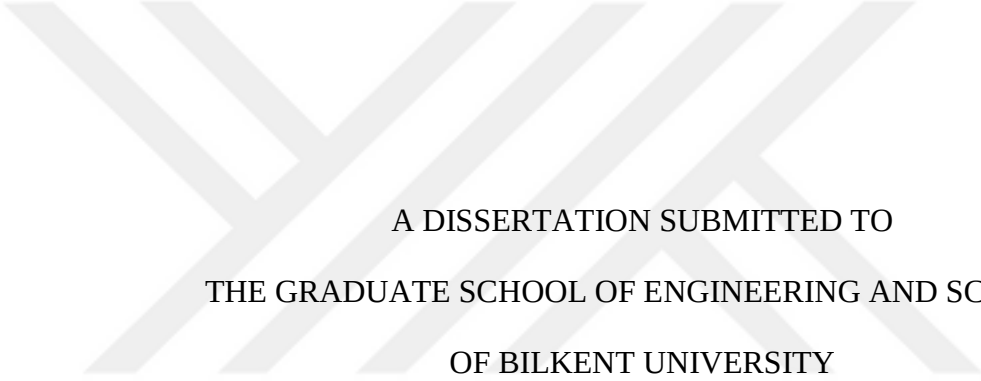


CATALYSIS WITH ENGINEERED PRUSSIAN BLUE ANALOGUES UNDER EXTERNAL BIAS, LIGHT, AND MAGNETIC FIELD



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THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
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By

Ramadan Chalil Oglou

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

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ABSTRACT

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M.S. in Materials Science and Nanotechnology

Advisor: Ferdi Karadaş

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The design of robust and feasible catalysts is one of the main concerns towards a carbon emission-free world. Prussian blue analogues (PBAs), the most well-known family of cyanide-based compounds, offer diversity and facile tunability of the structural components to achieve robust catalysts with high selectivities and reproducibilities. Herein this thesis, the catalytic performances of CoFe PBAs have been investigated for glucose and water oxidation processes. The structure of the Prussian blue (PB) framework has been engineered to tune the morphological and electronic properties for enhanced catalytic activity. In this regard, my thesis could be divided into three sections:

(i) Electrocatalytic glucose oxidation: In the first part of this study, a CoFe PB modified fluorine-doped tin oxide (FTO) electrode, which is prepared via an electrodeposition method, was investigated as a non-enzymatic glucose sensor under neutral conditions. The electrode exhibits a linear detection of glucose in the 0.1 – 8.2 mM range with a detection limit of 67 μM , and a sensitivity of 18.69 $\text{mA mM}^{-1} \text{cm}^{-2}$. Its stability is confirmed with both electrochemical experiments and characterization studies performed on the pristine and post-mortem electrodes. We also conducted a comprehensive electrochemical analysis to elucidate the identity of the active site and the glucose oxidation mechanism on the PB surface. In the second part, a series of PB modified carbon cloth (CC) electrodes were prepared with different cyanoferrate groups. A sensitivity as high as 145.43 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ in a 0.1 – 6.5 mM concentration range is

achieved with a response time below 2 s under physiological pH. The electrodes exhibit a superior selectivity of glucose in the presence of interfering agents, including sucrose, lactose, sodium chloride, ascorbic acid, and uric acid. The electrodes also show outstanding long-term stability over 15 days. Furthermore, we performed comprehensive electrochemical and characterization studies to elucidate the role of the cyanoferrate group on the morphologic and electronic properties of non-enzymatic glucose sensors.

(ii) Photocatalytic water oxidation: We present a simple and easy-to-scale synthetic method to plug common organic photosensitizers into a cyanide-based network structure for the development of photosensitizer-water oxidation catalyst (PS–WOC) dyad assemblies for the photocatalytic water oxidation process. Three photosensitizers, one of which absorbs red light similar to P680 in photosystem II, were utilized to harvest different regions of the solar spectrum. Photosensitizers are covalently coordinated to CoFe PB structures to prepare PS-WOC dyads. All dyads exhibit steady water oxidation catalytic activities throughout a 6 h photocatalytic experiment. Our results demonstrate that the covalent coordination between the PS and WOC groups enhances not only the photocatalytic activity but also the robustness of the organic PS group. We find that the photocatalytic activity of these “plug and play” dyads relies on several structural and electronic parameters, including the position of the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the PS with respect to the HOMO level of the catalytic site, the intensity and wavelength of the absorption band of the PS, and the number of catalytic sites.

(iii) Intermetallic charge transfer induced electrocatalysis: We report a novel route to enhance the sluggish kinetics of oxygen evolution reaction (OER) by manipulating the intermetallic charge transfer (IMCT) of PBAs. It is found that CoFe PBAs with dissimilar charge transfer abilities reveal a positive response for OER under external stimuli such as magnetic field and light illumination, in which the magnitude of enhancement can be correlated to the intensity of metal-to-metal charge transfer (MMCT) profiles rather than the catalytic activity. An enhancement of almost 57% for OER activity is observed under a 1 h light irradiation for the CoFe PBA that exhibits the strongest IMCT nature. Several control experiments are conducted correlating the direct relation of IMCT and external stimuli induced activity involving –electrochemical experiments at varying pH conditions.

Overall, this thesis indicates that CoFe PBAs could be engineered to design robust catalysts for oxidation reactions. Furthermore, they could also be fine-tuned to develop catalytic assemblies, which are responsive to applied bias, magnetic field, and light irradiation. Given the previous efforts in employing PBAs for catalytic applications, this thesis pushes the limits one step forward and brings a new level to this challenge.



Keywords: Prussian blue analogues, glucose oxidation, water oxidation, coordination chemistry, electrocatalysis, photocatalysis, external stimuli.

ÖZET

POTANSİYEL, IŞIK VE MANYETİK ALAN ALTINDA TASARLANMIŞ PRUSYA MAVİSİ ANALOGLARI İLE KATALİZ

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Dayanıklı ve uygulanabilir katalizörlerin tasarımı, karbonsuz bir dünyaya yönelik ana hedeflerden biridir. Siyanür bazlı bileşikler arasında en yaygın olarak bilinen Prusya mavisi analogları (PBA); yüksek seçicilik ve tekrarlanabilirlik ile sağlam katalizörler elde etmek için yapısal fonksiyon çeşitliliği ve kolay işlenebilirliği elverişli kılan önemli malzemeler sınıfına girmektedirler. Bu tezde, CoFe PBA'ların katalitik performansları glikoz ve su oksidasyonu için araştırılmıştır. Buna ek olarak, Prusya mavisi (PB) iskelet yapısının katalitik aktivitesini iyileştirmek üzere birtakım morfolojik ve elektronik tasarımlar gerçekleştirilmiştir. Bu bağlamda tezim üç bölüme ayrılabilir:

(i) Elektrokatalitik glikoz oksidasyonu: Bu çalışmanın ilk bölümünde, elektrodpozisyon yöntemiyle hazırlanan CoFe PB modifiye flor katkılı kalay oksit (FTO) elektrotu, nötr koşullar altında enzimatik olmayan bir glikoz sensörü olarak incelenmiştir. Elektrot, 0,1 – 8,2 mM aralığında, 67 μM algılama sınırı ve 18,69 $\text{mA mM}^{-1} \text{cm}^{-2}$ hassasiyetle doğrusal bir glikoz tespiti sergilemiştir. Stabilitesi, hem elektrokimyasal deneyler hem de kullanım öncesi ve sonrası elektrot üzerinde gerçekleştirilen karakterizasyon çalışmaları ile doğrulanmıştır. Ayrıca aktif bölgenin tanımı ve PB yüzeyindeki glikoz oksidasyon mekanizmasını aydınlatmak için kapsamlı bir elektrokimyasal analiz gerçekleştirilmiştir. İkinci bölümde, farklı siyanodemir gruplarıyla bir dizi PB modifiye karbon kumaş (CC) elektrot hazırlanmıştır. Sensör performansı olarak; 0,1 – 6,5 mM konsantrasyon aralığında 145,43 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ kadar yüksek bir

hassasiyet, fizyolojik pH altında 2 saniyenin altında bir tepki süresi elde edilmiştir. Elektrotlar; sakaroz, laktoz, NaCl, askorbik asit ve ürik asit dahil olmak üzere farklı etkin madde varlığında üstün bir glikoz seçiciliği sergilemiştir. Ayrıca, elektrotlar 15 gün boyunca başarılı uzun vadeli stabilite göstermiştir. Böylelikle, siyanodemir grubunun enzimatik olmayan glikoz sensörlerinin morfolojik ve elektronik özellikleri üzerindeki rolünü aydınlatmak üzere kapsamlı elektrokimyasal ve karakterizasyon çalışmaları gerçekleştirilmiştir.

(ii) Fotokatalitik su oksidasyonu: Fotokatalitik su oksidasyon işlemi için kromofor-su oksidasyon katalizörü (PS–WOC) ikili düzeneklerini geliştirilmek üzere bilinen organik kromoforları siyanür bazlı bir ağ yapısına bağlayarak basit ve ölçeklenebilir bir sentetik yöntem sunulmuştur. Güneş spektrumunun farklı bölgelerini soğurmak üzere, biri fotosistem II'deki P680'e benzer kırmızı ışığı soğuran olmak üzere, üç farklı kromofor kullanılmıştır. Kromoforlar, PS-WOC ikililerini hazırlamak üzere CoFe PB yapılarına kovalent olarak bağlanmıştır. Tüm sistemler, 6 saatlik bir fotokatalitik deney boyunca stabil katalitik aktivite sergilemiştir. Sonuçlarımız, PS ve WOC grubu arasındaki kovalent koordinasyonun sadece fotokatalitik aktiviteyi arttırmakla kalmayıp, aynı zamanda organik PS grubunun sağlamlığını da geliştirdiğini göstermiştir. "Tak ve çalıştır" ikililerin fotokatalitik aktiviteleri; PS'nin en yüksek dolu moleküler yörüngesinin (HOMO) ve en düşük boş moleküler yörüngesinin (LUMO) enerji seviyelerinin katalitik bölgenin HOMO seviyesine, PS'nin absorpsiyon bandının yoğunluğuna ve dalga boyuna, ve katalitik bölgelerin sayısı da dahil olmak üzere çeşitli yapısal ve elektronik parametrelere dayandığını göstermiştir.

(iii) Metaller arası yük transferine dayanan elektrokataliz: PBA'ların metaller arası yük transferini (IMCT) manipüle ederek oksijen üretimi reaksiyonunun (OER) durgun kinetiğini geliştirmek üzere yeni bir yöntem anlatılmıştır. Farklı yük transfer özelliğine sahip CoFe PBA'ların; manyetik alan ve ışık gibi harici uyaranlar altında OER için, katalitik aktivite performanslarından bağımsız ancak metal-metal yük transferi (MMCT) şiddetine bağlı olarak, pozitif bir sonuç ortaya koyduğu bulunmuştur. En güçlü IMCT yapısını sergileyen CoFe PBA için 1 saatlik ışığa maruz bırakıldığında OER aktivitesi için yaklaşık %57'lik bir artış gözlenmiştir. Bahsi geçen savı doğrulamak üzere; IMCT etkisi

ile dış uyarıların neden olduđu aktivite artışını ispatlayan kapsamlı kontrol deneyleri, MMCT profillerinin ortamın pH değeriine bağımlılıđı gösterilerek sağlanmıştır.

Genel olarak, bu tez CoFe PBA'ların oksidasyon reaksiyonları için sağlam katalizörler tasarlamak üzere geliştirilebileceđini göstermektedir. Bunun yanı sıra; PBA'lar harici potansiyel, manyetik alan ve ışığa yanıt veren katalitik yapıların tasarlanmasını elverişli kılmaktadır. Katalitik uygulamalar için PBA'ların kullanılmasına yönelik önceki çabalar göz önüne alındığında, bu tez sınırları bir adım daha zorlayıp bu alana özgün bir seviye getirmektedir.



Anahtar kelimeler: Prusya mavisi türevleri, glikoz oksidasyonu, su oksidasyonu, koordinasyon kimyası, elektrokataliz, fotokataliz, harici uyarımlar.



‘Ars Longa, Vita Brevis.’

Hippocrates

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CHAPTER 1

1. INTRODUCTION

By the 21st century, it is evident that a radical change in the chemical industry is required for a sustainable future. A more sustainable chemistry is inevitable for the production of high-value compounds and fuels to provide a low-cost energy supply. Catalysis is at the heart of most of the chemical processes in the industry as a reliable eco-friendly strategy.[1] A sustainable catalytic reaction should provide little to none polluting products, waste minimization, and valuable products with a high yield.[2] Understanding the catalysis at a molecular level is of great importance for the design of active, robust, and highly selective catalysts. For this reason, recent scientific studies have focused on the elucidation of catalytic mechanisms via characterization techniques, scientific computing, quantum chemistry, molecular modelling, thermodynamics and kinetics, and so forth.[3] In chemical industries, the catalytic oxidation of a compound plays a crucial role compared to other operations (distillation, separation, absorption etc.) which could be easily operated.[4]

Currently; water splitting, biomass upgrading, CO₂ reduction and light alkenes activation are the processes in high demand for selective and efficient catalyst development due to increasing global crises such as energy demand, healthy food and CO₂ emissions.[5] According to the Pimentel report in 1985 [6], catalysis is a significant field in chemistry that deserves high priority for the development of novel technologies which will shape mankind's future. For the advancement of the above-mentioned fields, the development of robust, low-cost, efficient catalytic architectures plays a crucial role.

1.1 CHEMISTRY OF CYANOMETALLATES AND PRUSSIAN BLUE ANALOGUES

More than 65 thousand scientific papers (Scopus Database) have been published on the cyanide-based compounds since the accidentally discovery of the first coordination compound by German artist Diesbach in 1704.[7] Mixing the animal refuse with sodium

carbonate in an iron pot gives a blue precipitate known as Prussian blue, which is followed by a labor work to isolate the main precursor of cyanide-based coordination polymers, potassium ferrocyanide, $K_4[Fe(CN)_6]$. [8] Thus, a new era was established allowing almost all transition metals excluding lanthanides and actinides to form cyanide-based compounds, which have potential applications in catalysis, magnetism, and electronics. [9] In these compounds, cyanide complexes are coordinated to metal ions with coordination numbers ranging from two to eight and oxidation states from 0 to +5. [8]

The cyanide ion (CN^-) has an electronic configuration of $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (4\sigma)^2 (1\pi)^4 (5\sigma)^2$, isoelectronic with N_2 , CO , and NO^+ , which corresponds to a triple bond between the carbon and nitrogen atom with a distance of 1.16 Å and vibrational frequency of 2080 cm^{-1} for the free cyanide ion. [7] A representative molecular orbital diagram of cyanide ion is presented in Figure 1.1. Herein, the highest occupied molecular orbital (HOMO) is a 5σ orbital while the lowest unoccupied molecular orbital (LUMO) is a $2\pi^*$ orbital.

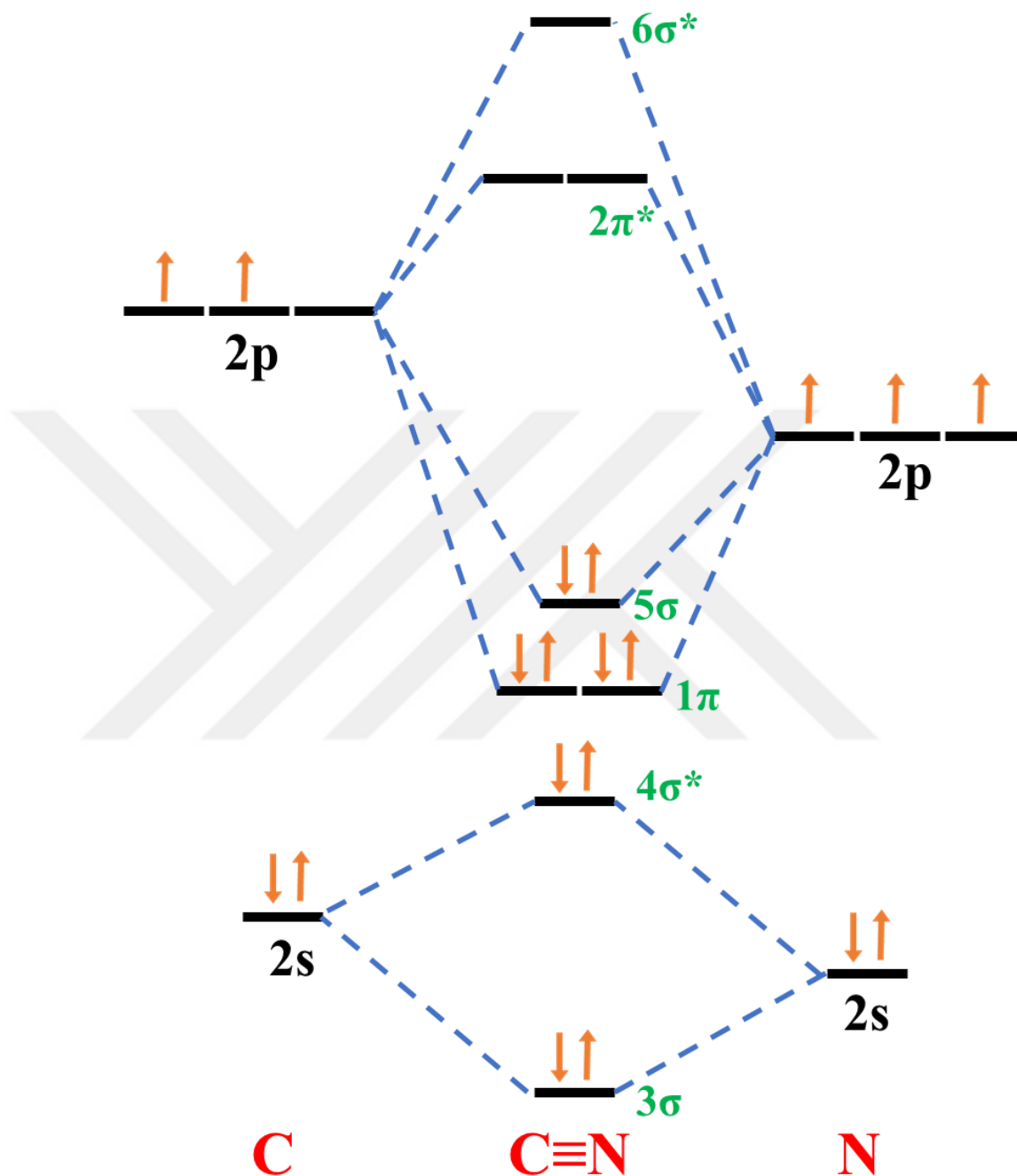


Figure 1.1 A representative illustration of cyanide ion molecular orbital diagram.

Computational studies indicates that the negative charge is equally distributed on both carbon and nitrogen atom and the cyanide ligand binds through the carbon atom (monodentate) since HOMO and LUMO are mainly carbon in character.[10] Carbon-bonded cyanide ligand is considered as a high-field ligand. For example, iron center is in

its low spin electronic configuration in $[\text{Fe}(\text{CN})_6]^{4-}$ and cobalt ion is a diamagnetic ion in the square planar Co complex, $(\text{PPN})_2[\text{Co}(\text{CN})_4]$, proving itself as a strong field ligand.[11] The resulting M–CN bond forms a strong σ -bond (electron donation from the ligand to the metal) and a relatively weak π -bond (electron donation from the metal to the ligand) as a result of interaction of HOMO and LUMO of cyanide ligand with metal d-orbitals.[12] The π -back bonding ability could easily be followed by bond distances of M–C provided from single X-ray diffraction and the cyanide shift from Infrared spectra of compounds. The coordination of cyanide to metal ions ($[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$) starting from Cr to Co (from left to right in the periodic table) leads to a decrease in the bond length of M–CN from 2.08 to 1.98 Å due to the increasing π -back donation towards electron rich metal site. Moreover, the Fe–C bond distances for Fe(II) and Fe(III) are found to be 1.90 and 1.93 Å, respectively, suggesting an increasing back-donation with decreasing the oxidation state of metal ions.[12] On the other hand, the M–CN coordination causes an increase in the $\nu(\text{CN}^-)$ stretch compared to free CN^- ion due to the removal of electrons from 5σ orbital, resulting in a weakening of the $\text{C}\equiv\text{N}$ bond.[13] Furthermore, cyanide group can also use its nitrogen atom to bind to metal ions to form a linear M–CN–M' coordination mode and the coordination of the second metal ion through the nitrogen atom weakens the cyanide bond even further due to the antibonding character of nitrogen lone pair. In addition, Infrared spectra reveal the cyanide peaks at 2098 and 2135 cm^{-1} for $[\text{Fe}^{\text{II}}(\text{CN})_6]^{3-}$ and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ complexes, respectively. Furthermore, the $\nu(\text{CN}^-)$ stretches of $[\text{V}(\text{CN})_6]^{n-}$ ($n=3,4$ or 5) for the oxidation states of V(I), V(II) and V(III) are found to be 1910, 2065 and 2977 cm^{-1} , respectively.[13] These trends clearly reveal that the $\nu(\text{CN}^-)$ stretches could be used to evaluate the electronic properties of the complex and allow a tunable property over the structure considering the electronegativity, coordination number, and the oxidation state of the metal site. Figure 1.2 briefly summarizes the above-mentioned issues.

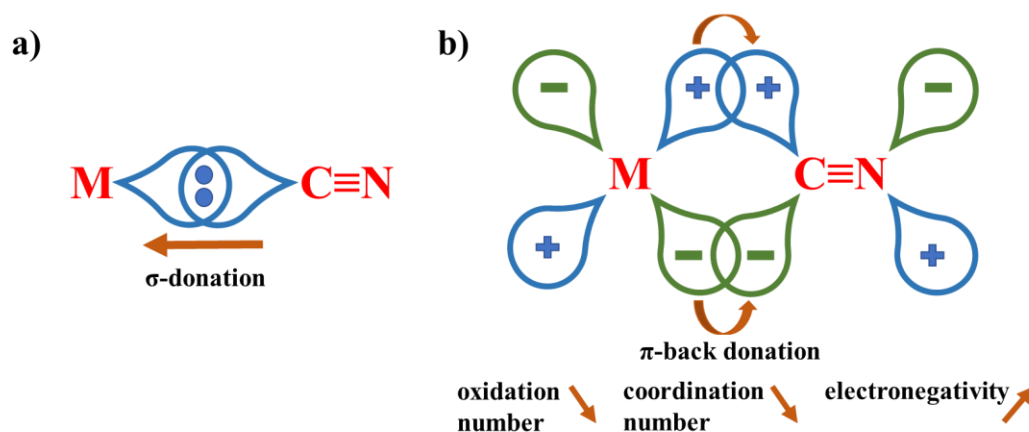


Figure 1.2 (a) σ -donation and (b) π -back donation of cyanide ion from the metal site through the bonding orbitals. The relating trends of the metal site for enhanced π -back donation ability is demonstrated.

The well-known Prussian blue (PB), $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$, has been described first by Woodward et al.[14] and characterized by Ludi et al.[15] as a 3D framework of Fe(II) and Fe(III) ions coordinated via a cyanide bridge to form a face-centered cubic structure. The extended network structure contains defects due to the valence ratio of 4:3 and these vacancies are filled by water molecules.

Prussian blue analogues (PBAs) could easily be synthesized by mixing a hexacyanometalate precursor with a 3d transition metal salt to form a bimetallic coordination compound. A typical PB has the molecular formula of $\text{A}_n\text{M}_x[\text{M}'(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$, where A is an alkali metal ion to provide the charge balance of the network formed by the coordination of M and M' transition metals with mixed oxidation states.[16]

Given the diversity of PBAs, their structures could easily be tuned to meet the requirements of a desired application. The rigid and short cyanide ligand ($\sim 5 \text{ \AA}$) allows an ideal pathway for the superexchange of metal sites offering promising optical, electronic, magnetic, and catalytic properties.[17] For example, the unique structure with counter cations in the microchannels allows easy transport of ions, which makes it an efficient electrode material for energy conversion and storage applications.[18] Moreover, the variation of oxidation states of metal ions has been utilized for the design of electrochromic and biosensing devices.[19–21] Besides these unique features, the earth-

abundance of structural components is another significant parameter for potential commercialization of PBAs.

Hexacyanoferrate complex is the most common precursor for the preparation of PBAs. The substitution of a ligand with one of the cyanide ligands in the octahedral coordination sphere of iron in hexacyanoferrate complex has also been studied to extend the potential applications of PBAs. Swinehart et al. [22] reported a decent approach, which involves the coordination of an acceptor nitrosonium ion to the complex to produce sodium pentacyanonitrosylferrate (II) complex, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$. The synthesis is achieved, although, with a relatively low yield due to strong coordination of CN^- ligand to iron. Asmus et al. [23] explained a straightforward method to substitute the NO ligand with weakly coordinated ligands, such as H_2O , NH_3 , and SO_3^{2-} to provide novel functionalities. Among them, pentacyanoamino-ferrate complex, $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$, has contributed significantly as a precursor due to the facile substitution of NH_3 ligand with pyridyl containing ligands (Figure 1.3). Wang et al. proved that the crystalline nature of PB could be reduced significantly by using pentacyanoferrate complex $[\text{Fe}(\text{CN})_5\text{L}]^{3-}$, $\text{L} = \text{NH}_3$, pyridine, 4-(dimethylamino)-pyridine (DMAP), and pyrazine) as a precursor.[24] A decrease in the crystallinity of PB framework enhances the number of defects, which, thus, enhances the number of active metal sites compared to highly crystal metal hexacyanoferrate compounds providing extended structural and morphological properties.

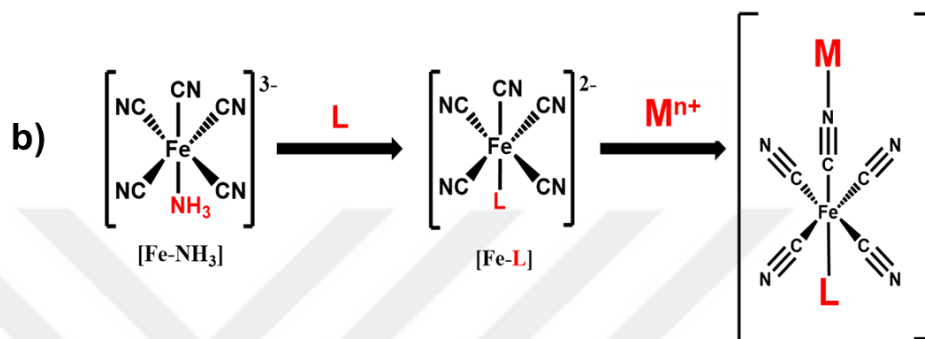
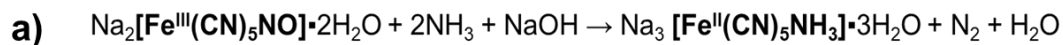


Figure 1.3 (a) The substitution of nitrosyl with ammonia ligand on pentacyanoferrate group and (b) two-step synthetic route starting with substitution of ammonia and coordination of second metal to afford [MFe-L] systems.

Cobalt hexacyanoferrate (CoFe) is one of the most known members of the PBAs since they have highly active cobalt sites and switchable physical properties using external stimuli, which have potential applications in photomagnetism, catalysis, and small molecule sensing (Figure 1.4). Co:Fe atomic ratio in a typical CoFe PBA could range from 1 to 2 depending on the reaction conditions and the required charge balance is compensated by the insertion of an alkali cation. Furthermore, the oxidizing ability of cobalt sites to higher oxidation states ($+2 \rightarrow +3 \rightarrow +4$) and the coordination of water molecules to cobalt sites, which are located on the surface of the complex, provides a suitable environment for water oxidation and reduction catalysis.[25] Up to now, cobalt-based PBAs are utilized as robust and stable water oxidation catalysts (WOCs) and the inactive iron site is found to serve as a donor group to the electron-deficient cobalt site during the water oxidation process.[26]

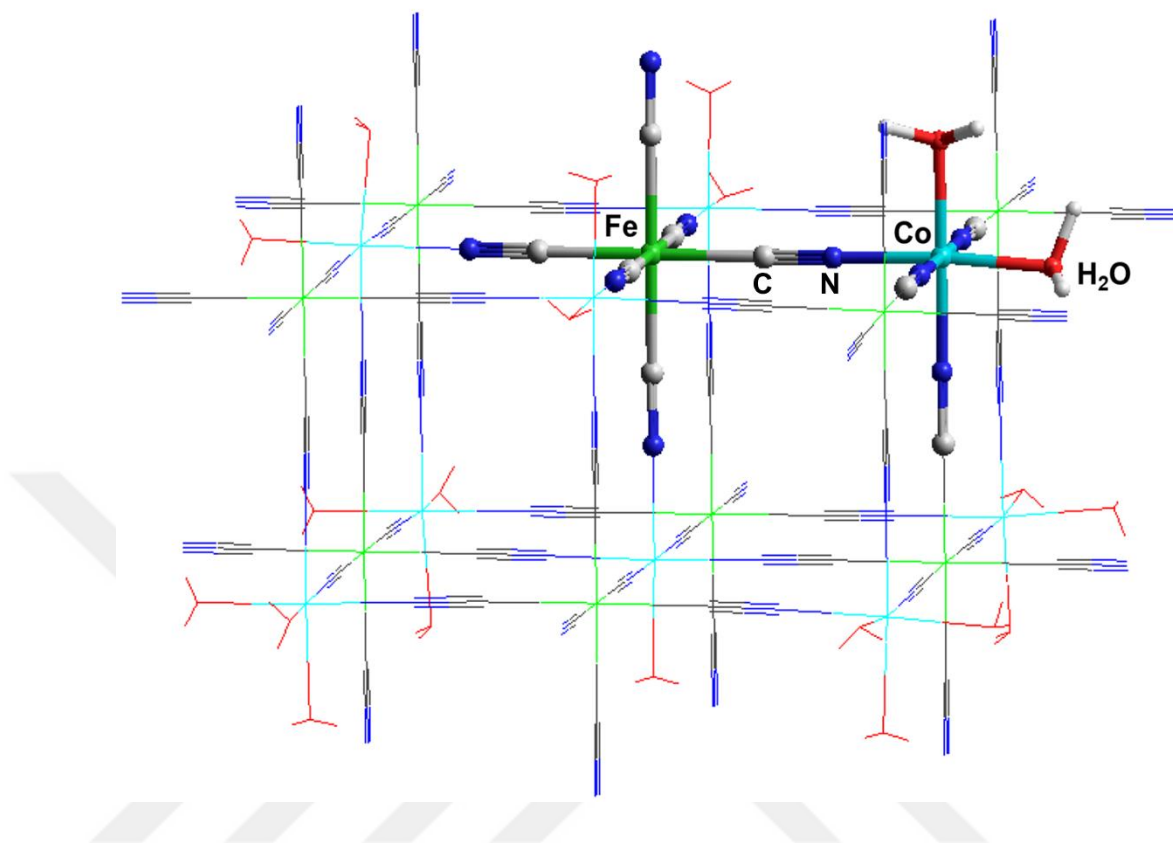


Figure 1.4 A typical unit structure of CoFe PB network.

1.2 CATALYTIC APPLICATIONS

1.2.1 Glucose Oxidation

Biomass has been considered as an earth-abundant alternative source to fossil-fuel based ones in chemical plants over the last years. Given the tremendous amount of organic waste (wood, food, plants etc.), lignocellulosic based materials are the pioneer of this class for the conversion of biomass into high-value chemicals. However, the treatment procedures like pyrolysis, gasification, or liquid-phase reforming increase the cost of such an inexpensive feedstock.[27] For this reason, catalytic oxidation processes are promising approaches for the conversion of biomass to beneficial chemicals by breaking a hydrogen bond (i.e. alcohol oxidation to aldehyde) or forming an oxygen bond (i.e. alcohol oxidation to carboxylic acid) on the organic molecule.

Cellulose accounts for nearly 50 % of lignocellulose and the rest is lignin and hemicellulose. [28] Therefore, cellulose is a crucial key for upgrading organic residues to

renewable chemicals and fuels. The high chemical and physical stabilities of cellulose limit their conversion under mild conditions[29] and the hydrolysis of this long-chain polymer to its monomer (glucose) is needed for further applications.[29,30] Therefore, glucose oxidation could play a pioneering role in biomass upgrading as it is the initial step in biomass conversion. Glucose is highly soluble in aqueous media and it is the primary ingredient of saccharides. It remains in an equilibrium with close and long-chain polyol structures in aqueous solutions (Figure 1.5).[31]

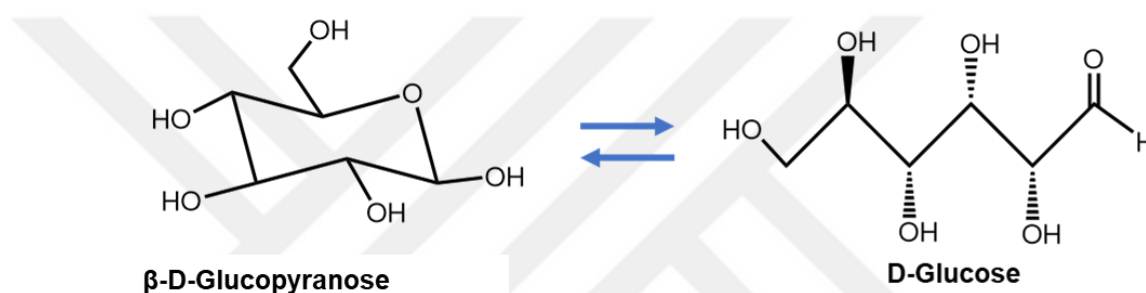


Figure 1.5 The equilibrium of glucose in close and long-chain polyol structures in the aqueous medium.

The catalytic oxidation of glucose has been widely investigated in recent years due to its abundance and facile processing. The oxidation of glucose could result in the formation of numerous products depending on the pH and temperature of the medium. Gluconolactone is known as the common product of the oxidation reaction and it is a high demand precursor in the food, textile, and pharmaceutical industries.[32] Further oxidation steps could produce various high-value chemicals as shown in Figure 1.6.

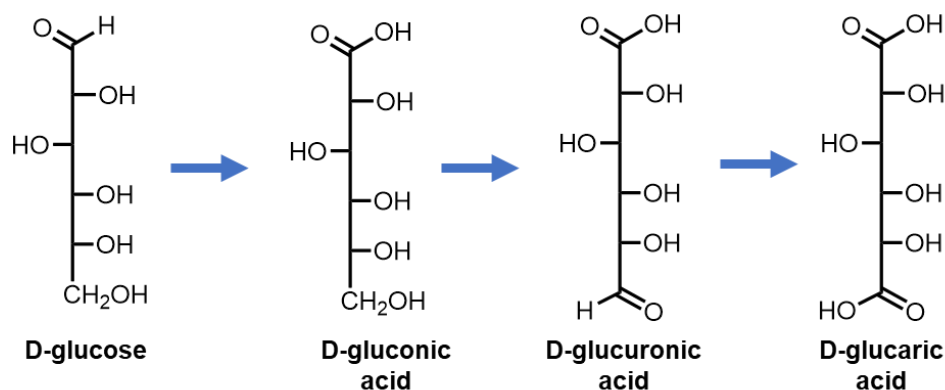


Figure 1.6 The possible products of the glucose oxidation process.

Another great significance of the glucose oxidation process is the fabrication of glucose sensors for diabetes monitoring, fermentation, and agricultural applications.[33–38] These high-tech products are already placed in our daily life and offer high standards of living. Glucose detection devices could operate using optical [39], electrochemical [37], and fluorescence-based [40] methods providing direct or indirect detection of glucose levels. Among them, electrochemical detection of glucose offers extremely low detection levels and facile synchronization with other electronic devices (i.e. mobile phones).

The first electrochemical enzymatic glucose sensor is reported by Clark and Lyons in 1962, which involves the use of glucose oxidase (GOx) enzyme on the surface of the electrode.[41] In the presence of glucose, the GOx converts the O_2 to H_2O_2 and, thus, a proportionality could be assumed by reduction of O_2 and increase of glucose level in the medium (Figure 1.7). The indirect measurement of glucose levels introduces a new platform for the design of sensors. However, Wilson and Turner stated that the restricted working conditions (anaerobic environment, pH 2–8 and $<40\text{ }^{\circ}\text{C}$) of enzyme shortens the shelf-life of the sensors.[42]

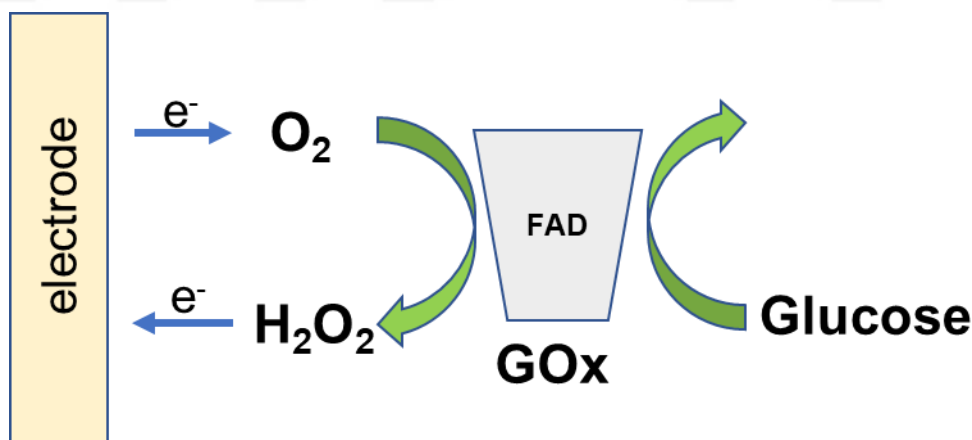


Figure 1.7 The first-generation enzymatic glucose sensor.

The design of enzyme-free electrodes for direct oxidation of glucose is of major significance in recent years. The utilization of noble metals such as Pt, Au, or Pd has been the first attempts in this field.[43] Figure 1.8 exhibits the reaction mechanism for the electrocatalytic oxidation of glucose by a Pt electrode in a neutral medium. However, the high cost and poor selectivity are the main problems to be addressed for these precious metals. On the other hand, low-cost transition metal oxides such as Co_3O_4 [44], CuO [45],

and MnO_2 [46] are able to oxidize the glucose with a high selectivity under alkaline conditions, while they exhibit poor activities in neutral environment. Therefore, it is clear that the oxidation environment is a significant parameter that affects the activity, selectivity, and stability of the non-enzymatic electrode. Recently, a few studies reported PB derived electrodes as efficient catalysts for the oxidation of glucose under alkaline conditions.[47–50] On the other side, the possible transformation of PBAs to oxides in alkaline conditions [51] raises the question whether the origin of the activity is from an oxide or a PB. The stability of PBAs in a wide range pH (1–13) and the need for glucose oxidation in ambient conditions put the PB modified electrodes at the center of interest for further investigation.

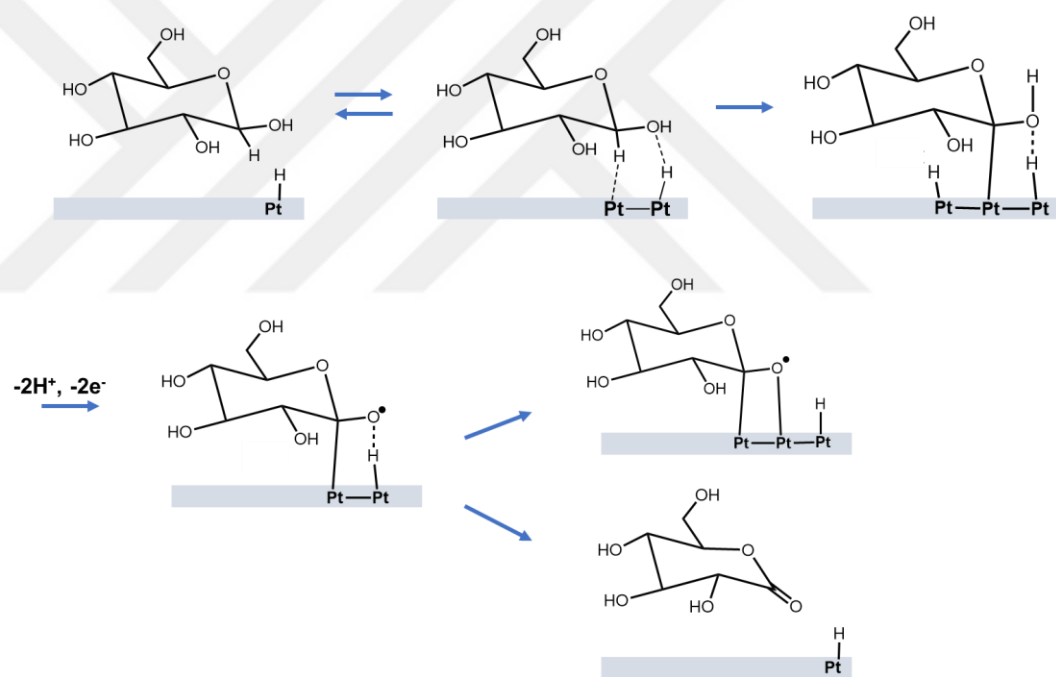
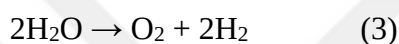
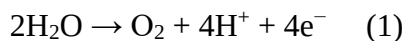


Figure 1.8 The glucose oxidation mechanism of Pt electrode in neutral pH.[43]

1.2.2 Water Oxidation

When cyanobacteria displayed the first oxygen evolution reaction 3.5 billion years ago, prokaryotic living forms took the initial steps toward the existence of life.[52] This fundamental reaction, later, evolved to *photosynthesis*, the essential cycle of life. Harvesting the sunlight to convert H_2O and CO_2 to O_2 and carbohydrate are the main processes of Photosystem I and II enzyme-cofactor complexes in natural

photosynthesis.[53] Mimicking this well-designed system could pave the way for clean and sustainable energy sources (O_2 or H_2) under mild conditions using water as an abundant and renewable feedstock.[54] An artificial photosynthetic system could be designed by splitting water into molecular oxygen and hydrogen coupling two half-reactions known as oxygen evolution reaction (OER) and hydrogen evolution reaction (HER),[55,56] (i) oxidation of H_2O to O_2 and (ii) reduction of protons to H_2 :



Nevertheless, the laborious thermodynamics and kinetics of OER necessitate the use of a catalyst to boost the sluggish kinetics. An ideal catalyst should accomplish a complete $4H^+/4e^-$ (proton-coupled electron transfer) oxidation to decrease the kinetic barrier for enhanced OER. For this reason, numerous studies focused on the development of effective and feasible water oxidation catalysts (WOCs) that operate at quite low overpotentials (<500 mV).[57] The utilization of solar or electrical energy to activate the catalyst for charge separation has been accepted as one of the most promising routes due to its cost-effective and eco-friendly aspects.[58]

1.2.2.2 Electrocatalytic water splitting

Electrocatalytic water splitting involves the OER ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) at the anode and HER ($4H^+ + 4e^- \rightarrow 2H_2$) at the cathode of the electrochemical setup (Figure 1.9). The use of an electrocatalyst has two main goals: (i) to reduce the overpotential of the reaction and (ii) to boost the reaction rate further, which will then allow a decrease in the total input electrical power.[59] Although the computational studies find it convenient to apply a potential of 1.23 V vs. NHE for overall water splitting, practical applications reveal that there is a need for higher potentials (overpotential) to overcome a series of resistances for the activation barrier of the electrode. Ir/Ru based electrode materials demonstrated significant activities for OER with comparable low overpotentials [60], and similarly, Pt-based electrode stand forward for HER [61]. However, their low abundance

and inadequate stabilities restrict further scale-up applications. On the other side, recent studies mainly focused on developing earth-abundant and promising electrocatalysts such as phosphides, oxides, nitrides, and carbides for both OER and HER.[59]

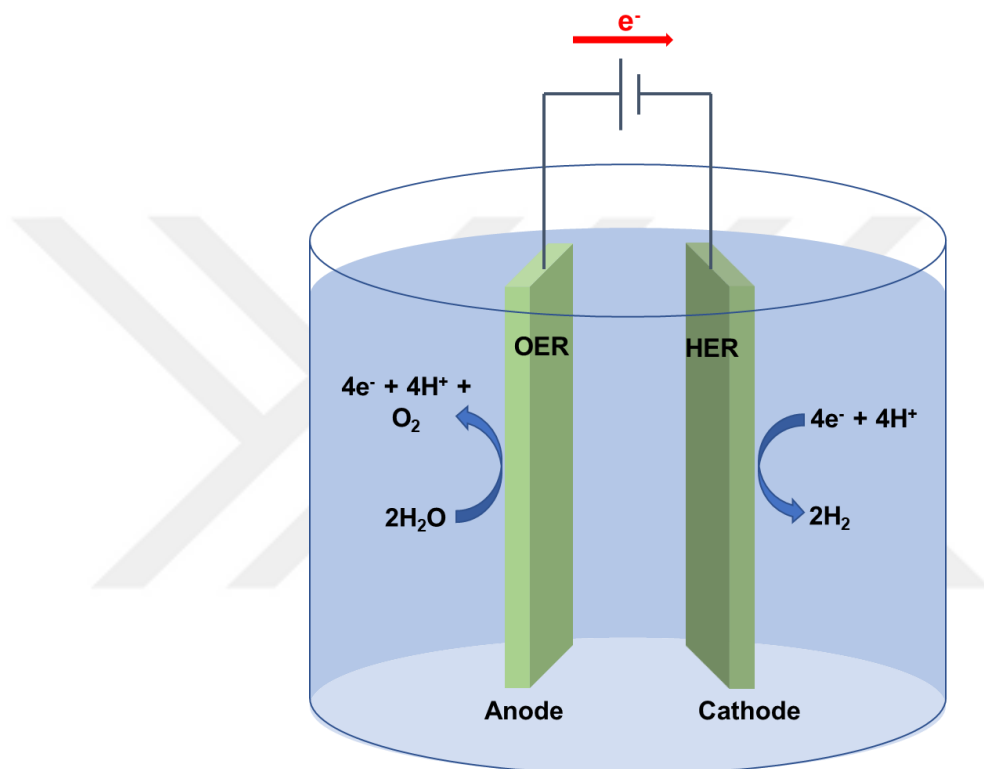
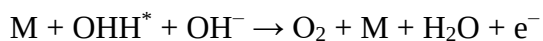
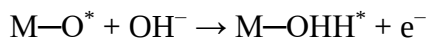
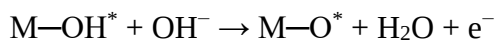
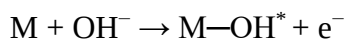


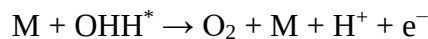
Figure 1.9 Electrocatalytic water splitting in a typical electrochemical setup.

Due to the highly complex mechanism and unfavorable kinetics of OER, a larger overpotential is essential to push the kinetics. The OER mechanism steps of a metal-based catalyst at the anode for the different environments are as follows [62]:

In alkaline solutions,



In acidic solutions,



Although the intermediate species exist in both acidic and alkaline media, the higher amount of OH^- species in alkaline media facilitates the water oxidation process offering much higher activities compared to the acidic media.[63] Moreover, access to the catalytic sites and electron transfer ability are other key parameters, which should be considered for the design of catalysts. Introducing new defects or making less crystalline structures could enhance the number of catalytic sites to afford a higher oxygen evolution rate.[59] In this regard, the insertion of heteroatoms is another reliable method for the enhanced conductivity of the catalyst for better charge transfer.[64] Tuning both morphological and electronic properties of a material is, thus, of great importance for the fabrication of promising catalysts.

PBAs are widely investigated for electrocatalytic water oxidation with various metal hexacyanoferrates ($M = Mn, Fe, Co$ and Ni), and among them, CoFe PB is proved as the most active catalyst in this family.[25,65] Compared to metal oxides and noble metal-based systems, CoFe is able to exhibit high stabilities in a wide range of pH (pH 1 – 13) as confirmed by long-term chronoamperometric studies.[51] The coordination environment of active catalytic sites, inactive cyanometalates, and the rigidity of the cyanide bridge are the key parameters that affect the catalytic performances of PB frameworks. The TOF value of the Co_3O_4 electrode is higher than the CoFe modified electrode [25] mainly due to the low surface concentration of active catalytic sites in a CoFe PBA (It is 1000 times lower than bulk oxide structures due to the long cyanide linkage). However, it is evident that this activity could be enhanced further by engineering the PB structures by utilizing their diverse and facile syntheses. The electrocatalytic water oxidation activities of PB based electrodes are represented in Table 1.1.

Table 1.1 Electrocatalytic water oxidation activities of PB electrodes.

PBA [M'–NC–M]	Formula	η_{onset} , mV	TOF, s ⁻¹	Tafel Slope, mV dec ⁻¹	Ref.
[Co–Fe]	K _{2x} Co _(2-x) [Fe(CN) ₆] (0.85<x<0.95)	N/A	2.6 × 10 ⁻³ at η =305 mV	85-95	[66]
[Co–Fe(CN) ₆ –P4VP]	Co _{1.5} [Fe(CN) ₅ P4VP]	360	2.6 × 10 ⁻³ at η =284 mV	111	[67]
[Co–Co ^{III}]	K _{0.38} Co _{0.131} [Co(CN) ₆]	283	5 × 10 ⁻² at η =400 mV	99	[65]
[Co–Cr ^{III}]	K _{0.41} Co _{0.129} [Cr ^{III} (CN) ₆]	303	5 × 10 ⁻³ at η =400 mV	96	[65]
[Co–Fe ^{III}]	K _{0.31} Co _{0.135} [Fe ^{III} (CN) ₆]	323	4.4 × 10 ⁻³ at η =400 mV	127	[65]
[Co–Fe ^{II}]	K _{0.70} Co _{0.165} [Fe ^{II} (CN) ₆]	343	3 × 10 ⁻³ at η =400 mV	121	[65]
[Co–Fe–isn]	Co ₂ [Fe(CN) ₅ isn]	324	7 × 10 ⁻³ at η =400 mV	146	[68]

An important parameter that affects the catalytic activity is the method of deposition. For example, electrodeposition has been found to give different activities compared to drop-casting since they reveal PBAs with different electronic properties and surface concentration.[25,65] In this regard, a higher TOF value of electrodeposited electrode emphasizes the significance of electronic properties. Furthermore, our group reported the synthesis of less crystalline CoFe PB structure using a polymer-bound pentacyanoiron precursor ([Co–Fe(CN)₆–P4VP]).[67] The asymmetry of structure caused by the polymer group introduced an increase in the number of active sites and a convenient environment for electrochemical reactions offering a better catalytic activity.[69] A similar approach was stated by Bonacin et al. using a [Fe(CN)₅(isn)] complex (isn=isonicotinate) to afford a CoFe PB.[68] Changing the coordination environment of cyanoiron precursor from hexa- to penta- is a beneficial approach to enhance the catalytic activity. Moreover, our group reported the effect of different cyanometallate precursors, which could give a better understanding of the electronic properties of PB for electrocatalytic water oxidation. It is

found that the $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$ is more active than the $\text{Co}^{\text{II}}\text{Fe}^{\text{II}}$ with around 15 times higher TOF value.[65] Common approaches to the above-mentioned methods were also published by making either nano-sized PB structures or Fe-doping networks elucidating both morphological and electronic properties of the PB framework for efficient electrocatalytic water oxidation processes.[51,70,71]

1.2.2.1 Photocatalytic water splitting

The photocatalytic water splitting process is a highly encouraging route due to the practically unlimited energy amount supplied by sunlight. Water splitting involves three main steps: (i) the photocatalyst absorbs photons based on its band gap to generate photoexcited electron-hole pair, (ii) the photoexcited charges separate and migrate to the surface of the catalyst without recombination, and (iii) adsorbed species are reduced and oxidized by the photogenerated electrons and holes to produce H_2 and O_2 , respectively (Figure 1.10).[72] The sluggish kinetics and the possible electron-hole recombination rates are the parameters that restrict the OER and the solar conversion efficiency. TiO_2 is considered the most investigated photocatalyst up to now, thanks to its high stability and activity. However, the photon absorption of this wide band gap (3.2 eV) semiconductor in the ultraviolet region (UV) limits its scale-up applications considering the tiny fraction of UV irradiation (~5 %) in the whole solar light. On the other hand, visible light accounts for 45 % of the solar spectrum pushing the demand for the development of a visible-light absorber photocatalyst with a narrow band gap and systems that can absorb a larger fraction of solar light.[73] Furthermore, efficient charge separation and transfer of photocatalyst could be achieved with a conduction band (CB) more negative than the redox potential of H^+/H_2 (0.0 V vs. NHE) and valence band (VB) more positive than the redox potential of $\text{O}_2/\text{H}_2\text{O}$ (1.23 V vs. NHE) for an ideal energy level alignment of overall water splitting as suggested by computational studies.[74]

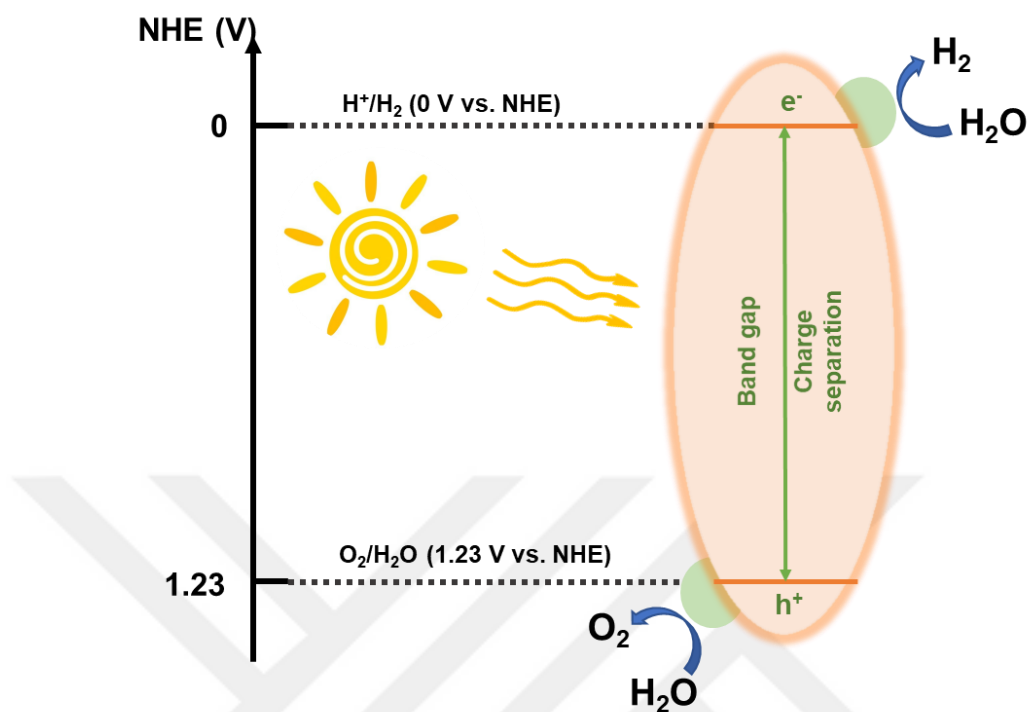


Figure 1.10 Primary steps of photocatalytic water splitting.

An efficient collaboration of a robust water oxidation catalyst (WOC) with a proper light absorbing unit (photosensitizer (PS) or semiconductor (SC)) is of great interest in the field of photocatalysis. On the other hand, many attempts have been proposed to connect a PS unit to a WOC (dyad assembly) via covalent coordination for a more efficient charge transfer compared to a physical mixture of components.[75] Thus, the efforts to mimic the natural photosynthesis have introduced several assemblies of donor and acceptor units with enlarged compartments such as triads, tetrads, or even pentads.[76–78] Due to their long excited-state lifetimes and efficient light-absorbing abilities, ruthenium-based units are widely investigated for the development of PS-WOC dyad assemblies. Thummel et al. proved that a covalently coordinated Ru-Ru dyad could demonstrate more than ten times higher TON compared to separate molecular systems and this photocatalytic activity pretty much depends on the ligand environment of the catalytic metal center.[79,80] Similarly, Sun et al. showed that the coordination of ruthenium diimine photosensitizer to ruthenium-based catalyst could increase the TON almost five times compared to the intermolecular systems.[81] Given the high cost and easy decomposition of ruthenium units under photocatalytic conditions, novel routes were proposed to avoid

photodegradation and to find alternative earth abundant components. In this regard, Sun et al. utilized a Co_4O_4 cubane system as a WOC with a promising performance [82], and several approaches, led by Waters et al. [83] and Hisaeda et al. [84], were reported, which involve the use of polymeric platforms to assemble PS-WOC systems to provide an intra-assembly charge transfer known as the hopping mechanism along the chain. It is obvious that the design of an entirely earth-abundant and robust PS-WOC assembly with comparable long excited lifetimes is still one of the greatest challenges in this field.

PBAs serve as prospective candidates for the development of earth-abundant WOCs for practical applications. CoFe PBA provides a proper HOMO level which is located below the redox potential of $\text{O}_2/\text{H}_2\text{O}$ for a suitable charge transfer.[26] A comprehensive work came by Galán-mascarós et al., which reported metal hexacyanometallates as an efficient and robust photocatalytic system for water oxidation in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$ ($\text{S}_2\text{O}_8^{2-}$ as an electron scavenger).[85] Among them, CoFe and CoCo photocatalysts demonstrated the highest TOF values of 4.5×10^{-4} and $8.1 \times 10^{-4} \text{ s}^{-1}$, respectively. This could be attributed to a proper energy alignment between the HOMO level of the photosensitizer and the HOMO of the cobalt-based PB WOCs to avoid charge recombination. A follow-up study that came up by our group, which demonstrated that the coordination of a pyridyl containing ruthenium PS to a pentacyanoferrate complex, then to the cobalt ion affords a CoFe–Ru dyad system with a TOF value of $4.5 \times 10^{-4} \text{ s}^{-1}$. This is considered as one of the first examples of Prussian blue-based PS-WOC dyad assemblies.[86] A breakthrough work, later, presented the first entirely earth-abundant PS-WOC assembly by coordinating a porphyrin PS to the PB analogue, CoFe–TPyP, with a relatively high TOF value ($3.2 \times 10^{-4} \text{ s}^{-1}$) compared to noble metal-based systems.[87] Given the simple synthesis, diversity, and robustness of these systems, their slight modifications could result in a significant enhancement in the performance.

1.3 MANIPULATING THE SWITCHABLE PROPERTIES OF PBAS USING EXTERNAL STIMULI

The design and development of tunable materials with switchable properties using external stimuli at the molecular level is the ultimate goal of nanotechnology. Compounds

that display electron-transfer-induced valence tautomerism are more favorable considering the structurally engineered molecules.[88] The ability of mixed oxidation state metal ions to transfer electrons between two metal sites via an external stimulus is a decent example for materials with switchable electronic properties, namely a metal-to-metal charge transfer (MMCT).[89]

In this concept, PBAs have been widely investigated due to their outstanding reversible MMCT features.[88] PBAs with different transition metals and cyanometal precursors that demonstrate MMCT property are represented in Table 1.2. Among them, CoFe is of utmost importance due to the more facile excitation of the Co spin state using a wide variety of induction including light [90–92], temperature [93,94], pressure [95], and electric field.[96] The first breakthrough study that involves the discovery of the photoswitchable bistable CoFe PB ($\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6] \cdot 6.9\text{H}_2\text{O}$) by Sato et al. [90] in 1996, reported that the red-light irradiation (660 nm) could result in an electron transfer between the cobalt and iron sites switching from a diamagnetic state ($\text{Fe}_{\text{LS}}^{\text{II}}\text{--CN--Co}_{\text{LS}}^{\text{III}}$) to a paramagnetic state ($\text{Fe}_{\text{LS}}^{\text{III}}\text{--CN--Co}_{\text{HS}}^{\text{II}}$) at around 5 K. The reversible scenario could be observed by blue light illumination (450 nm) for the same temperature, and all these transitions could be followed by pristine-post magnetic (increase and decrease in magnetization attributed to diamagnetism and paramagnetism, respectively) and Infrared spectroscopy (the cyanide peaks at 2162 and 2116 cm^{-1} are ascribed to $\text{Fe}^{\text{III}}\text{--CN--Co}^{\text{II}}$ and $\text{Fe}^{\text{II}}\text{--CN--Co}^{\text{III}}$, respectively) characterizations. Numerous follow-up studies came up by Sato et al. [97,98], Bleuzen et al. [99,100], and Verdaguer et al. [101,102] to elucidate this phenomenon. Sato et al. replaced the K^+ with Rb^+ cation ($\text{Rb}_{0.66}\text{Co}_{1.25}[\text{Fe}(\text{CN})_6] \cdot 4.3\text{H}_2\text{O}$) to afford a significant increase in $\text{Fe}^{\text{II}}\text{--CN--Co}^{\text{III}}$ configuration with a remarkable photo-enhanced magnetization and magnetic ordering temperature (from 16 to 22 K). Thus, it is found that the ligand field of cobalt ($\text{CoN}_{4.8}\text{O}_{1.2}$) is sufficiently strong to stabilize the diamagnetic $\text{Fe}_{\text{LS}}^{\text{II}}\text{--CN--Co}_{\text{LS}}^{\text{III}}$ state due to the fewer vacancies compared to CoN_4O_2 . A further study by Verdaguer et al. suggested the insertion of Cs^+ cation ($\text{CsCo}_{1.03}[\text{Fe}(\text{CN})_6] \cdot 3.3\text{H}_2\text{O}$) to the PB network introducing almost no vacancy (CoN_6), however, the photo-induced magnetization found to be relatively weak and it is concluded that the existence of diamagnetic pairs is a must but an excess of it diminishes the activity. It is obvious that the Co:Fe atomic ratio and coordination environment of cobalt sites are

crucial parameters for enhanced charge transfer. Over the years, the three-dimensional (3D) bulk PB structure is found to be consists of inactive diamagnetic or paramagnetic pairs which restrict the charge transfer for further efficiency.[103] Therefore, the construction of low dimensional MMCT networks has been introduced using building-block approaches including di-, tri-, tetra- or pentanuclear clusters.[88] The first well-known evidence of low dimensional pentanuclear PB is reported by Dunbar et al. proving a thermally induced MMCT between $[(\text{Co}^{\text{II}}_{\text{HS}})_3(\text{Fe}^{\text{III}}_{\text{LS}})]_2$ and $[(\text{Co}^{\text{II}}_{\text{HS}})_2\text{Co}^{\text{III}}_{\text{LS}}\text{Fe}^{\text{II}}_{\text{LS}}\text{Fe}^{\text{III}}_{\text{LS}}]$ states.[104] A few years later, Holmes et al. presented the first molecular fragment of a 3D PB network which is able to display both thermally and photo-induced charge transfer (transition between $(\text{Fe}^{\text{III}}_{\text{LS}}\text{Co}^{\text{II}}_{\text{HS}})_4$ and $(\text{Fe}^{\text{II}}_{\text{LS}}\text{Co}^{\text{III}}_{\text{LS}})_4$ states).[105] Regarding these distinguished studies, countless more have been published in recent years including Lescouëzec et al. [106] and Zhang et al. [107] with more extended contents. It is noteworthy to highlight that the coordination environment of a metal site such as accepting or donating ligands, the crystallinity of the structure, the oxidation state of metal ions and the solution medium are highly crucial parameters that affect the charge transfer between two metals.[89] Recently, Collet et al. studied in detail the ultrafast electronic and structural dynamics of CoFe PB under light illumination and it is found that spin transition initially takes place on Co site in ~ 50 fs, and thus, this triggers the following charge transfer from Fe to Co within ~ 200 fs.[108]

Table 1.2 PBAs with external stimuli tuned MMCT. T and $h\nu$ represent the thermal and light irradiation, respectively.

PBA [M'–NC–M]	MMCT coupled spin transition	External stimuli	Ref.
[Mn–Fe]	$[\text{Fe}^{\text{II}}\text{--CN--Mn}^{\text{III}}] \xrightarrow{\text{red}} [\text{Fe}^{\text{III}}\text{--CN--Mn}^{\text{II}}] \xleftarrow{\text{blue}}$	T, $h\nu$	[109–111]
[Mn–W]	$[\text{W}^{\text{IV}}\text{--CN--Mn}^{\text{III}}] \xrightarrow{\text{red}} [\text{W}^{\text{V}}\text{--CN--Mn}^{\text{II}}] \xleftarrow{\text{blue}}$	$h\nu$	[112]
[Fe–Fe]	$[\text{Fe}^{\text{II}}\text{--CN--Fe}^{\text{III}}] \xrightarrow{\text{red}} [\text{Fe}^{\text{III}}\text{--CN--Fe}^{\text{II}}] \xleftarrow{\text{blue}}$	T	[113]
[Fe–Os]	$[\text{Os}^{\text{II}}\text{--CN--Fe}^{\text{III}}] \xrightarrow{\text{red}} [\text{Os}^{\text{III}}\text{--CN--Fe}^{\text{II}}] \xleftarrow{\text{blue}}$	T	[114]
[Fe–W]	$[\text{W}^{\text{IV}}\text{--CN--Fe}^{\text{III}}] \xrightarrow{\text{red}} [\text{W}^{\text{V}}\text{--CN--Fe}^{\text{II}}] \xleftarrow{\text{blue}}$	T	[115]
[Co–Fe]	$[\text{Fe}^{\text{II}}\text{--CN--Co}^{\text{III}}] \xrightarrow{\text{red}} [\text{Fe}^{\text{III}}\text{--CN--Co}^{\text{II}}] \xleftarrow{\text{blue}}$	T, $h\nu$	[90,104,116,117]
[Co–Os]	$[\text{Os}^{\text{II}}\text{--CN--Co}^{\text{III}}] \xrightarrow{\text{red}} [\text{Os}^{\text{III}}\text{--CN--Co}^{\text{II}}] \xleftarrow{\text{blue}}$	T	[118]
[Co–W]	$[\text{W}^{\text{IV}}\text{--CN--Co}^{\text{III}}] \xrightarrow{\text{red}} [\text{W}^{\text{V}}\text{--CN--Co}^{\text{II}}] \xleftarrow{\text{blue}}$	T, $h\nu$	[119,120]
[Co–Mo]	$[\text{Mo}^{\text{IV}}\text{--CN--Co}^{\text{III}}] \xrightarrow{\text{red}} [\text{Mo}^{\text{V}}\text{--CN--Co}^{\text{II}}] \xleftarrow{\text{blue}}$	Dehydration- rehydration	[121]
[Ni–Fe]	$[\text{Fe}^{\text{II}}\text{--CN--Ni}^{\text{III}}] \xrightarrow{\text{red}} [\text{Fe}^{\text{III}}\text{--CN--Ni}^{\text{II}}] \xleftarrow{\text{blue}}$	Dehydration- rehydration	[122]
[Cu–Mo]	$[\text{Mo}^{\text{IV}}\text{--CN--Cu}^{\text{II}}] \xrightarrow{\text{red}} [\text{Mo}^{\text{V}}\text{--CN--Cu}^{\text{I}}] \xleftarrow{\text{blue}}$	$h\nu$	[123]

Over the last 25 years, the ability of PBAs to excite an electron from t_{2g} to e_g antibonding orbital using an external stimulus, namely Spin Crossover (SCO), is examined in-depth. However, its practical applications still remain as an effective beginning for the intro of the papers, and no concrete study has been proposed up to now. On the other hand, several studies (oxygen reduction reaction, HER, CO oxidation and CO_2 reduction) have been revealed to support the direct correlation of an increase in catalytic activity with the occupancy of antibonding orbitals.[124–127] Shao-Horn et al. [128] and Xu et al. [129] reported precise approaches on how to tune the catalytic sites in order to obtain respective e_g occupancy for enhanced OER. They concluded that fewer electron occupancy ($e_g < 1$) decelerates the proton separation of the M–OOH^- step and excessive electron occupancy ($e_g > 1$) slows down the molecular O_2 bond formation of the

M-OOH⁻ step (please see the Section 1.2 for OER mechanism). Overall, experimental studies demonstrate that the e_g occupancy close to unity ($e_g \sim 1$) provides better covalency for metal-oxygen bond formation decreasing the rate-limiting steps resulting in an enhanced OER activity. Much current fewer research reports are introduced the favorable outcome of this transition manipulating single Fe atoms for ORR [130] and Co-N doped carbon for OER [131], respectively. A more evident achievement of Zhou et al. proved the tunability of the thermal-differentiated superlattice feature of cobalt-based metal-organic frameworks (MOFs) via magnetic stimulation demonstrating a spin-dependent reaction pathway for an enhanced OER.[132] Consequently, López et al. demonstrated a comprehensive computational study proving that the electrocatalytic OER of CoFe PB could be enhanced significantly by tuning the SCO under an external field. Calculations revealed that the overpotential could be reduced from 0.7 to 0.3 V at room temperature following a SCO dependent pathway under a magnetic field.[133] Hereby, PBAs introduce a novel route for the production of renewable fuels thanks to their unique electronic properties.

1.4 OUTLINE OF THE THESIS

This thesis aims to present novel approaches on how to obtain the maximum efficiency from catalytic applications using the same catalyst by continuous engineering. It consists of three main parts, (i) the electrocatalytic oxidation of glucose, (ii) photocatalytic water oxidation and (iii) electrocatalytic water oxidation under magnetic field and light illumination (Figure 1.11).

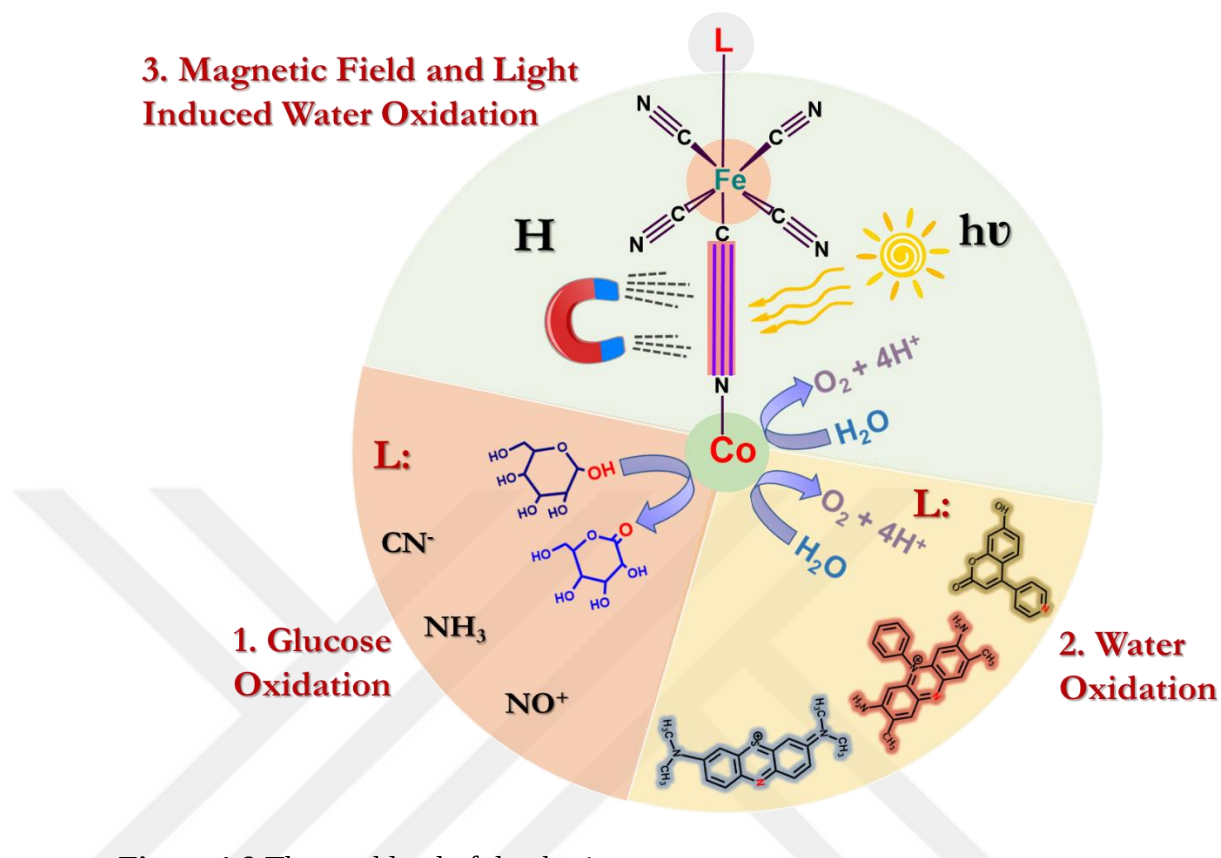


Figure 1.9 The workload of the thesis.

First part of study could be divided into two subdivisions. Initially, CoFe PB is proved as an efficient and robust catalyst for the electrocatalytic oxidation of glucose. The two-step electrodeposited PB modified FTO electrode is evaluated as a non-enzymatic glucose sensor and comprehensive mechanistic studies are presented. In the second glucose sensing study, a series of CoFe coated carbon cloth electrodes are prepared using different cyanoiron precursors ($[\text{Fe}(\text{CN})_6]^{2-}$, $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$, and $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$) to elucidate the effect of electronic and morphologic properties of PB structure on the electrocatalytic activity of glucose oxidation.

In the second part, we report a facile synthetic method to construct a series of photosensitizer–water oxidation catalyst (PS–WOC) dyad assemblies. We demonstrate that photosensitizers with different electronic and optical properties could easily be plugged to these CoFe PBAs to be utilized for photocatalytic processes. Three photosensitizers that absorb different regions of solar spectrum, including UV, green, and red-light region, were incorporated into dyads within this study. A red-light absorbing

dye, methylene blue ($\lambda_{\text{max}} = 664 \text{ nm}$), was also investigated to mimic P680 in photosystem II.

In the third part, we investigated the electrocatalytic water oxidation ability of CoFe PBAs under magnetic field and light illumination. Considering the intermetallic charge transfer property of materials, we prepared three different CoFe-PBAs, $[\text{Co-Fe}^{\text{II}}\text{NO}]$ with the highest catalytic activity but the lowest MMCT (due to strongly π -accepting NO ligand), $[\text{Co-Fe}^{\text{II}}]$ with the lowest activity and moderate MMCT, and $[\text{Co-Fe}^{\text{III}}]$ with moderate activity and the highest MMCT.



CHAPTER 2

2. METHODS AND INSTRUMENTATION

The experiments and characterization of materials are performed at the Chemistry Department (Karadas Group Laboratory) and National Nanotechnology Research Center (UNAM), Bilkent University.

The magnetic measurements of materials are conducted by Dr. Mehmet Burak Kaynar at Prof. Sadan Ozcan's lab, Hacettepe University.

2.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier-transform infrared spectroscopy (FTIR) spectra were measured using a Bruker ALPHA Platinum-ATR spectrometer in the 4000–400 cm^{-1} range with a resolution of 4 cm^{-1} and 64 scans to verify the formation of the complexes.

2.2 SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX)

Energy dispersive X-ray analysis and Scanning electron microscopy were performed by FEI - Quanta 200 FEG to characterize the morphology and depict the atomic ratios, respectively. Applied potentials are 5 kV for SEM and 15 kV for EDAX.

2.3 ULTRAVIOLET - VISIBLE (UV-VIS) SPECTROSCOPY

UV-Vis analysis was performed employing an Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer. Both solutions and FTO films characterized on the same spectrophotometer.

2.4 XRAY – PHOTOELECTRON SPECTROSCOPY (XPS)

XPS (Thermo Fisher Scientific; Al K-Alpha radiation; $h\nu = 1486.6$ eV) measurement was also operated at survey mode by operating a flood gun for surface charge neutralization with 30 eV pass energy and 0.1 eV step size, and it was performed for determining the elemental analysis. The correction of peak positions was calibrated by referencing the C1s peak position (284.8 eV) and shift other peaks in the spectrum accordingly.

2.5 POWDER X-RAY DIFFRACTION (PXRD)

Powder X-ray diffraction (PXRD) were conducted on powder samples by Panalytical X'pert Multi-Purpose to identify the phase structure, and the patterns were obtained in the range of $2\theta = 10^\circ - 90^\circ$ using Bragg-Brentano geometry (Cu K_α radiation; $\lambda = 0.15418$ nm).

2.6 GRAZING INCIDENCE XRAY-DIFFRACTION (GIXRD)

Grazing Incidence X-ray diffraction (GIXRD) were performed by Panalytical X'pert Materials Research Diffractometer to identify the phase structure of the FTO electrodeposited PB samples, and the patterns were obtained in the range of $2\theta = 10^\circ - 60^\circ$ using Bragg-Brentano geometry (Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation; $\lambda_1 = 0.15406$ nm and $\lambda_2 = 0.15444$ nm, respectively).

2.7 MAGNETIC MEASUREMENTS

Magnetic characterizations were conducted by a vibrating sample magnetometer (VSM) module of the physical properties measurement system (PPMS-Quantum Design). Temperature dependent magnetization ($M-T$) measurements were performed in the 2–300 K temperature range with an applied field of 500 Oe. Magnetic-field-dependent magnetization ($M-H$) measurements were performed at 2 K in the -2 to +2 T magnetic-field range.

2.8 ELECTROCHEMICAL SETUP

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) experiments were carried out by a Gamry Instruments Interface 1000 Potentiostat/Galvanostat in a standard three-electrode electrochemical cell configuration (Figure 2.1). PB coated electrodes, a Pt wire, and Ag/AgCl (sat.) serve as the working (WE), the counter (CE), and the reference (RE) electrodes, respectively. All potentials measured vs. Ag|AgCl|KCl(sat.), denoted as $V_{Ag/AgCl}$. All electrochemical experiments were performed in a 0.1 M PBS electrolyte containing 0.5 M KCl as a supporting electrolyte.

The potentials were converted to V_{RHE} using the Nernst equation:

$$V_{RHE} = V_{Ag/AgCl} (V) + 0.059 \times pH + V_{Ag/AgCl}^0 (V)$$

where V_{RHE} is the applied potential versus RHE, $V_{Ag/AgCl} (V)$ is the applied potential versus Ag/AgCl reference electrode, and $V_{Ag/AgCl}^0 (V)$ is the standard potential of the reference electrode (0.197 V_{RHE}).



Figure 2.1 The three-electrode configuration electrochemical setup. WE, RE and CE denote working electrode, reference electrode and counter electrode, respectively.

2.9 PHOTOCATALYTIC SETUP

The amount of photogenerated O_2 was recorded by gas chromatography (Agilent 7820A GC) equipped with a 5 Å molecular sieve column (Ar as the carrier gas) and a TCD detector (Figure 2.2). The photocatalytic experiments for oxygen evolution were performed in a 10 mL gas-tight Pyrex cell. The photocatalyst (10 mg) and $\text{Na}_2\text{S}_2\text{O}_8$ (20 mM) sacrificial agent was dispersed in a 10 mL phosphate buffer solution (PBS, pH 7.1). The reaction mixture was degassed with N_2 gas for 30 min. before each experiment. The reaction flask was coupled to a solar light simulator (Sciencetech, Model SLB-300B, 300 W Xe lamp, AM 1.5 global filter) and calibrated to 1 sun (100 mW cm^{-2}). The above

solution was also irradiated by visible light illumination ($\lambda > 420$ nm) through a 420 nm cut-off filter. The oxygen content in the headspace of the flask was sampled through the septum using a syringe and injected to GC for 2 to 3 times each time. During the experiments, the mixture was magnetically stirred and no leakage from air in the reaction flask was determined by monitoring the N_2 content. Each experiment was performed at least 3 times and the average of these values is considered as the amount of evolved oxygen.

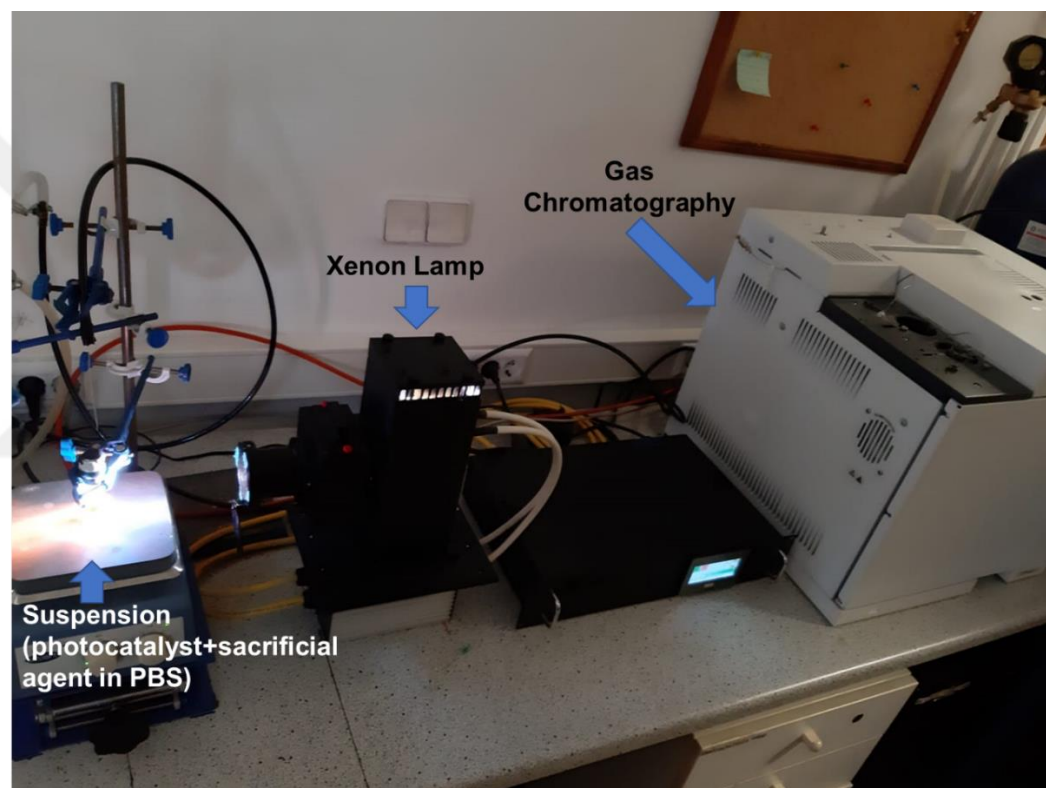


Figure 2.2 An illustration of photocatalytic setup including the Pyrex cell with suspension, solar simulator and gas chromatography.

2.10 MAGNETIC FIELD AND LIGHT ASSISTED ELECTROCHEMICAL SETUP

Magnetic field and light induced electrocatalytic water oxidation studies were performed by integration of electrochemical setup, electromagnet and solar simulator (Figure 2.3). For the magnetic field-assisted electrocatalysis, the three-electrode electrochemical setup is integrated inside the electromagnet between the magnetic poles

with a gap range of 50 mm. Electromagnet WD-50 (C-frame) magnetic field generator was used with variable air gap range of 0 – 80 mm (adjustable poles) and DC resistance of $9.2\ \Omega$ at $20\ ^\circ\text{C}$. The generated magnetic fields by the set electrical currents on the electromagnet were measured using a gauss-meter (Group3 DANFYSIK DTM133) to make a calibration plot of adjusted electrical current vs supplied magnetic field. Thus, the control of the magnetic field is provided for electrocatalytic experiments. For the light induced electrocatalytic studies a solar light simulator (Sciencetech, Model SLB-300B, 300 W Xe lamp, AM 1.5 global filter) calibrated to 1 sun ($100\ \text{mW cm}^{-2}$) was used without changing the position of electrochemical cell inside the electromagnet. LSV, CV and CA experiments were conducted under magnetic field and light illumination, respectively. PB electrode, Pt wire and Ag/AgCl (sat.) were used as WE, CE and RE, respectively, in PBS solution containing 0.5 M KCl as a supporting electrolyte.

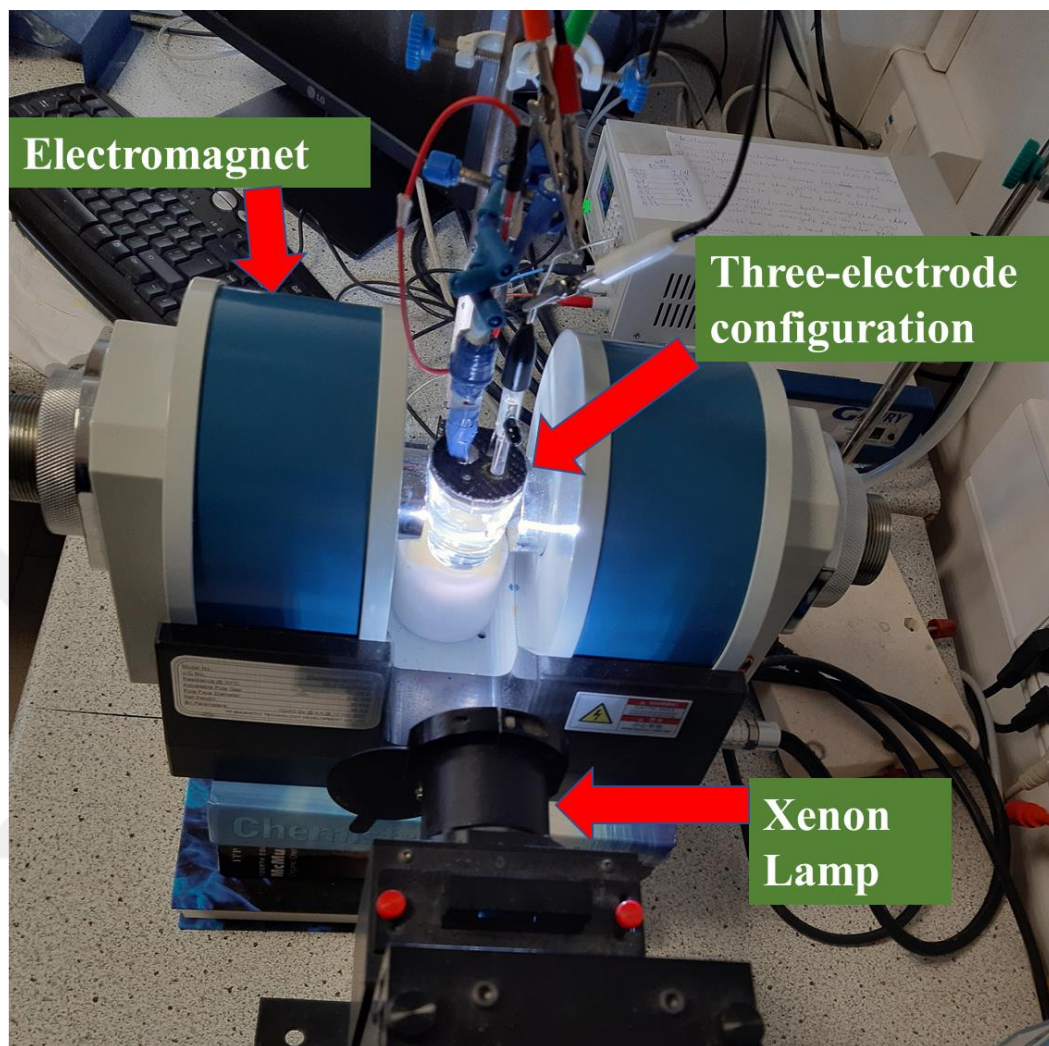


Figure 2.3 Magnetic field and light assisted electrochemical setup.

2.11 LOD CALCULATION

In general terms, the limit of detection (LOD) of an analyte may be described as the concentration, which gives an instrument signal significantly different from the blank signal. The LOD is determined according to the IUPAC definition [134,135], which is defined as

$$LOD = 3 * \frac{\text{Standard deviation of blank signal}}{\text{Slope of the calibration curve}}$$

The number 3 comes from the required 90% level of confidence in the difference between the observed signal and the blank response. We determined the LOD as follows:

The standard deviation of blank current (before the glucose injection) is determined. Then, the slope of the obtained calibration curve, which is the current response versus glucose concentration, is used with standard deviation of blank current for the LOD calculation.

2.12 CALCULATION OF SURFACE CONCENTRATION OF ACTIVE CATALYTIC SITES

Surface concentration of active catalytic sites on electrodes was calculated from the slope of the oxidation peak current I (mA) vs. sweep rate v (mV s^{-1}) plot. According to the equation below;

$$\text{slope} = \frac{n^2 F^2 A \Gamma}{4 R T}$$

where $n=1$ (1 e^- redox process), $F=96485 \text{ s A mol}^{-1}$ (Faraday's constant), A is the coated electrode surface area (cm^2), Γ =surface concentration (mol cm^{-2}), $R=8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1} \text{ mol}^{-1}$ (ideal gas constant) and T is the temperature.

2.13 STANDARD ERROR CALCULATION FOR OER ACTIVITY

The oxygen content in the headspace of the flask was sampled through the septum using a syringe and injected to GC for 2 to 3 times each time. Each experiment was performed at least 3 times and the average of these values is considered as the amount of evolved oxygen. The standard error is calculated by the ratio of the standard deviation of activities for each sampling hour to the square root of the number of samples as shown in below equation.

$$\text{Standard error} = \frac{\text{Standard deviation of oxygen evolution for each sampling hour}}{\sqrt{\text{Number of samples}}}$$

2.14 TON AND TOF CALCULATION

TON was obtained by dividing the moles of oxygen evolved from photocatalysis to the moles of cobalt in the catalyst. Since the TOF contains the unit time in its definition, the TON is divided by photocatalysis time in order to calculate the TOF.

$$TON = \frac{\text{the moles of evolved } O_2}{\text{the moles of Cobalt on dyad}}$$

$$TOF = \frac{TON}{\text{time}}$$

2.15 BAND ENERGY DIAGRAM CALCULATION

HOMO and LUMO levels were estimated from CV measurements and UV-vis spectroscopy, respectively. The reduction onset potential is utilized to find the LUMO level of the Fe-PS complexes from CVs and the HOMO is predicted by using optical band gap of the compound, which is acquired from UV-Vis absorption spectroscopy. Moreover, to find the Co oxidation level, the oxidation onsets are separately extracted from the CVs. It should be noted that the main electronic transition, responsible for photocatalytic water oxidation, is the electron transfer from the HOMO to the LUMO level. Therefore, the comparisons of the photocatalytic performances have been conducted by considering these two levels.[136]

CHAPTER 3

3. ELECTROCATALYTIC GLUCOSE OXIDATION USING CoFe BASED PBAS

This chapter of the thesis is based on the publications:

‘Electrodeposited cobalt hexacyanoferrate electrode as a non-enzymatic glucose sensor under neutral conditions’, R. Chalil Oglou, T.G. Ulusoy Ghobadi, E. Ozbay, F. Karadas, **Analytica Chimica Acta**, 2021, 1188, 339188. Adapted (or reproduced in part) with permission from Elsevier, Ref. [137]. Copyright 2021 Elsevier B. V.

‘Selective Glucose Sensing under Physiological pH with Flexible and Binder-Free Prussian Blue Coated Carbon Cloth Electrodes’, R. Chalil Oglou, T.G. Ulusoy Ghobadi, E. Ozbay, F. Karadas, **ChemElectroChem**, 2022, 9.2: e202101355. Adapted (or reproduced in part) with permission from John Wiley and Sons, Ref. [138]. Copyright 2022 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.1 CoFe ELECTRODE AS A NON-ENZYMATIC GLUCOSE SENSOR WITH COMPREHENSIVE MECHANISTIC STUDIES

3.1.1 Introduction

Efficient monitoring of glucose level and the strict control of its level is of great significance in diabetes and chronic diseases and other fields, including food processing, pharmaceutical monitoring, biotechnology industries, and environment managing.[139–142] In this regard, intensive efforts have been devoted to both in-vivo and in-vitro platforms to develop glucose-sensing schemes with high sensitivity, rapid response, and excellent reliability.

Amperometric electrochemical based sensing is one of the most promising approaches for glucose determination, which is based on the oxidation of glucose by an electrocatalyst. This class of sensors could be divided into enzymatic and non-enzymatic ones.[143] Current glucose sensors on the market for the detection of glucose in the blood

and wearable continuous glucose monitoring devices are mainly based on enzymatic sensors.[141] Enzymatic sensors rely on a glucose oxidase (GOx) enzyme, which exhibit great sensitivity and specific selectivity between glucose and other interfering agents in the blood. Enzymatic systems, however, suffer from scalability, enzyme manufacturing, high cost, and poor long-term stability.[144,145] Furthermore, a controlled environmental condition (temperature, humidity level, and pH range) and tedious immobilization procedures limit their efficiencies and reproducibilities.[146–148] Thus, enzyme-free electrochemical glucose sensors have become a highly desirable and attractive alternative to overcome the limitations of enzymatic ones.

Non-enzymatic glucose sensors based on nanostructured compounds generally exhibit high durability under harsh circumstances. Moreover, they are cost-effective, and they have simple fabrication routes. Besides the commonly used metallic nanoparticles and metal oxides, bimetallic Prussian Blue analogues (PBAs) have recently been investigated as non-enzymatic glucose sensors due to their large surface area, high electrocatalytic activity, effective electron transfer, high chemical stability, ease of preparation, and low cost of starting precursors [47–50,149,150]. The transition metal hexacyanometalates form an important class of insoluble mixed valence compounds [151,152]. Among them, cobalt hexacyanoferrate (denoted as CoFe) with a general formula, $A_nCo_x[Fe'(CN)_6].nH_2O$ (A = alkali-metal ions), is known as one of the first non-oxide heterogeneous electrocatalysts for water oxidation [25,67]. Their chemistry has been reviewed extensively in a variety of catalytic oxidation processes [65,153]. The cobalt site in a PB structure requires a relatively lower working potential compared to other 3d transition metals, which makes it a proper choice for selective oxidation reactions. Thus, Co based PBAs show an ideal platform for non-enzymatic glucose sensing application.

Herein this study, we report a comparative study of the non-enzymatic glucose sensing activities of CoFe and FeFe PB modified FTO electrodes, which are prepared via a facile electrodeposition method. We also scrutinize the electrocatalytic mechanism by performing comprehensive electrochemical studies under neutral conditions.

3.1.2 Experimental Procedure

3.1.2.1 Chemicals

Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Fischer Scientifics. Potassium hexacyanoferrate(III) ($\text{K}_3\text{Fe}(\text{CN})_6$) and Potassium chloride (KCl) were purchased from Sigma Aldrich. The sensing reagent D(+)-glucose was obtained from Aromel Kimya. The interference reagents D(+)-gluconolactone, L-ascorbic acid, uric acid, and D(+)-lactose were purchased from Acros Organics. Sucrose was obtained from Carlo Erba. All the reagents were analytical grade, and no further purification was applied. Millipore deionized water (resistivity; $18 \text{ M}\Omega\cdot\text{cm}$) was used for all experiments. Fluorine doped tin oxide (FTO) coated glass substrates (R_{sh} ; $20 \Omega/\text{sq.}$, 2mm in thickness) were used for electrodeposition experiments.

3.1.2.2 Preparation of the PB-modified FTO electrode

Each FTO electrode is immersed sequentially in a sonication bath containing deionized water, acetone, and ethanol, each for 15 min. The FTO electrode is then dried at 100°C for 1 h prior to use. Cobalt hexacyanoferrate (CoFe) modified electrodes were prepared by an electrodeposition method. First, the well-cleaned FTO electrode was immersed in an aqueous solution of $\text{Co}(\text{NO}_3)_2$ (10 mM) and KCl (0.5 M). A constant potential of $-0.9 \text{ V}_{\text{Ag}/\text{AgCl}}$ was applied for 100 s to afford metallic particles on FTO electrode (FTO/[Co]). Then, the rinsed FTO/[Co] electrode was immersed in a solution of $\text{K}_3\text{Fe}(\text{CN})_6$ (10 mM) and KCl (0.1 M) to perform a chronoamperometric experiment at $0.9 \text{ V}_{\text{Ag}/\text{AgCl}}$ for 100 s. Consequently, the electrodeposited FTO/[CoFe] electrode was rinsed with deionized water and dried at 100°C for 1 h.

3.1.2.3 Preparation of the Iron hexacyanoferrate modified FTO electrode

Iron hexacyanoferrate (FeFe) modified electrode was prepared by an electrodeposition method.[154] A well-cleaned FTO electrode immersed in a solution of $\text{K}_3\text{Fe}(\text{CN})_6$ (4 mM) and FeCl_3 (4 mM) containing a supporting electrolyte of KCl (0.5 M) in HCl (0.1 M). The deposition was performed by an applied constant potential of $0.4 \text{ V}_{\text{Ag}/\text{AgCl}}$ for 100 seconds. The film growth of the FeFe modified FTO electrode was

achieved by cycling in a potential range of -0.5 to 1.5 V for 10 to 15 times in an aqueous solution of KCl (0.5 M) in HCl (0.1 M).

3.1.2.4 Electrochemical measurements

All of the calculations are based on the geometric surface area and all potentials measured vs. Ag|AgCl|KCl(sat.). CV is performed at a scan rate of 50 mV s^{-1} with a potential range from 0.2 to $1.3 \text{ V}_{\text{Ag/AgCl}}$, while a potential of $1.15 \text{ V}_{\text{Ag/AgCl}}$ is applied for amperometric experiments in a N_2 -saturated 0.1 M phosphate buffer solution (PBS). For the amperometric detection of glucose, the current response is recorded while a specific concentration of glucose (from 0 to 10 mM) is added to a solution of 0.1 M PBS containing 0.5 M KCl at a specific potential. Each steady-state current response is recorded to obtain a steady-state current/glucose concentration profile to evaluate the sensing ability of the electrodes. Electrochemical experiments are performed also with the addition of interfering agents including fructose, sucrose, uric acid, and ascorbic acid.

3.1.3 Results and Discussion

3.1.3.1 Synthesis and Characterization

CoFe Prussian blue modified electrode is prepared according to the previously electrodeposition method with slight modifications.[25,155,156] The two-step process involves the reduction of Co^{2+} ions to metallic Co particles coated on FTO (FTO/[Co]) followed by the reaction of cobalt with $\text{Fe}(\text{CN})_6^{3-}$ ions to afford FTO/[CoFe] (Figure 3.1). In the second step, namely the derivatization process, metallic cobalt is slowly oxidized under a positive oxidation potential to produce a PB layer on FTO in the presence of $\text{Fe}(\text{CN})_6^{3-}$ ions.

The thickness of the film depends on several experimental parameters, such as the immersing time of the electrode in the plating and derivatizing solutions, the concentration of precursors, applied bias, and pH. These parameters are varied systematically to optimize the conditions for an electrode with uniform morphology and high stability. $2 \text{ cm} \times 1 \text{ cm}$ FTO electrodes were used as working electrodes, but only a surface of $1 \pm 0.05 \text{ cm}^2$ area was immersed in the solution.

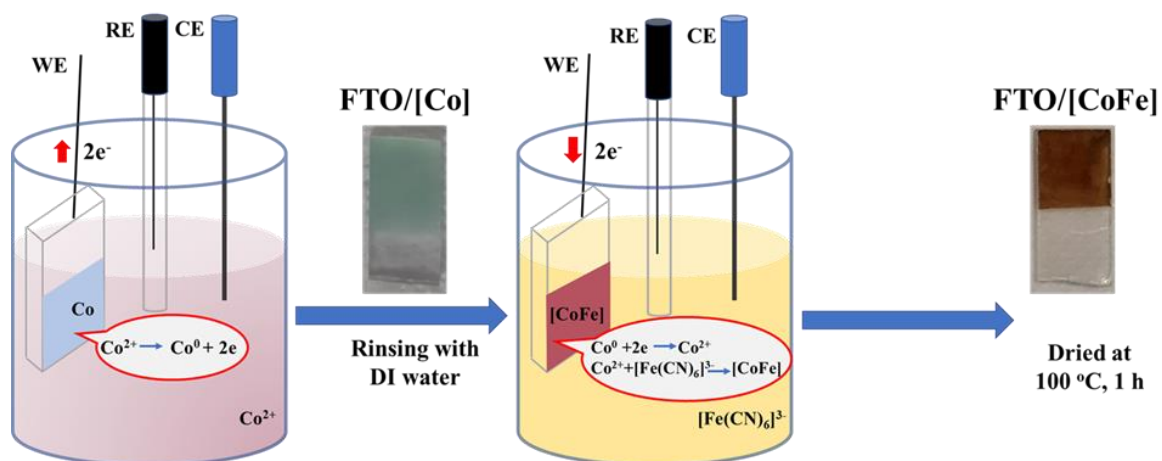


Figure 3.1 Schematic illustration of the fabrication of PB modified FTO electrode through a two-step electrodeposition process: (i) First, FTO coated glass substrate is treated with a negative bias in the presence of cobalt ions to obtain FTO/[Co], and then (ii) derivatization of the surface is performed in the presence of $\text{K}_3\text{Fe}(\text{CN})_6$ to afford FTO/[CoFe]. Finally, the electrode was left for drying at $100\text{ }^\circ\text{C}$. The electrode color changes from green-blue to brown during the formation of PB layer.

SEM technique is performed to investigate the structure and the morphology of FTO/[Co] and FTO/[CoFe]. Although the SEM image of FTO/[Co] exhibits a variety of clustered plate-shaped structures (Figure 3.2a), FTO/[CoFe] reveals randomly oriented needle-like structures having uniform sizes of around $1\text{ }\mu\text{m}$ long (Figure 3.2b). It can be observed that a complete structural transformation is obtained during the derivatization step. Energy-dispersive X-ray spectroscopy (EDAX) elemental scanning exhibits a Co/Fe elemental ratio of around 3:1 (Figure 3.3).

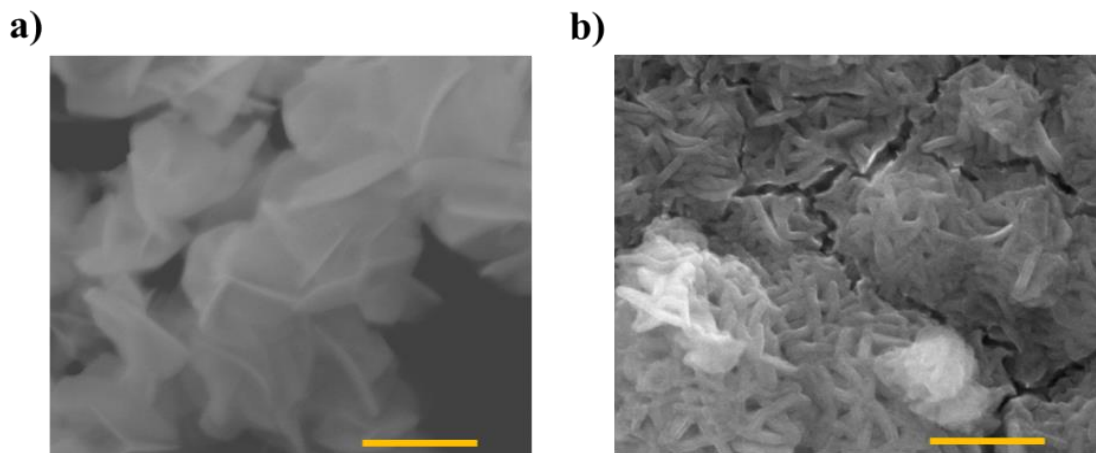


Figure 3.2 The SEM images (scale bar: 1 μm) of (a) FTO/[Co] and (b) FTO/[CoFe].

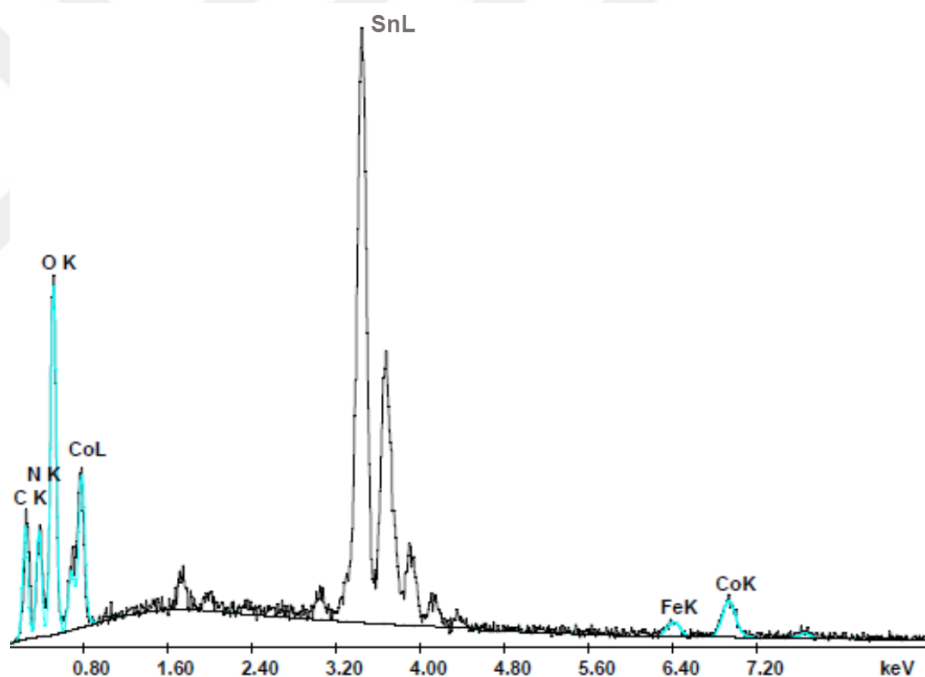


Figure 3.3 The EDAX analysis of FTO/[CoFe].

Moreover, the recorded XRD pattern of FTO/[CoFe] shows characteristic peaks of a face-centered cubic PB structure (Figure 3.4a). The peaks labeled with ‘*’ are located at 17°, 24°, and 35°, which correspond to PB (200), (220), and (400) crystal planes, respectively.[157] The XRD pattern of FTO/[CoFe] reveals sharp and intense peaks indicating the highly crystalline nature of the PB layer, and no impurity peaks are observed. Three major peaks are observed in the Infrared spectrum of FTO/[CoFe] (Figure 3.4b). The strong peak at 2107 cm^{-1} corresponds to the $\text{Co}^{\text{III}}\text{-NC-Fe}^{\text{II}}$ coordination mode.

This sharp peak also exhibits a shoulder at around 2074 cm^{-1} , attributed to the $\text{Co}^{\text{II}}\text{-NC-Fe}^{\text{II}}$ moieties in the structure. The broad band at 3350 cm^{-1} and the sharp one at 1605 cm^{-1} are assigned to M-O-H stretching and H_2O bending modes, respectively. Furthermore, the peaks at around $400\text{-}600\text{ cm}^{-1}$ are attributed to $\text{Co}^{\text{III}}\text{-N}$ and $\text{Fe}^{\text{II}}\text{-C}$ bond stretches.[65,70]

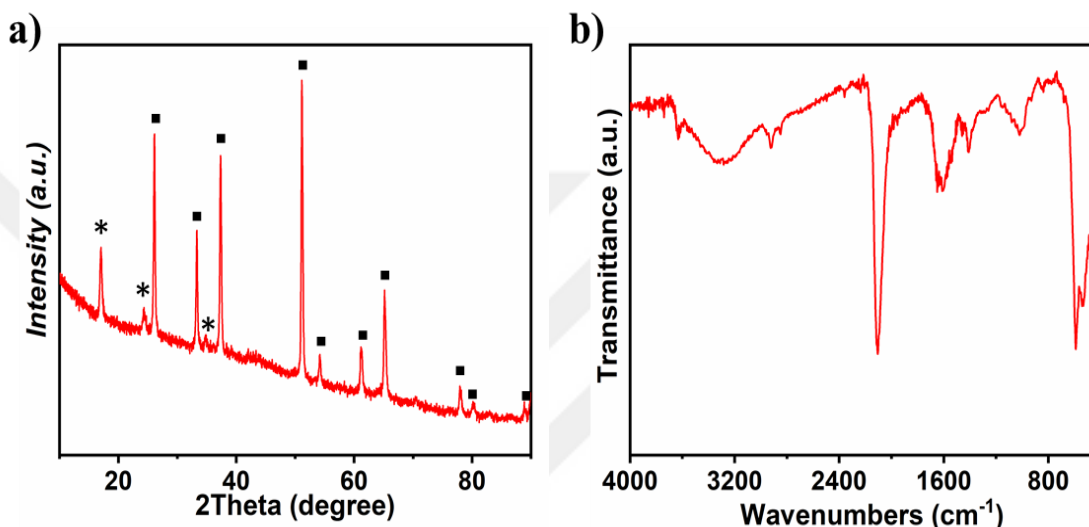


Figure 3.4 (a) The XRD pattern (the peaks labeled with * and ■ correspond to PB and FTO crystal planes, respectively) and (b) the ATR-FTIR spectrum of the FTO/[CoFe] electrode.

3.1.3.2 Electrochemical Experiments

Electrochemical studies are performed to evaluate the electrochemical glucose sensing performance of the FTO/[CoFe] electrode. Figure 3.5a shows the cyclic voltammograms of FTO/[CoFe] in a 0.1 M PBS solution at a scan rate of 50 mV s^{-1} and in a 0.2-1.3 V potential range. The characteristic irreversible peak above around $1.2\text{ V}_{\text{Ag/AgCl}}$ is due to the catalytic water oxidation process. The a quasi-reversible redox couple at an equilibrium potential of $0.95\text{ V}_{\text{Ag/AgCl}}$ is generally assigned to the $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ oxidation process ($\text{Co}^{\text{II}}\text{Fe}^{\text{II}} \rightarrow \text{Co}^{\text{III}}\text{Fe}^{\text{II}}$ process) in CoFe PB based electrodes.[26,67,158]

Prior to the detection experiment, the amperometric response of the electrode is recorded with an injection of glucose at various potentials to determine the optimum working/operating potential (Figure 3.5b). The currents were measured for each potential for 350 seconds. The worst sensitivity is obtained at $1.2\text{ V}_{\text{Ag/AgCl}}$ since the catalytic water

oxidation reaction competes with the catalytic glucose oxidation process. The highest sensitivity is obtained at 1.15 V_{Ag/AgCl}, and the sensitivity decreases gradually as the potential decreases from 1.15 to 1.0 V_{Ag/AgCl}. This trend indicates that Co^{III} site plays a crucial role in glucose sensing since the number of Co^{III} sites is in well-correlation with glucose sensitivity of FTO/[CoFe]. Since catalytic activity of FTO/[CoFe] towards glucose oxidation is confirmed by electrochemical studies, it is investigated further with amperometric experiments in the presence of glucose.

The sensitivity and the linear detection range are of critical importance for the performance of a glucose sensor. Figure 3.5c reveals the specific addition of glucose in a 0.1 M PBS solution during an amperometric measurement with FTO/[CoFe] electrode over 500 seconds under constant stirring. With the dropwise injection of glucose, the electrode exhibits a sharp increase in current with a fast current response, which reaches a steady state in less than 7 seconds. The current density then increases linearly with the addition of glucose up to a glucose concentration of 8.2 mM, which is well above the operating limit of a regular glucose sensing device.[159–161] Glucose concentration and the corresponding current are linearly fitted to derive a calibration curve for amperometric glucose detection (Figure 3.5c, inset). As shown in this figure, the calibration plot for FTO/[CoFe] electrode exhibits a good linearity in a 0.1–8.2 mM concentration range under neutral pH conditions.

On the other hand, the sensitivity with a unit of $\mu\text{A mM}^{-1} \text{ cm}^{-2}$ is obtained from the slope of the graph with a linear fit between the peak current density and the molarity. The sensitivity is calculated as $18.69 \mu\text{A mM}^{-1} \text{ cm}^{-2}$ ($R^2 = 0.98$) and the limit of detection (LOD) for the proposed sensor is determined as 67 μM according to the signal-to-noise ratio of three ($S/N=3$). Calculation details of LOD are given in the supporting information section.

One of the challenges in non-enzymatic glucose sensing is the current response caused by interfering reagents. Particularly, sucrose, fructose, ascorbic acid (typically 0.1 mM), and uric acid (typically 0.02 mM), which could be present in human blood, could interfere with the amperometric response due to possible side-oxidation processes.[159] As shown in Figure 3.5d, glucose (1mM), sucrose (0.1 mM), fructose (0.1 mM), ascorbic

acid (0.1 mM), and uric acid (0.02 mM) are sequentially injected into the electrolyte, followed by the final addition of glucose (1 mM). The interfering agents at concentrations determined according to human blood [142,162] produce negligible current signals to the response of FTO/[CoFe] compared to glucose, yet still provides significant responses to incremental glucose concentrations. As the results suggest, the FTO/[CoFe] sensor offers a quite selective catalytic glucose oxidation with high anti-interference ability.

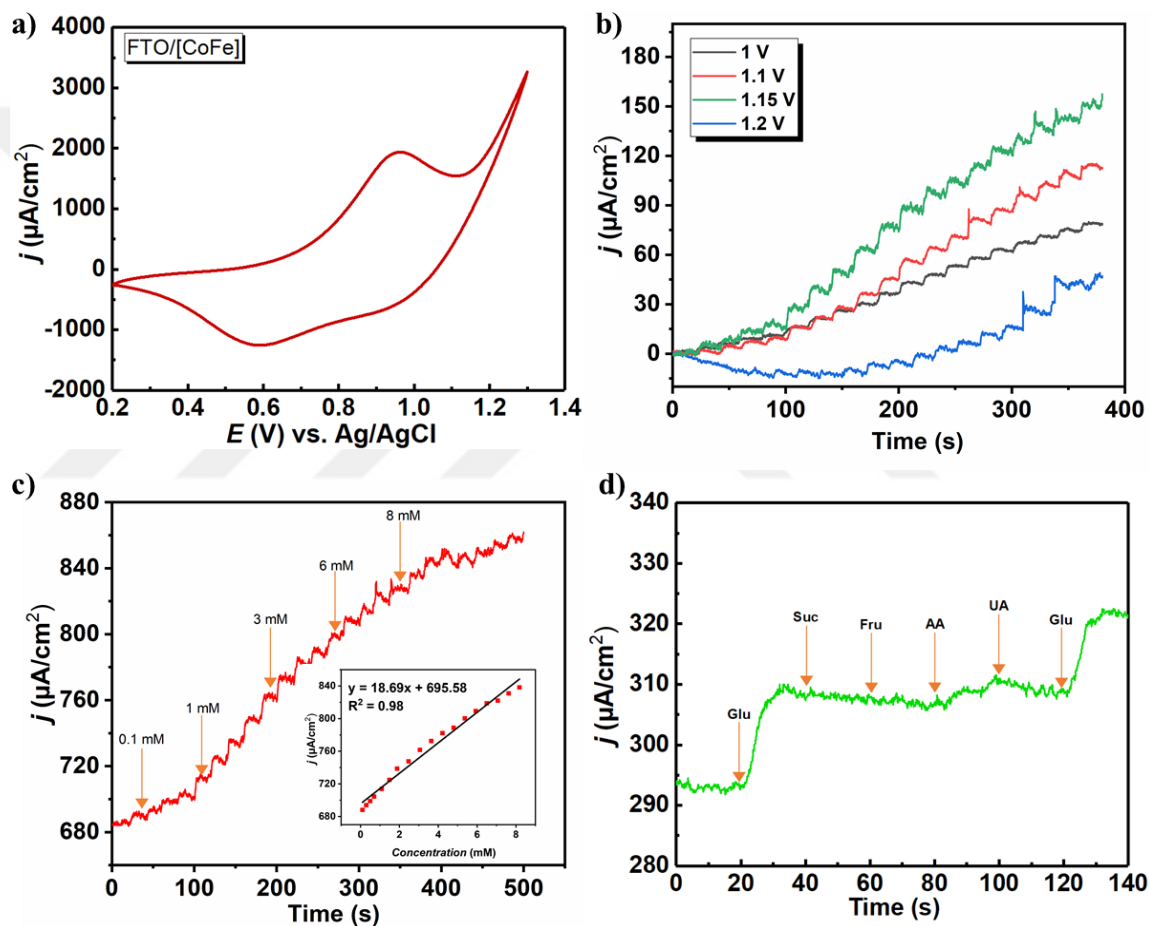


Figure 3.5 (a) CV curve of FTO/[CoFe] electrode at a scan rate of 50 mV/s in 0.1 M PBS. (b) The chronoamperometric profiles of FTO/[CoFe] electrode for consecutive injection of specific concentrations of glucose at different working potentials. (For better comparison, initial current densities are normalized to zero.) (c) Dose response curves; the chronoamperometric responses of FTO/[CoFe] electrode to successive additions of glucose. The arrow shows the concentrations of the overall solution for each injection time at an applied potential of 1.15 V_{Ag/AgCl}. Inset: Calibration curve of stable oxidation current versus the glucose concentration at the electrode. (d) The amperometric response of FTO/[CoFe] electrode in the presence of 1 mM glucose, 0.1 mM sucrose, 0.1 mM

fructose, 0.1 mM ascorbic acid, and 0.02 mM uric acid corresponding to concentrations of the overall solution.

Table 3.1 lists the glucose oxidation performance of previously reported PB-derived electrodes under basic conditions for comparison. While considerably high sensitivities are obtained with PB-derived electrodes, their working range (for people with diabetes, the range is 4 to 7 mM) and alkaline medium (pH 14) restrict their application for human blood. Similarly, the majority of the studies on non-enzymatic glucose sensors have been performed under basic media since OH^- ions also catalyze glucose oxidation, which leads to a dehydrogenation process at a slower rate.[163] The studies under neutral conditions are relatively limited, and they generally exhibit low sensitivity, restricted working range, relatively high cost, and complicated fabrication process.[159,160,163–165] It should also be noted that CoFe PB analogues are known to transform to metal oxides/hydroxides above $\text{pH} > 13$. [51,166] Herein this study, we performed all studies under neutral conditions to assure the stability of the electrode and to elucidate the glucose sensing mechanism in a PB structure.

Table 3.1 Comparison of working conditions for PB-derived electrodes

Electrode	Sensitivity , $\mu\text{A mM}^{-1}\text{cm}^{-2}$	Linear Range, mM	LOD, μM	Solution medium	Substrate	Synthesis method	Ref.
CuCo	567	Up to 0.825	3	NaOH	GC	Precipitation	[47]
NiFe	2392	0.0005-2	0.86	NaOH	GC	Precipitation	[48]
MOF-CoFe	5270	0.0014-1.5	0.02	NaOH	Ni Foam	Hydrothermal	[49]
Porous CoOx	426.8	Up to 1.92	0.16	NaOH	GC	Precipitation	[50]
CoFe	18.69	0.1-8.2	67	PBS	FTO	Electrodeposition	This work

Furthermore, the facile fabrication method for FTO/[CoFe] could be scaled easily for further practical applications. The use of a FTO electrode also allows comprehensive mechanistic and stability measurements, which are discussed in detail in the next section.

We also aim to elucidate the identity of the active site and the glucose oxidation mechanism in this study. For this purpose, we performed amperometric analyses also on FTO/[FeFe] electrode in the presence of glucose (Figure 3.6). In contrary to FTO/[CoFe], FTO/[FeFe] does not respond to a change in glucose concentration, which reveals that cobalt sites are the active sites in the FTO/[CoFe] electrode for glucose oxidation.

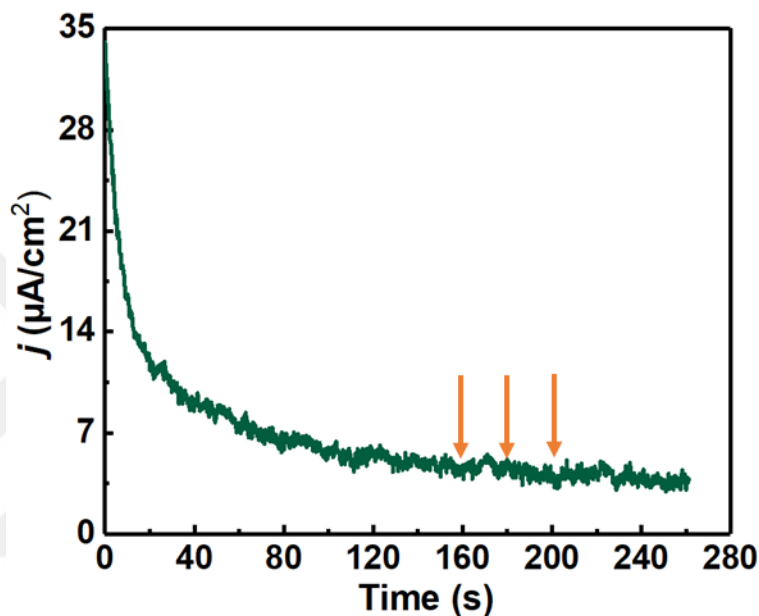


Figure 3.6 The i-t curve of FTO/[FeFe] electrode at an applied potential of 1.15 $V_{Ag/AgCl}$ in 0.1 M PBS (the arrows represent the injections of glucose concentrations at specified times).

Gluconolactone is considered the common product in glucose oxidation. Figure 3.7 presents the CVs of blank 0.1 M PBS electrolyte, and those with the addition of glucose (Figure 3.7a) and gluconolactone (Figure 3.7b) at a scan rate of 50 mV/s. Figure 3.7a reveals that the increase in glucose concentration causes a decrease in the intensity of the $Co^{II/III}$ oxidation peak at around 1 $V_{Ag/AgCl}$. In contrast, it increases with increasing the concentration of gluconolactone (Figure 3.7b). Moreover, the peaks shift to slightly more positive potentials in both cases.

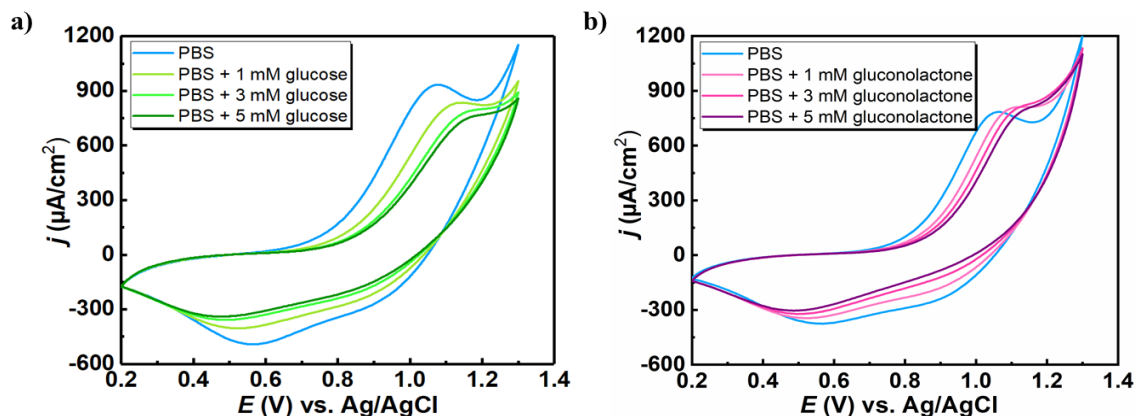


Figure 3.7 CV curves of FTO/[CoFe] electrode with sequential increase the presence of (a) glucose and (b) gluconolactone at a scan rate of 50 mV s^{-1} in 0.1 M PBS.

The similarity between the CV profile in the presence of gluconolactone and that obtained after the sensing experiment (Figure 3.8, orange curve) suggests that gluconolactone is produced on the electrode surface.

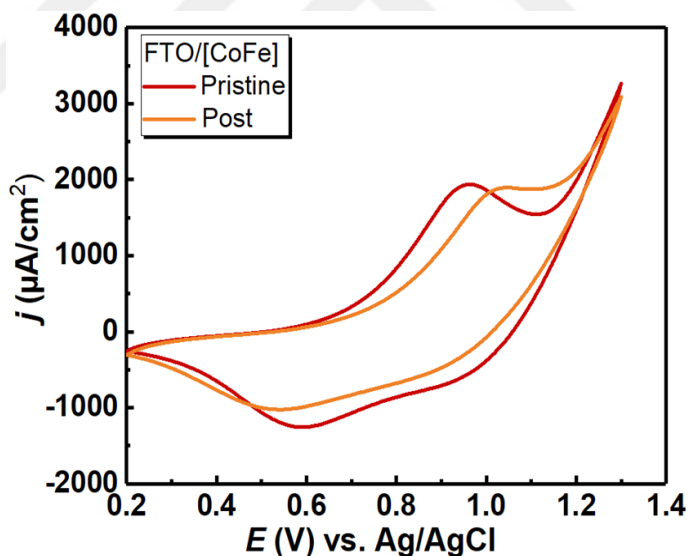


Figure 3.8 CV curves of pristine (red) and post (orange) FTO/[CoFe] electrode at a scan rate of 50 mV s^{-1} in 0.1 M PBS.

We also performed electrochemical experiments in the presence of fructose and sucrose (Figure 3.9 a and b). Of these, FTO/[CoFe] is observed to be sensitive only to fructose (Figure 3.9c). Both fructose and glucose have an $-\text{OH}$ group connected to the C1 atom, which can be oxidized to produce gluconolactone. The lack of an $-\text{OH}$ group on the C1 atom of sucrose, thus, suggests that glucose to gluconolactone transformation is the key process in the amperometric response of the FTO/[CoFe] electrode. Thus, glucose

oxidation on the PB surface involves the oxidation of the cobalt site, the coordination of the cobalt site to –OH group of the C1 atom, the oxidation of glucose to gluconolactone, and the release of the product.

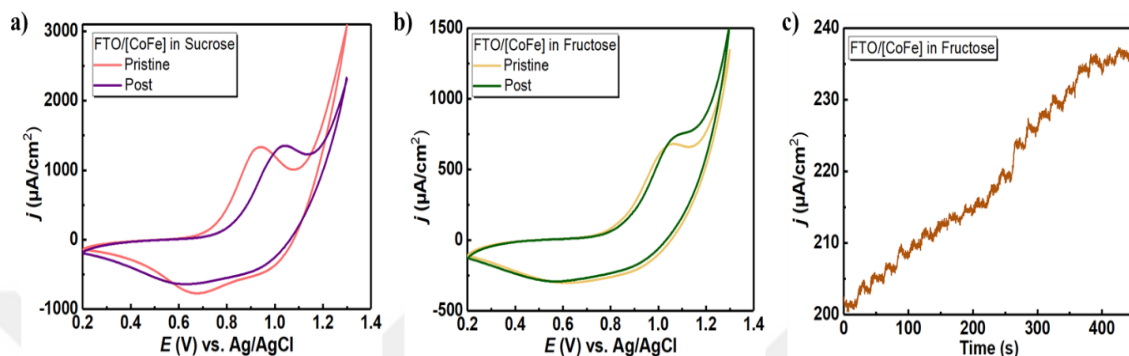


Figure 3.9 CV curves of FTO/[CoFe] electrode before and after the sensing applications for (a) sucrose, (b) fructose and the i-t curve of FTO/[CoFe] electrode at varied concentrations of fructose at an applied potential of 1.15 V_{Ag/AgCl} in 0.1 M PBS.

Post-mortem characterization studies are performed to further evaluate the stability of the electrode. In the following step, XPS analysis is utilized to explore the oxidation states of compositions. The XPS spectra of Fe2p and Co2p for both samples are shown in Figure 3.10 a and b. We focused on the metal sites in a cyanide-based network in previous deconvolutions [87,167,168], suggesting that partial oxidation is typical when metal ions are connected through a cyanide bridging group. The Co2p and Fe2p signals were examined in the binding energy region of 811 to 770 eV and 740 to 700 eV, respectively. The Co2p spectrum reveals two indicative peaks at 782.3 eV and 798.4 eV, which are assigned sequentially to 2p_{3/2} and 2p_{1/2}. Similarly, Fe2p spectrum shows two peaks corresponding to 2p_{3/2} at 708.5 eV and 2p_{1/2} at 721.4 eV. XPS studies, thus, reveal that PB layer in FTO/[CoFe] retains its structure during the electrochemical process [167,169]. The Infrared spectrum of pristine and post-catalytic electrodes exhibit similar stretches for the cyanide group without any considerable shift. A possible peak due to glucose or by gluconolactone is not observed (Figure 3.10).

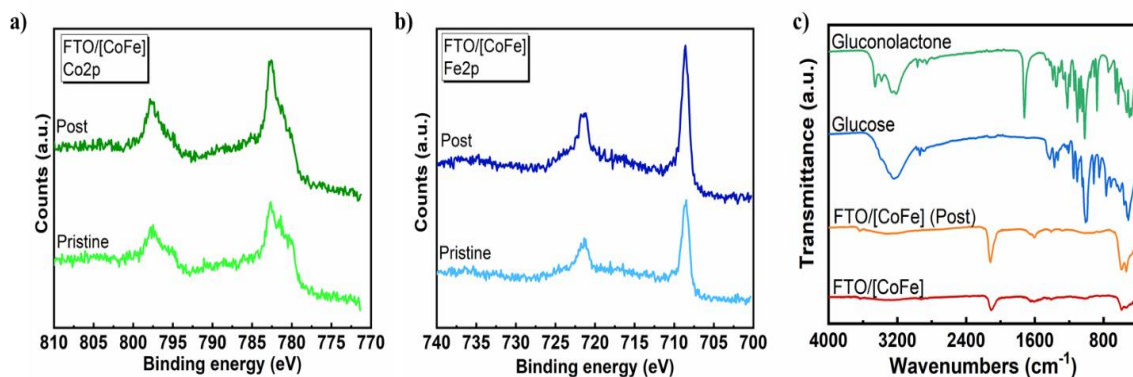


Figure 3.10 Pristine and post XPS spectra of FTO/[CoFe] electrode in the (a) Co2p, (b) Fe2p regions and (c) the ATR-FTIR spectrum of gluconolactone, glucose, post and pristine FTO/[CoFe] electrode (from top to bottom).

3.1.4 Conclusion

We prepared a CoFe Prussian blue analogue coated on an FTO electrode via a facile electrodeposition method. The electrode offers a high glucose-sensing sensitivity ($18.69 \mu\text{A mM}^{-1} \text{cm}^{-2}$) under neutral conditions in the 0.1–8.2 mM range, which covers the typical glucose concentration linear range (3–8 mM) in human blood. PB-based electrode provides a simple, promising and cost-effective sensing platform for the development of enzyme-free sensors. We find that the mechanism involves the oxidation of glucose at gluconolactone on the cobalt site, which is active towards the –OH group on the C1 atom of saccharides.

Overall, we report the first PB-based electrode operating efficiently under neutral conditions, which is required to test human blood. The electrode also overcomes most of the investigated electrochemical sensors due to its feasibility. Furthermore, the diversity of Prussian blue analogues and their easy synthesis allow easy tuning of their electrochemical properties. Thus, we anticipate that many Prussian blue modified electrodes will be investigated for non-enzymatic glucose sensing.

3.2 MORPHOLOGICAL AND ELECTRONIC PROPERTIES OF CoFe ELECTRODES ON ELECTROCATALYTIC OXIDATION OF GLUCOSE

3.2.1 Introduction

A glucose sensor with a fast response, a high sensitivity, and a wide working range holds a significant potential for diabetes monitoring, environmental detection, fermentation, and agricultural applications.[33–38] Electrochemical [37], optical [39], and fluorescence [40] based devices have been explored to achieve this target. Of these, electrochemical glucose sensors stand forward due to their low cost, facile fabrication, and high performance.[170] The enzymatic electrochemical glucose sensors rely on transforming glucose to gluconolactone with a glucose oxidase enzyme and sensing the by-product such as H_2O_2 with secondary electroactive material.[171–173] On the other hand, a non-enzymatic sensor consists of metallic or metal oxide nanoparticles, which can oxidase the glucose molecule to gluconolactone at a certain applied bias and the correlation of the generated current to concentration.[43]

Noble metals including platinum[174] and gold[175] have been examined to efficiently oxidize glucose to gluconolactone at low biases with relatively low selectivities.[176] Low-cost transition metal oxides such as Co_3O_4 [44], CuO [45], and MnO_2 [46] could also oxidize glucose with relatively high selectivity, though operating efficiently under basic conditions. While the high electrical conductivity of earth-abundant copper is utilized for catalytic oxidation of glucose, its limited working range and poor stability in neutral environment should be addressed.[177–179] CoFe Prussian blue analogues (PBAs), a well-known family of non-oxide coordination compounds, have also recently been found to be active towards glucose oxidation.[47–50] We recently showed that coordinatively unsaturated cobalt ions in Prussian blue (PB) structure could transform glucose to gluconolactone molecule once cobalt ions are oxidized to their 3+ oxidation states. Unlike metal oxides, PBAs are stable in a wide pH range (1-13), which make them promising candidates to explore glucose sensors operating under neutral and/or acidic conditions.

The substrate also plays an essential role in the selectivity and the sensitivity of sensors since it affects the conductivity and the morphology and, thus, the activity of the catalytic component.[45,176] For example, commonly studied metal oxides drop-casted on a glassy carbon electrode exhibit a high resistance in the catalyst-electrode interface, which could lead to a material loss over time.[180–182] Carbon electrodes could overcome the abovementioned issues since they offer direct fabrication of binder-free electrodes, low resistances, large surface area, and high number of active sites.[176,181,183] Hence, the choice of the substrate is another critical parameter to be investigated.

Recently, we fabricated CoFe PB modified fluorine-doped tin oxide (FTO) coated electrodes which operate as an efficient glucose sensor under neutral conditions.[184] Herein this study, we prepared CoFe PB modified carbon cloth electrodes with different cyanoiron precursors to elucidate the electronic and morphological effect of the iron sites on the activity and the sensitivity of PB based electrodes.

3.2.2 Experimental Procedure

3.2.2.1 Chemicals

Carbon cloth (CC) was purchased from Cetech Co. Ltd. Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and sodium pentacyanonitrosylferrate(III) dihydrate ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$) were obtained from Fischer Scientifics and Alfa Aesar, respectively. Potassium hexacyanoferrate(III) ($\text{K}_3\text{Fe}(\text{CN})_6$), potassium chloride (KCl), and sodium chloride (NaCl) were purchased from Sigma Aldrich. D(+)-glucose, D(+)-lactose, and sucrose were procured by Aromel Kimya, Acros Organics, and Carlo Erba, respectively. Potassium phosphate buffer solution (PBS) was prepared by mixing aqueous solutions of KH_2PO_4 (0.1 M) and K_2HPO_4 (0.1 M), which were supplied by Sigma Aldrich. All chemicals were used as obtained without any further purification. Deionized (DI) water (resistivity: 18 $\text{M}\Omega\cdot\text{cm}$) is used in all experiments.

3.2.2.2 Fabrication of PB-modified CC electrodes

Pieces of carbon cloth (2 cm x 1 cm) were sonicated in acetone three times. They were then washed with DI water several times and dried in an oven at 75 °C overnight. The dried carbon cloth pieces were treated with concentrated nitric acid (HNO_3) for 30

min to remove the natural oxide layer and then washed several times with DI water. The clean carbon cloths were put in the oven at 75 °C to obtain dry pieces.[185]

Cobalt hexacyanoferrate, cobalt aminopentacyanoferrate, and cobalt pentacyanonitrosylferrate modified carbon cloth electrodes were prepared by an electrodeposition method. Sodium aminopentacyanoferrate ($\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$) was synthesized according to our previous reports.[87] CC was immersed in an aqueous solution of $\text{Co}(\text{NO}_3)_2$ (10 mM) containing KCl (0.1 M) as a supporting electrolyte. Then a constant potential of $-0.9 \text{ V}_{\text{Ag}/\text{AgCl}}$ was applied for 100 s to form metallic cobalt particles on the CC surface (CC/[Co]). Then, the rinsed electrode was immersed in an aqueous solution of $\text{K}_3\text{Fe}(\text{CN})_6$ (10 mM) containing KCl (0.1 M), and a reverse potential ($0.9 \text{ V}_{\text{Ag}/\text{AgCl}}$ for 100s) was performed to oxidize the cobalt sites and form a CoFe PB on the surface of carbon cloth (CC/[CoFe]). The electrodeposited electrode was rinsed with DI water and kept in an oven at 75 °C for an hour. CC/[CoFe-NH₃] and CC/[CoFe-NO] working electrodes were also prepared with the same method by immersing CC/[Co] into a solution of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ (10 mM) and $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ (10 mM), respectively.

3.2.2.3 Electrochemical measurements

PB electrodeposited CC electrodes serve as working electrodes. All potentials measured vs. $\text{Ag}|\text{AgCl}|\text{KCl}(\text{sat.})$, denoted as $\text{V}_{\text{Ag}/\text{AgCl}}$. A constant potential of $1.15 \text{ V}_{\text{Ag}/\text{AgCl}}$ is applied for amperometric detection of glucose and, CV experiments are carried out at a scan rate of 50 mV/s with a potential range from 0.2 to 1.3 $\text{V}_{\text{Ag}/\text{AgCl}}$. All electrochemical experiments are performed in a 0.1 M PBS electrolyte containing 0.5 M KCl. Quantitative glucose detection was achieved by recording the current increases due to the specific glucose concentration injections to form a calibration plot under a CA experiment in 0.1 M PBS.

3.2.3 Results and Discussion

3.2.3.1 Synthesis and Characterization

PB modified CC electrodes were prepared via a two-step electrodeposition method.[25,156] A constant negative potential is applied to the CC electrode in a solution of Co^{2+} ions to afford metallic Co particles coated CC electrode, CC/[Co]. The electrode was then applied a positive potential in aqueous solutions of $[\text{Fe}(\text{CN})_6]^{2-}$,

$[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$, and $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complexes to afford CC/[CoFe], CC/[CoFe-NH₃], and CC/[CoFe-NO], respectively (Figure 3.11).

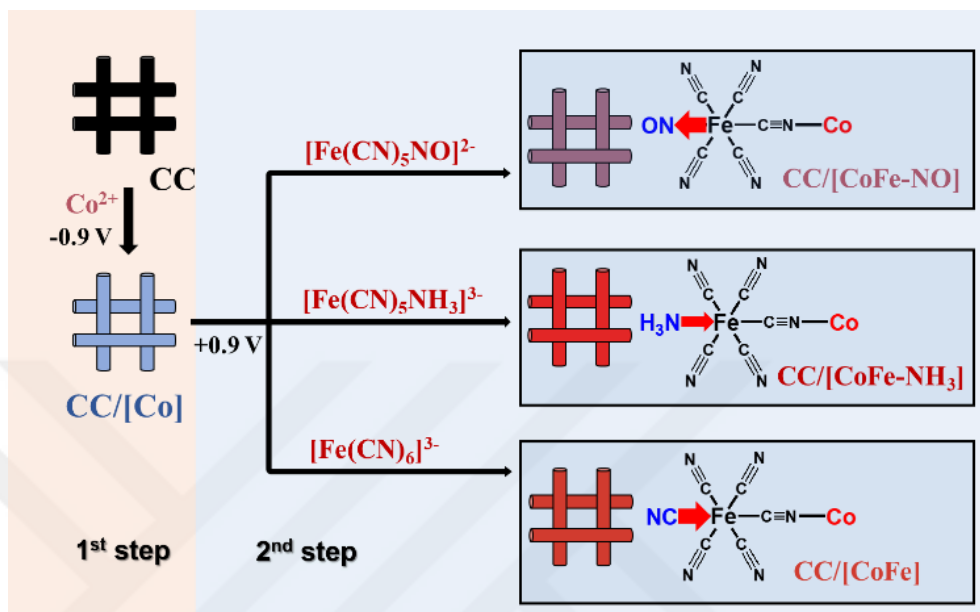


Figure 3.11 Synthetic strategy for the working electrodes. In the first step, the CC electrode is treated with a negative bias in the presence of cobalt ions to obtain metallic cobalt sites on the electrode (CC/[Co]), which is followed by the immersion of CC/[Co] electrodes to a solution containing the desired cyanoiron precursor under positive bias to form three different PB electrodes (2nd step).

PB coated CC electrodes exhibit different morphologies as depicted from SEM images (Figure 3.12 a-c). Although all electrodes exhibit spontaneously formed porosities, they differ from each other in terms of structural evolution. The SEM image of CC/[CoFe] illustrates a non-uniform and defective compound (Figure 3.12a), while a variety of clustered-ball-shaped structures are observed on the surface of CC/[CoFe-NH₃] (Figure 3.12c). On the other hand, CC/[CoFe-NO] exhibits well-organized nanoplatelet particles (Figure 1b). EDAX elemental scanning technique reveals a Co:Fe elemental ratio of 3:1 for all PB electrodes (Figure 3.13).

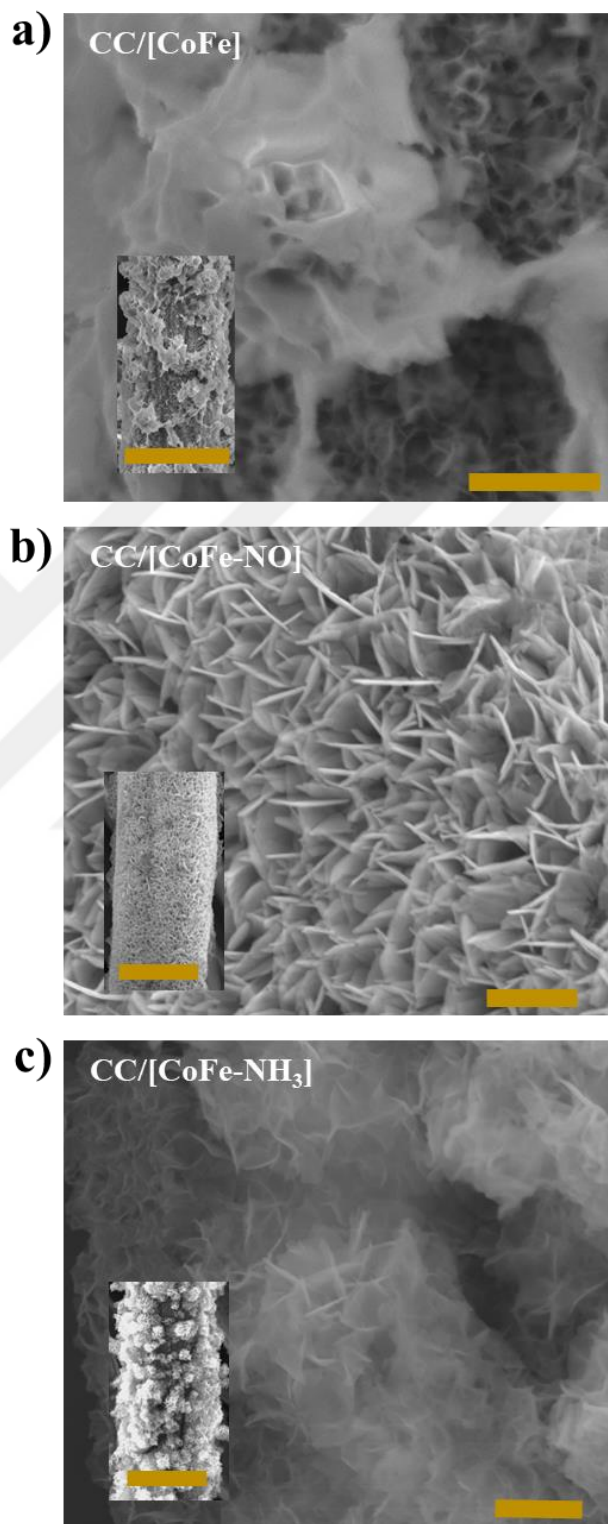


Figure 3.12 The SEM images of (a) CC/[CoFe], (b) CC/[CoFe-NO], and (c) CC/[CoFe-NH₃] (scale bar: 1 μ m). The inset images represent a single coated fiber with the relevant PB structure with a scale bar of 10 μ m.

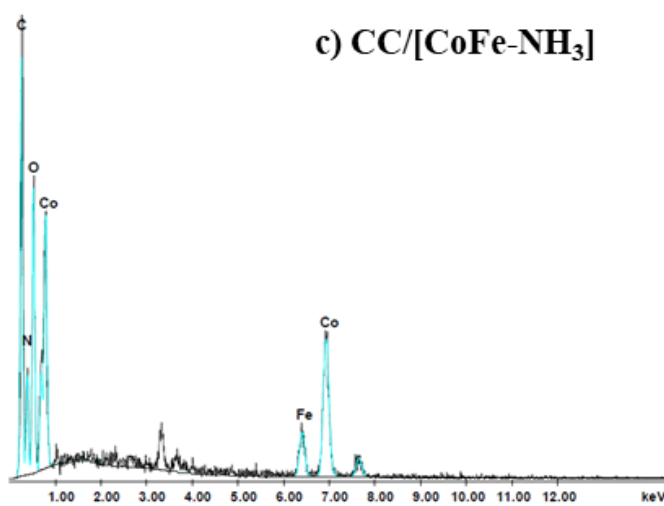
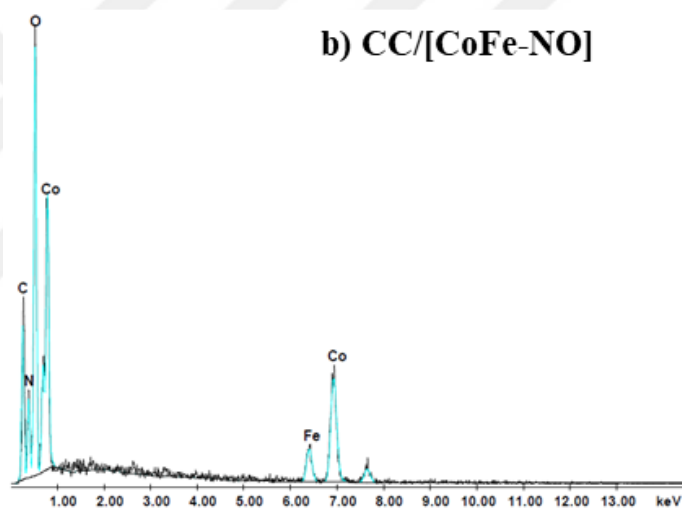
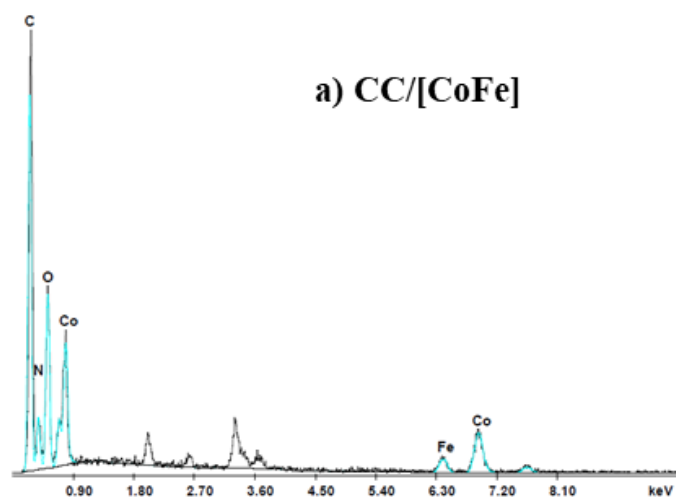


Figure 3.13 The EDAX analysis of (a) CC/[CoFe], (b) CC/[CoFe-NO], and (c) CC/[CoFe-NH₃].

Furthermore, the powder XRD pattern confirms a face-centered cubic PB structure (Figure 3.14a). [CoFe-NH₃] exhibits a less crystalline nature compared to [CoFe] and [CoFe-NO] as expected.[186,187] The Infrared spectrum of CC/[CoFe] shows weak peaks due to the low transmittance feature of CC (Figure 3.14b). The spectrum of blank CC electrode was used to define the characteristic peaks of PB structure. Both CC/[CoFe] and CC/[CoFe-NH₃] exhibit a strong peak at 2112 cm⁻¹, which corresponds to the Co^{III}-NC-Fe^{II} coordination mode.[65] The cyanide stretching mode for CC/[CoFe-NO] is observed at a much higher wavenumber (2188 cm⁻¹) due to the electron-accepting ability of the nitrosonium ligand. Moreover, the sharp peak of CC/[CoFe-NO] at 1940 cm⁻¹ is attributed to the -NO stretching mode.[188,189] Additional peaks observed for all samples belong to the components present in a typical PB structure. The peak at around 1605 cm⁻¹ is assigned to the H₂O bending mode, and the peaks in the 400–600 cm⁻¹ region correspond to Co–N and Fe–C bond stretches.[70]

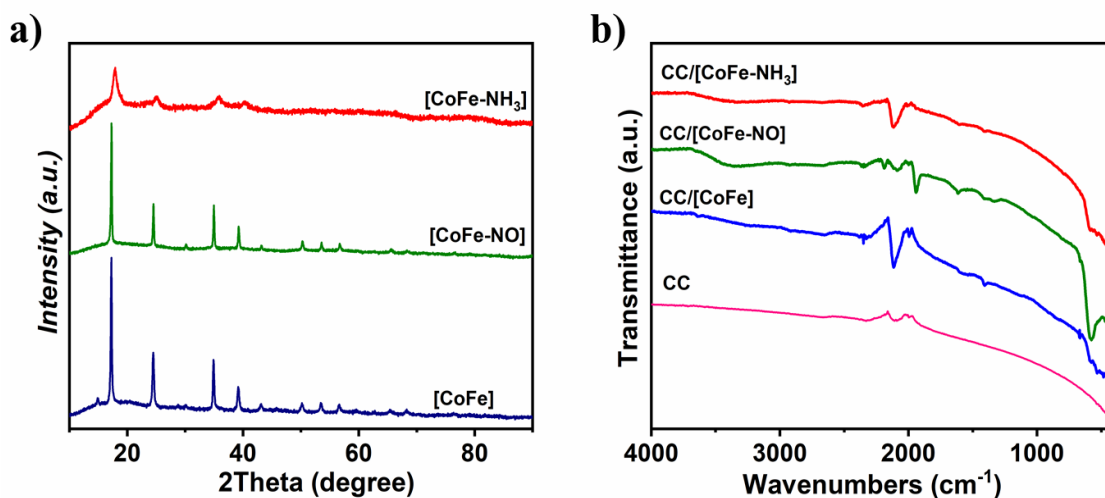


Figure 3.14 (a) The XRD pattern of powder PB analogues: [CoFe-NH₃], [CoFe-NO], [CoFe]; and (b) the ATR-FTIR spectra of the electrodes.

In the following step, XPS analysis is utilized to explore the oxidation states of compositions. The XPS spectra of Fe2p and Co2p for all three samples are shown in Figure 3.15. We focused on the metal sites in a cyanide-based network in previous deconvolutions [87,168,190,191] suggesting that the partial oxidation is typical when metal ions are connected through cyanide bridging group. Fe2p region, in Figure 3.15a, exhibits two dominant bands; the one at between 708–711 eVs for Fe2p_{3/2} and the other

one at between 721–723 eVs for Fe2p_{1/2}. The most pronounced difference is observed for the CC/[CoFe-NO] and CC/[CoFe] samples. The peaks for Fe2p_{3/2} (711 eV) and Fe2p_{1/2} (723 eV) indicate the formation of Fe³⁺ in the structures. Thus, the partial oxidation of Fe²⁺ to Fe³⁺ ions in CC/[CoFe] and CC/[CoFe-NO] is more dominant compared to CC/[CoFe-NH₃]. The peak for the iron atom in CC/[CoFe-NO] is observed at 711.37 eV (Fe 2p_{3/2}), which is around 1 eV higher than the one found for CC/[CoFe] (710.06 eV). This trend confirms the electron accepting ability of nitrosonium ligand and the electron donating ability of NH₃ ligand towards the iron site.

The dominant peaks of Co2p in all three samples are located at the binding energies of about 780 and 795 eVs, assigned to 2p_{3/2} and 2p_{1/2} of Co²⁺ cation, respectively. The binding energies of 782 eV and 797 eV also correspond to 2p_{3/2} and 2p_{1/2} doublet of Co³⁺, respectively (Figure 3.15b). ‘Shake-up’ satellites were also observed for all electrodes indicating the presence of mixed oxidation states for cobalt sites.

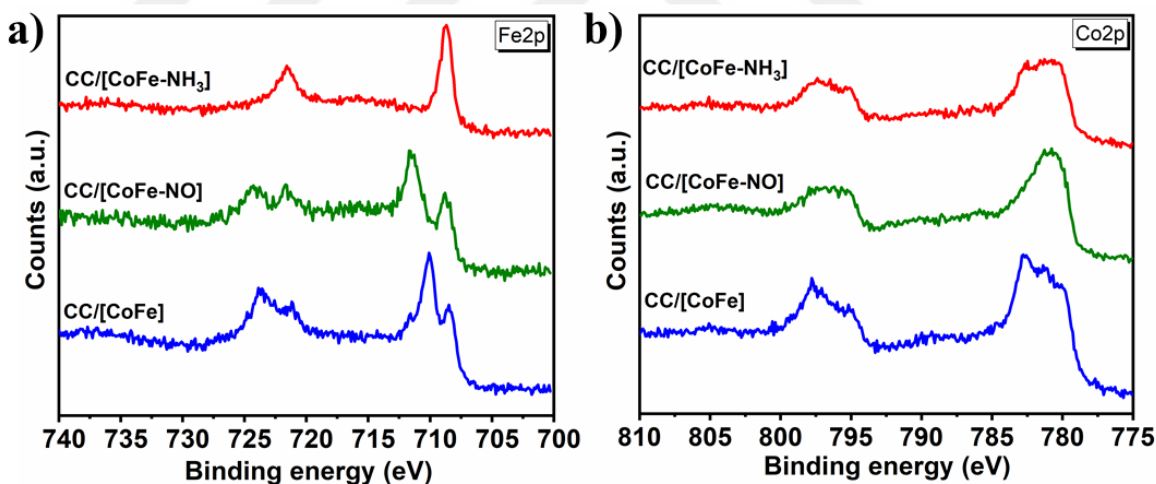


Figure 3.15 The XPS spectra of the electrodes in the (a) Fe2p and (b) Co2p regions.

3.2.3.2 Electrochemical Characterizations

Glucose sensing activities of PB modified CC electrodes were investigated with a series of electrochemical experiments performed in a 0.1 M PBS solution at pH 7. CV profiles exhibit a reversible redox couple, ascribed to the Co^{II}/Co^{III} redox process in a 0.2 – 1.3 V potential range (Figure 3.16a). CC/[CoFe-NO], however, exhibits a sharper intense oxidation peak compared to CC/[CoFe] and CC/[CoFe-NH₃]. The irreversible peak above 1.2 V is attributed to the catalytic water oxidation process. The optimum

working potential of PB sensors is determined according to the highest amperometric response when 1 mM glucose is injected to the neutral pH medium in a 1.00 – 1.20 V potential range (Figure 3.16b). The current responses of all electrodes increase gradually as the applied bias increases from 1.00 V to 1.15 V, then decrease significantly at 1.20 V due to the competitive catalytic water oxidation process. Since the highest sensitivity is observed at 1.15 V, further glucose sensing experiments are performed at this potential.

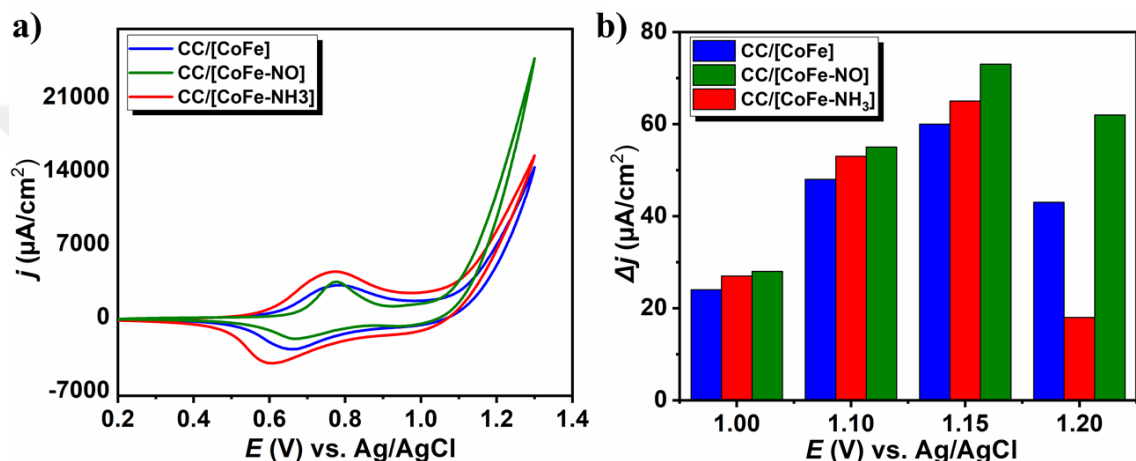


Figure 3.16 (a) CV curves of the electrodes at a scan rate of 50 mV/s and (b) the current responses of electrodes at different constant potentials in the presence of 1 mM glucose in CA measurements in a 0.1 M PBS.

Catalytic glucose oxidation activities of PB electrodeposited CC electrodes are examined with the addition of glucose at a constant concentration during amperometric measurements in 0.1 M PBS (Figure 3.17). Calibration plots are obtained by plotting steady-state current densities versus injected glucose concentration to evaluate their sensitivities (Figure 3.17, insets). Fabricated PB based electrodes reveal a fast response time and a wide concentration range under neutral conditions, making them suitable for industrial [192] and biological [193] applications. Moreover, CC/[CoFe], CC/[CoFe-NH₃], and CC/[CoFe-NO] offer a sensitivity of 43.07 ($R^2 = 0.98$), 43.84 ($R^2 = 0.98$), and 145.43 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ ($R^2 = 0.99$) with a detection limit of 54 μM , 63 μM , and 28 μM (based on $S/N = 3$), respectively. Among all, CC/[CoFe-NO] exhibits an activity three times higher than the other two electrodes.

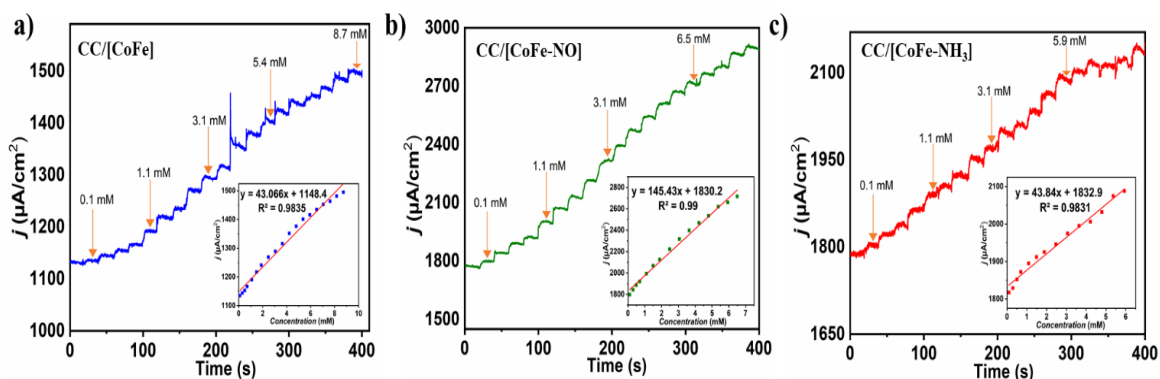


Figure 3.17 The CA profiles of (a) CC/[CoFe], (b) CC/[CoFe-NO], and (c) CC/[CoFe-NH₃] electrodes at varying concentrations of glucose (The arrow shows the concentrations of the solution at each injection time) and at an applied potential of 1.15 V. (Inset: Calibration curve of stable oxidation current versus the glucose concentration).

The lowest response time is obtained for CC/[CoFe-NO] (2 s in a 0.1 – 6.5 mM range) while it is 6 s (0.1 – 8.7 mM range) and 3 s (0.1 – 5.9 mM range), respectively for CC/[CoFe] and CC/[CoFe-NH₃] (Figure 3.18).

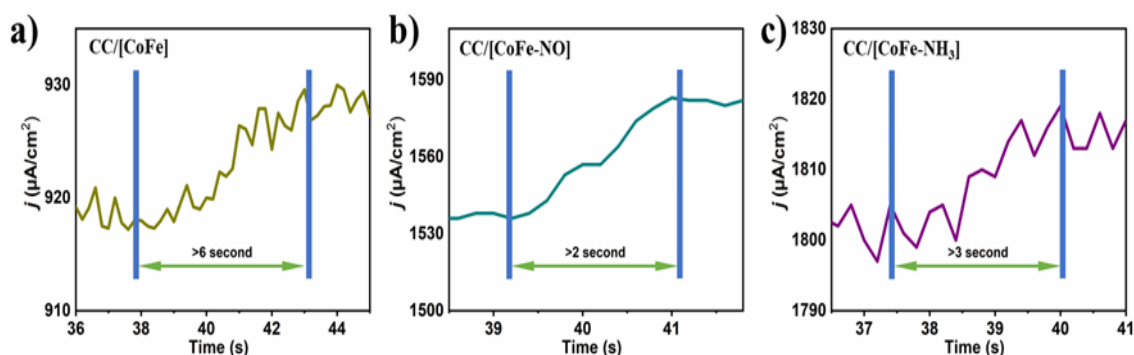


Figure 3.18 The magnified CA measurements during 0.3 mM glucose injection indicating the response time for (a) CC/[CoFe], (b) CC/[CoFe-NO], and (c) CC/[CoFe-NH₃].

While PB derived glucose-sensing electrodes have previously been studied under an alkaline medium (pH 14), we focus on the catalytic oxidation of glucose under a neutral medium (pH 7). We observe that they can operate in a wide working range compared to the previous reports.[47–50] PB derived CuCo and porous CoOx electrodes demonstrate a sensitivity of 567 and 426 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ with a working range up to 0.825 mM and 1.92 mM, respectively.[47,50] Besides, PB analogues have tendencies to transform to

metal oxides/hydroxides above $\text{pH} \geq 13$, which lead to poor shelf life.[51,166] Several studies clearly show that a sensor's performance decreases significantly as the pH of the working conditions is lowered.[194,195] Table 1 lists glucose-sensing electrodes studied under neutral conditions as a comparison.[159,160,163–165,195–197] Most non-enzymatic sensors that operate under neutral medium rely on a noble metal such as Pt and Au, which restrict their commercialization potential. Furthermore, Pt possesses a high oxidation ability with a relatively low selectivity.[170] While the tabulated sensors own similar linear ranges with the present work their sensitivities are considerably low. For example, nanoporous Pt exhibits a sensitivity of $5.67 \mu\text{A mM}^{-1} \text{cm}^{-2}$, [159] while it is $45 \mu\text{A mM}^{-1} \text{cm}^{-2}$ and $2.1 \mu\text{A mM}^{-1} \text{cm}^{-2}$ for 50 nm Au-TiO₂NTs[163] and Pt-Au nanocoral,[195] respectively.

Table 3.2 Glucose sensors studied under neutral conditions.

Electrode	Sensitivity, $\mu\text{A cm}^{-2} \text{ mM}^{-1}$	Linear Range, mM	LOD, μM	Substrate	Synthesis method	Ref.
Nanoporous Pt	5.67	1-10	800	Pt	Electrochemical roughening	[159]
Pt nanotubule array	0.1	2-14	1	Porous anodic alumina	Electrodeposition	[160]
50 nm Au-TiO ₂ NTs	45	0.05-3	50	Ti	Anodization + calcination	[163]
Au nanopillar arrays	13.2	0.5-9	60	Si wafer	Photolithography + sputtering + CVD	[164]
Pt-Au nanocatalyst	1.69	0.01-7.5	6.5	Boron doped diamond	Electrodeposition	[165]
Pt-Au nanocoral	2.1	Up to 22	28	GCE	Precipitation	[195]
PtAu/C nanocomposite	4.7	0-10	2	GCE	Precipitation	[196]
Au thin films	18.2	0-10	10	Carbon nanotube	Pulsed laser deposition	[197]
CoFe	18.69	0.1-8.2	67	FTO	Electrodeposition	[184]
CoFe	43.07	0.1-8.7	54	Carbon Cloth	Electrodeposition	This work
CoFe-NH ₃	43.84	0.1-5.9	63	Carbon Cloth	Electrodeposition	
CoFe-NO	145.43	0.1-6.5	28	Carbon Cloth	Electrodeposition	

The CV profiles of all electrodes present a shift to more positive potentials and a decrease in the intensity of Co^{II/III} redox peak as the glucose concentration is gradually increased (Figure 3.19). This behavior suggests that the redox process is dependent on the glucose concentration similar to water oxidation studies with PBAs.[65]

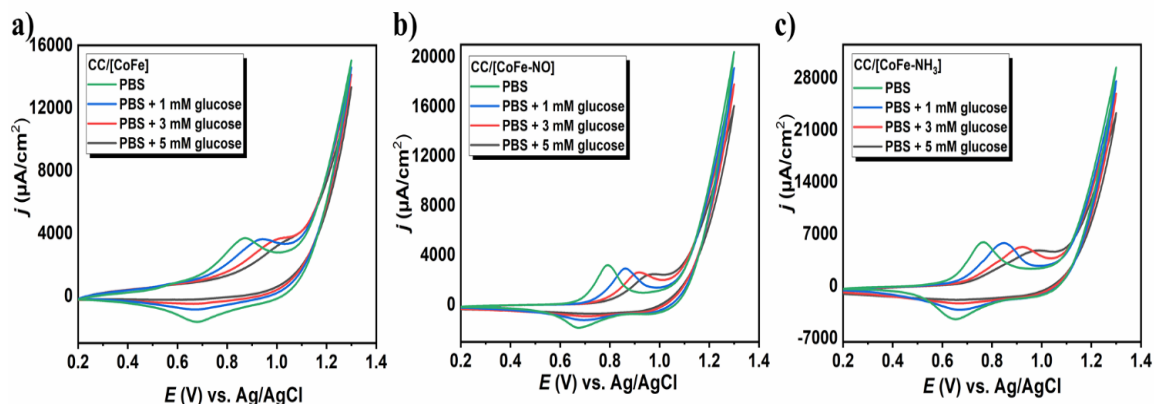


Figure 3.19 CV curves of (a) CC/[CoFe], (b) CC/[CoFe-NO], and (c) CC/[CoFe-NH₃] electrodes with sequential increase of the concentration of glucose at a scan rate of 50 mV/s in 0.1 M PBS.

Additionally, the CV profile of CC electrode does not suggest any interference to the sensing activity of PB analogues in the presence of glucose (Figure 3.20).

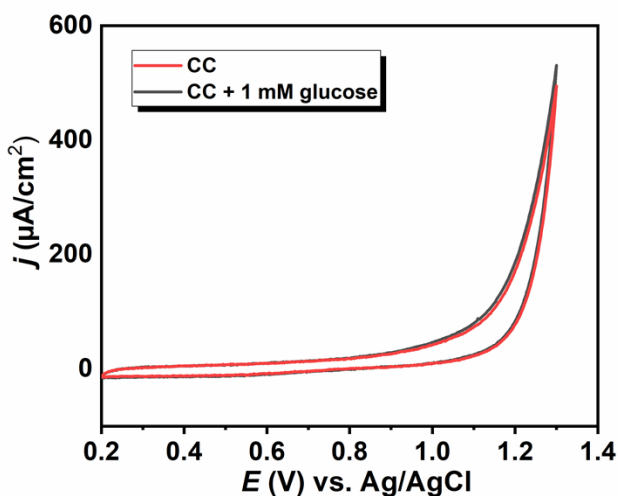


Figure 3.20 The CV curves of CC electrode in the absence (red) and presence (black) of glucose at a scan rate of 50 mV/s in 0.1 M PBS.

Moreover, CVs of all PB sensors indicate a similar trend after the sensing measurements when the solution is saturated with glucose (Figure 3.21). This trend suggests that glucose oxidation occurs on active Co^{III} sites, and the activity is diminished as the active sites are saturated with glucose molecules.

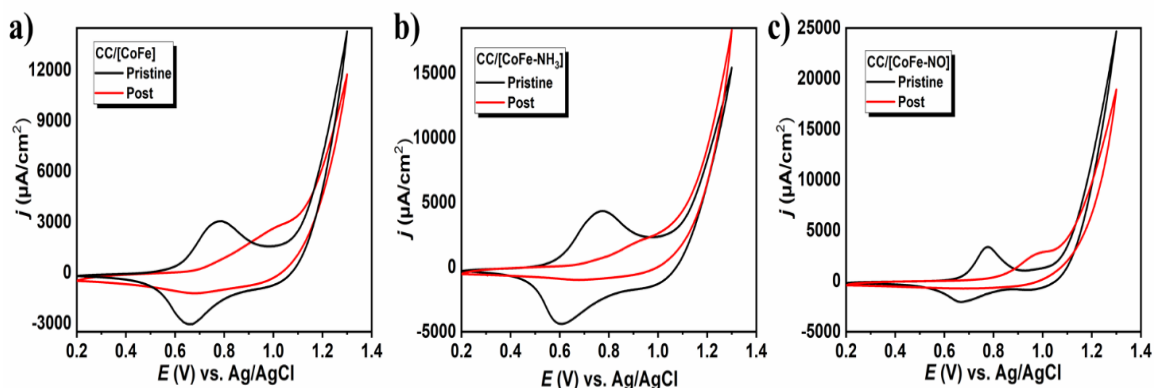


Figure 3.21 CV curves of pristine (black) and post (red) (a) CC/[CoFe], (b) CC/[CoFe-NO], and (c) CC/[CoFe-NH₃] electrodes at a scan rate of 50 mV/s in 0.1 M PBS.

CVs at different scan rates are recorded to estimate the surface concentrations of redox active cobalt centers (Figure 3.22).[67] A slight shift of Co^{II/III} redox couple towards the positive side is observed for the CVs of all electrodes with increasing scan rate due to the solution resistance.

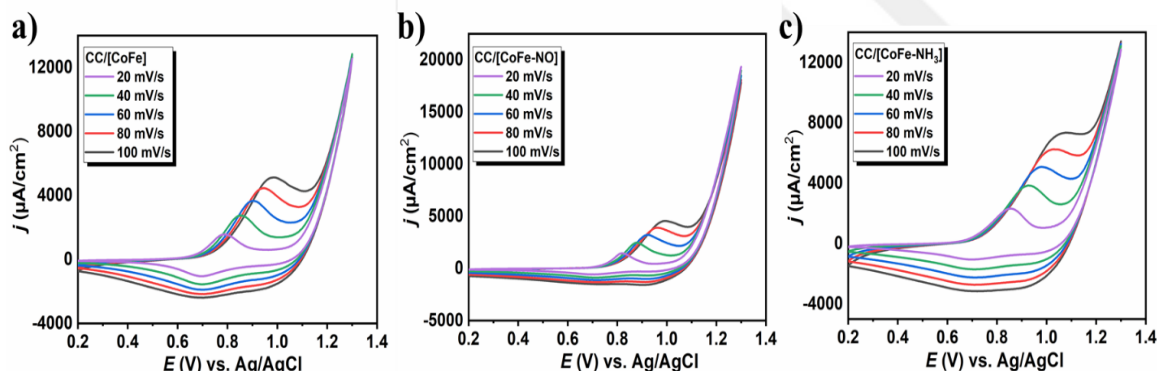


Figure 3.22 CV curves of (a) CC/[CoFe], (b) CC/[CoFe-NO], and (c) CC/[CoFe-NH₃] electrodes at different scan rates in 0.1 M PBS.

The coverage of active cobalt sites for CC/[CoFe], CC/[CoFe-NO], and CC/[CoFe-NH₃] is calculated as 47.6 nmol cm⁻², 41.8 nmol cm⁻², and 66.3 nmol cm⁻², respectively (Figure 3.23). The CC/[CoFe-NH₃] electrode presents 50% higher surface concentration compared to CC/[CoFe] and CC/[CoFe-NO]. The origin of high surface concentration could be the less crystalline nature of [CoFe-NH₃] as depicted from its powder XRD profile. Although CC/[CoFe-NO] exhibits the lowest active cobalt sites, it displays a glucose oxidation activity at least three times higher than the other two electrodes. The

faster response time and the higher amperometric response of CC/[CoFe-NO] compared to other electrodes suggests that the electronic effect of iron site plays an important role in the activity of cobalt sites in PB based sensors.

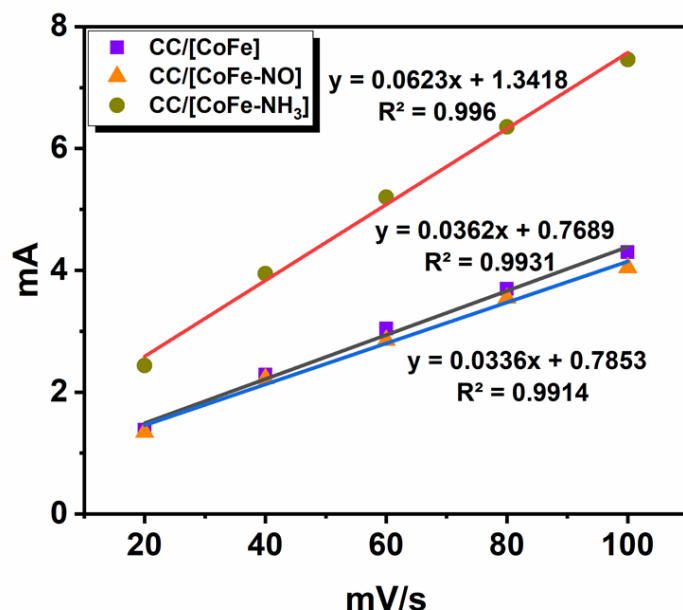


Figure 3.23 The linear relationship between peak current of CoII/III redox couple and sweep rates for CC/[CoFe], CC/[CoFe-NO], and CC/[CoFe-NH₃].

Selective detection of glucose is required from an ideal glucose sensor in a complex media of many different compounds. Studies in the literature exhibit diluted presence (at least 1/10) of various saccharides in the sensing medium compared to the glucose concentration.[47,198] In this study, however, we investigated the complete selectivity of glucose by injecting equimolar concentrations of glucose, sucrose, and lactose. The amperometric response of the electrodes towards glucose is at least ten times higher than lactose, and no observable change in current is observed in the presence of equimolar sucrose (Figure 3.24a). The slight change in the current obtained during the injection of lactose decreases rapidly to initial current levels. Moreover, the measurement is carried out with the addition of 2.5 mM NaCl, 12.5 μ M ascorbic acid, and 12.5 μ M uric acid (Figure 3.24a).[199] A visible activity is still not observed. The long-term stability of the fabricated PB sensors has also been investigated by examining their current response to a 1 mM glucose injection over 15 days (Figure 3.24b). While CC/[CoFe-NH₃] and CC/[CoFe] lose their activities, CC/[CoFe-NO] retains 93% of its activity even after 15

days, which could be attributed to the uniform morphology and strong interaction with the CC surface.

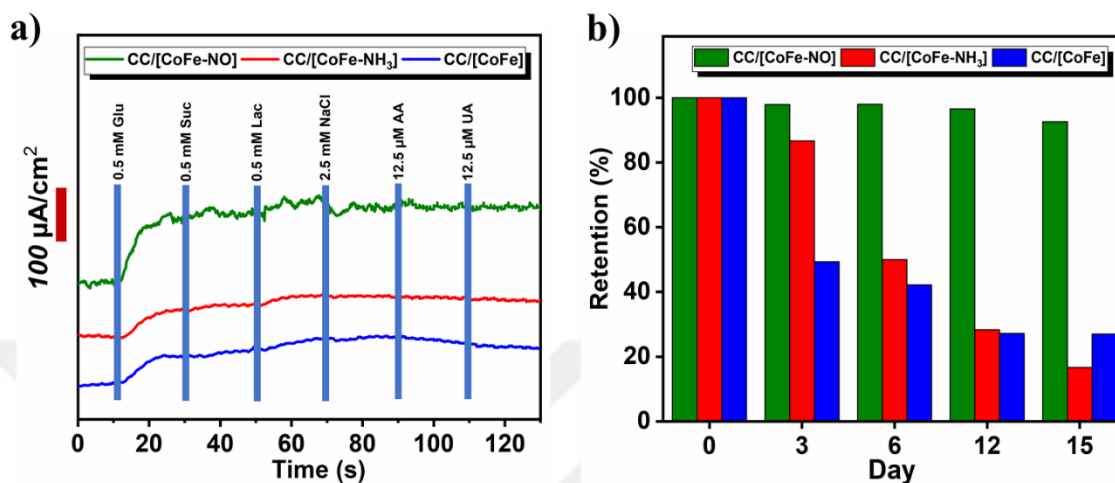


Figure 3.24 (a) The amperometric response of the electrodes in the presence of 0.5 mM glucose, 0.5 mM sucrose, 0.5 mM lactose, 2.5 mM NaCl, 12.5 μM ascorbic acid, and 12.5 μM uric acid. (b) The current response retention of the electrodes in percentage towards one mM glucose injection over 15 days.

3.2.4 Conclusion

We prepared a series of CoFe PB coated carbon cloth electrodes to elucidate the effect of electronic and morphologic properties of PB structure on the electrocatalytic activity of glucose oxidation. Characterization and electrochemical studies reveal that CC/[CoFe-NH₃] exhibit the highest surface concentration of active cobalt sites, which indicates that the crystalline nature of the PB structure could be reduced to enhance the number of defects and active sites by introducing asymmetric cyanoferrate precursors. Despite its higher surface concentration, CC/[CoFe-NH₃] exhibits a similar glucose oxidation activity to that of CC/[CoFe] and much less activity and selectivity compared to CC/[CoFe-NO]. The unprecedented high activity and fast response of CC/[CoFe-NO] suggests that the electronic effect plays a more dominant role compared to the morphological effect in the electrocatalytic activity of glucose oxidation. The electron-accepting ability of nitrosonium ion boosts the number of Fe^{III} and Co^{III} sites in these mixed-valence PB structures, which increases the catalytic activity of cobalt sites towards glucose.

The linear working ranges of all electrodes cover a concentration window under physiological pH. The electrodes also demonstrate superior selectivity for glucose in the presence of common interfering agents in human blood and sweat.[199,200] Furthermore, CC/[CoFe-NO] electrode retains 93 % of its initial activity even after 15 days.

In summary, we present a simple synthetic pathway, which allows easy-tuning of the activity and the operating range of the glucose sensor. The superior selectivity and robustness of the electrodes under physiological pH make them ideal platforms for glucose sensing from human blood and sweat.



CHAPTER 4

This chapter of the thesis is based on the publication “‘Plug and Play’ Photosensitizer–Catalyst Dyads for Water Oxidation’, R. Chalil Oglou, T.G. Ulusoy Ghobadi, E. Ozbay, F. Karadas, **ACS Applied Materials & Interfaces**, 2022, 14, 21131 – 21140. Adapted (or reproduced in part) with permission from American Chemical Society, Ref. [201]. Copyright 2022 American Chemical Society.

4. CoFe PB INCORPORATED PHOTOSENSITIZER DYADS FOR WATER OXIDATION

4.1 Introduction

Building covalently coordinated molecular dyad assemblies has been an attractive approach to mimicking photosystem II, which relies on coupling proper molecular chromophore and catalyst units for efficient charge separation.[202–205] The selection of the bridging ligand that connects a visible light absorbing molecular photosensitizer (PS) to either a hydrogen evolution catalyst (HEC) or a water oxidation catalyst (WOC) plays an essential role in the efficiency of the design. An ideal bridging ligand should have proper functional groups to coordinate the PS and the catalytic unit. Moreover, the studies reveal that the mechanism and the efficiency of charge transfer in donor-bridge-acceptor systems are mainly governed by the size, flexibility, and functional groups in the bridging ligand.[206,207] For example, a coherent superexchange mechanism could be accelerated by decreasing the length of the ligand, and a transition to a weakly distance-dependent incoherent hopping mechanism could be observed once relatively longer bridging ligands are used.[208–210] In coherent transport phenomena, conjugated π -systems, such as vinylene and acetylene groups, are preferred for facilitating an electron transfer through the π bonds.[211] It has also recently been found that the flexibility of the bridging ligand could also affect the charge transfer efficiency.[212] Therefore, short and rigid bridging groups should be chosen to construct a dyad assembly with an efficient electron transfer. Previously studied PS–WOC dyads are mostly limited to photosensitizer groups such as

porphyrin derivatives and ruthenium complexes that absorb light below 465 nm due to the difficulty in designing bridging ligands and properly matching energy levels between the PS and WOC units.[75,213–217] Iron-carbene photosensitizers have also recently been utilized for the development of dyads, although to date, only to address photocatalytic H₂ evolution process.[218,219]

We recently developed a new synthetic pathway to utilize the ability of cyanide bridging group to bind metal ions easily to form a linear M–CN–M' coordination mode, which provides a facile electronic communication between the metal ions (M–M' distance is around 5 Å).[26] The synthesis involves two straightforward steps: First, [Fe(CN)₅] is coordinated to a pyridyl-containing PS to prepare a molecular Fe(CN)₅–PS group, [Fe–PS]. Then, the binding ability of the terminal nitrogen atom of cyanide group to metal ions is utilized to react [Fe–PS] with cobalt ions, which yields a cyanide-based network structure, [CoFe–PS]. We first employed this method to coordinate a ruthenium PS to a CoFe PB structure.[220] Then, we prepared a [CoFe–porphyrin] compound to develop the first earth-abundant PS–WOC assembly.[87] We discovered that the porphyrin group serves not only as a light-absorbing component but also as a capping ligand to limit the dimensionality of cyanide-based network structure. The structure of a CoFe–PS architecture mainly differs from the well-known CoFe Prussian blue analogues (PBAs); CoFe–PS could be described as discrete and random-sized cyanide-based CoFe structures surrounded by PS groups, while CoFe–PBAs exhibit high crystallinity due to long-range structural order. Furthermore, our controlled experiment with a physical mixture of CoFe PBA and porphyrin reveals that the coordination bond between the porphyrin and [Fe(CN)₅] groups boosts the photocatalytic water oxidation activity due to enhanced charge transfer between porphyrin and catalytic cobalt sites. We used this method to further develop one of the first earth-abundant dye-sensitized photoanode in the literature.[87,221] A Prussian blue structure was incorporated to a phenazine-based organic group, Janus green B (JG), on a photoelectrode to prepare a JG-sensitized TiO₂ photoanode [CoFe–JG]. Irradiation of the working electrode with visible light ($\lambda > 420$ nm) under neutral conditions at the potential of 1.23V_{RHE} exhibits a steady photocurrent density of 50 $\mu\text{A cm}^{-2}$ for over 2 hours. In comparison, we prepared a CoFe–Safranine assembly coated on a visible light absorbing semiconductor, WO₃, and we measured

photocurrent density of 1.30 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ using solar irradiation under mildly acidic conditions (pH 3).[191]

Previous studies point out that cyanide-based heterogeneous PS-WOC assemblies are unique dyad assemblies since the distance between the PS and the catalytic site is minimized, which enhances the coupling between functional units. In one of our previous studies, this design has been highlighted as a “kissing assembly” since a partial mixing of molecular orbitals of PS and WOC units are observed due to short cyanide bridging ligand.[191] Moreover, the simplicity of the synthesis provides an ideal platform to prepare ‘plug and play’ PS–WOC assemblies with a large agenda of potential photosensitizers. In our pursuit of efficient noble metal free bulk devices, we chose a series of low-cost and well-known organic molecules as PS units, which exhibit various band alignments in the photoinduced oxygen evolution process. Each building block, PS, $\text{Fe}(\text{CN})_5$ group, and Co site, is integrated via a step-by-step strategy to achieve a PS–Fe–WOC coordination mode. This strategy also allows the preparation of PS, [Fe–PS], and [CoFe–PS] compounds separately and the comparison of the optical and structural properties of each component. Herein this study, we utilized three organic photosensitizers that absorb different regions of the solar spectrum: A green light absorbing dye, safranin O ([SF], $\lambda_{\text{max}} = 520 \text{ nm}$), is chosen to cover the region with the highest solar irradiation. A red-light absorbing dye, methylene blue ([MB], $\lambda_{\text{max}} = 664 \text{ nm}$), is studied to mimic chlorophyll in Photosystem II, which has not been achieved for a dyad assembly up to date. A UV light absorbing coumarin derivative, ([CM], $\lambda_{\text{max}} = 334 \text{ nm}$) is studied mainly for comparison. It is also used to elucidate the role of the Co:Fe atomic ratio on the activity since CM is a neutral molecule, while SF and MB are positively charged. In this study, we examined the optical, electrochemical, and photocatalytic properties of PS–WOC dyads to further verify the utility of our approach.

4.2 Experimental Procedure

4.2.1 Chemicals

All chemicals were used as obtained without any further purification. Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%) and safranin O ($\text{C}_{20}\text{H}_{19}\text{ClN}_4$, >94%) were supplied by Fischer Scientifics. 7-Hydroxy-4-(4-pyridyl)coumarin ($\text{C}_{14}\text{H}_9\text{NO}_3$, 95%) was

obtained from ABCR. Potassium chloride (KCl, 99-100%), methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, >97%), and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, >98%) were purchased from Sigma Aldrich. Chloroform (CHCl_3 , >99.9%) was procured by Carlo Erba. Potassium phosphate buffer solution (PBS) was prepared by 0.1 M potassium phosphate monobasic (KH_2PO_4 , Sigma Aldrich, 98-100%) and 0.1 M potassium phosphate dibasic (K_2HPO_4 , Sigma Aldrich, >99%). Deionized water (resistivity: 18 $\text{M}\Omega\cdot\text{cm}$) is used in all experiments. Coumarin, safranin O, and methylene blue photosensitizers are denoted as [CM], [SF], and [MB], respectively, throughout the manuscript. In addition, the iron source of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ is denoted as [Fe-NH₃] and synthesized according to our previously published procedure.[87]

4.2.2 Synthesis Procedures for [CoFe-CM], [CoFe-SF], and [CoFe-MB]

A two-step synthetic strategy was employed to prepare all PS-WOC assemblies, according to the published procedure.[191] First, a solution of the organic photosensitizer ([CM], [SF], or [MB]) was prepared with a proper solvent (6 mM [CM] in 100 mL CHCl_3 , 0.03 M [MB] and 0.03 M [SF] in 20 mL H_2O) and reacted with a solution of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ (a 20 mL aqueous solution of [Fe-NH₃] (0.03 M) for [MB] and [SF] and a 100 mL aqueous solution of [Fe-NH₃] (6 mM) for [CM]) in a 1:1 stoichiometric ratio. The resulting mixture is allowed to stir overnight at room temperature to prepare [Fe-PS] complexes. The suspension is kept in a fridge (+4 °C) overnight to settle down. It is then centrifuged to precipitate [Fe-PS] and decant it. The powder is dried for 2 days in an oven at 75 °C. Next, a solution of [Fe-PS] is reacted with a solution of $\text{Co}(\text{NO}_3)_2$ (2 eq.). For [CoFe-CM] and [CoFe-MB], [Fe-CM] and [Fe-MB] (0.03 M, 20 mL) were mixed with Co^{2+} (0.06 M, 20 mL) in an aqueous medium, respectively. For [CoFe-SF], [Fe-SF] (0.03 M in 20 mL acetonitrile) is reacted with $\text{Co}(\text{NO}_3)_2$ (0.06 M in 20 mL ethanol). The solution is stirred overnight at room temperature. The mixture is rinsed several times with cold ethanol and distilled water, then it is dried in an oven at 75 °C for 2 days to afford the photosensitizer-catalyst dyad assembly, [CoFe-PS]. The bulk precipitates were crushed in a mortar to obtain a powder form for further characterization and photocatalytic experiments.

4.3 Results and Discussions

4.3.1 Characterization Studies

[CoFe-PS] compounds were prepared via a two-step precipitation method (Figure 4.1). First, NH_3 ligand in $\text{Na}_3\text{Fe}(\text{CN})_5\text{NH}_3$ was substituted with a pyridyl containing PS to produce molecular [Fe-PS] complexes. Then, the lability of the terminal nitrogen atom of the cyanide ligand toward metal ions was utilized to react [Fe-PS] complexes with Co^{2+} ions. The reaction yields the formation of bulk CoFe PB structures, in which the coordination sphere of an iron site is identical to that of [Fe-PS]. On the other hand, cobalt sites are surrounded with a combination of nitrogen atoms of cyanide groups and water molecules, which make them ideal for catalytic water oxidation centers. PS-WOC assemblies with different organic light absorbing groups are characterized by ATR, SEM, XPS, and UV-Vis techniques. [CM], [SF], and [MB] have been examined as PSs for the photocatalytic oxidation of water.

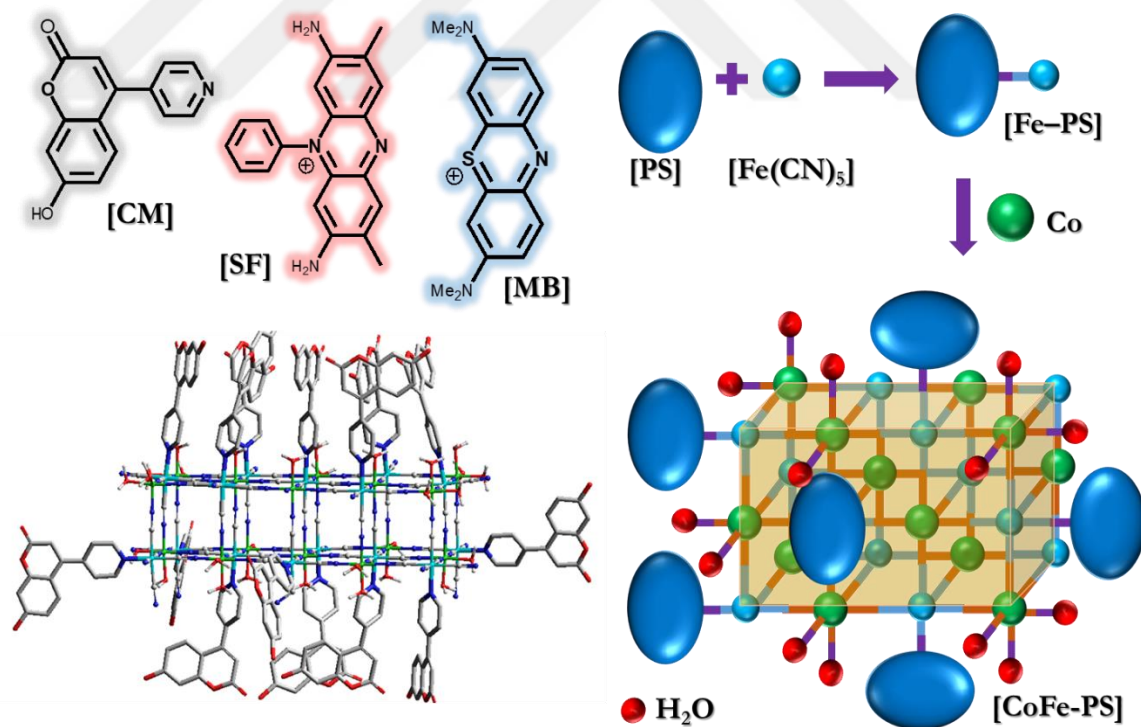


Figure 4.1 A visual two-step synthetic construction of PS-WOC dyad assemblies. The coordination of the PS ([CM], [SF], [MB]) to the $[\text{Fe}(\text{CN})_5]$ group yields molecular [Fe-PS] complexes, which are then reacted with cobalt ions to afford [CoFe-PS] assemblies. [CoFe-PS] exhibit random-sized network CoFe PB structures that are

surrounded with PS groups. Catalytic active cobalt sites are surrounded with a combination of N-atom of the CN group and H₂O molecules.

The nature of these organic groups and the coordination mode of cyanide groups in PS, [Fe-PS], and [CoFe-PS] compounds were monitored systematically with Infrared spectroscopy (Figure 4.2). The organic chromophores exhibit several sharp peaks in the 1600–740 cm⁻¹ region, which are assigned to the C–C and C–N ring stretching vibrations.[221] For [CoFe-CM], one additional peak is observed at 1711 cm⁻¹, which is attributed to the carbonyl group.[222] The revealed peaks at 1610 and 1410 cm⁻¹ are decent examples for the presence of α - β unsaturated ketone and C–H of methyl group for the [CoFe-SF] dyad sample, respectively. For [CoFe-MB], the peaks at 1595 and 900 cm⁻¹ are assigned to C=C bands for cyclic alkenes and vinylidene groups, respectively. The cyanide stretch shifts slightly to higher wavenumbers, when [Fe-NH₃] (ν CN = 2040 cm⁻¹) reacts with organic PSs to form [Fe-PS] complexes. The CN stretch is obtained at 2040, 2055, and 2107 cm⁻¹ for [Fe-CM], [Fe-SF], and [Fe-MB], respectively. The consistent trend in all cases indicates that the PS is coordinated to the iron site and that the electron densities in the iron sites decrease due to the electron-accepting abilities of organic groups.[191,221] The unusually high shift observed for [Fe-MB] indicates that iron sites are in their Fe^{III} states while [Fe-CM] and [Fe-SF] contain mainly Fe^{II} sites.[223] ν CN shifts further to higher wavenumbers once [Fe-PS] is reacted with Co²⁺ ions, which verifies the Fe–CN–Co coordination mode. ν CN stretch is obtained at 2070 and 2057 cm⁻¹ for [CoFe-CM] and [CoFe-SF], respectively. Contrary to the [CM] and [SF] cases, a shift to lower wavenumbers is observed for [CoFe-MB] (ν CN = 2055 cm⁻¹) compared to [Fe-MB] (ν CN = 2107 cm⁻¹), which could be attributed to the reduction in the oxidation state of Fe sites from 3+ to 2+ with the addition of cobalt ions.[157] Overall, [CoFe-CM], [CoFe-SF], and [CoFe-MB] depict the characteristic peak of cyanide group at 2070, 2057, and 2055 cm⁻¹, respectively.

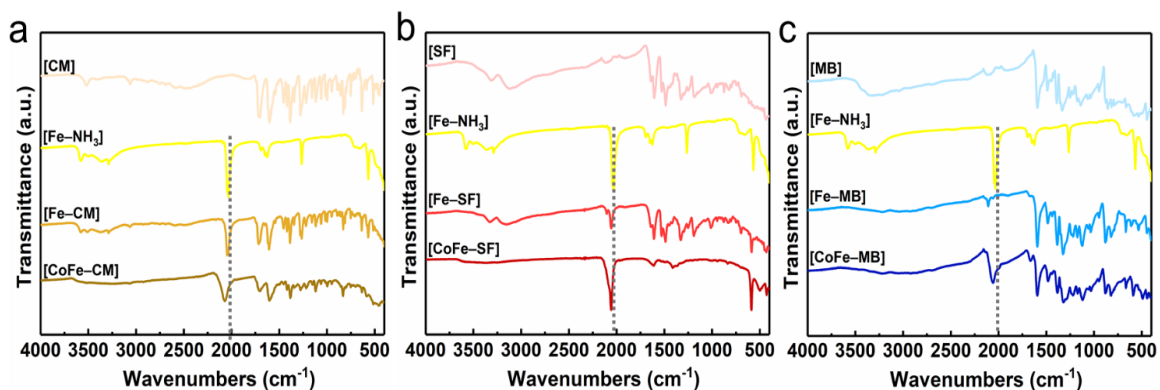


Figure 4.2 A systematic study of ATR-FTIR spectra for (a) [CM], (b) [SF], and (c) [MB] derived assemblies (The perpendicular dash lines demonstrate the shift in the cyanide stretch with respect to [Fe-NH₃]).

SEM analysis is performed to investigate the structure and morphology of [CoFe-PS] compounds. Figure 4.3 presents randomly evolved bulk particles for [CoFe-CM] while aggregated porous round and plate-shaped structures are observed for [CoFe-SF] and [CoFe-MB], respectively.

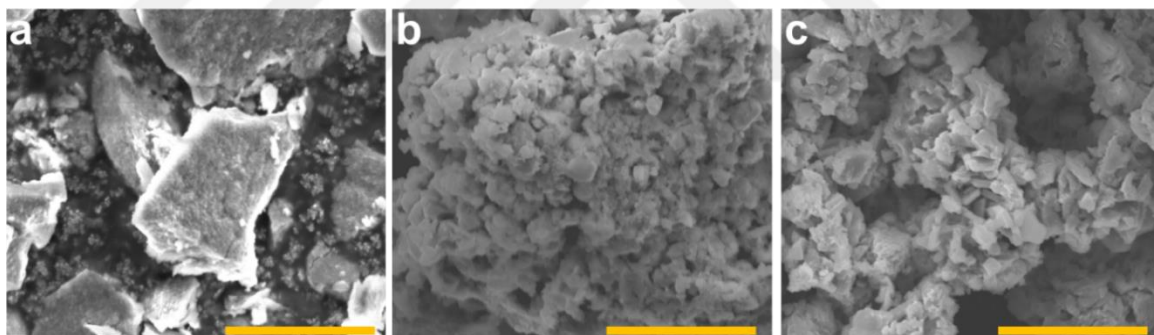


Figure 4.3 SEM images of (a) [CoFe-CM], (b) [CoFe-SF], and (c) [CoFe-MB] (scale bar: 5 μm).

EDAX analysis reveals slightly different Co:Fe atomic ratios. [CoFe-CM], which consists of neutral [CM] groups, exhibits a Co:Fe atomic ratio of 1.43, while positively charged [SF] and [MB] dyes yield lower Co:Fe ratios: 1.17 and 1.22 for [CoFe-SF] and [CoFe-MB], respectively (Figure 4.4). Based on these analyses, the following empirical formulas are derived: $\text{Na}_{0.14}\text{Co}_{1.43}[\text{Fe}(\text{CN})_5\text{CM}]$, $\text{Co}_{1.17}[\text{Fe}(\text{CN})_5\text{SF}](\text{NO}_3)_{0.25}$, and $\text{Co}_{1.22}[\text{Fe}(\text{CN})_5\text{MB}](\text{NO}_3)_{0.17}$, for [CoFe-CM], [CoFe-SF], and [CoFe-MB], respectively.

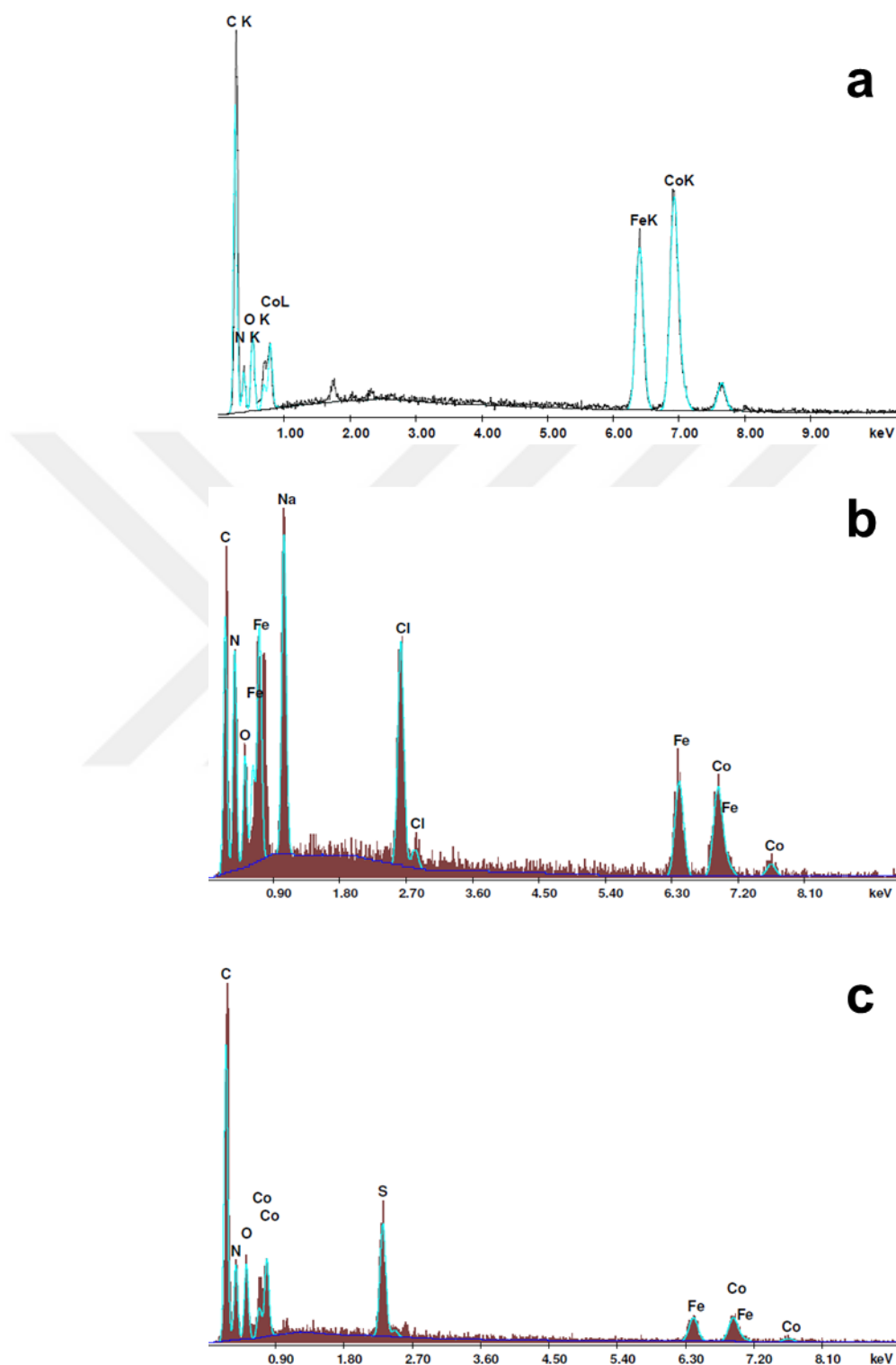


Figure 4.4 EDAX analysis of (a) [CoFe-CM], (b) [CoFe-SF], and (c) [CoFe-MB].

Figure 4.5 displays the comparison of optical absorption profiles of PS, [Fe-PS], and [CoFe-PS]. Both CM and [Fe-CM] exhibit a dominant absorption mainly in the

ultraviolet (UV) region ($\lambda < 400$ nm) with a weak molar absorptivity of $2.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ (at 334 nm).

When the iron site is coordinated to CM, an additional wide band appears at around 450 nm, attributed to a MLCT transition from the iron site to the CM group, which has been previously observed when $[\text{Fe}(\text{CN})_5]$ group is connected to pyridyl ligands and polymers.[67,224,225] The band edge for $[\text{Fe}-\text{CM}]$ is obtained at 536 nm that corresponds to a band gap of 2.31 eV (Figure 4.5a).

An additional broad band is observed at around 650 nm due to metal-to-metal charge transfer (MMCT) between Co and Fe sites. All the bands get broader due to the transition from a molecular structure, $[\text{Fe}-\text{CM}]$, to a network structure, $[\text{CoFe}-\text{CM}]$. On the other hand, the absorption profiles for $[\text{MB}]$ and $[\text{SF}]$ remain almost similar with the addition of $[\text{Fe}(\text{CN})_5]$ group to form $[\text{Fe}-\text{PS}]$ and Co ions to afford $[\text{CoFe}-\text{PS}]$. MB exhibits a strong absorption band at 664 nm with a shoulder at 617 nm.[226,227] The intense band at 664 nm shifts slightly to 654 nm for $[\text{Fe}-\text{MB}]$ and to 650 nm for $[\text{CoFe}-\text{MB}]$. The relative intensity of the shoulder at around 615 nm increases gradually from MB to $[\text{Fe}-\text{MB}]$ and to $[\text{CoFe}-\text{MB}]$. This pair of bands also get broader and cover a larger portion of the visible spectrum as MB is coordinated to $[\text{Fe}(\text{CN})_5]$ group. These changes could be attributed to the partial mixing of ligand with metal-based orbitals.[87,167,191] The absorption bands for MLCT and MMCT processes are not observed for $[\text{CoFe}-\text{SF}]$ and $[\text{CoFe}-\text{MB}]$ since i) they are likely concealed due to the intense absorption bands of $[\text{MB}]$ and $[\text{SF}]$ in the visible region and ii) relatively bulky phenazine groups lead to slightly weaker coordination between PS and Fe sites in $[\text{CoFe}-\text{MB}]$ and $[\text{CoFe}-\text{SF}]$ compared to $[\text{CoFe}-\text{CM}]$, which, in turn, afford relatively less efficient MLCT processes.

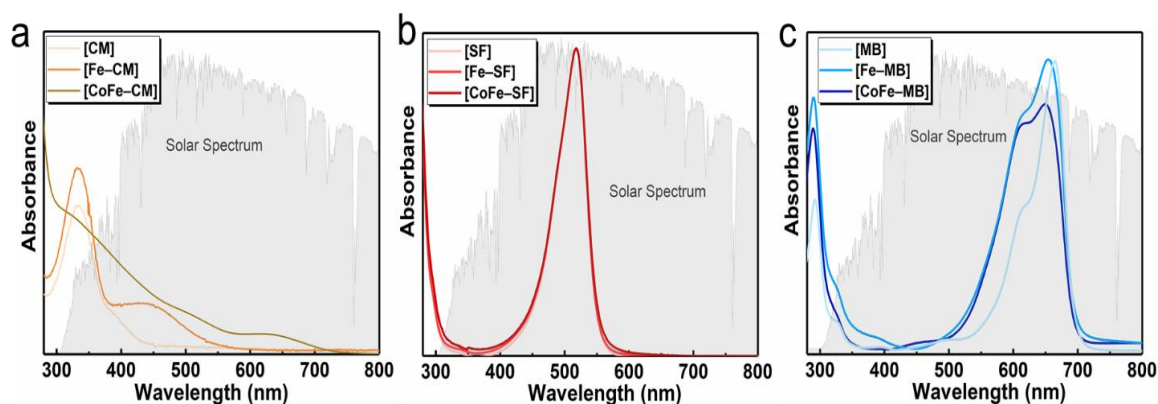


Figure 4.5 Absorption profiles for 10 μM aqueous solutions of (a) [CM], (b) [SF], and (c) [MB] derived compounds. The background depicts the normalized solar spectrum for comparison.

Given the dependence of MLCT process on the type of the solvent, UV-Vis absorption profiles are monitored in DMF as well (Figure 4.6).[228,229] The absorption bands that correspond to the $\pi \rightarrow \pi^*$ of the organic PS group remain as the major absorption bands for bare PS groups and dyads. In DMF, the MLCT and MMCT bands are more distinguishable for [CoFe-CM] compared to H_2O . For SF and [CoFe-SF], the $\pi \rightarrow \pi^*$ transition that is observed at 518 nm in H_2O shifts to 535 nm in DMF. More interestingly, a band at 390 nm and a broad one at around 620 nm appear, which could be attributed to the MLCT process from Fe sites to the SF group and MMCT process between metal sites, respectively. Similarly, [CoFe-MB] in DMF reveals an additional broad band at around 510 nm due to MLCT process. A band due to MMCT is not observed since the strong absorption bands of MB covers most of the 500-700 nm region. [Fe-SF] has a narrow resonant peak in the visible range with an edge positioned at 550 nm resulting a band gap of 2.25 eV (Figure 4.6b). [Fe-MB] has a broad visible light absorption profile with an edge at 693 nm and a band gap of 1.78 eV (Figure 4.6c). Both [Fe-SF] and [Fe-MB] also exhibit weak absorption bands in the UV region. Molar extinction coefficients are found as $5.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 660 nm for [Fe-MB] and $4.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 520 nm for [Fe-SF]. Note that their molar absorptivities are comparable to the benchmark $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer ($1.46 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at around 465 nm).[230] Overall, [Fe-CM] could be described as a UV active molecule, while [Fe-SF] and [Fe-MB] are visible light active photosensitizers. Therefore, [CoFe-MB] and [CoFe-SF] display the desired absorption profiles to harvest the visible light portion of the solar spectrum.

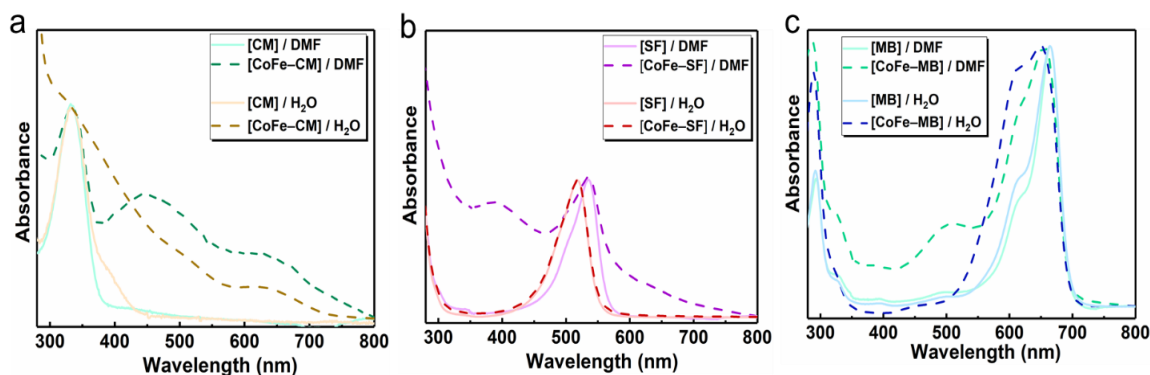


Figure 4.6 Comparison of absorption profiles for (a) [CM] and [CoFe-CM], (b) [SF] and [CoFe-SF], and (c) [MB] and [CoFe-MB] compounds in aqueous and DMF solutions.

4.3.2 Photocatalytic Water Oxidation Studies

The photoinduced O_2 evolution performances were evaluated in a neutral 0.1 M PBS containing the powder suspensions of the dyad compound in the presence of a sacrificial electron acceptor under both 1 sun illumination and visible light irradiation ($\lambda > 420$ nm). To consume the electrons in the LUMO level of the PS upon photoexcitation, persulfate anion, $S_2O_8^{2-}$, is used as an efficient electron scavenger (ES), which has been commonly used in previous PB-based solar driven water oxidation studies.[231]

As shown in Figure 4.7, a catalytic activity of approx. $71.3 \mu\text{mol g}^{-1} \text{h}^{-1}$ is obtained for [CoFe-MB], which is around 1.4 times higher than that obtained for [CoFe-CM] ($49.5 \mu\text{mol g}^{-1} \text{h}^{-1}$) and 2.5 times higher than that of [CoFe-SF] ($28.4 \mu\text{mol g}^{-1} \text{h}^{-1}$). Therefore, the following trend is obtained: [CoFe-MB] > [CoFe-SF] > [CoFe-CM] under solar irradiation (Figure 4.7a). The turnover frequency (TOF) values for the catalysts were also estimated to compare the activity of catalytic active sites. Based on obtained empirical formulas by EDAX analysis, all cobalt sites were assumed to be active sites for the determination of lower-bound TOF values. A similar trend is also obtained for the lower-bound TOF values as the catalytic activities, which are $(11 \pm 0.26) \times 10^{-4} \text{ s}^{-1}$, $(4.5 \pm 0.18) \times 10^{-4} \text{ s}^{-1}$, and $(5.5 \pm 0.19) \times 10^{-4} \text{ s}^{-1}$ for [CoFe-MB], [CoFe-SF], and [CoFe-CM], respectively. Therefore, [CoFe-MB] exhibits a much higher TOF value compared to the previous PB-based photocatalytic water oxidation studies including the ones even with a Ru PS.[87,220] Since the turnover number (TON) is defined as $\text{TOF} \times \text{time}$, [232] which is referred to the number of reactant converted per minute per catalytic site, the following

TONs of 3.78 ± 0.09 , 1.62 ± 0.07 , and 1.98 ± 0.07 are obtained for [CoFe–MB], [CoFe–SF], and [CoFe–CM], respectively. Moreover, [CoFe–SF] and [CoFe–MB] maintain their activities under visible light irradiation ($\lambda > 420$ nm) for three consecutive cycles, which is a total of 6-hours (Figure 4.7b). Figure 4.7c displays the O₂ evolution rates for dyad assemblies under solar and visible irradiation. [CoFe–MB] and [CoFe–SF] exhibit almost the same activities under both solar and visible light irradiation, indicating that their strong absorption bands in the visible region are utilized for light-driven water oxidation process. [CoFe–CM], however, shows no catalytic activity under the same conditions since most of its absorption is located dominantly below 400 nm.

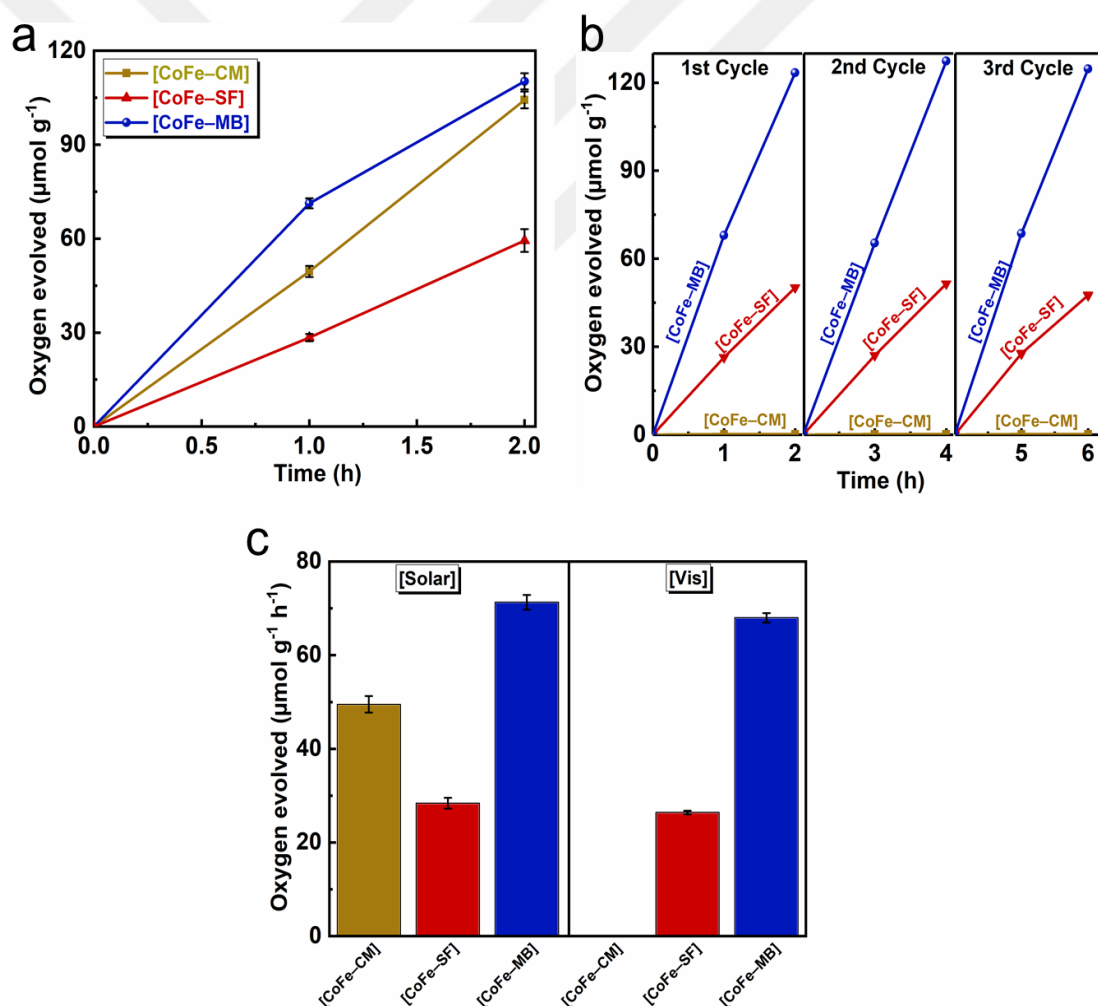


Figure 4.7 O₂ evolution rates of [CoFe–CM], [CoFe–SF], and [CoFe–MB]. Experiments are performed with 10 mg dyad sample and Na₂S₂O₈ (20 mM) at pH 7 in a 0.1 M PBS under (a) solar light irradiation (Xe lamp, 300 W), (b) visible light irradiation

(Xe lamp, 300 W, $\lambda > 420$ nm). (c) The comparison of activities based on the 1st hour of the photocatalytic experiment under solar and visible irradiation.

We performed a series of photocatalytic control experiments (Figure 4.8): i) No activity is obtained with MB/persulfate and bare persulfate solutions. ii) A mixture of [CoFe–MB] and persulfate in MeCN does not exhibit any activity, suggesting that the origin of evolved O_2 is water. iii) A physical mixture of [MB] and [CoFe] PBA exhibits a much poorer performance with around four-times lower activity than [CoFe–MB], which proves that the covalent coordination of the PS to the PB structure is essential to boost the charge transfer between the PS and the WOC.

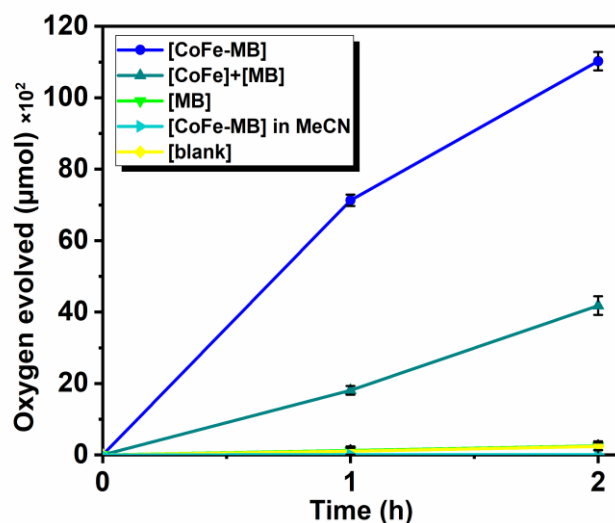


Figure 4.8 Comparison of photocatalytic performances for [CoFe–MB], physical mixture of [CoFe] + MB, MB alone and blank containing NaS_2O_8 as a sacrificial agent at pH 7 in a 0.1 M PBS under visible light irradiation. In addition, photocatalytic performance of [CoFe–MB] in MeCN electrolyte is demonstrated. All experiments performed with 10 mg of sample.

A combination of characterization techniques including cyclic voltammetry (CV) and absorption spectroscopy is utilized to estimate the energy levels of [Fe-PS] and Co site with respect to the water oxidation process. All PS-WOC dyads exhibit similar cyclic voltammograms in terms of a redox process attributed to the oxidation of catalytic cobalt sites at around 1.5 V_{RHE} .^[65,233] Therefore, the oxidation potential for the cobalt site is lower than the water oxidation potential (1.23 V_{RHE}), as deduced in our previous studies.^[191] The onset of oxidation and reduction potentials that are extracted from the

cyclic voltammogram could be correlated to the LUMO and HOMO levels of the [Fe–PS], respectively.[234–236] In our case, the onset reduction potentials (E_{red}) of [Fe–PS] components are extracted from their CV profiles to assign the LUMO potentials (Figure 4.9). Optical band gaps are then used to estimate the HOMO levels of [Fe–PS] groups.

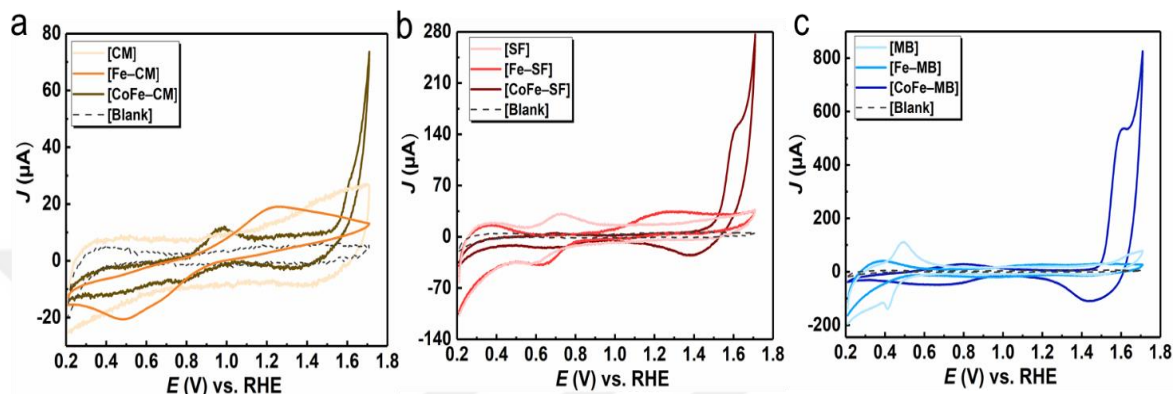


Figure 4.9 The cyclic voltammograms (CV) of homogeneous solutions (a) CM, (b) SF, and (c) MB based assemblies in 0.1 M PBS (pH 7) at a scan rate of 1000 mV s^{-1} . The CV profile of blank FTO coated glass is represented in dash lines. In each homogeneous measurement, fresh FTO coated glasses were used as a working electrode, Ag/AgCl as a reference electrode, and Pt wire as a counter electrode ($(V_{\text{RHE}} = V_{\text{Ag/AgCl}} (\text{V}) + 0.059 \times 7.1 + V_{\text{Ag/AgCl}}^0 (\text{V}))$). Assigned reduction potentials for [Fe–CM], [Fe–SF], [Fe–MB] are $0.89 \text{ V}_{\text{RHE}}$, $0.77 \text{ V}_{\text{RHE}}$, and $0.49 \text{ V}_{\text{RHE}}$, respectively. Co oxidations potentials deduced as $1.55 \text{ V}_{\text{RHE}}$ for [CoFe–CM], and $1.51 \text{ V}_{\text{RHE}}$ for both [CoFe–MB], and [CoFe–SF].

Based on all of the above-mentioned experimental evidence, the schematic representation of the operation mechanism for light driven O_2 production is proposed in Figure 4.10. The higher photocatalytic activity of [CoFe–MB] compared to [CoFe–SF] and [CoFe–CM] could be justified by their band alignments. The close proximity between the HOMO energy level of [Fe–MB] and Co provides a faster interfacial electron dynamic in [CoFe–MB] compared to [CoFe–SF] and [CoFe–CM]. Furthermore, the LUMO levels of [Fe–SF] and [Fe–CM] are positioned much closer to the energy level of catalytic Co site compared to their HOMO levels (Figure 4.10a and b). This mediates electron-hole recombination due to electron transfer from the LUMO level of the PS to the HOMO level of the catalytic cobalt site.[237] The HOMO and LUMO levels of [Fe–MB] are positioned more properly with respect to the HOMO level Co sites. [Fe–MB] also harvests a larger portion of the solar spectrum due to its strong and broad light absorption that overlaps with the solar spectrum. Therefore, upon excitation with solar light, the holes created in

the HOMO level of the [Fe–MB] are transferred to the HOMO level of the Co site to activate it for water oxidation process and electrons located on the LUMO are consumed with the sacrificial agent, persulfate ions, $S_2O_8^{2-}$ (Figure 4.10c).

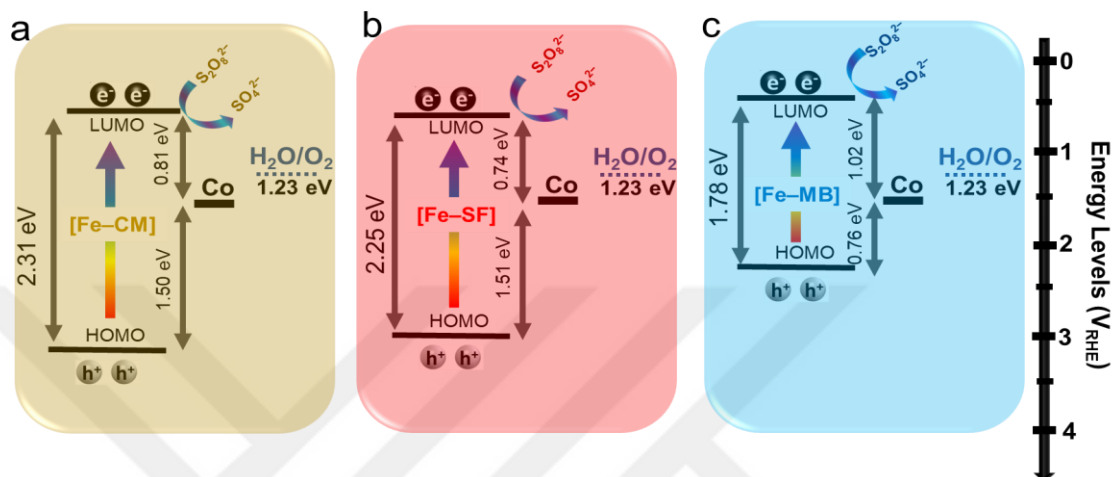


Figure 4.10 Estimated energy band diagrams for (a) [CoFe–CM], (b) [CoFe–SF], and (c) [CoFe–MB] for the photocatalytic water oxidation process involving the electron transfer mechanism.

In heterogeneous assemblies, the surface concentration of active catalytic sites is also an important parameter that governs catalytic activity.[51,65,238] The number of active catalytic cobalt sites is estimated by recording $Co^{2+/3+}$ redox wave at different scan rates (Figure 4.11). All dyad assemblies exhibit a relatively higher surface concentration compared to regular cobalt hexacyanoferrates due to the less crystalline nature of cobalt pentacyanoferrates.[26,66,239] [CoFe–CM] exhibits a surface concentration of 26 nmol cm^{-2} , which is around 25% higher than [CoFe–MB] (21 nmol cm^{-2}) and 65% higher than [CoFe–SF] (16 nmol cm^{-2}). This trend is also in good accordance with the Co:Fe atomic ratio obtained by EDAX analysis. This result indicates that the number of active catalytic sites could also be tuned by the charge of the PS. Relatively fewer cobalt sites are needed to provide a charge balance when positively charged [SF] and [MB] groups are used compared to the neutral [CM] case.

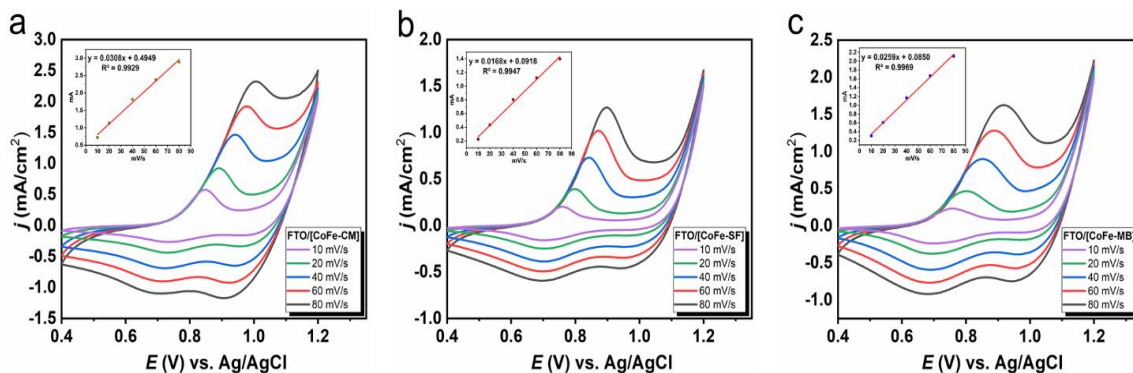


Figure 4.11 Surface concentrations of active cobalt centers calculated based on Cyclic Voltammograms (CVs) of PS-WOC dyad assemblies which were performed in 0.1 M PBS (pH 7) for (a) FTO/[CoFe–CM], (b) FTO/[CoFe–SF] and (c) FTO/[CoFe–MB] recorded at different sweep rates by using the slope of the linear trend for oxidation currents vs. sweep rates (Inset: The linear relationship between peak current of Co^{II/III} redox couple and sweep rates).[65] The electrodes of PS-WOC systems were prepared by a two-step electrodeposition method.[184,238] First, a well-cleaned FTO electrode was immersed in an aqueous solution of Co(NO₃)₂ (10 mM) to afford metallic cobalt particles on the electrode surface by applying a negative potential of -0.9 V_{Ag/AgCl} for 100 s. Then, the rinsed electrode was immersed in an aqueous solution of [Fe–PS] (10 mM) and a chronoamperometric measurement is conducted for 100 s under positive potential of $+0.9$ V_{Ag/AgCl}. Consequently, the electrode washed with DI water and kept in oven at 75 °C for 1 h.

Taking all of the above data into consideration, the origin of the obtained trend in the activity of dyads could be justified as follows: (i) [CoFe–CM] is a UV absorbing PS component, thus under visible light irradiation it has no photocatalytic activity. However, it exhibits a comparable activity under solar irradiation due to its absorption in the UV region and high surface concentration. Both [Fe–SF] and [Fe–MB] could be utilized as visible light active photosensitizers. [CoFe–MB] exhibits the highest activity since it exhibits a strong absorption, proper matching of energy levels, and relatively high number of cobalt sites that can participate in the photocatalytic process.

4.3.3 Stabilities of Dyads

Photocatalytic studies indicate that organic PS groups should be covalently coordinated to the CoFe Prussian blue structure for enhanced activity. Since all dyads preserve their photocatalytic activities throughout a 6 h experiment, the decomposition of the PS-WOC dyad via the leaching of catalytic cobalt sites or the degradation of organic PS group could be ruled out. We also performed characterization studies on the post-catalytic samples to support this thesis. XPS analysis was conducted for both pristine and

post catalytic samples (Figure 4.12). The Co2p and Fe2p signals were conducted in the 811–770 eV and 740–700 eV regions, respectively. Our previous reports reveal the partial oxidation of cobalt and iron sites after the photocatalytic process.[87,191,240] Co2p spectra exhibits two wide bands, one in the 780–785 eV region for Co2p_{3/2} and another one in the 795–800 eV region due to Co2p_{1/2}. According to the observed Co2p spectra, a similar trend for the chemical composition (a combination of Co(II) and Co(III) sites) is observed for all dyad assemblies (Figure 4.12a, b, and c). Both Co2p_{3/2} and Co2p_{1/2} peaks exhibit apparent shake-up satellites at the higher binding energy regions due to the presence of Co(II) ions. On the other hand, Fe2p region illustrates two apparent peaks for all samples; the one in the 707–712 eV region and the other one at around 721–723 eV correspond to Fe2p_{3/2} and Fe2p_{1/2}, respectively (Figure 4.12d, e, and f). The main observable difference is the secondary peaks for [CoFe–MB] (Figure 4.12f), which are revealed at 711.15 and 723.64 eV, which suggest a higher concentration of Fe(III) sites in [CoFe–MB] compared to [CoFe–CM] and [CoFe–SF].[241]

XPS studies on post-catalytic samples indicate a slight decrease of the shake-up satellites of Co2p signals of all the samples and a narrowing in the peaks of [CoFe–CM] and [CoFe–SF] (Figure 4.12a and b), both of which indicate the partial oxidation of cobalt sites from 2+ to 3+ oxidation states during the photocatalytic process.[242] Furthermore, the spin orbit splitting values of Co2p signals decrease from 15.24 and 15.51 eV to 15.02 and 15.05 eV for [CoFe–SF] and [CoFe–CM], respectively, which could be attributed to the relative increase in the concentration of Co(III) sites compared to Co(II) sites. However, the spin orbit splitting of [CoFe–MB] exhibits an increase of 15.48 to 15.97 eV for the post-catalytic sample due to the relative increase in the concentration of Co(II) sites (Note that spin orbit splitting values of 15 and 16 eV have been reported for [Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ complexes).[243,244] In addition, the Fe2p spectrum of the post-catalytic [CoFe–MB] sample reveals the reduction of the Fe^{III} sites during the water oxidation process as reported in previous studies.[157,223]

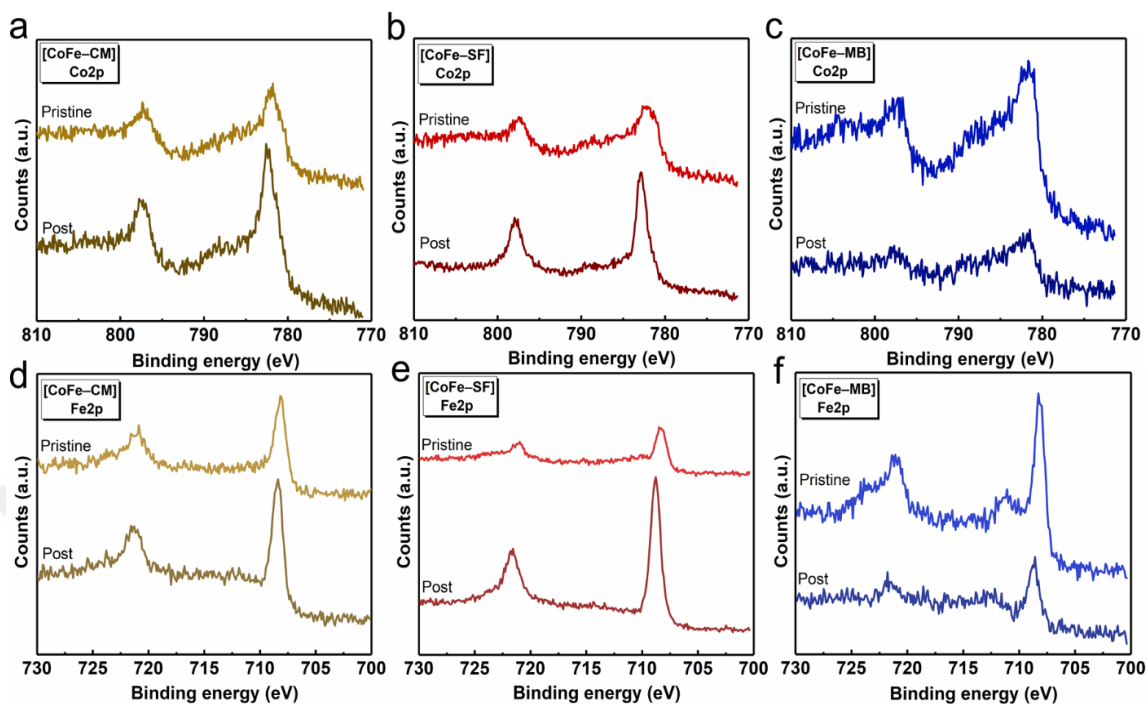


Figure 4.12 XPS studies performed on pristine and post-catalytic samples: Co2p for (a) [CoFe-CM], (b) [CoFe-SF], and (c) [CoFe-MB], and Fe2p for (d) [CoFe-CM], (e) [CoFe-SF], and (f) [CoFe-MB].

The O1s spectra of all pristine and post samples were examined for a possible metal oxide formation. All O1s features exhibit binding energies higher than 530 eV, which rule out the possible decomposition of the PB structure to a metal oxide (Figure 4.13).

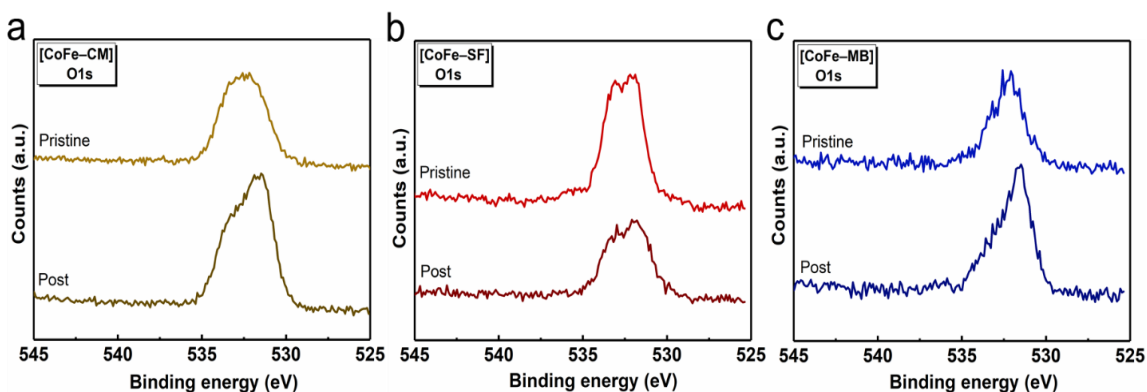


Figure 4.13 XPS studies of O1s signals for post and pristine (a) [CoFe-CM], (b) [CoFe-SF], and (c) [CoFe-MB] samples.

These results are also in good agreement with the Infrared spectra of post-catalytic samples (Figure 4.14). The post-catalytic samples of [CoFe-SF] and [CoFe-CM] exhibit a cyanide stretch at 2127 and 2110 cm^{-1} , respectively (Figure S7a and b), which are

assigned to a Co(III)–NC–Fe(II) coordination mode. For [CoFe–MB], however, the cyanide stretch is observed at 2087 cm^{-1} (Figure 4.14c), which corresponds to a Co(II)–NC–Fe(II) coordination mode.[90] Furthermore, the peaks that correspond to the organic PS group are still present in the post catalytic samples.

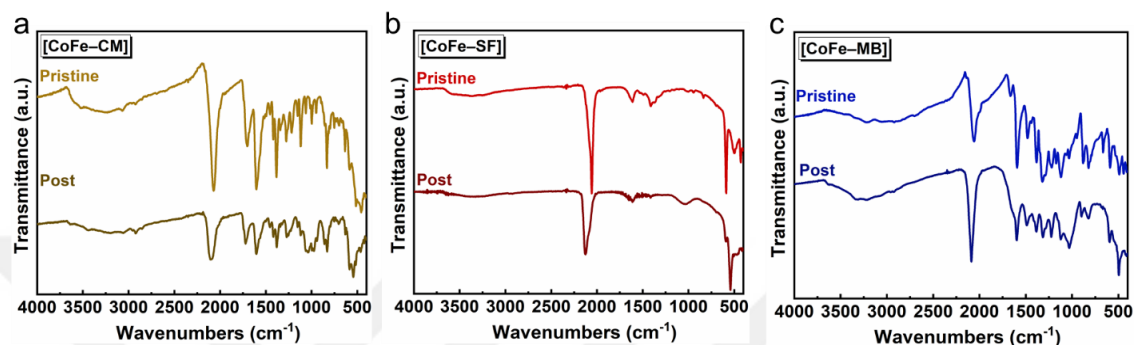


Figure 4.14 ATR-FTIR spectra for post and pristine (a) [CoFe–CM], (b) [CoFe–SF], and (c) [CoFe–MB] samples. The additional broad peaks that appear in the $1000\text{--}1200\text{ cm}^{-1}$ region for post-catalytic samples are attributed to the incorporation phosphate anions into the PB structure as counter anions to provide charge balance in partially oxidized CoFe PB structures.

The absorption profiles of [CoFe–SF] and [CoFe–MB] in DMF remain almost similar after the photocatalytic experiment (Figure 4.15). The intensities of MLCT bands increase slightly with respect to the absorption bands of photosensitizers due to the partial oxidation of metal ions. A significant decrease in the solubility of [CoFe–CM] is observed due to the precipitation of partially oxidized Prussian blue structure surrounded with phosphate counter anions and/or morphological changes during the catalytic process. Nevertheless, a weak absorption band at around 334 nm is observed, which indicates the presence of CM groups in the post-catalytic sample.

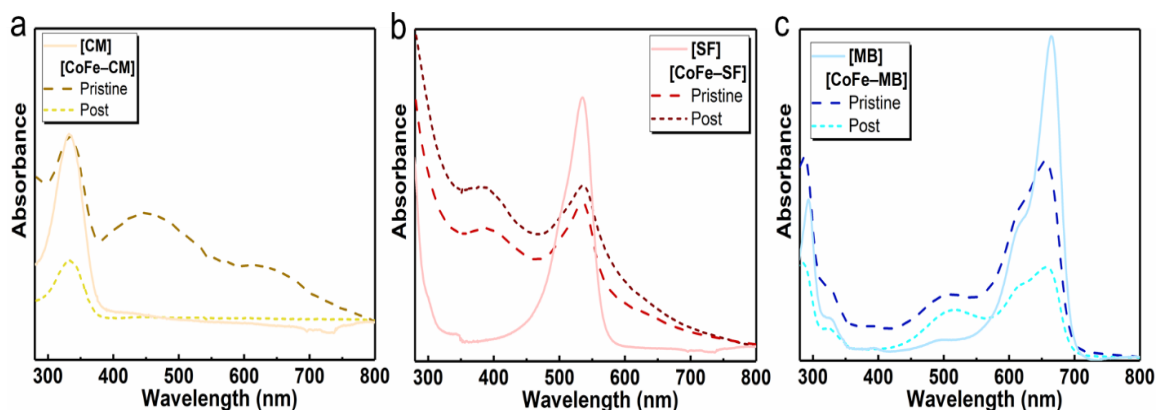


Figure 4.15 Absorption profiles for DMF solutions of (a) [CM], (b) [SF], and (c) [MB] derived [CoFe-PS] compounds.

4.4 Conclusion

A facile synthetic method was employed to prepare a series of PS-WOC dyad assemblies, which utilizes three photosensitizer groups that absorb different regions of the solar spectrum: a UV light absorbing [CM] (334 nm), a green light-absorbing [SF] (520 nm), and a red light-absorbing [MB] (664 nm). We found that all three PS-WOC assemblies are active and robust catalytic systems for the photocatalytic water oxidation process. Among these, [CoFe-MB] exhibits the highest activity as high as $68 \mu\text{mol g}^{-1} \text{h}^{-1}$ during a 6 h photocatalytic study under visible light. The relatively high activity of [CoFe-MB] could be attributed to the proper energy level matching between the HOMO and LUMO levels of the PS with respect to the HOMO of catalytic cobalt sites, and relatively high concentration of catalytic cobalt sites. Surprisingly, all organic PS groups including [MB], which degrades easily under photocatalytic conditions, exhibit high stabilities when they are incorporated into the PB network structure. As suggested by our controlled experiments with physical mixtures of PS groups and CoFe PB catalyst, the high activity and stability could be attributed to the efficient charge transfer and separation through short and rigid bridging cyanide groups.

We show that a variety of PSs with different absorption profiles and energy levels, even the ones with a narrow HOMO-LUMO gap and low stability under photocatalytic conditions, could be plugged to cyanide-based PS-WOC dyad assemblies. We demonstrate that this ‘plug and play’ synthetic strategy provides an ideal pathway to employ a large agenda of photosensitizers for photocatalytic applications including dye-

sensitized water oxidation. This study offers a guideline for the main parameters that affect photocatalytic activity.



CHAPTER 5

5. EXTERNAL STIMULI RESPONSIVE WATER OXIDATION PB-BASED ELECTROCATALYSTS

5.1 Introduction

The design and development of molecular level devices with switchable properties using external stimuli is one of the ultimate goals of nanotechnology. In this regard, Prussian blue analogues (PBAs) have been widely investigated particularly in the last two decades due to their electron-transfer-induced valence tautomerism features.[88] The pioneering work of Sato et al. proved that a CoFe Prussian blue (PB) undergoes from a diamagnetic state ($\text{Fe}_{\text{LS}}^{\text{II}}\text{--CN--Co}_{\text{LS}}^{\text{III}}$) to a paramagnetic state ($\text{Fe}_{\text{LS}}^{\text{III}}\text{--CN--Co}_{\text{HS}}^{\text{II}}$) at around 5 K under red-light illumination. Verdaguer et al. suggested a better understanding of this transition by controlling the vacancy of CoFe unit cell by insertion of cations.[245] Owing to great advances over the years, a facile excitation of the Co spin state on CoFe is extensively described under light [90,91], temperature [93,246], pressure [247], and electric field [96]. It is found that spin transition initially takes place on the Co site in ~ 50 fs, which thus, triggers a charge transfer from Fe to Co within ~ 200 fs.[248]

Current attempts in electrocatalysis have been sought for further innovations to push its limits by manipulating the intermediate electrochemical reactions of existing earth-abundant catalysts. Several catalytic reactions including oxygen reduction reaction (ORR) [124], hydrogen evolution reaction (HER) [125], CO oxidation [126] and CO₂ reduction [127] confirmed that the occupancy of antibonding orbitals of the catalyst could cause a positive effect on the performance. Shao-Horn et al. [128] and Xu et al. [129] reported that the e_g occupancy close to unity ($e_g \sim 1$) provides better covalency for metal-oxygen bond formation decreasing the rate-limiting steps and resulting in an enhanced activity on the sluggish kinetics of OER. Recently, the favorable outcome of spin conversion or spin crossover (SCO) was highlighted by manipulating single Fe atoms for ORR [130] and Co-N doped carbon for OER [131], respectively. A more evident achievement of Zhou et al. proved the tunability of the thermal-differentiated superlattice feature of cobalt-based

metal-organic frameworks (MOFs) via magnetic stimulation demonstrating a spin-dependent reaction pathway for an enhanced OER.[132]

Recently, a comprehensive computational study by Lopèz et al. proved that the possible spin-crossover phenomena of CoFe PB under a magnetic field could result in a much lower overpotential for OER, giving a new direction to electrocatalysis.[133] Herein, we extend this content further and present a series of CoFe PBAs, with dissimilar electronic properties, to demonstrate the first direct enhancement of OER by manipulating the SCO under magnetic field and light illumination.

5.2 Experimental Procedure

5.2.1 Chemicals

Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and sodium pentacyanonitrosylferrate(III) dihydrate ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$) were obtained from Fischer Scientifics and Alfa Aesar, respectively. Potassium hexacyanoferrate(III) ($\text{K}_3\text{Fe}(\text{CN})_6$), Potassium hexacyanoferrate(II) trihydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) and Potassium chloride (KCl) were purchased from Sigma Aldrich. Potassium phosphate monobasic (KH_2PO_4) and Potassium phosphate dibasic (K_2HPO_4), which are used for the preparation of Potassium phosphate buffer solution (PBS), were acquired from Sigma Aldrich. All the chemicals were obtained from commercial suppliers and used without further purification. Millipore deionized water (resistivity; 18 $\text{M}\Omega \cdot \text{cm}$) was used for all experiments. Fluorine doped tin oxide (FTO) coated glass substrates (R_{sh} ; 20 $\Omega/\text{sq.}$, 2mm in thickness) were used for electrodeposition experiments.

5.2.2 Preparation of the PB-modified FTO electrodes

A cleaning procedure of FTO electrodes is followed before further utilization. Each FTO electrode is immersed sequentially in a sonication bath containing deionized water, acetone, and ethanol, each for 15 min. The FTO electrode is then kept at 100 $^\circ\text{C}$ for 1 h before use. Cobalt hexacyanoferrate(III) ($\text{Co}-\text{Fe}^{\text{III}}$), cobalt hexacyanoferrate(II) ($\text{Co}-\text{Fe}^{\text{II}}$) and cobalt pentacyanonitrosylferrate ($\text{Co}-\text{Fe}^{\text{II}}\text{NO}$) modified electrodes were prepared by a two-step electrodeposition route. First, the well-cleaned FTO electrode was immersed in an aqueous solution of $\text{Co}(\text{NO}_3)_2$ (10 mM) and KCl (0.1 M) as a supporting electrolyte. The electrode was treated with a cathodic potential of $-0.9 \text{ V}_{\text{Ag}/\text{AgCl}}$ for 200 s to afford

metallic particles on the FTO electrode (FTO/[Co]). Then, the rinsed FTO/[Co] electrode was dipped in a solution of $\text{K}_3\text{Fe(III)(CN)}_6$ (100 mM) and KCl (0.1 M) to perform a chronoamperometric experiment at an anodic potential of 0.9 $\text{V}_{\text{Ag/AgCl}}$ for 200 s. The concentration of cyanoiron precursor is prepared 10 times higher than the cobalt salt solution in order to enhance the surface reaction of the electrode during the oxidation of cobalt sites to afford well-formed PB crystals. Consequently, the electrodeposited FTO/[Co- Fe^{III}] electrode was rinsed with deionized water and dried at 75 °C for 1 h prior to electrochemical experiments. The same procedure is also followed for $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$ (100 mM) and $\text{Na}_2[\text{Fe(CN)}_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (100 mM) cyanoiron precursors to afford FTO/[Co- Fe^{II}] and FTO/[Co- $\text{Fe}^{\text{II}}\text{NO}$] working electrodes as described above.

5.2.3 Electrochemical Measurement

PB coated FTO substrates are used as working electrodes with an area of $1 \pm 0.05 \text{ cm}^2$. All of the calculations are based on the geometric surface area. LSV is performed at a scan rate of 10 mV s^{-1} with a potential range from 0.5 to 1.5 $\text{V}_{\text{Ag/AgCl}}$, while a potential of 1.22 $\text{V}_{\text{Ag/AgCl}}$ is applied for amperometric experiments in a 0.1 M phosphate buffer solution (PBS).

For the magnetic field and light-assisted electrocatalysis, the three-electrode electrochemical setup is integrated inside the electromagnet between the magnetic poles with a gap range of 50 mm. The generated magnetic fields by the set electrical currents on the electromagnet were measured using a gauss-meter (Group3 DANFYSIK DTM133) to make a calibration plot of adjusted electrical current vs obtained magnetic field. Thus, the control of the magnetic field is provided for electrocatalytic experiments. The solar simulator was located perpendicular to the electromagnet, as well the working electrode surface, to have a direct standpoint.

5.3 Results and Discussions

5.3.1 Materials Synthesis and Characterization

Cobalt-iron (CoFe) based PB modified FTO electrodes were prepared by a straightforward two-step electrodeposition method. The electroreduction of cobalt ions to form a cobalt film on the FTO electrode (FTO/[Co]) is followed by the oxidation of cobalt

particles in the intended cyanoiron precursor ($[\text{Fe(III)(CN)}_6]^{-3}$, $[\text{Fe(II)(CN)}_6]^{-4}$ and $[\text{Fe(II)(CN)}_5\text{NO}]^{-2}$) to afford cobalt iron cyanide (Co–NC–Fe is abbreviated as Co–Fe) film under anodic bias. Thus, three different CoFe modified FTO electrodes are prepared FTO/[Co–Fe^{III}], FTO/[Co–Fe^{II}] and FTO/[Co–Fe^{II}NO] with dissimilar electronic properties. Figure 5.1 presents the schematic illustration of the prepared PB structures and highlights the increasing bond strength due to the enriching electron density from FTO/[Co–Fe^{II}NO], FTO/[Co–Fe^{II}] and FTO/[Co–Fe^{III}], respectively. The electrodeposited electrodes illustrate a homogeneous surface and characteristic color for all three samples.

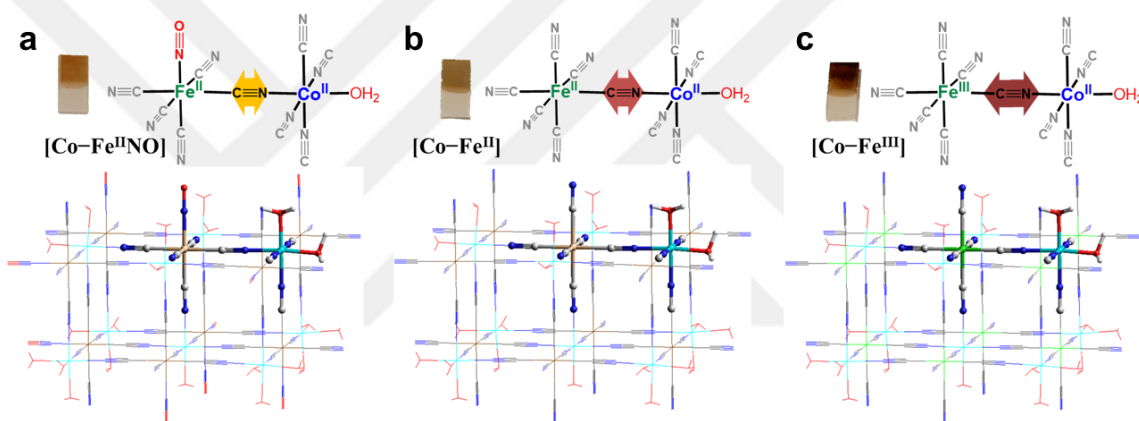


Figure 5.1 Schematic illustration and 3D representation with pictures of (a) [Co–Fe^{II}NO], (b) [Co–Fe^{II}] and (c) [Co–Fe^{III}] with relevant unit structures.

Several characterization techniques were conducted including SEM-EDAX, UV-vis spectroscopy, X-ray diffraction, IR spectroscopy, X-ray photoelectron spectroscopy, and magnetic measurements to evaluate both electronic and morphological properties of PB frameworks. The SEM images depict well-evolved high porous needle-shaped structures for all PB electrodes (Figure 5.2) and Co:Fe atomic ratios are obtained as 1.6, 1.6, and 1.9 for FTO/[Co–Fe^{II}NO], FTO/[Co–Fe^{II}], and FTO/[Co–Fe^{III}], respectively, from EDAX analysis (Figure 5.3). Considering the charge balance of structures, the Co:Fe atomic ratios ensure a good agreement.

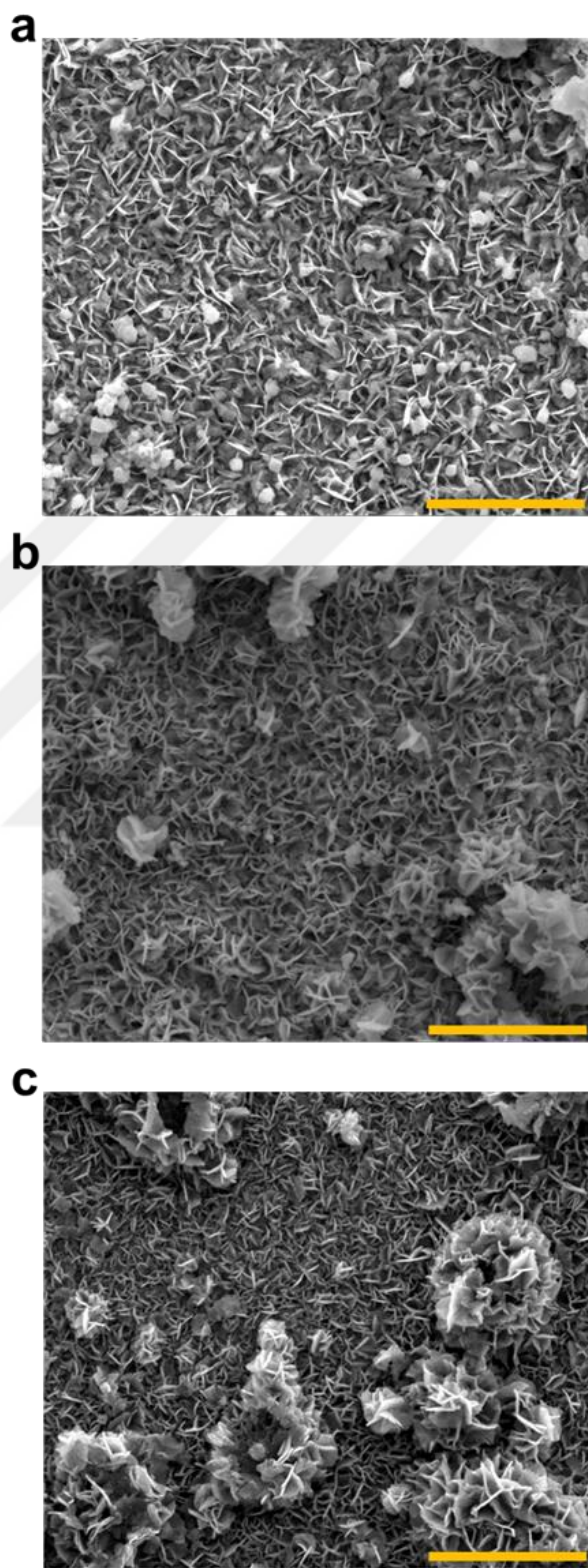


Figure 5.2 The SEM images of (a) FTO/[Co-Fe^{II}]NO, (b) FTO/[Co-Fe^{II}], and (c) FTO/[Co-Fe^{III}] (scale bar: 3μm).

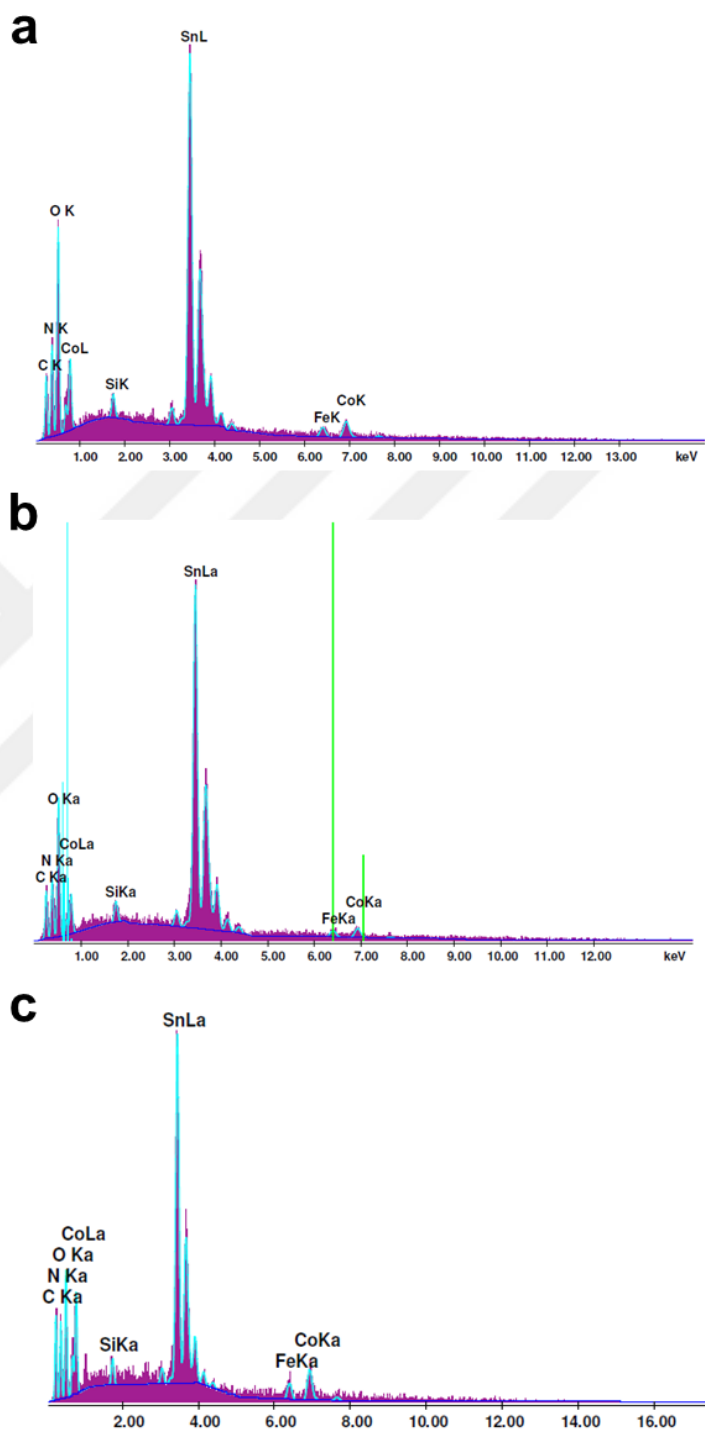


Figure 5.3 The EDAX analysis of (a) FTO/[Co-Fe^{II}]NO, (b) FTO/[Co-Fe^{II}], and (c) FTO/[Co-Fe^{III}].

Optical studies of FTO films are performed to evaluate the metal-to-ligand charge transfer (MLCT) and metal-to-metal charge transfer (MMCT) transitions of PBAs (Figure 5.4a). The main two bands that are shown for the three electrodes, the broad one at 570 nm and the sharp one at 400 nm, are attributed to MMCT and MLCT processes, respectively.[94,248] The more distinct shoulder of the FTO/[Co-Fe^{II}NO] electrode at 450 nm is due to the further MLCT process of the NO electron-accepting ligand which weakens the d→ π and d→d transitions of Fe sites.[249] It should be noted that the more dominant bands of the FTO/[Co-Fe^{III}] electrode are due to the more efficient charge transfer compared to FTO/[Co-Fe^{II}] and FTO/[Co-Fe^{II}NO].

The recorded thin film XRD patterns of PB modified FTO electrodes reveal a face-centered cubic crystalline structure for CoFe PBAs corresponding to (200), (220), and (400) crystal planes for the peaks located nearly at 17°, 24°, and 35° with slight variations to each other in the 2 θ range of 10–60° (Figure 5.4b).[137] The unit cell parameters are found as 10.2608 ± 0.0058 , 10.0642 ± 0.0095 , and 9.9322 ± 0.0023 Å for FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and FTO/[Co-Fe^{III}], respectively, which indicates a decreasing trend for the bond distance. This could be attributed to the increasing amount of Co^{III} sites which result in a shorter Co–N bond.[250] In this regard, FTO/[Co-Fe^{III}] exhibits the highest Co^{III} amount. For the FTO/[Co-Fe^{II}NO] case, the coordination of the -NO ligand could elongate the Fe–C bond distance more and, thus, it owns the largest unit cell parameter.[249]

To investigate the coordination mode of PB electrodes, Infrared spectroscopy studies were conducted (Figure 5.4c). The cyanide stretches are observed at 2187, 2076, and 2125 cm⁻¹ for FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}] and FTO/[Co-Fe^{III}], which correspond to the Co^{II}–CN–Fe^{III}, Co^{II}–CN–Fe^{II}, and Co^{III}–CN–Fe^{II} coordination modes, respectively.[90] It is noteworthy to remark that the electron-accepting ability of -NO ligand weakens the electron density of iron sites further and, thus, it is convenient to indicate the coordination mode of cyanide as Co^{II}–CN–Fe^{II}NO for FTO/[Co-Fe^{II}NO]. Furthermore, the sharp peak at 1940 cm⁻¹ for FTO/[Co-Fe^{II}NO] corresponds to -NO stretching mode.[138] All electrodes reveal the characteristic peaks of M–OH stretching and H₂O bending mode at 3600 and 1605 cm⁻¹ as a wide band and a sharp band. In

addition, the peaks at around $400\text{--}600\text{ cm}^{-1}$ are ascribed to Co–N and Fe–C moieties.[201]

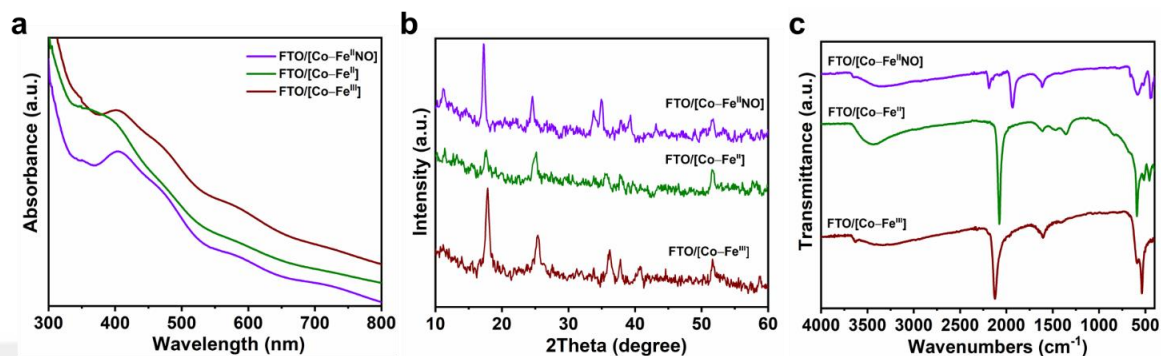


Figure 5.4 (a) Absorption profiles, (b) XRD patterns, and (c) Infrared spectra of FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and FTO/[Co-Fe^{III}].

Temperature-dependent magnetization (M–T) and magnetic-field-dependent magnetization (M–H) measurements are demonstrated in Figure 5.5. Temperature-dependent magnetization measurements reveal a mixture of two phases for all samples: diamagnetic (Co^{III}–CN–Fe^{II}) and ferrimagnetic (Co^{II}–CN–Fe^{III}) phases with an ordering temperature of around 24K.[90] Below 30 K, the CoFe PBAs exhibit similar ferrimagnetic behavior (antiferromagnetic interactions). On the other hand, magnetic-field-dependent magnetization measurements, collected at 2 K, reveal different heights for hysteresis loops of materials which indicate the difference between “magnetically ordered” and “paramagnetic/diamagnetic” ratios of CoFe PBAs.[91] According to that FTO/[Co-Fe^{III}] is the one that is able to utilize the Co^{II}–CN–Fe^{III} areas effectively providing higher magnetization and stronger interactions. In this regard, the FTO/[Co-Fe^{II}] seems to have a lower fraction of Co^{II}–CN–Fe^{III} sites resulting in a lower magnetization and this could be attributed to the high dominance of Fe^{II} areas which are diamagnetic. Consequently, FTO/[Co-Fe^{II}NO] exhibits the lowest magnetization due to the presence of Co^{III}–CN–Fe^{II} areas, this could be understood from the increasing magnetization with increasing field after the loop is over. This behavior presents the existence of Co^{II}–CN–Fe^{III} sites (the magnetically ordered part), and the rest of the material is either Co^{III}–CN–Fe^{III} or Co^{II}–CN–Fe^{II} (disordered = paramagnetic). In addition, the existing Fe^{III} areas are mostly ineffective owing to the coordination of the electron acceptor -NO ligand.

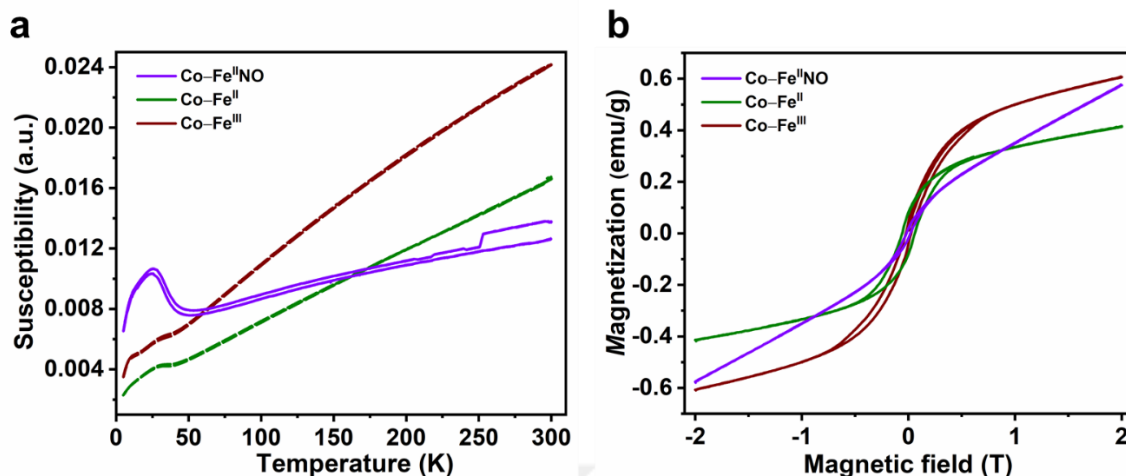


Figure 5.5 (a) Temperature and (b) magnetic field dependent magnetization of FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}] and FTO/[Co-Fe^{III}].

The oxidation states of metal ions are further elucidated with XPS analysis (Figure 5.6). The Fe2p signal of electrodes is deconvoluted into Fe2p_{3/2} and Fe2p_{1/2} peaks in the 700-730 eV range and the peaks are separately fitted to Fe^{III} and Fe^{II} areas. Similarly, the fitting of Co^{III} and Co^{II} peaks is carried out by the deconvolution of Co2p_{3/2} and Co2p_{1/2} peaks of the Co2p signal. The fittings show that FTO/[Co-Fe^{II}NO] consist of a mixture of Co^{II/III} and Fe^{II/III} ions while Co^{II} and Fe^{III} are the major ones. For the FTO/[Co-Fe^{II}] electrode, the Co^{II} and Fe^{II} are the dominant oxidation states as expected. On the other hand, Co^{III} and Fe^{II} features are the most distinct ones in FTO/[Co-Fe^{III}]. Moreover, the spin-orbit splitting values for Fe2p and Co2p are in good agreement with the fitting of Co2p and Fe2p signals and Infrared analysis, which suggest that the coordination modes of Co^{II}-CN-Fe^{II}NO, Co^{II}-CN-Fe^{II}, and Co^{III}-CN-Fe^{II} are the most favorable coordination modes for FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and FTO/[Co-Fe^{III}], respectively.[201] . The following empirical formulas were estimated based on EDAX and XPS analysis; Co^{II}_{0.7}Co^{III}_{0.9}[Fe^{III}(CN)₅NO]_{0.19}[Fe^{II}(CN)₅NO]_{0.81}(OH)_x(NO₃)_(1.29-x), for FTO/[Co-Fe^{II}NO], Co^{II}_{1.26}Co^{III}_{0.34}[Fe^{III}(CN)₆]_{0.03}[Fe^{II}(CN)₆]_{0.97}(OH)_x(NO₃)_(0.43-x) for FTO/[Co-Fe^{II}], and Co^{II}_{0.23}Co^{III}_{1.67}[Fe^{III}(CN)₆]_{0.11}[Fe^{II}(CN)₆]_{0.89}(OH)_x(NO₃)_(0.38-x) for FTO/[Co-Fe^{III}] (NO₃⁻ and OH⁻ anions, which are observed in Infrared spectra (Figure 5.4c), are added to provide charge balance).

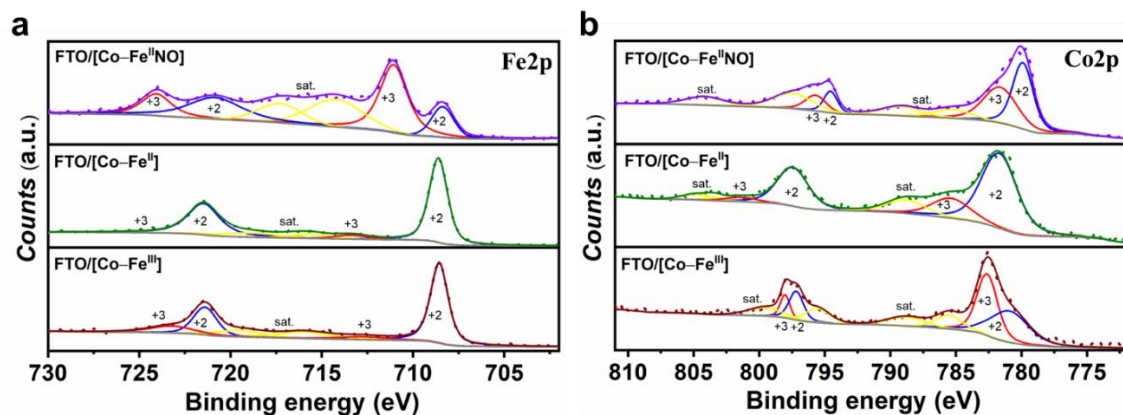


Figure 5.6 XPS analysis for (a) Fe2p and (b) Co2p signals of FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}] and FTO/[Co-Fe^{III}].

5.3.2 External Stimuli Assisted Electrocatalytic Water Oxidation

It is well-known that the PBAs are robust and stable OER electrocatalysts with diverse characteristics.[26] Herein, linear sweep voltammetry (LSV) and chronoamperometry (CA) studies are conducted under magnetic field and light illumination, respectively, to investigate the response of the electrocatalytic OER activities of CoFe based PB electrodes on external stimuli in 0.1 M PBS at pH 7. To begin with, several control experiments are performed to check the response of the electrochemical setup to the external fields, including the response of the bare FTO electrode and the effect of external stimuli below the OER region. The LSV profiles of PB electrodes reveal distinct OER activities in the absence of external fields with overpotentials 513, 540, and 530 mV at 1 mA cm⁻¹ for FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and FTO/[Co-Fe^{III}], respectively (Figure 5.7).

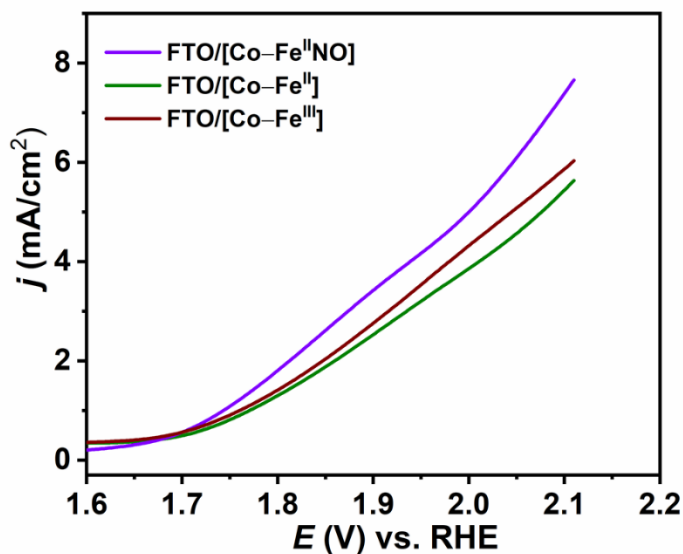


Figure 5.7 The LSV profiles of PB electrodes with a scan rate of 10 mV/s in 0.1 M PBS at pH 7.

Similarly, the Tafel slopes of FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and FTO/[Co-Fe^{III}] are found consistent with previous studies [51,65] and exhibit the same trend as 69, 86, and 79 mV dec⁻¹, respectively (Figure 5.8).

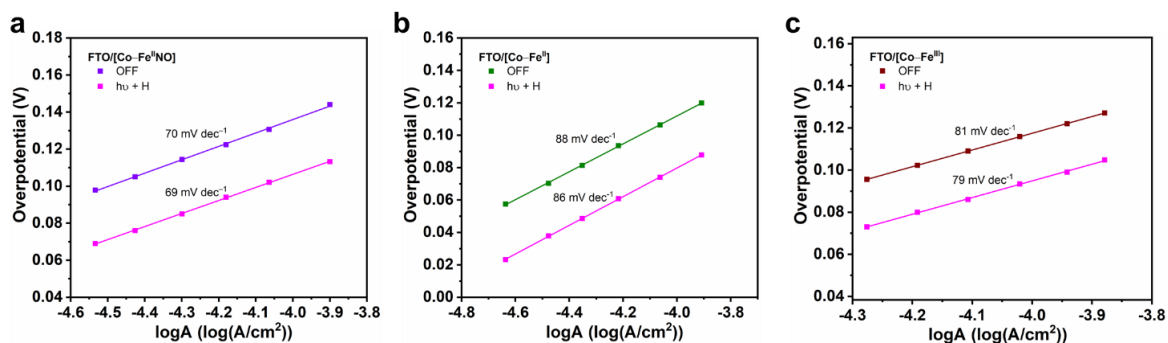


Figure 5.8 The Tafel plots of (a) FTO/[Co-Fe^{II}NO], (b) FTO/[Co-Fe^{II}], and (c) FTO/[Co-Fe^{III}] in the absence and presence of external fields.

The trend in the activity could be described with the change in calculated surface concentration of active catalytic sites, which are 49.35, 34.07, and 42.69 nmol cm⁻² for FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and FTO/[Co-Fe^{III}], respectively. (Figure 5.9).

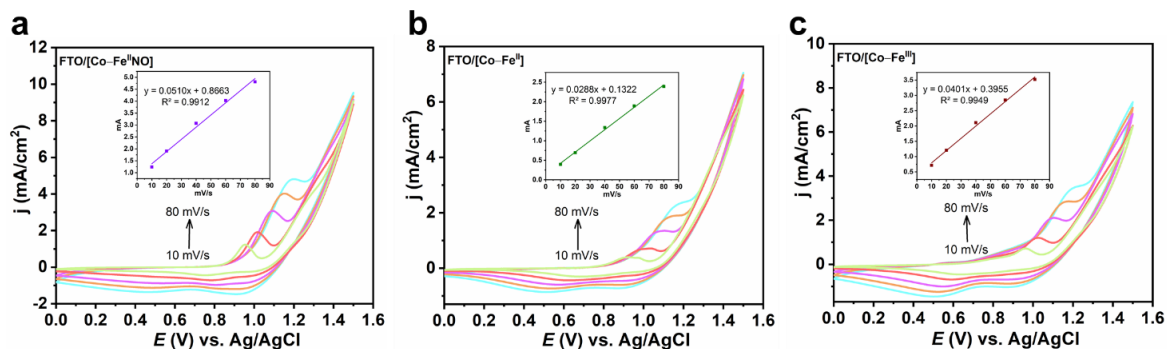


Figure 5.9 The cyclic voltammetry (CV) profiles of (a) FTO/[Co-Fe^{II}NO], (b) FTO/[Co-Fe^{II}], and (c) FTO/[Co-Fe^{III}] at different scan rates. The insets demonstrate the linear relation of oxidation processes with increasing scan rates.

Comprehensive electrochemical studies with PB electrodes are performed sequentially under magnetic field, light illumination, and both simultaneously (Figure 5.10). It is found that all electrodes demonstrate positive responses to external fields with different degrees. The LSV profiles reveal an increasing tendency for catalytic activity over the sequential exposure of the magnetic field, light illumination, and both stimuli. The most dominant enhancement of OER activity is observed for FTO/[Co-Fe^{III}], dissimilar to the catalytic activity trend of electrodes, and the improvement is more distinct over higher applied potentials. Although the Tafel slopes do not exhibit significant changes (Figure 5.8), the overpotentials decrease at least 15 mV at 1 mA cm⁻¹ for all electrodes ($\eta_{1\text{mA}}=502$, 526, and 503 mV for FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and FTO/[Co-Fe^{III}], respectively).

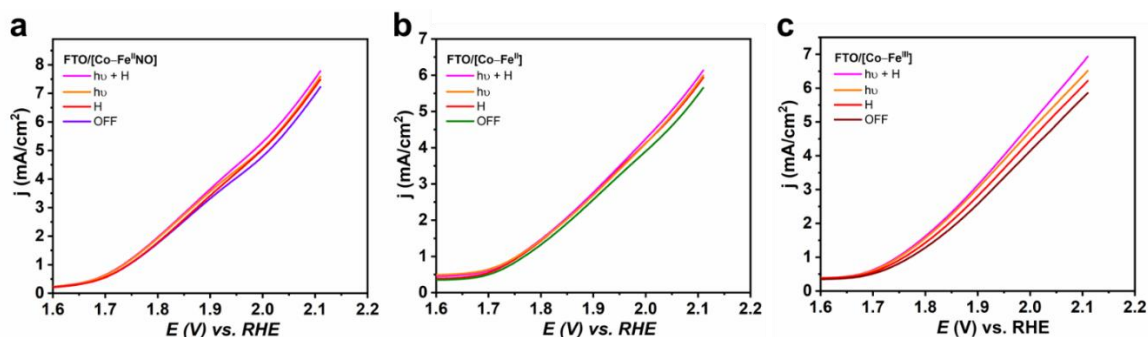


Figure 5.10 The LSV profiles of (a) FTO/[Co-Fe^{II}NO], (b) FTO/[Co-Fe^{II}], and (c) FTO/[Co-Fe^{III}] under consecutive applied external stimuli and non-stimuli.

Figure 5.11a illustrates the CA measurement for electrodes with respective five cycles under a 0.2 T magnetic field. FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and

FTO/[Co-Fe^{III}] indicate a reversible enhancement of OER under an external magnetic field with magnetocurrents, j_m , labelled as the enhancement in the magnitude of current density under magnetic field, of 24.8 ± 2.4 , 39.1 ± 3.0 , and $120.5 \pm 5.6 \mu\text{A cm}^{-1}$, respectively. The generated current density under the magnetic field corresponds to a 10.7 % enhancement of initial activity for FTO/[Co-Fe^{III}], while it is 1.9 and 3.0 % for FTO/[Co-Fe^{II}NO] and FTO/[Co-Fe^{II}], respectively. A similar OER enhancement of electrodes is also observed for solar light irradiation with the same trend but relatively higher generated currents are detected compared to magnetic field-assisted experiments (Figure 5.11b), which could be attributed to the larger energy supply of solar light than the minor magnetic field ($\sim 0.2 \text{ T}$). The photocurrents, j_s , labelled as the enhancement in the magnitude of current density under light illumination, are 176.7 ± 6.6 , 196.9 ± 4.6 , and $375.3 \pm 4.9 \mu\text{A cm}^{-1}$, which correspond to 9.7, 16.3, and 25.1 % enhancement of activity for FTO/[Co-Fe^{II}NO], FTO/[Co-Fe^{II}], and FTO/[Co-Fe^{III}], respectively.

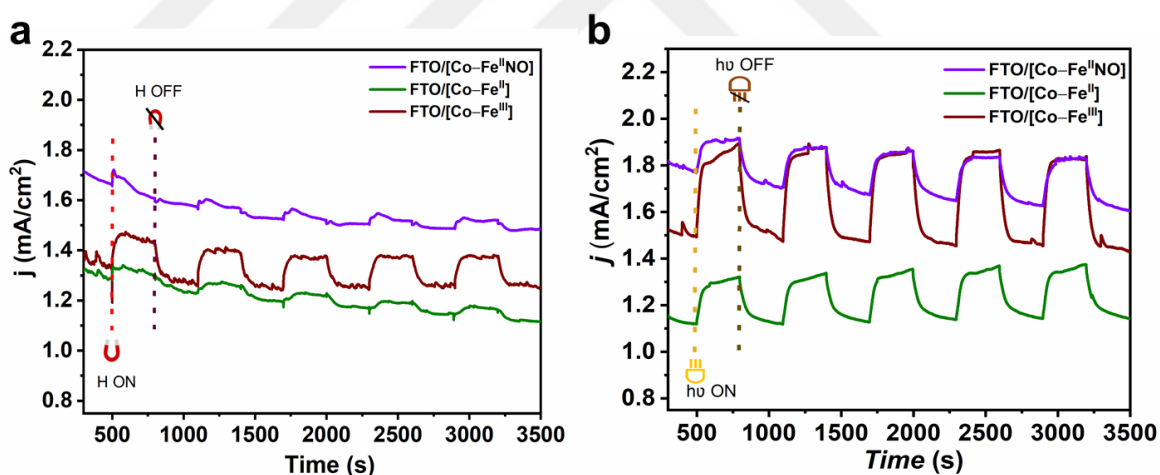


Figure 5.11 The CA measurements of PB electrodes at $\eta = 0.6 \text{ V}$ under (a) magnetic field and (b) solar light irradiation in 0.1 M PBS .

Figure 5.12 presents the CA measurement of FTO/[Co-Fe^{III}] with a continuous increase of the magnetic field and a corresponding linear increase of magnetocurrent is observed. A step increase on the j_m over the magnetic field set is detected up to 0.25 T and a continuous enhancement is found above 0.25 T .

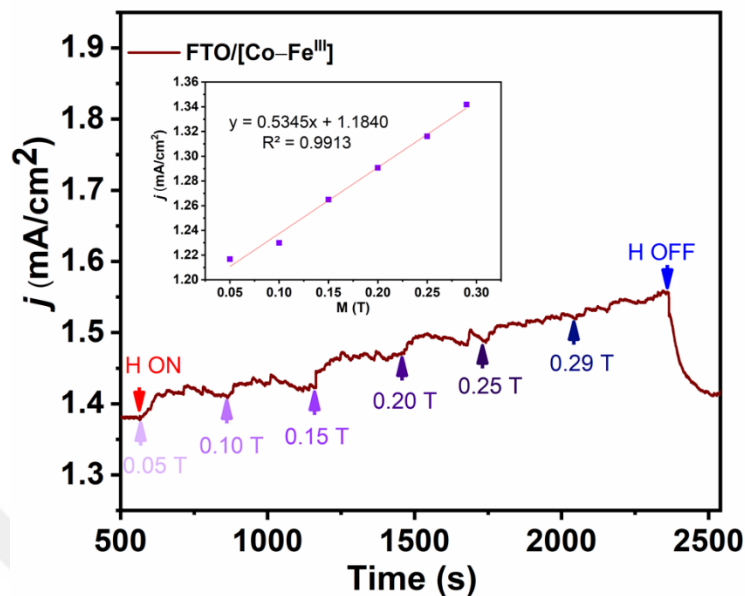


Figure 5.12 The CA measurement of FTO/[Co-Fe^{III}] with continuous increase of magnetic field at $\eta = 0.6$ V in 0.1M PBS. The inset indicates a linear increase in the current over the increasing magnetic field.

Figure 5.13 displays a 12 h long-term CA experiment of FTO/[Co-Fe^{III}] with sequent solar-light and magnetic field enhancement. At the end of the 1 h light illumination, the photocurrent reaches up to $850 \mu\text{A cm}^{-1}$ (57% enhancement) and a similar enhancement is also observed after 10 hours proving a decent reproducibility after a long-term experiment. It is noticed that the 30 min magnetic field does not suggest any further improvement at 0.2 T, which is in good agreement with the increasing magnetic field over j_m in Figure 5.12.

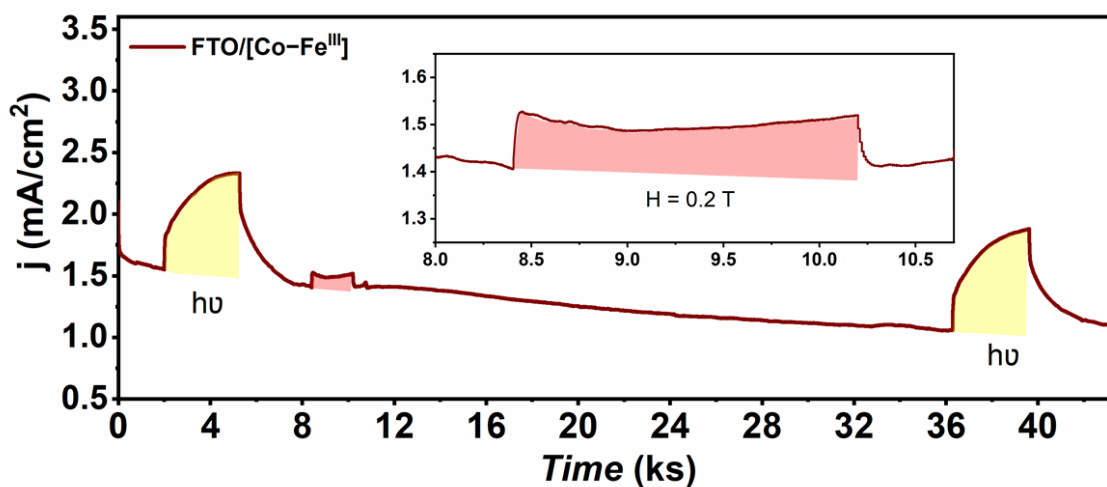


Figure 5.13 A 12 h long CA experiment of FTO/[Co-Fe^{III}] under consecutive light illumination and magnetic field at $\eta = 0.6$ V in 0.1 M PBS.

Recent studies on magnetic field enhanced water oxidation claim that enhancement under magnetic field could be attributed to either spin polarization [251–253] or magnetohydrodynamic effect [254,255]. To rule out these aspects, we performed several studies. It is found that spin polarization-based magnetocurrent is boosted at higher pH levels with increasing catalytic activity, while the magnetocurrent of CoFe-based PB electrode is diminished significantly at pH 9 beside the enhanced activity (Figure 5.14a). In this regard, solar light illuminated studies appeared to confirm the magnetic field response resulting in an almost 85% decrease in the photocurrent of FTO/[Co-Fe^{III}] at pH 9 (Figure 5.14b).

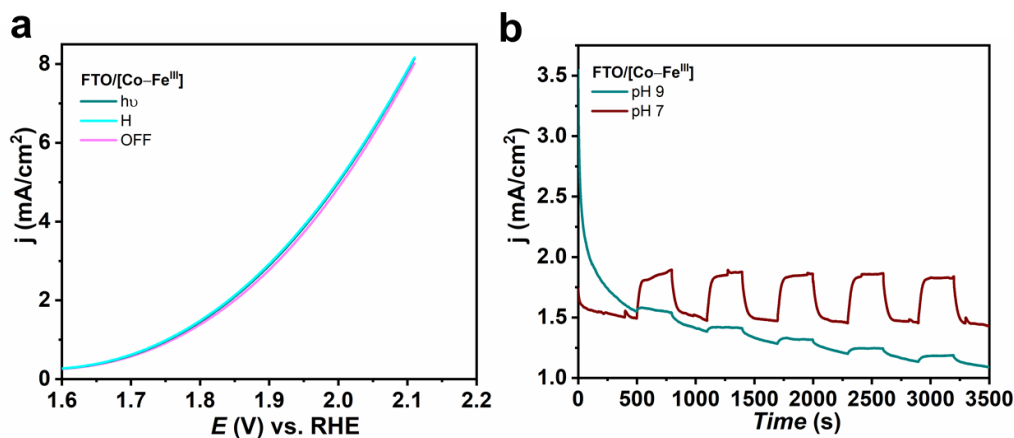


Figure 5.14 (a) The LSV profiles under external stimuli in 0.1 M PBS at pH 9 and (b) the CA experiment under light illumination in 0.1 M PBS at pH 7 and pH 9 of FTO/[Co-Fe^{III}].

In addition, the positive effect of the magnetic field is still present at pH 5 with lower activities (Figure 5.15a), and it reveals a similar enhancement of initial current over 0.2 T apply for the both pH 5 and 7 at the overpotential of 0.6 V (Figure 5.15b). On the other hand, the change in the direction of the electrode does not suggest any change in the magnetocurrent (Figure 5.15c), which rules out the magnetohydrodynamic effect in PB modified electrodes.[254]

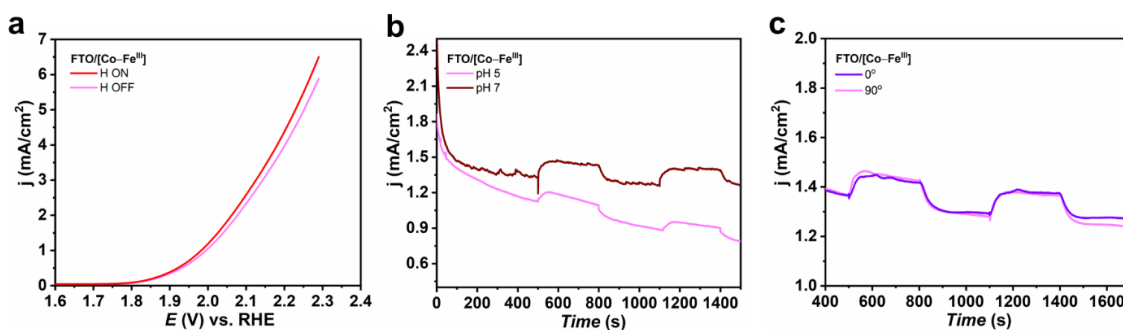


Figure 5.15 (a) The LSV profiles at pH 5, (b) the CA experiments at pH 5 and 7 and (c) the CA profiles at pH 7 by changing the direction of the FTO/[Co-Fe^{III}] under consecutive magnetic field apply.

The pH-dependent external stimuli enhancements pushed us forward to investigate the reason, and the optical studies reveal that the MMCT bands decrease dramatically as the pH is reduced (Figure 5.16).[256] So, an enhancement of intermetallic charge transfer is observed under acidic conditions.

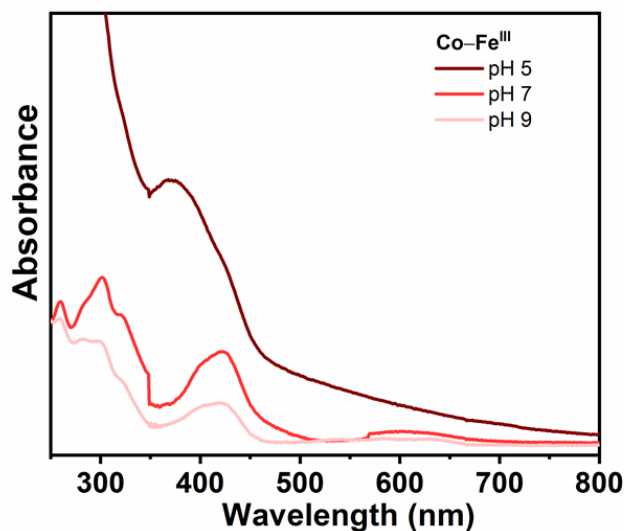


Figure 5.16 The absorption profiles of Co-Fe^{III} at different pH values of 0.1 M PBS.

Thus, the enhanced catalytic trend of PB electrodes under external stimuli provides a decent correlation with the intensity of MMCT profiles. Moreover, the utilization of a 420 nm cut off filter for the visible-light-induced CA experiment of FTO/[Co-Fe^{III}] revealed that there is a retention of 85 % in photocurrent compared to the solar light irradiated electrode (Figure 5.17). This minor decrease in photocurrent could be attributed to the broad shoulder of the MMCT band that slightly reaches below 420 nm.

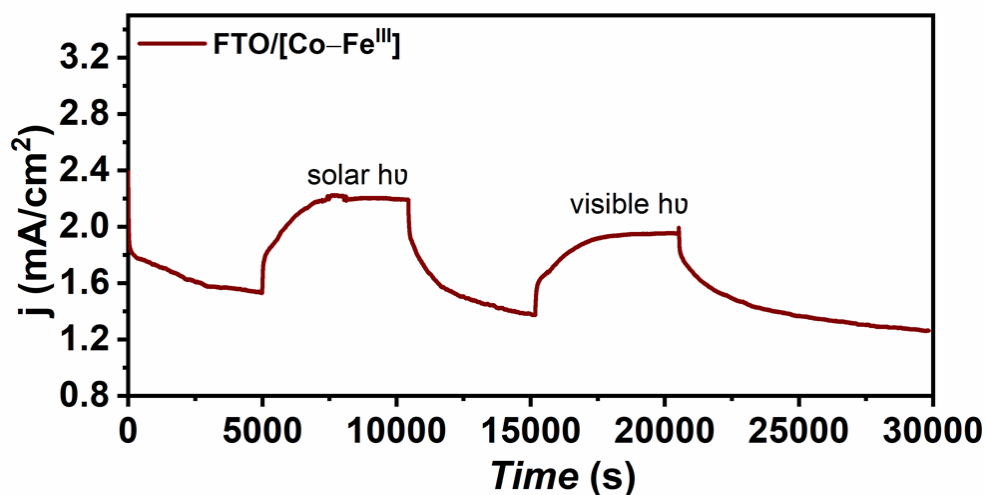


Figure 5.17 Solar and visible light irradiated CA experiment of FTO/[Co-Fe^{III}] at $\eta = 0.6$ V in 0.1 M PBS (pH 7).

All the above-mentioned characterizations and catalytic activities are summarized in Table 5.1. It is found that the prepared PB electrodes present a decent electronic correlation with the recorded catalytic enhancements under external stimuli.

Table 5.1 A summary of characterizations and enhanced electrocatalytic activities of PB electrodes.

PB electrode	j_m , $\mu\text{A cm}^{-2}$	$j_m/j \times 100$, %	j_s , $\mu\text{A cm}^{-2}$	$j_s/j \times 100$, %	Absorbance at 570 nm, A	H at 0.2 T, emu g^{-1}	Lattice constant, Å	$\text{Co}^{+3}/\text{Co}^{\text{All}}$ $\times 100$, % (spin-orbit splitting, eV)
[Co-Fe ^{III}]	120.5 ± 5.6	10.7	375.3 ± 4.9	25.1	0.2341	0.2258	9.9322 $\pm$ 0.0023	88% (15.12 eV)
[Co-Fe ^{II}]	39.1 ± 2.9	3.0	196.9 ± 4.6	16.3	0.1775	0.1750	10.0748 $\pm$ 0.0095	21% (15.79 eV)
[Co-Fe ^{II} NO]	24.8 ± 2.4	1.9	176.7 ± 6.6	9.7	0.1538	0.1284	10.2680 $\pm$ 0.0058	56% (15.44 eV)

5.4 Conclusion

A series of CoFe PBAs with different charge transfer abilities were prepared to elucidate the effect of magnetic field and light illumination on the catalytic activity through an intermetallic charge transfer. [Co-Fe^{II}NO] with the highest catalytic activity but the lowest MMCT (due to strongly π -accepting NO ligand), [Co-Fe^{II}] with the lowest activity and moderate MMCT, and [Co-Fe^{III}] with moderate activity and the highest MMCT were employed. It is found that all electrodes exhibit an enhancement under external stimuli and it is proportional to the intensity of intermetallic charge transfer rather than the catalytic activity. Among them, [Co-Fe^{III}] demonstrates the highest response over the external stimuli exposure, which could reach up to 10.7% and 25.1% enhancement under magnetic field and light illumination, respectively. Furthermore, a 1 h light irradiation boosted the OER activity by almost 57% and the reproducibility of this enhancement is confirmed after 10 h, similar to its initial enhancement. Moreover, the pH dependence of charge transfer is also observed for external stimuli induced activities. At

higher pH values (pH 9), a weaker MMCT band is observed and, although the catalytic activity increases the electrodes are observed to be insensitive to light irradiation and magnetic field. Although the catalytic performance is poor at lower pH values, the external stimuli effect on catalytic activity is found to be operating due to the increased intermetallic charge transfer.

Overall, a facile route is introduced in the field of electrocatalysis given the diversity of PBAs. By manipulating the intermetallic charge transfer of PBAs, various catalytic applications could exhibit enhanced activities to meet industrial expectations.



CHAPTER 6

6. CONCLUSION

In this thesis, several CoFe PBAs were synthesized using either a precipitation or an electrodeposition method for catalytic oxidation of glucose and water. Different strategies are employed to enhance the catalytic oxidation performance of CoFe PBAs. In this concept, the outcomes of these efforts could be evaluated in three sections:

(i) Electrocatalytic glucose oxidation: We demonstrated for the first time that CoFe PB modified FTO electrode could be utilized as a non-enzymatic glucose sensor under neutral conditions with relatively high activity and a proper working range. We observed that Co sites coordinate to the $-OH$ group on the C1 atom of saccharides to oxidize them with a possible gluconolactone formation. Then, we prepared a series of CoFe deposited carbon cloth electrodes to elucidate the effect of cyanoferrate group on the electronic and morphological properties of the electrodes. We found that the electronic effect is more dominant on PBAs for the electrocatalytic oxidation of glucose. Moreover, the long-term experiments revealed that PB based electrode is a robust and an efficient catalyst, which retains ~93% of its activity over 15 days. Given the poor selectivities of noble metals and the requirement for highly basic working conditions of metal oxides, CoFe PBAs provide a unique platform that unifies essential features of commercial glucose sensors including low-cost, proper working range, high stability, and high activity. Therefore, this study presents a potential pathway for the development of earth-abundant PB-based glucose sensors that operate under physiological pH in a wide working range.

(ii) Photocatalytic water oxidation: We reported a facile precipitation method for the construction of PS–WOC dyad assemblies using three different organic dyes as PSs that absorb different regions of solar spectrum. A UV-light (Coumarin, CM), a green-light (Safranin, SF) and a red-light (Methylene blue, MB) absorber dyes are plugged into the CoFe PB network and utilized for photocatalytic OER. It is found that all of them are active and robust systems for photocatalytic water oxidation. Among them, MB coordinated system demonstrates the highest activity owing to the proper band energy alignment for efficient charge transfer and relatively high surface concentration of active

sites. Furthermore, our study on MB is of significance due to its similar absorption profile with Photosystem II, which makes it a decent example for mimicking the natural photosynthetic process. We also found that organic dyes are stable under photocatalytic conditions when they are covalently coordinated to the PB structure. Our control experiments indicate that the coordination of PS and WOC components also improves the activity. The enhancement in the activity and the stability could be attributed to an efficient charge transfer between PS and WOC components through short rigid cyanide ligand. This ‘Plug and Play’ strategy introduces a novel route for the construction of PS–WOC systems, in which a wide agenda of photosensitizers with different band alignments could be integrated to CoFe PBAs to be utilized for water oxidation.

(iii) Intermetallic charge transfer induced electrocatalysis: We prepared a series of electronically dissimilar CoFe PB modified FTO electrodes via an electrodeposition method, by using different cyanoiron precursors to investigate their electrocatalytic OER responses under magnetic field and light irradiation. Characterization studies confirm that electronic properties of CoFe PBAs could be tuned by changing the cyanoferrate groups. We discovered that all the CoFe PB modified FTO electrodes demonstrate positive responses to OER activity during LSV and CA experiments under magnetic field and light irradiation. Furthermore, the highest enhancement under magnetic field and light irradiation is observed by the CoFe PBA that exhibits the most dominant MMCT feature. Several control experiments revealed that enhancement of intermetallic charge transfer on PB structure allows direct manipulation of OER activity with external stimuli. Since the catalytic enhancement is proportional to the intensity of MMCT feature, intermetallic charge transfer could play an important role on the rate determining step of water oxidation mechanism. The effect of intermetallic charge transfer could be explained by diminishing the intermediate sluggish kinetics of OER for enhanced catalytic performance as SCO abilities of active sites are boosted with increasing charge transfer ability of Fe sites. Thus, the utilization of this peculiar property of PBAs is not only a revolution for electrocatalysis but also, in an extended vision, a breakthrough for developing smart materials in a near future with earth-abundant CoFe-based materials.

In summary, we describe novel pathways to push the limits of catalysis by engineering PBAs for the development of easy-to-assemble ‘plug and play’ dyads and

electrocatalysts that are responsive to magnetic field and light irradiation. We could not claim ‘excellent’ or ‘perfect’ catalytic results for PBAs; however, we are aware that exciting steps have been made to develop PB-based catalytic systems in the last two decades. Taking into account this short period of progress, I have full faith that the PBAs could shape the world for a sustainable future.



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