

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**FABRICATION AND CHARACTERIZATION OF P3HT-WO₃ HYBRID
THIN FILMS AND DEVICE APPLICATIONS**

Ph.D. THESIS

Fatma Beyza YEDİKARDEŞ ER

Department of Nanoscience and Nanoengineering

Nanoscience and Nanoengineering Programme

MARCH 2024

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**P3HT-WO₃ HİBRİT İNCE FİLMLEİN ÜRETİMİ, KARAKTERİZASYONU
VE CİHAZ UYGULAMALARI**

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To my family,



FOREWORD

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January 2024

Fatma Beyza YEDİKARDEŞ ER
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ABBREVIATIONS

ACN	: Acetonitrile
AFM	: Atomic Force Microscopy
CA	: Chronoamperometry
CV	: Cyclic Voltammetry
ECD	: Electrochromic Device
EDX	: Energy Dispersive X-Ray Spectroscopy
EIS	: Electrochemical Impedance Spectroscopy
FTIR	: Fourier Transform Infrared Spectroscopy
HMDS	: Hexamethyldisilazane
HOMO	: Highest Occupied Molecular Orbital
ISFET	: Ion Sensitive Field Effect Transistor
ITO	: Indium Tin Oxide
LUMO	: Lowest Unoccupied Molecular Orbital
OFET	: Organic Field Effect Transistor
OLED	: Organic Light Emitting Diode
OPV	: Organic Photovoltaic
P3HT	: Poly (hexyl-3-thiophene)
PC	: Propylene carbonate
PET	: Polyethylene terephthalate
PL	: Photoluminescence
PMMA	: Poly(methyl methacrylate)
PVA	: Hierarchical Cluster Analysis
PVP	: Polyvinylpyrrolidone
SEM	: Scanning Electron Microscopy
SiO₂	: Silicon dioxide
WO₃	: Tungsten oxide
XPS	: X-Ray Photoelectron Spectroscopy
XRD	: X-Ray Diffraction



SYMBOLS

λ	: Wavelength
ϕ	: Work function
μ	: Mobility
ν	: Scan rate
c	: Concentration
C	: Capacitance
t	: Time
s	: Second
R	: Resistance
Q	: Charge
π	: Pi number
V	: Potential
α	: Absorption coefficient
I	: Current
Ω	: Ohm
mC	: Mili Coulomb
η	: Coloration efficiency
mA	: Mili Amper
nm	: Nanometer
cm	: Centimeter
ω	: Radial frequency
Z	: Impedance
τ	: Response time



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FABRICATION AND CHARACTERIZATION OF P3HT-WO₃ HYBRID THIN FILMS AND DEVICE APPLICATIONS

SUMMARY

Inorganic semiconductors, such as silicon and germanium, have underpinned the electronics industry since 1947. However, despite their high performance, the biggest drawback in the development of inorganic-based optical and electronic technology is that these materials can only be produced using expensive and impractical techniques, which require high temperatures and a vacuum environment. Instead of relying on expensive, time-consuming, and brittle inorganic-based materials in production, there is a need for new competitive materials. Especially after the introduction of inorganic solid-state devices to the market, the microelectronics sector began to rapidly develop with the discovery of the charge carrier capacities of organic materials. Since organic electronics can be coated using low-temperature and simple wet chemistry techniques (spin coating, dip coating, spray coating, inkjet printing, etc.), they can be applied to flexible substrates and large areas. Therefore, their easy processability expands the application areas of these materials.

Organic semiconducting polymers are solid materials composed of carbon, hydrogen, and other atoms (such as S or N) with -C and -C=C- bonds along the chain. Conjugated structures are formed along the chain by alternating the carbon atoms in their structures in the form of single bonds and double bonds. However, conjugation alone is not sufficient for high conductivity. In order to make conjugated polymers electrically conductive, either electrons are added to the structure or positively charges (holes) are created by withdrawing electrons from the structure, which is called the doping process.

Conjugated polymers like polyaniline, polythiophene, and polypyrrole have been commonly used in solid-state devices such as organic field-effect transistors (OFETs), organic photovoltaics (OPVs), solar cells, organic light-emitting diodes (OLEDs), electrochromic devices (ECD), photochromic devices, thermochromic devices, and sensors. Among these polymers, poly(3-hexyl thiophene) (P3HT), a derivative of polythiophene, stands out for several advantages. For instance, in comparison to conductive polymers like polyaniline, P3HT exhibits greater stability against environmental conditions due to its thiophene ring. It can be easily dissolved in a wide range of organic solvents, and it possesses both mechanical durability and flexibility. Beside its remarkable electrical conductivity, P3HT boasts chromogenic properties, presenting a significant advantage in its application in next-generation devices. The incorporation of various functional groups into its structure, or the alteration of conjugation length, allows for precise control over these chromogenic properties.

While conjugated polymers have several advantages, they do tend to exhibit lower electrical conductivity compared to inorganic semiconductors. They are also more susceptible to instability under the exposition of moisture, oxygen, or UV light when compared to their inorganic counterparts. Consequently, devices entirely composed of

organic polymers may operate with reduced efficiency and have a shorter lifetime in applications demanding high durability and long-term cyclic performance. To be able to overcome this issue, inorganic transition metal oxides with suitable work functions and energy bands are doped into organic semiconductor polymers. This provides both enhancing electrical conductivity and ensuring more stable operation under electrochemical conditions. Through the combination of advantages of both polymer and inorganic materials, superior properties are achieved in the resulting hybrid structures.

In this study, tungsten oxide (WO_3) was selected as the dopant material due to its advantageous properties, including high electron affinity, suitable band energy levels with P3HT and stability. In order to obtain hybrid thin films, different weight percentages of WO_3 powders were dispersed in a P3HT/1,2-dichlorobenzene solution. The efficiency of doping and the interaction mechanism between the two materials play crucial roles in determining the structural, optical, and electronic properties of the ultimate hybrid structure. Therefore, this thesis study is divided into two parts; the first part examines the use hybrid thin films in organic field effect transistors, while the second part examines their application in electrochromic devices.

The atomic composition of both doped and pristine thin films was quantitatively measured using Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM-EDX) and film morphology were investigated by Atomic Force Microscopy (AFM). The performance of the OFET devices was characterized by I-V characterization curves. Performance parameters such as threshold voltage, on/off current ratio, and field effect mobility were calculated. Considering the electronic characterizations, the optimum doping concentration was determined as 30% WO_3 by weight. It was found that the on/off current ratio and mobility for p-type hybrid thin films increased 10 times and 105 times, respectively. Moreover, reducing the charge traps at the gate insulator-semiconductor interface via doping led to a 20 V decrease in threshold voltage.

The electrochromic properties of both doped and pristine thin films were characterized by cyclic voltammetry (CV). Similarly to OFETs, the optimum doping concentration for the best electrochromic performance was again determined as 30% WO_3 by weight. For the hybrid films prepared by 30% WO_3 doping showed significant improvement in coloration efficiency, optical density and stability. Furthermore, it was found that efficient doping lowers the oxidation potential compared to the pristine P3HT film.

The interaction between P3HT and WO_3 was confirmed X-Ray Diffraction (XRD), Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Photoluminescence Spectroscopy (PL), and X-Ray Photoelectron Spectroscopy (XPS). XRD and Raman investigations indicated that the crystallinity of P3HT increased by the doping of 30% WO_3 , leading to better mobility of charge carriers and better optical contrast. Besides, increasing crystallinity in a polymer provides stability, which results long-term electrochemical cycling durability. Spectroscopic examinations revealed that the charge transfer between P3HT and WO_3 occurs electrostatically driven donor-acceptor interactions. Efficient charge transfer mechanism between WO_3 and P3HT reduces the band gap and oxidation potential, leading to an improvement in electrochromic performance.

Electrochemical Impedance Spectroscopy (EIS) was employed to examine capacitive properties thin films. It was found that double layer capacitance (C_{DL}) of P3HT increased from 5.7 μF to 105 μF with the incorporation of WO_3 . Also, lower charge

transfer resistance (R_{ct}) for hybrid films were obtained, which enables faster redox reactions.

Following the optimization of efficient doping concentration, doped (PW30) and pristine (P3HT) electrochromic films were sandwiched with a WO_3 counter electrode using a gel electrolyte. Regarding the chronoamperometric measurements, it was observed that the PW30-based solid device remains stable up to 1000 cycles without compromising coloration efficiency and exhibits shorter response times compared to the P3HT-based solid device.

Lastly, although not a primary focus of the thesis study, thermochromic behavior of both doped and pristine P3HT films was investigated in the 25°C - 225°C temperature range. The optical transmission at 550 nm of pristine P3HT film increased 17% with increasing temperature. However, no improvement was observed in case of WO_3 doped P3HT films. This suggests that the primary mechanism of thermochromism does not depend on charge transfer as seen in optical and electronic properties.

In summary, this thesis study involves comprehensive optical, electronic, and electrochemical characterizations of WO_3 -doped P3HT thin films, and the interfacial interactions. The application of resulting hybrid films in OFET and electrochromic devices are presented, and preliminary investigations devoted to potential technological applications are evaluated.



P3HT-WO₃ HİBRİT İNCE FİLMLEİN ÜRETİMİ, KARAKTERİZASYONU VE CİHAZ UYGULAMALARI

ÖZET

Silisyum ve germanyum gibi inorganik yarı iletkenler, 1947'den beri elektronik endüstrisinin temelini oluşturmaktadır. Ancak yüksek performanslarına rağmen inorganik temelli optik ve elektronik teknolojisinin gelişimini engelleyen en büyük faktör, bu malzemelerin yüksek sıcaklık ve vakum gerektiren pahalı ve pratik olmayan teknikler ile üretilmesidir. Üretimde pahalı, zahmetli ve esnek olmayan inorganik temelli malzemeler yerine, bunlarla rekabet edebilen yeni malzemelere ihtiyaç duyulmaktadır. Özellikle katı hal cihazlarının pazara sunulmasından sonra mikro elektronik sektörü ön plana çıkmaya başlamış ve geçtiğimiz yüzyılın ortalarında organik malzemelerin yük taşıma kapasitelerinin keşfiyle hızla gelişen bir sektör haline gelmiştir. Organik elektroniklerin vakum gerektirmeyen çözelti bazlı yöntemlerle (döndürerek kaplama, daldırarak kaplama, sprey ile kaplama, inkjet yazdırma, vb) kaplanabilmesi, esnek altlıklara ve geniş alana uygulanabilir olması üretimi daha ucuz hale getirmekte ve bu malzemelerin uygulama alanlarını genişletmektedir.

Organik yarı iletken polimerler, karbon, hidrojen ve diğer atomlardan oluşan, zincir boyunca -C ve -C=C- bağlarına sahip katı malzemelerdir. Yapılarındaki karbon atomlarının tek bağ-çift bağ şeklinde birbirini takip etmesi ile zincir boyunca konjuge yapılar oluşur ancak yüksek iletkenlik için konjugasyon tek başına yeterli değildir. Konjuge polimerlerin iletkenlik kazanması için katkılama işlemi ile yapıya ya elektron verilir ya da yapıdan elektron çekilerek artı yüklü boşluklar oluşturulur. Serbest yük taşıyıcıların (elektron ya da deşik) çift bağlarda zincir içi ya da zincirler arası hareket etmesi ile de elektriksel iletkenlik gerçekleşir. Polimer malzemeler uzun zincirli ve büyük moleküller olduğundan, yapılarında çok sayıda atom ve elektron bulundurlar. Elektronların bulunduğu bağ enerji seviyesi bağ orbitali olarak adlandırılırken, boş olan enerji seviyesi ise anti bağ enerji seviyesi olarak adlandırılır. Polimerlerin kalabalık elektronik yapısından dolayı sayıları sonsuza yaklaşan orbitaller üst üste gelerek birbirinden keskin şekilde ayrılmış enerji seviyeleri yerine, sürekli görünümde enerji seviyeleri oluştururlar. En yüksek dolu moleküler orbital (HOMO) ve en düşük boş moleküler orbital (LUMO) enerji seviyeleri arasındaki farka karşılık gelen bant aralığı, malzemenin optik ve elektronik özelliklerini doğrudan belirleyen bir parametredir. Katkılama işlemi ile polimerlerin bant aralığı ayarlanabildiğinden, iletkenlik, verimlilik, kararlılık, anahtarlama süresi, renklenme kabiliyeti, termal özellikler gibi bir çok parametre kontrol edilebilir. Ayrıca, konjuge polimerlerin elektriksel iletkenliği ve optik özellikleri, moleküler yapıları, kristalinite derecesi, katkı seviyeleri ve kaplama koşulları gibi faktörlere de bağlıdır. Örneğin, daha düzenli ve kristallenme derecesi daha yüksek bir polimerik yapı daha iyi iletkenlik sağlayabilmektedir.

Konjuge polimerler çok geniş bir aile olup; polianilin, politiyofen, polipirol gibi polimerler organik alan etkili transistörler (OFET), organik fotovoltailer (OPV), güneş hücreleri, organik ışık yayan diyotlar (OLED), elektrokromik cihazlar, fotokromik cihazlar, termokromik cihazlar ve sensörler gibi çok sayıda katı hal cihaz uygulamalarında kullanılmakta ve giderek yaygınlaşmaktadır. Konjuge iletken polimerler arasında bulunan ve bir politiyofen türevi olan poli(3-hekzil tiyofen) (P3HT); diğer iletken polimerlere kıyasla bazı avantajlar sağlamaktadır. Örneğin polianilin gibi iletken polimerlere kıyasla, sahip olduğu tiyofen halkası sayesinde çevresel koşullara karşı daha kararlı çalışabilmekte, çok çeşitli organik çözücülerde kolaylıkla çözünabilmekte, mekanik olarak daha dayanıklı ancak aynı zamanda daha esnek özellik gösterebilmektedir. İyi bir elektiksel iletkenlik sağlamanın yanı sıra, kromojenik özellikler göstermesi de yeni nesil cihazlardaki kullanımında önemli bir avantaj sağlamaktadır. Çeşitli fonksiyonel grupların yapıya katılması, katkılama ya da konjugasyon uzunluğunun değiştirilmesi ile, kromojenik özellikler istenilen şekilde kontrol edilebilmektedir. Her ne kadar konjuge polimerler çeşitli avantajlara sahip olsalar da, inorganik yarı-iletkenlere kıyasla daha düşük elektriksel iletkenlik göstermekte, nem, oksijen veya UV ışık altında da inorganik yarı-iletkenlere kıyasla daha kararsız çalışmaktadır. Bu sebeple tamamen organik polimerlerden oluşan cihazlar daha düşük verimle çalışabilmekte, dayanıklılık ve çevrimsellik gerektiren uygulama alanlarında daha kısa kullanım ömrüne sahip olabilmektedir. Hem organik yarı-iletken polimerlerin elektriksel iletkenliğini artırmak, hem de elektrokimyasal koşullar altında daha kararlı çalışmalarını sağlamak amacıyla, uyumlu iş fonksiyonuna ve enerji bantlarına sahip inorganik geçiş metal oksitleri ile katkılama yapılmaktadır. Böylece hem polimerin hem de inorganik malzemenin avantajları bir araya getirilerek, daha üstün özellikler gösteren hibrit yapılar oluşturulmaktadır.

Bu çalışmada yüksek elektron ilgisi, yüksek iş fonksiyonu, bant enerji seviyelerinin P3HT ile uyumlu olması, 300 nm – 1000 nm arasında optik absorpsiyona sahip olması, elektrokromik özellik göstermesi, yüksek sıcaklıklarda kararlı çalışması gibi avantajları sebebiyle, katkı malzemesi olarak tungsten oksit (WO_3) seçilmiştir. Ağırlıkça farklı yüzdelere WO_3 tozları, 1,2-diklorobenzen içerisinde çözünmüş P3HT çözeltisi içerisinde dağıtılarak, tek adımda ve çok kolay bir şekilde katkılama yapılmıştır. Katkılama verimi ve iki malzeme arasında oluşan etkileşimin türü, elde edilen hibrit yapının yapısal, optik ve elektronik özelliklerinin kontrol edilmesinde doğrudan belirleyici rol oynamaktadır. Bu kapsamda yazılan doktora tezi iki kısımdan oluşmaktadır; birinci kısımda WO_3 katkılı ve katkısız P3HT filmlerin organik alan etkili transistörlerde kullanımı incelenmiş, ikinci kısımda ise elektrokromik cihazlarda kullanımı incelenmiştir. Elde edilen hibrit çözeltiler, döndürerek kaplama yöntemi transistor performansının test edilmesi için silisyum dioksit test çipleri üzerine, elektrokromik performansının test edilmesi için ise indiyum kalay oksit (ITO) kaplı cam altlıklar üzerine kaplanmış ve kalınlığı 80 nm – 100 nm civarında değişen ince filmler elde edilmiştir. Katkılı ve katkısız filmlerin elementel içeriği Taramalı Elektron Mikroskopisi – Enerji Dağılımlı X-Işını Spektroskopisi (SEM-EDX) ile kantitatif olarak ölçülmüş, aynı zamanda filmlerin yüzey incelemeleri yapılmıştır. Film morfolojisi ve ortalama yüzey pürüzlülük incelemeleri Atomik Kuvvet Mikroskopisi (AFM) ile gerçekleştirilmiştir. OFET cihaz performansı I-V karakterizasyon eğrileri ile karakterize edilerek yük taşıma özellikleri incelenmiş, cihaz performansını belirleyen eşik voltajı, açık/kapalı akım oranı ve alan etkili mobilite gibi parametreler hesaplanmıştır. Yapılan hesaplamalar sonucunda, optimum katkılama konsantrasyonunun ağırlıkça %30 WO_3 olduğu ve bu katkılama oranında üretilen hibrit filmlerde, katkısız P3HT filmlere kıyasla mobilite değerinde 105 kat iyileşme

gözleendiği, açık/kapalı akım oranının yaklaşık 10 kat arttığı, katkılı ve katkısız filmlerin her ikisinde de p-tipi alan etkisi davranışı gözleendiği tespit edilmiştir. Ayrıca katkılama ile yalıtkan – yarı iletken ara yüzeyindeki yük tuzakları azaltılarak, eşik voltajında da yaklaşık 20 V azalma elde edilmiştir.

Farklı katkı oranlarında üretilen filmlerin elektrokromik özellikleri ise çevrimsel voltametri (CV) yöntemi ile karakterize edilmiştir. Elektrokimyasal karakterizasyonlar sonucunda OFET ile benzer şekilde optimum katkılama konsantrasyonunun, elektrokromik filmler için de ağırlıkça %30 WO₃ olduğu tespit edilmiştir. %30 WO₃ katkılı hibrit filmlerin, katkısız P3HT filme kıyasla 2 kat daha yüksek renklenme verimliliğine, daha yüksek optik geçirgenliğe, daha yüksek optik yoğunluğa ve daha düşük yükseltgenme potansiyeline sahip olduğu görülmüştür.

P3HT ve WO₃ arasındaki etkileşim mekanizmasını anlamak için X-Işını Difraksiyonu (XRD), Raman Spektroskopisi, Fourier Dönüşümlü Infrared Spektroskopisi (FTIR) Fotoluminesans Spektroskopisi (PL) ve X-Işını Fotoelektron Spektroskopisi (XPS) kullanılmıştır. XRD ve Raman incelemeleri sonucunda, ağırlıkça %30 oranında WO₃ katkılı olduğunda, P3HT'nin polimer zincirlerinin kristalizasyon derecesinin arttığı, buna bağlı olarak zincirler üzerinde daha iyi yük transferi sağlandığından elektriksel iletkenliğin arttığı tespit edilmiştir. Yapılan detaylı spektroskopik incelemeler sonucunda ise, P3HT ve WO₃ arasında elektrostatik etkileşimlere dayalı bir yük transferi gerçekleştiği tespit edilmiştir. WO₃ parçacıkları ve P3HT'nin tiyofen grupları arasında oluşan donör – akseptör etkileşimleri ile P3HT'nin bant aralığı ve yükseltgenme potansiyeli azaltılmış, böylece elektrokromik performansta katkısız P3HT filme kıyasla iyileşme elde edilmiştir. XPS analizleri ile tungsten (W) parçacıklarının P3HT'nin tiyofen halkasındaki kükürt atomu (S) ile etkileşiyor olabileceği düşünülmüştür.

Katkılı ve katkısız filmlerin yük transfer dirençleri ve kapasitif özellikleri Elektrokimyasal Empedans Spektroskopisi (EIS) ile incelenmiştir. Elektrot ve çözelti ara yüzeyinde oluşan elektriksel tabaka çift tabaka kapasitansı (C_{DL}), ara yüzeyde oluşan direnç ise yük transfer direnci (R_{ct}) olarak ifade edilmektedir. EIS incelemeleri sonucunda, çift tabaka kapasitansı katkısız P3HT film için 5.7 µF, ağırlıkça %30 WO₃ katkılı P3HT hibrit film için ise 105 µF olarak hesaplanmıştır. Bu durum, katkılı hibrit filmlerin çok daha yüksek kapasitif davranışa sahip olduğunu, yani daha iyi yük depolama kabiliyetine sahip olduğunu göstermektedir. Yüksek frekans bölgesinde ağırlıkça %30 WO₃ katkılı P3HT hibrit filmin katkısız P3HT filme kıyasla daha düşük R_{ct} değerine sahip olması, redoks ve elektrokromik reaksiyonların katkılı filmde daha hızlı gerçekleşmesini sağlamıştır.

Optimum katkı konsantrasyonu ağırlıkça %30 WO₃ olarak belirlendikten sonra, katkılı (PW30) ve katkısız (P3HT) elektrokromik filmler, iyonik jel elektrolit kullanılarak WO₃ karşıt elektrotu ile kapatılmış ve sandviç yapıda elektrokromik katı cihazlar elde edilmiştir. P3HT/WO₃ ve PW30/WO₃ katı cihazların oluşturulmasından sonra, cihazların elektrokromik performansı ve kararlılığı kronoamperometri (CA) ölçümleriyle incelenmiştir. Katkılı elektrokromik filmin kullanıldığı PW30/WO₃ katı cihazın, 1000 çevrime kadar bozulmadan kaldığı, P3HT/WO₃ katı cihazına kıyasla daha kısa anahtarlama süresine sahip olduğu, çok daha kararlı çalıştığı ve 1000 çevrim sonunda bile daha yüksek renklenme verimliliğine sahip olduğu gözlenmiştir.

Son olarak, elektrokromik çalışmaların çıktıları sonucunda P3HT'nin termokromik özellik de gösterebileceği düşünüldüğünden, katkılı ve katkısız filmlerin termokromik davranışları da incelenmiştir. Katkılı ve katkısız P3HT filmler 25°C - 225°C aralığında

ısıtıldığında, katkısız P3HT filmin 550 nm dalga boyundaki geçirgenliğinin %17 arttığı, ancak ağırlıkça %30 WO₃ katkılı filmin termokromik özelliğinde iyileşme olmadığı görülmüştür. Termokromizmin ana mekanizmasının, optik ve elektronik özelliklerde olduğu gibi P3HT ve WO₃ arasındaki yük aktarımına dayanmadığı görülmüş, WO₃ ilavesinin P3HT zincirlerinin üç boyutlu düzlemde konformasyonel yapıyı değiştirdiği için termokromik özellik üzerinde olumlu bir etkiye sebep olmadığı tespit edilmiştir.

Organik-inorganik hibrit malzemeler literatürde yaygın olarak kullanılmalarına rağmen, iki bileşen arasındaki ara yüzey etkileşimleri ve bu etkileşimlerin hibrit sistemin özelliklerini nasıl etkilediği detaylı olarak incelenmemiştir. Bu tez çalışmasında hem katkısız P3HT polimerinin hem de farklı oranlarda WO₃ katkılandıktan sonra elde edilen hibrit filmlerin elektronik, elektrokimyasal ve termal özellikleri detaylı bir şekilde incelenmiş, transistörlerde ve elektrokromik katı hal cihazlarında kullanılabileceği gösterilmiştir. Bu anlamda, bu doktora tezinde sunulan deneysel çalışmaların ve karakterizasyonların literatürde önemli bir açığı kapatacağı düşünülmektedir. Ayrıca katkılama konsantrasyonunun, hibrit ince film tasarımında ara yüzey özelliklerini önemli ölçüde etkilediği, sistematik deneysel çalışmalar ile de detaylı olarak incelenmiştir. Deneyler sonucunda, uygun katkılama konsantrasyonunun polimerin elektron taşınımını, moleküler yapısını ve elektrokimyasal özelliklerini iyileştirmesinden dolayı, hibrit ince filmlerin kullanıldığı transistör ve elektrokromik cihazların daha yüksek performansla çalıştığı tespit edilmiş, yüksek performanslı hibrit ince filmlerin kullanılabileceği potansiyel teknolojik alanların ön çalışmaları yapılmıştır.

1. INTRODUCTION

1.1 Scope and Structure of Thesis

Conjugated polymers have drawn great attention due to their low density, tunable band gap, easy processability, flexibility, low cost and solubility. These unique properties make conjugated polymers a specific class of innovative and distinctive materials with a wide range of applications such as photovoltaics (PV) [1], organic field effect transistors (OFET) [2], solar cells [3], light emitting diodes (OLEDs) [4] and electrochromics [5].

Although conjugated polymers are materials that can be produced easily and show advanced properties in terms of both optical and electronic properties, there are also some disadvantages that prevent their commercialization. Polyhexyl thiophene (P3HT) is one of the most commonly used conjugated polymers. The most significant issue with the development of conjugated polymers is the low charge carrier mobility. It is not comparable to that of silicon-based semiconductor materials. Besides, the electrical and optical performance in ambient atmosphere is unstable because of the moisture and oxygen sensitivity. To overcome these issues, organic and inorganic materials are generally combined with different methods and the ultimate material is called “hybrid (or composite)”. Hybrid materials are often designed to take advantage of the individual strengths of each component. For instance, combining the color diversity of organics and stability of inorganic materials provide higher charge transfer mobility, environmental durability, better reversibility, higher optical contrast and faster switching response.

Among the other metal oxides, tungsten oxide (WO_3) have drawn great attention due to their high electron mobility, excellent stability, high optical transmittance, transparency. Furthermore, WO_3 based devices can work under low operating voltages due to the lack of grain boundaries that restrict the electron movement. It is also a good light absorber under irradiation, heat and electrical field, which is called photochromism, thermochromism and electrochromism, respectively. Considering all

these promising properties, to improve electrical and optical properties of the P3HT based devices, WO_3 is proposed as an alternative to the other metal oxide dopant molecules. These organic – inorganic hybrid materials are promisingly used in sensor applications, chromogenics, electronics, supercapacitors, solar cells, batteries and so on.

The goal of this PhD thesis is to show how interfacial interactions affect the ultimate physical, chemical and optical properties of conjugated polymer based organic-inorganic hybrid systems and their usage in devices. To achieve these goals, the key hypothesis is to find a proper doping concentration of dopant molecules and structural control of the hybrid films. If the optimum doping and molecular control of hybrid structure can be achieved properly, efficient interfacial interactions between conjugated polymer (P3HT) and inorganic transition metal oxide (WO_3) may have a positive effect on several properties such as charge transport, optical and electrical switching, oxidation/reduction potentials, electrochemical stability, and ion storage property. Besides, in this thesis study, not only performance improvement was achieved, but also the interaction between these two materials was investigated in detail with several electronic, optical and structural characterization. Therefore, the fundamental physical and chemical aspects of performance improvement was reviewed and explained based on scientific foundations. In this respect, it is believed that the study will make significant contributions to the literature.

Within this context, the first chapter highlights the focus of the PhD thesis and demonstrate the outline of the thesis. The applicability of both P3HT and WO_3 hybrid materials in organic field effect transistors (OFETs) and electrochromic devices has been discussed in detailed via previous works from literature.

Chapter 2 provides a comprehensive account of the organic semiconductors, charge transport and doping mechanism of conjugated polymers and band theory. More specifically, the physical and chemical properties of polyhexyl thiophene (P3HT) are described since it has been chosen in this PhD study as the active polymer.

Chapter 3 deals with the principles of organic field effect transistors (OFETs) and the components, working principle and crucial device parameters are discussed. In addition, how different materials affect the device performance are shown by suitable examples from literature.

Chapter 4 gives a brief introduction about the concept of electrochromism. Then the fundamental mechanism of electrochromic materials, device components, and key parameters for device applications are described.

In chapter 5, preparation of hybrid films and the materials used are given. Different characterization techniques are represented including scanning electron microscopy (SEM), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), x-ray diffraction, Raman spectroscopy, Uv-Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), photoluminescence spectroscopy (PL), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and four point probe station.

In chapter 6, the major spectroscopic and structural characterizations of thin films to be able to explain interfacial interactions and morphological changes. Electrical measurements and parameter extractions are discussed for the usage of hybrid films in OFETs. Electrochemical measurements are discussed to explain optical behavior depending on the effects of doping concentration on electrochromic devices. Ion storage properties are also given with the impedance analysis. All characterizations of hybrid thin films are examined comparatively to undoped P3HT.

Chapter 7 encompasses a discussion on the impact of interfacial interactions on the polymer's morphology. Additionally, it provides a comprehensive summary of the improvements observed in the optical and electrical properties of WO₃ doped P3HT hybrid thin films.

1.2 Literature Review

Since 1947, the electronics industry has relied on inorganic semiconductors like silicon and germanium as its fundamental building blocks. However, despite the high transistor performance, the biggest factors preventing the inorganic technology development are the use of expensive and impractical fabrication techniques, which require vacuum and high temperature in production. Instead of expensive, troublesome and fragile inorganic-based field effect transistors; new materials that can compete with them are needed. Following the introduction of solid-state devices into the market, the microelectronics industry experienced significant growth, becoming a rapidly developing sector in the mid-twentieth century, particularly with the discovery

of organic materials' charge-carrying capabilities. The fact that organic electronics can be coated with solution-based methods (spin coating, dip coating, spray coating, inkjet...etc) at low temperatures and vacuum-free methods makes production cheaper and application areas wider.

1.2.1 Organic Field Effect Transistors (OFETs)

Most organic semiconductors exhibit lower conductivity than inorganic semiconductors due to their low mobility and lack of free charge carrier. For example, while the mobility of silicon is $>10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, the mobility of P3HT -the most commonly used conjugated polymer in organic semiconductor technology- is in the range of 10^{-5} - $10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [6]. However, by doping the organic polymer structure, important performance parameters can be controlled and thus improved.

Although organic-inorganic hybrid materials are used in photovoltaic devices, solar cells and organic light emitting diodes, solution based hybrid OFETs are still under investigation. Thus, distribution of an inorganic nanomaterial in an organic semiconducting polymer is of interest in both theoretical and application. The blends of organic-inorganic materials change the polymer film structure and increase the mobility by generating more localized energy levels [7].

In order to improve electrical properties, inorganic dopant molecules such as zinc oxide (ZnO) and titanium oxide (TiO_2) can be added into the organic polymers so that the free charge carriers can be controlled by doping concentration [8–12]. Besides, it is possible to improve transistor parameters including field effect mobility, on/off current ratio and threshold voltage.

Zinc oxide is the most widely used inorganic dopant molecule in thin film transistors. ZnO has a band gap around 3.1 eV – 3.3 eV and high binding energy [13], [14]. Large band gap provides durability against high electrical field, low noise and high power [15]. Band structure could be tailored depending on the crystalline structure so that it affects the electronic properties. ZnO based transistors have field effect mobility around 0.02 - $20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, threshold voltages around 1-20 V and on/off current ratio around $10^2 - 10^4$ [16], [17].

Navan and co-workers [18] dispersed 25 wt%, 40 wt% and 50 wt% of ZnO wires in 3 mg/ml P3HT/chloroform solvent and coated on bottom contact-bottom gate transistor by spin coating. Current-voltage and mobility measurements were performed for both

ZnO doped P3HT and pristine P3HT. Although ZnO is an n-type semiconductor, ZnO-P3HT composite showed p-type semiconductor behavior. Up to 40 wt% of ZnO, it was observed that hole mobility increased from 1.15×10^{-3} to 1.80×10^{-3} . Besides, it was reported that the on/off current ratio is not depending on the ZnO nanorods concentration and exhibited around 10^4 . When the concentration exceeds an optimum doping concentration, mobility decreased.

Xie [8] was prepared solution based P3HT:ZnO composites on bottom contact-bottom gate transistors and found that increasing film thickness causes a shift in threshold voltage from -12.8V to -6.1V. The mobility of the composite film increased 2 times from 1.30×10^{-3} to 2.62×10^{-3} . The improvement in mobility was supported by the X-Ray diffraction (XRD) analysis, and it was concluded that rod-shape ZnO nanostructures increased the crystalline domains of P3HT which are responsible for the charge transfer. Also, after the addition of ZnO, a joint area has been formed between p-type P3HT and n-type ZnO nanorods, called “heterojunction”. Since the work function of P3HT is smaller than the work function of ZnO nano rods, there has been an electron flow from P3HT to ZnO nanorods. In the p-type doped organic thin film transistor, electrostatic potential of the composite film decreased as the electron accumulates in the ZnO nanorods. In another work [10], 0.5 mg ZnO was dispersed in 3 mg P3HT/chloroform solution and coated on silicon dioxide (SiO_2) gate insulator by spin coating. It was found that hybrid composition increased the mobility 10 times and decreased threshold voltage from -1.9V to 0.7V, however on/off current ratio remained the same.

In another work [19], 10 mg P3HT was dissolved in 1 ml dichlorobenzene and 100 mg ZnO powders were dissolved in 1 ml dichlorobenzene, separately. After complete dissolution, two solution were mixed 1:1 volume ratio and spin coated on the chips at 5000 rpm for 60 seconds. The chip has 16 transistors with different channel lengths ($L=2.5 \mu\text{m}$, $5 \mu\text{m}$, $10 \mu\text{m}$, $20 \mu\text{m}$) on it. Since the electron affinity of ZnO is higher than the electron affinity of P3HT, ZnO tends to take electrons from HOMO level of P3HT leaving behind the holes. Thus, sub-threshold voltage decreases and field effect mobility increases for ZnO doped P3HT blends due to the efficient charge transfer between energy levels. Also, it is seen that short channel ($L=2.5 \mu\text{m}$) reduces the threshold voltage by increasing the mobility.

Similar to ZnO nanoparticles, molybdenum disulfide (MoS_2) was used as dopant molecule for P3HT to alter the electronic properties [20]. 1 mg MoS_2 were sonicated in 1 ml chloroform for 6 hours and 30, 60, and 90 μl MoS_2 solution added into the 3 mg/ml P3HT/chloroform solution. XRD data showed that MoS_2 incorporation was increased the crystallinity of P3HT chains and caused a reduction in exciton bandwidth, which means the extension of conjugation length of P3HT. Furthermore, due to the π - π stacking interactions, mobility of the 1% MoS_2 doped P3HT composite reached to $0.16 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is almost 50 time higher than undoped P3HT ($0.0038 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).

Among the other inorganic dopant molecules, WO_3 has drawn great attention in recent years due to its application in electrochromic, photochromic and solid state sensor devices [21]. They are also used in electrochromic transistors [22], [23], ion-sensitive field effect transistors (ISFETs) as gas detection [24] and in other areas of electrochemistry [25]. WO_3 is a semiconducting transition metal oxide having an adjustable wide band gap ($E_{\text{gap}} = 2.5\text{-}3.2 \text{ eV}$) at room temperature and high electron affinity [26], [24]. The electron affinity is a crucial parameter for effective charge transfer mechanism. For the first time, Barquinha [22] reported that the device coated with amorphous and crystalline WO_3 as a semiconductor layer exhibits transistor properties, and that the amorphous WO_3 shows better electronic performance than the crystalline WO_3 . The fact that this amorphous WO_3 -based transistor operates less than 4V and the current leakage is very small when the circuit is closed ($I_{\text{ON}}/I_{\text{OFF}}=106$).

1.2.2 Electrochromic devices (ECD)

Inorganic materials were typically employed in the first studies of electrochromic field. However, the poor color diversity, slow response times, production challenges, compatibility and performance issues, restricted their applications. Therefore, conductive polymers have been the focus of electrochromic research due to their fast reaction times, color diversity and easy processability.

Because of the fact that conjugated polymers have tunable band gap energies, mobile and delocalize π electrons, they can interact with light and store electrical charges so that they show superior electronic and optical properties in comparison with their inorganic counterparts. Furthermore, thanks to their tunable $\pi \rightarrow \pi^*$ transitions, light interaction and charge carrier transport can be controlled [27], [28]. Compared to other

conjugated polymers, polythiophenes become prominent due to their advantages such as being more stable, environmentally friendly, fast coloring response and having more pronounced $\pi \rightarrow \pi^*$ stackings thanks to their regioregular structure. Conjugated electrochromic polymers show at least one color and one bleach state. However, depending on the position of alkyl groups, repeating units and chain orientation, they could give different colors in the redox state.

However, the conjugated polymers are often unstable under atmospheric conditions and oxidation of the side chains and thiophene units in the backbone lead to degradation of the polymer [29], [30]. It was reported that [31] the P3HT films show higher optical contrast under high oxidation potentials but shorter lifetimes. It was thought that this shorter lifetime could be attributed to the degradation of P3HT forming sulfone and sulfide species. Therefore, the band gap of the conjugated polymers can be altered by proper incorporation of the dopant molecules to be able to overcome the short lifetimes and instability of the organic active materials used in EC devices [32].

In order to examine how interface interactions between organic and inorganic molecules affect the optical and electrochemical properties, P3HT was doped with mesoporous TiO_2 [33]. TiO_2 paste was dissolved in ethanol and spin coated on FTO substrates at 4000 rpm for 30 s. Then, 20 mg P3HT/1 ml chlorobenzene solution were spin coated at 2000 rpm for 60 s on both mesoporous TiO_2 coated FTO and uncoated FTO. It is seen that TiO_2 doping increased stability of the electrochromic device up to 1000 cycle and broadened the CV curve due to the strong interface interactions between TiO_2 and P3HT. Furthermore, with the addition of mesoporous TiO_2 , optical contrast increased from 24% to 32% and response time reduced from 30 s to 27 s.

Similarly, in electrochromic studies with polyaniline (PANI) and WO_3 hybrid films, it was found that electrochromic performance could be improved by interface modification. Song and co-workers [34] prepared WO_3 films by seed-assisted hydrothermal method and PANI was coated on WO_3 film by electrodeposition. Whilst there is almost no difference of the $\Delta T\%$ between WO_3 and PANI: WO_3 , coloration efficiency of the hybrid films increased from $57.84 \text{ cm}^2\text{C}^{-1}$ to $69.22 \text{ cm}^2\text{C}^{-1}$, resulting a fast color change. Due to the increased conductivity of PANI: WO_3 hybrid films in impedance measurements, it was asserted that WO_3 layer provided a proper surface modification for PANI layer and improved ion and charge transfer capability at the

interface. Nwanya and co-workers [35] deposited WO_3 on ITO substrates by chemical batch deposition and immersed the WO_3 coated ITO substrate into the PANI solution to get PANI: WO_3 hybrid films. Structural characterizations showed that the microporous structure and high specific area helped to improve charge transfer and capacitive properties of PANI: WO_3 hybrid films. Also, PANI: WO_3 hybrid films maintained its energy storage capability even after 1000 cycle charging - discharging. In another work [36], the electrochemical properties of P3HT on nanoporous WO_3 layers were investigated. P3HT: WO_3 composite structure changed the coloration states, and found that P3HT behaves like an ion storage layer by leading faster switching response compared to WO_3 .

Kim and co-workers [37] prepared surfactant assisted graphene oxide- octadecylamine (GO-ODA)-P3HT complex to improve long-term cyclability of P3HT. Although there is almost no difference between response times, (GO-ODA)-P3HT complex showed higher $\Delta T\%$ than pure P3HT ($\Delta T\%=22.4\%$ and $\Delta T\%=17.9\%$, respectively). In addition, the long-term stability of polymeric electrochromic materials with electrostatic interactions, π - π stacking and s- π interactions was considerably improved by the GO-ODA protective layer. Crystallinity is also one of the key parameters to affect the electrochromic performance. Huang and co-workers [38] investigated the effect of solvent evaporation on EC device performance and observed that larger optical contrast is directly affected to the polymer stacking and crystallinity degree. According to the research for which a brief overview of the literature is provided above, P3HT doped with different inorganic materials is often employed to improve electrical and optical properties in both electrochromic devices and electronic circuit components like OFETs.

1.3 Original and Significant Findings

Although organic-inorganic hybrid materials have been widely investigated for both electronic and electrochromic applications, a guided systematic study and detailed structural characterizations are not well established. Furthermore, despite the unique electronic and optical properties of P3HT, there are few studies on its application to electrochromic devices.

So far, the research mainly focused on the strong covalent bonds, coordination bonds and $\pi \rightarrow \pi$ stack interactions. However, there are a few study were addressed to

electrostatic interactions for superior properties in hybrid systems. As can be seen from the literature research, hybrid films is obtained mostly by layer-by-layer deposition methods, which is a multi-step production. In this work, WO_3 powders were dispersed in P3HT/1,2-dichlorobenzene solution by simple step solution blending doping without any covalent bonding. Subsequently, WO_3 doped P3HT solutions in different weight percentages were coated on prefabricated commercial test chips and ITO coated glass substrates for transistor and electrochromic applications, respectively. Doping concentration of WO_3 was optimized and a solid state electrochromic device was fabricated using the best hybrid thin film structure. Solid device was able to operate successfully with higher performance and stability compared to the pristine P3HT films.

In summary, this thesis work, it is hypothesized that efficient doping mechanism and electrostatic interactions between WO_3 and P3HT may enhance the optical and electrical properties of P3HT. Therefore, we discuss several important points in hybrid films in detailed as follows;

- Optimization of the proper P3HT: WO_3 doping concentration
- Doping effect and interfacial interactions on electron transport properties
- The effect of doping and interfacial interactions on ion transport properties
- The effect of proper doping and interfacial interactions on capacitive properties
- Putting into practice of the proposed hybrid systems to OFETs and solid state electrochromic devices.

Last but not least, the present research explores, for the first time, the effects of WO_3 doping on both transistor performance and electrochemical performance of P3HT thin films. Furthermore, this study will be helpful for designing high performance hybrid materials. It is also believed that these finding will shed light on to clarify the interactions at the interfaces between organic and inorganic components and will improve the understanding of optical and electrical behavior of hybrid systems for future applications.



2. ORGANIC SEMICONDUCTORS

2.1 Fundamentals of Organic Semiconductors

Organic semiconductors are substantially new class of materials, and due to their unique electronic, optic and mechanical properties, they have attracted attention as potential alternatives to traditional semiconductors in certain applications. With the discovery of organic semiconductor materials at the beginning of the 21st century, semiconductor technology gained momentum in several fields such as organic solar cells, organic light emitting diodes, low-cost integrated circuits, large-area and flexible displays, organic diodes and organic field-effect transistors. This is mainly due to the growing need to replace silicon with alternative materials, which are relatively simple and commercially available.

There are great differences between the bond structure of organic and inorganic semiconductors. Unlike the covalently bonded traditional inorganic semiconductors, organic semiconductors are weakly bonded based on the Van der Waals interactions. Due to such properties, organic semiconductors have a low melting point, low stability, and low interaction of electronic wave functions between neighboring molecules, which is directly related to optical properties and charge carrier transport. The intrinsic conductivities of low band gap inorganic semiconductors such as silicon (Si), germanium (Ge) and gallium arsenide (GaAs) are in the range of 10^{-8} to $10^{-2} \Omega^{-1}\text{cm}^{-1}$ [39]. In contrast, organic semiconductors have extrinsic conductivity, which is caused by the injection of charges, doping or electron hole pairs. This can be attributed to two distinct characteristics of organic materials; (i) absorption and emission in the visible region and (ii) significant coulomb interactions.

In inorganic semiconductors, free charge carriers are generated by the light absorption. This occurs when the incident light energy is higher than the band gap energy of a semiconductor. When a photon with sufficient energy is absorbed by the semiconductor, an electron from the valence band moves into the conduction band, where the electrons are free to move and conduct electricity. However, in organic

semiconductors, free charge carriers are generated through the dissociation of photoexcited excitons depending on the electric field [39]. When an organic molecule is exposed to light excitation, it has a potential to absorb a photon. The molecule, initially in the ground level energy, moves to a higher energy level, which is called "excited" state. This absorption of a photon results in the generation of an electron-hole pair. Electrostatic interaction between an electron and a hole might result to the formation of an exciton or electron-hole scattering.

2.2 The Basics and Band Theory of Organic Molecules

Organic semiconductors are polymeric materials that are largely made up of carbon, oxygen and hydrogen atoms, with a few sulfur and nitrogen atoms included. They can be classified as small molecules and polymers. Small molecules refer to organic compounds with low molecular weight, typically comprising aromatic hydrocarbons. These semiconductors can generally be deposited on a desired substrate by vacuum processes such as thermal evaporation. However, conjugated polymers are more advantageous since they can be dissolved in suitable solvents and deposited by simple, low-cost and low temperature techniques such as spin-coating, dip-coating or ink-jet printing. Most commonly used polymers and organic small molecules are given in Figure 2.1.

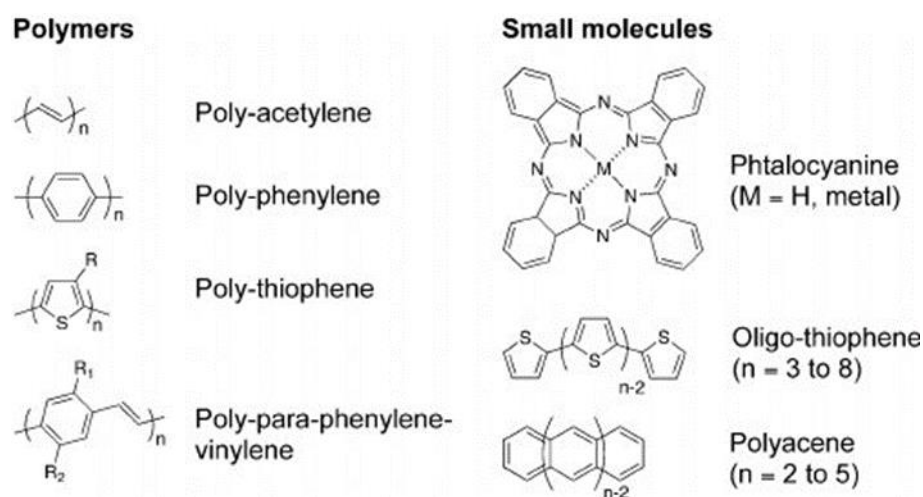


Figure 2.1 : Most commonly used polymers and organic small molecules.

Conductive polymers can be distinguished from the other polymers due to their conjugated chain structure consisting of alternating single and double bonds. If the bonds between carbon atoms in the polymer chain follow each other as single and

double bonds, this structure is called conjugation. A simple schematic representation of conjugation is given in Figure 2.2.

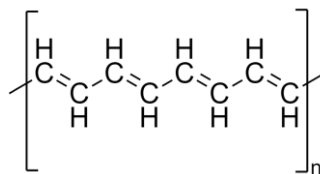


Figure 2.2 : A schematic representation of conjugated chain (polyacetylene).

In a conjugated system, each single bond between carbon atoms is called sigma bond (σ), which is a very strong bond consisting of sp^2 hybridization. In the double bonded parts, in addition to sigma bond, there is a weaker pi (π) bond, which is formed by the combination of overlapped p_y or p_z atomic orbitals along the x-axis of conjugated backbone. Charge carriers in these π bonds in organic semiconductors are called π electrons. In order to exhibit electronic conductivity, there must be suitable locations in the polymer backbone that can allow electron transportation along the chain. The conductivity of all organic semiconductors, irrespective of polymers or small molecules, depend upon conjugated π electrons. Polymers with conjugated double bonds in the main chain satisfy this condition so that only conjugated polymers can conduct the electricity.

The electrical and optical properties of a material depend on the difference between the bonding orbital (π) and the antibonding orbital (π^*). Since the bonding π orbital has lower energy, it is named as HOMO (Highest Occupied Molecular Orbital). The antibonding (π^*) orbital, which has a higher energy level, is called LUMO (Lowest Unoccupied Molecular Orbital). The HOMO energy band corresponds to the valence band in inorganic solid state physics, while the LUMO energy band represents the conduction band. The energy difference between HOMO and LUMO levels is also named as **band gap (E_{gap})**, which makes it possible to light absorption and emission in the visible region. For smaller molecules such as ethylene, energy gap between $\pi - \pi^*$ orbitals is large. When the number of repeating monomer units increases, HOMO and LUMO levels bring close to each other due to the large number of overlapped p orbitals, resulting the decrease in band gap [40]. Organic molecules with an energy difference of 1.5-3 eV between the bonding and antibonding orbitals are classified as semiconductors. However, band gap energy of a conjugated polymer can be easily altered by modifying π conjugation length, intermolecular interactions, substituents

and donor-acceptor structure. The schematic representation of energy band diagram for conjugated semiconductors is given in Figure 2.3.

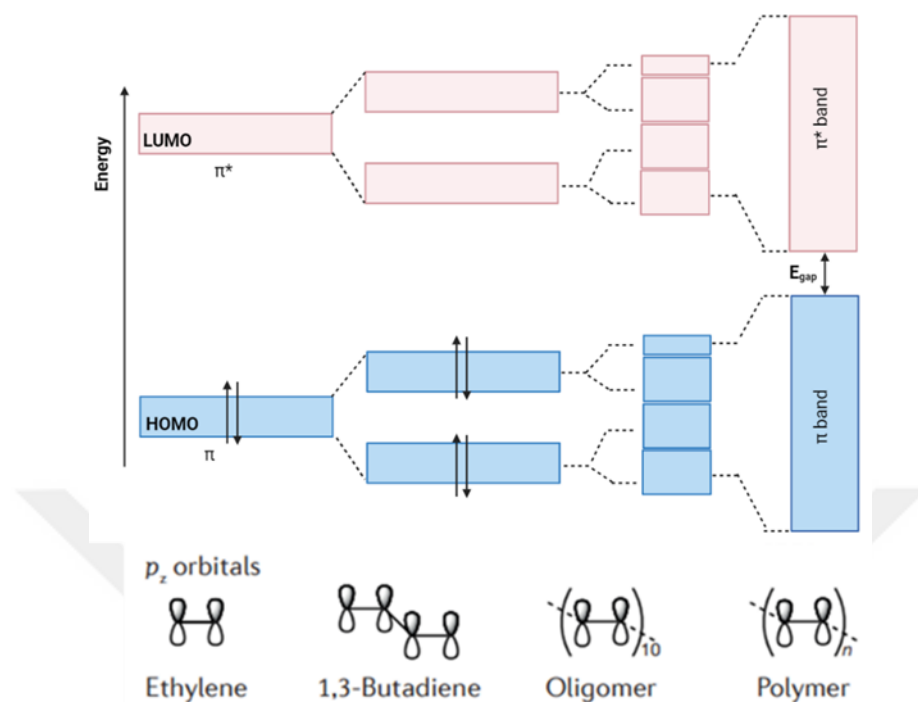


Figure 2.3 : The schematic representation of energy levels and band gap structure of organic semiconductors.

2.3 Conductivity of Organic Semiconductors

It has taken a long time to understand and characterize the conductivity mechanism of conductive polymers. The biggest reason why conductivity is difficult to explain is the movement of charge carriers. Potential charge carriers are created in the doping process, but they must be mobile in order to contribute to conductivity. This is achieved by introducing impurities or dopant molecules that either donate extra electrons (n-doping) or accept electrons (p-doping) into the semiconductor material. These extra charge carriers significantly influence the electrical conductivity and performance of the organic semiconductor. The conductivity of a semiconductor not only depends upon the doping level, but also molecular structure, chain crystallinity and environmental conditions.

In the following section we will discuss how charge transport occurs in organic semiconductors.

2.3.1 Charge transport mechanism

Polymers are semi-crystalline materials so that they have both aggregate domains and spaghetti-like amorphous regions. Aggregate domains are generated due to the π orbital overlaps between neighboring chains. These π orbitals are responsible for the charge carrier transportation between the inter-chain, which is called “ π -stacking”. Amorphous regions have inadequate π -stackings so that they have poor charge carrier mobility. Considering the chain structure of conjugated polymers as simply given in Figure 2.4, molecular arrangements can be classified as “inter-chain” and “intra-chain” interactions. The main charge transport mechanism is driven by these two interactions. Inter-chain interactions are π - π interactions so that charge carriers can travel in the crystalline domains of the polymer. This is called “**hopping mechanism**”. With a simpler definition, the electrons jump to the localized locations of the adjacent polymer chain. Inter-chain hopping prevents charge carriers from high energy traps formed in amorphous domains in the polymer backbone. Increasing the degree of π orbital overlapping between polymer chains, ordered crystalline domains are formed. The ordered crystalline domains formed by π -stacks increase crystallinity in the polymer chains. Therefore, the π -stacking and crystallinity correspond to efficient charge transport and lead to better conductivities [41], [42].

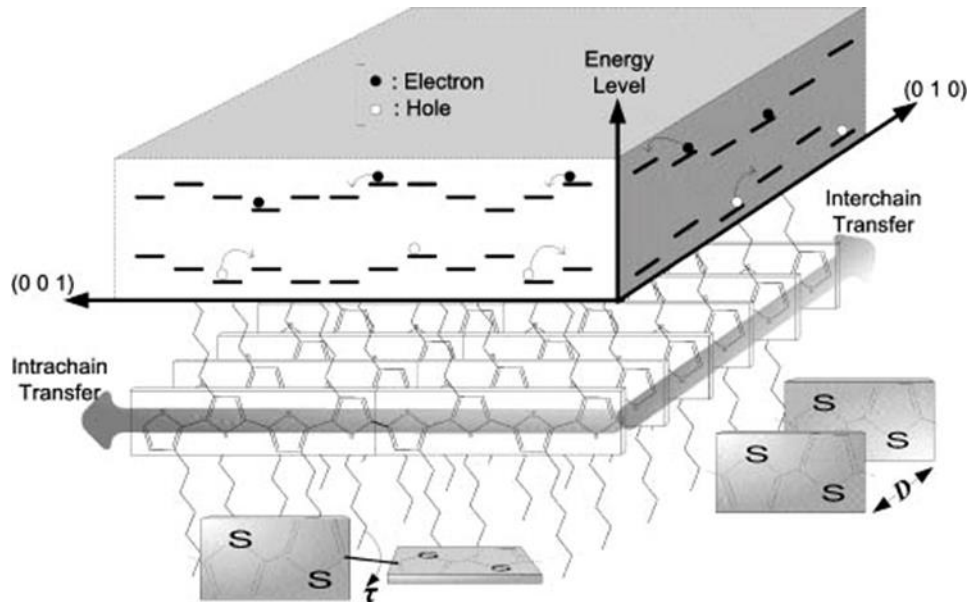


Figure 2.4 : The schematic representation of inter-chain and intra-chain interaction in P3HT thin film.

In many conjugated polymers containing aromatic groups such as thiophene units, two different densities of non-degenerate states arise due to their structural differences in

resonance states. The energetic states are different from each other. In conjugated polymers containing such aromatic groups, charge carrier transport occurs via polaron, exciton and bipolarons. In aromatic conjugated polymers, an excess charge can be created at LUMO or HOMO levels by photo-doping or electro-chemical doping. As a result of this excess charge formed in the structure, local shape alteration occurs in the structure of aromatic groups. This extra charge pair formed in the conjugated molecular structure as a result of doping is called “polaron”. “Bipolarons” are formed by removal of a second electron from polaron and are spinless. Polarons are formed at low oxidation levels whilst bipolarons are formed at high oxidation levels. Under the influence of an electric field, both polarons and bipolarons have the ability to travel along the polymer chain through the rearrangement of double or single bonds. Soliton is also one of the charge carriers which forms in in long-chain polyenes. Solitons can be charged (positive or negative charge with 0 spin) or neutral (0 charge and 1/2 spin). Therefore, the main mechanism of charge transport in conductive polymers is polarons, bipolarons or solitons. Figure 2.5 depicts the chemical or electrochemical doping processes of oxidation to polaron and soliton species [43].

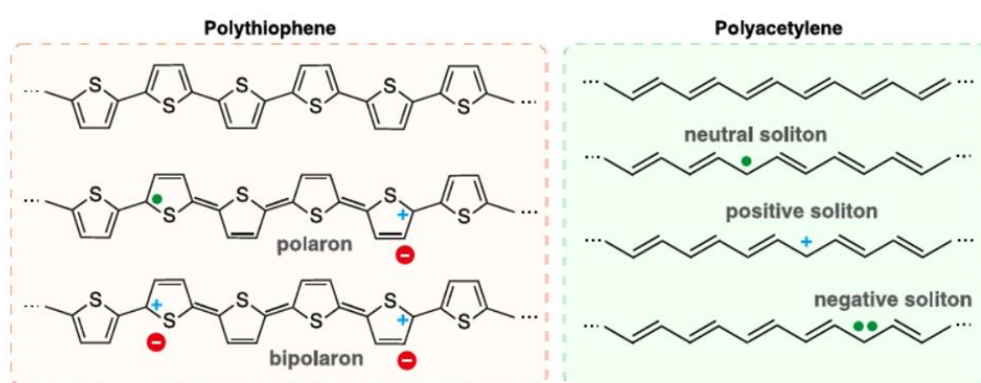


Figure 2.5 : Polaron, bipolaron and soliton species in conductive polymers.

2.4 Doping of Organic Semiconductors

Although the electrical properties can be improved with conjugation, unfortunately the conjugation alone may not be sufficient for electrical device applications. For example, the conductivity of undoped poly(3-hexyl thiophene) (P3HT) is around 10^{-5} S/cm, which is almost insulating. Hence, it is needed to introduce additional charge carriers (electrons or holes) into the polymer, called “doping”. In 1977, it was the first time Heeger, MacDiarmid and Shirakawa doped polyacetylene with halogen vapor and

enhanced conductivity almost 100 times [44], [45]. Since then, the research field in conductive polymers have gained momentum and researchers have proposed different doping mechanisms.

2.4.1 Electrochemical doping

In the electrochemical doping process, the oxidation or reduction of the polymer is driven by an electric current. The counter ion is drawn into the system from the electrolyte solution by the applied electric field. A positive potential is applied for an electron acceptor group to participate in the structure (oxidation). Electrochemical doping stops when the applied voltage is not sufficient to further oxidation of the polymer. The electrochemical doping process proceeds very similarly to the chemical doping process. However, in the electrochemical doping process, the energy required for oxidation or reduction is provided by the external bias, while the counter ion support of the ionized polymer is provided by the electrolyte. Furthermore, electrochemical doping is conducted in a three-electrode cell. Herein, typically a Ag/AgCl and platinum grid is used as reference electrode and counter-electrode, respectively. Herein, polymer acts as the working electrode which may be either oxidized or reduced until the electrochemical equilibrium is reached [46]. Also, electrochemical doping allows control to carrier density and doping levels under applied potential while in situ monitoring the change in both current and optical properties by UV–Vis–NIR absorbance spectroscopy. The p-type doping reaction for a conjugated polymer such as P3HT in electrolyte solution can be written as the reaction (2.1) [47];



where A indicates the injection/ejection of anions. By using different electrolyte solutions containing Br^- , ClO_4^- or PF_6^- anions, doping of organic semiconductors can be achieved.

2.4.2 Molecular doping

Molecular doping is driven by introducing a molecule that can add or withdraw electrons from the polymer backbone. This kind of doping may be chemical or electrostatic. In p-type molecular doping, an electron is transferred from the host polymer to the dopant molecule leaving behind a hole, since the LUMO level of the

dopant is lower than the HOMO level of polymer. On the contrary, in the n-type doping, an electron is transferred from the dopant molecule to the polymer leaving behind an excess free electron since the LUMO level of the dopant is higher than the HOMO level of polymer (Figure 2.6). This charge transfer mechanism is based on either physical or chemical interaction [48].

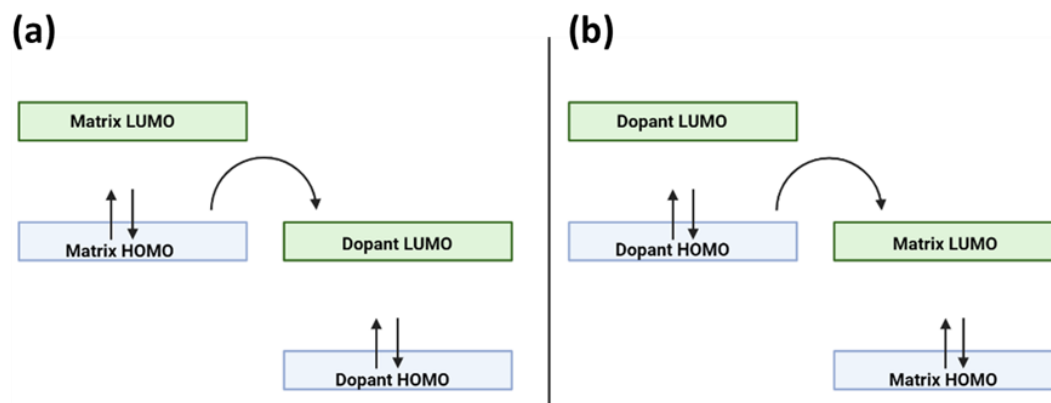


Figure 2.6 : A simple schematic illustration of (a) p-type doping and (b) n-type doping in organic semiconductors.

Molecular doping may be generated by two different mechanisms; ion-pair formation and ground-state charge-transfer complex (CPX) formation [49], [46]. In the CPX mechanism, regardless of n-type or p-type doping, a new hybridized bonding and anti-bonding orbitals are generated. In some cases, CPX mechanism might be observed where ion-pair mechanism could not happen. A schematic representation of these two mechanisms is given in Figure 2.7.

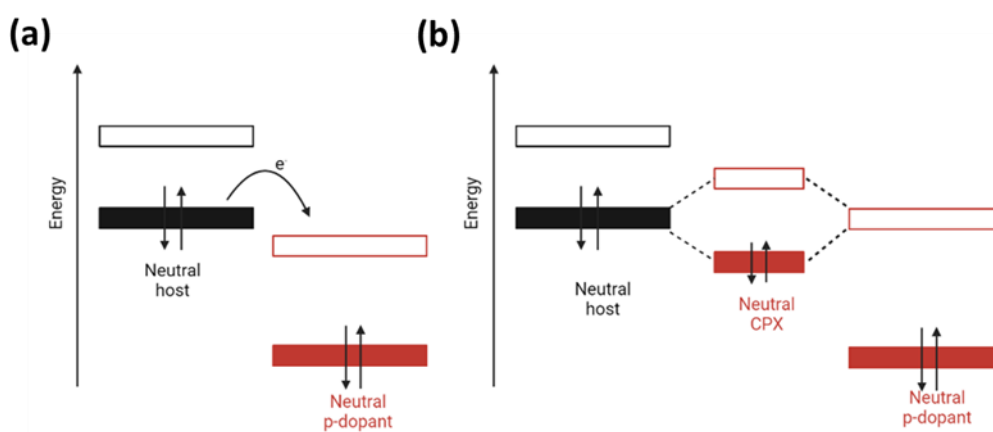


Figure 2.7 : A schematic representation of molecular doping mechanisms; (a) ion-pair formation and (b) ground-state CPX formation.

Molecular doping is widely used method to optimize electrical, optical and thermal properties of conjugated semiconductors. In this method, organic or inorganic dopant molecules that have better miscibility with polymer are introduced. The introduced dopants can increment extra charge carriers by oxidizing or reducing the polymer. Molecular doping techniques can be classified into several different techniques and summarized in Figure 2.8 [50].

- Solution blending doping

This method is one of the simplest doping methods and only involves mixing the polymer and dopant in the same solvent and coating them on a substrate by spin coating, dip coating or drop casting. Although this method is low cost and controllable method, there are major disadvantages such as the solubility difference of polymers and dopant molecules in the same solvent or excess amount of dopant molecules resulting phase separation.

- Solution sequential doping

The polymer solution is first coated on the substrate. Once the solvent has completely evaporated and the film has formed, the dopant solution is coated onto the polymer film by evaporation or spin coating.

- Solution soaking doping

The polymer solution is first coated on the substrate, then the polymer film is soaked into the dopant solution.

The ultimate material property strongly depends on the doping efficiency. For instance, when the good solvent is used for the proper doping method, crystallinity degree of the polymer chains increases due to the proper π - π^* stacking distances. When the excess amount of dopant molecules are introduced, crystalline domains on the polymer backbone may be destroyed and the transportation of charge carriers are blocked, resulting a decrease in mobility.

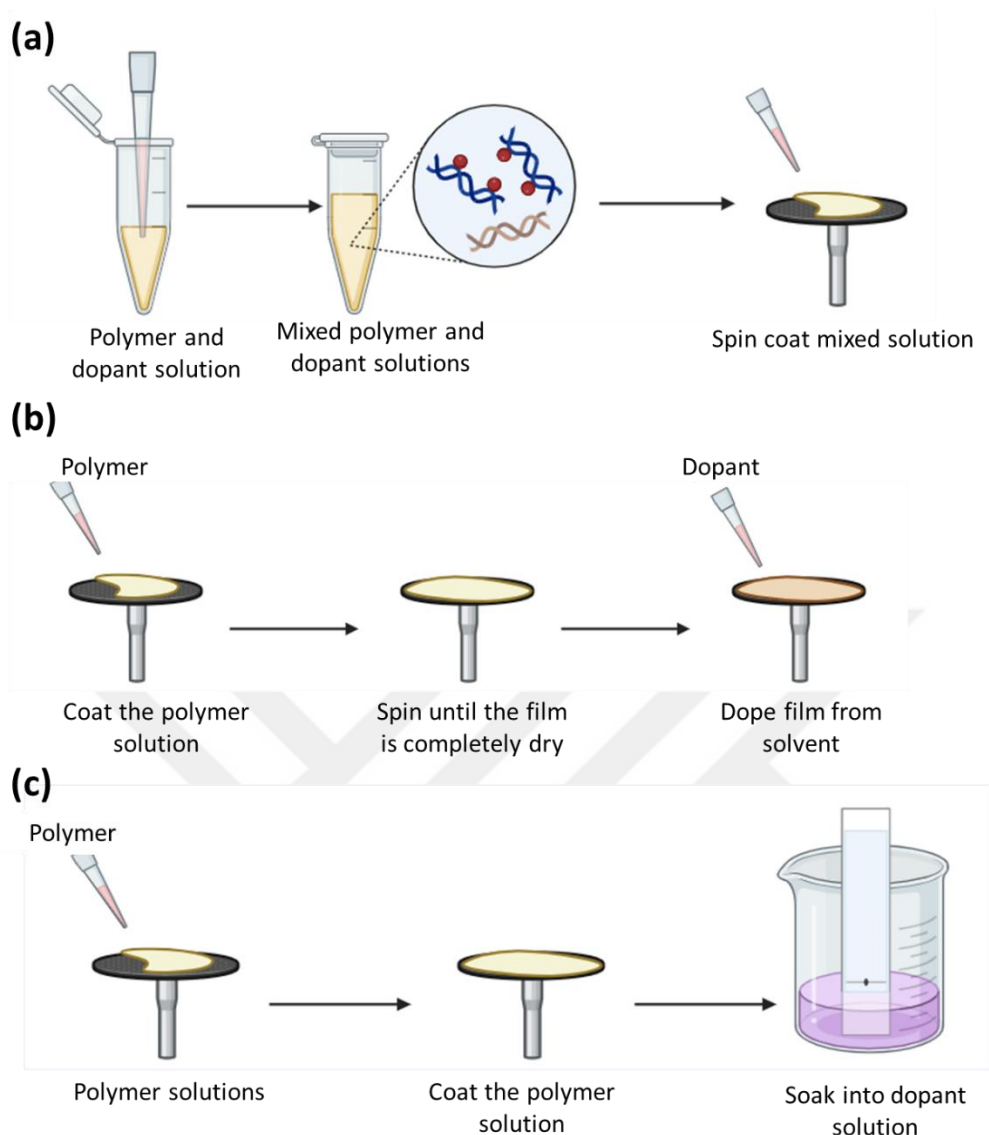


Figure 2.8 : (a) Solution blending doping method, (b) solution sequential doping method and (c) solution soaking doping method [50].

2.5 Properties of poly(3-hexyl thiophene) (P3HT)

While other conjugated polymers have been evaluated, poly(3-hexyl thiophene) (P3HT) is by far the most commonly studied conjugated polymer due to its superior electrical, optical and chromogenic properties [51], [52], [53]. Thanks to its extended light absorption up to 650 nm [54], higher hole mobilities [55], tunable band gap, synthetic versatility and high solution processability, P3HT is the excellent donor material for electronic and optical devices [56]. Its alkyl side chains provide good solubility, flexibility and easy processability. High mobilities of $0.1\text{--}0.4\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been recorded in P3HT based field effect transistors [57]. These studies have

made significant progress in establishing a relationship between nanoscale polymer structure and device performance. High regioregularity and shorter polymer chain are projected to result in better molecular packing and a higher degree of crystallinity [58], [59].

Since the 3-hexylthiophene units of P3HT is asymmetric regiochemistry, there are three possible orientations between thiophene units; head-to-head coupling, head-to-tail coupling and tail-to-tail coupling. If P3HT chains contain all these three orientations randomly, it is called “regiorandom”. If the P3HT chains extensively contain head-to-tail couplings, it is called “regioregular”. Regioregular conformation is highly desirable for both effective charge transportation and high absorption in the visible region. Both chain orientations are represented in Figure 2.9.

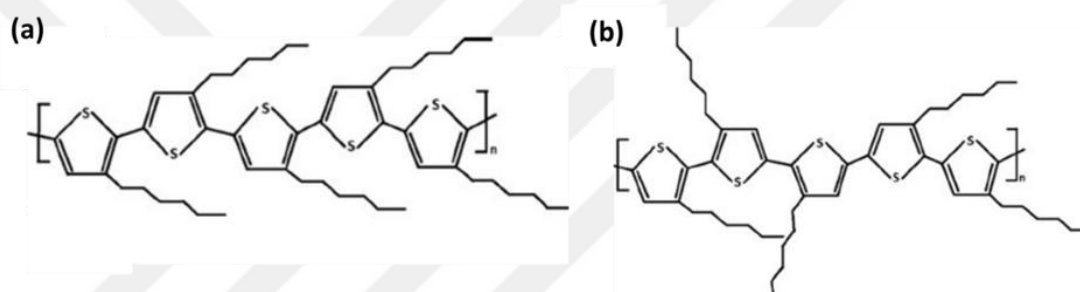


Figure 2.9 : The chain structure of (a) regioregular and (b) regiorandom P3HT.

Alkyl substituents in the 3 position of thiophene ring provide better solution processability and thin film forming capability [60]. By lipophilic interactions between the alkyl chains, these linear alkyl chains of appropriate length (usually 6–9 carbons) indirectly contribute to enhancing the long range order in the polymer. By placing an electronically inert substituent at the 3-position of the thiophene ring, steric hindrance to planarity may be used to significantly alter the effective conjugation length and therefore the band gap of polythiophenes. Thus, tuning of color states is strongly dependent to the relative positions of alkyl groups of thiophene backbone.

The majority of conducting conjugated polymers are affected by visible light and the transmitted wavelength is within the range of visible spectrum. When the molecule with sufficient energy absorbs the light, an electron moves from HOMO to LUMO level. The electron transition from HOMO to LUMO determines the optical properties of neutral conjugated polymers. The usual observation for the $\pi \rightarrow \pi^*$ transition of doped conjugate polymers is the red shift or blue shift. Red shift indicates the higher wavelengths because of extended conjugation by doping, whereas blue shift indicates

lower wavelengths because of the decreased conjugation. Optical characteristics of the polymer are considerably altered by these inter-gap transitions and cause strong color change. Since the absorption spectrum is dominated by strong $\pi \rightarrow \pi^*$ transitions in the visible region, some conjugated polymers with a low energy band gap can exhibit great transparency in the visible region after oxidation process. The change in optical absorption spectra of P3HT through ClO_4^- doping is given in Figure 2.10 [61].

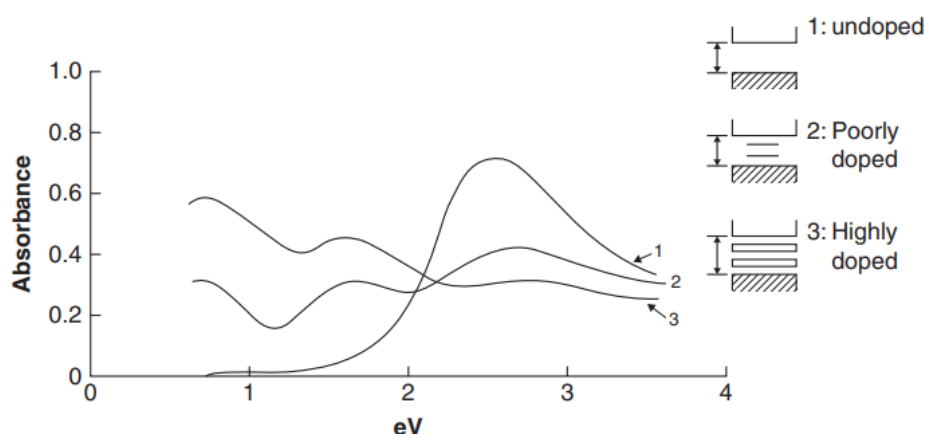


Figure 2.10 : The optical absorption spectra change of P3HT through ClO_4^- doping depending on the doping level.

The optical appearance of P3HT films can strongly be affected by molecular weight and packing. Not only crystallinity, conjugation length and inter-chain interactions also change the optical properties and charge carrier mobility. The extrinsic nature of charge separation mechanism of P3HT requires a contact between amorphous and crystalline domains in order to promote exciton dissociation [62], [63], [64]. In P3HT films, increased crystalline order could increase the exciton diffusion length. Several studies show that π -stacking affects the line shape of absorbance and emission [65], [66]. When P3HT is deposited from solutions onto a substrate, color of the thin film can change from orange to purple as solvent is evaporated. The absorption difference in the visible region depends on the solvent type, evaporation time and temperature, molecular weight, and crystallinity degree of P3HT film. When the thin film of P3HT is heated up to $\approx 200^\circ\text{C}$, the color of the film can change in the range of red – yellow depending on the molecular weight of P3HT. For a P3HT thin film, characteristic absorption bands generally appear in the range of 400 – 700 nm.

3. ORGANIC FIELD EFFECT TRANSISTORS (OFETs)

Compared to the Metal Oxide Semiconductor Field Effect Transistors (MOSFET), Organic Field Effect Transistors (OFETs) has drawn great attention past few decades due to their advantages such as low-cost, applicability on flexible substrates, large scale fabrication and low operation voltages. Although the working principle of OFETs and MOSFETs are almost similar, there are several major differences. One of the major differences is that OFET usually works in accumulation mode whereas MOSFET typically works in inversion mode. In MOSFET technology, there are three different regions depending on the gate voltage; accumulation, depletion and inversion. However, in OFET technology, only accumulation and inversion regions constitute the operating characteristics of transistors. In this chapter, the main working principle and key parameters of OFETs will be described in detail.

3.1 Architecture and components of OFETs

Organic field effect transistor consist of a semiconducting layer, source/drain/gate electrodes and an insulating dielectric layer. The distance between source and drain electrodes is named channel. When the voltage is applied between the source and the gate electrodes, an equal amount of charge of opposite sign is accumulated between insulator–semiconductor interfaces. By tuning the gate voltage, the charge density in the semiconductor channel can be modulated over a wide range. As such, device behaves like a switch and it constitutes the elemental backbone of logic circuits.

The semiconductors used in organic field effect transistors are usually intrinsic organic semiconductors, which makes the charge injection possible without intentional doping. If the Fermi level of electrode materials is corresponded with the energy band levels of semiconductor, charges could be injected from electrode to channel under an applied bias. Hence, the semiconductors which have higher HOMO energies show p-type device operation whilst the semiconductors which have lower LUMO energies show n-type device operation. Therefore, source and drain electrodes are separated from each other by the use of these p-type or n-type semiconductors.

According to the usage of device, there are four possible architectures for OFETs as given in Figure 3.1 [67]. Amongst these architectures, the most commonly used one is bottom gate-top contact configuration due to the ease of electrical field control in the channel. In the bottom gate-bottom contact configuration, a channel is easily generated at the interface between semiconductor and insulator. Also, another difference between transistor configurations is the amount of trap levels formed from insulator/semiconductor and electrode/semiconductor interfaces.

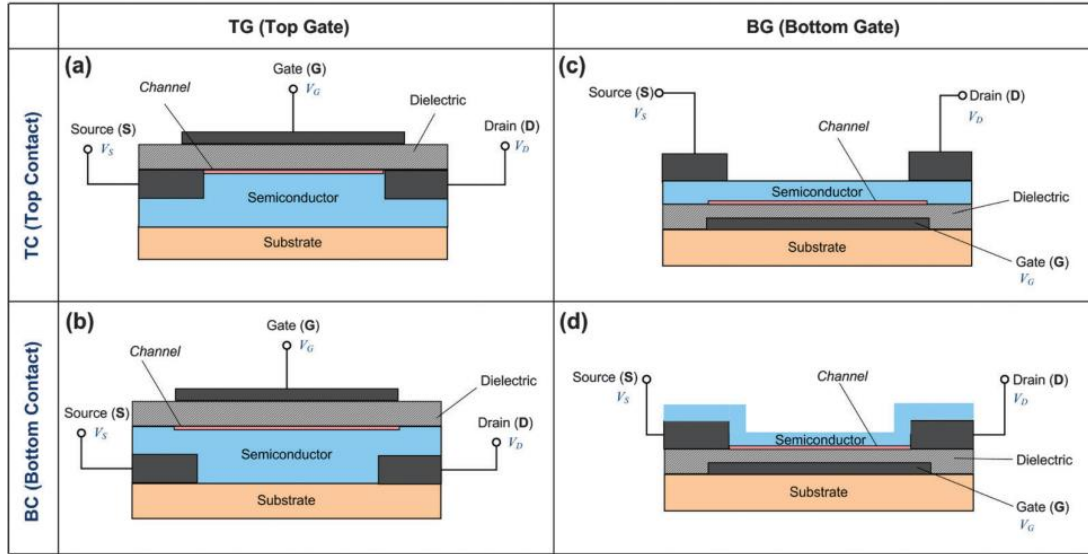


Figure 3.1 : Schematic cross-section configurations of OFETs. (a) Top gate-top contact, (b) top gate-bottom contact, (c) bottom gate-bottom contact, (d) bottom gate-bottom contact architectures.

- Substrate

The wide variety of substrates can be used in OFET fabrication such as glass, Si/SiO₂, polyethylene terephthalate (PET), polycarbonate (PC) or paper. It is worth noting that substrate materials should be smooth and clean since it is directly in contact with organic semiconductor. Furthermore, substrate should also be mechanically strength and chemically durable [68].

- Source/Drain/Gate electrodes

Metals with high work function such as gold (Au), copper (Cu), aluminum (Al) [69], [70], transparent electrodes such as indium tin oxide (ITO), graphene and carbon nanotubes [71] are frequently used as electrode materials.

– Semiconductor

The charge transport in the organic field effect transistors are based on the polymeric materials. Conjugated polymers including poly-alkyl thiophenes, small molecules including pentacene, tetracene, rubrene, TIPS-pentacene and carbon derivatives including carbon nanotubes and graphene are commonly used as active channel materials [72], [73], [74].

- Gate insulator

The gate insulator act as a barrier to the opposite charges on the gate and in the channel. The gate insulator layer should have a high dielectric constant (ϵ) to prevent current leakage and reduce the trap densities at the semiconductor/dielectric interface. Although high capacitance oxide materials (e.g. SiO_2 , Al_2O_3 , TiO_2) were preferred in the early years of OFET studies, insulating and mechanically resistant polymers such as polyimide, polyvinylphenol (PVP), poly(methylmethacrylate) (PMMA), poly(vinyl alcohol) (PVA) and Cytop have been started to draw attention in recent years [75].

3.2 Working Principle and Operation of OFETs

Organic field effect transistors are based on polymer semiconductors and operate by injecting free charge carriers (electron or hole) from electrodes to channel depending on the applied gate voltage. The channel dimensions are described with the width (W) of the source and drain electrodes and the distance (L) between them (Figure 3.2) [76]. The voltage difference between the source-gate electrodes is defined as V_{GS} , and the voltage difference between the drain-source is defined as V_{DS} . To operate the device, voltage is applied to the gate and drain electrodes when the source electrode is grounded. If negative gate voltage applies ($V_{GS} < 0\text{V}$), positive charges (holes) accumulate at the semiconductor/gate insulator interface whereas negative charges (electrons) accumulate at the interface under positive gate voltage ($V_{GS} > 0\text{V}$).

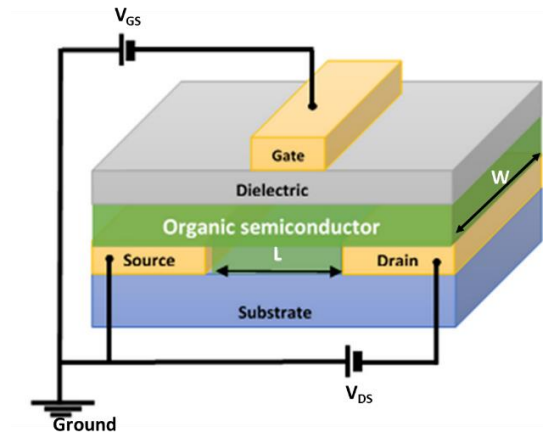


Figure 3.2 : A schematic representation of an OFET structure.

The type of conduction depends on the intrinsic properties of semiconductor and combination of contact materials. Although a few n-type organic semiconductors can be found in literature, organic semiconductors are mostly p-type materials. Hence, the most commonly observed operation mode in OFETs is p-type conductivity. A schematic representation of a p-type and n-type OFETs under certain bias is given in Figure 3.3. During the operation in case $V_{GS} < 0V$ and $V_{DS} < 0V$, p-type channel is observed since the majority charge carriers are holes in organic semiconductor. On the other hand, in case $V_{GS} > 0V$ and $V_{DS} > 0V$, n-type channel is observed since the majority charge carriers are electrons in organic semiconductor [6].

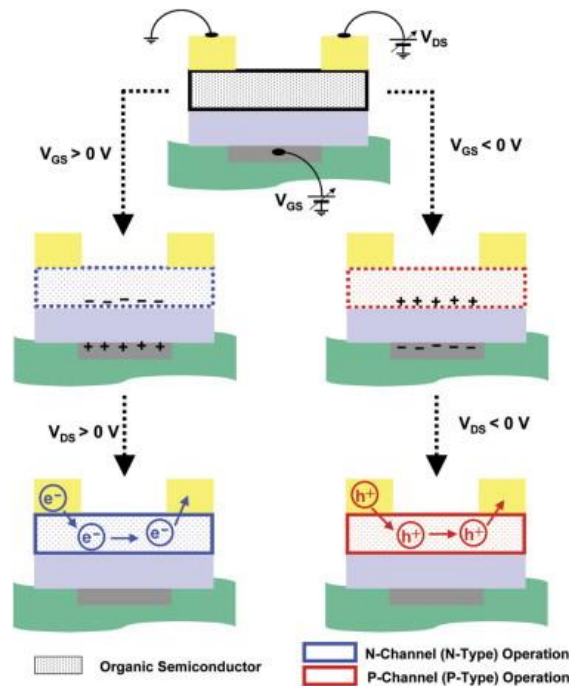


Figure 3.3 : A schematic representation of p-channel and n-channel operation modes in OFETs.

Considering the architecture of OFETs, electrode and organic semiconductor interface is crucial for operation. Since the metal electrodes are responsible for extraction or injection of charge carriers, it is preferred that HOMO (or LUMO) level of the semiconductor and the work function of electrode should match well for efficient charge transport [77].

If the interface between gate dielectric and semiconductor contains high trap densities, accumulated charge carriers must fill the traps before they can contribute to the charge transport. This slows down the field effect mobility. Depending on the band gap and trap density, field effect mobility can become gate voltage dependent. The semiconductor-gate dielectric interface is of critical importance, as most of the accumulated charges are localized in the first 10-15 nm region of the semiconductor. Since the electrical conductivity occurs at the very first nanometers of gate dielectric and organic semiconductor, surface roughness of the gate dielectric, molecular ordering of the semiconductor and trap densities at the interface play critical roles for the transistor operation and device parameters. In some cases, low wettability may be observed between the gate dielectric and organic semiconductor. This indicates that organic semiconductor cannot adequately spread across the gate dielectric since the surface energy between the organic semiconductor and the gate dielectric is not appropriate. To overcome this surface energy mismatch and improve the interface quality by passivating charge traps, a few nanometer thick self-assembled monolayers (HMDS, APTES...etc) are coated on the gate dielectric right before the deposition of organic semiconductor [78].

3.3 Key Parameters of OFETs

In order to operate the device as a transistor, two types of current graph emerges depending on the applied voltage; transfer characteristics and output characteristics (Figure 3.4 and Figure 3.5). By keeping the gate voltage (V_{GS}) constant, the V_{DS} voltage is swept and output curve is obtained. By keeping the voltage between source and drain (V_{DS}) constant, the V_{GS} voltage is swept and transfer characteristics were obtained.

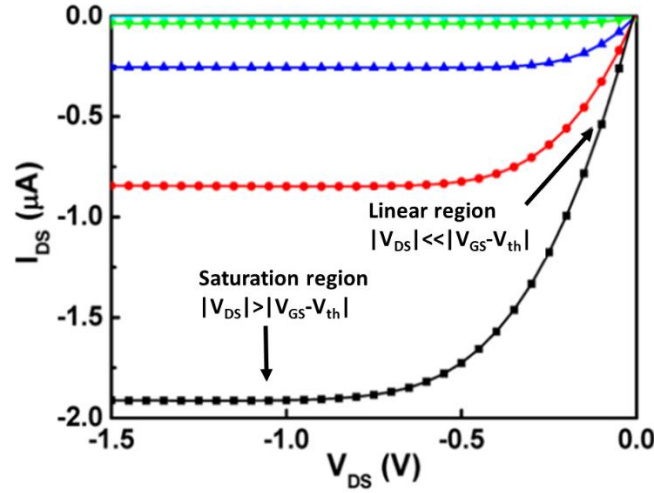


Figure 3.4 : Typical output characteristics of p-type thin film transistors.

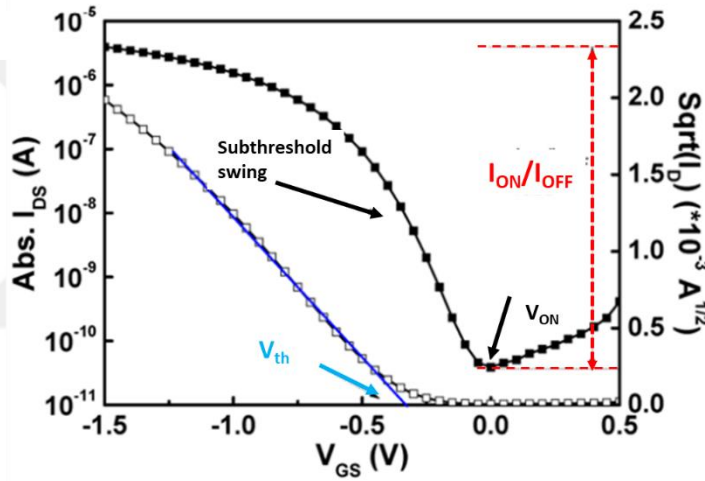


Figure 3.5 : Typical transfer characteristics of p-type thin film transistors.

As can be seen in Figure 3.4, I_{DS} current linearly increase depending on the V_{DS} in “linear region”. After exceeding a necessary V_{DS} voltage, I_{DS} current becomes independent of the drain bias and is almost constant. This region is called “saturation region”. At low drain voltages, a linear current region is seen as the gate and drain voltage magnitudes increase ($V_{DS} < V_{GS}$). When the drain voltage exceeds the gate voltage, saturation region is observed. The linear and saturation current can be calculated as given in equation (3.1) and (3.2) [68].

$$I_{DS_{linear}} = \frac{W}{L} \mu C_i (V_{GS} - V_{TH}) V_{DS} \quad (3.1)$$

$$I_{DS_{satur.}} = \frac{W}{2L} \mu C_i (V_{GS} - V_{TH})^2 \quad (3.2)$$

In equation (3.1) and (3.2), W is channel width, L is channel length, C_i is gate insulator capacitance, μ is mobility and V_{th} is threshold voltage. Device parameters such as on-off current ratio (I_{ON}/I_{OFF}), threshold voltage (V_{th}) and mobility (μ) can be extracted from the transfer curve of the OFET. For the good transistor performance; high mobility, large on-off current ratio and low threshold voltage is desired.

3.3.1 Field effect mobility (μ_{FET})

Field effect mobility (μ_{FET}) is a quantity of average charge carriers under a certain electrical field and is typically expressed in $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The field effect mobility can be calculated from the transfer curve (the slope of $\sqrt{I_{DS}}$ vs. V_{GS} curve measured in saturation regime). The drain current is linear with the source-gate voltage in the linear regime, which occurs when the source-drain voltage is much less than the source-gate voltage ($V_{DS} < V_{GS}$). However, drain current varies as the square root of the source-gate voltage when the source-drain voltage ($V_{DS} > V_{GS}$) is greater than the source-gate voltage. Hence, the field effect mobility can be estimated from the slope of I_{DS} vs. V_{GS} in the linear and saturation regime by using equation (3.3) and (3.4).

$$\mu_{linear} = \frac{2L}{WC_i V_{DS}} \frac{\partial I_{DS}}{\partial V_{GS}} \quad (3.3)$$

$$\mu_{saturation} = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_{DS}}}{\partial V_{GS}} \right)^2 \quad (3.4)$$

Herein, L is channel length, W is channel width, C_i is gate insulator capacitance, V_{GS} is gate-source voltage and I_{DS} is drain-source current.

3.3.2 Threshold voltage (V_{th})

Threshold voltage is the minimum voltage that must be applied accumulate charge carriers at the organic semiconductor and gate insulator interface. In other words, threshold voltage is the gate voltage at which the device starts to turn on. It is desired that threshold voltage is close to zero to provide better switching performance. It depends not only on the semiconductor and gate insulator, but also impurity and interface properties. Threshold voltage can be easily determined from the transfer

curve shown in Figure 3.5 by linear extrapolation. Typically, the transfer curve is plotted on a semi-logarithmic scale. The threshold voltage serves as a transition point, between an exponentially changing domain and a region characterized by linear drain current.

If the organic semiconductors have disorders or impurities, they are mostly suffer from high trap densities which result the high threshold voltages. Doping might be a good option to reduce the threshold voltage by incorporating extremely small amounts of dopants into the channel. Thus, the deep traps need to be filled in order to raise the Fermi level and build up an active channel. However, if the doping concentration is higher than favored, device works in depletion mode, which means opposite polarity gate voltages are needed to apply to turn off the channel [79].

3.3.3 On-off current ratio (I_{ON}/I_{OFF})

The on-off current ratio of a transistor is the comparison of the drain current in the on-state to the off-state. In order to obtain higher on-off current ratios, the geometry of the transistor can be optimized by adjusting the width (W) to length (L) ratio. When the gate voltage is lower than the threshold voltage, the off-current (I_{OFF}) corresponds to the drain current. The off-current is caused by leakage currents through the oxide and conduction due to charge carriers that are already stored inside the semiconductor.

The mobility of the transistor or dielectric constant of gate insulator must be as possible as high in order to obtain high on-state current (I_{ON}). On the other hand, in order to have low I_{OFF} current, channel conductivity of the organic semiconductor must be low and the gate insulator must not allow current leakages. Thus, the current flowing through the channel can be minimized when $V_{GS}=0V$. The on-off current ratio is determined by dividing the maximum current by the minimum current from I_{DS} vs. V_{DS} graph plotted on a logarithmic scale. High on-state current basically depends on the charge traps, capacitance of the gate dielectric and mobility of a transistor.

4. ELECTROCHROMIC DEVICES (ECDs)

Chromogenic materials are materials which can change their colors under an external stimulus such as temperature, voltage or light. If a material changes its optical properties with redox reactions (ion insertion/extraction) under a certain potential, it is called “electrochromic”. Electrochromic materials generally switch between two colored states or between one colored and one bleached states. Therefore, these materials are good candidates for sunglasses, smart windows and display technologies.

Electrochromic devices can be operated by transmission or reflection. Transmissive electrochromic devices are commonly used as smart windows in buildings. When controlling the light transmittance between bleach and colored states, heat must be dissipated in order to completely block sunlight. The emergence of some companies such as ChromoGenics, Heliotrope, Fraunhofer, View and SageGlass.. etc has continued to breathe new life into the heat and light controlled smart window industry. Moreover, for use in cars at night, self-darkening electrochromic mirrors prevent the lights of oncoming vehicles from blinding drivers or causing reflections in their side mirrors. For instance, Night-Vision System by Gentex is the best known example of reflective electrochromic devices.

Since electrochromic materials can change their optical behavior not only in visible region but also in NIR and microwave region, they can be used in defense or spacecraft applications, as well [80]. In spite of the fact that electrochromic materials and their device applications have been well studied by several scientists such as Deb [81], [82], [83] and Mortimer [84],[85], they are still highly attractive for electrochromic energy storage applications.

In order to understand better what an electrochromic device is, it must be first discussed the architecture of an electrochromic device. A typical electrochromic device consists of transparent conductive material (TCO), an electrochromic layer, an ion storage layer and an ion transport layer (electrolyte). The ion storage layer and the electrochromic layer are deposited on TCO coated glass substrates and laminated with an electrolyte in between (Figure 4.1). The conductive substrate coated on glass or

flexible plastic is being connecting to a power source. The electrochromic devices usually contain two conducting substrates as the working and counter electrodes. The electrochromic material is usually coated on either of the electrodes and the device is completed with the second conductive substrate. The second conductive substrate can be coated with an ion storage layer to enhance the switching speed and life cycle.

Under an external potential, electrochemical reactions in the electrochromic device result in a change in transmission (or absorption). If it is explained the working principle of the device through Figure 4.1, initially the device is transparent. After applying a negative voltage (or positive voltage) to the electrochromic layer side, electrochromic material is reduced (or oxidized) by injection of ions hidden in the ion storage layer and electrochromic layer becomes colored (or bleached).

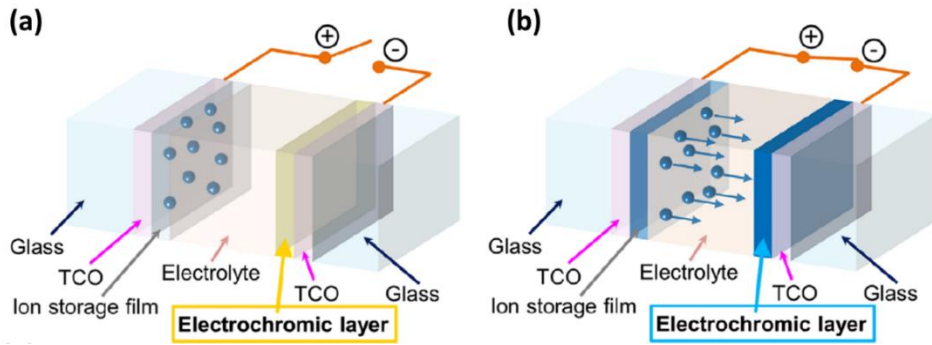
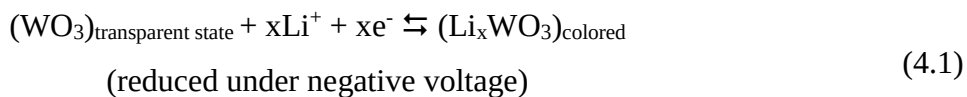
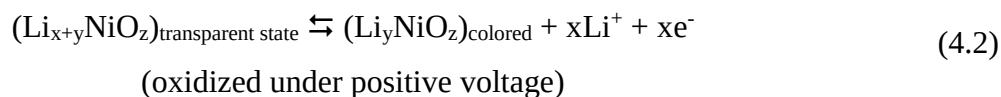


Figure 4.1 : Schematic drawing of an electrochromic device in (a) transparent (bleached) and (b) colored state.

An example of a dual electrochromic device configuration can be given as; glass / ITO / WO_3 (electrochromic layer) / electrolyte (LiClO_4) / NiO_x (ion storage layer) / ITO / glass. When a positive voltage is applied to the ion storage layer which is transparent in neutral state, ions are extracted from the film and it turns into colored by oxidation. At the same time, when the negative voltage is applied to the electrochromic layer which is transparent in neutral state, ions are injected into the film and it turns into colored by reduction. Therefore, one of the electrodes is oxidized while the other is simultaneously reduced, and the device appears either colored or transparent. In such a device structure, reversible colored and bleached states are observed by following equations (4.1) and (4.2).





4.1 Components of ECDs

The interface properties play crucial role in how efficiently charges are moved in the device. Hence, the material selection is very important to determine the device performance.

4.1.1 Conductive substrates

The conductive material is usually coated either on a rigid substrate or a flexible substrate. Rigid substrates for electrochromic devices usually include glass, quartz and polycarbonate. Flexible materials can be usually polymers including poly(ethylene terephthalate) (PET), polyethylene mine (PEI), polyimide (PI), polypropylene (PP), polycarbonate (PC), polyurethane(PU), and poly(dimethyl siloxane) (PDMS) [86], [87]. Indium tin oxide (ITO) and fluorine doped tin oxide (FTO) have been widely used for various electrochromic devices due to the low resistivity and high transparency. Also in last decades, graphene has received extensive research attention due to the high electrical conductivity, good optical properties, flexibility, and chemical durability [88], [89].

4.1.2 Electrochromic layers

Two major types of materials were reported to show electrochromic properties;

I. Inorganic materials

- Transition metal oxides (WO_3 , MoO_3 , TiO_2 , Ta_2O_5 , Nb_2O_5 , NiO , IrO_2 , Cr_2O_5 , MnO_2 , FeO_2 , and Co_3O_4) [90], [91], [92].
- Coordination complexes (Prussian blue, Co(II) and Zn(II) complexes) [93], [94]

II. Organic materials

- Conducting polymers (polyanilines, polythiophenes, polyselenophenes) [95], [96], [97], [53]
- Small molecules (viologens, aromatic diesters) [98], [99]
- Dyes (aromatic quinones and aromatic imides derivatives) [100], [101], [102]

Amongst these materials, organic electronic materials have drawn great attention due to the advantages of ease of structural modification, simple processability, low cost and adjustable coloration. However, inorganic materials are more stable in ambient conditions compared that of organic materials. From this point of view, organic and inorganic materials can be combined to fabricate hybrid structures which show both superior properties and stability. The coloration properties and efficiencies of some electrochromic materials from current studies in literature are given in Table 4.1.



Table 4.1 : The coloration properties and efficiencies of some electrochromic materials.

Color (reduced→oxidized)	Electrochromic material	$\lambda_{\max}$ (nm)	Coloration efficiency (cm^2C^{-1})	Coloration	Reference
Colorless→magenta	Viologen	517	103	Cathodic	[103]
Magenta→colorless	P3HT	460	230	Anodic	[104]
Deep blue→Colorless	PEDOT	620	530	Cathodic	[105]
Transparent Yellow→green	PANI	800	142	Anodic	[106]
Colorless→brown/grey	NiO	550	~115	Anodic	[107]
Colorless→blue	WO ₃	550	67	Cathodic	[108]
Colorless→brownish	MoO ₃	600	149	Cathodic	[109]
Colorless→blue	Nb ₂ O ₅	800	86	Cathodic	[110]
Colorless→grey	TiO ₂	550	56	Cathodic	[111]
Yellow→grey	V ₂ O ₅	700	8	Anodic/cathodic	[112]

Passerini [113] was first reported the electrochromic redox mechanism of NiO and was reported that it switches from transparent to brown color under oxidation potential. Although the electrochemical reactions of V_2O_5 (vanadium pentaoxide) and TiO_2 is highly reversible, coloration is not very strong. Therefore, V_2O_5 and TiO_2 are mostly used as ion storage layers in complementary electrochromic devices or batteries.

4.1.3 Electrolyte

In order to separate working and counter electrodes to avoid electrical contact, electrolyte layer is inserted between these two electrodes, which only allows the movement of ions enabling color switching. The materials to be used as ion conductive layer should have high optical transmittance and ion conductivity, but low electrical conductivity. Electrolyte materials can be classified as liquid electrolytes and solid/semi-solid (gel) electrolytes. Liquid electrolytes are generally prepared by dissolving Lithium salts (such as $LiClO_4$, $LiBF_4$) in appropriate organic solvents (such as acetonitrile or propylene carbonate). The small diameter of the metal ions (K^+ , Na^+ , H^+ , Li^+) to be formed in this layer allow the ions to move easily under the electric field. Although liquid electrolytes provide fast response due to the high mobility of ions in low viscous liquids, chemical stability and leakage can be challenging during the device operation. Therefore, many researches have attempted using plasticized gel polymer electrolytes as an alternative to liquid electrolytes. Gel polymer electrolytes compose of ionic conductive salts, host polymers, plasticizer polymers and organic solvents. Host polymer matrixes can be polyethylene glycol (PEG), polyvinylidene fluoride (PVDF), polyethylene oxide (PEO), polymethyl methacrylate (PMMA), polyvinyl alcohol (PVA), polyesters, polyurethanes, poly acrylonitrile (PANI), boronate esters and so on [114], [115], [116], [117], [118], [119]. The plasticizer polymer such as propylene carbonate (PC) or ethylene carbonate (EC) are responsible for increasing viscosity of solvent and dissociate ion aggregates leading to higher ionic conductivities of the electrolytes. Polymer electrolytes have superior mechanical and thermal stabilities within the applied voltage range. Due to the fact that they are lightweight, compact, easy processable and integrable to large-scale area for industrial applications, they are considered as the most promising materials in electrochromic and energy storage applications.

4.1.4 Ion storage layers

Ion storage layer actually keeps the ions that will cause the coloration in the electrochromic layer. When voltage is applied, the ions stored in the ion storage layer are moved to the electrochromic layer through the ion conductive layer. This movement is reversible under positive and negative bias. Ion storage layer itself could be electrochromic, as well. In this case, the electrochromic material used in the device must have opposite coloration properties with the electrochromic material on the other side of the electrolyte, which is called counter electrode. The main coloration mechanism here is ion exchange. One electrochromic layer is colored during ion insertion, while the other one is colored during ion extraction.

4.2 Chromogenic Materials Used in Thesis

4.2.1 Chromism of P3HT

P3HT has a good hole transporting and electron-donating ability. Besides, due to its reversible oxidation-reduction mechanism and significant absorption in both UV and NIR region, it has been studied for anodically coloring electrochromic applications.

When the electrical bias applied to the electrochromic polymer layer, the polymer can be either oxidized or reduced, leading a change in light absorbing properties. As can be seen in Figure 4.2, in the oxidation state, new charge carriers and lower energy intraband transitions are generated. As the oxidation level increases, HOMO-LUMO transition of the pristine P3HT and polaron absorption is fully depleted and becomes conducting state. These charge carriers are called polarons (partially oxidized) and bipolarons (fully oxidized). The changes in the electronic states under oxidation reduces the band gap of the polymer, so that the color and transmission of the polymer can be easily altered by applied voltage.

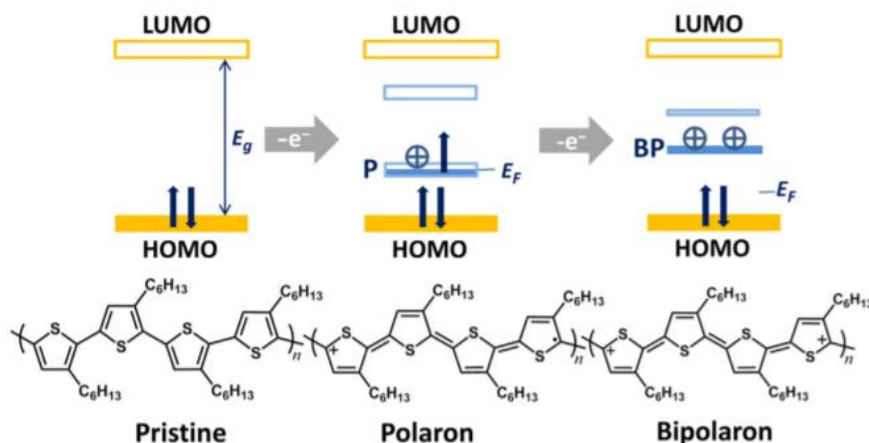
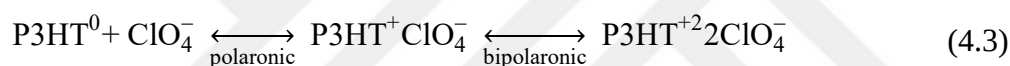


Figure 4.2 : The molecular structure of P3HT in the neutral state and positively charged state depending on the doping level.

Considering this doping mechanism, electrochromic behavior of P3HT can be explained through the equation (4.3). This reaction is reversible for electrochemical redox reactions.



When the positive potential is applied between the electrodes in a half cell containing LiClO_4 electrolyte solution, ClO_4^- counter anions migrate through the P3HT film. A layer is generated at the electrolyte/P3HT film interface, which is called Helmholtz double layer. Helmholtz layer consists of the accumulation of negative charge carriers in the P3HT film and positive charge carriers in the electrolyte, resulting in a double layer capacitance at the interface. Thus, ClO_4^- counter anions act as dopant for P3HT and oxidize (or reduce) P3HT film depending on the voltage applied.

It is also known that polyalkylthiophenes such as P3HT show thermochromic properties. P3HT absorbs light within the visible spectrum, resulting in a colored appearance. However, alteration of the conjugation length of the π -electron system within the polymer backbone or chain conformation with temperature might lead to a shift in the absorption wavelength. As a result, the polymer changes its color reversibly under different temperatures, which is called thermochromism. Even minor adjustments in the conformational structure can produce noticeable color variations, particularly if they impact the planarity of the polymer chain. Thermochromic behavior of P3HT will be explained more detailed in Chapter 6.4.

4.2.2 Chromism of WO₃

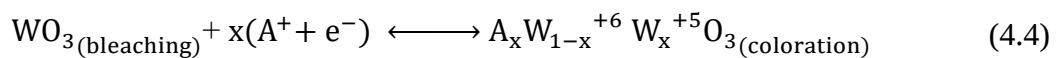
WO₃ is an n-type semiconductor with a large band gap in the range of 2.6–3.2 eV [120]. WO₃ films can be deposited by several techniques such as sputtering, thermal evaporation, pulsed laser deposition, chemical vapor deposition and wet chemistry. At the temperatures below 300°C, WO₃ is transparent and has amorphous structure. Above 300°C, it starts to crystalline and shows different crystalline phases depending on the heat treatment. As the temperature increases, crystalline phases of WO₃ form in the sequence of monoclinic, orthorhombic and hexagonal [121]. The crystalline phases of the WO₃ is given in Figure 4.3 [122].



Figure 4.3 : (a) Monoclinic, (b) orthorhombic and (c) hexagonal crystalline phases of WO₃.

Tungsten oxygen compounds can exhibit different electronic states such as W²⁺, W³⁺, W⁴⁺, W⁵⁺ and W⁶⁺. The conductivity mechanism of tungsten oxide is mainly driven by the oxygen vacancies in the material itself. Oxygen vacancies attract electrons due to the ionic character of the material. Since the vacancies are localized, local energy states are created for the electrons. These are often called "trap states" because the electron is trapped in the vacuum field due to its low energy. Hence, trap states are also called "band gap states" and are represented between the valence and conduction band on the band diagram. These oxygen vacancies may cause the formation of non-stoichiometric WO_{3-x} compound, which leads n-type semi-conductivity [123], [124].

Besides, tungsten oxide is one of the most studied cathodic electrochromic materials due to its great chemical stability, quick switching time and broad optical modulation range. The basic coloration mechanism of WO₃ is given in equation (4.4).



In equation (4.4), x is the number of inserted ions and A is the cations (Li⁺, H⁺, Na⁺) depending on the electrolyte. Although the WO₃ thin films are transparent in visible

region, it turns out to blue color during H^+ and Li^+ ion insertion. During the ion insertion, Fermi level band gets closer to the higher energy levels in the conduction band, giving rise in optical absorption. On the other hand, during ion extraction, Fermi level moves to lower energy levels and the film become transparent again. The coloration mechanism is reversible and illustrated in Figure 4.4.

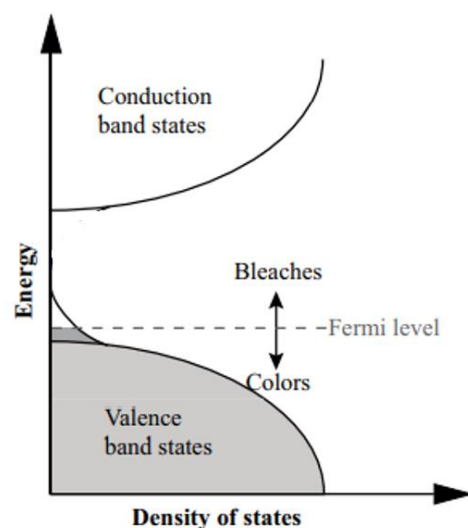


Figure 4.4 : Schematic representation of WO_3 energy level diagram.

Even though there is almost no studies which propose a certain mechanism, a few studies indicate that WO_3 exhibits reversible color change depending on the temperature. Ferro and co-workers reported that [125] WO_3 undergoes a transition from light green color at room temperature to a deep orange color at $500^\circ C$. Kumar and Mohanta [126] prepared nano-scale WO_3 powders at 5.5 pH. It was shown that monoclinic phase powders change their color from white to light-brown in $4^\circ C$ - $53^\circ C$ temperature range. It was also claimed that as the temperature changes, the transitions between crystalline phases leads to a change in color.

4.3 Key Parameters of ECDs

4.3.1 Optical contrast

Optical contrast is commonly defined as the percent transmittance difference ($\Delta T\%$) between the fully oxidized and fully reduced states according to the equation (4.5). Optical contrast is determined at the maximum wavelength (λ_{max}) where the difference in transmittance (or absorbance) between redox states is highest, which is often in the visible (UV) or near infrared (NIR) area.

$$\Delta T\% = T_{ox.} - T_{red.} \quad (4.5)$$

4.3.2 Coloration efficiency

Coloration efficiency (η) is calculated by dividing the optical density by the amount of inserted/ejected charges in per unit area with the help of equation (4.6) and the unit is defined as cm^2C^{-1} . In the equation (4.6), where $T_{ox.}$ and $T_{red.}$ is the transparency in oxidized and reduced states, Q is inserted or ejected charges in Coulomb and A is active area of the device in cm^2 . For the high performance electrochromic devices, high coloration efficiency is desired for higher energy efficiency and lower power consumption.

$$\eta = \frac{\log \frac{T_{ox.}}{T_{red.}}}{\frac{Q}{A}} \quad (4.6)$$

4.3.3 Switching response time

The switching time determines how rapid an applied voltage causes a change between the redox states. There are two unique processes taking place in the color change for colored to bleached state or vice versa. The coloration time (τ_c) describes the time needed to reach 95% of the electrochromic device's colored state. Similarly, the bleach time (τ_b) describes the time needed to reach the time its bleached state. While the human eye cannot see the remaining 5% of color shift, a value of 95% is commonly evaluated. The switching response time of an electrochromic material depends on the film homogeneity, film thickness, ion connectivity of the electrolyte, ion diffusion between electrolyte and electrochromic film and applied potential.

4.3.4 Life cycling

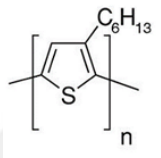
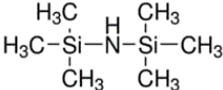
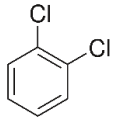
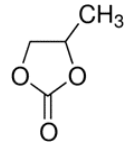
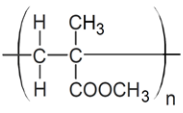
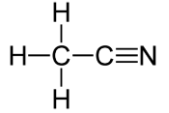
The device stability is determined through the way it preserves its electrochromic performance when subjected to repeated redox cycling and doping-undoping cycles. In order to determine device stability, the electrochromic device is being subjected to long redox cycles and recorded the change in optical contrast until significant degradation occurs. This gives an approximation of its life cycling.



5. MATERIALS AND METHOD

5.1 Materials Used

Table 5.1 : Chemicals used in experiments for both transistor and electrochromic studies.

Material	Molecular structure	Supplier
Regio regular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT) ($M_w = 25000-45000$ g/mol)		Sigma Aldrich
Hexamethyldisilazane (HMDS)		Sigma Aldrich
Tungsten oxide powders (>99.9%, $M_w = 231.84$ g/mol, Sigma Aldrich)	WO ₃	Sigma Aldrich
1,2-Dichlorobenzene anhydrous		Sigma Aldrich
Propylene carbonate (PC) (%99, $M_w:102.09$ g/mol)		Sigma Aldrich
Lithium perchlorate (>95%, $M_w:106.39$ g/mol)	LiClO ₄	Sigma Aldrich
Polymethyl methacrylate (PMMA) (>99.9, $M_w:350000$ g/mol)		Sigma Aldrich
Acetonitrile (ACN) (>99.9, $M_w:41.05$ g/mol)		Sigma Aldrich
Ethanol ($M_w:46.07$ g/mol)	H ₃ C-CH ₂ -OH	Merck

5.2 Preparation of Pure and Hybrid Formulations of P3HT

In this study, the electrical and optical properties of P3HT films depending on the dopant concentrations were investigated. Therefore, WO₃ doped P3HT thin films and undoped P3HT thin films were aimed to produce. Various concentrations of WO₃ powders (0 wt%, 10 wt%, 30 wt%, 40 wt%, 50 wt%) were directly mixed with 10 mg P3HT and dissolved in 1 ml 1,2-dichlorobenzene solution by stirring overnight at 70°C with magnetic stirrer. Both undoped and doped solutions were investigated for OFET and electrochromic applications. Figure 5.1 shows the steps of thin film fabrication and Table 5.2 shows the summary of preparation recipe of coating solutions and nomenclature of the samples. It is worth to say that all experiments were done by using both commercial and synthesized WO₃ powders [127],[128] but no difference were determined between the results.

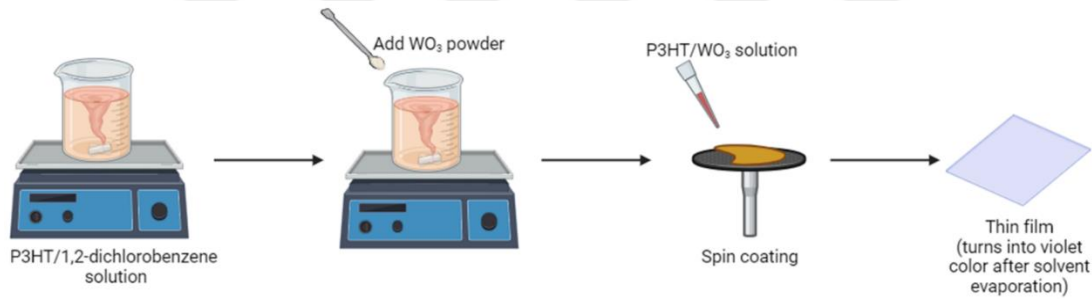


Figure 5.1 : Schematic illustration of solution preparation and thin film formation process steps.

Table 5.2 : Preparation recipe of coating solutions and nomenclature of the samples.

Sample Name	P3HT (mg)	1,2-dichlorobenzene (ml)	WO ₃ (mg)	Doping concentration (wt%)
PW0 (pure)	10	1	-	0
PW10	10	1	1.1	10
PW30	10	1	4.3	30
PW40	10	1	6.6	40
PW50	10	1	10	50

5.3 Applying Pristine and Hybrid Thin Films on OFET Test Chips

Pre-fabricated high density test chips with bottom-gate, bottom-contact (BGBC) structure were purchased from Ossila Ltd. Each test chip has 20 transistors, the highly p-doped silicon substrate with Au gate (G) electrode which covers the conductive edge of the substrate, the 300 nm-thick SiO₂ gate dielectric, and Au source (S) and drain

(D) electrodes. The channel length (L) and channel width (W) of each transistor are 30 μm and 1 mm, respectively. Figure 5.2 presents the top view of the test chip and the simplified schematic of a single BGBC transistor structure.

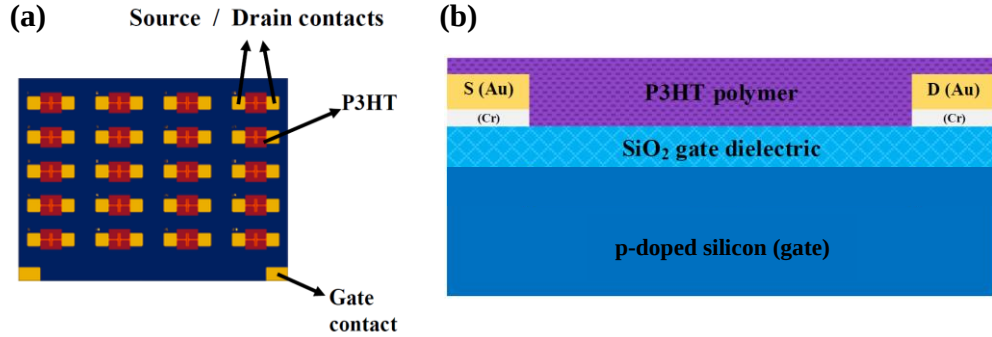


Figure 5.2 : (a) Top view of the pre-fabricated test chip [Image remains the copyright of Ossila Ltd. taken with permission from Ossila.com], (b) a simplified schematic drawing of BGBC structure.

Since the interface cleaning and film homogeneity of semiconducting layer is crucial for coating process and device performance, test chips have undergone a series of cleaning and surface treatment procedures. Since P3HT has a hydrophobic nature due to its long alkyl chain, it does not spread properly on the hydrophilic SiO₂ dielectric surface. In order to reduce surface energy at the interface and to increase wettability of P3HT solution on SiO₂, self-assembled monolayers such as alkyl silanes are coated between dielectric and semiconducting material. In this work, hexamethyl disilazane (HMDS) was spin coated on SiO₂ prior to P3HT thin film coating. Besides, HMDS treatment prevents the charge trap formation at the interface and strongly affects the device performance [129],[130]. At first, 10 min ultrasonic cleaning was performed with isopropyl alcohol and 1,2-dichlorobenzene, respectively. Then, test chips were dried with nitrogen gun and treated with Uv-ozone for 10 min to remove excess amount of organic residues. After Uv-ozone cleaning, to reduce surface energy at the interface between semiconducting layer and SiO₂, HMDS was spin coated at 4000 rpm for 40 s and annealed for 5 min at 100°C. Both pure P3HT and WO₃ doped hybrid solutions given in Table 1 were coated by spin coating over HMDS treated surface at 2500 rpm for 60 s and annealed for 30 min at 100°C. Source and drain contact pads and the rest of the chip surface except the channel region were gently wiped with a cotton swab to avoid short circuit. All solution preparation and coating process were carried out in inert glovebox ambient to avoid charge trap formation by oxygen and moisture.

5.4 Applying Pristine and Hybrid Thin Films on Single and Dual Electrochromic Devices

Indium–tin oxide (ITO) glass substrates coated by RF magnetron sputtering were supplied from Şişecam. ITO glass substrates ($\approx 17 \Omega/\text{sq}$) were sonicated in ethanol and deionized (DI) water for 10 min, respectively. Then, the ITO glass substrates were dried with a nitrogen gun. Both pure P3HT and WO_3 doped hybrid solutions given in Table 1 were coated by spin coating over the ITO coated glass substrates to be used as electrochromic layer. The optical performance of doped and pure thin films were investigated electrochemically in half cell configuration.

For solid state electrochromic device, WO_3 coated indium–tin oxide (ITO) glass substrates were supplied from Şişecam and used as counter electrode (or ion storage layer). Both pure P3HT and WO_3 doped P3HT solutions given in Table 1 were coated by spin coating at 2500 rpm for 60 s over the ITO coated glass substrates to be used as electrochromic layer. For the gel electrolyte preparation, 0.04 mg LiClO_4 was dissolved in 1 mg ACN. Then, 0.1 mg PMMA and 0.28 mg PC were added and stirred until a transparent gel is obtained. Dual electrochromic devices were fabricated with sandwich configuration are given in Figure 5.3.

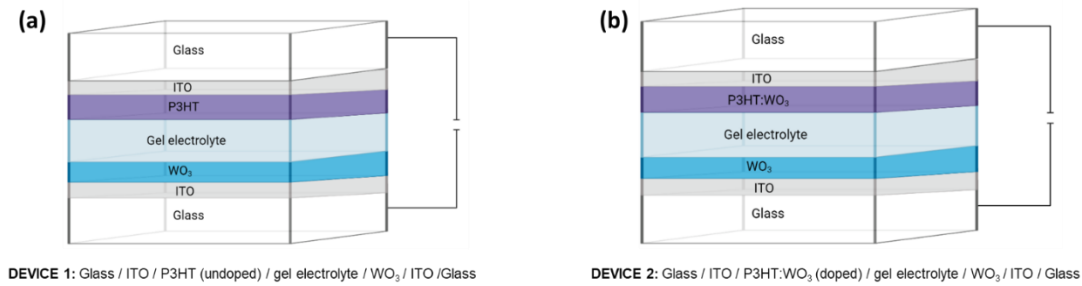


Figure 5.3 : Dual electrochromic devices were fabricated by using (a) undoped P3HT and (b) WO_3 doped P3HT electrochromic thin film layers.

5.5 Characterization Techniques Used

5.5.1 Surface and structural characterizations

When high energy electrons (2-30 keV) hit a solid surface, they can lead to various scattering events from the material. There are two types of electron scattering; elastic and inelastic scattering. In the event of an inelastic collision, the incident electron beam transfers some of its kinetic energy to the target atom. In the event of an elastic

collision, the kinetic energy of the incident electron beam does not change, only the velocity of the electron changes direction. Inelastic scattering includes secondary electrons, Auger electrons, characteristic and continuous x-rays whereas inelastic scattering includes backscattered electrons. Both elastic and inelastic scattering signals are used for quantitative analysis and imaging techniques. A schematic representation of electron-matter interaction is given in Figure 5.4 [131].

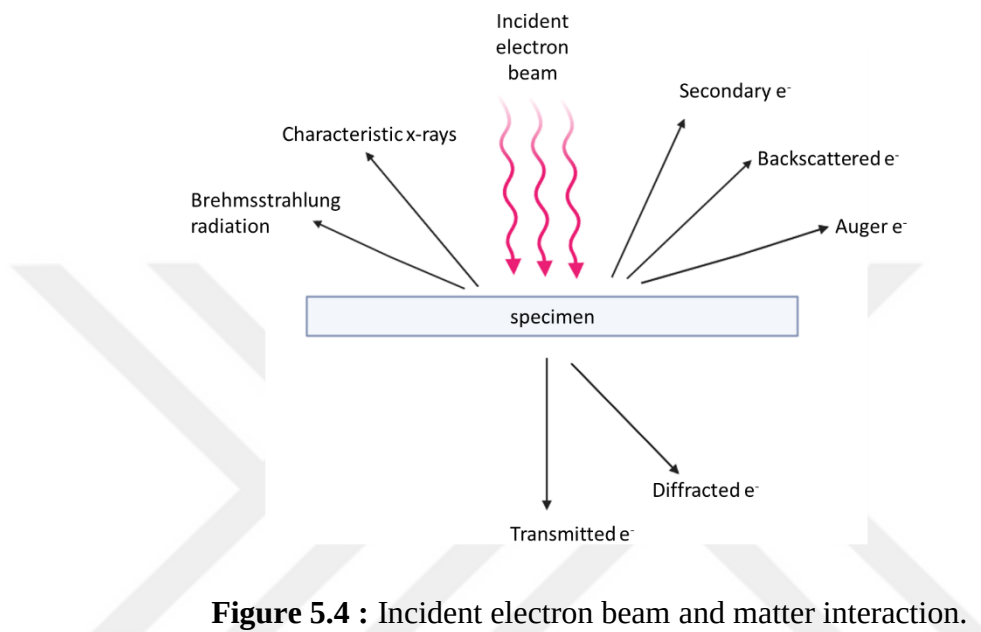


Figure 5.4 : Incident electron beam and matter interaction.

5.5.1.1 Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

Scanning Electron Microscopy (SEM) is an electron microscopy technique that can be used to image the surface by collecting secondary electrons' and backscattered electrons' signals while a focused beam of electrons scans the surface of a sample. The e-beam source used in this method can be W filament or LaB₆. In order for the accelerated electrons to reach the sample surface directly, the analysis is carried out in a high vacuum environment. The accelerated electron beam generates $\approx 50 \mu\text{m}$ spot size near the anode. However, this spot size is not enough to create a sharp image. Therefore, the spot size is reduced to $\approx 10 \text{ nm}$ by demagnifying with condenser and focused on the surface. When the focused electron beam interacts with the sample surface, x-rays, secondary electrons and backscattered electrons are emitted. X-rays and electrons are collected in separate detectors and converted into information.

Secondary electrons are electrons with energies $< 50 \text{ eV}$ and are scattered from the near surface region. The secondary electrons collected by the detector are accelerated in the

scintillation detector and converted into light. Thus, they provide a high-contrast and three-dimensional image of the surface. As well as depth resolution is dependent on acceleration voltage, horizontal resolution is generally in the range of 1-5 nm.

Backscattered electrons are electrons with energies >50 eV and are emitted from the deeper region (10-100 nm) as a result of elastic collisions. Since the heavy atoms produce more backscattered electrons, they create a brighter contrast. Backscattered electrons are mainly used for phase imaging and provides lower resolution compared to the secondary electron image.

With an accelerating voltage of about 5 kV, the wavelength of the incident electron beam is around 0.0173 nm, which is significantly less than the wavelength of light (≈ 400 nm). Therefore, SEM provides excellent image resolution compared to conventional optical microscopes.

While the surface is scanned and imaged with SEM, elemental analysis can be performed simultaneously. The characteristic x-rays scattered from the sample are collected in the EDX detector and separated according to their energies and elemental analysis is performed. Since He and H cannot produce x-rays, and elements with atomic number (Z) <5 produce very low x-ray signals, these elements cannot be quantified with EDX.

In this study, Hitachi SU 8220 model FEG-SEM was used to characterize the surface morphology of the thin films operated at 1.5 kV acceleration voltage. Atomic compositions of the thin films were calculated using EDX connected to SEM with Oxford software.

5.5.1.2 X-Ray Photoelectron Spectroscopy (XPS)

X-Ray photoelectron Spectroscopy is an advanced surface analysis technique, which is used to obtain chemical information about the surfaces of solid materials. In this method, an x-ray source excites the sample resulting the scattering of photoelectrons.

First, characteristic x-rays are produced by accelerated electrons from a target metal (Mg and Al) and sent to the specimen surface. As can be shown in Figure 5.5, the incident photon ($\text{MgK}\alpha$ or $\text{AlK}\alpha$) interacts with the electrons of inner shell orbitals ($1s2s2p$) in the specimen. If the energy of the incident x-ray is higher than the binding energy of the electrons, the sample ionizes by emitting an electron. This emitted

electron is called a photoelectron. Photoelectrons are separated due to their kinetic energies in analyzer. Since the kinetic energy of the incident beam and photoelectron is already known, binding energy can be calculated by using the equation (5.1). Herein, $h\nu$ indicates the kinetic energy of incident beam [132], [131].

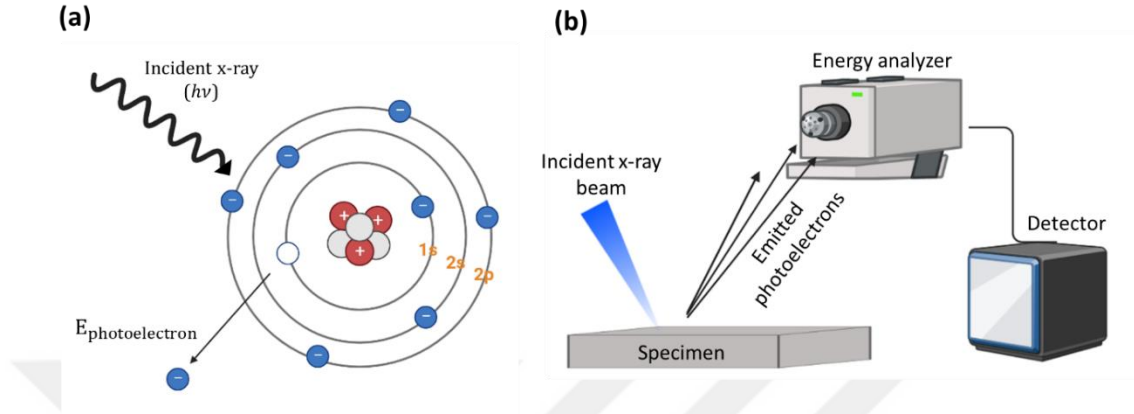


Figure 5.5 : A simple schematic representation of (a) x-ray and matter interaction and (b) working principle of XPS.

$$h\nu - E_{\text{binding}} = E_{\text{photoelectron}} \quad (5.1)$$

To be able to reach a photoelectron to the detector, it must escape from near surface region. Therefore, inelastic mean free path is crucial for XPS analysis. The 1s electrons emitted in the deeper region collide with other atoms in the sample until they reach the surface. Finally, they become trapped inside when they lost their energy. However, photoelectrons that have come as close as 10 nm to the surface can generate an XPS signal. Therefore, the XPS is quite surface sensitive technique.

The binding energy of an element strongly depends on its chemical environment. For example, the 1s energy of the carbon (C) atom cannot be the same as the 1s energy of the oxygen (O) atom. Similarly, the binding energy of the 1s electrons of the silver (Ag) element in the AgO compound and the binding energy of the 1s electrons of the Ag element in the Ag₂O compound cannot be the same. Therefore, the binding energy is fingerprint for an element and its chemical surroundings. Besides, quantitative analyzes can be performed with depth profiling. XPS can be effectively used to

determine elemental compositions and their electronic states, film thicknesses and thin film compositions.

5.5.1.3 X-Ray Diffraction (XRD)

X-ray diffraction is a non-destructive analysis method that enables the determination of the crystallographic properties of materials such as grain size, crystalline phases and orientations.

When an x-ray interacts with the material, it is diffracted in all directions by the atoms in the material. The diffraction waves can do either destructive or constructive interference. The resulting diffraction pattern also gives information about the reciprocal lattice structure of the material. Constructive interference is explained by Bragg's law as following equation (5.4). Diffraction occurs only at angles of incidence providing the Bragg's equation. As can be seen in Figure 5.6, the angle between the incident ray and the reflected ray is 2θ . The extra path taken between the two planes $|AB+CB|$ creates a phase difference between the two waves and causes different amplitudes [133].

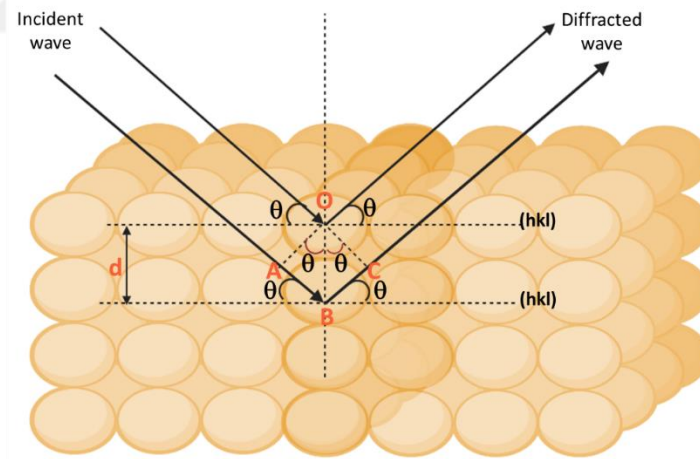


Figure 5.6 : The illustration of diffracted x-rays from crystalline planes of the material.

$$|AB|=|OB|.sin\theta \quad (5.2)$$

$$|CB|=|OB|.sin\theta \quad (5.3)$$

$$|AB+CB|=2d.sin\theta=n.\lambda \quad (5.4)$$

In Bragg's law given in equation (4.10), d is distance between the planes, θ is the incident and diffraction angle, n is integer (i.e.1,2,3) and λ is wavelength of incident x-ray. The wavelength of the photon used in XRD is $\lambda=0.5 \text{ \AA} - 2 \text{ \AA}$ ($E=40\text{-}500 \text{ eV}$), which is almost equal to inter-atomic distance. Therefore, XRD can provide extensive information about crystalline structures including lattice parameters.

The crystallinity degree of the pure and hybrid thin films were characterized by using Rikagu D/MAX-2200 model XRD instrument with $\text{CuK}\alpha$ radiation within the range of $20\text{-}60^\circ$ (2θ).

5.5.1.4 Atomic Force Microscopy (AFM)

Atomic Force Microscope obtains three-dimensional surface topography of a material by scanning the surface with a sharpened tip located on a cantilever. Cantilever has a metal coating that looks like a mirror. When laser beam is exposed to the cantilever, reflected light is detected by the photodiode and send to the computer to be create 3D image, respectively. The amplitude of the reflected light is depending on the bending motion of cantilever during surface scanning. As the displacement of cantilever changes, photodiodes generate more electrical current so that the bending amplitude of cantilever is measured. Imaging is performed as a result of interaction of the tip with the surface [131], [134]. A simple schematic working principle of AFM is given in Figure 5.7.

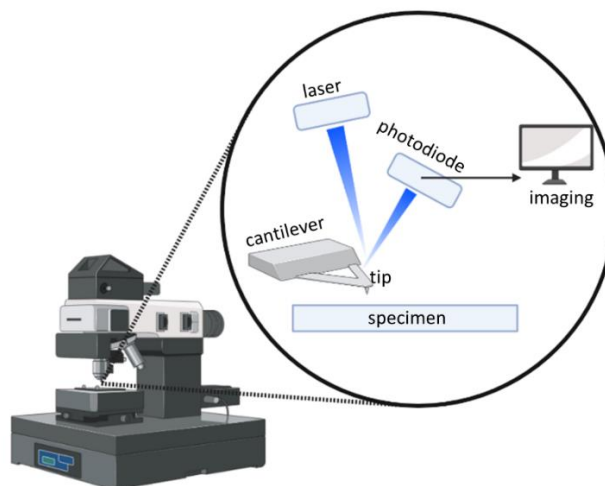


Figure 5.7 : A simple schematic working principle representation of AFM.

It is possible to make imaging in different modes with Atomic Force Microscope such as contact mode, non-contact and tapping mode. In contact mode, tip and material

surface is softly in contact and ionic repulsion forces is dominant. In non-contact mode a topographical image is created by bending the cantilever without touching the sample. The tip is kept very close to sample ($\approx 50\text{\AA}$ - $150\text{\AA}$) and Wan der Waals forces become dominant between the probe and the sample. Since these forces are relatively weak, the tip oscillates very fast by making this interaction detectable. The biggest advantage of this mode is that the tip is not damaged and soft materials can be measured more accurately. As for tapping mode, tip oscillates in its vibration frequency, leading the tip oscillates up and down. The biggest advantage of tapping mode is to get high resolution image and reduce damage to sample surface.

AFM is used to obtain various surface properties such as surface morphology, surface roughness, shape and size analysis of nanoparticles for all kinds of solid materials including metals, polymers, insulators and biomaterials. Morphologies of the both pure and hybrid thin films were performed by Veeco Dimension 3100 model AFM in tapping mode at ambient temperature and humidity.

5.5.1.5 Fourier Transform Infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) measures the vibrational and rotational modes of molecules in the near infrared (NIR) region. Infrared light is absorbed only by molecules which have a dipole moment between atoms. Infrared (IR) Spectroscopy is basically based on the absorption of infrared light by the material to be analyzed. The vibrational frequency of the sample is determined by the energy at which a signal appears in the absorption spectrum. IR spectra are often expressed as transmittance percentage (T%) versus the wave number of light in cm^{-1} unit.

When the IR beam passes from the high refractive index medium (Germanium or diamond crystal) to the low refractive index medium (sample), some of the light is reflected back from the sample. These reflected waves move away from the surface and gradually disappear. In this case, the intensity of the reflected light decreases, which is called “Attenuated Total Reflectance (ATR)”. The crystal surface is in contact with the sample surface and FTIR-ATR is one of the most popular reflectance techniques used in recent years.

ATR-FTIR device consists of IR source, laser, beam splitter, fixed and moving mirror system, interferometer, detector and computer. The beam splitters split the IR light in half and the beams pass through the mirrors. The reflected light from the mirrors are

reflected back to the beam splitter again. The light passes through the sample following the interferometer and is detected by the detector. By using the Fourier transform calculations in the computer, light is converted into a spectrum in the range of $400 - 4000\text{ cm}^{-1}$ [135]. Working principle of FTIR spectroscopy is sketched in Figure 5.8. In this study, Bruker Vertex 70 FTIR was used in the wavenumber $400\text{ cm}^{-1} - 4000\text{ cm}^{-1}$ with the ATR plugin.

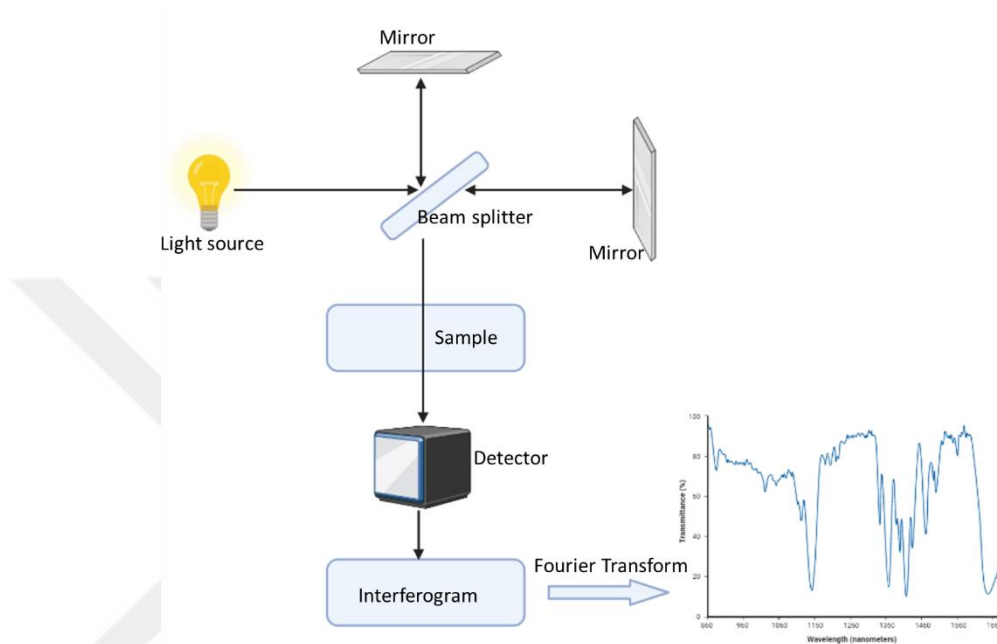


Figure 5.8 : A simple schematic working principle representation of FTIR.

5.5.1.6 Raman Spectroscopy

Raman spectroscopy also has a very similar working principle to the FTIR. However, unlike FTIR, it can also analyze non-polar groups. Both methods rely on the interaction of molecular vibration and light, but the incident light energies are different. FTIR measures the frequency of molecular vibrations in the sample, whereas Raman measures the inelastic scattering of two photons. In Raman spectroscopy, different optical events occur due to the interaction between the light and the sample. The incident light can be completely absorbed and scattered by the sample. If the energy of the incident monochromatic light and scattered photon is the same, Rayleigh or elastic scattering occurs. When the energy of the incident photon and the scattered photon are not the same, inelastic scattering occurs, which is called Raman scattering. If the scattered photon has lower energy than incident photon, Stokes scattering occurs. On the other hand, anti-Stokes scattering is occurred when the scattered photon energy is higher than the incident photon energy. Raman spectroscopy can be used not only

for molecular group identification, but also for the characterization of the crystalline samples. Working principle of Raman spectroscopy is sketched in Figure 5.9.

For the pure and hybrid thin films prepared in this study, Renishaw inVia™ model Raman spectroscopy instrument was used under 532 nm laser excitation.

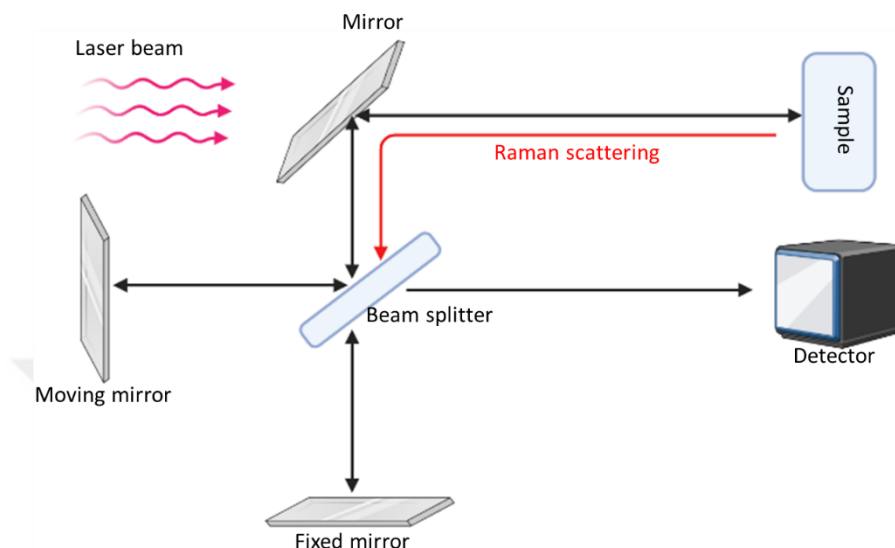


Figure 5.9 : A simple schematic working principle representation of Raman spectroscopy.

5.5.1.7 UV-Visible Spectroscopy

Ultraviolet visible spectroscopy corresponds to 200-800 nm region of the electromagnetic radiation, at which visible part is from 400-800 nm. When a molecule is exposed to the light, electrons are excited from the ground state to the higher energy states. The difference between these two energy levels is equal to $\Delta E = h\nu$, which induces electronic, vibrational and rotational excitations in the molecule. In other words, the transition from the HOMO level to LUMO level takes place, and this is the basis of UV-Vis spectroscopy.

UV-Visible spectroscopy consists of monochromator, reference and sample cells, detector, amplifier and computer. Most spectrophotometers are dual beam spectrophotometers. The incident beam is scattered with the help of rotating prisms. The beam passing through the slit is monochromatic and is split into two beams with the help of another prism. One beam passes through the sample whereas the other one passes through the reference cell. Since glass absorbs light in the UV region, silica or quartz cells are used as reference. The alternating current produced in the photocells

is transferred to the amplifier. After the signals are intensified in the amplifier, they are transferred to the computer and the final spectrum is obtained.

5.5.1.8 Photoluminescence Spectroscopy (PL)

Photoluminescence is the phenomenon of the molecule radiating its energy to the environment as a result of excitation with radiation. Photoluminescence can occur two forms depending on the excited state; fluorescence or phosphorescence. Fluorescence is the phenomenon of radiating from the first excited singlet state of an organic molecule excited by light. Radiation from triplet level is called phosphorescence, as well. As illustrated in Figure 5.10a, Jablonski diagram can be used to describe the PL phenomenon. S_0 indicates the ground state. S_1 indicates the first excited singlet state whereas T_1 indicates the first excited triplet state. The other states above S_0 and S_1 are vibrational energy states. When the light is absorbed, electrons are excited from ground state S_0 to S_1 . Once the molecule reaches the excited state, the energy of the excited state can be released (relaxation) can occur through many processes, such as heat dissipation (non-radiative), intersystem crossing, energy transfer through collisions with other molecules (quenching), phosphorescence or fluorescence. Fluorescence may compete with quenching, intersystem crossing, and phosphorescence in many molecules because of its short lifespan (10^{-8} s) [136],[137]. The setup of PL spectroscopy is given in Figure 5.10b. In this study, PL spectroscopy was used to investigate the interaction between WO_3 and P3HT.

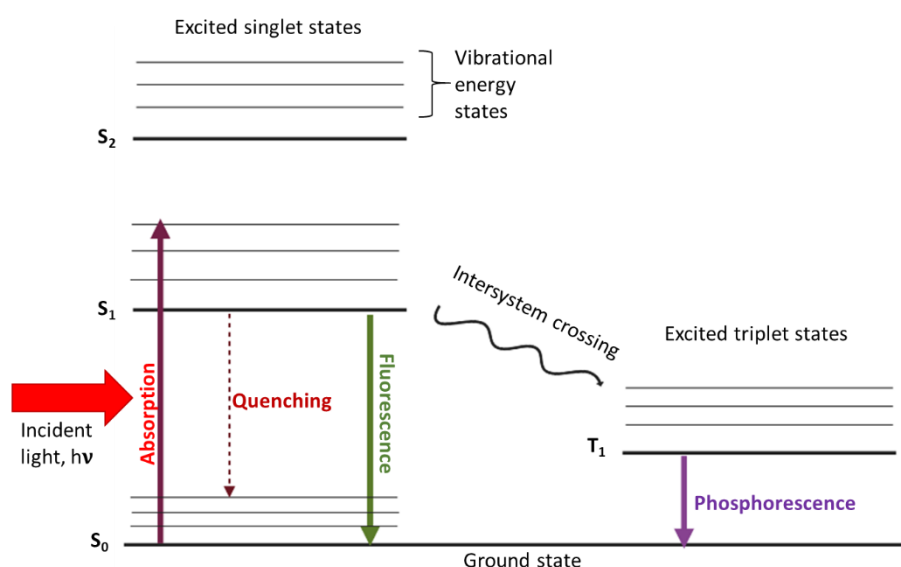


Figure 5.10 : Illustration of Jablonski diagram.

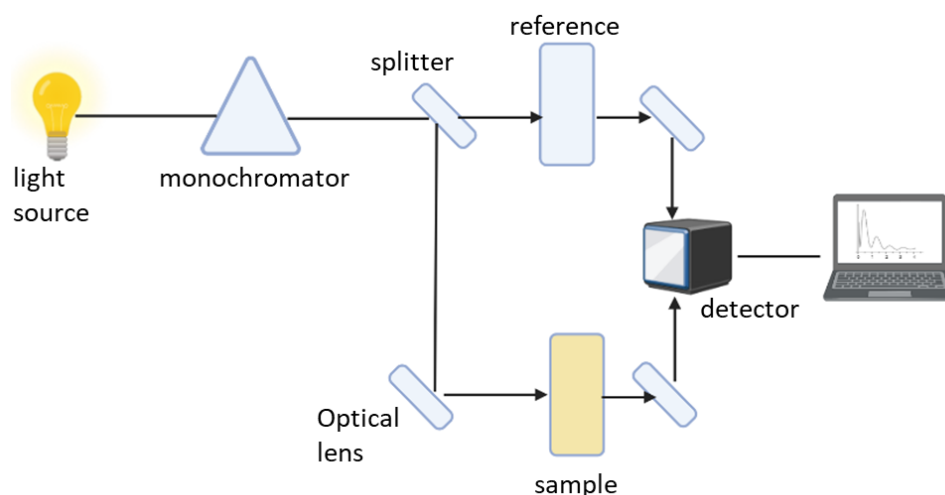


Figure 5.11 : Working principle of PL spectroscopy.

5.5.2 Electrochemical Characterizations

5.5.2.1 Three-electrode electrochemical cell

An electrochromic device or a super capacitor has to be wired into a circuit in order to be tested for electrochemical performance. As shown in Figure 5.11, three-electrode setup consists of a working electrode, reference electrode, counter electrode and a potentiostat. The counter electrode collects current from the working electrode, which links the sample to complete the circuit. Reference electrode controls the working electrode potential and reference electrode does not conduct any electricity (no current flow). In this study, P3HT films, Ag/AgCl electrode and platinum wire (Pt) were used as working electrode, reference electrode and counter electrode, respectively. All three electrodes are immersed in a liquid electrolyte. All electrochemical measurements were performed in atmospheric conditions in a three-electrode cell containing 1 M LiClO₄/PC electrolyte.

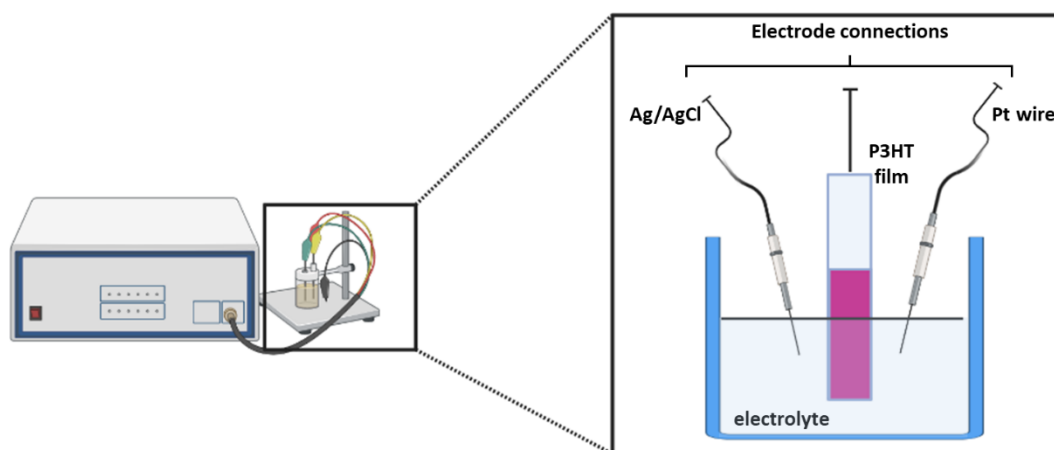


Figure 5.12 : Schematic illustration of a three-electrode system.

5.5.2.2 Cyclic voltammetry (CV) measurements

CV is a powerful tool to investigate redox reactions of materials and is performed in a three-electrode electrochemical cell. A potential is applied to the working electrode linearly with a constant scanning speed (V/s) from the initial potential value V_1 to the final potential value V_2 . The working electrode potential decreases to its original potential at the same rate after reaching the maximum potential. The cyclic scan can be performed repeatedly. To obtain the CV curve, the measured current is plotted against the potential. The voltage-current graph gives specific information to the working electrode immersed in the electrolyte. A typical cyclic voltammogram is given in Figure 5.12. The oxidation and reduction peak positions indicate the electrochromic properties of the working electrode and provide information about the selection of suitable switching potential.

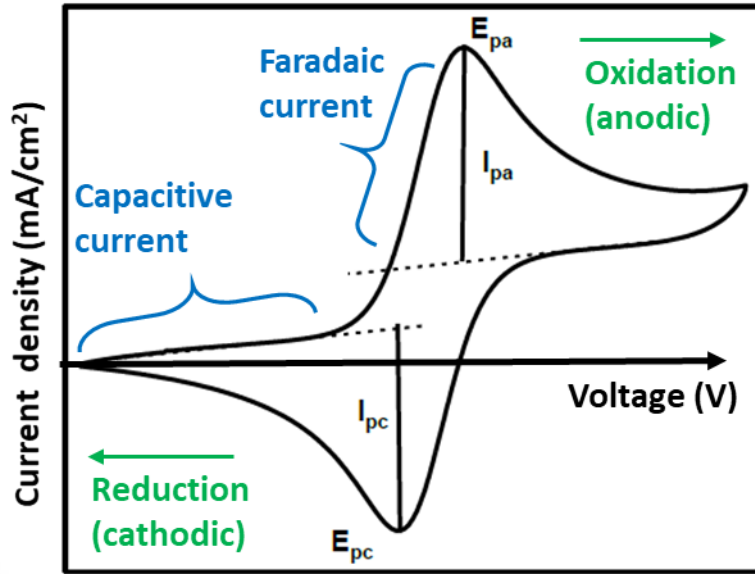


Figure 5.13 : A typical CV voltammogram curve.

Diffusion coefficient can also be calculated from the slope of peak current vs. square root of the scan rate using Randles-Sevcik equation (5.5).

$$I_p = 0.4463n^{3/2}F^{3/2}A \frac{D^{1/2}cV^{1/2}}{(RT)^{1/2}} \quad (5.5)$$

In equation (5.5), I_p is the peak current (A), n is the number of electrons transferred, F is the Faraday constant (96500 C.mol^{-1}), A is the electrode area (cm^2), c is the concentration of redox active species (mol.cm^{-3}), D is the diffusion coefficient ($\text{cm}^2.\text{s}^{-1}$), V is the scanning rate (V.s^{-1}), R is the gas constant ($8.31 \text{ J.K}^{-1}.\text{mol}^{-1}$) and T is the temperature (K). In this study, electrochromic thin films with an active area of $1 \times 1 \text{ cm}^2$ were characterized by means of cyclic voltammetry (CV) using CHI 6005D model CH Instrument.

5.5.2.3 Chronoamperometry (CA)

The chronoamperometry (CA) technique is based on the analysis of the current change over time, which occurs when the potential of the working electrode is suddenly changed from V_1 to V_2 potential. First, a V_1 voltage is applied to the working electrode as long as any reduction-oxidation reaction will not occur. Then, the voltage is rapidly changed to a V_2 voltage, where the electron transfer rate is very high. During a certain

period of time, the applied V_2 voltage is held constant while the change in current that occurs during that time is investigated.

5.5.2.4 Electrochemical Impedance Spectroscopy (EIS)

The circuit element that can resist the flow of electric current in a circuit is called resistance (R). Regarding to the Ohm's Law, resistance is equal to the ratio of voltage to the current. However, Ohm's Law is not sufficient to describe "resistance" in complex circuits. Instead, "impedance" is used to define total resistance of more complex alternative current circuits, such as capacitors. Therefore, the impedance (Z) is the ability of a circuit to resist an alternating current. Voltage (V) and current (I) become frequency dependent and formulated as equation (5.6).

$$Z_{\omega} = \frac{V_{\omega}}{I_{\omega}} \quad (5.6)$$

Electrochemical reactions at the electrode surface are studied using EIS. The electrode is subjected to a small AC voltage, the current response is monitored, and impedance is calculated as a function of AC frequency as given in equation (5.7). Herein, E_t is potential under t time, E_0 is amplitude of the signal and ω is radial frequency. The relationship between radial frequency (ω) and Hertz frequency (f) is also formulated as equation (5.8).

$$E_t = E_0 \sin(\omega t) \quad (5.7)$$

$$\omega = 2\pi f \quad (5.8)$$

Against this excitation signal, the response signal (I_t) has a different amplitude with a phase shift (θ) as shown in equation (5.9).

$$I_t = I_0 \sin(\omega t + \theta) \quad (5.9)$$

The equation to be able to calculate the system's impedance regarding Ohm's Law is as follows;

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \theta)} = |Z| \frac{\sin(\omega t)}{\sin(\omega t + \theta)} \quad (5.10)$$

The $|Z|$ is a vector combination of real (Z') and imaginary (Z'') parts of impedance and the relation between them is given in Figure 5.13.

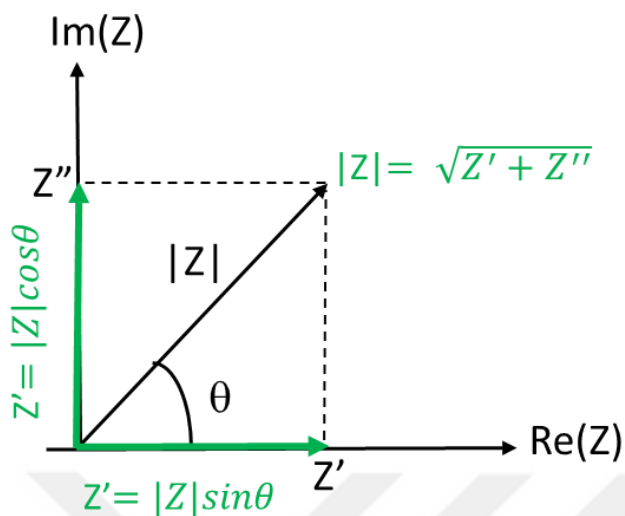


Figure 5.14 : A vector combination of real (Z') and imaginary (Z'') parts of impedance.

In this study, EIS measurements was used to investigate the capacitive and charge transfer properties of pure and doped P3HT thin films.

6. RESULTS AND DISCUSSION

6.1 Operation of P3HT Based Thin Films As OFET

P3HT thin films with different WO₃ concentrations were prepared as given in Chapter 5.2 and coated on pre-fabricated Ossila test chips to investigate transistor performance.

6.1.1 Structural characterization

In order to investigate thin film morphology and the distribution of WO₃ in P3HT, P3HT based pure and hybrid solutions were spin coated on SiO₂ test chips given in Figure 5.2a. Surface imaging was performed with SEM at 1.5 kV. Elemental analysis were also performed by EDX mapping mode. To able to confirm the presence of WO₃ in P3HT films, O, Si, S and W elements were quantified. It is clearly seen in Table 6.1, PW0 has no WO₃ on the coating and the amount of tungsten (W) increases when the doping concentration increases from PW10 to PW50, as well.

Table 6.1 : Elemental distribution of both pure and WO₃ doped P3HT hybrid coating solutions.

Sample Name	O%	Si%	S%	W%
PW0 (pure)	55.72	44.04	0.25	-
PW10	47.92	46.35	0.69	5.04
PW30	47.92	42.60	2.33	7.14
PW40	50.19	39.48	2.38	7.94
PW50	42.29	36.67	2.90	18.14

Considering the SEM images given in Figure 6.1, all doped formulations have well dispersion of WO₃ particles on the coating surface. However, it is observed that the WO₃ particles start to growth and agglomerate on the surface for PW50 coded thin film.

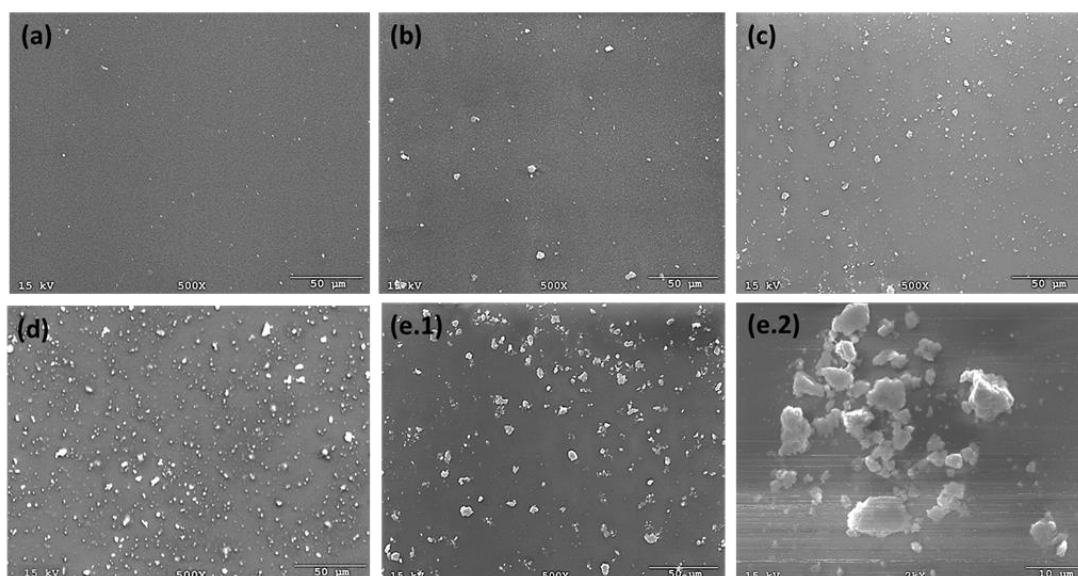


Figure 6.1 : SEM micrographs of (a) PW0, (b) PW10, (c) PW30, (d) PW40, and (e.1) PW50 coded samples at 500x magnification. (e.2) shows that the agglomerated WO_3 particles at 2000x magnification.

6.1.2 Transfer and Output characteristics of P3HT based OFETs

Output characteristic and transfer characteristic of pre-fabricated OFET test chips involving five different active channel material (PW0, PW10, PW30, PW40, PW50) were measured by using Agilent B1500A semiconductor characterization device. For the output characteristics, a drain-source voltage (V_{DS}) varying between 0V and -40V was applied in -2V steps while the gate-source voltage (V_{GS}) stepped from 40V to -40V was applied. The current between the source and drain electrodes (I_{DS}) is plotted as a function of the drain voltage (V_{DS}) are given in Figure 6.2. When the output curves given in Figure 6.2 are investigated, all OFET structures show p-channel transistor properties depending on the gate voltage ($V_{\text{GS}} = -40 \text{ V}$, $\Delta V_{\text{GS}} = 10 \text{ V}$). The linear increase of the I_{DS} current with the applied V_{DS} voltage indicates that ohmic contact is established between the P3HT based channel and Au electrodes of the transistor. The output characteristics of all samples are compared in Figure 6.2f at $V_{\text{GS}} = 10\text{V}$ and the saturation trend of the output curves can be clearly seen from the Figure 6.2.

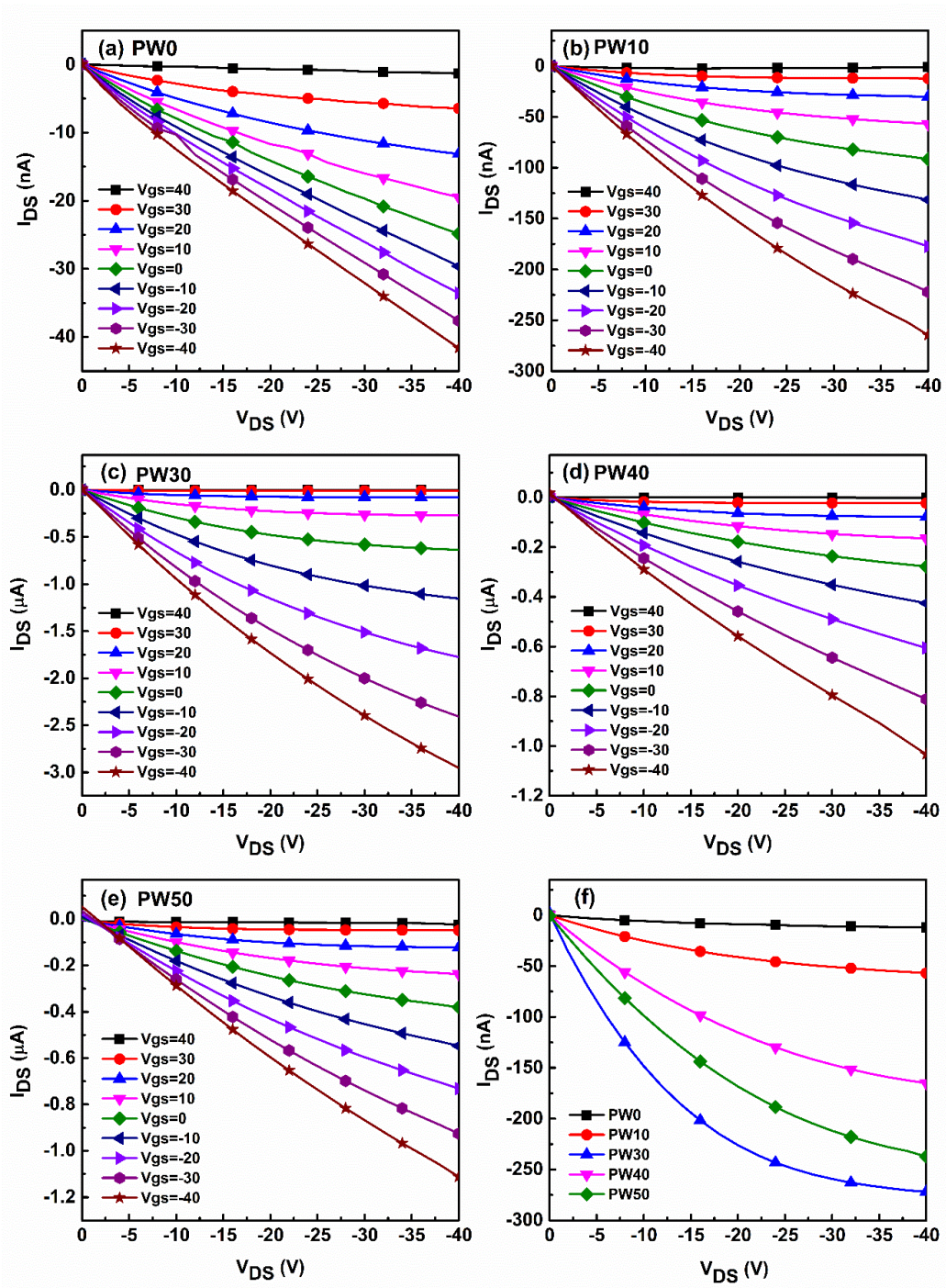


Figure 6.2 : Output characteristics of (a) PW0, (b) PW10, (c) PW30, (d) PW40, (e) PW50 OFETs, and (f) the comparison of output characteristics of pure P3HT and WO₃ doped P3HT hybrid OFETs when $V_{GS}=10$ V.

For the transfer characteristics, a gate-source voltage (V_{GS}) varying between 40V and -40V was applied in -5V steps while the drain-source voltage (V_{DS}) stepped from 0V to -40V was applied. The current between the source and drain electrodes (I_{DS}) is plotted as a function of the gate voltage (V_{GS}) are given in Figure 6.3. When the transfer curves given in Figure 6.3 are investigated, it is seen that maximum drain-

source current (I_{DS}) of P3HT was measured as 45 nA. However, I_{DS} current increases with the increasing WO_3 doping concentration. Maximum I_{DS} current, up to 3.3 μA , was obtained for sample PW30.

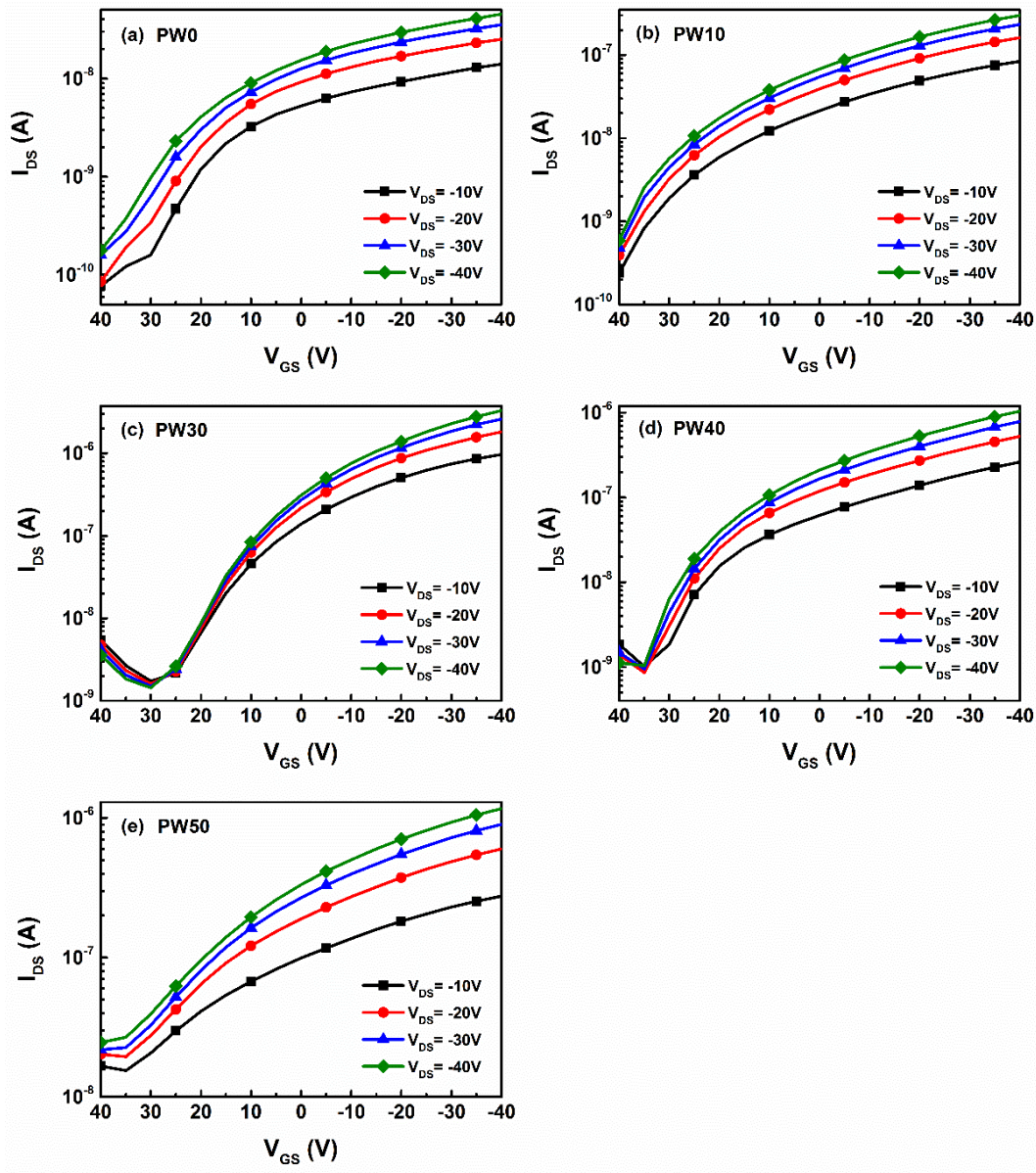


Figure 6.3 : Transfer characteristics of (a) PW0, (b) PW10, (c) PW30, (d) PW40, (e) PW50 OFETs.

Since the I-V curve becomes more linear at $V_{GS} = -40V$, performance parameters of the test chips were calculated at $V_{GS} = -40V$. Thus, the performance parameters of the OFETs were determined by the output and transfer characteristics and given in Table 6.1.

Table 6.2 : Comparison of basic transistor parameters based on pure and WO₃ doped P3HT hybrid structures.

Sample Name	I _{ON} /I _{OFF}	μ (cm ² V ⁻¹ s ⁻¹)	V _{th} (V)
PW0	2.5x10 ²	5.3x10 ⁻⁵	40.1
PW10	5.0x10 ²	2.8x10 ⁻⁴	37.2
PW30	2.3x10 ³	5.6x10 ⁻³	17.7
PW40	1.0x10 ³	1.1x10 ⁻³	32.7
PW50	5.0x10 ¹	9.0x10 ⁻⁴	45.1

As can be seen from Table 6.2, the on/off current ratio increases with the dispersion of WO₃ particles into the P3HT polymer until 30% WO₃ doping concentration. However, it starts to decrease when WO₃ concentration is increased further, since I_{ON} decreases and I_{OFF} increases for PW40 and PW50. It is thought that this may be due to the increased charge traps. Besides, the increase in on/off current ratio shows that more charge accumulation occurs in the transistor in a shorter time. Moreover, field effect mobility increases up to PW30 with the increasing concentration of WO₃, particularly showing an enhancement 105 times for PW30 compared to that of PW0. The threshold voltage also improved from 40.1V to 17.7V for PW30. Thus, it is understood that the traps at the insulator/semiconductor interface are reduced. Regarding the improvement in performance parameters, PW30 shows the best transistor performance among all.

6.1.3 Chemical characterization

In order to investigate the effect of different amounts of WO₃ doping on electrical properties, only the samples which have the highest (PW30) and weakest (PW50) device performance were chosen and analysed for further chemical characterizations.

The crystalline structure of pure P3HT and WO₃ doped P3HT thin films were investigated by XRD. Scanning was performed over 2 θ angles ranging from 20° to 60° to investigate characteristic peaks of both P3HT and WO₃ as seen in Figure 6.4. Like many conjugated polymers, P3HT films show different crystal structures depending on the solvent type, dissolution time, temperature and annealing conditions. Orientation, length and crystallinity degree is crucial for charge transport in the channel. In this study, pure P3HT shows a diffraction peak at 2 θ =23.4° due to the intermolecular $\pi \rightarrow \pi^*$ stacking corresponding to the (010) orientation [138], [139]. The distinct peaks of the XRD patterns exhibit at 2 θ values of 23.16°, 28.04°, 33.93°,

36.79°, 47.44° and 49.90° correspond to (002), (020), (112), (022), (004) and (220) planes of hexagonal WO₃ (ICDD: 98-008-0635). After the doping of WO₃ particles, characteristic P3HT peak slightly shifts to 2θ=23.6° due to some changes in interplane and interchain distances. Also, the peak becomes sharper which confirms improved crystallinity degree of P3HT. The appearance of prominent peak at 2θ=28.0 and other small peaks are attributed to the presence of WO₃ particles in the P3HT film. Considering the XRD spectrums, it can be estimated that there is a good interaction between polymer chains and WO₃ particles in PW30 film due to the more effective crystallization than PW0.

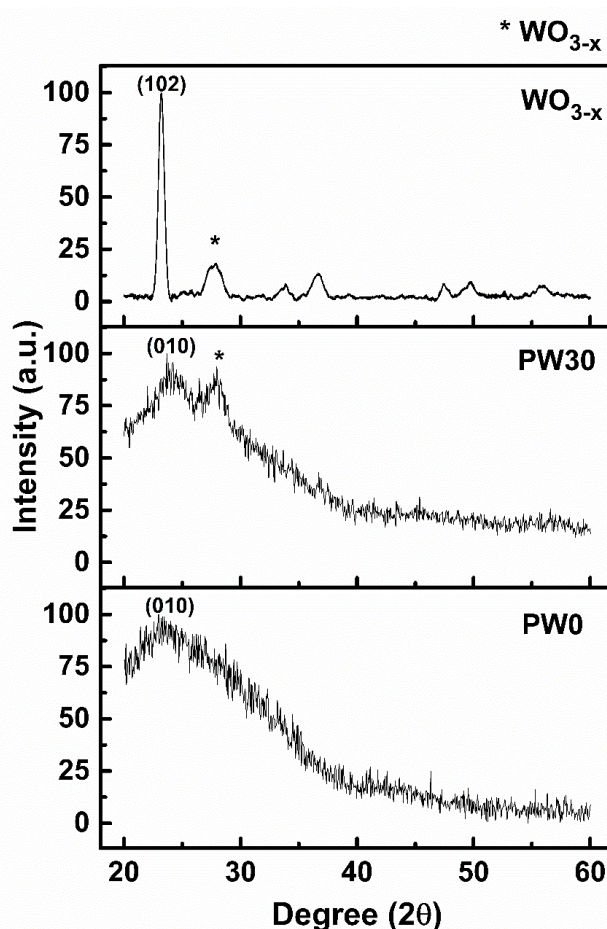


Figure 6.4 : XRD spectra of WO₃ powders, PW0 and PW30 thin films.

The interactions between WO₃ dopant molecules and P3HT are better understood when Raman spectroscopy is combined with XRD results. Raman spectrums at 600 – 1600 cm⁻¹ wavenumbers are shown in Figure 6.5. In the PW0 spectrum, Raman bands at 1452 cm⁻¹ and 1097 cm⁻¹ are assigned to C=C ring stretching and to C-H bending modes of inter rings, respectively. The small peak at 726 cm⁻¹ of WO₃ doped thin films indicates the C-S-C deformation vibration and is supposed to be related to electron

transfer between P3HT and WO_3 . Furthermore, it is observed that the C=C ring stretching peak at 1452 cm^{-1} shifts 6 cm^{-1} for PW30 while it shifts only 2 cm^{-1} for PW50. The peak intensity also increased after doping of WO_3 particles. The Raman shift towards lower wavenumbers refers that crystallinity degree of P3HT increases [140] with the doping of WO_3 particles and there is an effective conjugation throughout the polymer chain.

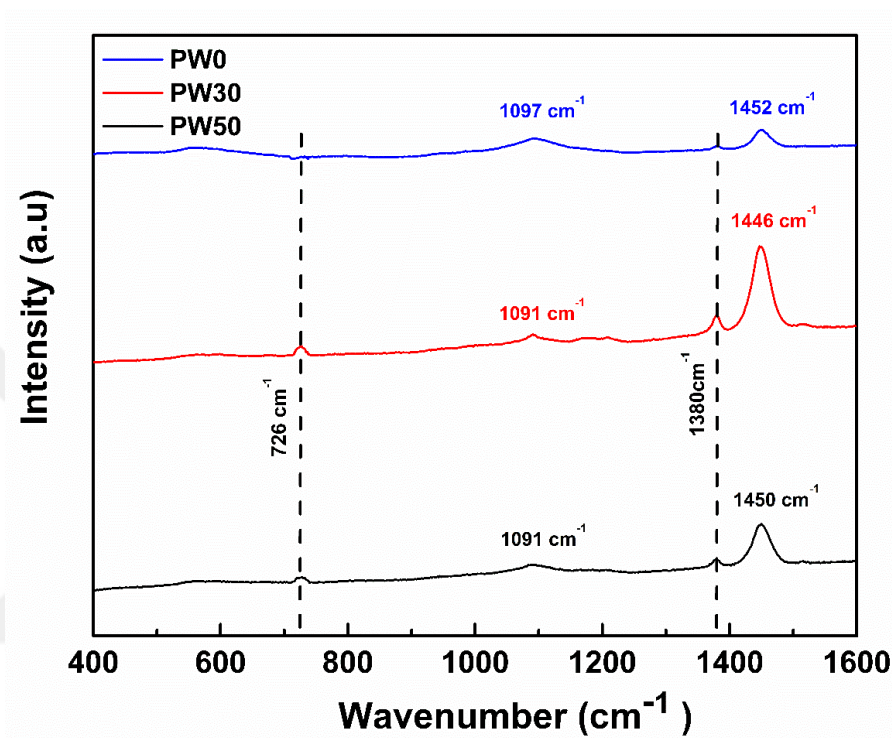


Figure 6.5 : Raman spectra of PW0, PW30 and PW50 thin films.

Furthermore, Raman peak shifting can be approximated by Hooke's Law given in equation (6.1); where ν is the frequency, k is the bond strength and m^* is the reduced mass. Regarding the equation (6.1), weakening the bond strength of thiophene chain causes a decrease in frequency. Since the wavenumber is directly proportional to the frequency, the Raman spectrum shifts to lower wavenumbers with the attachment of WO_3 particles. Exceeding 30% of WO_3 by weight, the polymer chain is completely occupied with an excess amount of WO_3 particles and the particles cannot find any suitable place to bond and to transfer electrons. Consequently, the Raman spectrum confirms that PW30 has the best transistor performance due to the better interaction and electrical charge transfer with P3HT network.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}} \quad (6.1)$$

FTIR spectrum given in Figure 6.6 is used to explain what kind of interaction occurs between WO₃ particles and P3HT. It is observed that the spectrums between 500 cm⁻¹ and 3000 cm⁻¹ wavenumbers indicate the fingerprint region for P3HT. The small peak at 3067 cm⁻¹, the intense peaks at 1573 cm⁻¹ and 1456 cm⁻¹ and the peak at 1252 cm⁻¹ are assigned to C-H stretching vibrations, C=C stretching modes and C-C vibrations in the thiophene unit of P3HT, respectively. The bands at 1126 cm⁻¹ and 1033 cm⁻¹ are due to the C-H₂ thiophene ring stretching vibrations. The characteristic C-S bands of P3HT appear at 943 cm⁻¹, 744 cm⁻¹ and 657 cm⁻¹. The characteristic band located at 806 cm⁻¹ is attributed to W-O-W stretching vibration of WO₃ [141]. It is clearly seen that doping of WO₃ particles into the P3HT network does not lead to any peak shifting since there is no covalent bonding. It is considered that WO₃ particles are attached to the P3HT polymer network with only electrostatic interactions such as cation- π or anion- π interactions, π - π stacking interactions and dispersion interactions. The absorption intensity of the peaks increases with the increasing content of WO₃ since the particles contribute to the system with extra absorption bands. These results verify that the P3HT polymer network is successfully incorporated with WO₃ particles.

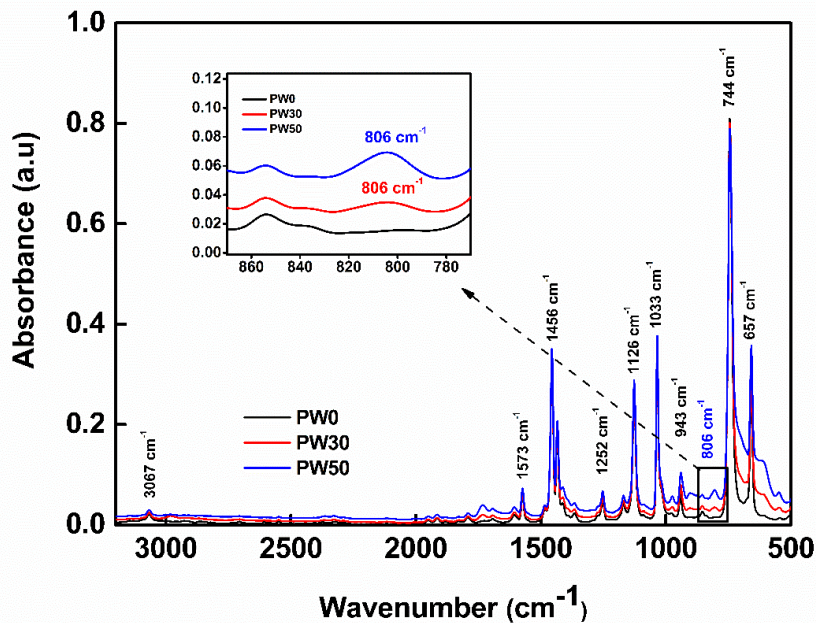


Figure 6.6 : FTIR spectra of PW0, PW30 and PW50 thin films.

The energy difference between conduction band of WO_3 and vacuum level is defined as electron affinity of WO_3 whereas the electron affinity of P3HT is defined as the energy difference between LUMO state of P3HT and vacuum level. The electron affinity of dopant molecule is responsible for the doping efficiency. Furthermore, when the HOMO state of the polymer and the conduction band minimum energy level of dopant molecule are close to each other, effective doping can be carried out [142]. Since the electron affinity of WO_3 ($E_{\text{EA}} > 4.4 \text{ eV}$) is higher than P3HT ($E_{\text{EA}} \approx 3 \text{ eV}$) [143],[144], WO_3 particles tend to take electrons from the HOMO level of P3HT leaving behind the holes. This type of doping is called p-type doping [12] and the enhancement of hole carriers in P3HT is responsible for high channel mobilities. Also, it is suggested that the proper amount of WO_3 doping into P3HT increases mobility and reduces threshold voltage. This enhancement is attributed to the passivation of charge traps existing in P3HT [145]. The charge transfer mechanism between WO_3 and P3HT is illustrated in Figure 6.7.

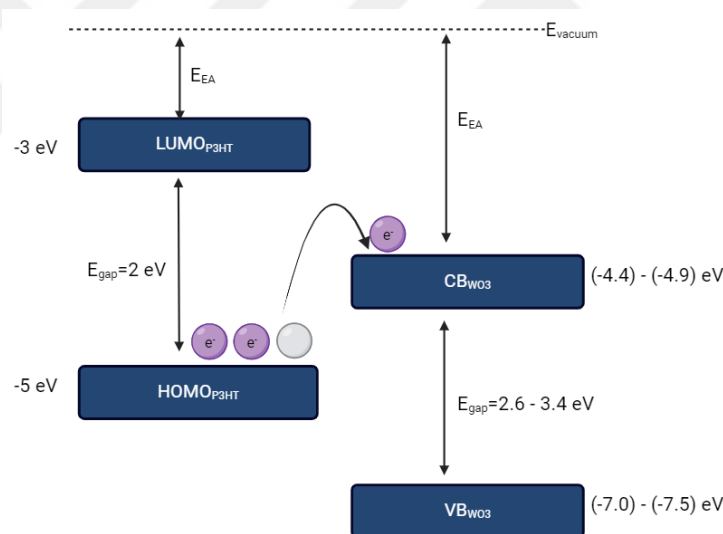


Figure 6.7 : Schematic illustration of charge transfer between WO_3 and P3HT.

Considering all these chemical characterizations confirming the interaction between WO_3 and P3HT, it is assumed that WO_3 particles can attach to the thiophene ring of P3HT to take unpaired electrons of sulphur element in the thiophene ring. Since the size of polymer fragments are very small compared to the size of WO_3 particles, it is assumed that WO_3 particles might engage with more than one thiophene units within the polymer network. In order to see if any W-S bonding exist in the hybrid structure, XPS analysis were performed. XPS survey scans of WO_3 powders, P3HT thin film

and PW30 thin film are shown in Figure 6.8a. As can be seen in Figure 6.8a, XPS signal at 36 eV is attributed to W4f core level whereas two sharp signals at 244 eV and 260 eV are attributed to W4d core levels. These signals are not observed in the survey spectra of P3HT. However, after the incorporation of 30% WO₃ into P3HT, which is coded as PW30 thin film, small XPS signals were obtained corresponding to the W4f and W4d core levels. This confirms that the presence of WO₃ in PW30 hybrid thin film. High resolution scan of W is given in Figure 6.8b. Figure 6.8b shows that the spin orbit coupling of 4f shell of WO₃ at 36.4 eV and 38.4 eV, which is attributed to W⁺⁶ oxidation states [146]. In Figure 6.8c, peaks at high binding energy of 164.0 eV (S2p_{3/2}) and 165.1 eV (S2p_{1/2}) are corresponding to sulfur atom in thiophene ring of P3HT. After the 30% WO₃ doping, small chemical shift is observed to the lower binding energies, which refers to the charge transport between S-W [147].

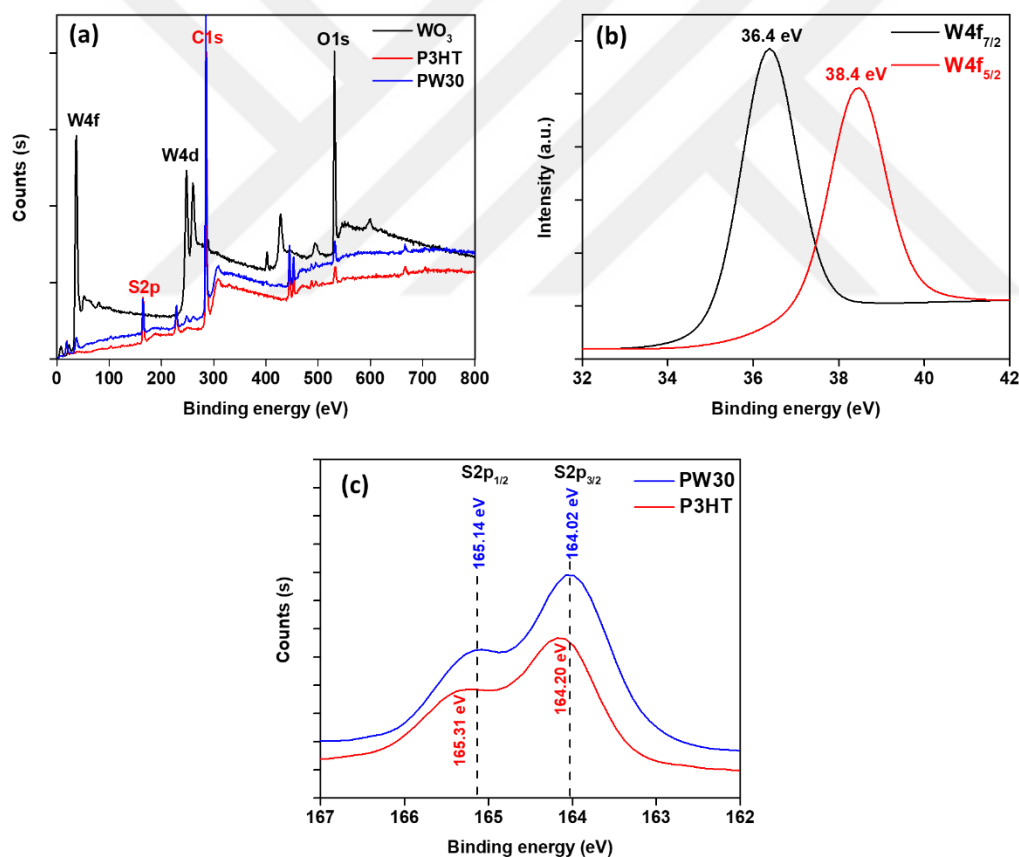


Figure 6.8 : (a) Survey scan of P3HT, WO₃ powders and PW30 thin film, (b) high resolution scan of W4f shell and (c) S2p spectra of P3HT and PW30.

The interaction between polymer chains and WO₃ particles influences the crystalline structure and molecular arrangement of P3HT chains, especially due to its impact on

charge transfer efficiency. Thus, the π -stacking and crystallinity correspond to efficient charge transport and lead to better field effect mobilities. The schematic structure of the coupling between WO_3 and P3HT is simply shown in Figure 6.9.

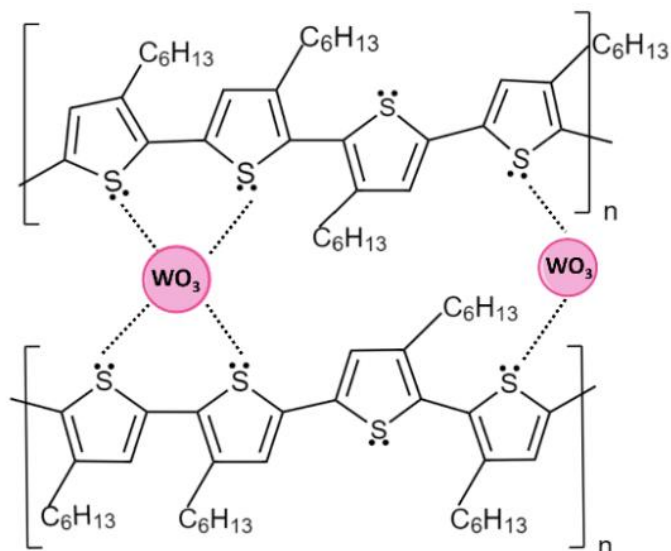


Figure 6.9 : Illustration of the interaction between WO_3 and P3HT.

6.2 P3HT Based Thin Films As Electrochromic Devices

P3HT thin films with different WO_3 concentrations were prepared as given in Chapter 5.2 and spin coated on ITO coated glasses to investigate electrochromic behavior of thin films.

6.2.1 Structural characterization

First, elemental analysis and surface imaging was performed to confirm the presence of tungsten in the prepared WO_3 doped hybrid films on ITO glasses. Elemental composition in weight percentages and FEGSEM images are given in Table 6.3 and Figure 6.10, respectively. As can be seen in Figure 6.10, the surface of undoped P3HT film has ordered crystalline domains under 60,000x magnification. However, the morphology of the film changes with WO_3 doping. It is observed that the WO_3 particles are homogeneously dispersed on the surface of PW10 ($\approx 28 - 35$ nm) and PW30 ($\approx 40 - 50$ nm) hybrid films whereas the particles grow and agglomerate in PW50 hybrid film. The AFM images given in Figure 6.11 also support the FEGSEM images. Undoped P3HT has regular branched and interconnected domains. However, it is seen that when 50% WO_3 in weight is added into the polymer, large-sized WO_3 particles

with a diameter of 150-450 nm agglomerate on the surface so that the average surface roughness significantly increases. The average surface roughness (R_a) was determined from AFM analysis and was found as 2.4 nm, 5.8 nm, 8.2 nm, 55.3 nm for undoped P3HT, PW10, PW30 and PW50, respectively.

Table 6.3 : Sample codes and elemental composition in weight percentages obtained from energy dispersive spectroscopy of prepared thin films.

Sample code	C%	O%	Si%	S%	W%	In%	Sn%
PW0	21.73	16.93	17.36	4.51	-	37.11	2.36
PW10	19.83	17.03	18.03	4.22	0.98	37.43	2.48
PW30	19.54	18.53	18.24	4.38	1.34	35.71	2.26
PW50	16.40	22.14	15.73	5.13	3.21	34.99	2.40

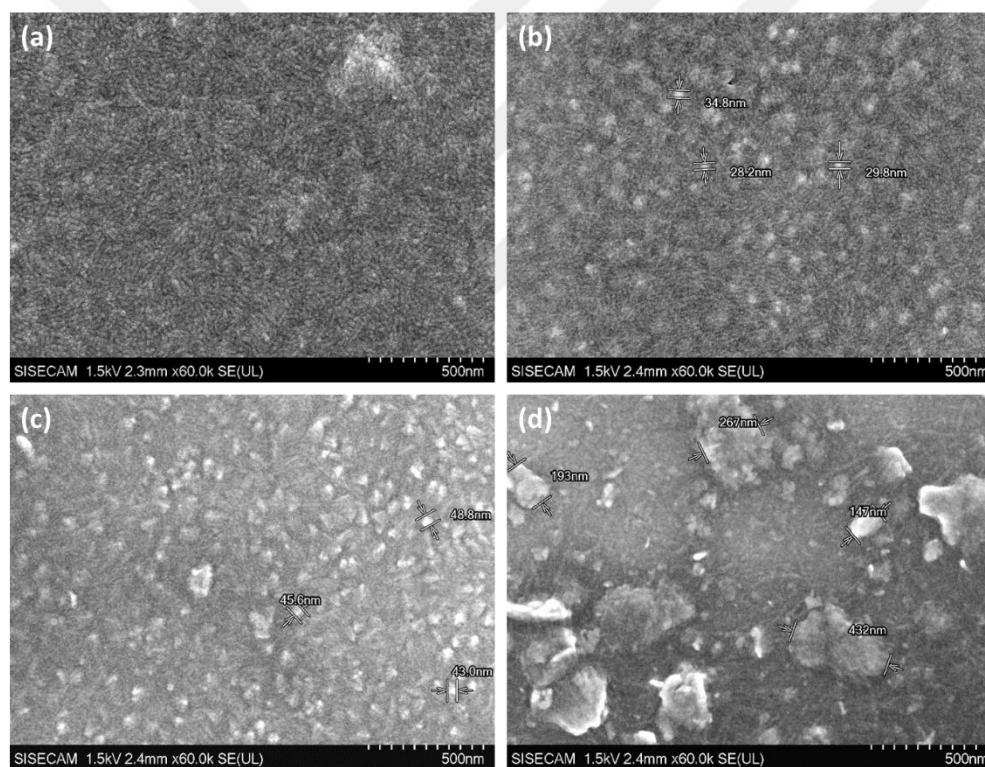


Figure 6.10 : Field emission scanning electron micrographs of (a) P3HT, (b) PW10, (c) PW30 and (d) PW50.

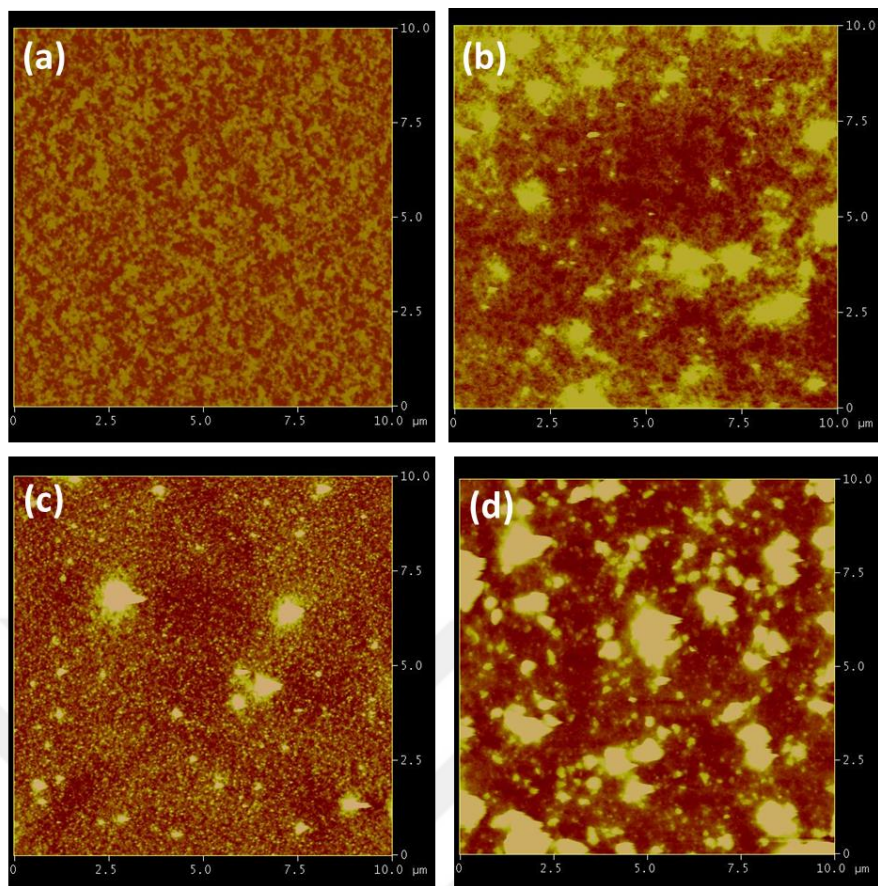


Figure 6.11 : Two dimensional AFM images of (a) P3HT, (b) PW10, (c) PW30 and (d) PW50.

6.2.2 Electrochemical characterization of half cells

To investigate the electrochemical behavior of P3HT films, the CV plot recorded at the different scan rates from 50 to 1000 mVs^{-1} in 1 M LiClO_4/PC electrolyte and shown in Figure 6.12a. The CV curve of the P3HT widens up to 1000 mVs^{-1} and maintain its characteristics. This shows that a typical electrochemical capacitive behavior with the rapid ion diffusion. Figure 6.12b shows the oxidation (I_{p1}) and reduction (I_{p2}) peak currents depending on the scanning rate. The good linear relationship between the square root of the scan rate and peak current, which means redox behavior is controlled by ions from the electrolyte solution through the electrode surface.

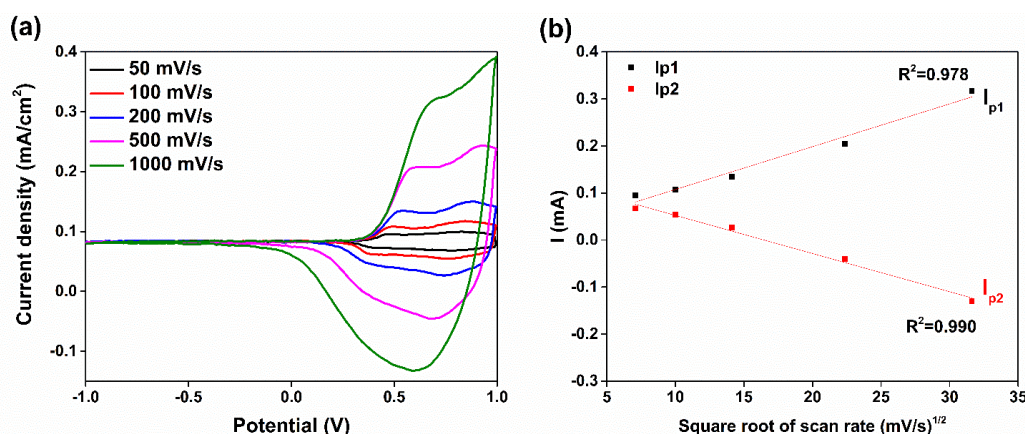


Figure 6.12 : (a) CV plot of P3HT at different scan rates and (b) peak current – scan rate square root graph of P3HT.

CV measurements were recorded for each hybrid film to investigate the effect of WO₃ incorporation on redox behavior. The CV curves of both doped and undoped P3HT films under 100 mV s⁻¹ scanning of ± 1 V potential range are shown in Figure 6.13.

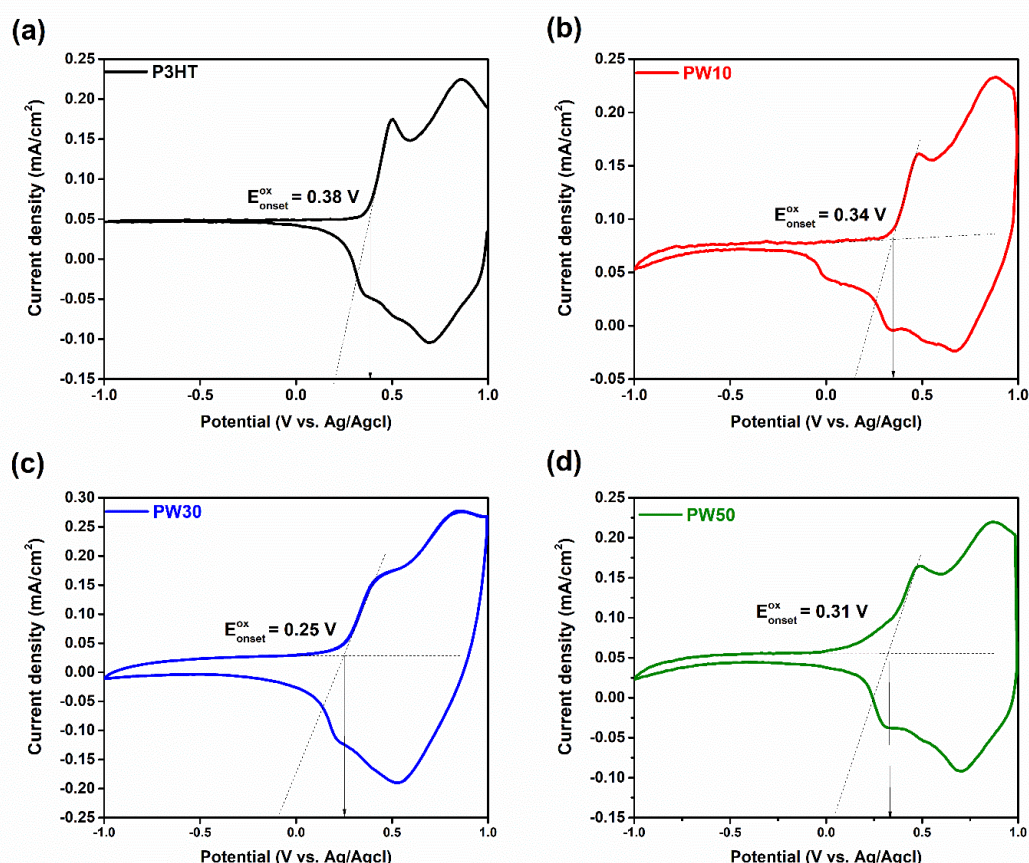


Figure 6.13 : Cyclic voltammograms at 100 mVs⁻¹ of (a) P3HT, (b) PW10, (c) PW30 and (d) PW50 in 1 M LiClO₄/PC electrolyte solution.

As can be seen from Figure 6.13, PW30 has the lowest oxidation potential ($E_{\text{onset}}^{\text{ox.}}=0.25$ eV). In order to be able to discuss the reason of this reduction in oxidation potential, HOMO energy levels of the each thin films were calculated by using the equation (6.2) [148].

$$E_{\text{HOMO}} = - (E_{\text{ox. onset vs. Ag/AgCl}} + 4.35) \text{ eV} \quad (6.2)$$

Considering this formula, HOMO levels of electrochromic films were determined as -4.73 eV, -4.69 eV, -4.60 eV and -4.66 eV for P3HT, PW10, PW30 and PW50, respectively. As can be clearly seen, PW30 has a higher HOMO energy level than the other electrochromic films. Strong donor-acceptor interactions can increase the HOMO energy levels, leading to a decrease in onset oxidation potentials [101], [149]. Therefore, it is thought that efficient WO₃ doping may change the electron density of donor groups in P3HT chain since it probably interacts with the thiophene groups by electrostatic interactions, leading to a decrease in oxidation potential. In similar studies [150], [33], significant broadening of CV curve and reduction in oxidation peaks refer to more efficient interaction between host material and dopant molecule, resulting a better charge transfer. This means that it is easier to excite electrons under an applied potential [151]. Besides, diffusion coefficient of P3HT and PW30 was calculated as $1.13 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $5.78 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. This means, optimum amount of WO₃ doping not only provides better charge transfer, but also increases the ion transport. These values are quite compatible with the previous studies reported in the literature, even better than some studies [152],[153], [154].

The oxidation potential corresponding to the onset potential depends on the interaction between electrodes and electrolyte interface. The areal capacitance (C_a) is calculated with the equation (6.3), where A is electrode area, ϑ is scan rate, ΔV is applied potential range and integrated i is total charge calculated from the area under the CV curve. [155].

$$C_a = \frac{1}{2A\vartheta(\Delta V)} \int i dV \quad (6.3)$$

PW30 showed the areal capacitance of 1.135 mF/cm^2 whereas P3HT showed the areal capacitance of 0.635 mF/cm^2 . These results are parallel to the charge transfer

resistance of P3HT and PW30 films measured by impedance spectroscopy. There is no further coloring observed between the potential range of 0V and -1V.

After electrochemical characterizations, the reversibility of the electrochromic films was tested by chronoamperometry (CA) cycling and UV-Vis spectra at 550 nm was recorded in situ in 0V-1V potential range within 8 s time interval. The response of current change occurred by charging/discharging of working electrode is given in Figure 6.14. When a positive bias (+1V) is applied to the thin films coated on ITO glass, both doped and undoped P3HT thin films oxidize and change color from purple to transparent following the reaction below;

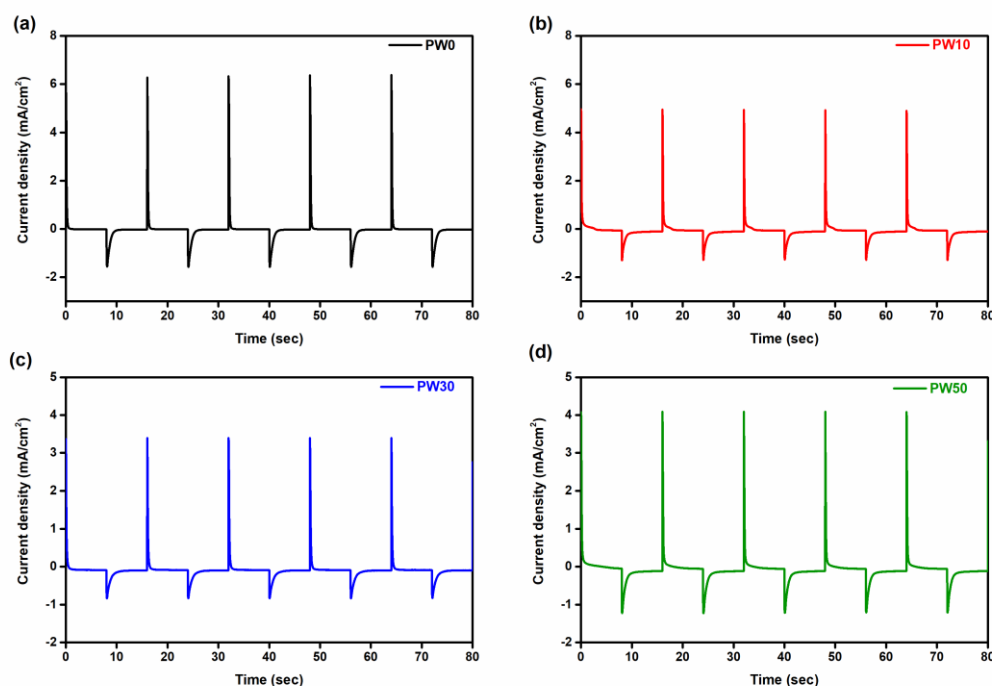
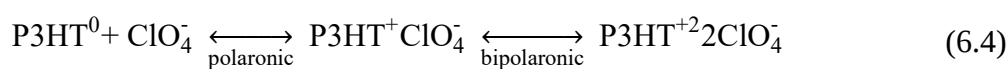


Figure 6.14 : Current stability of (a) P3HT, (b) PW10, (c) PW30, and (d) PW50 thin films with a residence time of 8 s.

Optical transmission of the thin films is given in Figure 6.15. Considering the Figure 6.15, the maximum transmittance difference ($\Delta T\% = T_{\text{bleach}} - T_{\text{color}}$) and the maximum optical density ($\text{OD} = \log(T_{\text{bleach}}/T_{\text{color}})$) was found as 36% and 0.26 for PW30 at 550 nm, respectively.

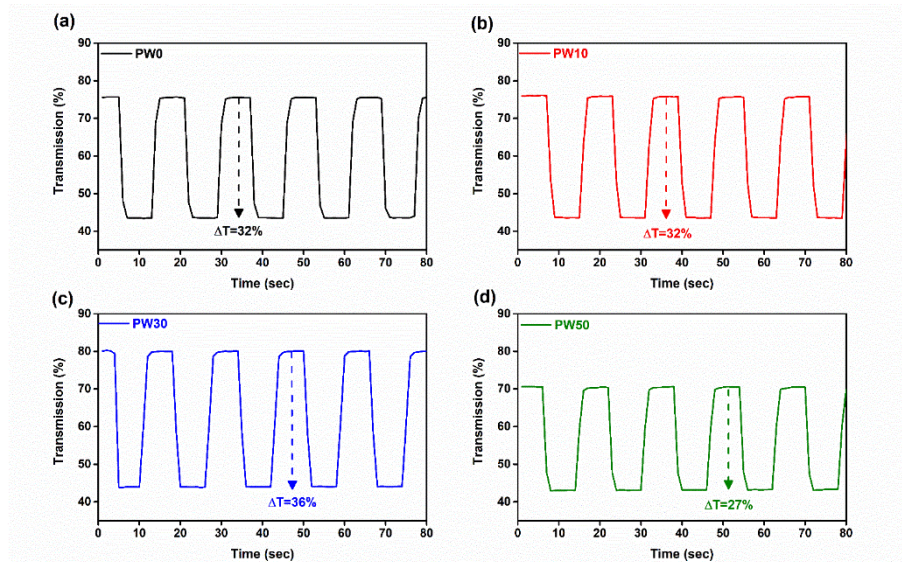


Figure 6.15 : Optical contrast of (a) P3HT, (b) PW10, (c) PW30, and (d) PW50 thin films with a residence time of 8 s.

The coloration efficiency (η) was calculated using the equation (6.5), where ΔOD and Q_{in} indicate the change of optical density and injected charges for 1 cm² electrode area, respectively.

$$\eta = \frac{\Delta OD}{Q_{in}} \quad (6.5)$$

Regarding the equation (6.5), maximum coloration efficiency was determined to be 464 cm² C⁻¹ for PW30. This value is almost twice that of the undoped P3HT film (220 cm² C⁻¹). The optical properties of electrochromic films are reported in Table 6.4. As can be seen in Table 6.4, the injected charge densities of 1.10 mC cm⁻² and 0.59 mC cm⁻² for P3HT and PW30 at +1V. Since the PW30 films show high transmittance modulation even in small charge injections, high coloration efficiency is obtained. This means a lower oxidation potential would suffice to induce bleaching, which makes the charges to be excited easier.

Table 6.4 : The optical properties of pure and doped P3HT thin films at 550 nm.

Sample code	T _{bleach} %	T _{color} %	ΔT%	ΔOD	Q _{in} (mC cm ⁻²)	Q _{out} (mC cm ⁻²)	η (cm ² C)
P3HT	75.57	43.27	32.3	0.24	1.10	1.02	220
PW10	75.66	43.76	31.9	0.24	1.01	0.78	233
PW30	79.70	42.70	37.0	0.26	0.59	0.61	464
PW50	70.53	43.01	27.5	0.21	0.50	0.53	422

The long-term performance of P3HT and PW30 was measured by observing the transmittance change over time while continuously switching between the colored and bleached states (Figure 6.16). There is almost no change in transmittance difference of PW30 during 1000 cycle whereas the transmittance difference decreases from 32% to 23% for P3HT. Since the stability and electrochromic performance parameters of PW30 is better than P3HT, further characterizations were performed comparatively for only PW30 and P3HT.

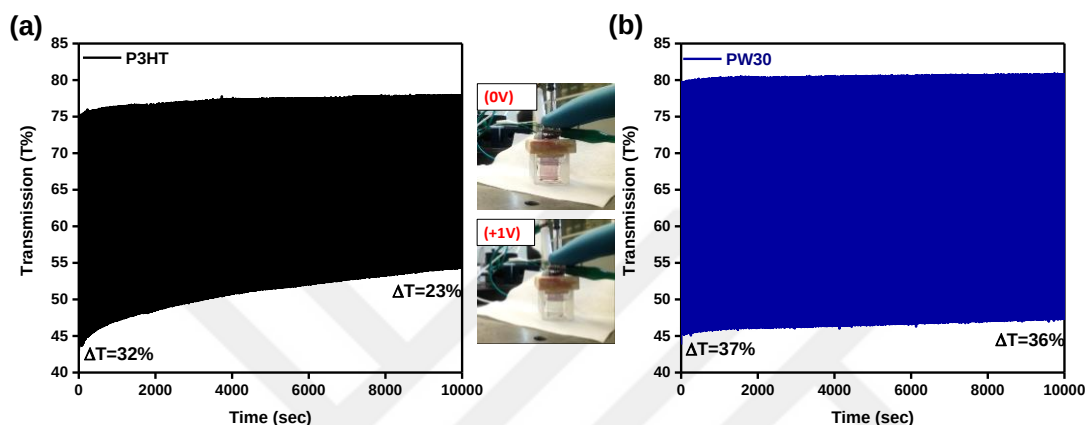


Figure 6.16 : Long-term electrochemical cycling stability measurements of the (a) P3HT and (b) PW30 thin films with a residence time of 5 s.

6.2.3 Optical characterization of half cells

The UV visible absorption spectra for P3HT and PW30 are given in Figure 6.17. For P3HT film, two distinct peaks at 512 nm and 546 nm and a shoulder at 603 nm are observed, showing the maximum peak at 546 nm. These peaks can be ascribed to $\pi \rightarrow \pi^*$ interactions in conjugated P3HT chains. After the doping of 30%wt. WO_3 into the P3HT, the absorption peak broadens. Similar to previous studies [156], [157], the broadening of the absorption spectrum with the addition of the dopant molecule to the host material indicates that there is an interaction between two materials. It can be said that the reason of this broadening is due to electrostatic interactions for this study. The vibrational energies of WO_3 molecules may contribute to the absorption band of P3HT.

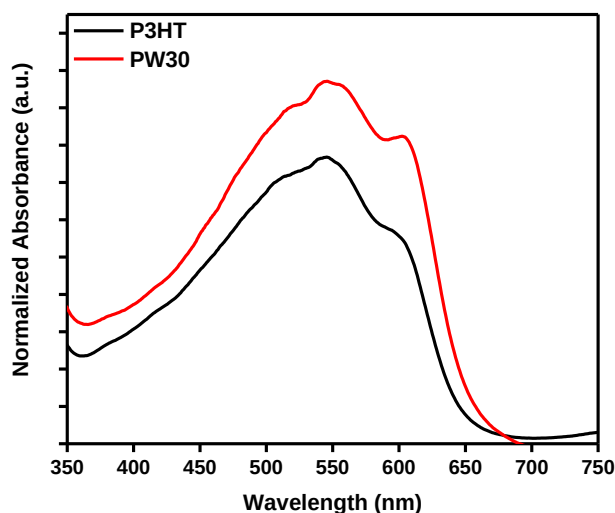


Figure 6.17 : UV-Visible absorption spectra of P3HT and PW30.

Moreover, since the peak intensity depends on the crystalline degree, the shoulder at 603 nm may indicate higher crystallization order of the P3HT chains in the PW30 hybrid structure. In our previous study [158], it was also confirmed the crystalline reflections of WO_3 particles became visible in PW30 hybrid film by XRD and Raman analysis.

Photoluminescence (PL) quenching is one of the powerful measurement methods for determining the charge transfer efficiency in the donor-acceptor blends. PL spectra of P3HT and PW30 excited at 422 nm is given in Figure 6.18. Maximum emission peak and a shoulder is observed at 598 nm and 632 nm, respectively. PL intensity quenches after the incorporation of 30% wt. WO_3 , which indicates the charge transfer and the creation/dissociation of the excitons between WO_3 and P3HT [157,159–163]. In the light of these findings, it is hypothesized that higher exciton dissociation efficiency and favorable donor – acceptor interactions between thiophene units of P3HT and WO_3 particles increase the HOMO energy level of P3HT by reducing the oxidation onset potential. Therefore, PW30 thin film shows a lower onset potential of oxidation than that of pure P3HT resulting an improvement in optical contrast.

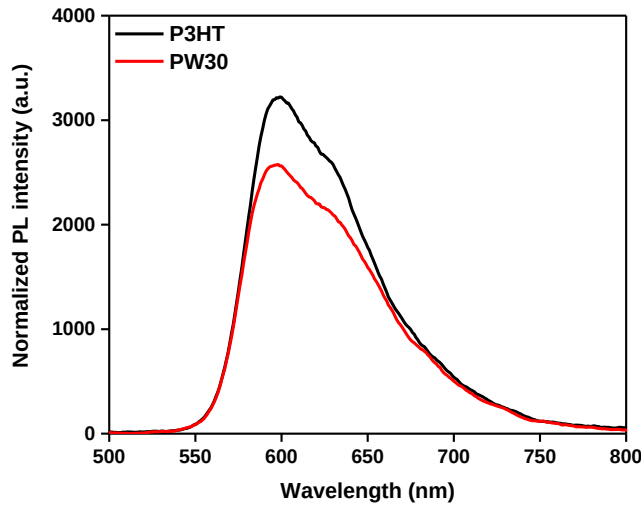


Figure 6.18 : PL spectra of P3HT and PW30.

The energy gap between the highest occupied π -electron band (valence band or HOMO) and the lowest unoccupied band (the conduction band or LUMO) determines the intrinsic optical properties of these materials. Hence, the optical band gap was calculated for both P3HT and PW30 films by using Tauc plot with the aid of the equation (6.6); where h is the Planck constant, ν is the frequency, E_{gap} is the optical band gap energy and the exponent n indicates the nature of the band transition with direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions which related to the value of $1/2$, 2 , $3/2$, and 3 , respectively.

$$(\alpha h\nu)^{\frac{1}{n}} = h\nu - E_{\text{gap}} \quad (6.6)$$

If the energy of the incident light is greater than the band energy, the electrons in the conduction band give their energy to the crystal after they are excited to a higher energy level and radiate by passing from the conduction band to the valence band. How much light is absorbed in the film depends on the absorption coefficient (α) and the film thickness (d_{film}). The absorption coefficient was calculated by using Beer Lambert law as a function of absorbance and film thickness ($\alpha = 2.303A/d_{\text{film}}$). Herein, d_{film} was found as ≈ 80 nm for P3HT and ≈ 88 nm for WO_3 doped P3HT. The optical band gap is obtained from the extrapolation of the linear part of the plot $(\alpha h\nu)^2$ versus $h\nu$. As can be seen in Tauc plot in Figure 6.19, E_{gap} values were found to decrease from 1.95 eV to 1.92 eV with the addition of WO_3 particles attributed the delocalization of charges [164]. Narrower bandgap and suitable energy levels lower the oxidation

potential and provide higher onset of absorbance resulting the substantial optical contrast [101].

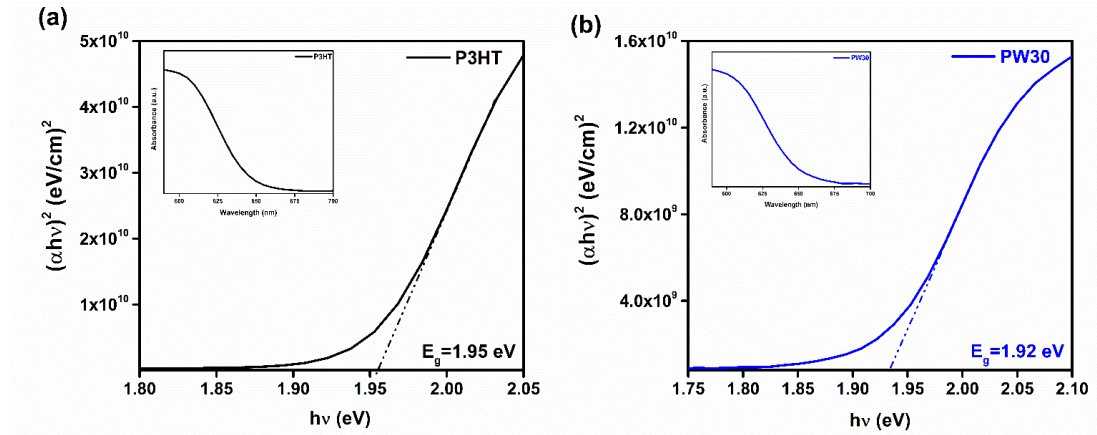


Figure 6.19 : Tauc plots derived from UV-Visible absorption spectra of (a) P3HT and (b) PW30.

6.3 Electrochemical Properties as Capacitor

Electrochemical impedance spectroscopy (EIS) measurements were also performed in the frequency range of 1 MHz–0.01 Hz to investigate the charge transfer at the electrochromic film and electrolyte solution interface. As shown in Figure 6.20, the diameter of the semi-circles in the high frequency region indicates the charge transfer resistance (R_{ct}) of the electrochromic films and decreases from 2.4 Ω to 1.3 Ω with the addition of 30% wt. WO₃ particles. PW30 film has a smaller circle radius due to the efficient donor-acceptor structure between thiophene units and better charge mobility. The switching time during bleaching (coloring) were 1.65 s (1.05 s) for P3HT and 1.04 s (0.95 s). PW30 has lower charge transfer impedance in high frequency region so that the redox and electrochromic reactions are proceeded easily due to the good ionic conductivity, and electrochromic performance of hybrid film was improved compared to undoped P3HT [165].

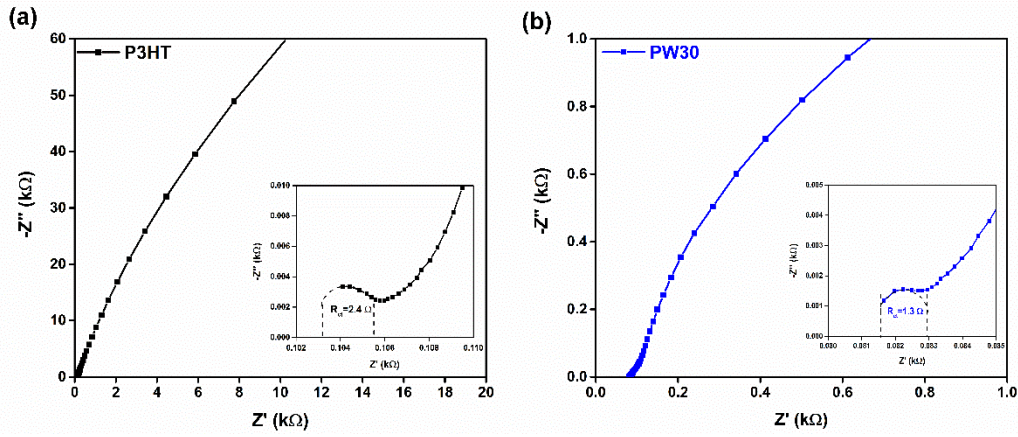


Figure 6.20 : Nyquist plots of (a) P3HT and (b) PW30 films.

Capacitive properties of P3HT and PW30 was determined by Bode plots at low frequency region (0.01–1 Hz). Low-frequency capacitance (C_{LF}) were calculated from the slope of $1/f$ vs. Z_{im} plot given in Figure 6.21 using the equation (6.7); where f is frequency and Z_{im} is imaginary part of the impedance. C_{LF} values were determined as 3.6×10^{-5} F for P3HT and 184×10^{-5} F for PW30.

$$C_{LF} = \frac{1}{2\pi f Z_{im}} \quad (6.7)$$

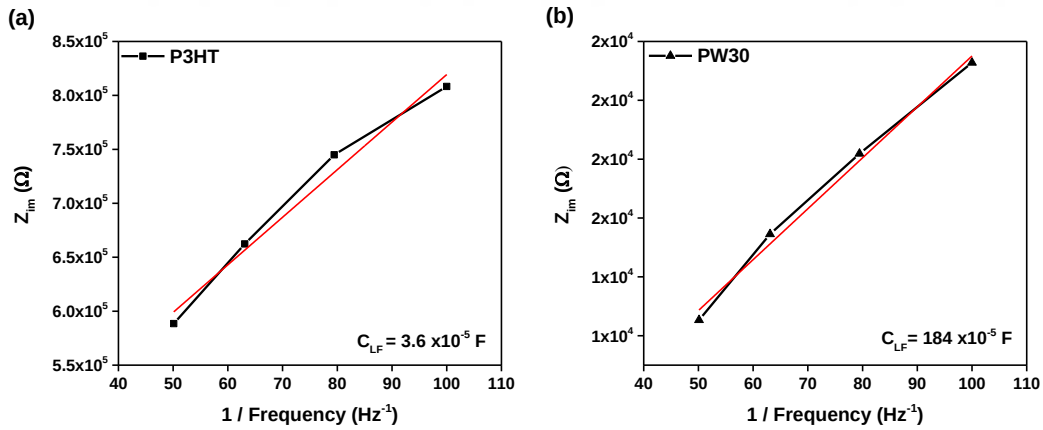


Figure 6.21 : Low-frequency capacitance (C_{LF}) values of (a) PW30 and (b) P3HT derived from Bode plots.

Double layer capacitance (C_{DL}) indicates the accumulation of charges at the electrode-electrolyte interface and it is calculated applying Bode magnitude ($|Z|$) at 0.16 Hz frequency ($\log \omega = 0$). As can be seen in Figure 6.22, C_{DL} is calculated as $5.7 \mu\text{F}$ and $105 \mu\text{F}$ for P3HT and PW30, respectively. EIS studies confirm that PW30 hybrid thin films have improved capacitive behaviour which means better storage.

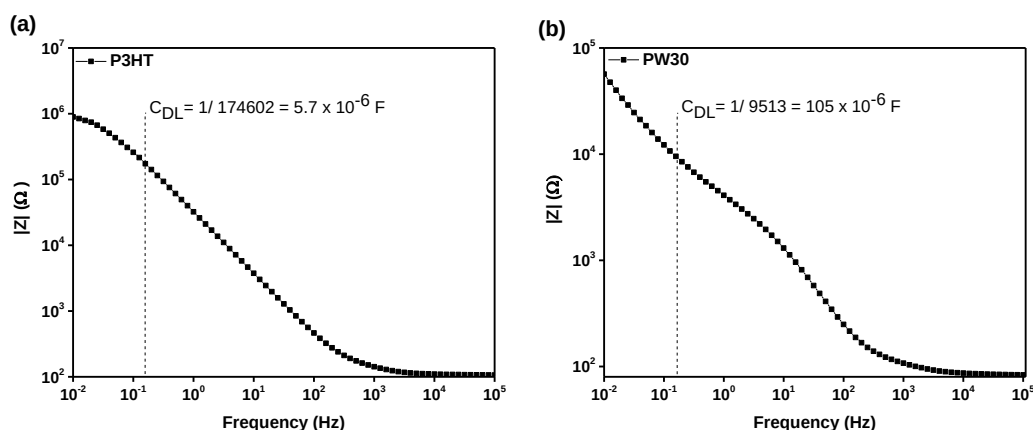


Figure 6.22 : Double layer capacitance (C_{DL}) values of (a) P3HT and (b) PW30 derived from Bode plots.

6.3.1 Electrochromic properties of complementary devices

A three-electrode system was used to electrochemical characterization of both P3HT and PW30. Considering the electrochemical measurements, two different complementary devices were fabricated using P3HT and PW30 as working electrodes and sandwiched with WO_3 film. The structure of the devices are given below (also given in Chapter 5);

DEVICE 1: GLASS / ITO / P3HT / GEL ELECTROLYTE / WO_3 / ITO / GLASS

DEVICE 2: GLASS / ITO / PW30 / GEL ELECTROLYTE / WO_3 / ITO / GLASS

Thin films were directly sandwiched with gel electrolyte, no sealing was applied to the solid state complementary devices. In order to determine the operation conditions, different potentials were applied to the complementary devices. As can be seen in Figure 6.23, in the neutral state (0V), device appears violet color since WO_3 film itself is almost colorless. When a positive bias (+1.4V) is applied to the P3HT coated ITO glass, the device turns bleach, whereas it turns violet again under negative bias (-1.4V). The reason for this switching from violet to bleach and redox mechanism have been already discussed in previous sections. As increasing the voltage up to +2V, bleach state of P3HT is obtained whereas WO_3 layer turns from transparent to deep blue (-2V). The coloration process of WO_3 under negative bias indicates the movement of Li^+ ions into the WO_3 . However, when negative bias (-2V) is applied to the P3HT coated ITO glass again, the device does not return to its transparent state and deep blue color is sustained, probably since P3HT film burned out at such a high potential. As a result, the optimum operation voltage range for reversible coloration has been

determined as $\pm 1.4\text{V}$. Since there is no further bleaching after $\pm 1.4\text{V}$, WO_3 film behaves like ion storage layer in solid state device in applied potential range. Same voltage range was applied to operate both devices, which are named as DEVICE 1 and DEVICE 2.

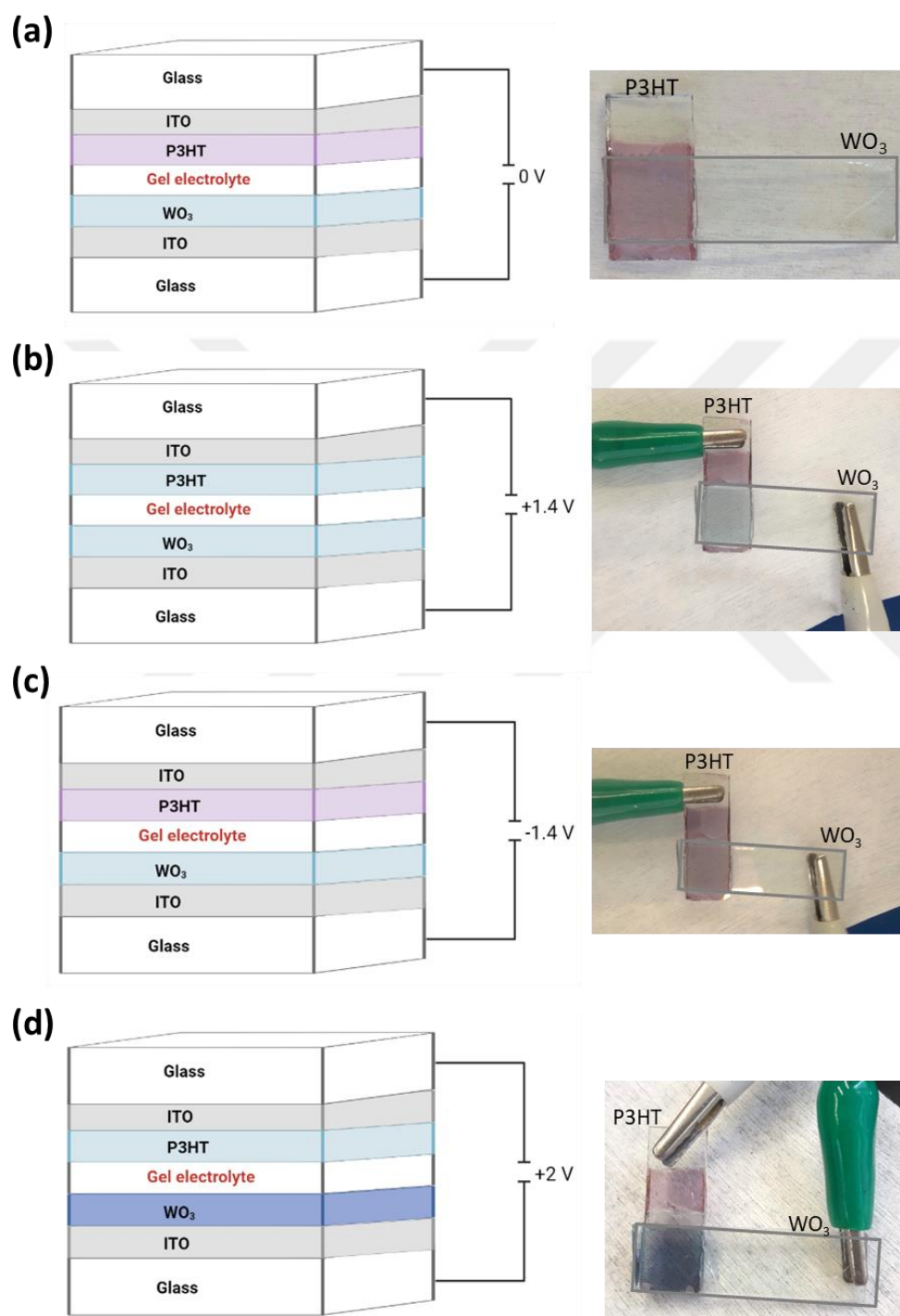


Figure 6.23 : Photographs of complementary devices displaying various colors with applied bias.

In order to confirm the color switching, UV visible spectroscopy was used. Transmission spectra and color of the P3HT based devices are given in Figure 6.24 and it is seen that transmission changes depending on the applied bias from 0V, -1.4V and +1.4V. The color switching behavior looks very similar for both devices; transmission values are higher at +1.4V than -1.4V in visible region (380–600 nm). On the other hand, transmission values are higher at -1.4V than +1.4V in IR region (700–1000 nm). In case of P3HT based device (coded as DEVICE 1), the largest transmittance difference ($\Delta T\%$) was found as 30% at 753 nm and 19% at 550 nm. In case of PW30 based device (coded as DEVICE 2), largest $\Delta T\%$ was found as 32% at 753 nm and 22% at 550 nm.

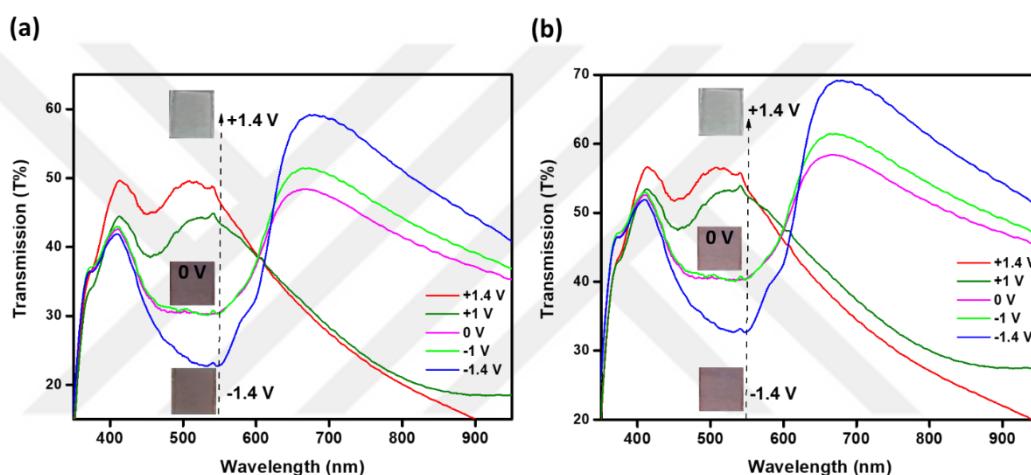


Figure 6.24 : Transmission spectra of (a) DEVICE 1 and (b) DEVICE 2 depending on the applied potential.

Cyclability and switching time are crucial parameters to determine the speed and electrochemical stability of the electrochromic device. Therefore, the long-term performance of P3HT and PW30 based complementary devices were measured by observing the transmittance change over time while continuously switching between the colored and bleached states at 550 nm. Chronoamperometric response of electrochromic devices is given in Figure 6.25 and Figure 6.26.

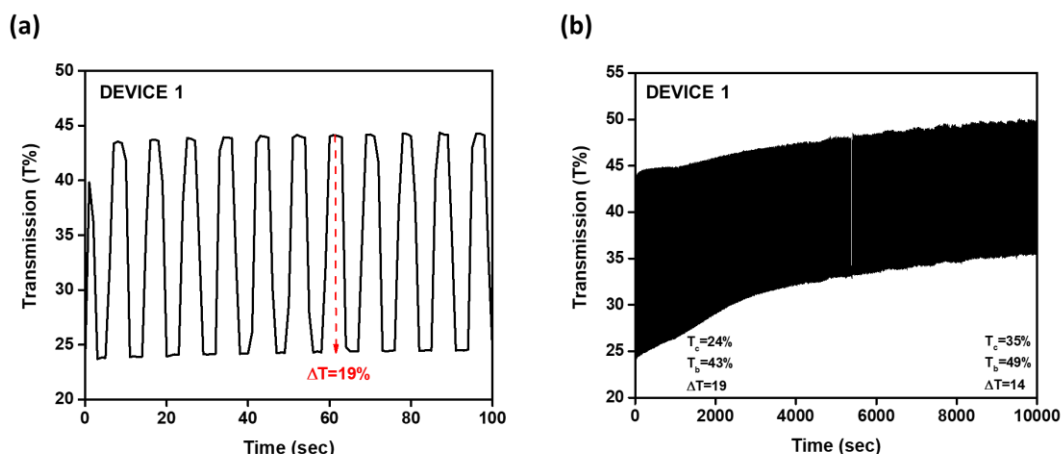


Figure 6.25 : (a) Optical contrast change through 10 cycle and (b) long term stability of P3HT based device with a residence time of 5 s in the range of $\pm 1.4V$.

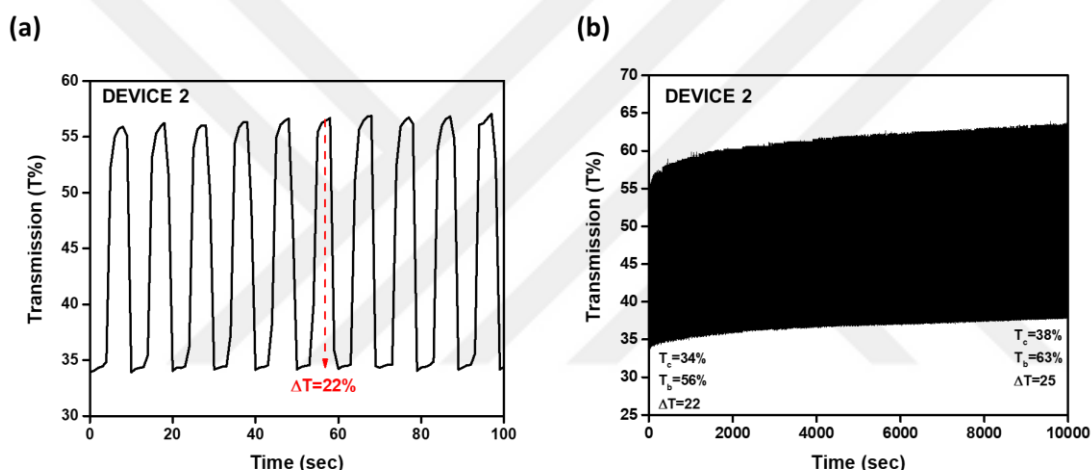


Figure 6.26 : (a) Optical contrast change through 10 cycle and (b) long term stability of PW30 based device with a residence time of 5 s in the range of $\pm 1.4V$.

For a better understanding of the switching response, a closer investigation was done. For the DEVICE 1, 2.40 s is needed to reach maximum transmission value (bleaching), whereas 1.53 s is needed to turn back to its colored state. For the DEVICE 2, 1.95 s is needed to reach maximum transmission value (bleaching), whereas 1.02 s is needed to turn back to its colored state. As obviously seen from Figure 6.27, a faster switching time is observed for DEVICE 2 even at the end of 1000 cycle.

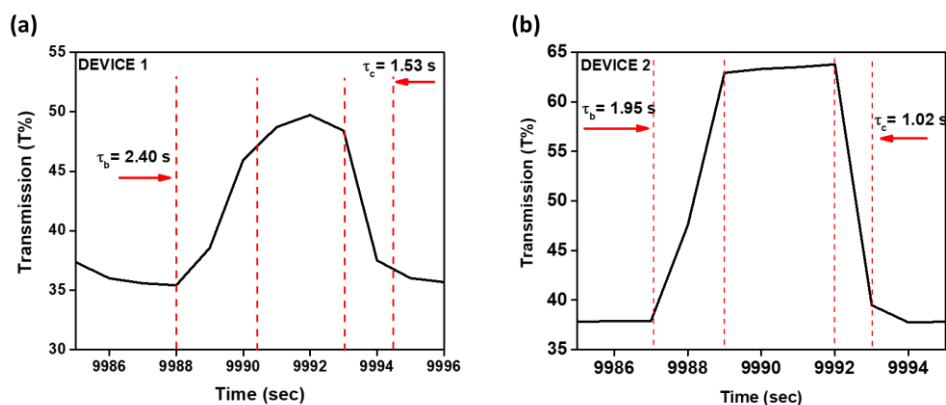


Figure 6.27 : Response time of (a) DEVICE 1 and (b) DEVICE 2 at the end of 1000 cycle.

Coloration efficiency, optical density and response time values were summarized in Table 6.5. In P3HT based device, the transmittance difference between the colored and bleach states gradually decreases from 19% to 14% through 1000 cycles (10,000 s). Correspondingly, optical density and coloration efficiency decrease 40% and 42%, respectively.

However, when PW30 is used as electrochromic layer, there is no change was observed in optical density at the end of 1000 cycle. Besides, coloration efficiency increases over time and response time improves. It means that PW30 based device switches 100 times during 10,000 s without almost any loss to the transmission values. This might be due to the increasing interface interaction at the PW30 layer over time. Hence, it can be said that PW30 based device operates more stable than P3HT based device.

Table 6.5 : The comparison of electrochromic performance parameters of complementary electrochromic devices.

Parameter	DEVICE 1		DEVICE 2	
	Initial	1000 cycle	Initial	1000 cycle
$T_{\text{bleach}} (\%)$	43	49	56	63
$T_{\text{color}} (\%)$	24	35	34	38
$\Delta T (\%)$	19	14	22	25
ΔOD	0.253	0.146	0.216	0.219
$Q_{\text{in}} (\text{mC cm}^{-2})$	0.902	0.900	0.640	0.603
$Q_{\text{out}} (\text{mC cm}^{-2})$	0.894	0.894	0.468	0.401
$\eta (\text{mC cm}^{-2})$	280	162	337	363
$\tau_{\text{bleach}} (\text{s})$	1.65	2.40	1.37	1.05
$\tau_{\text{color}} (\text{s})$	1.61	1.53	1.95	1.02

6.4 Thermochromic Behavior of P3HT Based Thin Films

Besides superior electrical and optical properties, conjugated polymers show reversible color change in oxidation state due to the solvent or temperature. In spite of the fact that temperature dependent color change of polythiophene derivatives is known in literature, there are a few studies which investigate the thermochromic behavior of polyalkyl thiophenes [166], [167].

Although not directly in the scope of this thesis, the thermochromic behavior of P3HT films has also been investigated. After the films are spin coated on glass substrates, evaporation of the 1,2 dichlorobenzene induces a color change, which means the orange solution transforms into purple thin films. For the thermochromic properties of P3HT based films, temperature-dependent spectral measurements were taken in the temperature range of 25°C-225°C by spectrophotometer and given in Figure 6.28. In Figure 6.28a, it is seen that P3HT film at 550 nm has a purple color and a transmittance value of 40% at 25°C room temperature. However, when the temperature increased up to 225°C, the color of the P3HT film turns into a yellowish color and transmittance increases to 57%. As for the absorption spectrum given in Figure 6.28b, the maximum absorption peak at 557 nm shifts to lower wavelengths (blue shift to 495 nm) as the temperature rises, and the purple colored polymer film turns into yellow. It is also worth to say that there is no significant optical change below 100°C, since there is no chain modification or orientation observed.

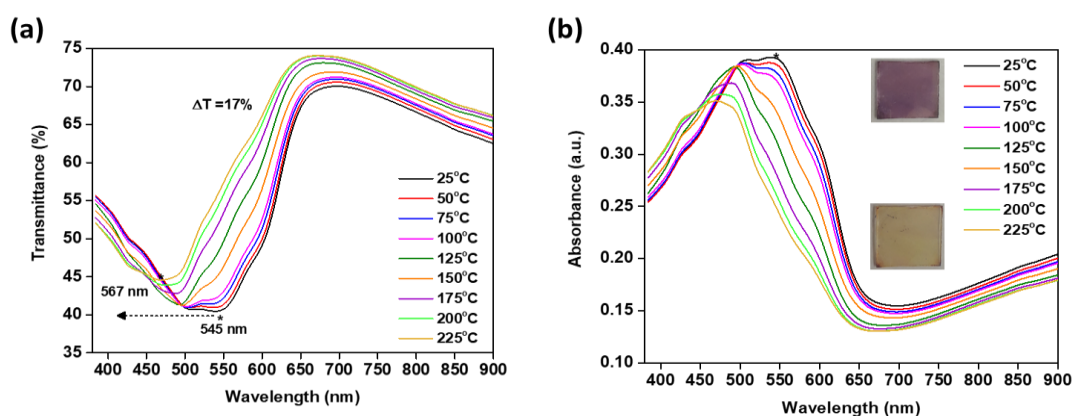


Figure 6.28 : (a) Transmittance and (b) absorbance change of P3HT with increasing temperature.

Figure 6.29 shows the change in transmittance during heating and cooling at a 550 nm constant wavelength. It is seen that, when the P3HT film is heated up to 225°C and

cooled back to room temperature, it returns to its initial transmittance value with an only 0.4% shift. This shows that the P3HT film can remain very stable even after heating to high temperatures.

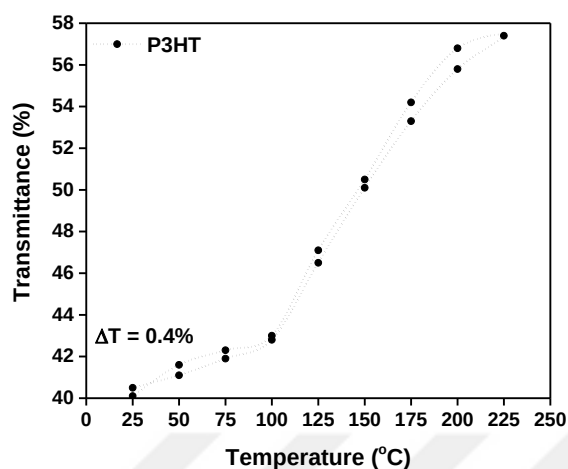


Figure 6.29 : Reversible color change of P3HT film as a function of temperature.

For the PW30 hybrid film, the change in transmittance and absorbance values is given in Figure 6.30. Comparison of thermochromic behavior of P3HT and PW30 is given in Figure 6.31, as well. As can be seen from Figure 6.30 and Figure 6.31, WO₃ doping has no effect on improving thermochromic properties. Above 100 °C, it is observed a dramatic increase in transmission of P3HT whereas it is observed a slight increase in transmission of PW30.

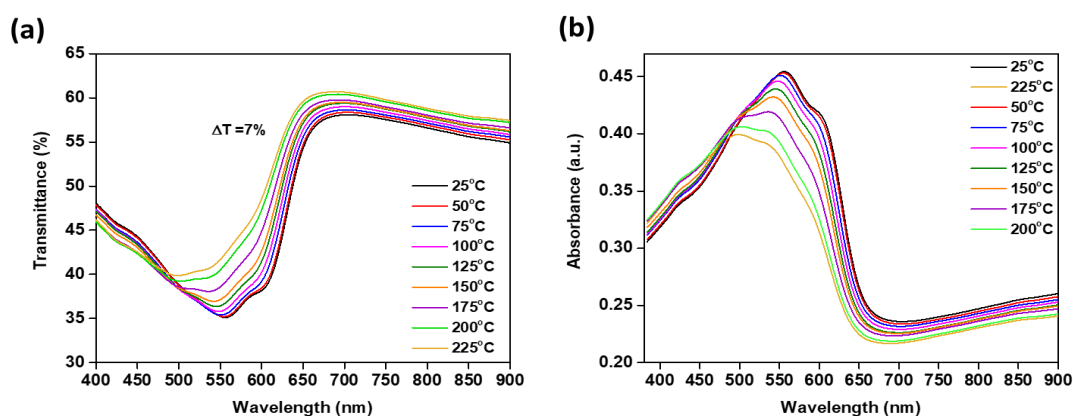


Figure 6.30 : (a) Transmittance and (b) absorbance change of PW30 with increasing temperature.

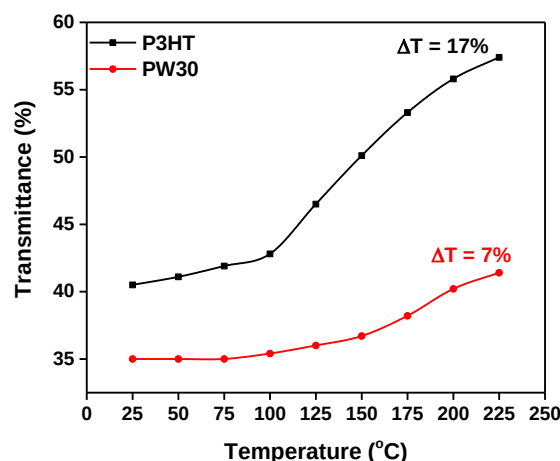


Figure 6.31 : Comparison of thermochromic behavior of P3HT and PW30 thin films.

Up to the present, there has been limited exploration into the development of hybrid organic–inorganic films that demonstrate thermochromism through charge-transfer formation. Thermochromic behaviour of oligothiophene derivatives such as P3HT are mainly due to the conformational changes instead of electronic interchain and intermolecular interactions [168], [169], [170]. The structure and distance of the repeating units or side chains (alkyl groups) can dramatically affect the thermochromic properties of the resulting polymers. From this point of view, the main mechanism of thermochromism is not the charge transport between WO₃ and P3HT. The attachment of WO₃ nanoparticles may be change the distance of repeating units and side chain conformation in three-dimensional space. Although the WO₃ addition improves the optical and electronic properties, it causes a negative effect on the thermochromic property as it changes the chain structure. Also, since the temperature dependent changes depend on the shape, size, or the particle distance [171], WO₃ particles may agglomerate at higher temperatures and may obstruct the thermochromic behavior.

Regarding these issues, as a future work, if P3HT and metal oxide dopant materials such as WO₃ can be chemically incorporated into the structure during synthesis, it is predicted that the thermochromic property might show different behaviors.

7. CONCLUSION

In this thesis work, it has been mainly focused on the application of P3HT based hybrid thin films in transistor and electrochromic solid state devices. The transition metal oxide WO_3 was doped into the semiconductor polymer P3HT in order to enhance its coloring, charge transport, and storage capabilities—but most significantly, to increase its chemical stability. When the literature is examined, it is seen that the doping process is generally carried out layer-by-layer coatings. In this study, unlike the literature, WO_3 powders were added directly to the P3HT solution, using a very easy and single-step method, called solution blending doping. In order to determine the optimum doping concentration, WO_3 powders with different weight percentages were added into P3HT solution and examined in comparison with undoped P3HT. Studies on doped and undoped P3HT films have shown quite different and remarkable results. Regarding of the electrical and optical measurements, it was determined that the best doping concentration is 30% WO_3 by weight.

More importantly, the largest gap in the literature is that the interactions between two materials in hybrid thin films have not been characterized in detail, while their performance in various application areas has been tested. However, the detailed investigation of the interaction mechanism between two materials is crucial for better understanding of any change in physical and chemical properties. For that purpose, the interaction between P3HT and WO_3 has been characterized thoroughly and based upon a scientific foundations. In this respect, it is thought that the outputs of this thesis work will make significant contributions to the literature.

Important findings have been obtained in this thesis study and allow the following conclusions to be drawn.

1. The optimum doping concentration can improve electrical, optical and electrochemical properties significantly. It has been observed that the excess amount of WO_3 doping results a decrease in electrical and electrochemical properties.

2. The surface morphology of the thin films were investigated by AFM and FEGSEM. It was determined that the average surface roughness increased with the addition of WO₃, and the particles began to agglomerate when more than 30% WO₃ was added.
3. When the hybrid thin films were tested in OFET chips, it was seen that the field effect mobility (μ_{FET}) increased from $5.3 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ to $5.6 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, and $I_{\text{ON}}/I_{\text{OFF}}$ current ratio was significantly increased 10 times for PW30 (30% WO₃ doped P3HT). Also, threshold voltage (V_{TH}) remarkably reduced from 40.1 V to 17.7 V. Regarding the improvement in performance parameters, PW30 shows the best transistor performance.
4. XRD and Raman spectroscopy reveals that 30 wt.% of WO₃ doping into P3HT generates new crystalline moieties on the P3HT-WO₃ hybrid chain resulting an increase in mobility.
5. Electrochromic performance of both PW30 and P3HT were also compared in a three-electrode system. 2-fold increase in coloration efficiency (from 220 cm²/C to 464 cm²/C) and improvement in optical density (from 0.24 to 0.26) was achieved in PW30 thin films compared to P3HT and long cycle device stability was significantly improved. The good cyclic stability is up to 1000 cycles.
6. The HOMO energy level for the PW30 hybrid film was calculated as -4.69 eV, whilst the HOMO energy level for P3HT was calculated as -4.73 eV. The increase in HOMO energy level with doping indicates that there are strong donor-acceptor interactions and effective charge transfer between P3HT and WO₃.
7. Efficient charge transfer between P3HT and WO₃ were also confirmed by peak quenching in photoluminescence.
8. The Tauc plot obtained from UV-Vis spectroscopy showed that the optical band gap decreased from 1.95 eV to 1.92 eV with doping. The increase in the optical contrast of PW30 hybrid film can be explained by narrower band gap and the increased HOMO level energy.
9. FTIR investigation showed that the charge transfer between P3HT and WO₃ is driven by the electrostatic interactions. XPS analysis makes us think that WO₃ particles might electrostatically attach to the unpaired electrons of sulphur element in the thiophene ring.

10. EIS measurements show that optimum amount of WO_3 doping improves the capacitive properties of P3HT. Low-frequency capacitance (C_{LF}) were calculated as 3.6×10^{-5} F for P3HT and 184×10^{-5} F for PW30. Double layer capacitance (C_{DL}) is calculated as 5.7 μF and 105 μF for P3HT and PW30, respectively. EIS studies confirm that PW30 hybrid thin films have improved capacitive behavior which means better storage property for capacitors.

11. After detailed examinations, it was determined that PW30 film performed better physically and chemically than P3HT, therefore it was used in the design of solid-state complementary electrochromic devices. It has been observed that the complementary EC device consisting of PW30 as active electrochromic layer works more stable even 1000 cycle, without compromising optical contrast and coloration efficiency, compared to the EC device consisting of P3HT as active electrochromic layer. It has also been found that PW30 based device responses in a shorter time.

These results provide important outputs that will shed light on the literature in designing conjugated polymer-based hybrid thin films for both transistor and electrochromic applications. The synergistic electrochromic and transistor performances are largely due to the effective electrostatic interactions between P3HT and WO_3 by simple mixing of two materials.

We believe that this systematic study and the results presented in this work will contribute to better understanding of doping mechanism in order to help fabrication of high performance transistors for flexible, solution-processed, low-cost, and large area electronics and chromogenics. Furthermore, it is thought that P3HT/ WO_3 organic-inorganic hybrid thin films can facilitate in development of electrochromic energy storage applications in near future.



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