Fabrication of Solid-State Electrochromic Device for Multifunctional Applications

Ph.D. THESIS

By Suchita Kandpal



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Fabrication of Solid-State Electrochromic Device for Multifunctional Applications

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Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

by Suchita Kandpal



DEPARTMENT OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE July 2023



Indian Institute of Technology Indore

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"Fabrication of Solid-State Electrochromic Device for Multifunctional Applications"** in the partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** and submitted in the **Department of Physics, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2019 to July 2023 under the supervision of Prof. Rajesh Kumar, Professor, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

03/07/2023 Signature of the student with date (Suchita Kandpal)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

03 July 2023 Signature of Thesis Supervisor with date

(Prof. Rajesh Kumar)

Suchita Kandpal has successfully given his/her Ph.D. Oral Examination held on.August 23, 2023

Signature(s) of Thesis Supervisor(s)

Date: 23 August 2023

Dedicated

to

my family

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-Suchily

Suchita Kandpal

Abstract

In the realm of modern science and technology, the field of nanoscience has emerged as a crucial catalyst for addressing numerous complex societal challenges. Over recent years, a notable increase in research areas with significant societal impact has been observed, with nanoscience and nanotechnology receiving particular attention, especially in the realm of nanodevices. This rapidly advancing field has been instrumental in generating innovative solutions to long-standing issues in domains such as energy and electronics. In the field of electronics, nanoscience and nanotechnology have gained increased significance due to their remarkable track record in applied research, particularly in sensing, energy storage, solar cells, memory devices, electrochromic devices, and more. The incorporation of nanotechnology in materials research has revealed numerous new features within compounds just by reducing them to the nanoscale. In this context, it is important to emphasize the importance of diverse materials for their functional utility across a wide range of applications, including oxides, polymers, and complex/hybrid compounds. Consequently, it has been demonstrated that better and more energy-efficient devices can be created by combining various inorganic and organic elements inside a well-designed framework.

Examining diverse aspects of materials and their practical applications, my research work, which is enclosed within this thesis, primarily centers around the fabrication of power-efficient electrochromic devices, understanding their working mechanism, and exploring their multifunctioning properties. Various inorganic, organic, and 2D-layered materials for making improved electrochromism in pre-designed displaylike structures have been explored. Structural morphologies and electrochemical properties of these materials were studied by varying different parameters in atomic layer deposition, hydrothermal and electrodeposition techniques. In this context, ALD deposition technique was used to deposit an atomically smooth and crackles thin film of nickel oxide. Thereafter, it was incorporated with organic electrochromic material i.e., viologen to fabricate a solid-state hybrid electrochromic device. The device was capable to change its color between transparent and blue states under the potential window of \pm 1.7V while taking less than 2s for toggling between the two-colored states. Its improved electrochromic behavior establishes the advantage over other methods through proper power utilization during color switching.

After its detailed study, the performance of the P3HT/EV-based organic electrochromic device was improved by doping with 2D-layered materials i.e., multi-walled carbon nanotubes (MWCNTs), molybdenum disulphide (MoS_2) and tungsten oxide/tungsten disulphide (WO_3/WS_2) nanocomposite. Their layered structure and the weak Van der Waals force present between these layers facilitate a large amount of charge movement between the electrochromic film and electrolyte promotes the high transfer rate of electrons, which was responsible to enhance the performance of the electrochromic device. Further, the effect of dopant concentration on the performance of the P3HT/EV electrochromic device was studied by taking different concentrations of MoS₂. The variation in electrochromic parameters as a function of dopant (MoS₂) concentration reveals that the highest (0.3 wt.%) MoS₂ doped device has faster switching whereas the lowest (0.1 wt.%) MoS₂ doped device has maximum color contrast and coloration efficiency under a very small external bias (±1.4V).

Additionally, a mixture of WS₂/WO₃, synthesized by hydrothermal technique was incorporated as a dopant with P3HT and EV active electrochromic layers. In-situ kinematics was performed to check the electrochromic performance of the device which shows the device is capable to switch its state in two wavelengths (visible ~ 515 nm and NIR ~ 800 nm) regions. A great color contrast ratio of 52%, fast switching time of less than one second along with excellent coloration efficiencies of 460 cm²/C and 288 cm²/C at these two wavelength regions shows the charge-facilitating nature of WS₂/WO₃ and make a device capable to modulate in dual-band region. Furthermore, the recorded cyclic voltammetry of the same device reveals its pseudocapacitive nature which was also validated

through galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements. It shows the specific capacitance value of the device is ~ 50 F/g at a current density of 1 A/g along with its fast response (charging/discharging) time and excellent energy density. Successful demonstration of its excellent capacitive performance along with the ability of electrochromic indicators paves the way for the integration of electrochromic energy storage indicators in various energy storage or energy-efficient buildings.

Further, a dual-purpose solid-state electrochromic diode was fabricated in P3HT/EV, pre-doped with MWCNTs and MoS₂. An asymmetric diodic I-V characteristic curve along with the enhanced electrochromic performance of the device was found which has been exploited for rectification applications. In-situ bias-dependent Raman spectroscopy has been performed to understand the operation mechanism of the electrochromic diode which reveals the formation of (bi-) polaron formation because of dynamic doping eventually leading to color change. A half-wave rectifier has been realized from the electrochromic diode which rectifies an AC voltage of frequency 1Hz or less making it suitable for low-frequency operation. This study will open a new possibility to design and fabricate multifunctioning and power-efficient electrochromic devices.

LIST OF PUBLICATIONS

(a) Peer-reviewed Journal (Thesis)

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List of Abbreviations

| Abbreviations | Full forms |
|--------------------|---|
| ACN | Acetonitrile |
| CE | Counter Electrode |
| CV | Cyclic Voltammetry |
| CIE | Commission Internationale de l'Eclairge |
| DCB | Dichlorobenzene |
| DI water | Distilled Water |
| EC | Electrochromic |
| ECD | Electrochromic Device |
| EIS | Electrochemical Impedance Spectroscopy |
| EV | Ethyl Viologen |
| FT-IR | Fourier Transform Infrared |
| FTO | Fluorine tin Oxide |
| GCD | Galvanostatic Charge Discharge |
| H_2O_2 | Hydrogen Peroxide |
| H_2SO_4 | Sulfuric acid |
| HNO ₃ | Nitric acid |
| IR | Infrared |
| ΙΤΟ | Indium Tin Oxide |
| LiClO ₄ | Lithium Perchlorate |
| MWCNTs | Multiwalled Carbon Nanotubes |
| MoS ₂ | Molybdenum Disulphide |
|------------------|------------------------------|
| NIR | Near Infrared |
| NiO | Nickel Oxide |
| РЗНТ | Poly(3-hexyl)thiophene |
| PPy | Polypyrrole |
| PEO | Polyethylene Oxide |
| PL | Photoluminescence |
| RE | Reference Electrode |
| SEM | Scanning Electron Microscopy |
| SR | Scan Rate |
| UV | Ultra-violet |
| WE | Working Electrode |
| WO ₃ | Tungsten Oxide |
| WS ₂ | Tungsten Disulphide |
| XRD | X-Ray Diffraction |

Chapter 1

Introduction

Rapid and revolutionary growth in nanotechnology has produced ground-breaking improvements in a variety of fields. Designing and synthesizing new nanomaterials is one major area of development. To synthesize nanomaterials with the required size, shape, composition, and surface qualities, researchers have created advanced controlled techniques[1–5]. The synthesis of nanomaterials at the atomic and molecular levels is now possible due to methods like chemical vapor deposition, sol-gel synthesis, self-assembly, and molecular beam epitaxy[6-9]. Design and production of nanodevices have made major advances in the field of nanotechnology especially due to real world applications[10-13]. Researchers have created new methods to create useful nanoscale devices with exact control over their characteristics and functions. Various electronic devices for application in optical and mechanical areas area created using methods like nanolithography, self-assembly, and bottom-up assembly. The development of nanoelectronics, nanophotonics, nanomechanics, and nanosensors, among other domains, has been made possible by these developments[14–18]. These technologies have a variety of uses in fields ranging from information technology and energy to healthcare and environmental monitoring. The significant development in the synthesis and fabrication of nanomaterials, characterization techniques, design and fabrication of nanodevices, nanomedicine, and energy applications have paved a way for transformative technologies and solutions across a wide range of industries, offering improved performance, efficiency, and novel functionalities. Immensely growing field of nanoelectronics has

inspired to take up the work in one such domain, i.e., electrochromism[19–27].

1.1 Nanomaterials in Various Fields

Nanomaterials are inherent constituent of the broad term "nanotechnology" which has significant impact on many different sectors, improving industrial production efficiency and creating new opportunities. Nanotechnology is the study and manipulation of matter at the nanoscale. Here are some of the synthesized nanomaterials showing different morphologies (Figure 1.1) that can be used in different applications[28–32]. Nanomaterials touch almost all disciplines as can be seen from following examples:



Figure 1.1: Electron micrographs of (a) polypyrrole, (b) carbon nanotubes, (c) tungsten oxide, (d) nickel oxide, and (e) molybdenum disulfide.

1.1.1 Physical Sciences

Nanoscience is important in physical sciences because it constitutes systems that allow observation and explanation of different physical processes that were previously unobservable in bulk materials. As an example, non-radiative transition is a critical phenomenon that has been effectively examined using Raman spectroscopy, proving to be a helpful approach. Non-radiative transitions in silicon

been detected nanostructures have using Raman spectroscopy[33,34]. Nanomaterials have unique features due to the quantum confinement effect, which does not exist in bulk materials, [35,36] Because these features become size-dependent when approaching nanometer scales, the concept of quantum confinement provides knowledge of diverse optical, electronic, and electrical phenomena in nanomaterials. The confinement effect changes energy levels when material dimensions reach the nanoscale range, resulting in discrete energy bands. Within nanomaterials, confined entities such as electrons, holes, phonons, and other bound states exhibit outstanding abilities, paving the way for applications in lasers, diodes, photovoltaics, and other fields. These applications are made possible by the combination of nanoscience and physical science.

1.1.2 Chemical Sciences

As shown by the recent development of many applications in the field, nanoscience plays an important part in different fields of chemical sciences. The development of nanoparticles allows significant developments in chemical research. The filtration of drinking water using nanopores in thin films of molybdenum disulfide is one significant application that shows the basic work of nanotechnology in chemical science. Highly sensitive and selective sensors are another explored field through nanoscience. Nanomaterials, such as quantum dots, nanoparticles, and nanowires, exhibit unique optical, electrical, and magnetic properties that can be used for sensing applications[37–43]. These nanosensors can detect and quantify various gases, pollutants, and biomolecules, with high sensitivity and specificity. The integration of nanomaterials with traditional sensing platforms has led to the development of miniaturized and portable sensors for real-time monitoring environmental, biomedical, and industrial in applications.

Other than sensors, nanoscience has greatly advanced catalysis, which is the acceleration of chemical reactions by catalysts. Nanomaterials offer a high surface area-to-volume ratio, providing a large number of active sites for catalytic reactions. This increased surface area allows improved reaction rates, selectivity, and efficiency. Nanocatalysts have been developed for various chemical reactions, including hydrogenation, oxidation, and carbon dioxide conversion/ neutralization. The precise control over the composition, size, and shape of nanoparticles allows the design of highly efficient catalysts with tailored properties for specific reactions[44,45].

1.1.3 Biological Sciences

Nanoscience has made important contributions to biological research by changing our understanding of biological processes and enabling the development of novel instruments and technologies. It plays an important role in the field of medicine by developing nanomedicine. Nanoparticles, nanocarriers, and nanoscale devices have been developed to carry medicines, target specific cells or tissues, and give medicines with controlled release[46-50]. These nanoscale platforms provide benefits such as better drug solubility, bioavailability, and targeted delivery, resulting in enhanced effectiveness for treatment and decreased side effects. Additionally, nanotechnology-based strategies, such as nanoscale drug delivery systems and nanofabrication techniques are employed to enhance tissue regeneration and promote healing. The interdisciplinary field of nanoscience and biology enhances the understanding of numerous applications such as DNA sequencing, transfer of genes, protein engineering, and nanoscale imaging. It opens up novel opportunities for understanding complex biological phenomena and allows researchers to investigate biological processes with neverbefore-seen accuracy at the molecular and cellular levels.

1.1.4 Materials Science

Nanoscience has transformed material science by enabling the design, fabrication, and characterization of materials at the nanoscale. The ability to change matter in such small dimensions has allowed the discovery of a wide range of novel characteristics and functionalities in materials. Nanomaterials, such as nanoparticles, nanocomposites, and nanowires, exceed their bulk counterparts in mechanical, thermal, electrical, and optical properties. These materials are used in various kinds of industries, including electronics, energy, aerospace, and healthcare. Nanotechnology offers exact control over material size, shape, composition, and structure, which creates specific characteristics and increased performance[14,48-56]. Understanding nanoscale phenomena and the ability to create materials at this level has paved the path for advances in nanoelectronics, energy storage, catalysis, and other fields.

1.1.5 Engineering

Engineering plays a crucial role in the fabrication of electronic devices for commercial use once materials have been prepared for a variety of application. Scientific industries today offer flexible, rollable, and stretchable electronic gadgets that can be incorporated into a variety of applications. By improving their flexibility, lightness, and stability, these device engineering adjustments increase their usefulness in daily life, including electronics, healthcare, aircraft, security and defense. The performance of electrical devices is further enhanced for the various applications by the introduction of effective materials like graphene and MXenes, which are 2D nanomaterials[57–60]. For many engineering applications, including memory, energy storage, sensing, photovoltaics, solar cells, and electrochromic devices, liverse engineering methods are used[19,35,61–63]. Electrochromic

devices (ECDs), which change their optical characteristics in response to electrical bias, offer enormous potential for use in electronics and display systems. ECDs that exhibit optical modulation in response to externally applied electrical bias. In order to improve performance, it is essential to understand the greater surface area nanostructure of the materials utilized in ECDs which will be covered in the next chapters.

1.2 Electrochromism

The phenomenon of reversible color change in materials on the application of an electrical bias or potential is known as electrochromism[5,9,64–69]. It's an interesting optical characteristic that has received a lot of interest in the field of materials science and technology. The ability of electrochromic (EC) materials to change their optical properties in response to an electrical input allows for dynamic control over their optical appearance. This unique characteristic has resulted in the development of ECDs, which have applications in a variety of industries such as smart windows, displays, electronic paper, and energy-efficient technologies (Figure 1.2)[5,68,70-77]. The reversible intercalation or ion insertion/extraction process within the material's structure provides the basis for electrochromism.



Figure 1.2: Applications of electrochromism in various technologies

The ECDs can be made up of many layers, including an EC layer, an electrolyte, and counter-electrodes. When an electrical potential is applied, the EC layer undergoes a redox reaction, which is accompanied by variations in light absorption or transmission. This causes the material's color to vary, which may be adjusted by changing the applied voltage. EC materials can exhibit various colored states, allowing for a wide range of optical effects. They can switch between transparent and opaque states or between many colors while remain (semi) transparent in nature. Different colored states depend on the material composition, structure, and applied potential. The ability to control the color or transparency of material through electrical means opens numerous applications in areas such as architecture, the automotive industry, aerospace, and smart devices[60,69,78-81]. Significant progress in the fabrication of advanced electrochromic materials with enhanced performance, durability, and efficiency has been made. In this thesis, 2D-layered materials have been used with transition metal oxides and conducting polymers to improve their performances in ECDs.

1.3 Electrochromic Materials

When electron transfer takes place through reduction (a gain of electrons) or oxidation (a loss of electrons), each EC active material exhibits a different optical absorption band and shows a different colored state. Based on the electron transfer mechanism, these materials can be categorized as either n-type or p-type EC materials. The "n-type or cathodic" and "p-type or anodic" EC active species are two families of materials used for fabricating ECDs. The redox polarity of the materials, which defines their electrochromic characteristics, is the basis for this categorization. These families include a broad spectrum of both organic and inorganic compounds.

1.3.1 Organic Electrochromic Materials

Organic molecules are one of the classes of EC active materials and are widely used in molecular electronics for a variety of purposes. Using organic materials in devices is simple because it involves simpler methods like spin coating, drop casting, and spray coating. A lot has been achieved from the invention of conducting polymers of thiophene, pyrrole, aniline, and their derivatives into various fields due to the presence of conjugated pi-electrons that enable the delocalization of electrons the along molecular backbone[41,53,70,82–92]. This delocalization allows for efficient charge transfer and redox reactions, leading to the modulation of optical properties. By applying an external electric potential, these materials undergo bias-induced reversible oxidation or reduction reactions, resulting in color changes.

Polythiophene (P3HT) lies in the "anodic" category of organic materials, which changes its color during the positive voltage from magenta to translucent to light blue due to the formation of polaron and bipolaron species in the thiophene polymer. On the other side, viologens are "cathodic" EC organic material that exhibits EC property while undergoing reversible redox reaction due to the formation of EV²⁺ and EV^{+•} (Viologen radical ion)[93,94]. Other than these materials polyaniline, poly(3,4-ethylenedioxythiophene) (PEDOT), polypyrrole, polycarbazole, and their derivatives are the available organic EC materials that offer unique electrochromic properties and applications in various areas. In this thesis, polythiophene, viologen, and polypyrrole have been used to fabricate ECDs, which will be discussed in the next chapters.

1.3.2 Inorganic Electrochromic Materials

In addition to organic EC materials, which are made of organic molecules or polymers, inorganic EC materials belong to another class of EC materials that are made of inorganic compounds or transition metal oxides. Because of their high stability, fast response times, and durability, these materials have acquired significant attention and importance in the field of optoelectronics. Tungsten oxide (WO₃) is an example of inorganic "n-type" electrochromic material, which changes its color between transparent and blue states when an electric current is applied[95]. Because of this ability, it has become an important inorganic EC material to fabricate smart windows, which can dynamically manage the quantity of light and heat entering a structure, resulting in enhanced energy efficiency. Nickel oxide (NiO) is the other inorganic "ptype" EC material, which can switch between translucent and reddish colors[96-99]. EC films based on NiO are extensively used in rear-view mirrors and smart windows to change reflectivity and transparency, resulting in improved visibility. Prussian blue, titanium oxide, cobalt oxide, iron oxide, etc are the other inorganic EC active materials that reversibly change their colors under biased conditions and take part in applications of electronic displays, sensors, and energy storage devices [2,38,57,100–105].

1.3.3 Herbal Electrochromic Materials

Herbal EC materials are an attractive and emerging category of materials that make use of the unique features of natural plant-based substances for electrochromic applications. These materials originate from plants such as leaves stems, roots, and flowers and have the ability to display bias and redox-dependent change in color. Nowadays, research is going on to investigate the utilization of extracts derived from natural flowers, such as hibiscus, aloe vera, etc. for the development of ECD[106,107].

1.4 The Electrochromic Device

As mentioned above, a typical ECD consists of two transparent conducting electrodes sandwiching at least one EC layer and a counter layer which are separated by an ion-conducting layer[54,84,108,109]. In a single ECD, the EC active material is deposited onto one transparent electrode, such as FTO (Fluorine-doped Tin Oxide) or ITO (Indium Tin Oxide) while the other electrode remains bare. The electrolyte will be placed between the two electrodes as a gel-like substance such as polyethylene oxide (PEO). The gel acts as a matrix, allowing electrolyte ions to move more freely.



Figure 1.3: Generic structure of an electrochromic device

In a double-layer device, both electrodes must be coated with EC active material and assembled in the device geometry using the same techniques (Figure 1.3). To enable the device to work in an active state in each polarity, it is necessary that both materials show complementary redox activity. The fabricated devices in their crossbar geometry can be utilized to evaluate their performance depending on their applications. Based on their properties and performance characteristics, these performance tests determine the suitability of the EC device for applications such as EC smart windows, protective shields, rear-view mirrors, supercapacitors, filters, etc.

1.4.1 The Device Performance Parameters

The performance of the fabricated ECD is checked by evaluating the various performance parameters. In-situ bias-dependent UV-Vis spectroscopy, electrochemical measurements, and Raman measurements are used to record these parameters which gives an idea about their utility. These necessary parameters are discussed here in detail.

1.4.1.1 Switching Time

Switching time measurement of an ECD is a key factor to determine how well the device will function in real-life applications. When an external bias is applied, a good ECD should be able to switch quickly from one colored state to another (or from a bleached state). The major optical change, either in absorption or transmission, which is differ by at least 90% between the two-color states at a particular wavelength, determines the switching time of the device. if sufficient contrast is seen, it is also acceptable to record a change of ~70% absorbance change to estimate switching time. The switching time is evaluated for both the ON state (transition from the bleached to the colored state) and the OFF state (transition from the colored to the bleached state) in order to evaluate the device's performance. The thickness of the material, the type of electrolyte, the composition of the material, and the conductivity of the sample also affect the switching time.

1.4.1.2 Color Contrast Ratio

The color contrast (CC) ratio is a mathematical quantity that can be used to quantify the visible optical changes that occur during the modulation of an ECD. This measurement is achieved by performing in-situ optical spectroscopy on the device or electrode during the color-changing process at a specified wavelength. For calculating the net change in the transmittance at the particular wavelength as the device changes between two colored states calculate the CC ratio. The below-mentioned equation (Eq. 1.1) is used to calculate the CC ratio of the device in percent.

Color Contrast Ratio(%) =
$$\frac{(T_f - T_i)}{T_i} \times 100$$
 (1.1)

where T_f , T_i are the initial and final transmittance values displayed by the device. Alternatively, this equation is also applicable to the initial and final absorbance values of the device.

1.4.1.3 Optical Density

The change in the optical property at a particular wavelength causes a change in the material's optical density (OD), which is expressed directly in terms of absorbance and logarithmic of the inverse of transmission expressed in the mentioned equation.

$$OD = A \tag{1.2}$$

$$OD = \log_{10}(\frac{1}{r})$$
 (1.3)

1.4.1.4 Coloration Efficiency

Coloration efficiency (η_{ce}) is one of the most important parameters for quantifying the performance of an ECD. At a given wavelength, the η_{ce} represents the ratio of the change in optical density (OD) between the colored and bleached states to the charge injected or extracted per unit area of the working electrode. Eq. (1.4) represents this relationship[110,111].

$$\eta_{ce} = \frac{\Delta OD(\lambda)}{Q} \tag{1.4}$$

where, $\triangle OD$ refers to the difference in absorbance values between the initial and final state of the ECD in two different colored states and Q indicates the charge density involved in the device's switching process. It can easily be calculated by obtaining the slope of the OD vs Q curve. A larger η_{ce} value implies that the device consumes less power to switch and retain a given colored state and is more suitable for commercial applications, as it achieves coloring and bleaching states more efficiently.

1.4.1.5 Stability/Cycle life

The stability of a device is an important parameter that determines its reliability which helps in knowing how long it can work. An ECD undergoes repeated cycles of coloration and bleaching, making it essential to evaluate its stability to ensure consistent performance over time. The stability of an ECD can be affected by various factors, including the choice of materials, fabrication techniques, environmental conditions, and operational parameters. Therefore, by carefully evaluating these parameters, the stability of the ECD can be quantified, which is an essential requirement for practical applications.

1.4.2 Multifunctional applications

In recent years, research in the area of ECDs has risen due to its multifunctional application especially in the area of energy generation, conversion and storage[20,111–117] which can be summarised in the schematic in Figure 1.4 below.



Figure 1.4: Electrochromism in various applications

1.4.2.1 Electrochromic Rectifier

An EC rectifier is a device that combines the functionalities of both an ECD and a rectifier. It exhibits the property of modulating its optical properties, such as color or light transmission, in response to an applied electrical bias, while also rectifying the input sinusoidal signal of electrical current. This unique combination makes EC rectifiers highly versatile and applicable in various fields. An ECD fabricated using organic EC conducting polymers P3HT and EV (doped with MoS₂/MWCNTs composites) shows reversible color modulation between magenta and blue colors when a bias of \pm 1.4V is applied[83]. The doping of MoS₂/MWCNTs makes it suitable for the rectification of low-frequency AC signals, which will be discussed in detail in the next chapters.

1.4.2.2 Electrochromic Supercapacitor

An EC supercapacitor is a hybrid device that combines the characteristics of both an ECD and a supercapacitor. It possesses the capability to store and deliver energy, while also exhibiting the ability to modulate its optical properties. Many transition metal oxides such as WO₃ have many oxidation states, which allow charge storage inside the material, making it useful for energy storage applications[118–124]. The chrono-amperometric response of ECDs is a useful measurement, which quantifies the amount of charge required to cause chromic modulation and increases the charge storage capacity of various devices. A composite of WS₂/WO₃ was used in the current research work with organic EC material to fabricate an energy storing ECD, which will be discussed in the upcoming chapters.

1.4.2.3 Electrochromic Memory

Electrochromic memory refers to a type of memory technology that utilizes the color-changing properties of EC materials to store and retrieve information. It takes advantage of the reversible and controllable electrochemical processes occurring within the electrochromic materials, allowing them to switch between different color states representing binary data (0 and 1). This unique characteristic makes EC materials promising candidates for optical memory applications. By applying an external electrical bias, the EC material can be selectively switched between its distinct color states, encoding information in the form of binary data. The stored information remains unaffected even after the power is removed, enabling non-volatile memory operation[40,125–128]. This unique characteristic makes EC materials promising candidates for optical memory applications. Current research work has been inspired by abovementioned application-oriented properties and the ability to display multifunctional applications. The research work has revolved around some main objectives as mentioned below.

1.5 Objectives

Main Objectives of the Presented work are as Follows:

- To develop an understanding of electrochemical-based electrodes for EC applications and their device fabrication.
- To utilize 2D layered materials for the fabrication of EC solid devices and investigate their role in enhancing the device's performance in EC and other diverse fields.
- To understand the mechanism of color change during the device's operation using in-situ techniques vis-à-vis, UVvis, and Raman spectroscopy.
- To redesign an organic ECD for enhanced performance by introducing a compatible counter ion, while also investigating the suitability of inorganic material for use in EC and energy storage applications.
- Optimizing the concentration of 2D layered materials in organic ECDs to make them flexible.
- Designing improved all-organic ECD by incorporating novel synthesized EC material and investigating its performance in both solid, flexible, and large-area electrodes.

1.6 Organization of Thesis

The above-mentioned studies (detailed results and discussion with experimental methodologies) have been complied in the thesis by adopting the following chapter-wise plan:

- Chapter 1 (the current chapter): Provide an overview of the pertinent topics related to the thesis work and establish the objectives that the thesis aims to achieve.
- Chapter 2: Deals with the details of the experimental methodology used for the experimental work carried out along with details of various experimental parameters and procedures followed for the fabrication of EC materials. It

also summarizes details of various equipment used for characterization.

- Chapter 3: It presents the work related to ECDs fabricated using ethyl viologen and it's all organic (with P3HT) and hybrid (with NiO) devices by the doping of multiwalled carbon nanotubes (MWCNTs) in different device paradigms and their corresponding performances.
- **Chapter 4:** It deals with the effect of MoS₂ nanoflower and its varying concentration in all-organic ECDs and corresponding applications.
- Chapter 5: It describes the role of WS₂ and WO₃ with allorganic and hybrid ECDs. A detailed study of the electrochemical and electrochromic properties of these devices has been discussed in this chapter.
- Chapter 6: It provides the study of multifunctional ECD to show EC rectifiers and EC supercapacitors with excellent performance of the devices. Certain rectifying and energy storage parameters of the devices have also been discussed which are beyond electrochromism.
- Chapter 7: It summarizes all the conclusions drawn based on the research work reported above. This also includes future scope of works that may be carried out to enhance the understanding in the field.

Chapter 2

Experimental Details

This Chapter provides a comprehensive overview of the methodology employed to fabricate various samples such as 2D layered materials, electrodes, and devices. Additionally, it will also cover the range of experiments that we used to characterize and explore their applications. Details of the instruments including X-ray diffraction (XRD), Scanning electron microscopy (SEM), Ultraviolet-Visible spectroscopy (UV-Vis), Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Electrochemistry and Raman spectroscopy have been provided. This chapter will also cover the fundamentals of electrochemistry i.e., voltammetry (CV), chronoamperometry, electrochemical cyclic impedance spectroscopy (EIS), and galvanostatic charge/discharge. These details will be provided in two different parts (sample preparation and instrumentation) as discussed below.

2.1 Sample preparation techniques

2.1.1 Hydrothermal technique

The term "Hydrothermal" derives from the combination of the words "hydro" and "thermal" which refers to a method of preparing nanocrystals through chemical reactions at high temperature and high pressure in a sealed aqueous solvent[129,130]. This process involves a Teflon beaker placed within a tightly sealed stainless-steel case, which is placed inside an oven/furnace reaching a maximum temperature limit of approximately 200°C. That high temperature creates high pressure, which plays a significant role to grow of nanostructures. Initially, the precursor solution is stirred gradually with the help of a magnetic stirrer to achieve a homogeneous mixture. Then it is transferred to the Teflon bath and sealed inside the stainless-steel chamber for further heat treatment in the oven (Figure 2.1). Externally controlling parameters such as time, and heating/cooling rates determine the shapes and size of the grown nanostructures.



Figure 2.1: Schematic illustration of a hydrothermal setup

One of the key advantages of the hydrothermal method is the precise control over crystal growth such as size, shape, and morphology of nanostructures by adjusting the temperature, pressure, and reaction time. This method is also compatible with a wide range of precursor materials, solvents, and substrates which enables the synthesis of various types of inorganic nanomaterials including oxides, sulfides, and metal nanoparticles. The Disadvantage of this method is the requirement of the sealed environment limits the scalability and increases the complexity of the experimental setup. The cost of acquiring and maintaining such vessels restricts the synthesis in large-scale production.

2.1.2 Electrodeposition technique

The term "electrodeposition" refers to the growth of thin films at the interface between the electrode and the electrolyte, driven by the flow of electric charge. In electrochemistry, a three-electrode system is chosen to facilitate the flow of charge using an external power source. This three-electrode setup contains the working electrode (WE), reference electrode (RE), and counter electrode (CE) connected through a conducting electrolyte medium within an electrochemical cell containing deposition precursors (Figure 2.2)[131].



Figure 2.2: Schematic diagram of electrodeposition setup with three electrodes

The CE and RE consist of Pt-wire and Ag/AgCl electrodes whereas the conducting substrates such as ITO/FTO and carbon cloth were used as a WE. Different morphology of thin films can be obtained by selecting the control parameters such as input voltage or current, electrolyte

concentration, and deposition time. The electrodeposition technique has unique advantages including homogenous and uniform film, strong adhesion on substrate, improved stability, and thickness control, which is a necessary requirement to fabricate devices in various applications[81,132].

2.1.3 Spin coating

Spin coating is one of the methods used to deposit thin films from a liquid state of material and its effect depends on the initial state of the material and the properties of the substrates[133]. In spin coating, a small quantity of the material is deposited onto the substrate, when it is subjected to the spinning motion (Figure 2.3). The substrate is attached to the spinning rotator, accelerates with a high speed, and the material spread uniformly over the substrate to form a film[87]. The thickness of the film depends on the solution concentration and the spinning speed of the rotator.



Figure 2.3: Schematic illustration showing the different stages of spin coating.

2.1.4 Drop-casting technique

The drop-casting technique is another method used to deposit a thin film by applying a liquid solution of material in droplet form. It is a relatively simple and versatile technique that involves placing a small droplet of the material onto the substrate surface using a pipette (Figure 2.4). The droplet spreads and assembles into a thin film due to the evaporation of the solvent and leaves behind the solid film of the material[134]. The thickness of the film can be controlled by adjusting the concentration of the solution and the volume of the droplet still achieving the uniform thickness across the entire substrate is challenging as the droplet tends to spread unevenly during the drying process.



Figure 2.4: Schematic representation of drop casting technique

2.2 Materials Synthesis

2.2.1 Molybdenum Disulfide (MoS₂)

The MoS₂ nano-flowers have been synthesized by a facile one-step hydrothermal route. In a typical synthesis, 1.7 g of ammonium heptamolybedate tetrahydrate [(NH₄)6Mo₇O₂₄.4H₂O] and 3 g of thiourea (CH₄N₂S) were dissolved in 60 mL deionized water by continuous stirring for 30 minutes. A homogeneous and colorless solution was obtained, which was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was heated to 220 °C in an oven for a period of 24 hours and then cooled down to room temperature. The MoS₂ nanoflower sample, in the form of a black-colored product, was collected after centrifugation and was washed with deionized water and ethanol several times. At the end, the reaction product was dried using a freeze dryer at -80 °C in a vacuum.

2.2.2 Tungsten Disulfide/Tungsten Oxide (WS₂/WO₃)

A facile one-step hydrothermal method was used for the synthesis of WS_2/WO_3 nanoflakes. The synthesis was performed using 1:3 weight ratio of ammonium paratungstate [(NH₄)10(H₂W₁₂O₄₂).4H₂O] and

thiourea [(NH₂)₂CS]. The precursors were dissolved in 70 mL of deionized water by continuous stirring for 30 minutes. A homogeneous and colorless solution was obtained after stirring. The solution was transferred into a 100 ml Teflon-lined stainless steel hydrothermal reactor. The reactor was heated to 240 °C in a muffle furnace for 3 h and then allowed to cool down to room temperature. The nanoflake sample in the form of a greyishblack precipitate was collected after centrifugation and then washed with de-ionized water and ethanol several times. The reaction product was dried overnight using a vacuum oven at 60 °C.

2.3 Electrode preparations

2.3.1 Poly (3-Hexylthiophene), P3HT film deposition

- 1. The ITO/FTO-coated glass substrates were cleaned with ultrasonication using acetone, ethanol, and distilled water successively prior to use.
- 0.3wt % P3HT was dissolved in dichlorobenzene (DCB) and prepared a homogeneous solution.
- 50μL of the prepared solution was spin-coated on ITO/FTO substrate for 120 s at 500 rpm.
- 4. The above-prepared film was dried at 80°C for 1 hour in the oven.

2.3.2 Ethyl Viologen (EV) film deposition

- 1. 4wt% ethyl viologen dipercholrate (EV) dissolved in acetonitrile solvent and stirred for 10 minutes to make a homogenous mixture.
- 5 wt.% polyethylene oxide (PEO) gel was prepared in acetonitrile (ACN).
- The prepared PEO solution was filtered through a 0.45μm PTFE filter and adding it to the EV solution.
- After preparing both solutions, EV solution (prepared in step 1) was mixed with PEO solution in a 2:3 ratio by the use of vortex, and 5µL prepared solution was drop-casted on the ITO/FTO

coated glass substrate, which was patterned by the double-sided tape.

2.3.2.1 Multiwalled carbon nanotubes (MWCNTS) doped Ethyl Viologen (EV) film deposition

- 1. 0.1wt% MWCNTs were dissolved in acetonitrile (ACN).
- 5μL mixed solution (4wt.% EV + 5wt.% PEO + 0.1 wt.% MWCNTs) was drop casted on ITO/FTO substrates patterned with the double-sided transparent tape.

2.3.2.2 Molybdenum disulfide (MoS₂) doped Ethyl Viologen (EV) film deposition

- 4wt% ethyl viologen dipercholrate (EV) and 0.1wt% MoS₂ dissolved in acetonitrile solvent and stirred for 10 minutes to make a homogenous mixture.
- 5wt% PEO solution in acetonitrile was prepared and filtered through a 0.45µm PTFE filter.
- After preparing both solutions, EV solution (prepared in step 1) was mixed with PEO solution in a 2:3 ratio by the use of vortex and 5µL prepared solution was drop-casted on the ITO/FTOcoated glass substrate.

2.3.2.3 Tungsten disulfide/Tungsten oxide (WS₂/WO₃) doped Ethyl Viologen (EV) film deposition

- 1. A solution of 0.1wt% (WS₂/WO₃) nanoflakes was prepared by dissolving them in acetonitrile (ACN).
- A mixed solution containing 4wt.% EV, 0.1 wt.% (WS₂/WO₃) and 5wt.% PEO was drop casted onto ITO/FTO substrates that had been patterned with double-sided transparent tape.

2.3.3 Nickel Oxide (NiO) film deposition

- 1. Nickel Oxide thin film was deposited by the atomic layer deposition (ALD) technique over FTO/Silicon substrates.
- 2. The substrates were placed in the reactor and synthesis was conducted at a temperature range of 160°C to 180°C.
- 3. Remote oxygen plasma with a power of 3000 W (frequency range of 1.9-3.2 MHz) was used as a counter-reagent (oxidizer).
- 4. NiCp2 pulse time, oxygen plasma processing time, and purge time was maintained at 1s, 14.5s, and 5s.
- 5. Prior to each stage of the nickel-containing reagent pulse, the reactor was purged with nitrogen for 10s.
- 1500 ALD (atomic layer deposition) cycles were performed to uniformly coat the substrates.

2.3.4 Tungsten Oxide (WO₃) film deposition

- 1. 1.25 g of tungstic acid (H₂WO₄) was added to the solution of 30 mL DI water and 10 mL H₂O₂ under stirring at 90°C. The prepared solution become transparent after a few minutes and then diluted with water to make 0.05 M.
- Another 3 mL aqueous solution was prepared by adding 0.035 g of thiourea [SC(NH₂)₂] and 0.040 g maleic acid (C₄H₄O₄) and then add aqueous HCl (3 M, 2mL), acetonitrile (18 mL) and (0.05 M, 1mL) H₂WO₄ solution prepared in the first step.
- Resultant solution was transferred into a Teflon autoclave containing FTO/carbon cloth substrates and heated at 180°C for 3 hours.
- 4. Lastly, these FTO/carbon cloth substrates were rinsed with water and dried in oven at 50°C for 1 hours.

2.3.5 Polypyrrole (PPy) film deposition

 Before starting the electrodeposition of the PPy film, the FTO/ITO electrodes are ultrasonically cleaned with acetone, ethanol, and distilled water.

- Electrochemical polymerization of pyrrole on FTO/ITO substrates was carried out in 0.1 M aqueous solution containing pyrrole in acetonitrile and tetrabutylammonium tetrafluoroborate (TBABF₄) by applying a constant current of 0.5 mA for 200 s with Ag/AgCl (reference), Pt wire (counter) and FTO/ITO as a working electrode.
- The reduction potential of magnitude (-1V) has been applied for 50 seconds to deposit a nominally undoped PPy thin film.

2.4 Characterization techniques

Various techniques were used to characterize the prepared samples to understand their properties. Different microscopy, spectroscopy, and electrochemical measurements were used to check the performance of the materials and devices. A brief description of their working mechanism has been discussed below:

2.4.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a technique utilized for studying the surface morphology of materials by employing a high-energy electron beam as a source[135,136]. When the material specimen is subjected to irradiation by these energetic electrons, it releases various signals consisting of both electrons and photons. These emitted signals include backscattered electrons, secondary electrons, auger electrons, and X-rays (Figure 2.5)[137]. These signals are employed to obtain information about the specimen.



Figure 2.5: Schematic representation of scanning electron microscopy

The secondary electrons, which are emitted with the interaction between the specimen and the incident electrons, are utilized to analyze the surface morphology. These secondary electrons are emitted from the surface of the specimen due to inelastic scattering from valence electrons. The SEM system contains various components, ranging from the generation of the electron beam to the detection of scattered or emitted electrons or photons. These components and their functionalities are discussed below.

2.4.1.1 Electron Gun

The electron gun in a Scanning Electron Microscope (SEM) is a crucial component responsible for generating the electron beam used in the imaging process. It is a source that produces a stream of high-energy electrons through the process of thermionic emission, in which a heated filament or cathode emits electrons when heated to a sufficiently high temperature. These emitted electrons are accelerated towards an anode, forming an electron beam. The electron beam is then focused and shaped using electromagnetic lenses to achieve a fine probe. The electron beam generated by the electron gun is typically accelerated to high energies, ranging from a few kilovolts to several tens of kilovolts, depending on the specific requirements of the imaging process. The high energy of the electron beam interacts with the specimen and leads to various signal emissions that are detected and utilized for imaging and analysis.

2.4.1.2 Condensor Lens

A condensed lens is a component used to focus the electron beam onto the specimen. It is an electromagnetic lens that plays a crucial role in controlling the convergence of the electron beam and determining the depth of field and resolution of the SEM imaging. The condensed lens consists of a set of magnetic coils that generate a magnetic field. This magnetic field interacts with the moving electrons in the beam, deflecting and focusing them. By adjusting the strength of the magnetic field, the condensed lens can control the convergence of the electron beam.

2.4.1.3 Objective Lens

The objective lens is responsible for further focusing and controlling the electron beam as it interacts with the specimen. The primary function of the objective lens is to focus the electron beam on a fine probe and maintain a small spot size on the specimen during scanning. This focused beam allows for high-resolution imaging and enables to visualize of the fine surface details and features of the specimen. Moreover, the objective lens can be used to control the working distance, which is the distance between the lens and the specimen surface. By adjusting the working distance, an operator can focus on different regions of interest within the specimen and obtain clear, detailed images.

2.4.1.4 Scanning Coils

The electron beam can be deflected by a varying magnetic field. This magnetic field can be controlled by passing varying currents through a coil and hence the electron beam that passes through the scanning coil may sweep over the samples. Sweeping the electron beam allows one to scan the sample in the broader region. Higher scanning speed results to lesser resolution and with greater noise.

2.4.1.5 Detector

The detectors in an SEM are vital components that enable the capture and analysis of various signals emitted or scattered by the specimen. They contribute to the generation of images with different contrasts and provide valuable insights into the specimen's surface morphology, elemental composition, crystallographic properties, and optical characteristics.

2.4.2 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a highly versatile imaging technique used to study surfaces at the atomic and molecular scale. The functioning of AFM involves a probe consisting of a sharp tip attached to a flexible cantilever. As the probe tip interacts with the sample surface, various forces start to act including van der Waals forces, electrostatic forces, magnetic forces, and chemical bonding forces. These interactions cause the cantilever to deflect, and this deflection is measured using a laser beam and a photodiode (Figure 2.6). AFM is also capable of providing threedimensional images, including the determination of particle size or depth of holes along the vertical dimension of surface structures. Beyond imaging, AFM is utilized for thickness measurement and measuring I-V characteristics at the atomic level[138–140].



Figure 2.6: Schematic illustration of atomic force microscopy

2.4.3 X-ray Diffraction (XRD)

X-rays are a form of electromagnetic radiation having short wavelengths, usually around 1Å. These X-rays diffract when they interact with a crystal, where the lattice planes within the crystal act as a diffraction element. X-ray diffraction (XRD) is one of the fundamental techniques used in crystallography to analyze and determine the composition and purity of samples[141,142]. Here are the description outlines of the mechanism of XRD from a sample.

2.4.3.1 X-ray Generation

When high-energy charged particles, such as an electron beam, collide with a metal target, X-rays are generated. This process involves in two steps:

- The transfer of kinetic energy from the electrons to the target, results in the emission of electromagnetic radiation known as continuous X-rays or white radiation.
- The high-energy electrons can displace core electrons from atoms in the target material. Subsequently, electrons from higher energy shells fill these vacancies and release electromagnetic radiation

corresponding to the energy difference between the transition levels. These emitted X-rays are referred to as characteristic or monochromatic X-rays.

2.4.3.2 Principle

When the X-rays fall on the electron of an atom of the material, which is placed on a sample holder positioned on a goniometer. Each atom within the crystal lattice acts as a diffraction center and collectively creates a grating-like effect for diffracting X-rays.

For the diffraction process, constructive interference should be there, and the total path length must be an integral multiple of the wavelength of the incident light i.e.,

$$2d\sin\theta = n\lambda \tag{2.1}$$

where (n) is an integer, (d) is interplanar spacing and (θ) represents the angle at which the X-rays are diffracted.

2.4.3.3 Instrumentation

The key components of X-ray diffraction are the X-ray source, sample stage, and detector (Figure 2.7). They all are arranged in a spherical geometry known as the Ewald sphere, where both the source and detector angles can be adjusted from 0° to 90°. Within this geometry, the detector captures all the constructive interference signals originating from the sample and represents them as a plot based on the diffraction angle (2 θ). This diffraction pattern contains valuable information about various Miller indices associated with specific lattice planes, allowing for the determination of sample phase purity, interatomic spacing, bond length/angle, and other related properties[143].



Figure 2.7: Schematic diagram of X-ray diffractometer with its components

2.4.4 Raman Spectroscopy

When a sample is exposed to monochromatic visible light, the light can be absorbed, reflected, or transmitted. A small fraction of the light undergoes scattering, resulting in frequencies equal to or different from the incident light. The scattered light with the same frequency as the incident light is known as the Rayleigh component, while the scattered light with different frequencies is referred to as the Raman component. These Raman lines have different frequencies from the incident light and are further categorized as Anti-Stokes and Stokes lines, corresponding to higher and lower frequency components, respectively. The degree of frequency shift observed in the Raman scattering depends on the vibrational energy levels of the sample, providing valuable information about its molecular or material properties. Despite being a weak process, Raman spectroscopy has become a widely used characterization tool in various research fields[144-150]. A typical Raman spectrometer consists of different components, as illustrated in Figure 2.8, which are discussed in more detail below.



Figure 2.8: Schematic illustration of Raman spectrometer

2.4.4.1 Light Source

The light source provides the incident monochromatic light that interacts with the sample. Common light sources include lasers, such as solid-state lasers or diode lasers, which emit a specific wavelength of light. Most used lasers include argon laser (514 nm and 488 nm), He-Ne laser (633 nm), diode lasers (532 nm, 785nm, 976 nm) etc.

2.4.4.2 **Optics**

A Raman spectrometer consists of various optical components that facilitate the excitation and detection of scattered light. Here are brief descriptions of these components:

Microscope: The microscope contains optical lenses with different magnifications and various apertures to focus the laser onto different areas of the sample. Increased magnification provides high resolution, enabling the detailed analysis of specific regions. The backscattered light from the selected area is collected through the same optical lens for further analysis.

Grating: The grating is composed of a series of parallel line spacings that disperse the incoming light. The density of the line spacing determines the

resolution of the spectrometer. Increasing the dispersion leads to higher resolution, but it may result in the reduced intensity of the scattered light.

Filter: Filters are used to selectively block or transmit specific wavelengths of light. They help remove any unwanted background noise or scattered laser light, allowing only the Raman scattered light to reach the detector. Optical filters, such as Rayleigh filters and notch filters are employed in Raman spectrometers to selectively block or transmit specific wavelengths of light. In backscattering mode, a Rayleigh filter is used to eliminate the Rayleigh scattering component, allowing only the Raman bands to pass. Notch filters are utilized to obtain both Stokes and anti-Stokes Raman lines.

2.4.4.3 Detector

CCD detectors are widely utilized in the design of Raman spectrometers due to their low signal-to-noise ratio and rapid response time, resulting in high quantum efficiency. The scattered light from the sample is directed onto the compact light-sensitive pixels of the CCD, which accurately capture the corresponding signal intensity at various positions, known as Raman shift.

2.4.5 UV-Vis Spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy is a commonly used analytical technique that involves the measurement of the absorption or transmission of ultraviolet and visible light by a sample. It provides valuable information about the electronic structure and properties of molecules, as well as the concentration of absorbing species in a solution. In a typical UV-Vis spectrometer (Figure 2.9), a Xenon lamp or a combination of Tungsten and Deuterium lamps is employed as the visible light source[151].


Figure 2.9: Schematic illustration of UV-Vis spectroscopy

A beam of light with a broad range of wavelengths in the ultraviolet and visible regions (from 200 to 800 nm) is passed through a sample. The sample may be in the form of a liquid, solid, or gas. As the light interacts with the sample, certain wavelengths are absorbed by the sample's molecules, while others are transmitted or scattered.

The absorption of light by the sample is recorded by a detector, usually a photodiode or a photomultiplier tube, and the resulting absorption spectrum is obtained. The spectrum represents the amount of light absorbed by the sample at different wavelengths. This absorption is caused by electronic transitions in the molecules, where the energy of the absorbed photons matches the energy difference between different electronic energy levels. The UV-Vis spectrum provides important information about the sample's absorption characteristics. It can be used to identify the presence of specific compounds based on their characteristic absorption peaks or to quantify the concentration of an absorbing species using the mentioned Beer-Lambert's law:

$$A \propto c. l$$
$$A = \in. c. l$$

where, \in is the molar absorptivity coefficient constant or \in is the absorbance for a solution of concentration 1mole/dm⁻³ and a path length of 1cm.

2.4.6 Electrochemical Measurements

Electrochemical measurements are a useful method for examining the electron transport characteristics of materials in an ionic electrolyte solution. As described in section 2.1.2, three-electrode systems are used in electrochemical measurements to reduce resistive effects outside of the material. The working electrode (WE), reference electrode (calomel or Ag/AgCl), and counter electrode (CE) constructed of Pt wire combine to form the three-electrode system. To avoid changing the material's characteristics, solutions containing ions such as KOH, NaOH, KCl, etc., are created at the lowest concentrations to create the ionic electrolyte. With the use of galvanostatic and potentiostatic measurements, input and corresponding output values can be get as discussed below.

2.4.6.1 Cyclic Voltammetry

In Cyclic Voltammetry (CV), constant increments of the potential are applied within a wide potential range. At least three potential terminals are utilized, where the applied potential varies at a given scan rate. Initially, the potential induces a current flow through the cathodic path (from V1 to V2), and after reaching V2, it returns through the anodic path (from V2 to V1). This completes a cycle within the specified potential window. The advantage of the cyclic scan from V1 \rightarrow V2 \rightarrow V1 is that it allows for the characterization of both the oxidation and reduction behavior of the material within a single cycle[152]. This means that the redox reaction of the material can be studied within a single potential window. Materials that exhibit only oxidation or reduction properties will not display any peaks during the respective scan direction.

2.4.6.2 Chronoamperometry

Chronoamperometry is a technique used to measure the current response over time for a specific applied potential. It involves the occurrence of a faradic reaction at the electrode surface, enabling the flow of current.

2.4.6.3 Chronopotentiometry

In the galvanostatic technique known as chronopotentiometry, the input current is kept constant while the potential changes during every step of the experiment[153]. In this method, the working electrode (WE) is given a constant current in relation to the counter electrode (CE), and the consequent potential between the reference electrode (RE) and the WE is measured. Chronopotentiometry has several uses, especially in battery and capacitor-related applications where it is used to investigate the charging and discharging characteristics of electrodes.

2.4.6.4 Linear Sweep Voltammetry

In Linear Sweep Voltammetry (LSV), a series of predetermined potentials is applied between the reference electrode (RE) and the working electrode (WE). The resulting current at each applied voltage is measured, allowing the construction of an I-V curve. The characteristics of LSV are influenced by several factors, including:

- 1. The rate of electron transfer reaction in the electrolyte.
- 2. The chemical reactivity of the material towards the electroactive species.
- 3. The voltage scan rate.

2.4.6.5 Electrochemical Impedance Spectroscopy

Resistance can come from a variety of sources during electrochemical experiments, affecting potentiostatic or galvanostatic readings. The Nyquist plot is used to identify the precise resistance connected to the electrode in contact with the electrolyte. The Nyquist plot analyses the impedance (Z) and can be used to see distinct semicircles between the imaginary component (Im(Z)) and real part (Re(Z)) of the impedance over a broad frequency range (10 mHz to 10 KHz). The diameter of these semicircles provides information on the effective impedance of various elements at the interface between the working electrode (WE) and the electrolyte. Semicircle behaviour can be studied at low and high frequencies to learn important details about the impedance at the electrode/material and material/electrolyte interfaces. The Nyquist plot

also used to identify materials that exhibit capacitive behavior, as evidenced by a vertical line at high frequencies, indicative of high impedance typically observed in capacitors[154].

Chapter 3

Improved Ethyl-Viologen based Organic Electrochromic Devices

This chapter deals with the methods to improve the performance of simple solid-state electrochromic devices fabricated based on the wellknown "Ethyl Viologen", an EC "cathodic" material. Apart from an individual species, choosing an appropriate combination of two different materials (cathodic & anodic) in a crossbar geometry makes it a favorable and improved performance of the device. This chapter will explore the relationship between the ethyl viologen-nickel oxide combination and ethyl viologen (doped with MWCNTs)-P3HT combination to improve the performance of the device in terms of its color switching (ST), contrast ratio (CR), stability, and its coloration efficiency (CE)[29,31]. In-situ spectroscopy like UV-Vis, Raman successfully explains the mechanism of the coloration/bleaching mechanism of the electrochromic active materials. The results have been published in international journals^{1, 2}.

¹ S. Kandpal et al, Opt. Mater., 2023, 136, 113494.

² S. Kandpal et al, Appl. Phys. Lett., 2021, 118, 153301.

3.1 Basic Electrochromic Device of Ethyl Viologen

As mentioned in earlier chapters, electrochromism is the reversible change of an electrochromic material between the redox states with distinguishable colors or transparency induced by the application of an electric bias. Numerous organic and inorganic materials such as derivatives of viologens or bipyridine, PEDOT: PSS, oxides of transition metals as cathodic or "n-type" electrochromic materials, and polythiophene, polypyrrole, nickel oxide, cobalt oxide, etc as anodic or "p-type" electrochromic materials have been investigated that exhibit changing color with electron injection and subsequently bleach upon ion extraction under bias stimuli condition. Among these mentioned materials, ethyl viologen has the possibility to change its state easily and hence can be a good cathodic active material in electrochromic devices. Here, the derivative of viologen i.e., ethyl viologen diperchlorate (EV(ClO₄)₂), shown in scheme 1, for its electrochromic properties have been discussed.



Scheme 1: Ethyl viologen diperchlorate molecule

By nature, viologens are "n-type" electrochromic active materials which means that they can change their color on the application of external bias of negative polarity. It was also confirmed by the recorded cyclic voltammetry (CV) of ethyl viologen (EV). For its CV measurement, EV has been carried out in a solution medium (EV in acetonitrile) along with a platinum electrode as counter, glassy carbon as working, and calomel as a reference electrode was used. Scanning from 0V to -2V, reduction peaks were observed at -0.7V and -1.7V (assigned by C1 and C2) and showed "n-type" behavior in electrochromism (Figure 3.1). Initially, it is colorless due to its dicationic form (EV^{2+}) and changes its appearance as it goes from dicationic form to radical form (EV^{++}) upon reduction. Again, it goes from (EV^{++}) to (EV^{0}) on further reduction whereas the anodic peaks assigned by A1 and A2 shows conversion of (EV^{0}) to (EV^{++}) and (EV^{++}) back to (EV^{2+}) states respectively and validates the redox behavior of viologen.



Figure 3.1: Cyclic voltammetry of ethyl viologen diperchlorate

Viologen-alone Electrochromic Device

Following the characterization discussed above, EV can be used as an "n-type" electrochromic active material for device fabrication. A device was fabricated by taking two ITO-coated glass substrates in which the layer of EV with PEO matrix (section 2.3.2, Chapter 2) was sandwiched between these two electrodes. The electrochromic performance of the fabricated device was investigated through in-situ bias-dependent absorbance spectroscopy, switching time, and cycle life. The black curve (Figure 3.2a) shows the transparent state of the fabricated device whereas the red curve was showing the colored (biased) state of the device. As the device is connected to the external bias (-2V) the device changes its color from transparent to blue due to the formation of viologen radical ion (Figure 3.2a).

To understand the color switching of the device between two colors (transparent-blue) state, the switching kinetics of the device was recorded. As the device experiences the external bias (-2V), its absorbance value gets changes but as soon as the bias polarity is reversed, the device doesn't completely return to its initial (transparent) absorbance value (Figure 3.2b) and takes ~3s/4s switching time (inset, Figure 3.2b). This is because the viologen layer sandwiched between two ITO electrodes was unable to identify the bias polarities individually and shows a lack of controllable reversible nature of the device. In other words, the single EC layer (EV) was getting oxidized or reduced in either of the biased states simultaneously at the two electrodes. Therefore, just one layer of viologen (via drop casting) along with a suitable electrolyte in the device limited its functionality and makes it of little importance from an application point of view.



Figure 3.2: (a) In-situ bias-dependent absorbance spectra of EV device and (b) switching kinetics along with the coloration/bleaching time (inset) of the device.

To address this issue, employing an additional layer (of counter ion) of an EC layer in combination with the electrolyte was a possible way to break the linearity and provide a separate path for electrons to move in both ways. So, the combination of EV-NiO in crossbar geometry was fabricated and studied in detail as has been discussed below.

3.2 Ethyl Viologen-Nickel Oxide-based Hybrid Electrochromic Device

As mentioned above, EV shows its color change in a negatively biased condition (-2V) due to the formation of ethyl viologen radical ions (EV⁺ & EV²⁺) and shows poor electrochromic performance. To improve the performance of that monolayer device, ethyl viologen is incorporated with other anodic material i.e., nickel oxide, which is a p-type material or tendency to oxidize itself at positive bias conditions. When the EV was alone in the device, the switching mechanism between oxidized (transparent) and reduced (blue) state is decreased because viologens degrade over the time, particularly in the presence of moisture and oxygen. This can be addressed by incorporating another p-type electrochromic material, having complementary redox behavior. Since the performance of viologen-based devices can be affected by the choice of electrochromic material used in complementary with the viologen. Different host matrices can have varying redox potentials, which can impact the reversibility, speed of the viologen redox reactions and enhance the performance of the viologen device. In this section nickel oxide (NiO) film has been used as an anodic or p-type electrochromic material in the fabrication of a double-layer electrochromic device (ECD). The device is prepared by taking two fluorine-doped tin oxide (FTO) electrodes or substrates separately, which are covered with the thin films of EC materials (EV & NiO) by using the appropriate technique through the flip-chip method. Its electrochemical and electrochromic performance parameters have been studied to investigate the switching mechanism of the device and the role of the individual material to improve the performance of the device.

3.2.1 Structural Characterization

Prior to exploring NiO as an anodic or p-type material in an actual device, atomically smooth NiO nanofilm has been deposited by plasma-assisted ALD technique. Although several literatures are reported on the synthesis mechanism of NiO thin film by various methods like chemical vapor deposition (CVD), hydrothermal, pulsed laser deposition (PLD), sol-gel, etc which often yield films with cracks. This has disadvantages while using them in devices because these cracks and uneven morphology can act as centers where power loss may take place during device operation thus decreasing the power efficiency. Thus, opting ALD technique can be an advantageous option due to the presence of flexibility to choose low synthesis temperature, exact control of the film thicknesses (up to monolayer), ability to grow smooth surfaces, to grow uniform coatings making them continuous and smooth thin films with excellent compatibility to grown on FTO substrates and used to fabricate a solid-state ECD.

The surface morphology of the NiO thin films deposited through the ALD technique on silicon or FTO substrates has been initially characterized by scanning electron microscopy (SEM). Figure 3.3a is the image captured in planner view which shows that the film is smooth and uniform. The EDS profile (inset, Figure 3.3a) clearly reveals the presence of Ni across the silicon substrate, which confirms its purity along with the obtained weight percentages of other elements present. The film thickness was determined by the cross-sectional SEM image (Figure 3.3b), which clearly indicates that the deposited layer is continuous on the top of the silicon substrate and the average film thickness comes around \sim 26–27 nm and it is a good agreement with the thickness determined using spectroscopic ellipsometry. Information about the crystal structure has been captured by the Grazing incidence X-ray diffraction (GI-XRD) technique. The surface sensing grazing incidence (GIXRD) pattern (Figure 3.3c) of deposited NiO film on silicon substrate clearly shows reflections at (111), (200), and (220), corresponding to cubic Fm3m modifications of NiO whereas reflections appear at angle 33° and 56.5° due to the imperfection of the crystal of silicon substrate. Elemental compositions of deposited NiO film have been investigated by recorded XPS spectrum after removing the outermost layer by etching for 30 seconds with argon ions. XPS spectrum in Figure 3.3d clearly shows that it contains only three elements i.e., nickel (47%), oxygen

(41%), and a small amount of carbon (12%). The excess of nickel and the presence of carbon is due to the presence of unreacted carbon. The most intense peaks belong to Ni2P_{3/2} and Ni2P_{1/2} agrees with the reported values of NiO and the peak appeared at ~284 eV corresponds to C–C and C–H ligands of nickel precursor. Thus, the film contains predominantly NiO however other residues are also present in less amount.



Figure 3.3: (a) SEM micrograph with EDS data (inset) displaying micro grain morphology and its cross-section micrograph in (b), (c) GI-XRD pattern, and (d) XPS survey spectrum of ALD grown NiO thin film on Silicon substrate. (Adapted from Ref 31, Opt. Mater., 2023)

3.2.2 Electrochemical Characterization

An electrochemical study of the above-mentioned ALD synthesized NiO film and drop casted EV has been done by cyclic voltammetry (CV) in a three-electrode system. The CV measurement of the EV has been carried out in a solution medium with a glassy carbon electrode as working (WE), platinum as counter (CE), and calomel as a reference electrode (RE). As mentioned above, the CV curve from EV shows two redox peaks, which is reversible in nature as evident from the obtained anodic peaks in reverse scan and clearly indicating the n-type behavior of EV. On the other hand, the CV curve of NiO film has been recorded in deionized (DI) water using KOH as a supporting electrolyte, which shows redox peaks in the positive potential window (Figure 3.4), indicating its p-type behavior. Since these two redox species show their complementary redox nature to each other and hence can be combined in making a solid-state ECD where NiO will support EV film under biased conditions for better performance of the device.



Figure 3.4: Cyclic voltammetry curve of the synthesized NiO thin film

3.2.3 Fabrication of Solid-State EC Device

After confirming the complementary behavior of NiO and EV, the solidstate electrochromic device has been fabricated through crossbar geometry by depositing the NiO-EV layer between two FTO substrates. As mentioned above, thin film of NiO having thickness ~26–27 nm has been prepared by ALD deposition technique over FTO substrate whereas a layer of EV in PEO matrix was obtained by drop casting method and then assemble together by flip-chip method, as shown schematically in Figure 3.5 along with the scheme showing the polarity in which the bias has been applied. The initial as-fabricated device (active area ~1 cm²) is transparent in nature because the thin film of NiO and EV both are transparent as the latter is colorless in its neutral state where it is present in EV²⁺ state. As the device is connected to the external bias (+1.7 V), such that the positive terminal of the battery is connected to the NiOcoated FTO electrode and the negative terminal is connected to the EVcoated FTO electrode, the color of the device changes from its initial transparent state to blue (left inset, Figure 3.5). This transparent to blue color switching is reversible which can be switched back on reversing the polarity. On changing the external bias polarity (-1.7 V), the device switches back to its initial transparent state, as shown in Figure 3.5 (right inset) showing the actual photographs of the device. Bias-dependent color change of the device is due to the simultaneous oxidation (reduction) of NiO (EV) from Ni^{II} to Ni^{III} (EV radical cation or EV⁺). Since the oxidation of Ni^{II}, results in a light grey in color and EV^{+•} is blue, thus the overall device starts to appear dark blue under this bias. The conversion of the transparent to blue color of the device is reversible, a requirement for ECD, due to the reversible redox nature of NiO and EV. Thus, the device switches back to its transparent state (as that of the as-fabricated state) on the application of -1.7 V bias.



Figure 3.5: Schematic diagram of the fabricated device under as fabricated and different applied bias (device states of ON/OFF) conditions along with the device's actual photographs. (Adapted from Ref 31, Opt. Mater., 2023)

3.2.4 Electrochemical and Electrochromic measurements of the Fabricated EC Device

The color changing of the device can also be correlated with the in-situ bias-dependent absorbance spectra, which was recorded at 0 V (initial) and ± 1.7 V. In the given voltage window of ± 1.7 V, the biased device shows maximum absorption at a particular wavelength of 604 nm (red curve, Figure 3.6). It can be seen that the initial color of the fabricated device is transparent (black curve, Figure 3.6) but when a positive bias (± 1.7 V) is applied, the maximum absorption is observed in the greenred region of the visible spectrum (red curve, Figure 3.6) at a wavelength of 604 nm and the device starts to show its blue color. Further, on reversing the polarity (± 1.7 V), the absorption spectrum imitates the curve obtained for the device when in its initial state (blue curve, Figure 3.6), and the device reappears its initial (transparent) state. Bias-dependent color switching of the device can also be understood using the corresponding transmission (%) response of the device.



Figure 3.6: In-situ bias-dependent UV–Vis absorption spectra along with the photographs of the device. (Adapted from Ref 31, Opt. Mater., 2023)

Switching stability between the colored and bleached states, an important parameter to examine device performance, has been displayed in Figure

3.7a. It can be noticed here that there is very less degradation in the absorption values of the device as a function of time, which shows that the device has good cycle life/cyclability between two colored states (transparent-blue) more than 250 s. No degradation in the absorbance values after 50 switching pulses, signifies a good stability, especially from a solid-state device.

Apart from the above-mentioned cycle life, knowing the switching time of the device taken to toggle between its two-colored states under commutative potential is also essential for calculating the performance of the ECDs. Single absorption cycle of the same device (Figure 3.7b), which reveals that the device takes 1.8 s to reach 77% (2.1 s for 90%) of the absorption change between the transparent and blue states and 1.4 s to come back to its 67% (1.8 s for 90%) of maximum absorption value, which is faster than the reported viologen based hybrid electrochromic devices. The most significant device performance parameter is the coloration efficiency (η) which is a measure of how power efficient an ECD is. It is defined as the slope of the curve plotted between the change in optical density (Δ OD) and the stored charge density (Q) required for the color modulation to take place. The bias-dependent color modulation curve (Figure 3.7b) is used to obtain the value of $\triangle OD$ whereas a current response under applied bias pulse train (Figure 3.7c) is used to obtain the value of Q. Variation of $\triangle OD$ (corresponding to $\lambda = 604$ nm) as a function of extracted charge density (Figure 3.7d) yields the value of the slope. The calculated value of the coloration efficiency (η_{ce}) was obtained to be \sim 118 cm²/C, which is significantly higher than the EV-based solid-state device. It is well known that the complementary solid-state ECD containing two electrochromic electrodes shows highly improved coloration efficiency. Our result indicates that a high coloration efficiency comparable to the EV-based complementary device could be achieved via introducing the ALD-grown NiO thin film.



Figure 3.7: (a) Multiple switching cycles of the device upto 250s, (b) single absorption cycle of the device with corresponding bias pulse (dashed line), (c) variation of current flowing through the device under a bias pulse train and (d) the variation of change in optical density as a function of stored used for estimating coloration efficiency. (Adapted from Ref 31, Opt. Mater., 2023)

From the above discussion, it is apparent that the performance of an inorganic/organic hybrid device is improved when the inorganic (NiO in the present case) film is deposited using the ALD technique than the other deposition techniques, which can be seen in the table below. Comparison table between the NiO films deposited with different techniques shows that the overall performance of ALD-deposited NiO film is superior to the other deposited film with different techniques. Such a device shows better performance not only in terms of switching time, one of the bottle-necks in inorganic devices, but also by making it power efficient as quantified using coloration efficiency.

| S.No. | Device Compositi on | Switching time(s) | Coloration Efficiency (cm ² /C) | NiO film Synthesis methods | Ref. |
|-------|---------------------------|----------------------|--|----------------------------------|---|
| 1. | NiO/EV | 1.8/1.4 | 118 | Atomic layer deposition (ALD) | This work |
| 2. | NiO | 5.62/4.31 | 13.66 | Electrodeposition | Kondal kar <i>et</i> <i>al.</i> [132] |
| 3. | NiO | NR | 24.5 | E-beam evaporation | Guo <i>et</i> <i>al</i> .[155] |
| 4. | NiO | 2.5/0.65 | 80.6 | Hydrothermal | Li et al.[156] |
| 5. | WO ₃ /NiO | 1.1/3.2 | 130.9 | Sol-gel | Xie <i>et</i> <i>al</i> .[157] |
| 6. | NiO | 5.4/3.6 | 43.5 | Spin coating | Zhao <i>et</i> <i>al</i> .[158] |

 Table 3.1: Performance parameters of various NiO-based ECDs:

The possible origin of such an improvement from ALD-grown film can be understood as follows. The inorganic films grown by employing techniques other than ALD lack control and develop cracks which may add to alternate channels for current flow thus making available letter current used for actual color modulation. This will put an additional power load on the whole coloration/bleaching process. On the other hand, the ALD-grown films are smoother and free from cracks thus the whole film participates in the color modulation process thus stopping the power wastage to yield a more efficient device. A controlled film can be grown using ALD, unlike other techniques, which might give an additional advantage in obtaining more batch-to-batch consistency in the devices. Overall, ALD appears to be a better technique for fabricating power-efficient organic/inorganic hybrid electrochromic devices.

3.3 Ethyl Viologen-P3HT based MWCNTs doped Organic Electrochromic Device

This section demonstrates another anodic (p-type) electrochromic material, polythiophene (P3HT) changes its optical states in the positive bias voltage. It can easily be dissolved in various organic solvents such as dichlorobenzene, chloroform, dichloromethane, etc, and can be used easily through spin coating or drop casting techniques to prepare their electrode for device fabrication. Here, the electrochromic device comprises polythiophene (P3HT) with an ethyl viologen (EV) layer doped with multi-walled carbon nanotubes (MWCNTs) in a bilayer geometry that has been fabricated. In this simple crossbar device, P3HT/EV acts as the electron donor/acceptor pair and MWCNTs facilitate easier and more efficient transfer of electrons required for the necessary redox process. Here, MWCNTs have been chosen for doping because the graphitic structure shows electron-holding properties where electrons can stay for some time before they are triggered to be released to take part in the redox process when required. Additionally, the "multiwalled" structure makes such sites available plenty in number to enhance the overall redox process. Electrochemical and electrochromic performance parameters have been studied to investigate the switching mechanism of the device and the role of the individual material to improve the performance of the device.

3.3.1 Structural Characterization

The MWCNTs, prepared for device use, are several micrometers long and 50–100 nm thick, as can be seen in the SEM micrograph (Figure 3.8a). The hollow tubular structures can be clearly seen in TEM (Figure 3.8b) and HRTEM images (Figure 3.8c) with the latter giving clear evidence of the multi-walled nature of the tubes. The structural phase of the MWCNTs has been confirmed using the XRD pattern (Figure 3.8d), which shows the most intense peak at ~26.2° corresponding to C (002) planes, a signature of a highly graphitic nature. The XRD peak marked with (110) corresponds to α -Fe (JCPDS-06–0696), whereas other peaks marked with (210), (131), and (230) arise from Fe3C present from the catalyst (JCPDS file no JCPDS-35–0772). The observed structural characteristic has been further confirmed using Raman spectroscopy (Figure 3.8e), due to its advantage in probing subtle characteristics of nanomaterials, superior that shows the three main characteristics D (1328 cm⁻¹, symmetric), G (1570 cm⁻¹, asymmetric due to D' hump at 1612 cm⁻¹), and 2D (2650 cm⁻¹, symmetric) bands, confirming the formation of good quality MWCNTs to be used in the electrochromic device.



Figure 3.8: Basic characterization of MWCNTs using (a) SEM, (b) TEM, (c) HRTEM, (d) XRD and (e) Raman spectroscopy. (Adapted from Ref 29, Appl. Phys. Lett., 2021)

3.3.2 Electrochemical Characterization

Electrochemical measurements of both the materials, used to fabricate the device, have been done through CV. As discussed above, EV is a cathodic or "n-type" active electrochromic material that changes its state during reduction (Figure 3.1). The CV of P3HT given in Figure 3.9 shows redox behavior in positive voltage bias and confirms its "p-type" electrochromic active behavior. For CV measurement, P3HT-coated ITO electrode, platinum and calomel electrodes were used as a working, reference and counter electrode with 1M LiClO₄ in acetonitrile solution. It shows oxidation peaks, which confirms the "p-type" behavior of P3HT. Both of them, P3HT/EV is a suitable combination for changing color in electrochromism. Further, the color-changing demonstration was done through the fabrication of an electrochromic device with the help of these two electrodes.



Figure 3.9: Cyclic voltammetry of P3HT

3.3.3 Fabrication of Solid-State EC Device

The solid-state electrochromic device was fabricated in a crossbar geometry using P3HT and CNT-doped EV (in PEO matrix) using the flip-chip recipe, explained in the above section (chapter 2). The finished solid-state device, consisting of the constituents in thin film form, is schematically shown in Figure 3.10 along with the bias polarity schemes. During the electrochromic operation, the as-prepared device (under 0 V bias) appeared magenta due to the natural color of P3HT (neutral), which changes to blue color on applying a bias of 1.4 V. The magenta to blue color is reversible, and the blue color switches back to magenta when a bias of -1.4 V is applied.



Figure 3.10: Schematic representation of the layered device showing the polarity scheme. (Adapted from Ref 29, Appl. Phys. Lett., 2021)

3.3.4 Electrochemical and Electrochromic Measurements of the Fabricated EC Device

Optical spectroscopic (absorption) variation corresponding to the biasinduced color change can be seen in Figure 3.11a. The device shows a clear change in the spectral response under different bias conditions and can be correlated with the actual color of the device as shown using the corresponding photographs. It is clear from Figure 3.11a that the unbiased device (black curve, Figure 3.11a) absorbs the maximum near the green band (\sim 525 nm) of the visible spectrum, giving the magenta color to the device as can be understood from the primarycomplementary color protocol. On applying 1.4 V, the overall absorption band shifts toward lower energy and starts absorbing in the green-red region (red curve, Figure 3.11b), leaving only "blue" to be perceived by the eye giving the same color to the device. On reversing the bias polarity (-1.4 V), the optical spectral response, thus the magenta appearance of device, changes to the one like for the as-prepared device (blue curve, Figure 3.11b), confirming that the bias reversal is followed by the color reversal, an important aspect from the application point of view. On simply leaving the device unhooked (no bias applied), it takes longer time to reverse the colored state because it has to rely on the atmospheric conditions for the necessary redox process to take place.



Figure 3.11: (a) In situ bias-dependent absorption spectra of the live device under different bias conditions, and (b) bias-dependent in situ Raman spectra (left panel) and Raman images (right panel) under different bias conditions. (Adapted from Ref 29, Appl. Phys. Lett., 2021)

The reason for the above-mentioned bias-dependent color switching (magenta to blue) is the process of following two phenomena taking place simultaneously at separate electrodes. At the positive terminal (connected to the P3HT layer), oxidation of P3HT from its neutral state (magenta) to the polaronic state (transparent) takes place due to biasinduced dynamic doping. At the same time, under this bias (1.4 V), the negative terminal is connected to the EV layer, which enables EV to reduce it from the transparent dicationic state (EV^{2+}) to the blue free radical state (EV^{+}) . The above-mentioned combination of redox processes yields a transparent polaron layer and a blue EV^{+•} later to give the overall perceived blue color to the device. On bias reversal, the P3HT polaron and EV^{+•} free radical gets reduced and oxidized (respectively) back to regain their neutral states of P3HT and EV²⁺ again through the process of dynamic (de-) doping where necessary electronic transaction is done through a bias rather than any involvement of the chemical redox process. This step is the most important aspect to achieve a liquid electrolyte-less device.

The validation of color switching mechanism has also been done through in situ bias-dependent Raman spectroscopy (left panel, Figure 3.11b) and Raman microscopy (right panel, Figure 3.11b) techniques. The Raman spectrum of the just-finished device (0 V, black curve) shows two peaks at 1379 cm⁻¹ and 1444 cm⁻¹, the signature of neutral P3HT, hence confirming its presence. Under a bias of 1.4 V (device turns blue) to the P3HT side of the device, both the above peaks come closer and can be seen as a dual peak (red curve, Figure 3.11b) at 1376 cm⁻¹ and 1411 cm⁻¹, which is identified as originating due to the dynamic doping-induced polaron formation. The necessary charge balancing for polarons to get stabilized is taken care of by diperchlorate ions available in the device from the viologen's layer participating in the redox process at the other electrode. As mentioned above, the device's color gets reinstalled to magenta (from blue) on reversing the bias (-1.4 V), which can also be seen in terms of reinstallation of neutral P3HT Raman modes (blue curve, left panel), confirming the process of dynamic de-doping. However, the Raman spectra in the left panel (Figure 3.11b) have been taken from a single spot from the active region of the device, but the P3HT/EV redox process takes place in the entire active region where the color modulation takes place. To confirm this, a linear Raman map has been recorded from the device, which also shows the reversible P3HT to polaron conversion in a 50 μ m long region in the active region of the device (right panel, Figure 3.11b). The linear map, recorded under different bias conditions confirms the above-mentioned dynamic doping process taking place in the whole active device and, thus, can be said to be responsible for the corresponding color switching.

The simultaneous redox process at the separate electrode can be obtained using the electrical measurement from the finished solid-state device, which shows an asymmetric I–V curve (Figure 3.12a) similar to a diode. When the device is biased with a positive voltage, more current flows, whereas a restricted current flows when the device is biased with a negative voltage, which can be understood as follows. In the positive bias, P3HT (EV) encounters the positive (negative) polarity, allowing the P3HT to release electrons, whereas the EV, at the negative terminal, receives the electrons to complete the cycle, which allows the current to continuously flow. On the other hand, under the negative polarity, the P3HT (EV) receives the negative (positive) polarity but cannot accept electrons to get reduced and similarly EV (already in EV²⁺ state) cannot lose electrons further to get oxidized. Such a mutual inability to receive/donate electrons restrict the current flow, making the I-V characteristic (Figure 3.12a) consistent with the dynamic doping-based mechanism.

It can be understood that since dynamic redox reactions are involved in the color-switching process, therefore, the speed and operating voltages at which the whole dynamic doping (and de-doping) takes place will decide the overall contrast ratio and speed of the device. In typical singleor double-layer solid-state devices, the necessary charge transfer is governed solely by the capability of molecules (P3HT and EV here) itself and makes the bottleneck in achieving a faster and more efficient device. To address this issue, the EV layer has been doped with the MWCNTs at the time of fabricating because of the following two reasons. First, materials with graphitic sheets like graphene nanoflakes, PCBM, etc. not only easily accept electrons but also are capable of holding them for release when required for necessary redox activity. Second, the multiwalled nature of the CNTs enables more graphitic sites for such charge storage and transfer, thus adding to the enhanced electrochromic activity. This faster and easier electron transfer is supposed to facilitate a fast electrochromic device, which is directly associated with the overall efficiency of the device, which is one of the most important parameters from the application point of view. Cyclability and switching time are other two very important parameters (along with contrast) to quantify the performance of any electrochromic device. The color switching dynamics of the device has been measured by recording the variation in absorbance with time by applying a rectangular 1.4/–1.4V bias pulse of 10 s duration (5 s each polarity) as shown in Figure 3.12b. The device takes only ~ 1 s (coloration time) to reach 77% of its maximum absorption while switching from magenta to blue and only 500 ms to toggle back to $\sim 67\%$ of the maximum absorption value during the blue to magenta switching. Such small



Figure 3.12: (a) I–V characteristic of the solid-state device and (b) single absorption switching kinetics of the device at the switching voltage from 1.4 V to -1.4 V, with multiple cycles in (c). (d) optical density variation with the charge density used to estimate device's efficiency. (Adapted from Ref 29, Appl. Phys. Lett., 2021)

coloration/bleaching times make the CNT-doped device one of the fastest in the family of P3HT and/or EV. Multiple pulse trains were applied to study stability and cyclability of the device (Figure 3.12c) to reveal that the cyclic response of the device continuously shows a reversible change in absorbance (515 nm). The device switches 80 times in the given duration with little compromise on the absorbance value, giving very good stability of the device. The next step to quantify the performance of the device is its coloration efficiency (η_{ce}), which is calculated from Eq. 1.4 (Chapter 1) and comes about to ~ 401 cm²/C, which is the highest coloration efficiency from a P3HT/doped-EV-based solid-state device is likely due to the fact that CNTs in the doped EV layer are playing their role by storing and enabling the EV counterion layer to release them appropriately for the redox process to become faster. This can also be appreciated from the observed low switching times, which is also supported by the fact that MWCNTs are good conductors.

Summary

The incorporation of "p-type" electrochromic active materials such as polythiophene (P3HT), and nickel oxide (NiO) with ethyl viologen (EV) leads to significantly enhanced performance of the electrochromic device. The ALD-grown crack-free and smooth NiO film appear to be advantageous with viologen due to its better utilization of applied power and its combination with the complementary redox counterpart. ALD has also better control for obtaining desired films in terms of thickness which in turn could help to achieve desired transparency from the ECD.

Further, the incorporation of viologen with polythiophene and MWCNTs exhibits most efficient performance of the device. The MWCNT-doped device demons trates a magnificent efficiency of $401 \text{ cm}^2/\text{C}$ and coloration/bleaching times of only 1s/500 ms while switching reversibly between magenta and blue colors at a voltage of as small as 1.4 V. Here, the improved performance of the device was obtained due to these two reasons. First, the complementary redox behavior of P3HT and EV, and second, the role of MWCNTs as a charge transferring facilitator. The latter enables an easy supply of electrons to the electrochromic layers when required, thus helping in achieving a fast color-switching response. This concludes the discussion on the improved performance of ethyl viologen-based electrochromic device, where we used suitable complementary anodic or "p-type" electrochromic active material along with the graphitic structured material i.e., carbon nanotubes. Some other 2D derivative material was explored as a dopant to get other interesting features of electrochromic device. This is the topic of next chapter and have been discussed in detail.

Chapter 4

Incorporation of 2D-layered material (MoS₂) for Improved Electrochromic Device

This chapter describes a recipe to improve the performance of ethyl viologen and polythiophene-based solid-state electrochromic devices through incorporating 2D materials. First, the device was appropriately designed and checked by performing the various electrochromic performance parameters and compared them with the undoped one. Choosing MoS₂ as a dopant improves the performance of the EV/P3HT device by facilitating the required charge carriers for redox reactions. This chapter also discusses the effect of MoS₂ doping concentration on the performance of the fabricated ECD in terms of its switching time, coloration efficiency, cycle life, and color contrast. These two aspects of the fabricated ECD were studied in detail. Results mentioned in this chapter are reported in journal publications^{2, 3}.

¹ S. Kandpal et al, Sol. Energy Mater. Sol. Cells, 2022, 236, 111502.

²S. Kandpal et al, J. Phys. D, 2022, 55, 375101.

4.1 Incorporating MoS₂ in EV/P3HT All-Organic Solid State Electrochromic Device

Two-dimensional materials like graphene, graphene oxide, and transition metal dichalcogenides hold great potential for the next generation of electronic applications due to their high electrical conductivity, large surface area, high optical transmittance, and good chemical stability. P3HT and EV are the most widely used polymers in the organic electronic world due to their high electrical conductivity, solution processibility in various solutions, and flexibility also but their low charge mobility limits their applications. Therefore, graphene-like layered structured materials and their weak Vander Waal's force present between layers might be helpful to resolve this issue by facilitating large amounts of charge movements between the electrochromic active layer and electrolyte and enhancing the performance of functionalized material[59,159–161]. Therefore, molybdenum disulfide (MoS₂) can be opted as a promising candidate for such types of organic electronic applications.

As discussed in chapter 3, multiwalled carbon nanotubes (MWCNTs) belong to the family of 2D derivative materials and have the property to facilitate the charge carriers in the ECD. Here another 2D layered material i.e., molybdenum disulfide (MoS₂), has been used as a dopant with P3HT/EV electrochromic active material to fabricate an ECD in an attempt to improve the performance of the device. Here, MoS₂ was synthesized hydrothermally as described in section 2.2 (chapter 2).

4.1.1 Structural Characterization of MoS₂

Prior to be used in the device, the synthesized MoS_2 has been characterized by SEM, XRD, and Raman spectroscopy to know its structural and morphological information. The SEM micrograph (Figure 4.1a) displays the nano-flower morphology of the sample, with petals oriented in random directions and thickness varying between 15 and 30 nm, and nanoflower dimensions of the order of approximately a micrometer. Further X-ray diffraction (Figure 4.1b) depicts the profile of final product obtained from the hydrothermal route. The most intense peak around ~14° represents (002) plane belonging to 2H–MoS₂. All other peaks in the XRD profile also were in good agreement with the 2H-phase of MoS₂ (indexed using JCPDS card no. 37–1492). Broadening in the XRD peaks reflects the nanosized crystallites present in the synthesized sample. Raman spectrum of the nano-flowers (inset, Figure 4.1b) also reveals the multilayer nature of the MoS₂ petals, which is in agreement with SEM (Figure 4.1a).



Figure 4.1: (a) Characterization of MoS₂ using SEM displaying nanoflower morphology, (b) XRD pattern and Raman spectroscopy (inset) showing multi-layered nature. (Adapted from Ref 30, Sol. Energy Mater. Sol. Cells, 2022)

Raman spectrum (inset, Figure 4.1b) shows in-plane (E_{2g}^1) and out-ofplane (A_{1g}) vibrational modes of hexagonal MoS₂ centered at ~ 379 cm⁻¹ and ~ 405 cm⁻¹ respectively. The difference in the vibrational shifts of these modes is sensitive to number of layers of MoS₂, and the value in this case is ~26 cm⁻¹ indicating the multilayer form of MoS₂ nanoflower. Another vibrational mode centered at ~ 451 cm⁻¹ corresponds to the second-order Raman mode 2LA(M), which has also been noticed. The structural analysis reveals that MoS₂ synthesized for ECD fabrication is multi-layered in nature with nanoflower architecture.

4.1.2 Fabrication of Solid-State EC Device

The solid-state ECD was fabricated in a crossbar geometry using P3HT and MoS_2 incorporate EV (say, $MoS_2 + EV$) in PEO matrix using the process mentioned in section 2.3 (chapter 2). The fabricated device consists of the thin films of P3HT and MoS₂ + EV sandwiched between two appropriate ITO electrodes as shown in the schematic in Figure 4.2. The device appears magenta in color in the as-deposited (initial) state due to the natural color of P3HT as $MoS_2 + EV$ layer is transparent. When a bias of 1.4 V is applied across the fabricated device, such that its P3HTcoated ITO electrode is connected to the positive terminal of the battery, the device color changes reversibly to blue (Figure 4.2). The abovementioned bias-dependent color change is due to the simultaneous oxidation (reduction) of P3HT (EV) to Polaron (EV radical cation). Since the polaron is transparent and EV radical is blue, the overall device appears blue under this bias. The magenta to blue color is reversible due to the reversible nature of the redox behavior of P3HT and the device switches back to magenta color on the application of -1.4 V (Figure 4.2).



Figure 4.2: Schematic representation of layered device (along with constituent layers) showing device colors under different bias. (Adapted from Ref 30, Sol. Energy Mater. Sol. Cells, 2022)

4.1.3 Electrochemical Measurements and Electrochromic Performance of the Fabricated EC Device

Varying color switching (between magenta and blue) of the device can also be understood using the corresponding variation in bias-ind optical spectra. In-situ bias-dependent transmittance spectra (Figure 4.3) show the change in optical transmittance of the device as a function of applied bias which can be correlated with the actual color of the device as shown using the corresponding photographs. The unbiased device (black curve, Figure 4.3) absorbs mostly near the green band (~ 525 nm) of the visible spectrum and transmits the remaining two primary colors (red + blue), which gives a magenta color to the device. On 1.4 V biasing, the overall transmittance band shifts towards lower energy and starts absorbing in the green-red region (red curve, Figure 4.3) with lower absorption to the blue wavelength. It leaves mostly the 'blue' to be perceived by the eye giving the same color to the device. On reversing the bias polarity (-1.4V) the optical spectral response, thus the magenta appearance of the device changes to the one for the as-prepared device (blue curve, Figure 4.3) confirming that the bias reversal is followed by the color reversal, an important aspect from the application point of view. This color modulation can also be appreciated from the bias-dependent transmission (%) variation response of the device. A maximum change in a transmission value of 12 % can be seen corresponding to the 515 nm wavelength. However, the device shows a color contrast (CC) of 42 % (for 515 nm wavelength) with an applied bias of as small as ± 1.4 V which is estimated using Eq. 1.1 (Chapter 1).

As mentioned above, the EV layer has been doped with MoS_2 in an attempt to enhance the electrochromic properties of electrochromic films due to its high charge transport properties and specific surface area. The layered graphene-like nanostructure of MoS_2 with sufficient microcracks and holes are expected to allow better electron transport in P3HT/EV+MoS₂ device to improve the device performance as measured

in terms of good response (coloration/bleaching or ON/OFF) time along with the cyclability of ECD.



Figure 4.3: In-situ bias-dependent optical spectra of the ECD under different bias conditions. (Adapted from Ref 30, Sol. Energy Mater. Sol. Cells, 2022)

To study the device stability during operation, a rectangular pulse of voltage 1.4 V/-1.4 V of 6 s duration (3 s each polarity) is used to operate the device and the cyclic response in absorbance (for 515nm) has been recorded (in Figure 4.4a), which shows that the device has good cyclability of more than 100 cycles as it shows only 3% decrease in maximum transmission after 500 s of continuous switching and remains constant for almost the entire duration (Figure 4.4a). Switching time is another device property that is important while commenting about the device performance. One of the switching cycles (Figure 4.4b) of the device shows that it takes only 0.8 s (coloration time) to reach 77% of maximum absorbance (sufficient to visible appreciate a color change) while switching from magenta to blue color. Furthermore, Figure 4.4b also shows that it takes only 0.4 s (bleaching time) to regain its 67% of maximum absorbance value during blue to magenta switching. A switching time of less than half second is very impressive speed of a solid-state device and certainly can be said to be one of the fastest in this family of all-organic device. Another most important parameter for

determining the electrochromic performance of a material is its coloration efficiency which gives information about the power efficiency as well. The efficiency (η_{ce}) is defined as the change in optical density (Δ OD) per unit of charge density (Q) and is expressed by Eq. 1.4, mentioned in chapter 1.



Figure 4.4: (a) Optical switching kinetics of the device under switching voltage from 1.4 V to -1.4 V with multiple cycles and (b) one switching cycle along with (c) Optical density variation as a function of charge density used to estimate device's efficiency. (Adapted from Ref 30, Sol. Energy Mater. Sol. Cells, 2022)

In order to calculate the value of the coloration efficiency of the device, a graph of optical density as a function of charge density is plotted (Figure 4.4c) and a very impressive efficiency of ~ 580 cm²/C has been calculated. It is clear from the above discussion that a solid-state P3HT/EV+MoS₂ device can be said to exhibit very good electrochromic performance with CC of 42%, switching times of 0.4 s (bleaching) & 0.8 s (coloration), coloration efficiency of 580 cm²/C and very good cycle life. A comparison between the performances of similar devices has been done in table 4.1 to highlight that the performance of the P3HT/EV+MoS₂ device is superior to other devices. It clearly indicates that the incorporation of a 2D layered material (MoS₂) in one of the active layers has helped in improving the performance as envisaged. It is important here to mention that however the device's speed and efficiencies increase on MoS₂ incorporation, the CC of the device is decreased because MoS₂ is dark in color which does change its color state even under bias. Due to this inert nature and inherent color, the CC is reduced in comparison with the EV/P3HT only device (without doping).

| Table | 4.1: | Comparison | of | various | viologen-based | ECDs | with | the |
|--------|--------|----------------|----|---------|----------------|------|------|-----|
| curren | tly re | ported device. | | | | | | |

| S.No. | Device Composition | Switching Time(s) | Coloration Efficiency (cm ² /C) | CC (%) | References |
|-------|--|----------------------|--|-----------|--|
| 1. | P3HT/MoS ₂ + viologen | 0.8s/0.4s | 580 | 42 | This work |
| 2. | P3HT/viologen | 1.5s/1s | 210 | 80 | Chaudhary <i>et al</i> [109]. |
| 3. | Viologen/V ₂ O ₅ | 10s/6s | NR | 70 | Li et al.[162] |
| 4. | Viologen | 5s/4s | 75.5 | 65 | Alesanco <i>et</i> <i>al</i> .[163] |
| 5. | Viologen/RGO | 6s/9s | NR | 90 | Gadgil <i>et</i> <i>al</i> .[86] |
| 6. | Viologen/FPP | 0.5s/0.4s | 460 | 56 | Chaudhary et al.[164] |
| 7. | Viologen | 6s/3s | 93.5 | 70 | Li et al.[165] |

The change in color of the device can also be understood by the coloration/bleaching mechanism through the schematic (Figure 4.5). As mentioned, the color of unbiased (as-prepared) device is magenta due to the presence of P3HT because viologen is in its transparent state. As the negative voltage (-1.4V) applied to the EV+MoS₂ electrode, the layer of EV^{2+} starts to receive electrons from the electrode and gets reduced to

 EV^{+} (Figure 4.5a), which is a well-known cationic state of EV exhibiting blue color. At the same time, (under the same bias of -1.4V) P3HT gets oxidized from its neutral (magenta) state to a polaronic (transparent) state by losing electrons to the positive electrode. As a result, the color of the device appears blue, and it will remain blue until the voltage is removed. Since the EV layer contains MoS₂ and can store some charge due to its 2D nature which is not utilized by either of the molecules. These electrons can be made available for necessary redox activity when required thus decreasing dependence on the active voltage source. When the reverse bias (1.4V) is applied to the viologen electrode, the reduced EV^{+} gets oxidized either by losing electrons to the power source or by transferring its excessive electrons to MoS₂ (Figure 4.5b).

On the other electrode, the polaronic state of P3HT (transparent) may get reduced to its neutral (magenta) state by taking electrons from the power source and finally, the device starts to show its initial (magenta) color. In this step too, charges stored on the MoS₂ in the EV layer are readily available for the P3HT molecules enables a faster redox activity. This is evident in terms of faster bleaching action which takes only 400 ms (Figure 4.4b). In the absence of MoS₂, the only source for electrons to participate in the redox process is through the power supply thus takes time which also can be appreciated from table 4.1. Overall, the MoS₂ acts as a redox process facilitator and improve device response.



Figure 4.5: Schematic illustration of the device showing electron motion during (a) coloration (magenta to blue) and (b) bleaching (blue to magenta) process. (Adapted from Ref 30, Sol. Energy Mater. Sol. Cells, 2022)
The electrical measurement recorded from the prepared device shows an asymmetric I-V curve resembling a diode (Figure 4.6). The I-V curve shown in Figure 4.6 has been obtained when the solid-state device is connected to the power supply in the polarity shown in the schematic in the inset. When the device is biased with positive voltage, P3HT (EV) encounters the +ve (-ve) polarity of the supply and starts to release the electrons and at the same time EV, at the negative terminal, receives the electrons so that the current starts to flow through the entire device after the application of bias sufficient enough to overcome the oxidation potentials as can be seen in Figure 4.6. On the other hand, under the negative voltage, P3HT and EV both are in their natural states thus do not tend to further reduce and oxidize, respectively, thus restricts the electron flow to yield little current through the device. Such a mutual inability to receive/donate electrons limit the current flow, making the I-V characteristic curve in consonance with the dynamic doping-based mechanism. Such an asymmetric I-V can be of technological importance as has been highlighted in later chapters.



Figure 4.6: Characteristic I-V curve of prepared solid-state device recorded (scan rate: 200 mV/s.) in two electrode geometry with biasing done in the polarity shown in the inset. (Adapted from Ref 30, Sol. Energy Mater. Sol. Cells, 2022)

It clearly indicated that the improved performance of the ITO/EV+MoS₂/P3HT/ITO solid state ECD is likely due to the incorporation of the MoS₂ layer, playing a key role by storing charge to facilitate the necessary redox process in a better way thus assisting in necessary charge transport during color switching of the device. Its large surface area and charge storage capabilities of the 2D-MoS₂ layer act in such a way that charge movement is easy between aligned P3HT interconnected network of P3HT and EV+MoS₂ layers, resulting to improve the carrier mobility to achieve faster coloration-decoloration cycles along with its improved coloration efficiency of EC device. Though increasing the performance of the device, device optimization and quantification of dopants is rather limited hindering the progress in the direction of MoS₂ on the overall performance of EV/P3HT-based solid state ECD has been investigated and discussed below.

4.2 Effect of MoS₂ doping concentration on device performance

This section deals with the effect of MoS₂ doping concentration on the performance of EV/P3HT-based solid-state ECD. As discussed in the above section, MoS₂ offers unique characteristics like high electrical conductivity, good chemical stability, and tunable bandgap which help in improving the performance of the ECD. Since the presence of MoS₂ doping concentrations influences the structural and morphological properties of EC films, which can help to control the optical switching behavior and efficiency of the device. Here optimization of the effect of MoS₂ concentration on the performance of the P3HT/EV ECD. The device works with optimal efficiency at a particular concentration, on doping beyond this value the CC gets compromised.

For device fabrication, hydrothermally synthesized MoS_2 in three different concentrations has been used as a dopant in the EV layer to fabricate P3HT/MoS₂+EV ECDs. Then the effect of dopant

concentrations has been studied in terms of device performance parameters like switching time, color contrast, and coloration efficiency.

4.2.1 Fabrication of Solid-State EC Device

The MoS₂ nanoflowers were doped in the EV to make the solid-state ECD using P3HT and the abovementioned MoS₂ doped EV (with different concentrations of MoS₂) in a PEO matrix. The fabricated device consists thin film of P3HT, and EV (doped with MoS₂) sandwiched between two ITO electrodes (Figure 4.7) and connected with the external bias. The color of the as-fabricated device is magenta, due to the presence of P3HT because EV is transparent. When the device is connected with (1.4 V) external bias, the positive terminal of the battery is attached with the P3HT electrode, the device changes its color from magenta to blue due to the oxidation (reduction) of P3HT (EV) to polaron (EV radical cation) formation governed by the process of dynamic doping. This process is reversible and the device switches back to its original color i.e., magenta and the overall device starts to appear back magenta in color. It was very interesting to study the effect of the concentration of MoS₂ on the performance to optimize the MoS₂ that should be doped to get the best performance of the device and discussed in detail. Identifying the appropriate doping percentage is important as it helps in increasing the efficiency at the cost of CC as has been discussed in detail later on.



Figure 4.7: Schematic diagram of the fabricated layered ECD. (Adapted from Ref 32, J. Phys. D, 2022)

4.2.2 Comparative Electrochromic Performance of the Fabricated EC Device

The electrochromic performance of the fabricated electrochromic solidstate devices (doped with 0.1 wt.%, 0.2 wt.%, and 0.3 wt.% MoS₂) was studied by measuring the absorbance (A) modulation corresponding to the wavelength of 515 nm with respect to time (t), when the device is under the influence of ± 1.4 V bias (Figure 4.8). The device doped with 0.1 wt.%, 0.2 wt.%, and 0.3 wt.% MoS₂, reveals that the device takes 0.80 s, 0.61 s, and 0.47 s to reach the 77% absorbance of its maximum value and 0.4 s, 0.38 s, and 0.30 s to switch back to its 67% value of maximum absorbance (Figure 4.8) respectively. It is evident from Figure 4.8 that switching time decreases with increasing the doping concentration thus making the switching faster. As MoS₂ has the ability to enhance the charge transfer between conjugated polymer and dopant, it facilitates the carrier transport in the device. Resultantly, makes them respond faster in the doped device when biased.



Figure 4.8: Single switching cycle between colored and bleached state for device doped with (a) 0.1 wt.%, (b) 0.2 wt.%, and (c) 0.3 wt.% MoS₂ in the EV layer. (Adapted from Ref 32, J. Phys. D, 2022)

To understand the effect of doping on other device performance parameters like color modulation and coloration efficiency, these parameters have been studied using in-situ bias-dependent optical spectroscopy. In-situ bias-dependent transmittance spectra (Figure 4.9) also show the change in optical transmittance of the device as a function of applied bias and dopant concentration in different panels. The unbiased device with the lowest dopant concentration of 0.1wt.% (blue curve, Figure 4.9a) absorbs mostly near the green band (~525 nm) of the visible spectrum and transmits the remaining two primary colors (red & blue), which gives a magenta color to the device. On positive biasing, the overall transmission band shifts towards lower energy and starts absorbing in the green-red region (red curve, Figure 4.9a) with lower absorption to the blue wavelength. Thus, the blue color of the device starts appearing. Transmission modulation has been calculated from these bias-dependent transmission (%) variation responses of the devices and estimated using Eq. 1.1 (chapter 1). The calculated CC was 42.3% for the lowest concentration which decreases to 30% for the maximum dopant concentration of 0.3 wt.% as can be appreciated from Figures 4.9a - 4.9c. The continuous reduction in the value of CC with dopant concentration is expected due to the electrochromic importance of MoS₂ which additionally, is dark in color and does not change its color state even under bias. This suggests that the 0.1 wt.% doping concentration of MoS₂ is the most suited concentration if one wishes to use these devices for an application where better CC is desired.

Another important parameter, i.e., coloration efficiency was also calculated by Eq. 1.4 (chapter 1) and comes around ~ 583 cm²/C for the device having 0.1 wt.% doping concentration of MoS₂, which is larger than the un-doped device. With increasing the doping concentration of MoS₂ from 0.1 wt.% to 0.2 wt.%, its coloration efficiency decreases from 583 cm²/C to 378 cm²/C and further increases from 378 cm²/C to 490 cm²/C at 0.3 wt.% MoS₂ concentration, shown in Figures 4.9d - 4.9f. This can be understood from Eq. 1.4 (chapter 1), that the coloration efficiency of any device depends on the change in optical density as well as the stored charge. There is a slight variation between the optical densities among these dopant concentrations resulting in



Figure 4.9: (a-c) In-situ bias-dependent (%) transmission spectra and (df) corresponding coloration efficiency of the device fabricated with different concentrations of MoS₂. (Adapted from Ref 32, J. Phys. D, 2022)

small but noticeable difference in the coloration efficiencies of these devices. This is because the stored charge is $0.2 \text{ wt.}\% \text{ MoS}_2$ doped device is greater than $0.1 \text{ wt.}\% \text{ MoS}_2$ doped device. Thus, the coloration efficiency of the device reduces with increasing the dopant concentration. On further increasing the dopant concentration, there is appreciable changes between optical densities and stored charge (Q), so that the increased coloration efficiency has to be obtained than the 0.2 wt.% MoS₂ doped device.



Figure 4.10: Variation of (a) switching time, (b) color contrast, and (c) coloration efficiency as a function of MoS₂ dopant concentration. (Adapted from Ref 32, J. Phys. D, 2022)

It indicates that the appropriate doping concentration of MoS_2 plays an important role in improving the performance of ECD. A MoS_2 dopant concentration-dependent comparison between the switching time, CC, and coloration efficiency is shown in Figure 4.10. There is an evident correlation between MoS_2 doping concentration and the electrochromic performance of fabricated devices (Figure 4.10). This figure summarizes the variation in electrochromic properties of the device with three different concentrations of MoS_2 incorporation with viologen thin film. It is evident that switching becomes faster (decreasing switching times) on increasing the dopant concentration (Figure 4.10a). On the other hand, on increasing dopant concentration, the contrast (as measured using CC) and the efficiency gets compromised on increasing the dopant concentration. The comparison of performance displayed by devices with different MoS₂ concentrations helps in optimizing the device fabrication which can be summarized as follows. The MoS₂ doping improves the overall performance of P3HT/EV-based ECD but while doping the dopant concentration should be optimized depending on the application requirement. For applications, where faster speed is needed, high MoS₂ doping can be used if compromising the contrast ratio is not of much concern. On the other hand, for power-efficient operations with good color contrast, low to moderate doping is appropriate and should be chosen.

Summary

An all-organic layered ECD consisting of polythiophene and viologen (doped with MoS₂) shows fast, power-efficient, and stable performance of the device. Two-dimensional MoS₂ layers provide a large number of active sites in which charges can be trapped and de-trapped when an external voltage is applied to participate in the redox activity that eventually switches the color of the device. This property of the 2D-MoS₂ layer decreases the dependency on the power source for redox activity and thus reduces the overall switching time between two colored states i.e., magenta and blue. With the MoS₂ concentration of 0.1 wt.%, the device takes 0.8 s/ 0.4 s switching time to change its states whereas on further increasing the doping concentration of MoS₂ to 0.2 wt.% and 0.3 wt.%, the switching time becomes (0.61 s/0.38 s) and (0.47 s/0.3 s) respectively.

Additionally, among the three MoS₂ doped solid state ECDs, the 0.1 wt.% MoS₂ doped EC device showed excellent coloration efficiency (~ 583 cm²/C) and CC (~ 42.3%), at a wavelength of 515 nm in the potential range of ± 1.4 V but compromised with the device's color contrast. The study reveals that low to moderate doping of MoS₂ must be chosen for power-efficient operation whereas high dopant concentration is more appropriate for faster device operation. In a broader context, it can be said that doping with 2D materials can help in managing the charge sites which in turn can help in making the device switching faster. Tungsten

disulfide (WS₂) is another such material that can also improve the electrochromic performance of the device, but its inherent color decreases the color contrast. Therefore, we have introduced the mixture of WS₂/WO₃ as a dopant for device fabrication using well-established electrochromic materials as it will help in managing the redox activity without hindering the electrochromic operation. The detailed discussion has been explored in the next chapter.

Chapter 5

Tungsten chalcogenides doped Organic and Hybrid Electrochromic Device

This chapter deals with the synthesis and fabrication of organic and hybrid electrochromic (EC) solid-state devices fabricated with two tungsten chalcogenides. A mixture of WS₂/WO₃ nanoflakes was synthesized by a simple hydrothermal technique and characterized by SEM, XRD, and Raman spectroscopy. The device was appropriately designed and checked by performing various EC performance parameters and compared them with the performance of a device fabricated without any doping. Using the mixture of WS₂/WO₃ as a dopant improves the performance of the ECD. This chapter also reports the EC performance of WO₃ with other conducting polymers i.e., polypyrrole (PPy) in terms of switching time, contrast, and efficiency. This improved study of the device has been discussed here in detail. The research work has been published in journals^{4, 5}.

⁴ S. Kandpal et al, J. Appl. Phys., 2023, 133, 023101.

⁵ S. Kandpal et al, Communicated...

5.1 Doping of WS₂/WO₃ in viologen/P3HT Organic Electrochromic Device

ECD of P3HT/EV with the incorporation of tungsten An disulfide/tungsten oxide (WS₂/WO₃) has been fabricated by following the recipe discussed earlier (section 2.3, chapter 2) to improve its performance. Transition metal dichalcogenide (WS₂) exhibits remarkable electrical conductivity and enhances the charge transfer properties of the P3HT/EV matrix. Additionally, the incorporation of WO₃ enhances the EC performance and stability of the device. The doping of WS₂/WO₃ into the P3HT/EV device creates a synergistic effect that combines the advantage of each component by contributing the effect of both WS₂ and WO₃. In this section, the electrochemical and EC properties of the P3HT/EV (doped with WS₂/WO₃) device has been investigated for optimizing the device architecture to achieve superior EC performance from the device.

5.1.1 Structural Characterization of WS₂/WO₃

A mixture of WS₂/WO₃ nanoflakes was synthesized by a one-step hydrothermal technique, as discussed in section 2.2 (chapter 2). Prior to making the device it was characterized by SEM, XRD, and Raman spectroscopy. The FESEM micrograph (Figure 5.1a) depicts the morphological aspect of hydrothermally synthesized WS₂/WO₃ nanoflakes. It can be clearly observed that the synthesized nanoflakes have thicknesses of a few nanometers. The structural characteristics were analyzed using XRD data (Figure 5.1b). The diffraction peaks at ~ 13.7°, 28.7°, 31.3°, 39.0°, 43.0°, 49.47°, 59.3°, 65.4° and 75.8° correspond to the (002), (004), (101), (103), (006), (105), (112), (114) and (205) which corresponds to the planes of 2H-phase of WS₂ [JCPDS card no: 08-1398] and the peaks at 24.0°, 27.7°, 34.0°, 36.9°, 42.1°, 47.1°, 54.0° and 57.7° corresponds to the (001), (200), (111), (201), (300), (002), (221) and (400) planes of the hexagonal phase of WO₃ [JCPDS card no: 75-2187]. The peak marked by an asterisk (*) represents the (111) plane of orthorhombic WO₃.(0.33H₂O). The structural feature of the nanoflake sample has been further verified using Raman spectroscopy (inset, Figure 5.1b). The peaks centered at ~ 351.5 and 420.5 cm⁻¹ are attributed to the E_{2g}^1 and A_{1g} modes of WS₂. The E_{2g}^1 mode is associated with the interlayer atomic vibrations of the W-S bond with both the atoms moving in opposite directions whereas the A_{1g} mode is related to the intralayer vibrations of S atoms. The peaks at ~ 173 and 269 cm⁻¹ represent the bending (W-O-W) mode of bridging oxygen whereas the peak at ~ 788 cm⁻¹ corresponds to the stretching (O-W-O) vibrational mode of tungsten atoms and adjacent oxygen atoms of hexagonal WO₃.



Figure 5.1: (a) FESEM micrograph; (b) XRD pattern of WS_2/WO_3 nanoflakes along with the Raman spectrum (inset).

5.1.2 Fabrication of solid-state EC Device

The ECD having the structure "ITO glass/P3HT/(WO₃/WS₂+EV)/ITO" glass was fabricated by sandwiching the P3HT and EV (doped with WO₃/WS₂) in PEO gel electrodes, as shown in the schematic (Figure 5.2). The finally prepared device appears magenta in color due to the inherent color of pristine P3HT with the EV layer being transparent. As the external power supply (+1.5 V, with respect to P3HT) is applied across the two different electrodes of the device, the device changes its initial magenta color to blue color as shown in the actual photographs of the device (inset, Figure 5.2). This is because of the reduction of the EV²⁺ ion to its EV⁺⁺ radical cation and comes from its transparent state to a blue state. Subsequently, neutral P3HT gets oxidized by losing its

electron to the electrode and changes its magenta color to its transparent color through a dynamic doping process.



Figure 5.2: Schematic representation of layered device along with its actual photographs (inset) under different bias conditions.

5.1.3 Electrochemical Measurements of the Fabricated EC Device

The color change of the device can also be understood by the biasdependent transmission spectra of the device (Figure 5.3), which shows the change in optical transmittance of the device as a function of applied bias and can be correlated with the perceived color of the device. The maximum transmission occurs in the blue and red wavelength regions of the visible spectrum which gives the initial (magenta, OFF) color to the device (blue curve, Figure 5.3a) whereas the colored (blue or "ON") state is characterized by the overall transmission band in the lower energy (blue wavelength) region (red curve, Figure 5.3a) and giving the blue appearance to the device. There is an increased transmission of IRradiation in the OFF state of the device whereas suppressed transmission in the IR-radiation value, as a function of applied bias. It can be appreciated from Figure 5.3b which shows the multiwavelength transmission modulation of the device in the visible (~515 nm) as well as NIR (~800 nm) wavelength regions. The device has sufficiently good color contrast in the visible wavelength region with a maximum value of ~ 52% at 515 nm.



Figure 5.3: (a) In-situ bias-dependent transmission spectra of the device in the visible (~515 nm) as well as NIR (~800 nm) wavelength region in (b).

The device shows reversible color switching between the two colors represented through the CIE color coordinates (u',v') of (0.381, 0.362) in the OFF state and (0.198, 0.262) in the ON state (Figure 5.4) without compromising the good contrast value corresponding to the higher wavelength in the near-infrared (NIR) region. Therefore, these two wavelength regions have been chosen to carry out investigations related to the EC switching behavior of the device by measuring its switching kinetics.



Figure 5.4: CIE color coordinates of the fabricated device as well as the corresponding images.

In addition to the CC of the device, switching stability/cyclability is another important parameter, which is also examined through the EC performance parameters of the device (Figure 5.5). The device shows excellent switching stability of at least 1000 seconds when the device is continuously toggled between ON/OFF states with an applied square pulse of ± 1.5 V amplitude of 5 s time interval each at 515 nm and 800 nm wavelength regions respectively. The ECD exhibited less variation in absorbance even after 200 repeated operation cycles at the visible (~ 515 nm, Figure 5.5a) wavelength region whereas the repeated switching cycles at IR (~ 800 nm) region show some spikes in the absorbance values due to the external environmental disturbance while recording the repeating switching cycles of the device (Figure 5.5b). The significantly less variation in absorbance in the repetition of such switching steps up to 1000 s or 200 switching cycles shows a great stability/cyclability of the device in both wavelength regions.

One of these absorbance switching cycles has been used to measure the switching time taken by the device to toggle between it's ON and OFF states (Figures 5.5c &5.5d). The switching time is defined as the time taken by the device to show 90% change in the absorbance value. The as-prepared device takes 500 ms to switch from its OFF state (magenta) to its ON state (blue), while 700 ms is required to switch back to the OFF state from the ON state at visible (~515 nm) wavelength region (Figure 5.5c) whereas its switching time at IR-wavelength (~ 800 nm) region is 0.8 s (coloration, ON)/0.8 s (bleaching, OFF) respectively (Figure 5.5d).

A switching time of less than a second shown by the device represents a fast switching that has been achieved due to the presence of the mixture of WS₂/WO₃ as it can store charge carriers under external bias, which facilitates the necessary charges to take part in a reversible redox reaction to P3HT in an ECD. Additionally, the coloration efficiency, calculated using Eq. 1.4 (chapter 1), of the device was obtained to be ~ 460 cm²/C and 288 cm²/C (Figures 5.5e – 5.5f) for visible (~ 515 nm) and IR (~ 800 nm) wavelength regions respectively. These values of a few hundred represent moderately high coloration efficiency from a device in its solid-state form making it a good option for power-efficient operation.



Figure 5.5: (a) In-Situ bias-dependent multiple switching cycles of the device between ON and OFF states in the voltage window (± 1.5 V) at visible and IR wavelength region in (b), (c) single switching cycle at 515 nm wavelength, (d) response time of the device in the same fixed voltage window at 800 nm wavelength, and the corresponding estimated coloration efficiencies of the device in (e), (f).

The better performance of the device is also evident from the comparison table below (table 5.1). As mentioned above, the possible reason for improved color switching performance is the charge storage capabilities of WS_2/WO_3 which gives the device a possibility to be explored for

charge storage applications. The charge storage capabilities have been exclusively studied and reported separately in the next chapter.

Table 5.1: Comparison table of various reported P3HT-based solid-state

 ECDs.

| S.No | Device Composition | Switching Time | Coloration Efficiency (cm ² /C) | Reference |
|------|---|-------------------|--|--|
| 1 | РЗНТ-NTTO | 0.8s | 1055 | Bansal et al.[166] |
| 2 | PANI/P3HT | 0.5s | 534 | Pathak et al.[167] |
| 3 | РЗНТ/РСВМ | 0.5s | 320 | Chaudhary <i>et</i> <i>al</i> [168] |
| 4 | P3HT/IAI/PET | 0.3s | 252 | Kim <i>et al.</i> [169] |
| 5 | P3HT/Viologen | 1.5s | 200 | Chaudhary et al.[164] |
| 6 | P3HT/WO ₃ +WS ₂ +EV | 0.5s | 460 | This work |

Based on the above discussion, it is very clear that incorporation of WS₂/WO₃ plays the key role by storing charge to facilitate the necessary redox process efficiently thus assisting in necessary charge transport during color switching of the device. This yields a better way to make an improved performing device, capable to show dual-band EC modulation in visible as well as NIR ranges.

5.2 Organic-Inorganic Hybrid Polypyrrole/WO₃ Electrochromic Device

This section demonstrates another hybrid ECD made using the organic (polypyrrole) and inorganic (tungsten oxide) combination. Another "p-

type" EC material i.e., polypyrrole (PPy) with tungsten oxide (WO₃) has been introduced here to fabricate an ECD. PPy has been chosen here because it along with its derivatives is a well-known electroactive and conducting polymers, which can be synthesized both chemically and electrochemically in organic solvents. It is the most considered conducting polymer than others because of its high conductivity, stability, flexibility, good mechanical property, and low cost of its monomer (pyrrole)[85,170,171]. The EC performance of that hybrid device was studied through various performing parameters like switching time, efficiency, cycle life that are discussed below.

5.2.1 Structural Characterization

The thin film of WO₃ was deposited over the FTO glass substrate by hydrothermal synthesis technique (a detailed recipe is discussed in section 2.3, chapter 2). The uniformity of the deposited thin film was characterized by recorded SEM micrographs. It clearly shows that the film covers the substrate fully and it is likely that the devices, fabricated using them, will not result in short devices as has been confirmed later on. It can also be seen that WO₃ nanoparticles are present with a particle size in the range of nanometers (Figure 5.6a). The structural characteristics has further validated by using Raman spectroscopy, shown in Figure 5.6b. Peaks observed at 717 cm⁻¹, and 813 cm⁻¹ are attributed to the stretching vibration of tungsten atoms and adjacent oxygen atoms while the peak at 270 cm⁻¹, 327 cm⁻¹ arise due to the bending mode.



Figure 5.6: (a) Top view of SEM micrograph of synthesized WO₃ thin films along with its Raman spectrum (b). (Adapted from Ref 28, J. Appl. Phys., 2023)

Another counter electrode was deposited by electro-polymerization of pyrrole. Polymeric PPy film was deposited on the FTO substrate using the solution containing pyrrole in acetonitrile and tetrabutylammonium tetrafluoroborate (TBABF4) as a supporting electrolyte (as explained in chapter 2). Electropolymerization of pyrrole begins with the formation of small globules and these small globules lead to cluster formation (Figure 5.7a). Further, Raman spectrum (Figure 5.7b) shows two intense peaks at 1597 cm⁻¹ and 1314 cm⁻¹, corresponds to the stretching vibration of carbon atoms while 1040 cm⁻¹ and 980 cm⁻¹ peaks arise due to the formation of radical cation (polaron). These experimental pieces of evidence lead to the confirmation of successfully deposited PPy and WO₃ thin films.



Figure 5.7: (a) Surface morphology of electrodeposited PPy film and (b) corresponding Raman spectrum. (Adapted from Ref 28, J. Appl. Phys., 2023)

5.2.2 Electrochemical Characterization

Further electrochemical properties of both the deposited films have been studied through cyclic voltammetry (CV) measurements, which was performed in 0.1 M LiClO₄ in acetonitrile electrolyte at a scan rate of 10 mV/s. Calomel as a reference, platinum as a counter, and deposited film (on FTO) as the working electrode have been used to study their CV. The

CV curve of the PPy thin film (Figure 5.8a) shows redox peaks in the positive potential window when it scans from (-0.75 V) to (2V) voltage window. Similarly, the CV of the WO₃ thin film (Figure 5.8b) shows its redox behavior in the negative potential window. It is expected that the combination of these two complementary redox active species will support each other on a biased induced color change mechanism.



Figure 5.8: Cyclic voltammetry curves of synthesized (a) PPy and (b) WO₃ films at a scan rate of 10 mV/s

5.2.3 Fabrication of solid-state EC Device

Solid-state ECD was fabricated using the above two electrodes (WO₃ and PPy) in a crossbar geometry. The detailed stepwise recipe of device fabrication was the same as mentioned in section 1.4 (chapter 1). The finished device containing thin films of these two constituents has been schematically shown in Figure 5.9 along with the device photographs under different bias conditions. The color of the as-prepared device (under 0V bias) is greenish-blackish due to the presence of PPy, as WO₃ is transparent. During the bias condition (+1 V), the color of the device changes from greenish-blackish to bluish-greenish color due to the oxidation/reduction of PPy/WO₃ whereas on reversing the polarity of bias voltage (-1 V) the color of the device switches back to its initial (greenish blackish) color.



Figure 5.9: Schematic representation of layered device along with their original photographs in different biased states. (Adapted from Ref 28, J. Appl. Phys., 2023)

5.2.4 Electrochromic Measurements of the Fabricated EC Device

In-situ bias-dependent transmission measurement has also been recorded at 0 V and \pm 1 V (Figure 5.10). The black (dotted) curve (Figure 5.10) shows the initial color (i.e., greenish-blackish) of the fabricated device. It can be seen here the maximum transmission of the fabricated device is observed at wavelength ~ 650 nm. When a positive bias (+1 V) is applied across the device, such that the positive terminal of the battery is connected to the PPy-coated electrode while the WO₃ electrode is connected to the negative terminal, the maximum transmission shifts from its initial position (red curve, Figure 5.10) and the device starts to show its greenish bluish color. Further, on reversing the bias polarity, the optical spectral response changes to the one like for the as-prepared device (blue curve, Figure 5.10) confirming that the bias reversal is followed by the color reversal which is an important aspect from the application point of view.



Figure 5.10: In-situ bias-dependent transmission spectra of the hybrid device. (Adapted from Ref 28, J. Appl. Phys., 2023)

Two phenomena can be considered to be responsible for changing the colors which is simultaneously taking place between the two separate electrodes. When the PPy layer is connected to the positive terminal of the battery, neutral PPy is changing to its oxidized (polaronic) state whereas the WO₃ layer, connected to the negative terminal of the battery, is getting reduced from its W^{VI} (transparent) to W^{V} (blue) state. Consequently, the device changes its greenish-blackish color to bluish greenish color. Again, on reversing the bias polarity, the polaronic state of PPy converts to its reduced (neutral) state, and simultaneously (W^{V}) state gets oxidized to its neutral (W^{VI}) state, consequently, the device reappears its initial (greenish blackish) color. The maximum CC of the device was more than 47% at the wavelength of 650 nm, so the other parameters were calculated at the same wavelength.

Furthermore, to check the performance of the fabricated device, various parameters have been measured by applying the voltage pulse between +1 V (for 5 s) and -1 V (for 5 s). The switching kinetics of the device has been measured at 650 nm wavelength because it is the wavelength in which the maximum optical density change of the device is produced between colored and bleached states. The cyclic stability of the device

has been tested up to 500 seconds (Figure 5.11a) showing very less degradation in the transmission values during its coloration/bleaching states, which is a very good sign of the stability or cyclability of the ECD. A zoomed portion, showing a single transmission switching cycle (Figure 5.11b), is used to estimate the switching time of the device between coloration and bleaching states under a commutative voltage window. The Switching time is defined as the time required for the fabricated device to reach 90% of the transmission/absorbance change between the steady colored and bleached states. For the PPy/WO₃ hybrid solid-state ECD, the switching time (Figure 5.11b) is 1.1 s and 1.8 s respectively, which is faster than the pristine WO₃-based ECDs. The switching in the transmission values is due to the reversible nature of the fabricated device. which also validates by the cyclic chronoamperometric response in Figure 5.11c. A finite current is flowing through the device in the forward as well as reversed bias, which is a consequence of the charging and discharging of the used EC materials.



Figure 5.11: (a) Absorption switching kinetics of the device under switching voltage from 1 V to -1 V with multiple cycles, (b) Single absorption switching, (c) current response of the device under \pm 1 V

voltage pulse train and (d) estimated device's efficiency. (Adapted from Ref 28, J. Appl. Phys., 2023)

Another important parameter i.e., coloration efficiency (η_{ce}) provides a large optical modulation with low charge insertion or extraction, which is one of the crucial parameters for practical ECDs. (Eq. 1.4, chapter 1) Figure 5.11d shows a plot of change in optical density (Δ OD) versus the stored charge density at \pm 1 V (for 650 nm wavelength). The calculated value of the coloration efficiency is the slope of the curve between the change in optical density (Δ OD) and stored charge density (Q) and comes out to be 304 cm²/C. This high value is due to the complementary nature of the used electrode materials, as mentioned above. This can also be possible by using of PPy electrode, which reduces the required redox potential of WO₃ electrode to switch its color between coloration and bleaching states. Obtained values of various parameters is quite high as compared with those of the best-known tungsten oxide based ECDs, which can also be seen in table 5.2 below:

| S.No. | Device/Film Composition | Switching Time(s) | Coloration Efficiency (cm ² /C) | Color contrast (%) | References |
|-------|----------------------------|----------------------|--|--------------------------|---------------------------------------|
| 1. | PPy/EV | 1.35s/0.8s | 194 | 34 | This work |
| 2. | PPy | 1.5/2 | 23.33 | 38.3 | Bhosale <i>et</i> <i>al</i> .[172] |
| 3. | PPy/WO3 | 0.6/0.8 | 153.33 | 48.5 | Bhosale <i>et</i> <i>al</i> .[172] |
| 4. | NiO/PPy | 0.6/0.4 | ~ 300 | NR | Sonavane <i>et</i> <i>al</i> [173] |
| 5. | PPy/TiO2 | 1.5/9 | NR | ~ 50 | Takagi <i>et</i> <i>al</i> .[174] |
| 6. | PPy/PEDOT | 6/9 | 100 | 28.2 | Silva <i>et</i> <i>al</i> .[175] |

Table 5.2: Comparison table of various polypyrrole based- ECDs:

Further, its electrochemical cyclic stability was studied by the double step potential technique of chronoamperometry. Recorded

chronoamperometric curves (Figure 5.12) clearly show that there is no significant change in the curve shapes whereas the change in magnitude of the peak current is very less from the first cycle to the 200th cycle, indicating that PPy/WO₃ ECD has good stability and remarkable durability under coloration/discoloration process. In brief, using an electrodeposited PPy layer when used as a complementary layer with a hydrothermally grown WO₃ layer makes an efficient EC solid-state device with improved switching time, stability and good coloration efficiency which can be used in various EC applications.



Figure 5.12: Chronoamperometry curves of WO₃/PPy hybrid ECD at the different cycles under the step potential of +1V/-1V for 5s each step time. (Adapted from Ref 28, J. Appl. Phys., 2023)

Summary

All-organic solid-state ECD was fabricated using well-characterized WS₂/WO₃ nanoflakes with the organic electrochromic materials, P3HT and EV displays power efficient device with a color-switching between magenta and blue colors with a small bias of \pm 1.5V. The device shows a great color contrast ratio of 52%, fast switching time of less than one second along with excellent coloration efficiencies of 460 cm²/C and 288 cm²/C at wavelengths ~ 515 nm (visible), and ~ 800 nm (NIR)

respectively. The improved EC performance of the device is originating from the mutually supporting redox behavior of the P3HT, EV, and the charge-facilitating nature of WS₂/WO₃. The WS₂/WO₃ doping in an all-organic material improves dual-band EC modulation in visible and NIR ranges respectively.

Furthermore, an organic-inorganic hybrid device fabricated by another anodic EC active material (PPy) with WO₃ shows a power-efficient color modulation performance. Obtained values of switching time, and coloration efficiency indicate the faster insertion/desertion kinetics between PPy/WO₃ films and lead to a fast and efficient application-based solid-state liquid electrolyte-less ECD. Some other interesting features of electrochromism have also been observed in these organic ECDs when doped with 2D-layered materials. This is the topic of the next chapter and has been discussed in detail.

Chapter 6

Multifunctional Operation: Electrochromic Supercapacitor and Rectifier

This chapter describes the multifunction application of the ECD fabricated with EV and P3HT electrochromic materials by the doping of 2D-layered material's composite i.e., MoS₂/MWCNTs or WS₂/WO₃. The device was appropriately designed and checked by performing various measurements to test it as a rectifier and supercapacitor. Doped MoS₂/MWCNTs add an additional function i.e., rectifying behavior in the ECD whereas WS₂/WO₃ adds an energy-storing behavior without modulation with the electrochromic performance of the device. This chapter will demonstrate the multifunctional properties of an ECD as well as a rectifier in a single solid-state device, which can be used in a rectifying circuit to rectify less frequency of sinusoidal signals[83]. Another interesting feature to store energy in a single device will also be explored in this chapter. These two additional features of the fabricated electrochromic device were studied in detail which makes the solid-state ECD future ready. The results described here have been reported as journal publications^{6, 7}.

⁶ S. Kandpal et al, ACS Materials Au, 2022, 2, 293-300.

⁷ S. Kandpal et al, Communicated...

6.1 Co-doping MoS₂ & MWCNTs in P3HT/EV for Fabricating Electrochromic Rectifying Device

The integration of molybdenum disulfide (MoS₂) and multiwalled carbon nanotubes (MWCNTs) into an organic electrochromic device holds great potential to create a hybrid system with rectifying properties in addition to its inherent bias induced color changing behavior. MoS₂, a 2D-layered material, enhances charge transport properties within the device and facilitates the flow of current in a specific direction[161]. This feature is essential for rectification, where the device allows the current to flow preferentially in one direction while inhibiting it in the opposite direction. On the other hand, MWCNTs improve the electrical properties and stability of the organic electrochromic materials in the device. Additionally, the unique structure of MWCNTs provides a well-defined pathway for charge transport, contributing to rectification behavior in the device.

The incorporation of MoS₂/MWCNTs as dopants in the ECD allows the synergistic effects of both materials that can enable efficient charge transfer, rectifying the flow of current through the device. Here we explored the additional functionality i.e., rectifying property with electrochromism in P3HT/EV (doped with MoS₂/MWCNTs) based ECD.

6.1.1 Structural Characterization

The MoS₂ nano-flowers and MWCNTs used in the device, have been synthesized by facile one-step hydrothermal route and ferrocene-toluene pyrolysis respectively, using the recipe discussed in section 2.2 (chapter 2). The synthesized MWCNTs and MoS₂ nano flower was characterized by SEM, XRD, and Raman spectroscopy, which is already explained in the structural characterization section of section 3.2 (chapter 3) and section 4.1 (chapter 4).

6.1.2 Fabrication of Solid-State EC Device

A fabricated ECD contains two layers on two ITO-coated glass electrodes, which are complementary to each other. One of the ITO electrodes is coated with P3HT, an EC material, and the other one is coated with an MWCNT-MoS₂ mixture doped EV. The two electrodes are connected by ion-conducting PEO gel-type electrolyte as shown in the schematic (Figure 6.1), which provides the path for ions to move from one electrode to another electrode under the application of external bias. It important mention is here to that the ITO/P3HT/EV(MoS₂+CNT)/ITO device is actually an ECD that shows color modulation between magenta and blue color under appropriate electrical bias.



Figure 6.1: Schematic illustration of the layered device with its constituent layers. (Adapted from Ref 83, ACS Materials Au, 2022)

6.1.3 An Electrochromic Rectifier

The fabricated device shows an asymmetric I-V curve exhibiting diodic nature (Figure 6.2) when measured in two-terminal geometry with connections made with polarities shown in the inset. Initially (0V or no bias applied), the EC rectifying device is magenta (pristine color of

P3HT) in color as the EV layer is transparent in this state. When 1.4 V bias across the ECD is applied, the device turns its color from magenta to blue due to the simultaneous oxidation (reduction) of P3HT (EV) to polaron (EV radical ion). This complementary redox reaction, taking place at appropriate terminals, provides the continuous supply of charge which is reflected as the current (~ 0.25 mA at 1.4 V, Figure 6.2) in this bias polarity state (say forward bias). The above-mentioned EC rectifying device is reversible in nature due to the reversible redox activity of P3HT and it switches its color back from blue to magenta on reversing the polarity (-1.4 V). When a negative bias is applied to an asprepared device where the (doped-) EV layer receives a positive voltage and P3HT layer receives a negative voltage, no current flows because at this polarity (say reverse bias) EV (P3HT) layer cannot oxidize (reduce) hence do not allow current to flow (0 mA at -1.4 V, Figure 6.2). As a consequence of the above complementary redox nature of EV and P3HT, an asymmetric diodic I-V curve is observed which can be used for rectifying purposes as has been discussed later on.



Figure 6.2: I-V characteristic curve of the device (inset) at scan rate 100 mV/s. (Adapted from Ref 83, ACS Materials Au, 2022)

Before utilizing the diodic I-V behavior of ECD, its color-switching property has been studied using in-situ UV-Vis spectroscopy to see bias-

induced modulation in absorbance from the device (Figure 6.3a) and its ability to switch multiple times (Figure 6.3b). The bias-dependent optical modulation from the device can be seen very clearly from the corresponding change in the absorption spectra recorded from the device (Figure 6.3a). The device in its as-prepared state absorbs mostly in the green region of the visible spectrum thus appearing magenta as can be understood from the complementary color scheme.

On the other hand, when forward biased, the optical response changes and the device starts absorbing red as well as green light thus leaving only blue to be perceived and giving the blue appearance as can be seen from the actual photograph of the device shown in the insets. On bias reversal (reverse bias), the optical spectrum retraces the spectrum obtained from the as-prepared device which again looks magenta, and it means that the bias-induced color modulation is reversible.



Figure 6.3: (a) In-Situ bias-dependent absorption spectra of the fabricated device along with photographs of the device and (b) stability of absorption cycles of the device. (Adapted from Ref 83, ACS Materials Au, 2022)

Stability, or cycle life, is another very important property of a device especially when one intends to use it for rectification purposes. The device has been tested to check its cyclability by observing cyclic color modulation corresponding to 515 nm wavelength by applying a constant square pulse function of (\pm 1.4 V, 3 s duration). The device shows a very good cycle life of at least 200 cycles (Figure 6.3b) without much change in the absorbance values in either of the colored states of the device. A

good cycle life suggests that it is suitable for application as a rectifier as has been discussed later.

As mentioned above, the color switching and diodic nature of the I-V curve (Figure 6.2) is a consequence of bias-induced redox change. To ensure that this is the mechanism for the device's working, in-situ Raman spectroscopy has been carried out from the device under different bias conditions. The Raman spectrum of the as-fabricated device shows (0 V, black curve in Figure 6.4) two peaks at 1379 cm⁻¹ and 1444 cm⁻¹ which are signatures of the presence of neutral P3HT (magenta appearance). On increasing the bias to 1.4 V the Raman spectrum changes where the above peaks shifted (red curve, Figure 6.4) at 1411 cm⁻¹ and ~1460 cm⁻¹ ¹, which indicates the formation of polaron and bipolaron which are formed after oxidation of P3HT as expected. The transparent and blue color of polarons and bipolarons, respectively, also explains the blue appearance of the device in this forward bias condition where the EV also converts to its radical cationic state which is also blue. On bias reversal, the Raman spectrum from the device (green curve, Figure 6.4) mimics the spectrum obtained from the as-prepared device (black curve, Figure 6.4) confirming the reinstallation of neutral P3HT phase as can be seen as its magenta color appearance.



Figure 6.4: In-situ Raman spectra of prepared solid-state device under different bias conditions. The corresponding device color is shown in the respective insets. (Adapted from Ref 83, ACS Materials Au, 2022)

For utilizing the asymmetric I-V characteristic of the device, the ECD diode has been used in a half wave rectifier circuit (Figure 6.5a) where the typically used semiconductor p-n junction diode (inset, Figure 6.5a) has been replaced by the ECD diode. An equivalent rectifying circuit was connected using the ECD diode with a load of 10 Ω resistance whereas a function generator was used to give a sinusoidal wave of 1Hz. A digital oscilloscope was used to monitor the input (sinusoidal wave) and the output at the load resistance (rectified signal) simultaneously in an arrangement shown in Figure 6.5b. The half wave rectification of a 1 Hz sine wave signal was achieved using the ECD diode as can be seen in Figure 6.5c which shows the AC input voltage (1.4 V, yellow curve) and rectified signal (violet curve), in which only positive half of the sinusoidal wave input is present and negative half cycle is almost absent and appears as noise due to poor signal to noise filtration in the circuit. Low-frequency negative voltages from sinusoidal signals can be
successfully filtered using the electrochromic diode fabricated using 2D material doped EV/P3HT all-organic device.



Figure 6.5: (a) Schematic illustration of the fabricated EC rectifier with the basic circuit rectifier in the inset, (b) rectification measurement experimental setup, and (c) input sine function signal (yellow curve) and rectified signal (purple curve) using EC diode at 1Hz. (Adapted from Ref 83, ACS Materials Au, 2022)

The layered 2D-like nanostructures of MoS_2 , the unique 1-dimensional electronic structure of CNT, and their tendency to trap the charges between layers and de-trap under external bias leads to enhance the charge carrier mobility in one direction that eventually improves the rectification of ECD and can allow one to filter frequency upto 1 Hz. In the absence of these dopants, the device takes up to a few seconds to switch thus restricting such diodes to filter only very small frequencies. At higher frequencies, the diodic nature is not present and thus acts as a short circuit for sinusoidal inputs.

An all-organic EC diode fabricated using P3HT and (MoS₂-CNT doped) EV layers switches faster than the undoped device and enables one to use these diodes for rectifying sinusoidal functions of frequency up to 1 Hz. It is important here to mention that the color contrast of the device incorporated with MoS_2 and CNT is less than that of the device without these. Since $CNTs/MoS_2$ incorporation decreases the contrast, the amount to be incorporated in the device (to increase the coloration speed and efficiency) is limited by the desired contrast as decided by the specific application. Since color contrast is not much of a concern for rectifiers therefore one can use the maximum amount of these dopants to achieve the fastest possible rectifier.

It can be said that a solid-state EC diode, fabricated using organic electrochromic conducting polymer P3HT and EV (doped with MoS₂/MWCNTs composites) shows reversible color modulation between magenta and blue colors when a bias of \pm 1.4 V is applied. Doping of MWCNTs and MoS₂ makes the device switch faster as compared to the basic EV/P3HT device making it suitable for rectification of AC voltages up to 1 Hz. Its charge-holding property between conducting polymer layer (P3HT and EV) enhanced the forward-bias current and rectification ratio. The use of EC devices in rectifier circuits and their frequency response also has been evaluated, which indicates its low frequency rectifying nature with an input oscillating voltage of \pm 1.4 V.

6.2 Electrochromic Supercapacitor using WS₂/WO₃ doped P3HT/EV Solid State Device

As discussed in chapter 5, WS₂ possesses sufficient electrical conductivity and storage capacity to be used in a device whereas WO₃ allows reversible color change on external bias and contributes to maintaining the contrast of an electrochromic device. Additionally, its ability to store and release energy quickly contributes to the overall energy storage capacity of the device.

Keeping this in mind, the doping of WS_2/WO_3 in an organic electrochromic device is expected to offer the combine functionalities i.e., electrochromism and energy storage in a single device that can

exhibit both energy storage and visual display capability. The EC energy storage behavior of this co-doped integrated device has been studied in terms of device performance parameters such as UV-Vis, cyclic voltammetry, galvanostatic charging/discharging, EIS, etc.

6.2.1 Structural Characterization

A one-step hydrothermal technique was used to synthesize WS_2/WO_3 nanoflakes and then characterized by scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. Its detailed description has already been discussed in the structural characterization of section 5.1 (chapter 5).

6.2.2 Fabrication of Solid-State EC Device

For the fabrication of a multifunctional ECD, thin films of P3HT and WS₂/WO₃ doped ethyl viologen, grown through the spin coating and drop casting techniques over ITO-coated glass substrates, have been used. For this, three different solutions i.e., 0.3wt% P3HT in DCB, 5wt% PEO in ACN, and 4wt% EV in ACN were prepared by using vortex mixing. The P3HT film (~ 1µm thick) was spin-coated on ITO-coated glass substrate at 500 rpm for 120 s and then annealed at 80°C for one hour whereas a layer of EV (premixed with WS₂/WO₃) in PEO matrix was drop casted on another ITO coated glass substrate and then assemble together with the help of double-sided tape using simple flip-chip method. The finally prepared device (Figure 6.6) shows its magenta color that changes to blue under the potential bias of +1.5 V (with respect to P3HT). On reversing the bias polarity (-1.5 V), the device comes back to its magenta color (Figure 6.6) due to the bias reversal redox behavior of both the EV and P3HT electrodes, as can also be seen in the actual photographs of the device.

As discussed in chapter 5, the device having the structure $[ITO/P3HT/(WS_2/WO_3)+EV/ITO]$ shows electrochromism in two wavelengths (visible ~ 515 nm and NIR ~ 800 nm) regions. The device shows its improved EC performance in terms of switching time, color

contrast, efficiency, and stability/cyclability in both wavelength regions of the electromagnetic spectrum.



Figure 6.6: Schematic diagram of the layered device

6.2.3 Supercapacitive Charge Storage Properties

The (super-) capacitive property of the solid-state ECD has been studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD) curves. The CV curves of the fabricated solid-state ECD at different scan rates from 100 mV/s to 400 mV/s in the potential range of (-1.5 V) to (2 V) have been recorded (Figure 6.7) scanned in the direction marked with arrow. These curves show a pair of redox peaks at (0.1 V) and (-0.2 V) indicating the presence of pseudocapacitive material i.e., WS₂/WO₃ nanoflakes in the device.



Figure 6.7: Cyclic voltammetry of the device recorded at different scan rates. The arrows show the scan direction.

Furthermore, the movement of ion diffusion in an ECD has been investigated by EIS using a Nyquist plot (Figure 6.8a) up to the frequency range of 100 kHz to 10 mHz. The Nyquist plot exhibits a semicircle and linear regiment representing high- and low-frequency regions, respectively. The semi-circle in the high-frequency region is associated with the contact resistance between solution and electrolyte whereas the linear regiment at the low-frequency region associated with the redox mechanism occurs at the electrode-electrolyte interface, which indicates the capacitive behavior of the fabricated solid-state ECD. To fit the EIS analysis data an equivalent electrical circuit (inset, Figure 6.8a) has been plotted which shows the small charge transfer resistance, indicating fast charging and discharging response time of the device.

Further, the electrochemical performance of the device has been investigated through the galvanostatic charge/discharge curve with different current densities (1 A/g to 2 A/g) using a potential window from 1.6 V to -1.6 V (Figure 6.8b). The deviation from the ideal triangular shape of the GCD curves indicates the contribution from the pseudocapacitive charge storage behavior of the device. The small IR drop present in the GCD curves of the device also shows the small charge

transfer resistance offered by the electrolyte ions as also expected from the EIS plot. It is also clearly seen that the discharging time decreases with the increase in current density due to the faster diffusion of electrolyte ions on the active material of the device. A bit longer discharging time, than charging time, indicates the high coulombic efficiency of the device, which makes it suitable for practical applications.



Figure 6.8: (a) Nyquist plot (inset: equivalent electric circuit), (b) charging-discharging curves with increasing current densities of the device.

The energy storage behavior of the device was evaluated by estimating the specific capacitance values from a GCD plot using the equation mentioned below:

$$C_s = \frac{I\Delta t}{m\Delta V} \tag{6.1}$$

where *I* is the discharge current, Δt is the discharge time, ΔV is the potential window and *m* is the active material mass over the electrode. The obtained maximum specific capacitance value for the device is ~ 50 F/g at a current density of 1 A/g and shows a typical variation with current density (Figure 6.9). A gradual decrease in specific capacitance with current density also indicates the pseudocapacitive nature of the device. Since high energy density is desired and is one of the factors which makes supercapacitor device suitable for practical applications

therefore the energy density of the device has been calculated using the equation mentioned below:

$$E_D = \frac{1}{2}C_s(\Delta V)^2 \tag{6.2}$$

where C_s is the calculated specific capacitance of the device and ΔV is the working potential window. The maximum energy density of the device is calculated to be ~ 60 Wh/kg (inset, Figure 6.9) at a current density of 1 A/g. Based on the above discussion, it is very clearly evident that an ECD vis-e-vis ITO/(EV+WS₂/WO₃)/P3HT/ITO shows not only an improvement in EC performance but also displays moderately high super capacitive performance.



Figure 6.9: Variation of specific capacitance as a function of value along with the energy density with the increasing current density in the inset.

It is evident that the two properties, namely improved EC performance and charge storage capabilities, are complementary to each other and support mutual operation. The WS₂/WO₃ doping enables one to achieve (i) improved dual-band EC modulation (chapter 5) in the visible and NIR range and (ii) multifunctional operation by adding charge storage making it an overall multifunctional EC solid-state device.

Summary

An appropriately designed solid-state ECD can be used in multifunctional applications. A solid-state EC diode fabricated using organic EC conducting polymer P3HT and EV (doped with MoS₂/MWCNTs composites) shows reversible color modulation between magenta and blue colors when a bias of \pm 1.4V is applied. Insitu Raman spectroscopy establishes that the color modulation is caused by the bias-induced redox switching as a consequence of dynamic doping in P3HT. It has been observed that doping of MWCNTs and MoS₂ makes the device switch faster as compared to the basic EV/P3HT device making it suitable for rectification of AC voltages up to 1 Hz, which was also validated through obtained asymmetric I-V characteristic curve.

Further, doping of WS₂/WO₃ nanoflakes with P3HT/EV can be used to fabricate an EC supercapacitor. The device combines the two applications namely, electrochromism and energy storage. The device shows a great contrast ratio and coloration efficiency while operating in dual-band color modulation. Additionally, it also exhibits a maximum capacitance of ~ 50 F/g and an energy density of ~ 60 Wh/kg at a current density of 1 A/g. The designed EC supercapacitor device demonstrates its excellent capacitive performance along with the ability of electrochromic indicators.

Chapter 7

Conclusions, Summary and Future Scope

This chapter outlines the main conclusions drawn from the research work reported in the thesis. Additionally, the scope for future extension of the work has also been highlighted.

7.1 Conclusions and Summary

7.1.1 Electrochromic display devices

- Extensive studies have been done to investigate the spectroelectrochemical properties of organic and inorganic materials along with the understanding of color-changing mechanisms.
- The electrochromic performance of these materials was studied by preparing thin film electrodes using different-different methods, with optimization of various parameters for achieving the desired composition.
- Two different combinations of all-organic and organic/inorganic hybrid devices were designed with the help of the flip-chip technique to investigate the electrochromic behavior of the device under different bias conditions.
- In-situ bias-dependent spectroscopy measurements including Raman measurements were conducted to understand the working mechanism of bias-induced color switching of the fabricated EC solid state device.
- 5. For improving the performance of an ethyl viologen (EV) solidstate electrochromic device, an all-organic and hybrid device of

EV/ P3HT and EV/NiO were fabricated, and their EC performance were investigated.

- Two-dimensional layered materials such as molybdenum disulfide (MoS₂), multiwalled carbon nanotubes (MWCNTs) and tungsten disulfide (WS₂) were identified and characterized to enhance the EC performance of devices.
- A bilayer device of P3HT and EV (doped with MWCNTs) showing three colored states (magenta – transparent – blue) was demonstrated under appropriate bias conditions.
- 8. Electrochemical measurements were performed on individual electrodes to identify the factors affecting in device performance.
- Plasma-assisted atomic layer deposition technique was employed to deposit smooth, atomically thin, and homogenous nickel oxide thin films, leading to improved performance of ethyl viologen EC device.
- Different concentrations of molybdenum disulfide (MoS₂) were used to optimize its effect on EC performance.
- 11. A hybrid device containing tungsten oxide (WO₃) and polypyrrole (PPy) was fabricated and exhibited a switching time of (1.1s / 1.8s), coloration efficiency of 304 cm²/C, good color contrast (47%) and remained stable upto 500 seconds at a low operation voltage of 1V.
- 12. An all-organic device based on P3HT-EV (doped with WS₂/WO₃ nanoflakes) demonstrated dual-band optical modulation in visible (~ 515nm) and NIR (~ 800nm) wavelength regions along with stable and power-efficient EC performance.

7.1.2 Multifunctional Role of the electrochromic device

 The incorporation of MWCNTs/MoS₂ in an all-organic electrochromic device containing P3HT and EV electrochromic active materials exhibits an asymmetric I-V characteristic curve, making it a promising candidate for dual applications in electrochromism and rectifying sinusoidal signals.

- Demonstration of the EC rectifier has been done and it was capable to rectify the sinusoidal signal having a frequency less than 1 Hz without losing its electrochromic behavior.
- A P3HT/EV device when doped with WS₂/WO₃ nanoflakes shows energy storage properties and an electrochromic supercapacitor can be made.
- The presence of WS₂/WO₃ nanoflakes in P3HT/EV device makes a device suitable for electrochromic as well as energy storage applications without compromising the electrochromic performance of the device.
- 5. The device exhibited a fast-switching time of less than one second along with excellent coloration efficiencies of $460 \text{ cm}^2/\text{C}$ and $288 \text{ cm}^2/\text{C}$.
- 6. Additionally, the device shows a maximum capacitance of ~ 50 F/g and an energy density of ~ 60 Wh/kg at a current density of 1 A/g shows their potential for multifunctional usage.

7.2 New Findings Reported in the Thesis

- The introduction of appropriate 2D-layered materials enhances the redox activity of the active electrochromic material within the device.
- Plasma-assisted atomic layer deposition technique used to deposit thin, smooth, and uniform metal oxide thin films, exhibiting excellent electrochromic performance with EV in a hybrid solid-state electrochromic device.
- In-situ bias-dependent Raman spectroscopy has been successfully employed to investigate the working mechanism of the electrochromic device.
- 4. A dual-wavelength filtering device comprising EV and P3HT with suitable dopant in its device geometry has been fabricated that filters 515 nm (visible) and 800 nm (NIR) wavelengths with biasing switching of +1.5V and -1.5V.

- The incorporation of suitable 2D material as a dopant makes an organic EC device suitable for a bifunctional role and expands its potential applications.
- 6. Devices are also demonstrated beyond electrochromism i.e., their use in rectifier and supercapacitor are also elaborated.

7.3 Future Scope of the Work

The research work can be extended in the following direction in the future:

- 1. To study the effect of the thickness of active material on the performance of ECDs.
- 2. Scaling up device fabrication for commercialization.
- 3. Fabrication of devices on large-scale flexible substrates.
- 4. Exploring other 2D-layered materials to understand the effect of their morphology, electrical property, and stability for improving the existing electrochromic devices.
- 5. Optimizing various properties of materials that can influence the electrochromic performance.
- Exploring additional applications of ECDs such as memory devices, heat shielding, sensors, and energy storage (battery), solar cells.

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Annexure

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