rev. B*, vol. 49, no. 20, pp. 14251–14269, 1994.
- [141] G. Kresse and J. Hafner, “Ab initio molecular dynamics for liquid metals,” *Phys. Rev. B*, vol. 47, no. 1, pp. 558–561, 1993.
 - [142] G. Kresse and J. Furthmüller, “Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set,” *Comput. Mater. Sci.*, vol. 6, no. 1, pp. 15–50, 1996.
 - [143] J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Phys. Rev. Lett.*, vol. 77, no. 18, pp. 3865–3868, 1996.
 - [144] P. E. Blöchl, “Projector augmented-wave method,” *Phys. Rev. B*, vol. 50, no. 24, pp. 17953–17979, 1994.
 - [145] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. Ángyán, “Screened hybrid density functionals applied to solids,” *J. Chem. Phys.*, vol. 124, no. 15, p. 154709, 2006.
 - [146] F. S. Hegner, J. R. Galán-Mascarós, and N. López, “A Database of the Structural and Electronic Properties of Prussian Blue, Prussian White, and Berlin Green Compounds through Density Functional Theory,” *Inorg. Chem.*, vol. 55, no. 24, pp. 12851–12862, 2016.
 - [147] W. Kohn, A. D. Becke, and R. G. Parr, “Density functional theory of electronic structure,” *J. Phys. Chem.*, vol. 100, no. 31, pp. 12974–12980, 1996.
 - [148] A. D. Becke, “Density-functional exchange-energy approximation with correct asymptotic behavior,” *Phys. Rev. A*, vol. 38, no. 6, pp. 3098–3100, 1988.
 - [149] A. D. Becke, “Density-functional thermochemistry. III. The role of exact exchange,” *J. Chem. Phys.*, vol. 98, no. 7, pp. 5648–5652, 1993.
 - [150] R. G. Parr and W. Yang, “Density-functional theory of atoms and molecules,” *Oxford Univ. Press N.Y.*, 1989.
 - [151] D. J. F. G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M., “Gaussian 09,” *Gaussian 09*, vol. 37, p. 785, 1988.
 - [152] C. Lee, W. Yang, and R. G. Parr, “Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density,” *Phys. Rev. B*, vol. 37, no. 2, pp. 785–789, 1988.
 - [153] P. J. Hay and W. R. Wadt, “Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg,” *J. Chem. Phys.*, vol. 82, no. 1, pp. 270–283, 1985.
 - [154] P. J. H. T. H. Dunning, “Methods of Electronic Structure Theory,” in *Springer US, Boston, MA*, 1977, pp. 1–27.
 - [155] R. A. Kendall, T. H. Dunning, and R. J. Harrison, “Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions,” *J. Chem. Phys.*, vol. 96, no. 9, pp. 6796–6806, 1992.
 - [156] T. Yanai, D. P. Tew, and N. C. Handy, “A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP),” *Chem. Phys. Lett.*, vol. 393, no. 1–3, pp. 51–57, 2004.

- [157] S. Miertuš and J. Tomasi, "Approximate evaluations of the electrostatic free energy and internal energy changes in solution processes," *Chem. Phys.*, vol. 65, no. 2, pp. 239–245, 1982.
- [158] S. Miertuš, E. Scrocco, and J. Tomasi, "Electrostatic interaction of a solute with a continuum. A direct utilization of AB initio molecular potentials for the prediction of solvent effects," *Chem. Phys.*, vol. 55, no. 1, pp. 117–129, 1981.
- [159] J. L. Pascual-Ahuir, E. Silla, and I. Tunon, "GEPOL: An improved description of molecular surfaces. III. A new algorithm for the computation of a solvent-excluding surface," *J. Comput. Chem.*, vol. 15, no. 10, pp. 1127–1138, 1994.
- [160] "Chemcraft - graphical software for visualization of quantum chemistry computations.," <http://www.chemcraftprog.com>.
- [161] D. G. Nocera, "The artificial leaf," *Acc. Chem. Res.*, vol. 45, no. 5, pp. 767–776, 2012.
- [162] M. G. Walter *et al.*, "Solar Water Splitting Cells," *Chem. Rev.*, vol. 110, no. 11, pp. 6446–6473, 2010.
- [163] D. L. Ashford *et al.*, "Molecular Chromophore-Catalyst Assemblies for Solar Fuel Applications," *Chem. Rev.*, vol. 115, no. 23, pp. 13006–13049, 2015.
- [164] S. Berardi *et al.*, "Molecular artificial photosynthesis," *Chem. Soc. Rev.*, vol. 43, no. 22, pp. 7501–7519, 2014.
- [165] M. Yamamoto, J. Föhlinger, J. Petersson, L. Hammarström, and H. Imahori, "Artificial Photosynthesis A Ruthenium Complex – Porphyrin – Fullerene-Linked Molecular Pentad as an Integrative Photosynthetic Model Communications Angewandte," *Angew. Chem. Int. Ed. Engl.*, vol. 56, pp. 3329–3333, 2017.
- [166] L. Favereau *et al.*, "A Molecular Tetrad That Generates a High-Energy Charge-Separated State by Mimicking the Photosynthetic Z-Scheme," *J. Am. Chem. Soc.*, vol. 138, no. 11, pp. 3752–3760, 2016.
- [167] T. Schlottbauer, R. Schroot, S. Glover, L. Hammarström, M. Jäger, and U. S. Schubert, "A multidonor–photosensitizer–multiacceptor triad for long-lived directional charge separation," *Phys. Chem. Chem. Phys.*, vol. 19, no. 42, pp. 28572–28578, 2017.
- [168] F. Li *et al.*, "Organic Dye-Sensitized Tandem Photoelectrochemical Cell for Light Driven Total Water Splitting," *J. Am. Chem. Soc.*, vol. 137, no. 28, pp. 9153–9159, 2015.
- [169] F. Li, K. Fan, L. Wang, Q. Daniel, L. Duan, and L. Sun, "Immobilizing Ru(bda) Catalyst on a Photoanode via Electrochemical Polymerization for Light-Driven Water Splitting," *ACS Catal.*, vol. 5, pp. 3786–3790, 2015.
- [170] L. Li, L. Duan, Y. Xu, M. Gorlov, A. Hagfeldt, and L. Sun, "A photoelectrochemical device for visible light driven water splitting by a molecular ruthenium catalyst assembled on dye-sensitized nanostructured TiO₂," *Chem. Commun.*, vol. 46, no. 39, pp. 7307–7309, 2010.
- [171] H. Li, F. Li, B. Zhang, X. Zhou, F. Yu, and L. Sun, "Visible Light-Driven Water Oxidation Promoted by Host-Guest Interaction between Photosensitizer and Catalyst with A High Quantum Efficiency," *J. Am. Chem. Soc.*, vol. 137, no. 13, pp. 4332–4335, 2015.
- [172] B. D. Sherman *et al.*, "Light-driven Water Splitting by a Covalently Linked Ruthenium-based Chromophore–Catalyst Assembly," *ACS Energy Lett.*, vol. 2, pp. 124–128, 2017.
- [173] B. D. Sherman *et al.*, "A Dye-Sensitized Photoelectrochemical Tandem Cell for Light Driven Hydrogen Production from Water," *J. Am. Chem. Soc.*, vol. 138, pp. 16745–

16753, 2016.

- [174] L. Alibabaei *et al.*, "Chromophore-Catalyst Assembly for Water Oxidation Prepared by Atomic Layer Deposition," *ACS Appl. Mater. Interfaces*, vol. 9, pp. 39018–39026, 2017.
- [175] M. Yamamoto *et al.*, "Visible light-driven water oxidation with a subporphyrin sensitizer and a water oxidation catalyst," *Chem. Commun.*, vol. 52, no. 94, pp. 13702–13705, 2016.
- [176] M. Yamamoto *et al.*, "Visible light-driven water oxidation using a covalently-linked molecular catalyst–sensitizer dyad assembled on a TiO₂ electrode," *Chem. Sci.*, vol. 7, pp. 1430–1439, 2016.
- [177] J. T. Kirner and R. G. Finke, "Sensitization of Nanocrystalline Metal Oxides with a Phosphonate- Functionalized Perylene Diimide for Photoelectrochemical Water Oxidation with a CoO," *ACS Appl. Mater. Interfaces*, vol. 9, pp. 27625–27637, 2017.
- [178] M. Shatruk, C. Avendano, and K. R. Dunbar, "Cyanide-Bridged Complexes of Transition Metals : A Molecular Magnetism Perspective," *Prog. Inorg. Chem.*, vol. 56, pp. 155–334, 2009.
- [179] Y. Aratani, T. Suenobu, K. Ohkubo, Y. Yamada, and S. Fukuzumi, "Dual Function Photocatalysis of Cyano-Bridged Heteronuclear Metal Complexes for Water Oxidation and Two-Electron Reduction of Dioxygen to Produce Hydrogen Peroxide as a Solar Fuel," *Chem. Commun.*, vol. 53, pp. 3473–3476, 2017.
- [180] Y. Aratani, K. Oyama, T. Suenobu, Y. Yamada, and S. Fukuzumi, "Photocatalytic hydroxylation of benzene by dioxygen to phenol with a cyano-bridged complex containing FeII and RuII incorporated in mesoporous silica-alumina," *Inorg. Chem.*, vol. 55, no. 12, pp. 5780–5786, 2016.
- [181] D. H. Macartney, "Properties and Reactions of Substituted Pentacyanoferrate (II) Complexes," *Rev. Inorg. Chem.*, vol. 9, no. 2–3, pp. 101–152, Jan. 1988.
- [182] K. Szaciłowski and Z. Stasicka, "Molecular switches based on cyanoferrate complexes," *Coord. Chem. Rev.*, vol. 229, no. 1–2, pp. 17–26, Jul. 2002.
- [183] J. R. Eskelsen, Y. Qi, S. Schneider-Pollack, S. Schmitt, K. W. Hipps, and U. Mazur, "Correlating elastic properties and molecular organization of an ionic organic nanostructure," *Nanoscale*, vol. 6, pp. 316–327, 2014.
- [184] N. Kumar, V. Kumar, and H. S. Panda, "Enhanced tortuosity for electrolytes in microwave irradiated self-organized carbon-doped Ni/Co hydroxide nanocomposite electrodes with higher Ni/Co atomic ratio and rate capability for an asymmetric supercapacitor," *Nanotechnology*, vol. 28, no. 44, p. 445405, 2017.
- [185] M. Kuang, T. Tao Li, H. Chen, S. Mao Zhang, L. Li Zhang, and Y. Xin Zhang, "Hierarchical Cu₂O/CuO/Co₃O₄ core-shell nanowires: synthesis and electrochemical properties," *Nanotechnology*, vol. 26, no. 30, p. 304002, 2015.
- [186] Y. Li *et al.*, "Denitrification performance of non-pitch coal-based activated coke by the introduction of MnO_x–CeO_x–M (FeO_x, CoO_x) at low temperature," *Mol. Catal.*, vol. 445, pp. 21–28, 2018.
- [187] S. C. Petitto, E. M. Marsh, G. A. Carson, and M. A. Langell, "Cobalt oxide surface chemistry: The interaction of CoO(1 0 0), Co₃O₄(1 1 0) and Co₃O₄(1 1 1) with oxygen and water," *J. Mol. Catal. A Chem.*, vol. 281, no. 1–2, pp. 49–58, 2008.
- [188] T. G. Ulusoy Ghobadi, A. Ghobadi, and A. K. Okyay, "Surface engineered angstrom thick ZnO-sheathed TiO₂ nanowires as photoanodes for performance enhanced dye-

- sensitized solar cells," *J. Mater. Chem. A*, vol. 2, no. 40, pp. 16867–16876, 2014.
- [189] A. Ghobadi, H. I. Yavuz, T. G. Ulusoy Ghobadi, K. C. Icli, M. Ozenbas, and A. K. Okyay, "Enhanced Performance of Nanowire-Based All-TiO₂ Solar Cells using Subnanometer-Thick Atomic Layer Deposited ZnO Embedded Layer," *Electrochim. Acta*, vol. 157, pp. 23–30, 2015.
- [190] R. Zou *et al.*, "Chain-like NiCo₂O₄ nanowires with different exposed reactive planes for high-performance supercapacitors," *J. Mater. Chem. A*, vol. 1, no. 30, pp. 8560–8566, 2013.
- [191] E. P. Alsaç, E. Ülker, S. V. K. Nune, Y. Dede, and F. Karadas, "Tuning Electronic Properties of Prussian Blue Analogues for Efficient Water Oxidation Electrocatalysis: Experimental and Computational Studies," *Chem. - A Eur. J.*, vol. 24, pp. 4856–4863, 2018.
- [192] R. N. Sampaio, M. M. Silva, A. A. Batista, and N. M. B. Neto, "Investigation of the photophysical and electrochemical properties of a free base tetrapyrrolyl porphyrin with meso carbon linked ruthenium(II) groups," *J. Photochem. Photobiol. A Chem.*, vol. 315, pp. 98–106, 2016.
- [193] A. M. López *et al.*, "A Co(II)-Ru(II) dyad relevant to light-driven water oxidation catalysis," *Phys. Chem. Chem. Phys.*, vol. 16, pp. 12000–12007, 2014.
- [194] M. Grätzel, "Dye-sensitized solar cells," *J. Photochem. Photobiol. C Photochem. Rev.*, vol. 4, no. 2, pp. 145–153, Oct. 2003.
- [195] A. Hagfeldt and M. Grätzel, "Light-Induced Redox Reactions in Nanocrystalline Systems," *Chem. Rev.*, vol. 95, no. 1, pp. 49–68, 1995.
- [196] P. Li *et al.*, "Infrared hyperbolic metasurface based on nanostructured van der Waals materials," *Science (80-.)*, vol. 359, pp. 892–896, 2018.
- [197] R. L. House *et al.*, "Artificial photosynthesis: Where are we now? Where can we go?," *J. Photochem. Photobiol. C Photochem. Rev.*, vol. 25, pp. 32–45, 2015.
- [198] J. J. Concepcion, R. L. House, J. M. Papanikolas, and T. J. Meyer, "Chemical approaches to artificial photosynthesis," *PNAS*, vol. 109, no. 39, pp. 15560–15564, 2012.
- [199] P. Xu, N. S. McCool, and T. E. Mallouk, "Water splitting dye-sensitized solar cells," *Nano Today*, vol. 14, pp. 42–58, 2017.
- [200] T. Rawling, C. Austin, F. Buchholz, S. B. Colbran, and A. M. McDonagh, "Ruthenium phthalocyanine-bipyridyl dyads as sensitizers for dye-sensitized solar cells: Dye coverage versus molecular efficiency," *Inorg. Chem.*, vol. 48, no. 7, pp. 3215–3227, 2009.
- [201] A. Pannwitz and O. S. Wenger, "Photoinduced Electron Transfer Coupled to Donor Deprotonation and Acceptor Protonation in a Molecular Triad Mimicking Photosystem II," *J. Am. Chem. Soc.*, vol. 139, no. 38, pp. 13308–13311, 2017.
- [202] M. V. Sheridan *et al.*, "Evaluation of Chromophore and Assembly Design in Light-Driven Water Splitting with a Molecular Water Oxidation Catalyst," *ACS Energy Lett.*, vol. 1, pp. 231–236, 2016.
- [203] J. W. Youngblood *et al.*, "Photoassisted overall water splitting in a visible light-absorbing dye-sensitized photoelectrochemical cell," *J. Am. Chem. Soc.*, vol. 131, no. 3, pp. 926–927, 2009.

- [204] D. Wang *et al.*, "Stabilized photoanodes for water oxidation by integration of organic dyes, water oxidation catalysts, and electron-transfer mediators," *Proc. Natl. Acad. Sci.*, vol. 115, no. 34, pp. 8523–8528, 2018.
- [205] J. T. Kirner and R. G. Finke, "Water-oxidation photoanodes using organic light-harvesting materials: A review," *J. Mater. Chem. A*, vol. 5, no. 37, pp. 19560–19592, 2017.
- [206] G. F. Moore *et al.*, "A visible light water-splitting cell with a photoanode formed by codeposition of a high-potential porphyrin and an iridium water-oxidation catalyst," *Energy Environ. Sci.*, vol. 4, no. 7, pp. 2389–2392, 2011.
- [207] M. Yamamoto *et al.*, "Visible light-driven water oxidation with a subporphyrin sensitizer and a water oxidation catalyst," *Chem. Commun.*, vol. 52, no. 94, pp. 13702–13705, 2016.
- [208] J. T. Kirner, J. J. Stracke, B. A. Gregg, and R. G. Finke, "Visible-light-assisted photoelectrochemical water oxidation by thin films of a phosphonate-functionalized perylene diimide plus CoOx cocatalyst," *ACS Appl. Mater. Interfaces*, vol. 6, pp. 13367–13377, 2014.
- [209] P. Tang *et al.*, "Enhanced photoelectrochemical water splitting of hematite multilayer nanowire photoanodes by tuning the surface state via bottom-up interfacial engineering," *Energy Environ. Sci.*, vol. 10, no. 10, pp. 2124–2136, 2017.
- [210] Y. Yamada, M. Yoneda, and S. Fukuzumi, "A robust one-compartment fuel cell with a polynuclear cyanide complex as a cathode for utilizing H₂O₂ as a sustainable fuel at ambient conditions," *Chem. - A Eur. J.*, vol. 19, no. 35, pp. 11733–11741, 2013.
- [211] E. P. Alsaç, E. Ülker, S. V. K. Nune, and F. Karadas, "A Cyanide-Based Coordination Polymer for Hydrogen Evolution Electrocatalysis," *Catal. Letters*, vol. 148, no. 2, pp. 531–538, 2018.
- [212] M. Szkoda, J. Rysz, J. Ryl, A. Lisowska-Oleksiak, and K. Siuzdak, "Fabrication and photoactivity of organic-inorganic systems based on titania nanotubes and PEDOT containing redox centres formed by different Prussian Blue analogues," *J. Alloys Compd.*, vol. 723, pp. 498–504, 2017.
- [213] J. R. Swierk, K. P. Regan, J. Jiang, G. W. Brudvig, and C. A. Schmuttenmaer, "Rutile TiO₂ as an Anode Material for Water-Splitting Dye-Sensitized Photoelectrochemical Cells," *ACS Energy Lett.*, vol. 1, no. 3, pp. 603–606, 2016.
- [214] E. A. Turhan, S. V. K. Nune, E. Ülker, U. Şahin, Y. Dede, and F. Karadas, "Water Oxidation Electrocatalysis with a Cobalt-Borate-Based Hybrid System under Neutral Conditions," *Chem. - A Eur. J.*, vol. 24, no. 41, pp. 10372–10382, 2018.
- [215] NIST X-ray Photoelectron Spectroscopy Database, "NIST X-ray Photoelectron Spectroscopy Database," https://srdata.nist.gov/xps/EngElmSrchQuery.aspx?EType=PE&CSOpt=Retri_ex_dat&Elm=N.
- [216] L. Chen, X. Wang, X. Zhang, and H. Zhang, "3D porous and redox-active prussian blue-in-graphene aerogels for highly efficient electrochemical detection of H₂O₂," *J. Mater. Chem.*, vol. 22, no. 41, pp. 22090–22096, 2012.
- [217] H. Maaoui *et al.*, "A Prussian blue/carbon dot nanocomposite as an efficient visible light active photocatalyst for C-H activation of amines," *Photochem. Photobiol. Sci.*, vol. 15, no. 10, pp. 1282–1288, 2016.
- [218] H. Yang, L. Sun, J. Zhai, H. Li, Y. Zhao, and H. Yu, "In situ controllable synthesis of

magnetic Prussian blue/graphene oxide nanocomposites for removal of radioactive cesium in water," *J. Mater. Chem. A*, vol. 2, no. 2, pp. 326–332, 2014.

- [219] T. Ogata *et al.*, "Phenazine-photosensitized reduction of CO₂ mediated by a cobalt-cyclam complex through electron and hydrogen transfer," *J. Phys. Chem.*, vol. 99, no. 31, pp. 11916–11922, 1995.
- [220] J. C. Dean, D. G. Oblinsky, S. Ra, and G. D. Scholes, "Methylene Blue Exciton States Steer Nonradiative Relaxation: Ultrafast Spectroscopy of Methylene Blue Dimer," *J. Phys. Chem. B*, vol. 120, pp. 440–454, 2016.
- [221] D. Ke *et al.*, "Hidden Relaxation Channels in Aqueous Methylene Blue after Functionalization of Graphene Oxide Probed by Transient Absorption Spectroscopy," *Chin. J. Chem. Phys.*, vol. 30, no. 4, pp. 389–394, 2017.
- [222] S. Verma, A. Ghosh, A. Das, and H. N. Ghosh, "Ultrafast Exciton Dynamics of J- and H-Aggregates of the Porphyrin-Catechol in Aqueous Solution," *J. Phys. Chem. B*, vol. 114, pp. 8327–8334, 2010.
- [223] T. G. Ulusoy Ghobadi *et al.*, "Pushing the limits in photosensitizer-catalyst interaction via a short cyanide bridge for water oxidation," *Cell Reports Phys. Sci.*, vol. 2, no. 2, p. 100319, 2021.
- [224] D. Wang *et al.*, "A stable dye-sensitized photoelectrosynthesis cell mediated by a NiO overlayer for water oxidation," *Proc. Natl. Acad. Sci.*, pp. 1–8, 2019.
- [225] H. J. Son *et al.*, "Dye stabilization and enhanced photoelectrode wettability in water-based dye-sensitized solar cells through post-assembly atomic layer deposition of TiO₂," *J. Am. Chem. Soc.*, vol. 135, no. 31, pp. 11529–11532, 2013.
- [226] C. L. Gray *et al.*, "Oligomeric Ruthenium Polypyridyl Dye for Improved Stability of Aqueous Photoelectrochemical Cells," *J. Phys. Chem. C*, vol. 124, no. 6, pp. 3542–3550, 2020.
- [227] J. K. McCusker, "Electronic structure in the transition metal block and its implications for light harvesting," *Science*, vol. 363, no. 6426, pp. 484–488, 2019.
- [228] E. R. Young and A. Oldacre, "Iron hits the mark," *Science*, vol. 363, no. 6424, pp. 225–226, 2019.
- [229] O. S. Wenger, "Is Iron the New Ruthenium?," *Chem. - A Eur. J.*, vol. 25, no. 24, pp. 6043–6052, 2019.
- [230] T. C. B. Harlang *et al.*, "Iron sensitizer converts light to electrons with 92% yield," *Nat. Chem.*, vol. 7, no. 11, pp. 883–889, 2015.
- [231] J. D. Braun *et al.*, "Iron(ii) coordination complexes with panchromatic absorption and nanosecond charge-transfer excited state lifetimes," *Nat. Chem.*, vol. 11, no. 12, pp. 1144–1150, 2019.
- [232] K. S. Kjær *et al.*, "Luminescence and reactivity of a charge-transfer excited iron complex with nanosecond lifetime," *Science*, vol. 363, no. 6424, pp. 249–253, 2019.
- [233] G. F. Moore *et al.*, "A visible light water-splitting cell with a photoanode formed by codeposition of a high-potential porphyrin and an iridium water-oxidation catalyst," *Energy Environ. Sci.*, vol. 4, no. 7, pp. 2389–2392, 2011.
- [234] D. Wang *et al.*, "Stabilized photoanodes for water oxidation by integration of organic dyes, water oxidation catalysts, and electron-transfer mediators," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 115, no. 34, pp. 8523–8528, 2018.

- [235] Z. Jiao, X. W. Sun, J. Wang, L. Ke, and H. V. Demir, "Hydrothermally grown nanostructured WO₃ films and their electrochromic characteristics," *J. Phys. D: Appl. Phys.*, vol. 43, no. 28, pp. 1–6, 2010.
- [236] J. Su, X. Feng, J. D. Sloppy, L. Guo, and C. A. Grimes, "Vertically aligned WO₃ nanowire arrays grown directly on transparent conducting oxide coated glass: Synthesis and photoelectrochemical properties," *Nano Lett.*, vol. 11, no. 1, pp. 203–208, 2011.
- [237] T. Oshima *et al.*, "An Artificial Z-Scheme Constructed from Dye-Sensitized Metal Oxide Nanosheets for Visible Light-Driven Overall Water Splitting," *J. Am. Chem. Soc.*, vol. 142, no. 18, pp. 8412–8420, 2020.
- [238] M. Tong, J. Yang, Q. Jin, X. Zhang, J. Gao, and G. Li, "Facile preparation of amorphous carbon-coated tungsten trioxide containing oxygen vacancies as photocatalysts for dye degradation," *J. Mater. Sci.*, vol. 54, no. 15, pp. 10656–10669, 2019.
- [239] B. Shan *et al.*, "A Silicon-Based Heterojunction Integrated with a Molecular Excited State in a Water-Splitting Tandem Cell," *J. Am. Chem. Soc.*, vol. 141, no. 26, pp. 10390–10398, 2019.
- [240] B. Shan *et al.*, "Binary molecular-semiconductor p–n junctions for photoelectrocatalytic CO₂ reduction," *Nat. Energy*, vol. 4, no. 4, pp. 290–299, 2019.
- [241] K. Hayat, M. A. Gondal, M. M. Khaled, Z. H. Yamani, and S. Ahmed, "Laser induced photocatalytic degradation of hazardous dye (Safranin-O) using self synthesized nanocrystalline WO₃," *J. Hazard. Mater.*, vol. 186, no. 2–3, pp. 1226–1233, 2011.
- [242] P. Wang *et al.*, "A broadband and strong visible-light-absorbing photosensitizer boosts hydrogen evolution," *Nat. Commun.*, vol. 10, no. 1, 2019.
- [243] S. Guo, K. K. Chen, R. Dong, Z. M. Zhang, J. Zhao, and T. B. Lu, "Robust and Long-Lived Excited State Ru(II) Polyimine Photosensitizers Boost Hydrogen Production," *ACS Catal.*, vol. 8, no. 9, pp. 8659–8670, 2018.
- [244] M. K. Gish, A. M. Lapides, M. K. Brennaman, J. L. Templeton, T. J. Meyer, and J. M. Papanikolas, "Ultrafast Recombination Dynamics in Dye-Sensitized SnO₂/TiO₂ Core/Shell Films," *J. Phys. Chem. Lett.*, vol. 7, no. 24, pp. 5297–5301, 2016.
- [245] D. F. Zigler *et al.*, "Disentangling the Physical Processes Responsible for the Kinetic Complexity in Interfacial Electron Transfer of Excited Ru(II) Polypyridyl Dyes on TiO₂," *J. Am. Chem. Soc.*, vol. 138, no. 13, pp. 4426–4438, 2016.
- [246] S. E. Bettis *et al.*, "Photophysical characterization of a chromophore/water oxidation catalyst containing a layer-by-layer assembly on nanocrystalline TiO₂ using ultrafast spectroscopy," *J. Phys. Chem. A*, vol. 118, no. 45, pp. 10301–10308, 2014.
- [247] O. S. Wenger, "Photoactive Complexes with Earth-Abundant Metals," *J. Am. Chem. Soc.*, vol. 140, no. 42, pp. 13522–13533, 2018.
- [248] Y. Liu, P. Persson, V. Sundström, and K. Wärnmark, "Fe N-Heterocyclic Carbene Complexes as Promising Photosensitizers," *Acc. Chem. Res.*, vol. 49, no. 8, pp. 1477–1485, 2016.
- [249] M. Yang, D. W. Thompson, and G. J. Meyer, "Charge-transfer studies of iron cyano compounds bound to nanocrystalline TiO₂ surfaces," *Inorg. Chem.*, vol. 41, no. 5, pp. 1254–1262, 2002.
- [250] M. Yang, D. W. Thompson, and G. J. Meyer, "Dual Pathways for TiO₂ Sensitization by Na₂ [Fe(bpy)(CN)₄]," *Inorg. Chem.*, vol. 39, no. 17, pp. 3738–3739, 2000.

- [251] D. C. Ashley and E. Jakubikova, "Ironing out the photochemical and spin-crossover behavior of Fe(II) coordination compounds with computational chemistry," *Coord. Chem. Rev.*, vol. 337, pp. 97–111, 2017.
- [252] Y. Liu *et al.*, "Towards longer-lived metal-to-ligand charge transfer states of iron(ii) complexes: an N-heterocyclic carbene approach," *Chem. Commun.*, vol. 49, no. 57, pp. 6412–6414, 2013.
- [253] P. Chábera *et al.*, "FeII Hexa N-Heterocyclic Carbene Complex with a 528 ps Metal-To-Ligand Charge-Transfer Excited-State Lifetime," *J. Phys. Chem. Lett.*, vol. 9, no. 3, pp. 459–463, 2018.
- [254] B. J. Coe *et al.*, "Pentacyanoiron(II) as an electron donor group for nonlinear optics: Medium-responsive properties and comparisons with related pentaammineruthenium(II) complexes," *J. Am. Chem. Soc.*, vol. 128, no. 37, pp. 12192–12204, 2006.
- [255] I. Deligkiozi, E. Voyiatzis, A. Tsolomitis, and R. Papadakis, "Synthesis and characterization of new azobenzene-containing bis pentacyanoferrate(II) stoppered push-pull [2]rotaxanes, with α - And β -cyclodextrin. Towards highly medium responsive dyes," *Dye. Pigment.*, vol. 113, pp. 709–712, Feb. 2015.
- [256] S. Tan *et al.*, "Molecular oxygen adsorption behaviors on the rutile TiO₂(110)-1 $\times$ 1 surface: an in situ study with low-temperature scanning tunneling microscopy," *J. Am. Chem. Soc.*, vol. 133, no. 6, pp. 2002–9, Feb. 2011.
- [257] A. Bhattacharyya, M. P. Schmidt, E. Stavitski, and C. E. Martínez, "Iron speciation in peats: Chemical and spectroscopic evidence for the co-occurrence of ferric and ferrous iron in organic complexes and mineral precipitates," *Org. Geochem.*, vol. 115, pp. 124–137, 2018.
- [258] B. M. Weckhuysen, R. Heidler, and R. A. Schoonheydt, "Electron Spin Resonance Spectroscopy," *Mol. Sieves*, vol. 4, pp. 295–335, 2004.
- [259] Y. Zhao *et al.*, "Ultrafine NiO Nanosheets Stabilized by TiO₂ from Monolayer NiTi-LDH Precursors: An Active Water Oxidation Electrocatalyst," *J. Am. Chem. Soc.*, vol. 138, no. 20, pp. 6517–6524, 2016.
- [260] P. Chábera *et al.*, "A low-spin Fe(III) complex with 100-ps ligand-to-metal charge transfer photoluminescence," *Nature*, vol. 543, no. 7647, pp. 695–699, 2017.
- [261] M. Glöckle and W. Kaim, "An Exceedingly Stable Diiron(ii,iii)," *Angew. Chemie - Int. Ed.*, vol. 38, no. 20, pp. 3072–3074, 1999.
- [262] S. I. Ohkoshi and H. Tokoro, "Photomagnetism in cyano-bridged bimetal assemblies," *Acc. Chem. Res.*, vol. 45, no. 10, pp. 1749–1758, 2012.
- [263] L. M. Baraldo, P. Forlano, A. R. Parise, L. D. Slep, and J. A. Olabe, "Advances in the coordination chemistry of [M(CN)₅L]ⁿ⁻ ions (M=Fe, Ru, Os)," *Coord. Chem. Rev.*, vol. 219–221, pp. 881–921, Oct. 2001.
- [264] B. J. Coe *et al.*, "Nonlinear Optical and Related Properties of Iron (II) Pentacyanide Complexes with Quaternary Nitrogen Electron Acceptor Units," *Inorg. Chem.*, vol. 48, no. 4, pp. 1370–1379, Feb. 2009.
- [265] H. E. Toma and C. Creutz, "Pentacyanoferrate(II) Complexes: Evaluation of Their Formal Potentials and Mechanism of Their Quenching of Tris(2,2'-bipyridine)ruthenium(II) Luminescence," *Inorg. Chem.*, vol. 16, no. 3, pp. 545–550, 1977.
- [266] R. Papadakis and A. Tsolomitis, "Study of the correlations of the MLCT Vis absorption

maxima of 4-pentacyanoferrate-40'-arylsubstituted bispyridinium complexes with the Hammett substituent parameters and the solvent polarity parameters E NT and AN," *J. Phys. Org. Chem.*, vol. 22, no. 5, pp. 515–521, 2009.

- [267] R. Papadakis, "Preferential Solvation of a Highly Medium Responsive Pentacyanoferrate(II) Complex in Binary Solvent Mixtures: Understanding the Role of Dielectric Enrichment and the Specificity of Solute–Solvent Interactions," *J. Phys. Chem. B*, vol. 120, no. 35, pp. 9422–9433, Sep. 2016.
- [268] S. Ardo and G. J. Meyer, "Photodriven heterogeneous charge transfer with transition-metal compounds anchored to TiO₂ semiconductor surfaces," *Chem. Soc. Rev.*, vol. 38, no. 1, pp. 115–164, 2009.
- [269] E. Jakubikova and D. N. Bowman, "Fe(II)-polypyridines as chromophores in dye-sensitized solar cells: A computational perspective," *Acc. Chem. Res.*, vol. 48, no. 5, pp. 1441–1449, 2015.
- [270] D. N. Bowman, J. H. Blew, T. Tsuchiya, and E. Jakubikova, "Elucidating band-selective sensitization in iron(II) polypyridine-TiO₂ assemblies," *Inorg. Chem.*, vol. 52, no. 15, pp. 8621–8628, 2013.