CONJUGATED POLYMER AND TRANSITION METAL OXIDE BASED HYBRID MATERIALS:
SYNTHESIS, CHARACTERIZATION, AND ELECTROCHROMISM

LING HAN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Electrochromism is a phenomenon that some materials involving reversible color changes through redox reactions under electrical stimulus. This PhD work is aimed at developing hybrid materials based on conjugated polymers (CPs) and transition metal oxides (TMOs), which combine the advantages of both materials and exhibit enhanced electrochromic properties, and understanding the underlying mechanisms. Tungsten trioxide (WO₃) and poly(3,4-ethylenedioxythiophene) poly(styrene sulfate) (PEDOT:PSS) or its derivatives were employed to produce hybrid EC materials and devices.

Firstly, the hybrid EC materials based on WO₃ nanoparticles (NPs) and PEDOT:PSS were synthesized through the layer-by-layer (LBL) assembly method. Polyethylenimine (PEI) was applied to promote the electrostatic force between the two components. Single component films, namely PEDOT:PSS and WO₃-NP films, were also fabricated as reference films through the same method. The hybrid films exhibit enhanced EC properties, especially the coloration efficiency (117.7 cm²/C), compared with the reference films. The enhancement may be attributed to the efficient charge transfer process between components, since the hybrid film exhibit enhanced electrical conductivity during switching as verified by the scanning electrochemical microscopy (SECM). According to literature and SECM results, the WO₃ films experience conductive-to-nonconductive transition as applied potentials go from positive to negative, while the PEDOT:PSS presents high conductivity at its oxidized state. Therefore, in the hybrid system, the synergistic interactions between components promote the enhanced charge transfer process, resulting in improved EC performance. However, the nonconductive PEI layers involved may prohibit the redox reactions and the charge transfer process in the hybrid system, which would lower the EC performance.

Secondly, to further improve the EC performance, the hybrid films based on WO₃ and PEDOT:PSS were synthesized by one-pot sequential
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electrodeposition method without any PEI component. Single component films of same thickness were also produced as reference films. Compared with the reference films, the hybrid films exhibit significantly improved EC properties, especially the optical contrast (47%) and electrochemical stability. It’s resulted from the simultaneous switching and synergistic interactions of two components. The morphology and structure of the hybrid films can be manipulated through tailoring the electrodeposition parameters to enlarge the interfacial area, leading to efficient interactions between the components.

Thirdly, the charge-balancing dopant PSS involved in the aforementioned hybrid systems is an electrical insulator, which may block the charge transfer process between WO₃ and PEDOT, and lower the EC performance. Poly(4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butane sulfonic acid (PEDTS) is a self-doped PEDOT derivative bearing a sulfonate group in each repeat unit. It was employed to replace PEDOT:PSS in the hybrid systems. A hybrid aqueous suspension was obtained through mixing the EDTS monomers and WO₃ NPs in acidic solutions, where the PEDTS were obtained through air-assisted chemical oxidation and spontaneously attached onto the WO₃ NPs. The electrochromic devices (ECDs) assembled based on the hybrid films through air-brush spraying exhibit significantly improved optical contrast and electrochemical stability owing to the enhanced synergistic interactions between the two active components.

In conclusion, the combination of WO₃ and PEDOT:PSS or its derivatives is an effective way to improve the electrochromic properties owing to the synergistic interactions between the components. The polymers may act as buffer components for WO₃, while the WO₃ can prevent the over-oxidation of the polymers in the hybrid systems. And the combination of the two components also facilitates the charge transfer process in the hybrid system.
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### Abbreviations

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<td>c</td>
<td>crystalline</td>
</tr>
<tr>
<td>CE</td>
<td>Coloration Efficiency</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
</tr>
<tr>
<td>CP</td>
<td>Conjugated Polymer</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DIW</td>
<td>Deionized Water</td>
</tr>
<tr>
<td>EC</td>
<td>Electrochromic</td>
</tr>
<tr>
<td>ECD</td>
<td>Electrochromic Device</td>
</tr>
<tr>
<td>EDOT</td>
<td>3,4-ethylendioxythiophene</td>
</tr>
<tr>
<td>EDTS</td>
<td>4-(2,3-dihydrothiieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butane sulfonyl acid sodium salt</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>FeMeOH</td>
<td>Ferrocene Methanol</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>Hn</td>
<td>[PEI/WO₃/PEI/PEDOT:PSS]n</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>KCl</td>
<td>Potassium Chloride</td>
</tr>
<tr>
<td>LiClO₄</td>
<td>Lithium Perchlorate</td>
</tr>
<tr>
<td>LBL</td>
<td>Layer-By-Layer</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PAMPS</td>
<td>Poly(2-acrylamido-2-methylpropanesulfonic acid)</td>
</tr>
<tr>
<td>PANI</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PB</td>
<td>Prussian Blue</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene Carbonate</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butane sulfonic acid)</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethylenimine</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>Pn</td>
<td>[PEI/PEDOT:PSS]n</td>
</tr>
<tr>
<td>Ppy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrene sulfonate)</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
</tr>
<tr>
<td>RE</td>
<td>Reference Electrode</td>
</tr>
<tr>
<td>Redox</td>
<td>Reduction-Oxidation</td>
</tr>
<tr>
<td>Ru(NH₃)₆Cl₃</td>
<td>Hexaammineruthenium(III) Chloride</td>
</tr>
<tr>
<td>SECM</td>
<td>Scanning Electrochemical Microscopy</td>
</tr>
<tr>
<td>SEI</td>
<td>Secondary Electron Images</td>
</tr>
<tr>
<td>SWE</td>
<td>Second Working Electrode</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TMO</td>
<td>Transition Metal Oxide</td>
</tr>
<tr>
<td>UME</td>
<td>Ultra-Microelectrode</td>
</tr>
<tr>
<td>UV-vis-NIR</td>
<td>Ultraviolet-visible-Near Infrared</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
</tr>
<tr>
<td>Wn</td>
<td>[PEI/WO₃]n</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

In this chapter, the motivation, hypothesis, objectives, and scope of my PhD study are presented. First of all, the background of electrochromism including the definition of electrochromic (EC) materials and their applications are introduced. The motivation of my PhD research is to design and synthesize high-performance hybrid EC materials and devices via combination of organic and inorganic EC materials. With the motivation, the key hypothesis of my research is that synergistic combination of WO$_3$, PEDOT:PSS or its derivatives can give novel hybrid materials with enhanced EC properties from the interfacial interactions between components. To verify the hypothesis, different synthesis methods can be used to control the structures and morphologies of the hybrids. Various characterization techniques, including SECM and spectro-electrochemical measurements, can be applied to study the EC properties, and the synergistic effects and interactions between components. Based on the above, the detailed objectives and scope of this work are stated. Furthermore, an overview is given to show the organization and structure of the thesis. Last but not least, the novelty and the major findings of this work are highlighted.
1.1 Background and Motivation of the Research

Electrochromism refers to the reversible color changes brought about by the reduction-oxidation (redox) reactions stimulated by sufficient electric potentials or currents.[1] It was first coined in 1961 by Platt, and widely accepted in 1969 when WO$_3$ was first suggested to make electrochromic devices. Various materials that display reversible color change during redox reactions are defined as electrochromic (EC) materials.[2] Nowadays, the demand for novel electrochromic materials is increasing significantly, since they can be used in flexible displays, smart windows, and many other applications. The smart windows have already been commercialized as airplane windows to lower the energy consumption of air conditioners. Thus, EC materials and devices with high optical contrast, fast switching speed, and good electrochemical stability attract much attention in research area.

The EC materials can be divided into several categories, including transition metal oxides (TMOs), conjugated polymers (CPs), metal complexes, viologens, hybrid composite materials and so on. The TMOs and CPs attract most attention, since they are the most widely applied EC materials at present. Most electrochromic TMOs exhibit colour change owing to the inter-valance charge transfer and show good electrochemical stability compared with organic EC materials. Some TMOs, such as tungsten oxide (WO$_3$) and nickel oxide (NiO), show intense colour change from transparent to colored states, whereas some other TMOs, like titanium oxides (TiO$_2$), present low optical contrast and are usually used as optical passives or electrodes. However, the coloration efficiency of TMOs is relatively low, especially compared with conjugated polymers.[2] The conjugated polymers are also widely used as EC materials nowadays, since they present high optical contrast, fast switching speed, high coloration efficiency and low cost. In addition, the band gap or the colour of CPs can be easily modified through tailoring their chemical structures. Nevertheless, the electrochemical stability of CPs is always limited by the
over-oxidation or degradation of polymers.[3, 4] Therefore, the organic-inorganic hybrid EC materials are very popular in the EC field, since they can in theory combine the advantages of both components.

To enhance the performance of hybrid EC materials, the first issue is that ideally the organic and inorganic active components should be able to switch in the same potential window so as to contribute to the optical contrast of the hybrid materials simultaneously. The second issue is to promote the synergistic effects of the components. In this case, the hybrid materials are expected to present enhanced properties compared with the simple addition of the single components or single component films of same thickness owing to the interactions among the components. Large interfacial area is preferred to enhance the interactions and charge transfer process among the active components.

The motivation of this thesis is to design and synthesize novel hybrid EC materials with enhanced EC performances, including optical contrast, switching response and electrochemical stability for various applications. The hybrid materials are produced from transition metal oxides and conjugated polymers via various thin film fabrication methods, such as Layer-By-Layer (LBL) assembly, electrodeposition, and air-brush spraying. The studies on the electrochemical and electrochromic performance of hybrid materials can demonstrate the synergistic effects resulting from the interactions among the components.

1.2 Hypothesis

Hybrid EC materials based on conjugated polymers and transition metal oxides have been synthesized and characterized by several research groups.[5-8] Tungsten oxide (WO$_3$) is one of the most popular EC materials among TMOs, which has already been used in commercially available smart windows. With applying reductive potential, it allows the colour transition from transparent to blue, which is one of the most intense colour changes among TMOs.[2, 9-11]
On the other hand, the most common electrochromic CPs are polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and their derivatives. PEDOT doped with poly(styrene sulfonate) (PSS) and its derivatives are widely used cathodically colored EC polymers owing to the high optical contrast, good processability, and low cost.\cite{2, 12} It also changes colour from light blue to dark blue at reductive potentials. The hybrid films based on WO$_3$ and PEDOT:PSS reported by Deepa et al. were fabricated through spin coating PEDOT:PSS layer on top of electrodeposited WO$_3$ films. They exhibit enhanced EC properties, including optical contrast and electrochemical stability, since both components are cathodically colored.\cite{13} However, the reasons for enhanced electrochemical stability haven’t been clarified or studied. In addition, according to the literature, the WO$_3$ shows metallic conductivity at its reduced states and low conductivity in the fully oxidized state. By contrast, the PEDOT:PSS exhibits high conductivity in its doped (oxidized) states.\cite{2} Therefore, it was hypothesized that the hybridization of WO$_3$ and PEDOT:PSS with large interfacial area may improve charge transfer process in the hybrid materials, leading to enhanced electrochromic properties. LBL assembly method can be employed to enlarge the interfacial area between components so as to promote synergistic effects. Scanning electrochemical microscopy (SECM) is proposed as a tool to verify the conductivity and study the charge transfer process of the hybrid materials.

Secondly, many hybrid films, such as the WO$_3$ and PEDOT:PSS films mentioned above, are fabricated through multi-step processes, where the components are deposited from separate solutions via various processes. It is always difficult to control the morphology and structures of the resulting hybrid films. Electrochemical synthesis methods are commonly employed to fabricate uniform thin films of WO$_3$ and PEDOT:PSS from their corresponding solutions. As reported by Zou et al., cyclic voltammetry has been employed to electrodeposit WO$_3$ and polyaniline from aqueous one-pot solution, leading to uniform morphology and structure.\cite{14} In this case, it was hypothesized that it
may be possible to fabricate hybrid materials based on PEDOT:PSS and WO$_3$ via sequential electrodeposition from one-pot solution. It would simplify the synthesis process and provide an easy way to tailor the structure of hybrid materials by adjusting the deposition parameters. As a result, enhanced EC performance could be achieved with efficient charge transfer process owing to optimized interfacial area between the two components.

Thirdly, it is worth noting that the PSS, which act as a dopant for PEDOT, is an insulator. It also doesn't show any electrochromic properties. Thus PSS in the hybrids may block the charge transfer between components according to Karlsson’s study.[15] Poly(4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butane sulfonic acid (PEDTS) is a self-doped water soluble PEDOT derivative with high conductivity and stability compared with PEDOT:PSS. Therefore, it was hypothesized that replacing PEDOT:PSS with PEDTS can enhance interfacial charge transfer and hence EC properties of the hybrids.

1.3 Objectives and Scope

With the above hypotheses, the overall objective of my PhD study is to synthesize and characterize inorganic-organic hybrid materials based on WO$_3$ and PEDOT or its derivatives with enhanced electrochromic properties, and study the underlying mechanisms of the enhancements.

The first study was aimed at clarifying the roles played by WO$_3$ and PEDOT:PSS, respectively, in the hybrid EC materials. LBL assembly method is applied to produce sample films from WO$_3$ nanoparticles and PEDOT:PSS suspensions to provide large interfacial area. The optical contrast of obtained hybrid film is expected to be enhanced, since both WO$_3$ and PEDOT:PSS can switch simultaneously under reductive potentials. The charge transfer process of the hybrid materials may be improved owing to the complementary conductivity of components in the switching potential range. SECM was employed to verify the conductivity change of sample films during redox
reactions, establishing a basic understanding of the mechanism for the potential EC performance enhancement.

The second objective of this work is to further improve the EC performance of the hybrid materials based on WO₃ and PEDOT:PSS by tailoring their morphology at nanometer-scale. The hybrid thin films are synthesized through one-pot sequential electrodeposition from aqueous solutions containing EDOT, PSS and peroxotungstic acid (PTA). The structure and morphology of sample films can be well controlled through manipulating the deposition parameters. The hybrid film is expected to exhibit enhanced EC properties owing to the improved interactions between components.

The third objective of this work is to remove PSS in hybrid system by replacing PEDOT:PSS with PEDTS so as to enhance the charge transfer process. PEDTS was synthesized via simple air-assisted chemical oxidation of 4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butane sulfonic acid sodium salt (EDTS) and employed to hybridize with WO₃ nanoparticles (NPs). EDTS monomers can be easily oxidized and attached to WO₃ NPs in acidic conditions. The EC performance of these hybrid film based electrochromic devices (ECDs) is expected to be improved owing to the enhanced charge transfer process.

1.4 Dissertation Overview

In this thesis, the studies of the aforementioned hybrid electrochromic material systems are reported.

In Chapter 1, rationales for the research, hypotheses, detailed objectives, and scope of the studies are provided. The structure of the thesis is outlined and the originality of the work is also highlighted at the end.

In Chapter 2, a literature review is presented. Firstly, a brief history of electrochromism is introduced. Then, previous studies on typical EC materials of different categories, such as transition metal oxides, conjugated polymers, viologens, hybrid materials, and so on, are reviewed. Electrochromic devices
(ECDs) and their applications, like commercially available smart windows, are also introduced. The last section of this chapter is focused on key performance parameters of electrochromic devices, namely optical contrast, switching speed, coloration efficiency, long term reversibility, and their characterization methods.

Chapter 3 is the experimental methodology section. In this section, the principles underlying the synthesis and characterization techniques employed and the methods of data analysis are included. The synthesis techniques, such as LBL assembly, electrodeposition, chemical oxidation, and air-brush spraying, are well introduced and demonstrated, since they are employed to fabricate hybrid EC materials with desired morphology and structures. The principles for various methods used to characterize the chemical structures and morphologies, and measure electrochemical and electrochromic properties, as well as data analysis methods, are also explained in detail. An explanation of why a particular method is chosen is also given. Last but not least, the data analysis processes are also covered in this chapter.

In Chapter 4, the first part of my PhD study is reported to elaborate the changes of conductivity and EC properties of the hybrid materials based on WO₃ NPs and PEDOT:PSS. The hybrid materials obtained through LBL assembly are proved to have enhanced EC properties compared with single component films, which resulted from the improved charge transfer and interactions between components. The conductivity improvement in hybrid materials studied by the SECM technique is also discussed in this chapter.

In Chapter 5, the second work of my study is elaborated. It presents the enhanced electrochromic properties of the hybrid materials obtained through one-pot sequential electrodeposition from EDOT, PSS and PTA mixed aqueous solution. In this work, hybrid materials with well controlled morphology and structures are obtained. The EC performance of hybrid films is characterized and studied. Finally, the reasons for the enhancement are also explained.

In Chapter 6, the assembly of electrochromic devices based on the hybrid
suspensions consisting of WO$_3$ and PEDTS hybrid nanoparticles is reported. The hybrid synthesis process involves air-assisted oxidative polymerization of EDTS and the simultaneous attachment of the polymerization products to WO$_3$ NPs. The ECDs assembled from the hybrid suspensions exhibit enhanced electrochromic properties, especially the optical contrast and electrochemical stability, compared to the WO$_3$ based devices. In summary, the materials synthesis, device fabrication, and electrochromic properties of the materials and devices are all discussed in detail.

In Chapter 7, a summary of my PhD work is presented firstly, where all the studies of hybrid EC materials based on WO$_3$ and PEDOT:PSS or its derivatives are put together to prove the hypotheses. The implications of my work in three areas are then elaborated: (1) the significance of using SECM technique to study the conductivity change of EC materials in redox switching processes; (2) the possibility of applying the one-pot sequential electrodeposition method to obtain various hybrid materials with controllable morphology and structure; (3) the significance of fabricating hybrid suspensions with catalyst-free oxidation of EDTS and simple electrostatic attachment process. Moreover, some suggested future work is also presented in this chapter.

1.5 Significant Findings and Outcomes

This research led to several significant findings and novel outcomes by:

I. Employing SECM Technique in EC Material Conductivity Studies

Scanning electrochemical microscope is a widely used electrochemical analysis technique to study the in-situ surface reactions in electrochemical cells. It provides various information including the conductivity, kinetics of surface reactions, and so on. The electrochromic materials experience redox reactions that give colour changes under external potentials. According to literatures, the
conductivities of some EC materials are changing during the redox process. In my PhD study, for the first time, the SECM technique was applied to verify the conductivity changes of the EC films, including WO$_3$, PEDOT:PSS and their hybrid films, in their electrochromic switching processes. Compared with the traditional four-probe conductivity measurement, this technique reflects the conductivity changes under dynamic potentials sweep, and hence is more suitable for mechanism studies.

II. One-pot Sequential Electrodeposition

Electrodeposition is a common thin film fabrication method for both inorganic and organic materials. Cyclic voltammetry has been employed to produce organic-inorganic hybrid materials from one-pot solution for many purposes. Differently, in this research, hybrid EC materials based on WO$_3$ and PEDOT:PSS are synthesized via one-pot sequential electrodeposition process for the first time, where the morphology and structure can be easily tailored. The hybrid films can be simply electrodeposited from an aqueous solution containing EDOT, PSS, and PTA by applying positive and negative square wave potential in sequence. The morphology and structure of the obtained hybrid can be easily manipulated through adjusting the deposition parameters, leading to hybrid electrochromic materials with significantly enhanced performance.

III. Hybrid EC Suspensions

Electrochromic inks are quite common nowadays, since they can be used by various coating/printing techniques, such as air-brush spraying, spin coating, bar rolling, and inkjet printing, to fabricate large-scale devices. However, the additives used to stabilize the ink are usually not electrochromic materials, which may hinder the charge transfer process and lower the EC performance. In my work, the hybrid suspensions based on water soluble PEDTS and WO$_3$ NPs
were fabricated through air-assisted oxidation polymerization of monomers and directly attached to the WO$_3$ NPs in the acidic aqueous suspensions. There is no catalyst or other additives involved in this hybrid EC suspension, which can be directly coated on substrates through air-brush spraying. Therefore, the ECDs assembled from the hybrid materials exhibited enhanced EC performance owing to the efficient charge transfer process.

**References**


Chapter 2

Literature Review

In this chapter, the literatures regarding electrochromism, typical electrochromic (EC) materials and devices, and the key parameters used to characterize EC properties are reviewed. Firstly, the discovery of electrochromism and its developing history are presented. Then, the structures and properties of common EC materials, such as transition metal oxides (TMOs), conjugated polymers (CPs), metal complexes, and viologens, are described. The applications of the EC materials and devices as smart windows, flexible displays, are also introduced in this chapter. Finally, the key parameters widely used to characterize the performance of EC materials and devices are discussed, which provide a basis for spectro-electrochemical studies performed in this PhD study.
2.1 Introduction to Electrochromism

Electrochromism indicates the phenomenon of visible colour changes initiated by external electric stimulus accompany with reversible reduction-oxidation (redox) reactions.[1-4] Electrochromic materials exhibit a change of spectra during redox reactions, since the energy band shifts upon electron uptake or release. The term electrochromism only covers spectra change in the visible region of electromagnetic spectrum. Electrochromic materials exhibit coloured and bleached states during redox switching.[2] Materials with more than one coloured states in redox reactions are defined as possessing multielectrochromism (or polyelectrochromism). [4]

The term ‘electrochromism’ was first coined in 1961 by Platt to indicate a colour generated through electric stimulus.[5] The electric field shifted the orbital energies of materials, which was reflected in colour changes. In fact, colour changes generated from redox reactions were observed by chemist Berzelius as early as 1815. In his studies, the pale yellow WO$_3$ turned blue upon reduction.[6] And in 1840s, the development of photography, where Prussian blue (PB) was applied, initiated the redox-colouration process with electron transfer.[7] The study of redox-colouration process continued in the twentieth century. Early electrochromic devices based on iodine, silver, MoO$_3$, WO$_3$ and other materials were developed during this period. The first widely accepted concept of ECDs was suggested by Deb in 1969.[8] The device he built with WO$_3$ film immersed in ion-containing electrolyte reported in 1973 indicated the true birth of electrochromic technology.[9] Since then, EC materials and devices have attracted much attention. Metal oxides, organic polymers, and other EC materials have been synthesized and studied. Many researchers focused on this field to understand the colouration mechanism, and even established a model of electro-bleaching and electro-colouring. [10, 11]

Nowadays, EC materials and devices have developed into a popular topic, continuously attracting people’s attention. Thousands of researchers and
engineers are working in this field to fabricate EC materials and devices with novel properties and better performances. The EC materials and devices are widely used in various applications, such as smart window, flexible display, and so on.[3, 12, 13] The smart windows have already been commercially available for vehicles and houses, which switch colours with applied potential of a few volts. As shown in Fig. 2.1 the smart windows installed in the airplane can block out at most 90% of sunlight at its colored state. Flexible display based on EC materials has great potential in replacing the current liquid crystal display (LCD), considering its low cost, flexibility and multi-coloration properties.

![Figure 2.1](AirlineReporter.com)

**Figure 2.1** Electrochromic smart windows showing different states from AirlineReporter.com.

### 2.2 Electrochromic Materials

Electrochromic materials can be divided into inorganic, organic, and other materials, such as metal complexes and polynuclear transition-metal hexacyanometallates.[1] And nowadays, hybrid materials based on inorganic and organic EC materials are becoming more and more popular due to the synergistic effects obtained through hybridization.

#### 2.2.1 Typical Inorganic EC Materials

Most of the inorganic EC materials are transition metal oxides (TMOs), which exhibit intense coloration and good photochemical stability.[14] The oxides of the following transition metals possess electrochromic properties:
cerium, chromium, cobalt, copper, iridium, iron, manganese, molybdenum, nickel, niobium, palladium, praseodymium, rhodium, ruthenium, tantalum, titanium, tungsten and vanadium. Some TMOs, such as WO₃, MoO₃, IrO₂ and NiO, present intense coloration, since they can switch from transparent to dark color states, while others can switch from one intense color to a light color. [15]

The redox switching of TMOs always involves a charge transfer process inducing electrons uptake/release and complementary ion insertion/extraction. The electron transfer in TMOs usually occurs in the valence band among the metal sites, which is termed as optical intervalence charge-transfer transition. It is considered as the major reason for EC coloration of TMOs. And the solid-state TMOs can provide numerous interstitial sites for guest ions through various structural arrangements, such as corner-sharing or edge-sharing. The EC information for some common TMOs is provided in Table 2.1. [1, 12, 15, 16]

Table 2.1 Electrochromic transition metal oxides and its EC properties from ref.[16]

<table>
<thead>
<tr>
<th>No.</th>
<th>Cathodically ion insertion materials</th>
<th>Anodically ion insertion materials</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoO₃</td>
<td>Transparent</td>
<td>Blue</td>
</tr>
<tr>
<td>2</td>
<td>V₂O₅</td>
<td>Yellow</td>
<td>Blue-black</td>
</tr>
<tr>
<td>3</td>
<td>Nb₂O₅</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>4</td>
<td>WO₃</td>
<td>Transparent</td>
<td>Blue</td>
</tr>
<tr>
<td>5</td>
<td>Ir(OH)₃</td>
<td>Blue-black</td>
<td>Transparent</td>
</tr>
<tr>
<td>6</td>
<td>Ni(OH)₂</td>
<td>Brown-bronze</td>
<td>Transparent or pale-green</td>
</tr>
</tbody>
</table>

WO₃ is one of the most widely studied EC materials among all TMOs, and has already been employed in many commercialized applications. The thin film of WO₃ usually are colorless (or pale yellow shown in the picture below) with
W\textsuperscript{VI} as the oxidized state. Upon reduction, it turns blue (shown in the picture below) since some W\textsuperscript{VI} sites are reduced to W\textsuperscript{V} with electron uptake and cation insertion shown in Eq. 2.1. The inserted cation M\textsuperscript{+} can be Li\textsuperscript{+}, H\textsuperscript{+}, Na\textsuperscript{+} and other metal ions, which play an important role in EC switching process.\cite{17, 18} The size of inserted cations can affect the reversibility of this redox reaction. Small cations, such as H\textsuperscript{+} and Li\textsuperscript{+} are most commonly applied in EC applications. The subscript \(x\) is the insertion coefficient, which indicates the fraction number of filled interstitial sites in WO\textsubscript{3} lattice. \cite{12, 14, 19}

\[ W^{VI}O_3 + xM^+ + xe^- \rightarrow M_x(W^{VI})_{(1-x)}(W^{V})_xO_3 \]  

(Eq. 2.1)

In addition, the WO\textsubscript{3} and its reduced form M\textsubscript{x}WO\textsubscript{3} (short for M\textsubscript{x}(W\textsuperscript{VI})\textsubscript{1-x}(W\textsuperscript{V})\textsubscript{x}O\textsubscript{3}) experience a non-metal-to-metal transition during the redox switching as shown in Figure 2.2. \cite{20, 21} At fully oxidized W\textsuperscript{VI} state (\(x=0\)), the WO\textsubscript{3} acts as an insulator with low electronic conductivity, since it is conducted by electron site-to-site hoping. With increasing \(x\), the electronic conductivity of M\textsubscript{x}WO\textsubscript{3} increases from non-metallic to metallic owing to the increasing number of delocalized transferable electrons. The critical composition of M\textsubscript{x}WO\textsubscript{3} for this transition to occur is defined as \(x_c\), which is varied from different cations and structure. Therefore, the electronic conductivity of M\textsubscript{x}WO\textsubscript{3} is highly dependent on the insertion coefficient \(x\). On the other hand, the electrochromic switching is limited by the charge transfer process, which can be affected by the conductivity (\(\sigma\)) of the material. Thus, \(x\) can also influence the rate of coloration during the electrochromic switching process.\cite{20-22}
The morphology of WO₃ applied in EC applications can be amorphous, polycrystalline or a mixed phase, which is sensitive to the synthesis method. Amorphous WO₃ (a-WO₃) thin film is usually prepared through electrodeposition or thermal evaporation in vacuum.[11, 21, 23] The crystalline WO₃ (c-WO₃) has a perovskite structure with monoclinic phase, which can be obtained through sputtering, hydrothermal synthesis, and annealing of amorphous or mixed phases WO₃. [24] However, the actual crystal structure is dependent on both synthesis methods and conditions. For instance, the a-WO₃ can also be obtained through sputtering method with well controlled conditions reported by Wittwer et al.[21] Compared with c-WO₃, the a-WO₃ contains large portion of defects that strongly influence the electronic structure based on the study by Chadwick et al.[25] Since a-WO₃ is more electronically conductive than c-WO₃, the electrochromic coloration rate of a-WO₃ can be higher than that of c-WO₃. And in terms of coloration efficiency, the a-WO₃ can be better than that of c-WO₃ as well. Therefore, the electrochromic properties of WO₃ with different morphology and structure are varied from each other.

### 2.2.2 Typical Organic EC Materials
In organic EC materials, conjugated polymers (CPs) as well as small molecular materials, such as viologens can exhibit electrochromic properties.

I. Conjugated Polymers

Conjugated polymers (CPs), also called conducting polymers, are organic polymers that conduct electricity. Their backbone chains of alternating double- and single-bonds create a system of delocalized π-electrons, which result in interesting and useful optical and electronic properties. They can be produced by polymerizing aromatic monomers, such as pyrrole, aniline, thiophene, furan, carbazole, azulene, indole, etc.[26] Similar to TMOs, the ions and electrons insertion and extraction will modify the electronic structure in polymers, resulting in optical color change. The color presented is determined by the band gap, which is defined as the energy gap \( E_g \) between the highest occupied π-electron band (valance band) and the lowest unoccupied band (conduction band). Charge carriers can induce new states in band gap, which in turn changes the optical properties. [26, 27]

The charge carrier insertion process is also called doping, which can be divided into two categories, p-doping and n-doping. P-doping means oxidation process, which indicates anions inserted or doped into CPs, leading to the delocalization of π-electrons.[26-28] Anodically colored EC material presents color change under oxidation. Reduction process is to remove the dopants in CPs (also known as undoping process), and returns to its neutral states.[26, 29] Fig. 2.3 illustrates the typical p-doping process of poly(pyrrole) and its corresponding undoping processe. [1] On the other hand, n-doping is a reduction process, where the cations are doped into CPs causing cathodic coloration. The material will switch back to neutral state, when the dopants exit from CPs (undoping process).[30] However, to date, the majority of CPs that investigated in electrochromic properties are p-doped conjugated polymers, since the n-doped CPs are less stable.
The intrinsic color exhibited by materials is directly related to the band gap. The larger the band gap, the more visible light will transmit through; while the lower the band gap, the more light is absorbed by the materials. CPs with band gap energy of 3.0 eV are transparent (absorption band in the UV region) in undoped thin film form. If it is p-doped, the anions inserted into the CP will lower the $E_g$, resulting in light absorption in lower energy part of the spectrum (visible region). Those with $E_g$ equal to or less than 1.5 eV are highly absorbing in the undoped form, but after doping, the free carrier absorption is relatively weak in the visible region as it is transferred to the NIR part of the spectrum.

The color change or contrast of the conjugated polymers in doping/undoping process relies on the band gap change. As shown in Fig. 2.4, the PEDOT exhibits deep blue color in neutral state and a light blue color upon oxidation. And the electronic band structure change of conjugated polymers can be followed by recording in-situ spectrum as a function of applied potential. In neutral state, the PEDOT is undoped with strong absorption band at 621 nm (2 eV), which is characteristic of a $\pi-\pi^*$ interband transition. In oxidation state, the inserted anions induced new energy levels between conduction and valence bands (Fig. 2.4b) corresponding to the presence of a polaronic charge carrier, where the interband transition decreases, and two new optical transitions (1.25 eV and 0.8 eV) appear at lower energy. Further oxidation leads to formation of a bipolaron and the absorption is enhanced at lower energies (shown in Fig. 2.4).
The reversible electronic structure changes of the conjugated polymers in doping/undoping process leads to reversible color change. Polymers with a bandgap of intermediate magnitude have distinct optical changes throughout the visible region, and can be made to induce many color changes. To obtain multicoloration, copolymerization of different monomers with several distinct units is widely used. Simply blending or mixing of two or more EC materials can combine their properties to achieve complex colors. [26, 28, 31-33]

**Figure 2.4** (a) Spectroelectrochemistry for a PEDOT film on an ITO glass substrate. The film had been deposited from EDOT (0.3 M) in propylene carbonate solution containing tertrabutylammonium perchlorate (0.1 M) and spectra are shown on switching in tertrabytylammonium perchlorate (0.1 M) in acetonitrile. The insert shows absorbance vs. potential. The bandgap is determined by extrapolating the onset of the $\pi$ to $\pi^*$ absorbance to the background absorbance. The $E_{b1}$ transition is allowed and is visible at intermediate doping levels. (Figure reproduced from Thomas, C. A. ‘Donor-Acceptor methods for band gap reduction in conjugated polymers: the role of electron rich donor heterocycles’. Ph.D. Thesis, Department of Chemistry, University of Florida, 2002, p. 41.) (b) Illustration of the bandgap structure of CPs during doping process reprinted from ref.[16]

CPs have increasingly drawn people’s attention in past few decades owing to their excellent EC properties, such as good switching response, high optical contrast, low cost, ease of processability, and high degree of color tailorability.
However, the disadvantages of CPs are their poor chemical and thermal stability. Besides, in the long term usage, polymer degradation may occur, which will greatly affect the EC properties.[26, 34] Some typical CPs, including polythiophene, polyaniline, and polypyrrole will be briefly introduced below.

Polythiophene is one of the most common CPs due to its good EC properties and ease of synthesis. Numerous polythiophenes with special substitutes have been synthesized to tuning the color states and enhance the electrochromic properties.[30, 35, 36] The coloration of polythiophene and its common derivatives are summarized in Table 2.2.[16]

<table>
<thead>
<tr>
<th>Serial number</th>
<th>Monomer</th>
<th>Polymer λ&lt;sub&gt;max&lt;/sub&gt; (nm) and color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oxidized state</td>
</tr>
<tr>
<td>1</td>
<td>Thiophene</td>
<td>730 (blue)</td>
</tr>
<tr>
<td>2</td>
<td>3-Methylthiophene</td>
<td>750 (deep blue)</td>
</tr>
<tr>
<td>3</td>
<td>3,4-Dimethylthiophene</td>
<td>750 (deep blue)</td>
</tr>
<tr>
<td>4</td>
<td>2,2’-Bithiophene</td>
<td>680 (blue-grey)</td>
</tr>
</tbody>
</table>

Poly(3,4-ethylenedioxy thiophene) (PEDOT) and its alkyl derivatives are cathodically colored CPs, which turn from pale blue to dark blue under reduction. It contains extra alkylenedioxy rings in its formula and is usually doped with poly(styrene sulfonate) (PSS) refer to the thiophene. The oxygen atoms near the thiophene ring contribute to lower the band gap energy of polythiophene. The band gap energy of PEDOT is about 1.6-1.7 eV, which is 0.5 eV lower than that of polythiophene. As discussed, the absorption band will shift to lower energy regions in spectrum. Besides, as reported, the alkylenedioxy ring in general poly [3,4-(alkylenedioxy) thiophene] (PXDOT) materials can strongly affect the optical contrast and switching process.[37-39]

For example, the 3,3-diethyl-3,4-dihydro-2H- thieno-[3,4-b][1,4] dioxepine
(ProDOT-Et₂) preserves larger size of alkylenedioxy ring than that of PEDOT, leading to high optical contrast ratio to 75% and high composite coloration efficiencies up to 505 cm²/C.[39]

PEDOT is a widely used EC material with high optical contrast, fast switching speed, and moderate band gap.[33] The spectroelectrochemistry of its thin films are present in Fig. 2.5 with corresponding colors of PEDOT in different states. [40] The PSS can be added to form a macromolecular salt PEDOT:PSS with better chemical stability and higher water solubility. Many techniques can be applied to synthesize the PEDOT:PSS films, such as electropolymerization, dip coating, spin coating etc.

**Figure 2.5** Spectroelectrochemistry for a PEDOT film on an ITO glass substrate. The insert shows the variety of hues produced on application of various biases. (adapted from ref. [40])

Polythiophene

PEDOT

PEDOT:PSS

sulfonic acid (PEDTS) is a PEDOT:PSS derivative bearing a sulfonate group in
each repeat unit as illustrated below. It is commonly used as a replacement of PEDOT:PSS in sensors, electrochromic and other applications, since the nonconductive PSS may form an insulating layer around the PEDOT, especially in the commercially available Baytron PEDOT:PSS.[41] It is a self-doped cathodically colored CP with high water solubility and electrical conductivity. Similar to PEDOT:PSS, it turns from light blue to dark blue under reductive potentials. Initially, the monomer EDTS was reported as cation-exchange material for synthesis of water soluble polymers. The monomer can be copolymerized with EDOT via electrolyte-free oxidative electropolymerization to obtain EC active CPs. [42, 43] The PEDTS polymers or oligomers have been fabricated from its monomer through chemical and electrochemical methods in aqueous solutions with FeCl₃ as catalyst. The obtained PEDTS exhibits high water solubility and electrical conductivity, and high EC performance owing to the sulfonate functional groups in the chain.[41]

![PEDTS](image)

**Polyaniline** (PANI) is a multicolored EC material, which can switch between being transparent, yellow, green, dark blue and even black colors. The coloration of PANI is dependent on the oxidation state and the pH value of the electrolyte.[44] It is generally accepted that the redox reaction contains several complex processes involving the H⁺ and/or anions insertion/expulsion as shown in Fig. 2.6. [45]
In the cyclic voltammetry (CV) scan, different oxidation states of PANI appear in the potential sweep shown in Fig. 2.7. Two oxidation peaks are observed at around 0.2 and 0.6 V; and the corresponding reduction peaks appear at -0.1 and 0.45 V. As potential increasing (oxidation process), the absorption band shifts from about 430 nm towards 810 nm, where many interconversions colors appears during this process. Electropolymerization and spin coating are the most commonly used coating methods to fabricate PANI thin films.

**Figure 2.6** Proposed redox mechanism of PANI: different forms and inter-conversions reprinted from ref.[45].

**Figure 2.7** Cyclic voltammetry and the color changes in the PANI film coated on Pt and dipped in a 10^{-2} M aqueous HCl solution containing 0.2 M LiCl, scan rate: 10 mV/s reprinted from ref.[45].
Poly(pyrrole) (Ppy) is a typical p-doping CP with its redox reaction process shown in Fig. 2.3.[1] The Ppy film exhibits blue-violet (λ=670 nm) color in its oxidized state, and then turns to yellow-green (λ=420 nm) color upon reduction. A pale-yellow color is presented without any dopants inside Ppy films. Considering the EC properties, Ppy films shows fast switching and high contrast, especially the poly(3,4-disubstituted pyrrole). However, the durability of Ppy film is not that promising due to the polymer degradation during redox cycles. The film can be produced by electropolymerization from pyrrole monomers as well.[1, 48, 49]

II. Organic Small Molecules

Viologens (4,4’-dipyridinium compounds), that can be reduced to deep blue-purple color, are typical organic small molecular EC materials. Fig 2.8 shows the common redox states of viologens, which may experience one-electron and two-electron reductions.[1] The first electron reduction is reversible and exhibit electrochromic properties; while the second electron reduction process is electrochemically nonreversible. [50]

![Diagram of viologen redox states](image)

**Figure 2.8** Common redox states of viologens with attached group R\(^1\) and R\(^2\). X\(^-\) refers to charged anion. This figure is reprinted form ref.[1].
2.2.3 Other EC Materials

I. Metal Complexes

Metal complexes or coordination complexes consist of metallic center ions (or atoms) and surrounding ligands.[51] The electrochromic color switch of a metal complex is caused by the charge transfer process from either the center cations or the bound ligands, where the redox reactions occur. Ferroin ([Fe\textsuperscript{II}(phen)\textsubscript{3}]\textsuperscript{2+}, phen = 1,10-phenanthroline) is one of the metal complexes applied in electrochromic devices, where the red color becomes pale blue. During the switching, the center cation Fe\textsuperscript{II} is oxidized into Fe\textsuperscript{III} in the reaction.[52] In addition, some ligand-based redox reactions can also occur in the metal complex, accompanying with the centre cations’ reactions. So the electrochromism of the metal complexes can be altered by the bound ligands. For example, the surface-modified [Ru(L)\textsubscript{3}]\textsuperscript{2+} (L shown below) film can exhibit seven color states in the redox reactions, which cover almost the entire visible spectrum. [53]

![Ferroin](image)

Currently, people are also focused on the metal complexes for electrochromism in NIR regions, which can be employed in smart windows to control the indoor environment.
II. Prussian Blue Systems

Prussian blue (PB) systems are a series of polynuclear transition metal hexacyanometallates, which are insoluble mixed-valence compounds.[54] The general formula $M^\prime_i[M^\prime \prime(CN)_6]_l$ shows that the transition metal M exhibits different oxidation states. For instance, the blue colored PB contains $Fe^{II}$ and $Fe^{III}$, which can be partially or fully oxidized to green or golden yellow respectively, and reduced to white.[1, 55] Therefore, the PB systems usually present multiple color states in redox reactions owing to the mixed valence of the metals.

2.2.4 Hybrid EC Materials

At present, the research community is particularly interested in hybrid materials owing to their synergetic properties from combining two or more EC components. Based on Z. Wang and X. Hu’s work, the inorganic hybrid system based on titanium dioxide (TiO$_2$) doped WO$_3$ has greatly improved electrochromic properties after a certain storage time.[56] The most popular system is the organic-inorganic hybrid system, which benefits from the combination and interactions among organic and inorganic components. Many hybrid systems with enhanced EC properties, such as PANI/TiO$_2$ and PANI/WO$_3$, have been studied and reported in the past few decades.[23, 57, 58]

As discussed in the conjugated polymer section, most CPs have a durability problem caused by polymer degradation. The performance gradually declines over increasing switching cycles. The inorganic EC materials display better long term stability during redox switching cycles. However, the switching speed of inorganic EC materials is much slower than that of organic materials.[16] Thus, the organic-inorganic hybrid system may combine the advantages of each material, which can enhance the overall EC performance. Many inorganic-organic hybrid EC materials have been studied by researchers recently. Some characteristic hybrid system with enhanced EC performance will
be reviewed below.

I. **WO$_3$ – PANI Systems**

The hybrid system based on WO$_3$ and PANI is produced by several different methods. As reported by Cai *et al.*, the core/shell nanowire array based on WO$_3$ and PANI were fabricated with significantly improved EC performance.[58] Another structure is produced by a one-pot molecular assembling method, in which a secondary bonding is formed to enhance the interactions between two components.[23] The films show a porous morphology with nanorod arrays on the surface, and WO$_3$ is uniformly incorporated into the polymer network. The obtained hybrid thin film exhibits high coloration efficiency and comparable durability compared to PANI film; while the switching response of hybrid film is faster than that of WO$_3$ films.

II. **WO$_3$ – PEDOT Systems**

The hybrid system based on WO$_3$ and PEDOT:PSS shows single coloration under reduction process. Many inorganic-organic hybrid materials have a problem of low optical contrast, since most conjugated polymers are anodically colored while the inorganic ones are mostly cathodically colored. In this system both components can switched simultaneously, leading to a high optical contrast. The hybrid system based on WO$_3$ and PEDOT:PSS were obtained and studied by several research groups. As reported by M. Deepa *et al.*, a two-layer hybrid film with enhanced long term stability composed of WO$_3$ and PEDOT has been obtained from a two-step process including surfactant-mediated electrochemical deposition of WO$_3$ and spin coating of PEDOT:PSS.[59] Another group fabricates hybrid films with effective charg propagation and storage through voltammetric potential cycles from a mixed solution containing EDOT and sodium tungstate dehydrate (Na$_2$WO$_4$·2H$_2$O).[60] The obtained hybrid materials usually exhibit significantly enhanced electrochemical stability.
compared with neat WO$_3$ and PEDOT:PSS films.

2.3 Electrochromic Devices

Electrochromic devices (ECD) are electrochemical cells that can control the optical properties, such as transmission, reflection and so on, in a reversible way on applied potentials.[16] As an electrochemical cell, the device is composed of a working electrode, a counter electrode, and an electrolyte, which forms a sandwich structure with the electrolyte in between the electrodes. Based on the optical properties displayed, the ECDs can be categorized into two classes: transmission ECDs and reflection ECDs. The transmissive ECDs switch colors reversibly in the visible range, while the reflective ECDs are usually applied in the IR range.[61] The following section of this thesis will focus on the transmission ECDs, which are usually used as smart windows, rear mirrors, and so on.

2.3.1 Configurations of ECDs

As mentioned above, the electrochromic device is a multi-layer device, which is composed of a working electrode, a counter electrode, with an electrolyte in between. There are two typical configurations of transmission electrochromic devices, namely single-layer ECDs and complementary ECDs illustrated in Fig. 2.9. The substrate is used to provide mechanical support for devices. And the electrodes are made of transparent conductors, which allow light to pass through. The electrolyte between the two electrodes provides pathways for ions, which requires high ionic conductivity. In single layer electrochromic devices, only one layer of electrochromic materials are deposited onto the working electrode; while the complementary ECDs have a dual-active-layer of electrochromic materials on both working and counter electrodes. The single layer ECD exhibits the basic electrochromic features, which is usually applied to characterize the properties of EC layers. In the
complementary ECD, an additional layer of EC materials, also called complementary EC layer, is deposited on the counter electrode, where both EC layers can switch simultaneously to enhance the optical contrast. The complementary EC layer normally switches into colored state at the opposite potential to the primary EC layer. And the potential windows of switching and the color of the complementary EC materials should match with the primary EC layers.[44] For example, if the primary EC layer is a cathodically colored material, the complementary EC layer must be anodically colored so as to enhance the optical contrast during switching. In addition, the charges generated by the primary EC layer can be consumed by the complementary EC layer during the redox reactions, which greatly enhance the electrochemical stability compared with single-layer ECDs.

![Schematic illustration of (a) single-component and (b) complementary electrochromic devices](image)

**Figure 2.9** Schematic illustration of (a) single-component and (b) complementary electrochromic devices (not to scale).

### 2.3.2 Components of Transmission ECDs

Based on the configuration of EC devices, the components that compose the ECDs are elaborated in the following sections, namely transparent conductors, electrolytes, EC materials.

**I. Transparent Conductors**
For transmission ECDs, the transparency of the electrodes is essential, since it allows the light to pass through the devices. Normally, they are fabricated by transparent substrates coated with conductive materials, such as indium tin oxide (ITO), fluorine-doped tin oxide (FTO), silver grid, and etc. And the substrates are non-conductive glasses or flexible polyesters, such as polyethylene terephthalate (PET), which provide the mechanical support and protection for the device.

The transparent conductors serve as the electrodes and charging balancing layers in the ECDs. In single-layer ECD, the working electrode delivers charges to the electrochromic materials; while the counter electrode serves as the charging balancing layer. In addition, a complementary layer of electrochromic materials is deposited on the counter electrode (transparent conductor) in the dual-layer ECDs. Overall, the transparent conductors require high transparency and good conductivity to deliver charges in ECDs.

II. Electrolyte

Electrolyte layer in the ECDs separates the electrodes, and provides source and pathways of ions to transfer between two electrodes. It is usually an electronic insulator to prevent short circuit of the device, and exhibits high ionic conductivity for ion transfer.

The electrolytes commonly used in ECDs are gel and liquid electrolytes. Gel electrolytes are most widely applied, which can be divided into polymer electrolytes and polyelectrolytes. Polymer electrolytes include neutral macromolecules that are dissolved in the solvent to increase the viscosity. Some common polymers used in the electrolyte are poly(methyl methacrylate) (PMMA), poly(vinyl alcohol) (PVA), and poly(ethylene oxide) (PEO). Similar to the liquid solution electrolyte, the salt or acid is dissolved in the solvent as well to provide the ionic conductivity. By contrast, polyelectrolytes, also called polysalts, are polymers with ion-labile groups, which exhibit properties of both polymer and the electrolyte. For example,
poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) is a strong anionic polyelectrolyte, and it can form gel when cross linked. In addition, the gel electrolyte can tightly glue two electrodes together to assist the fabrication of ECDs. And its disadvantages are insufficient ionic conductivity, thermal instability and so on.[62]

As the name states, liquid electrolyte refers to an electrolyte in the liquid state. Most liquid electrolytes are either liquid solutions or ionic liquids. Liquid solution is the salt or acid dissolved in solvent to provide the mobile ions; such as lithium perchlorate dissolved in propylene carbonate (LiClO₄/PC). The ionic liquid is a salt in liquid state with its melting point lower than 100°C, which is largely composed of ions. The ionic liquid used as electrolyte in ECDs is usually liquid at room temperature, such as 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]).[63] Their good thermal stability, low cost, and high ionic conductivity make ionic liquids a popular option as electrolytes in ECDs. The advantage of liquid electrolyte is the efficient ionic transfer between two electrodes. However, the leakage or solvent evaporation of liquid electrolyte in ECDs is still problematic. Thus, it is always completely sealed inside the device.

III. EC layers

The EC layers are the functional materials in electrochromic devices, which exhibit optical changes with applied potentials. They are composed of the electrochromic materials introduced in section 2.2 and fabricated through various techniques, such as electrodeposition, layer-by-layer assembly, spraying, and so on. The synthesis and fabrication methods will be introduced in chapter 3.

2.4 Electrochromic Key Performance Parameters
The performance of transmissive EC materials and devices can be evaluated in terms of optical contrast, switching response, electrochemical stability, cycle life, and even memory effects. The widely used key parameters for EC performance characterization are listed below.

### 2.4.1 Optical Contrast

The optical contrast indicates the optical property of EC materials. It is defined as the optical transmittance change ($\Delta \%T$) between bleached state and colored state at a wavelength of interest ($\lambda_{\text{max}}$), where optical contrast reaches the highest value (shown in Eq. 2.2).[64] The optical contrast can be measured by the UV-vis spectrometers over the visible region so as to define the optical contrast at a specific wavelength. Another parameter related with optical contrast is the contrast ratio (CR) shown in Equation 2.3, which refers to the transmitted light of colored state over that of the bleached state at $\lambda_{\text{max}}$. [2, 47]

\begin{equation}
\Delta \%T = \%T_{\text{bleach}} - \%T_{\text{color}} \\
\text{(Eq. 2.2)}
\end{equation}

\begin{equation}
\text{CR} = \dfrac{\%T_{\text{color}}}{\%T_{\text{bleach}}} \\
\text{(Eq. 2.3)}
\end{equation}

### 2.4.2 Switching Response

Switching response is a very important part of electrochromic performance properties, including parameters as coloration efficiency, switching time, and bleaching time.

**Coloration efficiency** (CE) is a key parameter defined as the optical absorbance change ($\Delta A$) at certain wavelength ($\lambda$) for inserted charges (Q) per unit area, can be calculated by Eq. 2.4, where $\Delta A$ is calculated by the transmittance between bleached ($\%T_{\text{bleach}}$) and colored ($\%T_{\text{color}}$) states, expressed in Eq. 2.5.[2, 35, 65] This parameter quantitatively expresses that the color change is stimulated by the charges insertion of the materials. Usually, the CE of organic EC materials is higher than that of inorganic ones owing to the
higher molar absorption.

\[
CE(\lambda) = \frac{\Delta A}{Q} \text{ (cm}^2/\text{C)} \tag{Eq. 2.4}
\]

\[
\Delta A = \log_{10} (\%T_{\text{bleach}} / \%T_{\text{color}}) \tag{Eq. 2.5}
\]

**Switching time** (or coloration time) stands for the time required for an electrochromic material to switch from its bleached state to the 90\% of its fully colored state. Similarly, the **bleaching time** stands for the time required to switch back. Numerous factors can affect the switching process, such as ion diffusion in thin film, applied potential (or current), film thickness, morphology and so on. The switching time of organic materials is usually less than that of inorganic ones.\[2, 66\]

### 2.4.3 Stability and Cycle Life

In repeating redox cycles, the electrochromic performance will decline. The stability refers to number of switching cycles without significant electrochromic performance loss. The degradation of EC materials is usually caused by high applied potential (over oxidation or reduction), ionic conductivity loss of electrodes or electrolyte, side reactions, oxygen involved irreversible reactions and so on.\[2\]

### 2.4.4 Optical Memory

Optical memory is also called the open-circuit memory, which refers to the phenomenon that EC materials will sustain the color after the potential or current is removed. The time of EC materials retain color state is called the optical memory.\[2\] For some material, such as viologens, the color will disappear immediately after removal of electric field; while some EC material, such as inorganic transition metal oxides, can sustain the colored states for days or even weeks. The difference is based on the diffusion process of ions after termination of electric field.
2.5 Questions and Strategies from Literature

In this literature review section, electrochromism, electrochromic materials and devices, and their applications were introduced. Based on the literature studies, most electrochromic materials and devices have their advantages and drawbacks that are difficult to overcome. The most commonly employed EC materials TMOs and CPs are reviewed here.

Transition metal oxides, which are well studied as electrochromic materials owing to its dense coloration and good photochemical stability, exhibit disadvantages as relatively slow switching process, high cost, and limited number of colors compared with most conjugated polymers. While, the conjugated polymers used as electrochromic materials are very popular nowadays, since it shows high optical contrast, ease of processability, fast switching process. Moreover, the color of CPs can be tailored by modification of the monomers with different functional groups. However, the CPs show relatively poor thermal and photochemical stability compared with TMOs. The electrochromic switching of CPs are based on doping and undoping process, leading to degradation of polymer chains during the redox cycles. Therefore, the electrochemical stability of CPs is usually poor. Nowadays, researchers are focusing on the above issues to improve the EC properties of materials through various methods, such as fabrication of nanostructured materials, tailoring the band gap of CPs, hybridization of organic/inorganic materials, and etc.

In this study, the hybridization of organic/inorganic materials is employed to address the above issues and further improve the electrochromic properties. Based on the literature, the hybrid EC materials can achieve enhanced electrochromic properties by combining the advantages of components through adjusting the composition, morphology, and chemical bonding. Many successful hybrid composites exhibit better performance compared with single component materials in terms of optical contrast, switching response, and electrochemical stability. Gu’s group reported the WO_3/PANI hybrid system
with chemical bonding that presents fast switching response and better reversible stability compared with single component materials.\[23\] However, the optical contrast of this hybrid material has not been developed, since WO$_3$ and PANI cannot switch simultaneously. Based on the literature study, cathodically colored PEDOT:PSS or its derivatives are employed to hybridize with WO$_3$ to achieve enhanced EC properties in my PhD works, since both of the materials colored at negative potentials and their electrical conductivities are complementary to each other.

In conclusion, there are numerous unsolved issues in electrochromic materials and devices currently. As this review of the literature shows, novel hybrid systems, new synthesis methods, fabrication techniques, and even innovative characterization methods can be proposed and verified to solve the problem and achieve high EC performance. This thesis is focused on the hybrid system based on WO$_3$ and PEDOT or its derivatives with enhanced optical contrast and electrochemical stability.

References


[54] K.R. Dunbar, R.A. Heintz, Chemistry of Transition Metal Cyanide


Chapter 3

Experimental Methodology

In chapter 3, the experimental methodology is elaborated in terms of materials synthesis, thin film fabrications, characterization methods, and data analysis processes for EC materials and devices. In this PhD study, thin film fabrication methods, namely LBL assembly, electrodeposition, and air-brush spraying, were applied to obtain hybrid EC materials with desired structure. Various techniques, such as SEM, TEM and AFM, were used to characterize the morphology and topology of the EC materials. Chemical composition and structure were verified by EDX, XPS, Raman and FTIR spectroscopy. Electrochemical analysis methods, including cyclic voltammetry and SECM were applied to monitor the electrochemical behaviour of the sample materials. The spectroelectrochemistry and electrochromic performances of sample materials and devices were studied in electrochemical cells. In this chapter, a general introduction of the above techniques is presented first followed by discussion on the underlying principles, and why these particular techniques are appropriate for this study.
3.1 Materials Synthesis and Thin Film Fabrication Methods

EC materials can be synthesized through various methods, which may strongly affect the performances. And they are usually fabricated as thin films for EC applications. The transition metal oxides are normally produced by hydrothermal method, sol-gel process, electrodeposition, chemical vapor deposition, and etc. The polymers can be obtained through polymerization from monomers and deposited as films via electrodeposition, spin coating, spray coating and layer-by-layer assembly. The synthesis techniques employed to obtain desired EC materials and thin film fabrication methods applied to deposit the EC materials on substrates are introduced and illustrated below.

3.1.1 Synthesis of WO₃ NPs

As discussed in the literature review section, the EC performance of WO₃ is strongly affected by the synthesized methods. The WO₃ nanoparticles (NPs) reported by Costa et al., exhibit high EC performance with stable crystal structure owing to the large surface area. And it can be easily obtained through hydrothermal method and well dispersed in water without any additives.[1, 2] Therefore, WO₃ NPs can be a promising EC material for inorganic/organic hybrid system.

Hydrothermal method is a common synthesis technique to produce crystals from solvent at high temperature. The structures and shapes of the obtained materials can be altered through adjusting the synthesis parameters, such as temperature, vapor pressure, and even the solubility. According to the literature, the WO₃ NPs can be synthesized through oxidation of W powder with hydrogen peroxide (H₂O₂) in aqueous solution at 100 °C in a sealed flask for about 3 hours, followed by freeze drying. The yellow WO₃ NPs obtained have crystalline structures and can be well dispersed in water without any additives.

3.1.2 Synthesis of PEDTS
PEDTS is a self-doped PEDOT derivative that presents good conductivity and water solubility. It is involved in this work to replace the PEDOT:PSS in the hybrid system to further enhance the charge transfer and EC performance. Before the synthesis of PEDOT, the monomer EDTS can be synthesized from hydroxymethyl EDOT (EDOT-OH) according to Stephan’s study. [3] And the PEDTS can be obtained from the polymerization of the monomers via chemical and electrochemical methods.[4] The polymerization of EDOT is an oxidization process, where the thiophene rings are forming polymer chains. The detailed synthesis procedures will be elaborated in chapter 6.

3.1.3 LBL Assembly

Layer-By-Layer (LBL) assembly is a simple thin film fabrication method to produce multilayer films based on the attractions of opposite charges between components.[5] A schematic illustration of LBL synthesis process is shown in Fig. 3.1. Many conjugated polymers, such as PEDOT:PSS and PANI, have been successfully deposited on conductive substrates by LBL method with well controlled structure and outstanding EC performance. And it can also be applied to incorporate different functional materials, such as Au nanoparticles, into polymer matrix with nano-size controlled structure. [6] Thus, LBL assembly is commonly applied in the fabrication of hybrid films with tailored morphology.

Figure 3.1 Schematic illustration of LBL assembly.
In the first work of this thesis, the conductivity changes of hybrid films based on WO$_3$ nanoparticles and PEDOT:PSS were studied compared with single component films. As discussed in materials selection above, the electron transport properties of WO$_3$ and PEDOT:PSS are complementary to each other, which make multilayer hybrid films attractive for electrochromic applications. The LBL assembly was applied to produce the hybrid multilayer films owing to low cost, ease of production, and precisely controlled morphology and structure.[7] The hybrid multilayer films can be easily deposited via LBL assembly by immersing the substrate into sample solutions alternatively. Both WO$_3$ NPs and PEDOT:PSS can be well dispersed in DI-Water, which makes it even more suitable for LBL assembly. And theoretically only single molecular layer of sample films will be deposited in this way. Therefore, with the precisely controlled morphology, it is also a very useful technique for underlying mechanism studies.

The polyelectrolyte is an important part in the LBL assembly, which assists the incorporation of different functional materials. It is used to modify the charges of components so that the components can be attracted to each other.[7] As reviewed in literature study, the polyelectrolyte is an ionic conductor, assisting the ionic transportation (ion insertion or extraction) in the EC films. On the other hand, most polyelectrolytes are electrical insulators that may hinder the electron transfer between components. As in the first work of this thesis, the polyelectrolyte polyethylenimine (PEI) used to provide charges is an electrical insulator, which prohibits the electron transfer in sample films.[8] Regarding this issue, conductive materials can be used to modify the charges of components. While, in our case, WO$_3$ NPs that prevent the formation of complete insulating PEI layers create pathways for electron transfer between components. It can also be a solution for this concern.

In summary, LBL assembly is a simple multilayer thin film fabrication
technique, which is suitable for hybrid films synthesis and mechanism study. In the first work of my PhD study, the hybrid films based on WO$_3$ NPs and PEDOT:PSS are obtained through this method, and studied by SECM techniques to understand the conductivity changes.

### 3.1.4 Air-brush Spraying

Air-brush spraying is a coating method for many applications, especially painting. The airbrush gun as shown in Fig. 3.2 uses the fast moving air flow to spray various materials, such as inks and dyes. The pressure near the venture will decrease as the air flowing, which leads to the material fluid to spray out. The droplet come out can be controlled by the needle and cone in the airbrush gun. This technique allows mixing of different materials as long as they can be dissolved or dispersed homogeneously in solutions. Therefore, it is a suitable preparation method for hybrid films on substrates.

![Figure 3.2 Schematic illustration of airbrush gun.](from http://hubpages.com/art/How-to-keep-your-airbrush-working)

The air-brush spraying method was used to fabricate electrochromic devices in the third work of this thesis owing to the simple coating process.[9] In the third work, a hybrid suspension has been prepared based on homogeneously dispersed WO$_3$ nanopartiles with CPs attached in DI-water. The hybrid EC films can be prepared through various techniques from the
suspension, such as air-brush spraying, roll coating, spin coating, or even inkjet printing. Air-brush spraying is simple and easily controlled method, and also very suitable for large area fabrications. Thus, it was applied in the EC film fabrications. In addition, many other techniques can be employed as well.

3.1.5 Electrodeposition

Electrodeposition is a widely used electrochemical synthesis and coating method for both inorganic and organic materials.[2, 10] It is applied to coat a uniform thin layer on the electrode, where electrochemical reactions occur. Many electrochromic materials are fabricated and deposited on the transparent conductors through electrodeposition, and present good electrochromic properties. And the deposition process can be easily controlled through adjusting the parameters, including applied potential, current, and deposition time. Most EC transition metal oxides can be easily electrodeposited from aqueous solutions containing the metal ions.[11, 12] The hydroxide ions generated in solutions are always associated with the metal ions and deposited as the insoluble layers on the electrode surface. The deposited layers usually contain metal oxides and hydroxides, and exhibits amorphous morphology prior to annealing. The CPs, such as PEDOT:PSS and PANI, can be electropolymerized from their monomers and deposited on the electrode surface. The polymer structure can be easily tailored through copolymerization or grafting functional groups by adjusting the monomer solutions.[13] Thus, the electrodeposition is a common synthesis technique to obtain uniform EC films with controllable deposition process.

In this work, electrodeposition was employed to deposit both WO$_3$ and PEDOT:PSS from one-pot aqueous solution with well controlled structure. The WO$_3$ can be electrodeposited from the peroxytungstic acid (PTA) aqueous solution. And the acidity is adjusted by hydrochloride acids to pH 1-2 in the dilute solutions, which assists the sol-gel electrodeposition process of WO$_3$ thin films. PEDOT:PSS can be electropolymerized from monomers dissolved in
acidic aqueous solution, which provides the possibility to deposit it with the WO$_3$ from a single solution. The monomer EDOT and PSS can be dissolved in the PTA to form a relatively stable solution. Excess peroxy species are removed by decomposition, while the presence of catalyst Pt-black prevents the oxidation of EDOT in solution. Both components can be electrodeposited as thin films with controllable structure by tailoring the deposition parameters, such as applied potentials or deposition time. This leads to large interfacial areas, enhancing the interactions between components. The amorphous WO$_3$ deposited exhibits better EC performance in terms of switching response and optical contrast as mentioned in the literature review section. In addition, compared with the LBL method, PEI layers or other additives are not involved to hinder the charge transfer between components. However, annealing process is not suitable for the obtained EC films, since the polymer cannot sustain high temperature. As a result, some uncertain species, such as tungsten hydroxides or functional groups, were presented in the obtained EC films and cannot be clearly identified.

In conclusion, the electrodeposition is a simple and easily controlled method for both synthesis and thin film coating of inorganic and organic materials. In the second work of this thesis, electrodeposition is employed to fabricate hybrid films with desired structure from one-pot solutions. Compared with LBL synthesis method, the electrodeposition can easily alter the morphology and structure of the hybrid thin films so as to improve the interactions between components.

3.2 Characterization Techniques

The obtained EC materials were tested and analyzed through various techniques to study their morphology, structure, chemical composition, electrochemical and electrochromic properties. These techniques are introduced in details; and the reasons to employ the particular technique are also presented below.
3.2.1 Morphology and Structure

The properties of materials can be strongly dependent on their morphology and structure. Various techniques can be used to characterize them, including surface profiler, X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). A basic and brief introduction of these techniques will be presented below, since they were only involved for basic morphology characterization in this thesis.

I. Surface Profiler

The surface profiler is an instrument that used to measure the thickness and roughness of thin films. It can be divided into two categories as contact and optical profilometers.[14] The contact surface profiler provides the surface information through a diamond stylus in contact with the sample surface and moving across it. The thickness or roughness can be determined by measuring the feedback of the tracking force. The measurement ranges from 10 nm to 1 mm based on the size of stylus. And the measurement cannot be affected by the environment owing to the contact between the stylus and the sample surface. However, the surface morphology may be damaged by the stylus during measurement. The optical profilometer measures the surface without contact, which prevents damaging the sample surfaces. Compared with the stylus based profilometer, the optical one provides more reliable information but can be easily affected by the environment, where the light can be reflected or absorbed by the contaminants. [15-17]

For the EC films obtained in my work, the contact surface profiler was employed to measure the thickness of thin films, since it is simple and unaffected by the environment with reasonable resolutions. In addition, the thicknesses of sample films are in the measurement range of contact surface profiler. Practically, a step was created on the film, where the stylus can easily
measure the depth when moving across it as shown in Fig. 3.3.

![Schematic illustration of thickness measurements through surface profiler.](image)

**Figure 3.3** Schematic illustration of thickness measurements through surface profiler.

II. XRD

X-ray diffraction (XRD) is a common characterization method for identifying the crystal structure of materials, which provides information on atomic or molecular arrangements.[18] X-ray waves passing through materials will be scattered by the atoms inside, generating secondary spherical waves. If the atoms are regularly arranged (crystalline), the constructive wave will appear in certain directions following Bragg’s law (Eq. 3.1) of diffraction.

\[
2d\sin\theta = n\lambda
\]

(Eq. 3.1)

Here \(d\) refers to the distance between the diffracting planes, \(\theta\) is the incident angle, \(n\) can be any integer number, and \(\lambda\) indicates the wavelength of incoming beam. Therefore, the diffraction pattern can be collected and shown as a function of incident angle (\(\theta\)), which indicates the atomic or molecular arrangements of materials.[18, 19] The resolution of XRD spectrum can be sometimes limited when measuring the crystals with complex or large repeating unit for a given number of observed reflections. For example, the macromolecular usually present less well-resolved crystal structures.[20]

The electrochromic properties can be strongly affected by the crystalline structures of EC materials, especially the transition metal oxides. XRD was involved in this work to provide information on the crystalline structure of sample films, which can help to understand the charge insertion and extraction process. For example, the WO\(_3\) films prepared through sol-gel process and electrodeposition were both characterized by XRD to identify their crystal structures. The WO\(_3\)-NP film with crystalline structure exhibits relatively slow
switching process compared with the electrodeposited amorphous WO$_3$ films.

III. AFM

The atomic force microscopy (AFM) technique provides topography information of materials with resolution around nanoscale. In an AFM, a mechanical probe is used to “touch” the surface while moving across it. A laser beam is employed to reflect and transfer the information collected by the probe as shown in Fig. 3.4. With the collected surface information, a 3 dimensional (3D) image (surface topography) can be presented with resolution of a few nanometers. In addition, different phases of materials can be identified through the force between the probe tip and sample surface. Compared with other morphology characterization methods, AFM is a relatively non-destructive technique with easy sample preparation process. Also unlike SEM, the detection is not affected by the environment. However, the sample may be damaged by the scanning probe, since it is in contact with the sample surface. And the scanning area and speed of SEM are better than that of AFM technique.

The hybrid sample films obtained are based on inorganic TMOs and organic CPs, which exhibit different phases and structures. The AFM technique can be applied to characterize the surface structure, study the materials morphology and topology, and differentiate the organic and inorganic phases in hybrid systems.

Figure 3.4 Schematic illustration of AFM working mechanism based on laser deflection detection. (from https://en.wikipedia.org/wiki/Atomic-force_microscopy)
IV. SEM

Scanning electron microscopy (SEM) is another morphology characterization method, which provides surface morphology information through scanning electron beams. Compared with conventional optical microscope, the SEM images are formed through the scattered electrons instead of light. With the incident electron beam, various signals are generated owing to the interactions among sample atoms and the incoming beams, including secondary electrons, back-scattered electrons, photons and even light. As a result, images and atomic composition information of samples can be obtained from these signals. Secondary electron images (SEI) are the most common SEM images, where the secondary electrons near the sample surface are detected and presented. They can provide information of surface morphology and topology at a high resolution of around 1 nm. Back-scattered electron images (BSE) are based on the elastic-scattered electrons generated in deeper positions. The BSE images are significantly dependent on the atomic number (Z) of materials, which indicate the atomic distribution within materials. Thus, it is usually applied in companion with atomic analysis techniques, such as energy dispersive X-ray spectroscopy (EDX).[26] In addition, the EDX in company with the SEM is a technique to detect and analysis the photons of characteristic X-ray signals.[26] The details of this technique will be elaborated in the chemical structure and composition characterization section. As the incident electron beams can be easily scattered, the samples should be placed in a vacuum environment to limit the unwanted scattering by contaminants. Moreover, the sample needs to be conductive so as to prevent the electron accumulations. Therefore, to obtain better images, a thin layer of Pt or Au, usually around 10 nm thick, is coated on the sample surface to increase the conductivity. In addition, the electron beam may damage the sample surface during scanning process owing to the high energy of the incident beam. Overall, the SEM technique is a very common image technique to provide surface
morphology and topology information with high resolution at various magnifications.[27]

Another morphology characterization technique AFM is always applied with SEM together. In addition to SEM, AFM provides better lateral resolution and can differential phases in materials. Therefore, both techniques were used for EC materials characterizations to study the morphology, topology, atomic and phase distribution.

V. TEM

Transmission electron microscopy (TEM) is similar to SEM using the focused electron beam to produce images of sample materials. However, the TEM images are based on the electrons that transmit through the ultrathin samples. The incident electron beam is emitted from the filament, then accelerated by high voltage (100-300 kV) and focused by the magnetic coils (lens in TEM), so that it can pass through the materials at desired positions. After that, the electrons are converted into light and produce images on the fluorescent screen. The characterization on desired position at various magnifications can be easily achieved through adjustments. Fine details of materials are presented by the TEM images based on the interactions between electrons and sample atoms. The materials with high atomic numbers or thickness will appear dark in the TEM images, since they absorb more electrons.[28] It is always used in companion with the EDX technique to present the atomic distribution of samples. Besides the image mode, diffraction mode is another commonly applied mode, providing crystallographic information of materials. A diffraction pattern is generated in this mode as well arranged dots or a series of rings for different structures. Each dot represents an atomic plane in single crystalline materials with certain orientations refer to the electron beam. And the rings can be obtained when analysing amorphous or polycrystalline materials. Overall, TEM can provide material information of morphology, composition, and crystallography at high resolution of atomic
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level. However, the TEM instrument is very complex and expensive, since it must precisely control the electron beam movements in high vacuum environment. In addition, the sample preparation process is tedious, as ultrathin specimens of few micrometres or nanometres are desired in this process. [29-31]

TEM technique was involved to characterize morphology and structure of hybrid materials. In the second part of this work, the one-pot electrodeposition method can alter the morphology and structure of the hybrid films. The TEM technique is the straightforward method to image the lateral structure and present it directly. The sample preparation method is also presented here: A small piece of sample film is glued to the copper rings vertically and mechanically supported by the epoxy resin. It is then polished and ion-milled into only few nanometres so that the electron beam can pass through it. The contrast of the TEM image indicates the components inside the hybrid films owing to different atomic numbers. In the third part of this work, the TEM is also employed to show the morphology of the hybrid nanoparticles. Thus, TEM technique was suitable for the characterization at high resolution despite its tedious sample preparation process.

3.2.2 Chemical Structure and Composition

The materials obtained through various synthesis methods can be confirmed or defined by analysing the chemical structures. It can be verified by Fourier transform infrared (FTIR) and Raman spectroscopy. And composition of each component in hybrid materials is very important, since it can significantly affect the properties. Thus, energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopies (XPS) can be applied to characterize the composition of hybrid materials. The techniques used are briefly introduced and discussed below, since they were employed for basic analysis in this work.

I. FTIR
Fourier transform infrared (FTIR) spectroscopy is a chemical structure analysing technique for identifying materials. IR spectroscopy with a wide range of wavelengths is passing through the sample, which absorbs the light of certain wavelengths. The absorption peaks are then displayed on the spectrum plot as intensity versus wavenumbers. The absorption is caused by the chemical bonds vibrations, where the frequencies are corresponding to that of incident light. Thus, the spectrum represents a molecular fingerprint of materials. Moreover, the size of peaks can be an indication for the amount of materials, which can be used for quantitative studies. Compared with the monochromatic spectroscopy, FTIR can scan sample with a broad range of IR frequencies simultaneously. And the scan process can be repeated to increase the accuracy and sensitivity of measurements. Therefore, FTIR is a non-destructive technique that is suitable to identify unknown materials, determine the quality of materials, and verify the amount of components in mixtures. Conventionally, the samples for FTIR examination are prepared mixing with the IR-transparent material potassium bromide (KBr). The attenuated total reflection (ATR) technique is developed in FTIR measurement, where the solid or liquid samples can be directly measured as fabricated. Nowadays, the FTIR is usually equipped with the ATR compartments for simple sample preparation process. [32, 33]

The FTIR is applied in this work to identify the EC materials after synthesis. Characteristic absorption peaks observed indicates the existence of the components in sample films. Moreover, the synthesis process could also be examined by FTIR scans to identify the products of each step. So FTIR (including ATR-FTIR) is a desired chemical structure analysis technique to identify different materials.

II. Raman

Raman spectroscopy is another chemical structure identification technique to verify the molecular structures. Unlike the FTIR technique, it is a
monochromatic spectroscopy based on the inelastic scattering of incident light. The specimen can interact with the incident light of certain wavelength, resulting in the energy shift of the incident photon, which gives information of vibration modes in the system. The signals of energy shift of incident laser photons caused by the excitation of sample materials are collected and presented as Raman spectrum, which is plotted as intensity versus Raman shift (or frequencies). And the Raman shift presented as wavenumbers can be calculated through Eq. 3.2, where Raman shift ($\Delta \omega$) is derived from excitation wavelength ($\lambda_0$) and scattered wavelength ($\lambda_1$).

$$\Delta \omega = \frac{1}{\lambda_0} - \frac{1}{\lambda_1}$$

(Eq. 3.2)

The signals detected are very weak, since the elastic scattering signals are excluded. Silver, gold or copper are commonly applied to coat on the sample surface, since they have enhanced Raman scattering signals compared with non-metallic surfaces.[34] Other techniques, such as surface resonance, are employed for modern Raman spectroscopy. The FTIR spectroscopy with a wide range of wavelengths provides similar, but complementary information, compared with Raman spectroscopy. In Raman spectroscopy, the intensity of Raman scattering is proportional to the change in the molecular electric dipole-electric dipole polarizability. However, in IR technique, the interaction between the molecule and light is determined by the electric dipole moment derivative. Therefore, some transitions may be not IR active but can be analysed through Raman spectroscopy for some centre symmetric molecules. Bands which have large Raman intensities in many cases have weak infrared intensities and vice versa. However, for some very symmetric molecules, certain vibrations can be inactive in both IR and Raman spectroscopy. Other techniques may be applied for further analysis. Different information can be obtained through the different interactions between the molecule and the electromagnetic radiation in both techniques.[35] The FTIR technique is usually applied together with Raman spectroscopy to provide comprehensive
information of chemical structure to identify the unknown samples. In this work, both techniques are employed to identify the components obtained through various fabrication methods mentioned above.

III. EDX

Energy dispersive X-ray (EDX) spectroscopy is a commonly used elemental analysis technique that provides quantitative information of elements in samples. It is based on the X-ray excitation of samples when reacting with external energy sources, such as electron beams in SEM and TEM. The energetic electron or proton beam will excite electrons in the inner shell of sample atoms, leading to the ejection of the inner shell electrons. In this case, the outer shell electrons will jump into the inner shell with energy released as X-ray. The X-ray released is usually corresponding to the energy difference between shells in sample atom, which is unique for each element. Therefore, the X-ray spectrum, detected by the energy dispersive spectrometer, can be used to determine the elements. So it can be applied to measure the atomic distribution in samples as element maps. In addition, the intensity of EDX peaks can be used to determine the quantities of each sample element. However, overlapping of characteristic peaks of different elements is common in the EDX measurements, which may strongly affect the accuracy. And this technique is always being equipped in SEM and TEM instruments, since it is significantly dependent on the energy of incident beams (electrons beams in this case). The accelerating voltage of electron beams is required to be high enough to excite the inner shell electrons, resulting in sufficient emitted X-ray. Moreover, the energy of the incident beams can also determine the penetration depth of this technique, which usually ranges from 2 to 6 μm. [26, 36-38]

The EDX is applied in this work together with SEM and TEM characterization techniques. It semi-quantitatively determines the elements shown in SEM and TEM images. In this case, it can also provide information of sample composition based on the characteristic elements of each component.
Because of its low accuracy, it is usually applied in companion with other techniques to provide comprehensive atomic and composition information of samples.

IV. XPS

Similar to EDX, X-ray photoelectron spectroscopy (XPS) is another commonly used quantitative elemental analysis technique. Unlike the EDX, XPS is a surface sensitive technique, which provides elemental information of sample from 10 nm to its surface. The sample interacts with the incident X-ray, where the electrons are excited to eject from sample atoms. The signals of kinetic energy and numbers of ejected electrons are measured to calculate the binding energy of the electrons. Then the electronic structure can be determined by the binding energy of electrons ejected from different shells. As the electronic structure of each atom is unique, the wide range XPS survey can be used to determine the elements inside samples. XPS is also used to analysis the chemical environment of specific elements in particular energy range, since the electronic structure can be easily affected by chemical bonds. For example, in tungsten oxides, the binding energy of tungsten at its fully oxidized state will be higher than that of less oxidized ones. So it is also used to determine the oxidation states and other chemical environment of sample elements. As a surface technique, the XPS requires ultra-high vacuum environments to conduct measurement and sensitive detectors to sense the ejected photoelectrons.[39, 40]

Compared with EDX, XPS provide more accurate elemental information in samples, including the chemical environment of specific element. On the other hand, XPS only provides information of sample surface up to around 10 nm; while EDX measurement can penetrate to a few micrometers. And the measurement process of XPS is much more tedious than that of EDX. XPS and EDX are both employed in characterization of EC sample films in our work. The XPS is used to provide the surface information with the chemical
environment of W in neat WO₃ and hybrid film. And EDX is applied to determine the composition of each component in bulk hybrid samples.

3.2.3 Electrochemical Analysis

The electrochromic switching is mainly based on the reversible redox electrochemical reactions. So it is essential to study the electrochemical properties of EC materials to understand the redox reactions during switching process. Cyclic voltammetry (CV) method is most commonly used technique to study the redox processes. A novel technique scanning electrochemical microscopy (SECM) is also involved to study the conductivity of EC materials in redox switching potential windows.

I. CV

Cyclic voltammetry (CV) is a measurement method that collects the current passing through the working electrode under ramped potentials. The CV measurement is usually conducted in the standard three-electrode electrochemical cells containing electrolyte, working, reference, and counter electrodes. The applied potential is swept and repeated in a certain range as a function of time shown in Fig. 3.5a. The slope indicates the voltage changes at unit time interval, which is defined as the scan rate (V/s). The current passing through the working electrode is recorded and plotted versus the applied potentials as the CV graphs. A typical CV graph of reversible redox reaction is shown in Fig. 3.5b, where the cathodic and anodic peaks are labelled.
The cathodic peak indicates the reduction reaction; while the anodic peak refers to the oxidation reaction. And cathodic peak current is equal to the anodic peak current. The CV graphs of non-reversible species exhibit unequal cathodic and anodic peak currents. Some species with multiple oxidation states may show several peaks in CV graph. The difference between cathodic and anodic potential peaks is attributed to the diffusion of reversible species. Therefore, the CV is commonly applied to characterize the redox reactions through analysis the cathodic and anodic peaks. Quantitative studies can be achieved through the amount of charges recorded during the reactions. However, the CV method is a sensitive technique, which may be affected by the dissolved contaminants.[41]

The CV method is employed to analysis the switching reactions of EC sample films, since the reactions are mostly reversible redox reactions. The sample films coated on ITO (or FTO) glasses are used as the working electrode, and analysed at various scan rates. The peaks shown in CV curves refer to the redox reactions, which indicate the switching process of materials. Multiple redox peaks exhibit in CV curves of hybrid films suggest both components switching in the system. In addition, the plot of potential peaks as a function of scan rate may advise the diffusion process as well. The CV method involved in the EC materials analysis can provide the information of redox reactions, including coloration/bleaching potentials, diffusion process, and charges transfer process in the EC films.

II. SECM

Scanning electrochemical microscopy (SECM) is a novel technique based on the study of electrochemistry with a small electrode called
ultramicroelectrode (UME). The radius ($a$) of UME can be ranged from a few nanometers to 25 μm. The operation of SECM is conducted in an electrochemical cell with UME held or moved across the substrate in a solution as shown in Fig. 3.6a. The current passing through the UME is recorded as a function of applied potential or movement of UME. It provides the information about nature and properties of substrates. There are several operation modes of SECM as feedback mode, tip generation/substrate collection (TG/SC) mode, and substrate generation/tip collection (SG/TC) mode. The TG/SC mode means that reactants is generated at the UME tip and detected at the substrates. Similarly, the SG/TC mode refers to the reactants generated in the substrate and detected by the UME tip. The most commonly applied feedback mode can be employed to study the reactions on substrate surface. In this mode, the tip current is recorded as the UME approaching towards the substrate surface. For example, the SECM feedback mode experiment is conducted as shown in Fig. 3.6a with a solution containing species O that can be reduced at the UME tip on applied potentials. As shown in Fig. 3.6b, if the substrate is far from the UME tip, the oxidation will occur at the counter electrode (auxiliary electrode) leading to a steady-state current. As the UME tip approaching the conductive substrate, the tip current will be increase dramatically, since the oxidation occurs at the substrate (Fig. 3.6c). On the other hand, the tip current will decrease significantly upon approaching a non-conductive substrate, since the diffusion has been hindered by the substrate (Fig. 3.6d). [42]
Figure 3.6 (a) Schematic illustration of an electrochemical cell for SECM experiment containing electrodes, electrolyte, redox species, and substrate. Basic principles of SECM: UME tip is (b) far from substrate, (c) near conductive substrate, and (d) near non-conductive substrate. (Reproduced from ref. [42].)

Base on the feedback, the approach curves or even conductivity images of substrate can be plotted and analysed. Therefore, the SECM is suitable to study the in-situ reactions on substrate and its underlying mechanism. However, this SECM method is a sensitive surface technique, which can be easily affected by contaminate, physical vibrations, UME size, and etc. Various and tedious simulation processes may be involved in data analysis process. Despite the drawbacks, the feedback mode of SECM technique was employed in this work to study the EC films, including WO$_3$-NP, PEDOT:PSS and multilayer hybrid films. In this case, the EC films were used as the substrates and been monitored by the UME during redox reactions. It provided the conductivity information of substrate films at either constant potentials or CV scans so as to study the conductivity changes of EC films during redox reactions.

### 3.2.4 Electrochromic Performance Study

The electrochromic performance is characterized in terms of optical contrast, switching speed, coloration efficiency, and electrochemical stability as discussed in literature review section. Herein, the experimental set-up and practical procedures are elaborated and discussed.

The EC properties are characterized in a standard three-electrode electrochemical cell as shown in Fig. 3.7, which is a simple and widely used EC
characterization tool. The EC films coated on the ITO or FTO glasses serve as the working electrodes. Silver (Ag) and platinum (Pt) wires are employed as the reference and counter electrodes, respectively. And the Ag wire is calibrated by reversible redox species in electrolyte solutions. Electrolyte is filled into the quartz cuvette with all the electrodes immersed inside. Another cuvette containing only electrolyte is used as reference during the EC performance characterization. The transmittances (or absorbance) of this electrochemical cell are recorded with various applied potentials on working electrodes. All the EC properties are characterized through this set-up.

Figure 3.7 Image of three-electrode electrochemical cell used for electrochromic performance characterization.

**Optical spectrum characterization** is to obtain optical contrasts of EC materials under various potentials through recording the transmittance of EC materials at a wavelength range. For example, the transmittances of an EC film are recorded at wavelength from 300 to 900 nm (visible range) with applied potentials. The optical contrast can be obtained as the maximum transmittance difference ($\Delta T$) between the bleached and colored states at wavelength of interest as in Eq. 2.2.

**Dynamic performance characterization** is to record the transmittance of EC films under square-wave potentials. The transmittance is measured at the wavelength of interest and plotted as a function of time. In this plot, the
transmittance change (ΔT) between colored and bleached states can be directly observed. In addition, the corresponding current passing through the working electrode (EC film) is also monitored during the switching process. The coloration efficiency (η) is defined as the change of absorbance (ΔA) or optical density (ΔQD) at wavelength of interest (λ) per unit of inserted charges (Q) (shown in Eq. 2.4). It can be derived from the recorded dynamic transmittance and its corresponding current (i) as in Eq. 2.4, 2.5 and 3.3, where A means the area of EC film.

\[ Q = \left( \frac{\int i \Delta t}{A} \right) \]  

(Eq. 3.3)

The electrochemical stability or reversibility is tested by monitoring the transmittance of EC films at wavelength of interest under square-wave potentials for many reversible cycles. The transmittance difference between bleached and colored state will be reduced owing to the degradation of EC materials. It is presented as the transmittances recorded at completely bleached and colored state versus the number of cycles. And the transmittance change as increasing reversible cycles can be directly observed and analyzed.

3.3 Overview of Methodologies

In this chapter, the experimental methodologies including materials selection, synthesis and fabrication, characterization of EC materials and devices are introduced, and the reasons to use particular technique are elaborated. First of all, to achieve high performance EC materials and devices, proper EC materials are employed to build hybrid system with desired morphology and structures. WO₃ and PEDOT:PSS or its derivatives are applied to fabricated EC materials and devices, since all components exhibit good EC properties. Secondly, the properties of materials can be strongly affected by morphology and structures. Various synthesis and fabrication techniques, such as hydrothermal methods, chemical oxidation, LBL assembly, air-brush spraying, and electrodeposition, are applied to obtain hybrid EC materials with
desired morphology and structures. Large interfacial areas are achieved through these techniques, leading to efficient interactions between components and enhanced EC performances. Thirdly, the morphology and structure of obtained materials are characterized by surface profiler, AFM, SEM and TEM techniques. And the chemical structure and composition of obtained EC materials are verified by FTIR, Raman, EDX, and XPS techniques. The general working mechanism, advantages and disadvantages of these techniques are presented and discussed. Sometimes, more than one technique is employed to provide comprehensive information of chemical structure and composition of obtained materials. The electrochemical and electrochromic properties are all tested in electrochemical cells. The CV and SECM techniques are applied to study the electrochemical behaviours of EC materials. The EC performance is measured in a simple and widely used electrochemical cell with sample films as the working electrode. The spectroelectrochemical tests are presented to characterize the key factors of EC performance.

Reference


Chapter 4*


In this chapter, structure, morphology and properties of multilayer hybrid EC films obtained through LBL assembly of PEDOT:PSS and WO₃ nanoparticles (NPs) are presented. In the LBL process, insulating polyethylenimine (PEI) is deposited in between PEDOT:PSS and WO₃ NPs to introduce electrostatic force. In the hybrid films, WO₃ NPs are homogeneously distributed in the polymers and form an interdigitated structure. The very rough surface morphology hinders the formation of a continuous PEI layer between the electrochromic layers. The coloration efficiency of the obtained hybrid film is significantly improved to 117.7 cm²/C at wavelength of 633 nm. The SECM technique is employed to study the enhancement through probing the conductivity changes of obtained EC films under potential sweeps. The study verified that the complementary electrical conductivity of the two components in the studied potential range can enhance charge transfer in the hybrid system during the switching process.

4.1 Introduction

As introduced in previous chapters, WO\textsubscript{3} is currently the most widely used inorganic EC material owing to its high performance among TMOs. Electrochromic CPs usually exhibit fast switching speed and high coloration efficiency, and hence have been combined with WO\textsubscript{3} to improve its electrochromic properties.\cite{1, 2} In particular, poly(styrene sulfonate) doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) and WO\textsubscript{3} are both cathodically colored materials, and can be simultaneously switched to colored or bleached state.\cite{3} As reported by Deepa et al., PEDOT:PSS/WO\textsubscript{3} composite films with PEDOT:PSS as the major component can exhibit a high coloration efficiency comparable to that of PEDOT:PSS; while the electrochemical response of WO\textsubscript{3} was preserved in the hybrid.\cite{4} The interactions between the organic and inorganic components also stabilize the defects in WO\textsubscript{3}, leading to good electrochemical stability of the hybrids with WO\textsubscript{3} as the major component.\cite{2} Furthermore, although with cations (M = H\textsuperscript{+}, Na\textsuperscript{+} and Li\textsuperscript{+}) inserted, M\textsubscript{x}WO\textsubscript{3} displays metallic conductivity due to its oxygen-vacancy defects, the fully oxidized WO\textsubscript{3} is an n-type semiconductor with extremely low electrical conductivity.\cite{5} By contrast, PEDOT exhibits high electrical conductivity in its oxidized state.\cite{5} Thus under positive potentials, the high conductivity of PEDOT:PSS may facilitate electron transport in WO\textsubscript{3}/PEDOT hybrids. So far, the effects of redox reaction induced electrical conductivity change on electrochromic properties of TMO/CP hybrid systems have, however, been rarely studied.\cite{6}

As mentioned in section 3.2, LBL assembly is a versatile thin-film fabrication method for organic and inorganic materials. As for WO\textsubscript{3}-based layered electrochromic structures, Wang and Zeng et al. reported LBL-assembled electrochromic films based on crystalline WO\textsubscript{3} nanosheets, which have good electrochemical stability.\cite{7} However, although in principle the small thickness of the nanosheets could shorten the ion diffusion path, in
reality the stacking of nanosheets leads to a slow coloration process. Several research groups also reported the LBL assembly of electrochromic thin films based on polyoxometalates (POMs) and polyelectrolyte, such as tungstophosphate anion (P₂W₁₈⁻) and poly(allylamine hydrochloride) (PAH).[8] Gold nanoparticles (AuNPs) have also been incorporated into POMs/polyelectrolyte system to enhance its electrochromic properties.[9] Thus, the LBL is feasible to fabricated hybrid thin film based on WO₃ and PEDOT:PSS with enhanced EC properties, since both components simultaneously switched and their electric conductivity are complementary. Furthermore, understand charge transfer process in such layered electrochromic structures may provide useful design guideline for other electrochromic TMO/CP hybrid systems.

In this work, the LBL assembly method was employed to fabricate electrochromic hybrid films from crystalline WO₃ nanoparticles (WO₃ NPs), PEDOT:PSS and polyethyleneimine (PEI). Herein we demonstrate that the hybrid system with WO₃ as the major component exhibits enhanced electrochromic properties, especially remarkably improved coloration efficiency compared with those of WO₃/PEI and PEDOT:PSS/PEI systems. Moreover, for the first time, the SECM technique was employed to verify the conductivity changes of sample films during their redox switching processes under potential sweep, providing insight into the mechanism underlying the enhanced electrochromic properties.

4.2 Experimental Methods

4.2.1 Materials

All chemicals, namely PEI (50 wt.% in H₂O), PEDOT:PSS (1.3 wt.% dispersion in H₂O, conductive grade, 1 S/cm), W powder, H₂O₂ (30 wt.% in water), H₂SO₄ (98%), NH₃OH (28~30% in water), LiClO₄ and propylene carbonate (PC), were purchased from Sigma-Aldrich and used without further
purification. Unless otherwise specified, all solutions or suspensions were prepared using deionized water (DIW, 18 MΩ/cm²), which was purified by Milli-Q integral water purification system. The substrates used were Si wafer (Sigma-Aldrich), quartz glass, and indium tin oxide (ITO) coated glass with sheet resistance $R_s = 5-15 \ \Omega$ (Delta Technology, USA). The Si wafers were cleaned by sonication in 1:1 (vol. ratio) DIW/acetone mixture for 20 mins, followed by immersing in 3:1 (vol. ratio) $H_2SO_4$ (98%)/$H_2O_2$ (30%) solution for 30 min. The glass and ITO coated glass were cleaned by sequential bath sonication in ethanol, 1:1 (vol. ratio) $NH_4OH/H_2O_2$, and DIW for 10, 30, and 10 min respectively. After cleaning, they were washed by DIW and blow dried by $N_2$ gas before use. Standard three-electrode electrochemical cell was employed in electrochromic studies. Pt and Ag wires were used as counter and reference electrodes, respectively. While, in electrochemical tests, Ag/AgBr wire was used as reference electrode.

### 4.2.2 Sample Preparation

The WO$_3$ NPs were prepared via a hydrothermal process from metallic W powder, which could be dispersed in water without any additives.[10, 11] The electrochromic thin films were obtained by LBL assembly. Clean substrates were immersed into 1 wt.% PEI and 0.2 wt.% PEDOT:PSS (or 0.4 wt.% WO$_3$-NPs) solutions for 30 min and 1 hour alternatively to obtain single component films. Multilayer hybrid films were fabricated by immersing the substrates sequentially into PEI, PEDOT:PSS, PEI, and WO$_3$-NP solutions for 30 min, 1 hour, 30 min, and 1 hour repeatedly. Between any two adsorption steps, the substrates were washed by DIW, and also blow-dried by $N_2$ gas for building uniform assembled layers. The obtained thin films are denoted as P$n$, W$n$ and H$n$, where $n$ represents the number of layers. The meanings of P$n$, W$n$ and H$n$ are listed in the Abbreviation section.
4.2.3 Characterization

The XRD pattern of WO$_3$ NPs was measured using a Shimadzu diffractometer with Cu Kα radiation. The thickness of the multilayer films was measured using a surface profiler (alpha-step 500 profilometer) on Si substrate. The surface morphology of the films were examined on a scanning electron microscope (SEM, SIRION, FEI Ltd.), which is equipped with energy dispersive X-ray spectrometer (EDX, X-Max 20, Oxford Instruments, UK) system for examining the composition. The topography of the films was also characterized by atomic force microscope (AFM Dimension ICON, Bruker) using tapping mode at a scale of 5 µm. The chemical structure and composition of the films were studied by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA, Kratos Analytical) using Al Kα (1486.7 eV) X-ray source.

The spectra-electrochemical properties were measured by potentiostat (1470E, Solartron) and a UV-Vis-NIR spectrophotometer (UV3600, Shimadzu). The transmittance of each film was recorded at potentials of +0.8, 0, and -1.0 V in a wavelength range of 300 to 800 nm. Moreover, to obtain dynamic transmittance, square-wave potentials oscillating between +0.8 and -1.0 V were applied to sample films at time interval of 40 and 50 s for hybrid and PEDOT:PSS/WO$_3$-NPs films respectively. A standard three-electrode system was used in all tests, where sample films coated on ITO glass served as working electrode, and platinum (Pt) and silver (Ag) rods were used as counter and reference electrode, respectively, in a solution of 1 M lithium perchlorate (LiClO$_4$) in propylene carbonate (PC).

Scanning electrochemical microscope (SECM, CHI 920C) was employed to conduct cyclic voltammetry (CV) and other electrochemical tests. CV was also carried out with the same apparatus and solution as the electrochromic tests. Approach curves were measured by approaching a Pt microelectrode (25 µm diameter, RG = 10, $E = +300$ mV vs. Ag/AgBr quasi reference electrode (QRE)) to the sample surface in an aqueous solution of 0.1 mM ferrocenemethanol.
(FcMeOH) and 10 mM potassium chloride (KCl). The surface was either floated or controlled at a fixed potential (ca. −300, −200, −100, and 0 mV) by connecting as the second working electrode. The effect of potential on conductivity of the films was also studied by SECM. A Pt microelectrode was positioned closely above the sample and kept at +300 mV (vs. Ag/AgBr QRE) in the same redox solution, and its current was recorded as the potential applied on the sample was scanned from 0 to -0.8 V (vs. Ag/AgBr QRE) at a scan rate of 5 mV/s.

4.3 Results and Discussions

4.3.1 LBL Assembly of Sample Films

In this work, LBL assembly method was employed to obtain the hybrid films. Since both WO$_3$ NPs (crystalline structures determined by XRD pattern shown in Fig. 4.1) and PEDOT:PSS colloidal particles have negatively charged surfaces, to facilitate the electrostatic adsorption of the components, polycationic PEI was used as intermediate layers to attract the anionic species, as illustrated in Fig. 4.2. The substrate was firstly treated with the PEI solution, and then immersed into PEDOT:PSS and WO$_3$-NP suspensions alternatingly with a PEI layer in between. By repeating the processes, multilayer hybrid films can be obtained and for simplicity they are denoted as hybrid films. PEI/PEDOT:PSS and PEI/WO$_3$-NP multilayer films were also prepared as reference samples and they are denoted as PEDOT:PSS and WO$_3$-NP films. Herein, a film composed of PEI/PEDOT:PSS (or PEI/WO$_3$-NP) is defined as one layer for PEDOT:PSS and WO$_3$-NP films, while a film of PEI/PEDOT:PSS/PEI/WO$_3$-NP is defined as one layer for the hybrid films.
Figure 4.1 X-ray diffraction pattern of WO$_3$ NPs on ITO glass substrate.

Figure 4.2 Scheme for the formation of electrochromic multilayer hybrid film [PEI/PEDOT:PSS/WO$_3$-NPs]$_n$ (H$n$).

The thickness of PEDOT:PSS and hybrid films is plotted against the number of layers in Fig. 4.3, showing approximately linear relationships for both systems. Based on the growth curves, the average thickness of a hybrid layer is about 12 nm, while the average layer thickness of PEDOT:PSS film is only around 5 nm. The WO$_3$ NPs have irregular disk-like shape with a diameter of around 50 nm and height of only few nanometers (Appendix, Fig. A.1). By first few steps of adsorption, WO$_3$ NPs could not form a continuous layer like the polymers. Thus, the surface of these films is too rough to precisely determine the thickness of each layer. However, after 5 steps of adsorption, the average thickness of WO$_3$-NP films can be roughly measured, which is about 35 nm.
Figure 4.3 Thickness of electrochromic films with different numbers of layers measured by surface profiler.

4.3.2 Morphologies and Compositions of Sample Films

AFM can provide detailed information about surface morphology, topography and homogeneity of the films. The AFM micrographs in Fig. 4.4 show the surface features of the PEDOT:PSS, WO$_3$-NP and hybrid films adsorbed on Si substrates. From Fig. 4.4A, it is obvious that as the number of layers increases, the thickness and roughness of the PEDOT:PSS films gradually increase. By contrast, the WO$_3$ NPs are adsorbed homogeneously (Fig. 4.4B). In addition, as the number of layers increases from one to three, clearly more WO$_3$ NPs are observed in the AFM height images, implying that the WO$_3$ NPs adsorbed on top layer may be interdigitated with the ones adsorbed in the underneath layers owing to the much smaller thickness of the PEI layer than the size of the WO$_3$ NPs. Similar trend is also observed for the hybrid films (Fig. 4.4C) because the thickness of a PEI/PEDOT:PSS layer is also much smaller than the size of WO$_3$ NPs. The surface morphology of the hybrid films is also observed by SEM and the typical images are shown in Fig. 4.5. Clearly, the WO$_3$ NPs are uniformly distributed on the surface of the films. The lateral size of the disk-like WO$_3$ NPs is around 50 nm (Appendix, Fig. A.1), which is indeed much larger than the thickness of a PEI/PEDOT:PSS layer (less than 10 nm as indicated by Fig. 4.3). The orientation of the NPs with
respect to the surface is fairly random. Similar to that observed by AFM, more WO$_3$ NPs are observed in the ten-layer hybrid film in comparison with that in the one-layer hybrid film, again suggesting the interdigitated arrangement of the WO$_3$ NPs in the thicker hybrid films. Thus, the AFM and SEM results corroborate each other, indicating that the WO$_3$ NPs are well incorporated and homogenously distributed in the polymer layers.

Figure 4.4 AFM images of one (a), two (b) and three (c) layers of (A) PEDOT:PSS (B) WO$_3$-NP, and (C) hybrid films on Si substrates.
XPS and EDX analysis were performed to determine the chemical composition of the LBL assembled films. Although both techniques can be used to quantitatively measure elemental compositions of materials, XPS provides the information for material surfaces of around top 10 nm, whereas EDX can be used to characterize the compositions of thicker films of several micrometers. Thus, XPS is suitable for analyzing thin films, while EDX is more reliable for thick films. In this work, XPS was used to characterize the compositions of the thin films with only few layers. Fig. 4.6a shows the trends of the atomic percentage of tungsten (W at%) in the WO$_3$-NP and hybrid films of 1-3 layers measured by XPS. The W at% increases with increasing the number of layers for both the WO$_3$-NP and hybrid films, which is in agreement with the AFM results (Fig. 4.4B). As the number of layers increases, the substrate surface is gradually covered by WO$_3$ NPs, which leads to limited increase in adsorption of WO$_3$ NPs in the two-layer and three-layer WO$_3$-NP films. The surface of the PEDOT:PSS films is however rougher (Fig. 4.4A) and hence the surface area is larger, resulting in enhanced adsorption of WO$_3$ NPs, i.e., higher W at% of the hybrid films than that of the corresponding WO$_3$-NP films (Fig. 4.6a). The XPS spectra of one-, two- and three-layer PEDOT:PSS, WO$_3$-NP and hybrid films are provided in Appendix, Fig. A.2 to illustrate the adsorption process of PEDOT:PSS and WO$_3$ NPs. For thin layers (one-, two-, and three-layer films as shown in Fig 4.6b), the intensities of the characteristic peaks of S and W
gradually increase as the number of layers increases, and meanwhile the intensity of the peak from the ITO substrate gradually decreases. The surface atomic ratio of S to W for the hybrid films of 1-3 layers is all around 0.05 (Fig. 4.6b and Table A.1a, Appendix), indicating that the composition of hybrid film is consistent as increasing no. of layers. Therefore, the LBL process can produce homogenous hybrid film in first few layers.

**Figure 4.6** (a) Atomic concentration of W in WO$_3$-NP single component and hybrid films as a function of No. of layers. (b) Atomic concentration and ratio of elements (blue squares) VS No. of hybrid layers. Results derived from XPS measurement.

As the thickness of the sample film increases, the peak from ITO will disappear in XPS scan. Then, the chemical compositions were further characterized by EDX, which is suitable for element analysis of thick films. As shown in Fig. 4.7, initially both the atomic ratios of S to In and W to In increase stably with increasing the number of layers. The atomic ratio of S/W increases gradually as the number of layers increases but it is smaller than 1 for the hybrid films with up to 20 layers (Table A.1b, Appendix). It is worth noting that the atomic ratio of S/W obtained by EDX is significantly larger than that measured by XPS because the EDX results reflect the bulk compositions while XPS gives only the surface compositions of the films. Nevertheless, it demonstrates that both WO$_3$ NPs and PEDOT:PSS can be well incorporated into the hybrid films in the first 10 layers. For even thicker hybrid films, such as a 20-layer hybrid film, the atomic ratio of S/W becomes substantially larger,
suggested that WO$_3$-NPs are more difficult to be adsorbed onto the films than polymers once the films are covered with a layer of closely spaced WO$_3$-NPs. Therefore, the hybrid films with 10 layers or less have relative uniform compositions and so they were used for electrochemical and electrochromic characterization.

![Figure 4.7](image)

**Figure 4.7** EDX measurements shows the atomic ratio between elements as a function of No. of hybrid layers. Blue squares indicate the atomic ratio between S and W to the blue axis on right.

### 4.3.3  Electrochemical Behaviors of Sample Films

To understand the electrochemical behavior of the multilayer films, cyclic voltammetry (CV) was conducted using a standard three-electrode system. The CV curves of the one-, two-, and three-layer PEDOT:PSS, WO$_3$-NP and hybrid films at a scan rate of 25 mV/s are presented in Fig. 4.8(a-c). For all the three types of films, the area enclosed by the CV curves increases as increasing the number of layers, which verifies the successful LBL deposition of the components.[8] Figs. 4.8a and 4.8b show that the PEDOT:PSS films exhibit a significant oxidation peak at +0.05 V and a reduction peak at −0.70 V, while the WO$_3$-NP films show a broad oxidation peak at around −0.72 V. For the one-, two- and three-layer hybrid films, the PEDOT:PSS redox peaks are covered by WO$_3$ peaks in the potential range from +1.0 to −1.0 V (Fig. 4.8c). The reduction peak of PEDOT:PSS can only be observed at a slower scan rate of 10 mV/s, as...
shown in the inset of Fig. 4.8c. For the hybrid films with more layers, a clear reduction peak can be observed at −0.76 V, and a strong oxidation peak appears at around −0.45 V (Fig. 4.8d). The redox peaks shift may be caused by the chemical and electrostatic interactions between the components.[12, 13] It also suggests that both components contribute to the redox reactions in the hybrid films.

![Cyclic voltammetry graphs](image)

**Figure 4.8** Cyclic voltammetry of one, two, and three layers of (a) polymers (P1, P2 and P3), (b) WO$_3$-NP (W1, W2 and W3), (c) hybrid (H1, H2 and H3), and (d) six, eight, and ten layers of hybrid (H6, H8 and H10) films deposited on ITO in 1 M LiClO$_4$/PC at a scan rate of 25 mV/s (or 10 mV/s in inserted graph in (c)).

To probe the charge transfer process between the active components in the hybrid films, SECM technique was used to study the surface conductivity change of the films *in-situ* as a function of applied potential. The scanning probe is a microelectrode, which is held or moves in a solution in the vicinity of a substrate. The substrate conductivity can affect the faradic feedback steady-state current through the microelectrode tip when the tip is moving...
towards the substrate surface. A standard three-electrode electrochemical cell is employed with the film bathing underneath the solution. FcMeOH is dissolved in the solution as the redox mediator. In bulk solution, the oxidation process of the Red species occurs at the microelectrode tip with applied potential, while a reduction process occurs at the counter electrode. When the microelectrode tip approaches a conductive substrate, the species electrochemically generated at the tip diffuse to the surface and are regenerated, leading to a positive feedback, i.e., an increase in tip steady-state current with decreasing distance between microelectrode tip and substrate surface. On the other hand, when the microelectrode tip approaches an insulating substrate, the redox reaction is hindered since the substrate block the diffusion of the redox species. Thus, a negative feedback, i.e., a decrease in tip current with decreasing distance between microelectrode tip and substrate surface, can be observed. [14-16]

In this work, approach curves are recorded for the films coated on both conductive (ITO) and non-conductive (glass) substrates when the microelectrode tip, under a constant potential of +300 mV, approaches the sample surfaces. The distance between the microelectrode tip and sample surfaces is determined by fitting the experimental data to the theoretical feedback approach curves (Appendix, Fig. A.3).[14, 17, 18] The normalized feedback curves are presented in Fig. 4.9. Positive feedbacks are obtained when microelectrode approaches the PEDOT:PSS (1 S/cm) films coated on ITO surface at different substrate potentials (−300, −200, −100 and 0 mV) (Fig. 4.9a). The WO$_3$-NP films coated on ITO surface exhibit, however, typical positive feedback only at substrate potential of −300 mV, and typical negative feedback is recorded at −100 and 0 mV. Obviously, the WO$_3$-NP films experience a conductive-to-nonconductive transition, and the transition completes at −100 mV (Fig. 4.9b), at which M$_x$WO$_3$ is fully oxidized to WO$_3$ based on the CV studies (Fig. 4.8b). The results are consistent with the literature, showing that WO$_3$ is only conductive in its reduced state (M$_x$WO$_3$) (>10$^3$ S/cm) with sufficient negative charges injected, while it becomes non-conductive in
the completely oxidized state ($<10^{-8}$ S/cm). On the other hand, the hybrid film coated on ITO surface exhibits positive feedbacks at different potentials (-300, -200, -100 and 0 mV), suggesting that the hybrid film is conductive over the tested potential range (Fig. 4.9c). It can also be clearly seen in Fig. 4.9d that the conductivity of the hybrid film is not affected by WO$_3$ NPs, since positive feedback is observed on the 5-layer hybrid film coated on glass substrate.

![Figure 4.9 SECM normalized approach curves recorded above 5 layers of (a) PEDOT:PSS, (b) WO$_3$-NP, and (c) hybrid films coated on ITO glasses at potentials of -300, -200, -100, and 0 mV (d) SECM normalized approach curves recorded above glass, 5 layers of PEDOT:PSS, WO$_3$-NP and hybrid film coated on glass substrates. The mediator is 0.1 mM FcMeOH in 10 mM KCl aqueous solution.]

To further study the conductivity change of the films at various potentials, a SECM feedback mode was applied to the films coated on ITO substrates. The general idea is illustrated in Fig. 4.10a. Briefly, the microelectrode tip is close to the sample coated on ITO glass, where the substrate is under potential scanning from −0.8 to 0 V. At the same time, the current through the microelectrode tip,
under the same constant potential of +300 mV, is monitored. The tip current is normalized to the current on the microelectrode tip when the substrate potential is −0.8 V. When the microelectrode is moving towards the sample surfaces, the reaction on the substrate surfaces can be reflected by the current through the microelectrode tip.

**Figure 4.10** (a) Schematic diagram showing the redox reaction occurred between microelectrode tip and substrate surface. (b) Plot of normalized microelectrode tip current recorded above ITO, 5 layers of PEDOT:PSS, WO$_3$-NP and hybrid film coated on ITO glasses as substrate potential cycled from 0 to -0.8 V at a scan rate of 5 mV/s. The mediator is 0.1 mM FcMeOH in 10 mM KCl aqueous solution. The tip current is normalized to the current on the UME tip when the substrate potential is -0.8 V, (The plateau values of all four curves at right end are normalized to 1.)

As mentioned, the substrate conductivity can affect substantially the current measured at the tip because of the conductivity effect on the kinetics of electron transfer occurring at the surface. Fig. 4.10b shows that in the potential range applied to the substrate, the normalized microelectrode tip current for the ITO with 5 layers of PEDOT:PSS maintains at the same level, indicating that the conductivity of these films does not change in this potential range. By contrast, the WO$_3$-NP film experiences a conductive-to-nonconductive transition in a potential range of −0.25 to 0 V, where the tip current drops sharply. The half-cell reduction reaction is gradually blocked by the substrate surface because it becomes more insulating. However, the hybrid film exhibits no
significant conductivity change in this potential range, indicating that the PEDOT:PSS layers may form a conductive network to enhance the conductivity of the hybrid film. Thus, the result agrees with the approach curves that the conductive-to-nonconductive transition has been eliminated in the potential range of −0.25 to 0 V in the hybrid film, since the PEDOT:PSS may enhance the overall conductivity.

4.3.4 Electrochromic Properties of Sample Films

To compare the electrochromic properties of the hybrid films with those of their PEDOT:PSS and WO$_3$-NP counterparts, spectro-electrochemical characterization were conducted on 10-layer PEDOT:PSS and WO$_3$-NP films, and 5-layer hybrid films. In this case, all samples contain the same number of electrochromic layers, whereas they have slightly different thickness, i.e. 55, 50, and 60 nm for the PEDOT:PSS, WO$_3$-NP and hybrid films, respectively; noting that the surface of the WO$_3$-NP film is very rough so that the thickness is only a rough estimation.

The transmittance of WO$_3$-NPs, PEDOT:PSS and hybrid thin films were recorded at constant potentials of +0.8, 0 and -1.0 V, respectively. The optical transmittances against the wavelength of all three films are shown in Figs. 4.11a-c. All the three films exhibit maximum transmittance differences ($\Delta T$) between the bleached and colored states at wavelength of around 633 nm, which is defined as optical contrast. With comparable thickness of each film, the optical contrast of the hybrid film ($\Delta T$=20%) is significantly higher than that of WO$_3$-NP ($\Delta T$=7.3%) and PEDOT:PSS ($\Delta T$=9.6%) films. Dynamic transmittance was also recorded under oscillating potentials stepped between +0.8 V and -1.0 V for the three films, respectively. The results are shown in Fig. 4.11d. The dynamic contrasts of the sample films are consistent with the optical contrasts measured in Fig. 4.11(a-c). The switching time for WO$_3$-NP, PEDOT:PSS and hybrid thin films is 6, 20, and 8 seconds, respectively. The coloration efficiency of the films, which is defined as the optical absorbance
change divided by the corresponding injected charges per unit area, were derived from the dynamic transmittance plot in Fig. 4.11d.[5, 19] As illustrated in Fig. 4.11e, the coloration efficiency of the hybrid film is dramatically improved to 117.7 cm$^2$/C, compared with 58.6 cm$^2$/C and 86.4 cm$^2$/C for WO$_3$-NP and PEDOT:PSS films respectively. It indicates that more electrochromic materials are activated per unit area, considering similar thickness of the three films. The electrochromic property data, including optical contrast, switching time and coloration efficiency, are summarized in Table A.2 (Appendix). In addition, to investigate electrochromic reversibility of the hybrid films, the optical transmittances of the 5-bilayer hybrid film and corresponding WO$_3$-NP and PEDOT:PSS reference sample films were recorded for 1000 reversible cycles (Fig. 4.11f). The results show that the hybrid thin film can maintain 75% of its original optical contrast after 1000 repeating cycles, indicating its reasonably good electrochromic stability.

![Graphs showing transmittance vs wavelength](image1.png)
Figure 4.11 UV-Vis spectrum of 10 layers of (a) WO$_3$-NP, (b) PEDOT:PSS, and 5 layers of (c) Hybrid thin films under different potentials of +0.8, 0, and -1.0 V. (d) Dynamic optical transmittance curves of 10 layers of (I) WO$_3$-NP, (II) PEDOT:PSS, and 5 layers of (III) Hybrid thin films obtained under square wave potential oscillating between +0.8 V and -1.0 V at a time step of 50 (I & II) and 40 (III) seconds respectively. The horizontal axis on the top shows the time scale for hybrid film. (e) Coloration efficiency of 10 layers of (I) WO$_3$-NP, (II) PEDOT:PSS, and 5 layers of (III) Hybrid (blue axis on top and right) thin films. (f) Optical transmittance between bleached (up triangle) and colored (down triangle) states of 10 layers of (I) WO$_3$-NP, (II) PEDOT:PSS, and 5 layers of (III) Hybrid thin films measured under square wave potentials oscillating between +0.8 and -1.0 V for 1000 cycles. The transmittances were measured at wavelength of 633 nm.

The significant enhancement of electrochromic properties may be attributed to two main factors: (1) effective charge transfer process between the two active components; and (2) relatively high electrical conductivity of PEDOT:PSS and WO$_3$ NPs at oxidized and reduced states, respectively. In the PEDOT:PSS film, the PEI layers may work as interlayer barrier for electron hopping between PEDOT:PSS layers [20], leading to inefficient charge transfer and hence lower coloration efficiency and slow switching speed than that of neat PEDOT:PSS films. However, in the WO$_3$-NP film, the very rough surface created by randomly oriented disk-like WO$_3$ NPs and their interdigitated arrangement hinder the formation of a continuous PEI barrier layer between the
WO$_3$ NPs, giving similar coloration efficiency as electrodeposited WO$_3$-NP film.[11] Similarly, WO$_3$ NPs in the hybrid film may effectively interact with PEDOT:PSS, and the PEI layers cannot hinder the charge transfer between the electrochromic components. As a result, the hybrid film exhibits an efficient charge transfer between active electrochromic components and a relatively fast switching speed. Moreover, the coloration efficiency is also enhanced compared with the electrodeposited hybrid films reported in our previous publication (81.8 cm$^2$/C), which has similar components and composition.[2] The enhancement can be attributed to the interdigitated structure of the LBL hybrid film, providing large interfacial area and assisting the charge transfer process. In addition, as verified by SECM studies, the conductivity of the hybrid film is not affected by the applied potential. It suggests that the PEDOT:PSS may facilitate the charge transfer among WO$_3$ NPs at fully oxidized state. As a result, the hybrid film may possess more accessible WO$_3$ units during redox switching. Therefore, compared with PEDOT:PSS and WO$_3$-NP films, the hybrid film exhibits enhanced optical contrast and remarkably high coloration efficiency.

4.4 Conclusions

The hybrid electrochromic films consisting of WO$_3$ NPs, PEDOT:PSS and PEI have been successfully prepared by LBL assembly. The WO$_3$ NPs are homogeneously distributed in the hybrid system, and form an interdigitated structure. Compared with the PEDOT:PSS and WO$_3$-NP films, the hybrid films exhibit significantly improved electrochromic properties in terms of optical contrast and coloration efficiency. Especially, the coloration efficiency is remarkably improved to 117.7 cm$^2$/C. The enhancement in electrochromic properties may be attributed to the efficient charge transfer between the active components and high conductivity of the hybrid film during the switching process. The underlying mechanism is verified by SECM studies. According to the literature, the WO$_3$ exhibits metallic conductivity at reduced states and acts
as insulator in its fully oxidized states. In this work, the conductivity change process is directly presented from the SECM results. A significant conductive-to-nonconductive transition is observed for the WO$_3$-NP films in potential range of 0 to -0.25 V. However, it is not seen for the PEDOT:PSS and hybrid films. This indicates that PEDOT:PSS facilitates the charge transfer among fully oxidized WO$_3$ NPs in the hybrid system, providing more accessible active units during redox switching.

References

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Chapter 5*


In this chapter, the synthesis, characterization, and EC properties of hybrid films composed of PEDOT:PSS and WO$_3$ fabricated via one-pot electrodeposition will be presented. The hybrid films were deposited on indium tin oxide (ITO) glasses from one-pot solution using square-wave galvanostatic method. The morphology of the hybrid films could be easily manipulated to optimize their EC properties by adjusting deposition conditions. In the hybrids, both components can be simultaneously switched to colored or bleached states. The optical contrast of the hybrid film is higher than that of PEDOT:PSS or WO$_3$ films of the same thickness. Moreover, the stability of the hybrid film is significantly enhanced. The enhancement may be attributed to the favorable interactions between the two components, as well as the large interfacial area created using this unique one-pot sequential deposition method.

5.1 Introduction

The work presented in chapter 4 demonstrated that hybridization of WO₃ and PEDOT:PSS may lead to enhanced EC properties, especially the electrochemical stability.[1] According to literature, various methods have been applied to synthesize TMO/conjugated polymer hybrid electrochromic materials with well controlled structure and morphology, especially the interfacial area between the two components. For example, Xiong et al. reported that in electrochromic polyaniline (PANI)/titanium oxide (TiO₂) hybrids with interfacial covalent bonds, significant electron donor (PANI)-acceptor (TiO₂) interactions could cause a reduction in HOMO energy that enables PANI be oxidized at a lower potential and hence leads to greatly improved electrochemical stability.[2] More recently, a hybrid system based on PANI/tungsten trioxide (WO₃) was reported by J. Zhang et al.[3] The hybrids exhibit both long cycle life and fast switching speed as the interactions between PANI and WO₃ help to slow down surface-defect-induced degradation of amorphous WO₃ and at the same time depress over-oxidation of PANI.[3] In the aforementioned hybrid systems, the organic and inorganic components are, however, anodically and cathodically colouring materials, respectively. Thus, the optical contrast of such hybrids is mainly contributed by switching of one component to different redox states, whereas the redox reactions of the other component have to be eliminated by controlling potentials in order to avoid their negative effect on optical contrast, i.e., the second component does not act as an electrochromic material effectively.

The hybrid systems based on PEDOT:PSS and WO₃, where both components are cathodically colouring materials, exhibits enhanced optical contrast compared with single component films.[1] As reported in last chapter, the hybrid systems composed of these two components have been prepared and studied by several research groups, including ourselves.[1, 4-6] The EC properties of hybrid films obtained in last work are improved compared with
WO₃-NP and PEDOT:PSS films, but still can be further enhanced via removing the nonconductive PEI layers. And it remained a challenge to establish a simple synthesis method that allows tailoring the hybrid structures at nanoscale so as to optimize electrochromic properties of the hybrids.

In this chapter, a novel multilayer PEDOT:PSS/WO₃ hybrid system prepared by one-pot sequential electrochemical deposition is reported. This facile method allows us to control the morphology through adjusting deposition time for each layer, and hence the interfacial area and resultant electrochromic properties of the hybrids can be easily optimized. Herein, it is demonstrated that by optimizing the morphology, both components in the hybrids can be simultaneously switched to colored or bleached state, giving rise to high optical contrast, while the cycle life of the hybrid greatly benefits from the interfacial interactions and large interfacial area created using such an one-pot sequential deposition method.

5.2 Experimental Methods

5.2.1 Materials

All chemicals used in this work were purchased from Sigma-Aldrich and used as received. Unless specified, all experiments were conducted under ambient conditions and all solutions were prepared using de-ionized (DI) water. All electrodeposition/electropolymerization experiments were performed using a three-electrode system. Silicon dioxide-passivated, indium tin oxide-coated glass (ITO glass) with sheet resistance $R_s = 5\text{-}15\ \Omega$ and dimensions of $7 \times 50 \times 0.7\ \text{mm}$ (Delta Technologies, USA) was used as the working electrode. Before any deposition, the ITO glass was sonicated in acetone, iso-propanol, ethanol and DI water for 5 minutes, respectively, and then blow-dried with nitrogen gas. A platinum (Pt) sheet with the dimension of $1\times2\ \text{cm}$ was used as the counter electrode. The reference electrode used was silver/silver chloride (Ag/AgCl in sat. KCl).
5.2.2 Sample Preparation

Appropriate solutions were first prepared for electrodeposition of PEDOT:PSS, WO₃ and PEDOT:PSS/WO₃ hybrid thin films on ITO glass substrates, respectively. For PEDOT:PSS film, a solution containing 0.02 M EDOT and a certain amount of PSS (weight ratio EDOT:PSS = 1:1.6) was electropolymerized at the current density of +0.5 mA/cm² for 50 seconds.[7] For WO₃ synthesis, 0.9 g tungsten (W) powder was dissolved in 30 ml of a 30 wt.% H₂O₂ aqueous solution and the solution was refluxed at 60 °C until W powders were completely oxidized, giving a peroxotungstic acid (PTA) solution.[8, 9] Excess H₂O₂ in the solution was removed by Pt black, and then 70 ml DI water was added to dilute the solution to achieve a PTA concentration of 0.05 M. The WO₃ films were obtained by applying current density of -0.6 mA/cm² to the working electrode for about 500 s. To prepare the hybrid thin films, EDOT and PSS were added into the PTA solution to achieve a solution with 0.02 M EDOT:PSS and 0.05 M PTA. The pH of the resultant solution is around 1.5-2.0. The hybrid thin films were then deposited using galvanostatic square wave method. For example, in a typical process, a positive current density of +0.5 mA/cm² and negative current density of -0.6 mA/cm² were alternately applied for 10 s and 60 s, respectively, to the working electrode for 5 cycles. The deposition area of all films is about 2 cm². The obtained films were rinsed with DI water and blow dried with nitrogen gas.

5.2.3 Characterization

The film thickness was measured using an Alpha-step 500 profilometer. A transmission electron microscope (TEM JEOL 2100F) equipped with energy dispersive X-ray spectrometer (EDX) system was used to examine the cross-section of electrochromic films. A field-effect scanning electron microscope (FESEM 6340F) was employed to examine surface morphology of the films. The chemical structure and compositions of the thin films were
characterized using Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum GX), X-ray photoelectron spectroscopy (XPS, Theta-probe, Thermo Scientific) and Raman spectroscopy (Witec confocal Raman spectrometer with excitation light of 488 nm). The FTIR scan was conducted on a diamond attenuated total reflection (ATR) unit (Graseby Specac ATR10500) from 4000 to 600 cm\(^{-1}\), with 16 scans collected for signal averaging. To compensate for the surface-charging effects in XPS scans, the binding energy level of C1s was set at 285 eV for further data analysis. An X-ray diffraction spectrometer (Shimadzu) with Cu Kα radiation was used to identify crystalline structure of WO\(_3\) and hybrid thin films.

Cyclic voltammetry (CV) was measured using a multi-channel AC/DC electrochemical impedance test station (Solartron Model 1470E) in 0.1 M lithium perchlorate (LiClO\(_4\))/propylene carbonate (PC) solution. It was performed at a scan rate of 5, 15, 25, 50, and 100 mV/s within a potential range from -1.0 to +1.0 V. The spectro-electrochemical properties of the films were measured using Solartron Model 1470E and a UV-Vis-NIR spectrophotometer (Shimadzu UV 3600). The UV-Vis spectra of the thin films were recorded in the wavelength range from 300 to 800 nm at potentials of -1.0, 0, and 0.8 V. For each thin film, dynamic optical transmittance was also recorded at wavelength of interest under a square wave potential oscillating between +0.8 and -1.0 V at a time step of 50 s. The coloration efficiencies and switching times of the electrochromic thin films were measured according to the methods discussed in chapter 3.

### 5.3 Results and Discussions

#### 5.3.1 One-pot Sequential Electrodeposition of Sample Films

In this work, a constant-current-density electrodeposition method was used for one-pot sequential deposition of multilayer WO\(_3\) and PEDOT:PSS thin films. The electropolymerization of EDOT:PSS occurred at the positive current
density,[7] while the electrodeposition of WO$_3$ was driven by electroreduction at negative potentials.[8-10] For hybrid films, the two components were co-deposited from the same aqueous solution. First, EDOT:PSS underwent oxidation electrochemical polymerization to form a PEDOT:PSS layer on ITO glass under positive current, and then PTA was reduced under negative current to form a WO$_3$ layer on top of the PEDOT:PSS layer; the reduction process may be accompanied by dehydration of the WO$_3$ layer as the reaction medium was highly acidic. The two layers together are defined as a bilayer in this thesis. The process was repeated several times to achieve a multilayer hybrid thin film (Fig. 5.1).

![Diagram showing the synthesis process for the multilayer PEDOT:PSS/WO$_3$ hybrid thin films.]

A: Positive current density +0.5 mAcms$^{-2}$
B: Negative current density -0.6 mAcms$^{-2}$

**Figure 5.1** Synthesis process for the multilayer PEDOT:PSS/WO$_3$ hybrid thin films.

Both neat WO$_3$ and PEDOT:PSS films show approximate linear relationships between the film thickness and deposition time (Fig. 5.2a and 5.2b), while the electrodeposition of WO$_3$ is much slower than the electropolymerization of EDOT. For the deposition of PEDOT:PSS/WO$_3$, the growth curve is also approximately linear (Fig. 5.2c). In this work, unless otherwise specified, the hybrid films used for property characterization all have
5 bilayers with an overall thickness of about 200 nm. WO$_3$ and PEDOT:PSS thin films of the same thickness were also fabricated as reference samples. Pictures of the as-deposited PEDOT:PSS, WO$_3$ and hybrid thin films on ITO glass are shown in Fig. 5.2d.

![Figure 5.2](image)

**Figure 5.2** Thickness of (a) WO$_3$, (b) PEDOT:PSS, (c) hybrid films as a function of total deposition time. (d) Pictures of ITO glasses and the electrochromic thin films of same thickness. The three films were all at their oxidized states, blow dried after electrodeposition.

### 5.3.2 Morphologies of Sample Films

To directly demonstrate the capability of this one-pot method for fabrication of multilayer PEDOT:PSS/WO$_3$ hybrid thin films, a TEM image of a hybrid thin film with relatively thick WO$_3$ and PEDOT:PSS layers is shown in Fig. 5.3. This hybrid thin film was deposited by applying 30 s of positive current density and 300 s of negative current density repeatedly. It can be seen that there are alternating dark and light layers. Within each bilayer, the dark
region should be WO$_3$ or a WO$_3$-rich region owing to the high atomic mass of W. It can also be observed that when a WO$_3$ layer is added onto a PEDOT:PSS layer, there is no clear boundary between the two layers, i.e., the dark shade increases gradually. The likely reason for this is that upon applying the negative potential, the PEDOT:PSS layer may be reduced first. At the same time, the PTA ions may be attracted by the PSS anions in the partially reduced PEDOT:PSS to diffuse into PEDOT:PSS. Since the PEDOT:PSS layer is conductive, it may act as a porous electrode for the deposition of WO$_3$ inside the PEDOT:PSS layer, especially in the near surface region. Only after PEDOT:PSS is fully reduced or the PTA ions cannot diffuse into the PEDOT:SS layer anymore, would a neat WO$_3$ layer forms. And it may be reduced to M$_x$WO$_3$ simultaneously with insertion of cations (M$^{x+}$). On the other hand, when it is switched to the positive potential, M$_x$WO$_3$ would be oxidized to WO$_3$ and become more insulating. Hence, the oxidization of EDOT would not occur in the partially oxidized M$_x$WO$_3$ layer significantly because the very low conductivity inside, whereas the electropolymerization of EDOT:PSS would still occur on the surface of the WO$_3$ layer to some extent and once some conductive PEDOT:PSS species are formed on the surface, a layer of PEDOT:PSS would quickly form. Thus a sharp boundary appears only when a PEDOT:PSS layer is added onto a WO$_3$ layer.
A unique advantage of this one-pot multilayer deposition method is that the morphology of the hybrid thin films can be facilely manipulated by controlling the deposition time for each layer. By shortening deposition times, the layer thickness of both PEDOT:PSS and WO₃ could be reduced substantially to cause PEDOT:PSS and WO₃ interpenetrating each other, resulting in “layerless” morphology. The morphology of a “layerless” hybrid film fabricated by applying alternating positive current for 10 s and negative current for 60 s were examined using FESEM to compare with those of neat WO₃ and PEDOT:PSS films. As shown in Fig. 5.4a and 5.4b, both neat WO₃ and PEDOT:PSS films have relatively compact and smooth surfaces. However, when WO₃ is deposited on PEDOT:PSS (for 60 s only), the PEDOT:PSS/WO₃ film exhibits a loosely packed surface morphology (Fig. 5.4c); the discrete nanoparticles on surface are likely to be WO₃ particles with PEDOT:PSS underneath. When PEDOT:PSS is deposited on PEDOT:PSS/WO₃ (for 10 s only), the PEDOT:PSS/WO₃/PEDOT:PSS film shows a very uneven surface morphology (Fig. 5.4d), implying that the surface may not be fully covered by a PEDOT:PSS layer. By repeating such short-time depositions, a “layerless” morphology would be formed. In later sections, the electrochemical and electrochromic properties presented are all based on the hybrid film with such “layerless” morphology as it provides much larger interfacial area, benefiting electrochromic properties.
Figure 5.4 FESEM micrographs showing surface morphologies of (a) neat WO₃, (b) neat PEDOT:PSS, (c) PEDOT:PSS/WO₃ and (d) PEDOT:PSS/WO₃/PEDOT:PSS films of the hybrid films.

5.3.3 Structure of Sample Films

Chemical structures of the hybrid films are verified by ATR-FTIR spectroscopy. Fig. 5.5a shows the spectrum of the hybrid film with 5 bilayers in comparison with that of WO₃ and PEDOT:PSS reference films. From the WO₃ reference sample, two strong bands at 969 and 916 cm⁻¹ are observed, which can be attributed to asymmetric stretching vibrations of W=O double bonds of an amorphous WO₃ network.[3, 11] While, the PEDOT:PSS reference sample exhibits bands at 1513 and 1310 cm⁻¹, which are attributed to the stretching of C=C and C-C bonds in the thiophene rings. The vibration of C-S bond can also be observed at 685 cm⁻¹ and stretching of ethylenedioxy group at 1083 cm⁻¹.[12, 13] The hybrid film clearly exhibits the characteristic bands of both WO₃ and PEDOT:PSS, proving the existence of both components. To further confirm the
multilayer structure, ATR-FTIR measurements were also carried out on the hybrid films with different number of layers, namely PEDOT:PSS, PEDOT:PSS/WO$_3$ (WO$_3$ on top), PEDOT:PSS/WO$_3$/PEDOT:PSS (PEDOT:PSS on top), and PEDOT:PSS/WO$_3$/PEDOT:PSS/WO$_3$ (WO$_3$ on top), respectively (Fig. 5.5b). In the hybrid thin films of PEDOT:PSS and PEDOT:PSS/WO$_3$/PEDOT:PSS, indeed the characteristic bands of PEDOT:PSS can be clearly observed, whereas the bands corresponding to WO$_3$ are relatively weak. By contrast, the spectra of the PEDOT:PSS/WO$_3$ and PEDOT:PSS/WO$_3$/PEDOT:PSS/WO$_3$ thin films exhibit relatively strong characteristic bands of both PEDOT:PSS and WO$_3$, implying that when switched to the negative current, a significant portion of WO$_3$ is formed inside of the PEDOT:PSS layer. This is consistent with the TEM result shown in previous section (Fig. 5.3).

To further confirm the structure of the electrodeposited WO$_3$ layer, Raman spectroscopy and X-ray diffraction studies were conducted. Fig. 5.5c shows that the electrodeposited WO$_3$ film has two distinct Raman bands at 780 and 945 cm$^{-1}$. The band at around 780 cm$^{-1}$ can be attributed to W$^{VI}$-O bonds, while the one located at 945 cm$^{-1}$ can be assigned to the stretching of the terminal oxygen atoms in W$^{VI}$=O on surface of the thin films.[14, 15] In addition to the two strong Raman bands, a relatively weak Raman band is also noticeable at 620 cm$^{-1}$, which corresponds to the symmetric stretching mode of W$^{VI}$(O$_2$), indicating that the reduction of peroxotungstates to WO$_3$ is not fully completed in the deposition process.[16] Moreover, the X-ray diffraction pattern shown in (Fig. A.4, Appendix) confirms that the electrodeposited WO$_3$ and hybrid thin films are all amorphous in nature.
Figure 5.5 ATR-FTIR spectra of (a) WO$_3$, PEDOT:PSS and the 5-bilayer hybrid thin film, and (b) the hybrid thin films with different number of layers: PEDOT:PSS (I), PEDOT:PSS/WO$_3$ (II), PEDOT:PSS/WO$_3$/PEDOT:PSS (III), PEDOT:PSS/WO$_3$/PEDOT:PSS/WO$_3$ (IV). (c) Raman spectra of ITO glass and the electrodeposited WO$_3$ thin film.

XPS was used to further confirm the chemical structures of the hybrid films and probe interfacial interactions. Fig. 5.6 shows XPS spectra for W4f and S2p peaks of the hybrid thin films with the corresponding spectra of PEDOT:PSS and WO$_3$ films as references. The full XPS survey of the hybrid thin films with different numbers of layers is provided in Appendix as Fig. A.5. For the neat WO$_3$ film, the two characteristic peaks at binding energy of 37.9 eV (W4f$_{7/2}$) and 35.7 eV (W4f$_{5/2}$) correspond to oxidation state of W$^{VI}$, indicating that W is at its highest oxidation state. The single-layer PEDOT:PSS hybrid thin film exhibits no characteristic W4f peaks. When a layer of WO$_3$ is deposited on top of the PEDOT:PSS layer, the PEDOT:PSS/WO$_3$ hybrid thin
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Film shows two characteristic peaks at 38.2 eV (W4f₁/₂) and 36.0 eV (W4f₃/₂) respectively, which are 0.3 eV higher than that of the neat WO₃ film (Fig. 5.6a).

![XPS spectra](image)

Figure 5.6 XPS spectra in (a) W4f and (b) S2p region for neat PEDOT:PSS (I), PEDOT:PSS/WO₃ (II), PEDOT:PSS/WO₃/PEDOT:PSS (III), PEDOT:PSS/WO₃/PEDOT:PSS/WO₃ (IV) and WO₃ films.

The up-shift in binding energy is likely to be associated with the presence of a large amount of defects, which are mainly caused by incomplete reduction of peroxotungstanes and –OH groups on surface.[17] It is striking to see that in the spectrum of the PEDOT:PSS/WO₃/PEDOT:PSS hybrid film that has PEDOT:PSS as the top layer, although the intensities of the W4f peaks become lower owing to the coverage by PEDOT:PSS, the binding energies of the W4f peaks shift back to the positions for neat WO₃. This implies that driven by the anodic potential, EDOT molecules may be able to diffuse into the defect sites to form PEDOT:PSS. The PEDOT may interact with the defects in the WO₃ layer to reduce the electron withdrawing effect of the peroxide groups. Fig. 5.6b shows that the neat PEDOT:PSS thin film exhibits characteristic S2p peaks for two types of distinctly different sulphur (S) atoms; the broad peak with higher binding energy can be attributed to the overlap of S2p₃/₂ and S2p₁/₂ peaks of the S atoms in PSS, while the duplet at lower binding energy is from the S atoms in PEDOT.[12, 18] In comparison with neat PEDOT:PSS, the hybrid films all exhibit slightly lower binding energies for the S2p peaks of PEDOT, implying that there may be some interactions between WO₃ defect sites and PEDOT.
Such interactions may play important roles in influencing electrochromic properties of the hybrids, which will be discussed in following sections.

5.3.4 Electrochemical Behaviour of Sample Films

To understand the electrochemical behaviour of the hybrid films, three-electrode CV tests were conducted for WO$_3$, PEDOT:PSS and 5 bilayer hybrid thin films in a 0.1 M LiClO$_4$/PC solution, and the CV curves at various scan rates are shown in Fig. 5.7. In the scan rate range of 5 to 100 mV/s, WO$_3$ shows an obvious oxidation peak (Fig. 5.7a), while PEDOT:PSS shows a couple of redox peaks (Fig. 5.7b). The shape of the CV curves of the hybrid film in general is more similar to that of WO$_3$ at relatively high scan rates, while distinct PEDOT:PSS redox peaks can be observed at relatively low scan rates (Fig. 5.7c). It suggests that both components in the hybrid film are electrochemically active. Thus, both components can be switched simultaneously to colored/bleached state under negative/positive potentials.

The area enclosed by the CV curves quantifies the inserted and extracted charges. Comparing the CV curves of the three films at the scan rate of 100 mV/s, the hybrid film has the largest enclosed area, suggesting that more active units in the hybrid can be effectively oxidized/reduced probably because the PEDOT:PSS layer facilitate charge transfer,[19] making charge insertion/extraction into/from WO$_3$ easier. Indeed when the peak current densities for the anodic and cathodic peaks of the hybrid are plotted against the square root of the scan rate ($\nu^{1/2}$), resulting in a nonlinear relationship (Fig. 5.7d).[19] This signifies that both the oxidation and reduction in the hybrid are non-diffusion-controlled processes in the studied scan rate range.[20, 21]
**Figure 5.7** Cyclic voltammetry plots of (a) WO$_3$, (b) PEDOT:PSS, (c) 5-bilayer hybrid thin films of the same thickness at scan rates of 5, 15, 25, 50, and 100 mV/s. (d) Plots of peak current density versus square root of scan rate for the 5-bilayer hybrid thin film.

### 5.3.5 Electrochromic Properties of Sample Films

To characterize their electrochromic properties, all the films were tested in a three-electrode electrochemical cell with 0.1 M LiClO$_4$/PC solution as electrolyte. With applied potentials from +0.8 to -1.0 V, WO$_3$ changes from transparent to blue, PEDOT:PSS changes from pale blue to dark blue, while the hybrid changes from pale blue to grey blue. The optical contrast of the electrochromic films at the wavelength of interest ($\lambda$) can be expressed as the transmittance difference between the bleached and colored states at $\lambda$.\[22\] Fig. 5.8(a-c) shows UV-Vis transmission spectra of WO$_3$, PEDOT:PSS and 5 bilayer hybrid thin films under various potentials. The neat WO$_3$ thin film (Fig. 5.8a) exhibits optical contrast of more than 25% in the wavelength range of 600 nm to 800 nm. At $\lambda$ of 633 nm, where human eye is most sensitive, an optical contrast of 29% is achieved. \[23\] Beyond 633 nm, the optical contrast of WO$_3$
increases slowly and reaches \(\sim 35\%\) at 800 nm. The PEDOT:PSS thin film exhibits its maximum optical contrast of 32\% at \(\lambda\) of 600 nm (Fig. 5.8b) as there is an obvious absorption peak at 600 nm at its colored state. The UV-vis spectrum of the hybrid thin film is obviously a combined spectrum of the two components (Fig. 5.8c). At negative potential \(-1.0\) V, the hybrid thin film exhibits an optical transmittance curve similar to that of neat \(\text{WO}_3\) in shape, but with significantly lower transmittance. Moreover, a broad absorption peak caused by PEDOT:PSS reduction is noticeable at wavelength of about 600 nm, indicating the simultaneous reduction of both components. At positive potential \(+0.8\) V, the transmittance of the hybrid film is generally in between those of \(\text{WO}_3\) and PEDOT:PSS films, implying that both components are switched to their bleached state. Not only the two components can be simultaneously switched, the hybrid thin film also exhibits higher optical contrast than the corresponding \(\text{WO}_3\) and PEDOT:PSS films in wavelength range from 600 to 800 nm, and the hybrid film maintains a nearly constant contrast beyond 645 nm. The enhanced optical contrast may again be attributed to the easier charge insertion/extraction into/from \(\text{WO}_3\) caused by its interactions with PEDOT:PSS. Therefore more \(\text{WO}_3\) units can be effectively switched in the hybrid film, leading to higher optical contrast.

The transmittance of the three electrochromic thin films at their \(\lambda\) of interest under square-wave potential oscillating between \(+0.8\) and \(-1.0\) V at a time interval of 50 s are illustrated in Fig. 5.8d. The dynamic contrast of the hybrid film is about 45\%, which is again much higher than that of neat \(\text{WO}_3\) or PEDOT:PSS films. From the plot, the transmittance of the hybrid is in between those of the \(\text{WO}_3\) and PEDOT:PSS films in either bleached or colored states. It reconfirms that both components contribute to the bleaching and coloration process. The coloration efficiency of the hybrid film is also in between those of \(\text{WO}_3\) and PEDOT:PSS films (Fig. 5.8e). Regarding the switching kinetics, the PEDOT:PSS, \(\text{WO}_3\) and hybrid films exhibit similar fast bleaching behaviour, whereas their coloration is slower. The coloration time for neat \(\text{WO}_3\) film (10 s)
is significantly longer than that of neat PEDOT:PSS film (5 s) presumably owing to the slower ion diffusion in WO₃. The coloration time of the hybrid film is 8 s, implying that the PEDOT:PSS surrounding WO₃ domains could facilitate the charge transfer process of WO₃ in the hybrid film.

**Figure 5.8** UV-vis optical transmittance spectra in visible range of (a) WO₃, (b) PEDOT:PSS, and (c) 5-bilayer hybrid thin films under different potentials of 0.8, 0, and -1.0 V. (d) Dynamic optical transmittance of the thin films of (I) WO₃ (blue dashed line), (II) PEDOT:PSS (red dash-dot line), and (III) 5-bilayer hybrid (black line).
solid line) under square wave potential oscillating between +0.8 and -1.0 V at a time step of 50 s recorded at (I) 633, (II) 600 and (III) 645 nm, respectively. (e) Coloration efficiencies of (I) neat WO₃, (II) neat PEDOT:PSS, and (III) 5-bilayer hybrid (blue aixs on top and right) thin films.

To investigate electrochemical stability of the hybrid film, the transmittance at bleached and colored states of the WO₃, PEDOT:PSS and hybrid thin films were measured under a square wave potential oscillating between +0.8 and -1.0 V for 1000 cycles (Fig. 5.9). In first 100 cycles, the optical contrast of the WO₃ film decreases dramatically from 29% to about 20%. This is likely to be caused by the presence of structural defects in as-deposited hybrid film, which provide many interstitial sites initially. Such defect sites may be consumed in the redox switching, since the Li⁺ ion could be entrapped in these interstitial sites, causing the initial reduction in contrast. It then maintains most of the optical contrast in the following cycles. For the PEDOT:PSS thin film, the optical contrast continuously deteriorates and it completely loses its electrochromic activity after about 500 cycles as a consequence of over-oxidation of PEDOT:PSS. The hybrid thin film exhibits remarkably improved stability, retaining 97% of its original contrast after 1000 cycles. The enhanced stability of the hybrid can be attributed to two major factors: 1) PEDOT:PSS may enter the defect sites in the WO₃ lattice, as suggested by the XPS result presented in Fig. 4a, acting as a buffer layer to prevent the surface-defect-induced anodic dissolution and cyclic erosion in the first 100 cycles; 2) the surface functional groups of WO₃ may act as dopants to prevent the over-oxidation of PEDOT:PSS.
5.4 Conclusions

In summary, multilayer hybrid thin films consisting of PEDOT:PSS and WO$_3$ were readily prepared using a one-pot sequential electrochemical deposition method. The method provides a simple and efficient way to produce hybrid thin films with large interfacial area between components without any additives. Moreover, the morphology of the hybrid thin films can be easily manipulated by adjusting the deposition parameters, such as deposition time or potentials. Thus, the interactions between the two phases can be well controlled to optimize the electrochromic performance of the thin films. In the hybrid thin films, PEDOT:PSS and WO$_3$ can be simultaneously switched to colored/bleached states, exhibiting significantly improved optical contrast and stability compared with neat PEDOT:PSS or WO$_3$ films.

References


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Chapter 6*

Facile Preparation of Aqueous Suspensions Composed of WO$_3$/Sulfonated PEDOT Hybrid Nanoparticles

In this chapter, a novel aqueous suspension based on WO$_3$ NPs and PEDTS is prepared for the fabrication of electrochromic devices (ECDs). The suspension is obtained through dissolving the monomers of PEDTS in the dispersion of WO$_3$ NPs, where the air-assisted oxidative polymerization of EDTS occurs. The PEDTS is attached to the WO$_3$ NPs owing to the electrostatic forces in the suspension. The electrochromic devices are fabricated from the hybrid suspension via air-brush spraying and its EC properties are presented in this chapter. Compared with single component based ECDs, the hybrid ECDs exhibit enhanced EC properties, especially the optical contrast and electrochemical stability. In this hybrid system, the synergistic interactions between the components and efficient EC material loading, where the PEDTS fill in the voids among WO$_3$ NPs leading to more EC materials per unit volume, contribute to the improved EC properties.

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6.1 Introduction

As reported in chapter 4 and 5, the electrochromic hybrid films based on PEDOT:PSS and WO₃ were fabricated and exhibited enhanced EC properties owing to the interactions between components. Tungsten trioxide nanoparticles (WO₃ NPs) used in the first work reported in Chapter 4 present outstanding reversible colour change and coloration efficiency among transition metal oxides.[1-3] The double insertion/extraction of electrons and small ions, such as Li⁺, into/from WO₃ can result in coloration or bleaching process, respectively.[4] As reported by Liu et al., the porous morphology of the EC films composed of WO₃ nanoparticles (NPs) facilitates the ion insertion/extraction process, resulting in improved EC performance.[2] However, WO₃ at its fully oxidized state exhibits low conductivity as a semi-conductor as studied in chapter 4.[5] To address this issue, the combination of WO₃ with a cathodically colouring EC polymer that is electrically conductive under positive potentials and has fast switching speed is an attractive approach.[5, 6] Poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) is a widely used cathodically colouring polymer owing to its high optical contrast, fast switching speed, high coloration efficiency, ease of deposition, and good stability in doped state.[7-10] In the previous work reported in chapter 4 and 5, WO₃ and PEDOT:PSS have been combined at the nanoscale through LBL assembly and one-pot sequential electrodeposition techniques.[5, 11] In these systems, PSS, which serves as charge balancing dopant for PEDOT, is an insulator with no electrochromic properties. The commercial PEDOT:PSS exhibits a core-shell structure, where the PEDOT is surrounded by the PSS. In this case, the PSS may inhibit the charge transfer process, hindering the electrochromic redox reactions.[12, 13]

A sulfonated PEDOT (shown in the figure below) named as poly(4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid) (PEDTS) can be used to replace the PEDOT:PSS in the hybrid system. It
Hybrid Suspensions of PEDTS/WO$_3$  

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is a water soluble self-doped conjugated polymer with high electrical conductivity, as reported by Karlsson et al.[13] The –SO$_3^-$ groups in the monomer can serve as the charge balancing dopants for PEDTS, leading to an enhanced charge transfer process. PEDTS has been involved as EC materials via different synthesis methods, such as electrochemical copolymerization of 3,4-ethylenedioxythiophene (EDOT) and 4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid sodium salt (EDTS) and oxidative polymerization of EDTS by ferric ions.[12-14] The EDOT-EDTS copolymers still show some degree of water solubility as well as relatively poor electrochromic properties. Moreover, the composition and chemical structure of compolymers is less controlled. While using the chemical oxidation method, PEDTS films can be obtained through various filtration steps, whereas they still contain some dark-colored iron ions.

PEDTS

In this chapter, it is reported that an aqueous suspension of WO$_3$/PEDTS hybrid NPs can be facilely prepared simply by adding EDTS monomers into a WO$_3$-NP aqueous dispersion followed by moderate heating. The PEDTS oligomers are fabricated through air-assisted chemical oxidation of EDTS monomers and simultaneously attached to the WO$_3$ NPs.[15] It is also demonstrated that the as-prepared suspension can be directly used to fabricate EC films by air-brush spraying; and single-active-layer ECDs, commonly applied to characterize the EC properties of materials, are assembled based on the hybrid and references films in this work. The hybrid based ECDs exhibit much higher optical contrast and electrochemical stability than the single
component based ones. The synthesis processes of the hybrid suspension and electrochromic properties of the ECDs are presented and analyzed below.

6.2 Experimental Methods

6.2.1 Materials

All chemicals involved in this work were purchased from Sigma-Aldrich and used without further purifications, including hydroxymethyl EDOT (EDOT-OH, 95%), tungsten (W) powders, hydrogen peroxide solution (H₂O₂ 30 wt.% in water), hydrochloric acid (HCl, 37%), lithium perchlorate (LiClO₄), and anhydrous propylene carbonate (PC, 99.7%). The solutions or suspensions involved in this work were all prepared with deionized water (DIW, 18 MΩ/cm²) from Milli-Q integral water purification system unless specified. The fluorine-doped tin oxide (FTO) coated glasses were applied as transparent electrodes for ECDs, with surface resistivity around 7 Ω/sq. They were cleaned by bath sonication in ethanol, isopropanol (IPA), acetone, and DIW for 5 minutes, respectively, and blow-dried by nitrogen gas before use. The electrochemical and electrochromic measurements were conducted in the electrochemical cells that were introduced in the experimental sections.

6.2.2 Sample Preparations

I. Preparation of EC Layers

The EDTS monomers were synthesized from EDOT-OH by chemical substitution according to Stephan’s procedures. [14] WO₃ nanoparticles were prepared using the sol-gel method as in previous reports.[2, 16, 17] WO₃ NPs (100 mg) was dispersed in 20 mL DI-Water and sonicated for 20 mins. And EDTS (40 mg) was then dissolved in the dispersion. Four sample dispersions were prepared with same contents and named as S1, S2, S3 and S4. The original sample dispersion present as milk-like liquid. The experiments were conducted as listed below:
S1 was stirred and heated at 80 °C for 4.5 hours in N₂ condition. No colour change observed.

S2 was stirred and heated at 80 °C for 4.5 hours in air. No colour change observed.

The pH of S3 was adjusted by HCl to around 1~2, and then stirred and heated at 80 °C for 4.5 hours in N₂ condition. No color change observed.

The pH of S4 was adjusted by HCl to around 1~2, and then stirred and heated at 80 °C for 4.5 hours in air. Blue colored observed. The blue colour indicated the change of oxidation states of both components. The PEDTS (light blue) can be formed by oxidation of EDTS. And the reduced tungsten oxides also exhibit blue colour. From the above experiments, the EDTS can only be oxidized by oxygen in strong acidic conditions. And the WO₃ NPs cannot oxidize the EDTS under the same conditions (S3). Without WO₃ NPs, EDTS can also be oxidized to form PEDTS under the same conditions, but the polymerization product can be dissolved in water to form a blue polymer solution, instead of suspensions of hybrid nanoparticles.

Therefore, the hybrid suspension was prepared as an aqueous dispersion containing 0.5 wt% WO₃ NPs and 0.2 wt% EDTS with pH around 1~2. The pale white suspension was heated in air at 80°C for about 4 hours, and turned blue owing to the air-assisted chemical oxidative polymerization of EDTS.[13] The dispersion with 0.5 wt% WO₃ NPs and the 0.2 wt% EDTS solution were also prepared, respectively, for reference ECDs assembly. To fabricate the EC layers, both the hybrid suspension and the WO₃-NP dispersion were separately sprayed onto FTO glasses at 60 °C through air brush spray. The thickness of EC layers was controlled by the spray time; and the area of EC layers are around 3.5 x 3.5 cm². And the PEDTS films were fabricated through drop casting, since the sprayed films were too thin to be show any EC properties. The obtained EC films were dried and stored in the vacuum desiccator for ECD fabrication.

The products of EDTS oxidization is likely to be a mixture of polymers and oligomers. By applying positive potentials to the PEDTS and hybrid thin films.
fabricated, the PEDTS can be further polymerized. Therefore, before the spectro-electrochemical characterization, the thin films were subjected to positive potential of +1.3V vs. Ag/Ag⁺ for 250 s in 1 M LiClO₄/PC solution to further polymerize PEDTS. The spectro-electrochemical measurements were all taken at the stable condition of the films. It means that the transmittance values of the hybrid films are stable under positive potentials.

II. Preparation of Electrolyte

In this work, an electrolyte solution of 1 M LiClO₄/PC was prepared for electrochemical analysis and ECD fabrication.

III. Assembly of ECDs

Electrochromic devices (ECDs) based on WO₃ and hybrid films were assembled with EC films coated on FTO glass as the working electrodes and neat FTO glasses as the counter electrodes. The obtained ECDs were named as hybrid ECDs and WO₃ based ECDs with the structure demonstrated as [FTO/glass | hybrid EC film | electrolyte | FTO/glass] and [FTO/glass | WO₃-NP film | electrolyte | FTO/glass], respectively.

6.2.3 Characterization

The size distribution of the particles in the suspension was measured by Malvern zeta potential analyser. For the EC films obtained, the thicknesses were measured by surface profiler (Alpha-step 500). The topology and phase distribution of EC films were characterized by atomic force microscope (AFM Dimension ICON, Bruker) with tapping mode at a scale of 1 µm. The field-effect scanning electron microscope (FESEM 7600F) equipped with energy dispersive X-ray spectrometer (EDX, Oxford INCA) system were employed to characterize the morphology and atomic composition of sample films. Fourier transform infrared spectroscope (FTIR, Perkin Elmer Spectrum GX) was applied to verify the chemical structure and composition. The FTIR
scan was conducted on a diamond attenuated total reflection (ATR) unit (Graseby Specac ATR10500) from 4000 to 600 cm\(^{-1}\), with 16 scans collected for signal averaging. The electrochemical behaviors of sample films were monitored by potentiostat (1470E, Solartron). Cyclic voltammetry was performed at a scan rate of 25 and 50 mV/s within a potential range from -1.0 to +1.0 V. And the potentiostat was also involved to characterize the spectroelectrochemical properties with a UV-Vis-NIR spectrophotometer (UV3600, Shimadzu). Neat FTO glasses were used as the references during the tests. The electrochemical set-up for the tests was demonstrated in experimental methodology section.

6.3 Results and Discussions

6.3.1 Hybrid Suspension Synthesis

The hybrid suspensions were obtained through three steps, including dispersion of WO\(_3\) NPs in DIW, dissolving EDTS in the dispersion, and the air-assisted oxidation of EDTS under acidic conditions. The size distribution analysis of the dispersion was conducted at each step of the synthesis process as shown in Fig. 6.1a. The size distribution peak for the WO\(_3\)-NP dispersion (red curve) is located at ~100 nm, indicating the average size of the pristine WO\(_3\)-NPs. After adding the EDTS monomers, initially the peak is at approximately the same position (blue curve) as the monomers can be completely dissolved in water. After the air-assisted chemical oxidation, the peak shifts to around 1000 nm (olive curve), indicating the attachment of the polymerization products onto WO\(_3\) NPs. It is believed that the highly acidic condition provides excess H\(^+\) ions to balance the negative charges of -SO\(_3\)\(^-\) functional groups, and they may exchange with the sodium ions (Na\(^+\)).[12] Thus the positively charged thiophene rings (radical cations) may be attracted to the negatively charged WO\(_3\) NPs. Without WO\(_3\) NPs, a blue solution, which shows no size distribution peak, was obtained because the polymerization products are completely soluble in water. In Fig. 6.1b, a transmission electron
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microscopic (TEM) image shows a typical hybrid nanoparticle, corroborating the above result. The particle size observed by TEM is much smaller probably, since the polymers could be detached during the sonication in TEM sample preparation process. While in water, the PEDTS chains may be only partially attached to the WO$_3$ NPs and hence could well stretch into the solvent.

![Figure 6.1](image)

**Figure 6.1** (a) Size distribution of dispersed WO$_3$ NPs (red), WO$_3$ NPs with dissolved EDTS monomers (blue), and WO$_3$ NPs with attached PEDTS (olive). (b) TEM micrograph of a typical WO$_3$ nanoparticle attached with PEDTS.

### 6.3.2 Morphology and Structure of Sample Films

The hybrid and WO$_3$-NP films were fabricated via air brush spray at 60°C. The thicknesses of both films are around 400 nm, so that the WO$_3$-NP films can be the reference sample for further comparison. The morphologies and topology of both films were characterized by AFM and SEM. WO$_3$ NPs with small gaps in-between can be observed clearly in AFM images (Fig. 6.2a), whereas the hybrid film exhibits smaller roughness because the gaps are partly filled by PEDTS (Fig. 6.2c). Moreover, the two components can also be differentiated in AFM phase images (Figs. 6.2 b & d). Clearly, in the hybrid film the WO$_3$ NPs (bright) are dispersed in the PEDTS matrix (dark). The SEM image of neat FTO glasses, WO$_3$-NP and hybrid films are presented in Fig. 6.3, where the FTO surface is shown as the references. The WO$_3$-NP film shows a coarse surface owing to the stacked nanoparticles. In consistent with the AFM results, SEM
micrograph of the hybrid film shows a smoother surface as the WO$_3$ NPs are well incorporated into the polymer matrix.

**Figure 6.2** AFM images of WO$_3$-NPs (a & b) and hybrid (c & d) films on FTO glasses.

**Figure 6.3** SEM images of FTO glasses at different magnifications: 25K(a) and 50K (b). SEM images of WO$_3$-NPs (c) and hybrid (d) films on FTO glasses; and the inserts are the images taken at higher magnifications.
6.3.3 Chemical Composition of Sample Films

The composition and chemical structure of obtained sample films were verified by Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray microscope (EDX). The ATR-FTIR spectra of WO$_3$-NP, PEDTS (obtained from drop casting), and hybrid films are shown in Fig. 6.4a. Compared with WO$_3$-NP and PEDTS reference films, the hybrid film spectrum exhibits characteristic bands of WO$_3$-NP and PEDTS, further confirming the existence of both materials. EDX analysis was also conducted on sample films, since it can provide elemental composition of materials semi-quantiitatively. As shown in Fig. 6.4b, the atomic ratio of W/Sn in both WO$_3$-NP and hybrid films are roughly at the same level, indicating approximately the same amount of WO$_3$ deposited on FTO glasses. Other than W, the hybrid film also contains S with W/S atomic ratio of roughly 2/1, as illustrated in Fig. 6.4b; noting that each WO$_3$ unit has only one W atom, whereas each EDTS unit contains two S atoms. This translates into a fairly low PEDTS content, suggesting that PEDTS mainly fills the voids among the WO$_3$ NPs since they are attached on WO$_3$ NPs in the suspension. WO$_3$ NPs are still the major component in the hybrid film. Considering that the two films have roughly the same thickness, the hybrid film should contain more EC active materials per unit volume than the WO$_3$-NP film.

![Figure 6.4](image)

**Figure 6.4** (a) ATR-FTIR spectra of WO$_3$-NP, WO$_3$/PEDTS hybrid, and PEDTS films. (b) Atomic ratios (W/Sn and S/Sn) of WO$_3$-NP and hybrid films measured by EDX.
6.3.4 Electrochemical Behaviours and Electrochromic Properties

Both WO₃ and PEDTS are cathodically blue colored EC materials. As in the obtained hybrid films, the WO₃ NPs and PEDTS can be switched to their colored/bleached states simultaneously under negative/positive potentials, contributing to the EC performance of hybrid films. The simultaneous switching is confirmed by the cyclic voltammetry (CV) plots of the WO₃-NP and hybrid films (Fig.6.5), which show oxidation and reduction peaks of both components in the potential range from +1.0 V to −1.0 V.

![Figure 6.5 Cylic Voltammetry plots of (a) WO₃-NP and (b) hybrid films of the same thickness coated on FTO glasses in 1 M LiClO₄/PC solution at scan rates of 25 and 50 mV/s. The reference electrode for the measurement is Ag/Ag⁺.](image)

Single-active-layer electrochromid devices were fabricated using WO₃-NP, PEDTS and hybrid films of the same thickness, respectively, to characterize their electrochromic performances. The ECDs were assembled as described in section 6.2.2 and characterized as two-electrode electrochemical cells. Fig. 6.6 shows the optical transmittance spectrum, dynamic transmittances, photoelectrochemical stability, and coloration efficiency of the ECDs assembled using WO₃-NP, PEDTS and hybrid films as the active layer, respectively. As studied in literature, the optical contrast means the maximum transmittance difference (ΔT) between bleached and colored states at a wavelength of interest (λ).[18] As shown in Figs. 6.6a-c, the transmittances of the ECDs based on WO₃-NP, PEDTS and hybrid films were recorded at potentials of +2, 0, and -3 V

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in visible wavelength range. The ECDs based on WO3-NP, PEDTS and hybrid films exhibit optical contrast of 33.7%, 29.4% and 58.0%, respectively, at wavelength of interest. With comparable thickness of all EC films, the optical contrast of the hybrid ECD is significantly higher. Dynamic transmittances of the ECDs were measured under oscillating potentials between +2 and -3 V at a time interval of 50 s and plotted in Figs. 6.6d. The dynamic contrasts for WO3-NP and hybrid based ECDs show the same trend as observed under constant potentials, i.e., the hybrid film gives much higher contrast than the reference films. The bleaching process of the hybrid ECD is, however, slower, which may be attributed to the slower bleaching of the WO3-NP component owing to the hindered ion extraction from the WO3 NPs brought by filling the voids among the WO3 NPs by PEDTS. Nevertheless, the initial bleaching of the hybrid ECD is very fast; it can achieve higher contrast than both WO3-NP and PEDTS ECDs in just few seconds. The coloration efficiencies of the ECDs are illustrated in Fig. 6.6e, which is derived from the dynamic transmittance and the corresponding charges as demonstrated in Eq. 2.5 and Eq. 3.3. [10, 19, 20] The hybrid ECD with WO3 NPs as major component exhibits enhanced coloration efficiency of 84.6 cm²/C compared with ca. 54.2 cm²/C for WO3-NP based ECD, while the PEDTS based ECD presents much higher coloration efficiency of 208.0 cm²/C. The electrochemical stability of all the ECDs were analysed by recording the transmittance of the ECDs under oscillating potentials between +2 and -3 V for 1000 cycles (Fig. 6.6f). After 1000 switching cycles, the hybrid ECD sustains more than 95% of its original contrast, whereas the WO3-NP and PEDTS based ECD only retains 35% and 30% of their original contrasts, respectively. Since the stability of an ECD is crucial for its practical applications, we can conclude that the hybrid ECD has better overall EC performance than its counterparts with neat WO3-NP or PEDTS alone as the active material. The hybrid ECD presented here also exhibits significantly enhanced coloration efficiency and electrochemical stability compared with the previously reported electrodeposited high-performance WO3-NP films, and
improved coloration efficiency compared with the hybrid films based on amorphous \( \text{WO}_3 \) and PEDOT:PSS reported in our previous works.[2, 11]

Figure 6.6 UV-vis optical transmittance spectra of ECDs based on (a) \( \text{WO}_3 \)-NP, (b) PEDTS and (c) hybrid films under potentials of +2, 0 and -3 V. (d) Dynamic optical transmittance of ECDs based on \( \text{WO}_3 \)-NP (red), PEDTS (blue) and hybrid (black) films under square-wave potentials oscillating between +2 and -3 V at a time interval of 50 s. (e) Coloration efficiency of ECDs based on \( \text{WO}_3 \)-NP, PEDTS (red axis on top and right) and hybrid films (black axis on bottom and left). (f) Optical transmittance of ECDs based on \( \text{WO}_3 \)-NP (red), PEDTS (blue) and hybrid films (black) at their colored and bleached states as a function of switching cycles. The transmittances of \( \text{WO}_3 \)-NP and hybrid based ECDs were collected at wavelength of 633 nm, and the PEDTS based
ECDs were characterized at 580 nm. The WO$_3$-NP and hybrid films were fabricated via air-brush spraying, while PEDTS films were prepared by drop casting.

Based on the EC properties results discussed above, the hybrid ECD exhibits remarkably enhanced EC properties, especially the optical contrast and electrochemical stability. The enhanced EC performance can be attributed to the attachment of PEDTS to WO$_3$ NPs, which facilitates the filling of the voids among the WO$_3$ NPs by PEDTS. Firstly, the hybrid film, with almost the same thickness as the WO$_3$-NP film, contains more EC active materials per unit volume than the WO$_3$-NP film. Both WO$_3$ and PEDTS contribute to the electrochromic switching process of hybrid films, leading to greatly enhanced optical contrast of hybrid ECDs. The lower transmittance of the hybrid ECD at bleached state is mainly brought by PEDTS, which is light blue at oxidized state. Secondly, the self-doped PEDTS exhibits higher electrical conductivity than PEDOT:PSS. The attachment of PEDTS on WO$_3$ NPs, which are the major active component, may benefit charge transfer process of WO$_3$ NPs in coloration process, and hence more WO$_3$ units can be effectively switched, also contributing to the increased optical contrast. The PEDTS may block the ion extraction from the WO$_3$ NPs in the hybrid films at oxidized state, resulted in relatively slow bleaching process. The improved charge transfer during coloration process also leads to enhanced coloration efficiency as compared with that of the neat WO$_3$-NP film. Last but not least, the interactions between PEDTS and WO$_3$ NPs may prevent the erosion of the WO$_3$ NPs and the over-oxidation of PEDTS during switching cycles, significantly improving long-term stability of the hybrid ECD.

6.4 Conclusions

In this work, a novel aqueous suspension containing WO$_3$/PEDTS hybrid nanoparticles has been developed, which can be used for ECD fabrication. In this suspension, the hybrid nanoparticles are formed through air-assisted
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oxidation polymerization of EDTS and simultaneous attachment of the PEDTS to WO$_3$ NPs. This process leads to efficient EC material loading in the hybrid system, meaning more active electrochromic materials per volume compared with neat WO$_3$-NP film. Moreover, good conductivity and stability of PEDTS facilitate the charge transfer during coloration process in the hybrid film, and the interactions between the two components improve the electrochemical stability of the hybrid ECDs. This synthesis method is very simple and environmental friendly. Besides the air-brush spraying, with proper rheological modification, other coating/printing techniques may also be applied to fabricate hybrid EC films using this easily produced EC suspension.

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Conclusions and Suggestions for Future Work

As described in previous chapters, in my PhD study, three hybrid EC systems based on WO$_3$ and PEDOT:PSS or its derivatives were developed using different synthesis and fabrication methods. The EC properties of the hybrid films were characterized and correlated to their structures. The enhanced EC performances of the hybrid materials have been demonstrated, and the underlying mechanisms of the enhancements were also investigated. In this chapter, these works will be summarized, and conclusions will be drawn to answer the questions raised in first chapter (hypotheses). In addition, the most significant findings of my study will be highlighted and the implications of these findings will be elaborated. Possible future research will be also suggested based on my PhD study.
7.1 Summary and Conclusions

My PhD work was focused on developing hybrid EC materials based on WO$_3$ and PEDOT:PSS or its derivatives with enhanced EC properties, especially better optical contrast and electrochemical stability. The electrochemical and electrochromic behaviour of the obtained EC hybrid materials and devices were studied and the results are summarized below.

7.1.1 Hybrid EC Materials through LBL Assembly

In the first section of this work, the hybrid films were fabricated based on PEDOT:PSS, PEI and WO$_3$ NPs via LBL assembly process and exhibited improved EC properties in terms of optical contrast and coloration efficiency (CE). In the hybrid system, both components can color/bleach in the same potential range, resulted in enhanced optical contrast. The charge transfer process is greatly improved owing to the interdigitated structure with WO$_3$ NPs homogeneously distributed in the polymer matrix, leading to significantly improved CE of 117.7 cm$^2$/C. The underlying mechanism of the enhancement was also studied and verified by SECM technique. The WO$_3$ films experience a nonconductive-to-conductive transition during potential sweep from negative to positive. On the other hand, the PEDOT:PSS films present high conductivity in the oxidized state. According to the SECM results, the hybrid films show enhanced conductivity in both oxidized and reduced states during the potential sweep, which suggests that the PEDOT:PSS can assist the charge transfer process of WO$_3$ in oxidized states during switching.[1, 2] It also indicates there are more accessible active units in the hybrid film during redox switching process, leading to enhanced EC properties.

The obtained multilayer EC thin films also present some drawbacks. The PEI layers involved to introduce the electrostatic force are nonconductive, which hinders the charge transfer between EC active components in the obtained EC films.[3, 4] For example, the PEI layers in the PEDOT:PSS films
obtained in this work inhibit the redox reactions of PEDOT:PSS layers, leading to a slow switching process. However, the hybrid films are less affected by the PEI layers owing to the improved charge transfer process. The irregularly shaped WO$_3$ NPs can prevent the PEI from forming a complete layer, and enlarge the interfacial area between WO$_3$ and PEDOT:PSS. Therefore, the EC performance of hybrid materials is improved compared with single component films, but, can be further enhanced without the nonconductive PEI layers.

From this first section, it can be concluded that the hybrid films based on WO$_3$ and PEDOT:PSS present enhanced EC properties, especially the optical contrast and coloration efficiency, owing to the simultaneous switching and synergistic interactions between components. The underlying mechanism of the enhancement has been verified by the SECM techniques. Nevertheless, the nonconductive PEI layer may prohibit the charge transfer process in hybrid system and lower the EC performance. Therefore, the hybrid system can be developed based on PEDOT:PSS and WO$_3$ without PEI layers to further improve the EC performance.

### 7.1.2 Hybrid EC Materials through Electrodeposition

In the second piece of work, the hybrid thin films were developed based only on WO$_3$ and PEDOT:PSS through a simple one-pot sequential electrodeposition method in the second section of this work. Both components were sequentially electrodeposited onto ITO substrates from one-pot aqueous solution. The morphology and structure of hybrid materials can be easily tailored to achieve large interfacial area between two components through adjusting the electrodeposition parameters during fabrication process. The obtained hybrid thin films exhibit significantly improved optical contrast and electrochemical stability. In the hybrid system, both components are contributing to the electrochromic switching, since they can simultaneously switch to colored/bleached states at negative/positive potentials. In addition, it sustains more than 97% of its original optical contrast after 1000 reversible
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redox cycles, which is mainly caused by the synergistic interactions between two components. The PEDOT:PSS is able to serve as a buffer component for WO$_3$ to prevent the degradation of EC performance.

Compared with the first work, the hybrid thin films obtained in this work are composed of purely WO$_3$ and PEDOT:PSS with controllable morphology and structures. The one-pot sequential electrodeposition is employed to deposit both components from aqueous solution directly without PEI and other additives. As a result, the charge transfer process is more efficient in all obtained EC films. And the interfacial area between components can be easily manipulated during electrodeposition process. In addition, the hybrid films exhibit enhanced interactions between PEDOT:PSS and WO$_3$ that stabilize the hybrid structure, leading to significantly improved electrochemical stability, even compared with LBL assembly hybrid films. However, like PEI, the PSS involved in the hybrid system as charging balancing dopant for PEDOT is also nonconductive, which may hinder the charge transfer between WO$_3$ and PEDOT. Thus, self-doped PEDOT derivative can be applied to replace the PEDOT:PSS in hybrid system to further enhance the charge transfer process so as to improve the EC performance.

In conclusion, the hybrid EC films based on WO$_3$ and PEDOT:PSS obtained through one-pot sequential electrodeposition show enhanced electrochromic performance, especially the optical contrast and electrochemical stability. The large interfacial area between components can be easily obtained to promote the synergistic interactions in the hybrid system, leading to enhanced EC performance. To further improve the interactions, self-doped PEDOT derivatives can be employed to exclude the nonconductive PSS in hybrid systems to achieve better performance.

7.1.3 Hybrid EC Aqueous Suspensions

As discussed in the last section, the self-doped PEDOT derivatives can be used to replace the PEDOT:PSS in hybrid systems to further enhance the charge
transfer between polymers and WO$_3$. In this work, the self-doped sulfonated PEDOT (PEDTS) was obtained through air-assisted chemical oxidation of EDTS monomers in aqueous solution. The polymers (or oligomers) were attached to the WO$_3$ NPs dispersed in the solution immediately owing to the electrostatic force, resulted in an aqueous hybrid particles suspension. The hybrid EC films obtained via air-brushing spraying from the suspensions were applied to assemble single-active-layer electrochromic devices. Consistant with previous work, the hybrid films based ECDs exhibits enhanced EC properties, especially the optical contrast and electrochemical stability. The optical contrast is remarkably improved to 58% at wavelength of 633 nm, and it can sustains more than 95% of its contrast after 1000 reversible cycles. The significant enhancement in EC performance may be mainly caused by large interfacial area and the synergistic interactions between components. The PEDTS possess high conductivity, since it is highly doped without the nonconductive PSS, which facilitates the charge transfer process in hybrid films. In addition, the polymers filling in the voids among WO$_3$ NPs, leading to large interfacial area and efficient EC material loading in hybrid films compared with neat WO$_3$-NP films.

In this work, an aqueous suspension containing EC hybrid particles were obtained through simple chemical oxidation and the electrostatic force promoted attachment. The PEDOTS is easily obtained through air-assisted chemical oxidation without any catalyst or additives. Large interfacial area between components could also be achieved, since the PEDTS is attached to the WO$_3$ NPs in the hybrid films. The air-brush spraying was employed to fabricate EC thin films, which can produce homogenous thin films on substrate with large surface area. Compared with the LBL assembly, the films obtained through air-brush spraying are less affected as increasing thickness. However, the morphology and structure of hybrid thin film obtained in this work cannot be easily tailored. And the thin film preparation process is still more tedious than one-pot electrodeposition, since polymers need to be synthesized from
monomers before film fabrications. Hence, to further improve the EC performance and simplify the fabrication process, self-doped conjugated polymers that can be electrodeposited with WO₃ from one-pot solutions may be applied in the hybrid systems to achieve controllable morphology and structures.

In summary, the ECDs based on hybrid thin films consisting of WO₃ NPs and self-doped PEDTS exhibit enhanced EC properties in terms of optical contrast and electrochemical stability. The PEDTS with good conductivity assists the charge transfer process in hybrid system. And the synergistic interactions between two components also contribute to the significantly improved EC performance. With proper modifications, the suspensions obtained in this work may be applied to fabricated EC films through various techniques besides air-brush spraying, such as one-pot electrodeposition, roll coating, spin coating, inkjet printing, and etc.

7.1.4 Overall Conclusions

In my PhD study, the hybrid EC materials based on WO₃ and PEDOT:PSS or its derivatives have been fabricated using various methods. Significantly enhanced EC properties, especially the optical contrast and electrochemical stability, are achieved. The electrochromic performances of the hybrid materials and devices obtained in this work are listed in table 7.1 below. And the performances of the reference films and devices are included as well. In the first piece of work, the hybrid materials based on WO₃ and PEDOT:PSS promote the synergistic effects in the system due to the enhanced conductivity and simultaneous switching process. In the second piece of work, the non-conductive PEI layers have been removed to enlarge the interfacial area so as to further improve synergistic effects in the hybrid system. As listed in the table below, the obtained sample films present enhanced EC performance owing to the enhanced synergistic effects. In the third piece of work, the non-conductive PSS have been removed by using a self-doped PEDOT
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derivative PEDTS in the hybrid system. It may enhance the interfacial interactions between two components so as to further promote the synergistic effects in the system. As a result, the obtained electrochromic devices based on the sample films show enhanced EC performance compared with the reference ones.

Table 7.1 The electrochromic performances of both the reference and hybrid materials and devices obtained in the three works reported in this thesis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potential step (V)</th>
<th>CT %</th>
<th>CE (cm²/C)</th>
<th>Switching time (s)</th>
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<td><strong>LBL Assembly Work</strong></td>
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<td>WO₃-NPs</td>
<td>+0.8V/-1.0V</td>
<td>7.3</td>
<td>58.6</td>
<td>9</td>
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<tr>
<td>PEDOT:PSS</td>
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<td>86.4</td>
<td>15</td>
</tr>
<tr>
<td>Hybrid</td>
<td>+0.8V/-1.0V</td>
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<td>117.7</td>
<td>6</td>
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<td></td>
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<tr>
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<td>29</td>
<td>78.4</td>
<td>11</td>
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<td>WO₃ ECD</td>
<td>+2.0V/-3.0V</td>
<td>35</td>
<td>54.2</td>
<td>10</td>
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<tr>
<td>PEDOT:PSS ECD</td>
<td>+2.0V/-3.0V</td>
<td>30</td>
<td>208.0</td>
<td>3</td>
</tr>
<tr>
<td>Hybrid ECD</td>
<td>+2.0V/-3.0V</td>
<td>58.0</td>
<td>84.6</td>
<td>5-6</td>
</tr>
</tbody>
</table>

The enhancements may be attributed to three factors: 1) Simultaneous switching processes, where both components are coloured/bleached simultaneously. 2) Promoting the synergistic interactions between components through tailoring the structure to enlarge the interfacial areas. The electrical conductivity of hybrid films are verified to be enhanced owing to the complementary electrical conductivity of the two components in the redox potential ranges. And the polymers may act as the buffer layer for WO₃, and the WO₃ can prevent the over-oxidation of polymers during switching process. 3) Effective materials loading by removing the insulating components. More EC
active materials can be deposited in the hybrid system through removing the PEI or PSS components. Thus, the hypotheses raised in chapter 1 are verified.

### 7.2 Implications of the Work

This section covers the major findings of my PhD work and its contribution towards the development of hybrid EC films based on conjugated polymers and transition metal oxides. The work presented in this thesis proves that the hybridization of WO$_3$ and PEDOT:PSS or its derivatives is able to achieve enhanced EC performance, especially the optical contrast and electrochemical stability owing to the synergistic interaction between components. Novel synthesis methods and analysis techniques employed to fabricate and characterized the obtained EC materials can also be used in other hybrid EC systems. The key implications of my study in this field are given below.

#### 7.2.1 SECM for Design of Novel Hybrid EC Systems and Mechanism Studies

As reported in chapter 4, the SECM technique is innovatively employed to verify the conductivity changes of EC materials under dynamic potential sweeps and facilitate the mechanism studies. It is a powerful technique with the UME scanning the substrate surfaces, providing information about images of conductivity and chemical reactions, charge transfer among interfaces, surface reactions, and so on.[6] To develop novel hybrid EC system, the SECM can be employed to closely monitor the conductivity changes of each component during the redox reactions so as to promote efficient charge transfer process in hybrid system. For examples, EC materials A and B are nonconductive in potential range [0, +0.6V] and [+0.4V, +0.8V], respectively. If both of them switch at +0.5V, then the hybridization of A and B may not result in enhanced EC performance, since the both of them are nonconductive and may prohibit the charge transfer process. In addition, the in-situ heterogeneous reactions on
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semiconductor surfaces, such as WO$_3$, can be also studied.[7, 8] The underlying mechanism of redox reactions and its kinetics of EC materials can be well investigated and understood through the SECM characterizations. Therefore, the SECM characterization technique can be widely applied for developing novel hybrid EC systems and study the underlying mechanism.

7.2.2 Possibility of One-pot Electrodeposition for other Hybrid Systems

At present, more and more people are focusing on the inorganic-organic hybrid EC materials, since it may combine the advantages of both categories. These hybrid systems are usually fabricated through multistep methods with limited control on the morphology and structures. For example, the hybrid system based on WO$_3$ and PEDOT:PSS were fabricated in two steps as spin coating the polymer layers and then electrodepositing the WO$_3$ layers.[9] However, the one-pot sequential electrodeposition reported in chapter 5 can be a reasonable and effective way to synthesize inorganic-organic hybrid materials with controllable structures.

According to the literature, most inorganic TMOs can be formed through electrodeposition, and commonly used CPs, such as PANI, PEDOT, and poly(pyrrole), are also able to be electropolymerized from their monomers.[10] Therefore, one-pot sequential electrodeposition may be a good method to synthesize hybrid materials based on other systems besides WO$_3$ and PEDOT:PSS to achieve well controlled morphology and structures.

7.2.3 Hybrid Suspensions for Large-area Coating/Printing

The solutions or suspensions containing electrochromic materials can be used to fabricate EC films and devices through spin coating, air brush spray, inkjet printing and etc. In chapter 6, we reported an easily obtained aqueous suspension containing hybrid EC particles used for large-area coating through air-brush spraying. On one hand, the nanoparticle based hybrid suspensions can
be applied to other hybrid systems, where the conjugated polymers or other components can attach onto the nanoparticles. On the other hand, with proper modifications, the hybrid suspension can be employed to many coating techniques besides the air brush spray. For example, with certain additives, the suspension may meet the requirements, including viscosity, particle size and so on, for inkjet printing or spin coating. So the hybrid suspension may be a promising candidate for large-area coating/printing of EC hybrid materials.

7.3 Recommendations for Future Research

As mentioned in section 7.1.3, the morphology and structure of hybrid thin films based on PEDTS and WO₃ cannot be easily tailored through the air-brush spraying techniques. The novel one-pot electrodeposition may be a better option to obtain hybrid films with controllable structures. However, the major issue is that the PEDTS cannot be electrodeposited from aqueous solutions, since it is soluble in water. According to literature, the self-doped conjugated polymer can be obtained through electrochemically co-polymerization of EDOT and EDTS from aqueous solutions.[12] Hence, the copolymer may be a promising material to hybridize with WO₃ through one-pot sequential electrodeposition to obtain tailorable morphology and structure so as to achieve high EC performance. Some preliminary results based on the synthesis and characterizations of the copolymers are shown below.

The copolymers were electropolymerized from aqueous solution containing EDTS and EDOT monomers with molar ratio of 1:2. The PEDOT:PSS films were also fabricated as reference samples of the same thickness (~200 nm). The chemical structure of the copolymer was verified by FTIR as shown in Fig. 7.1a, where the characteristic peaks were shifted compared with the PEDOT:PSS spectrum. Moreover, the redox reaction of copolymer was shown in CV graphs (Fig. 7.1b) in comparison to that of PEDOT:PSS. The copolymers present similar oxidation and reduction peaks as PEDOT:PSS at -0.1 and -0.8 V, respectively.
Figure 7.1 (a) FTIR scan of conjugated polymers of PEDOT/PEDTS copolymers (blue) and PEDOT:PSS (red). (b) Cyclic voltammetry plots of PEDOT/PEDTS copolymers (blue) and PEDOT:PSS (red) in 1 M LiClO$_4$/PC at scan rate of 50 mV/s. The reference electrode for the measurement is Ag/Ag$^+$. 

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As reviewed in literature, the PEDTS (~5 S/cm) exhibits improved conductivity compared with PEDOT:PSS (~0.1 S/cm).[11-13] The SECM studies were conducted similar to the experiments illustrated in Fig 4.10a. The EC films were served as the substrate under linear scan voltammetry; and the UME tip was placed at the approached position to monitor the surface reactions. The recorded results are present in Fig. 7.2 below. The constant tip currents recorded above the substrates of copolymers and PEDOT:PSS films indicate that both films are conductive at potential range from 0 to +0.8 V (Fig. 7.2a). On the other hand, the conductivity of both films decrease at negative potentials as reflected in the tip current shown in Fig. 7.2b. The tip current recorded above PEDOT:PSS film experiences an obvious drop at -0.45 V; while the tip current above copolymer films gradually reduced at potential range from 0 to -0.8 V. So the conductivity of copolymer films is slightly better than that of PEDOT:PSS at potential range from 0 to -0.8V.
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Figure 7.2 (a) Tip current recorded as linear scan voltammetry of copolymer (blue) and PEDOT:PSS (red) films from 0.8 V to -0.3 V at scan rate of 1 mV/s in 1 mM Ru(NH$_3$)$_6$Cl$_3$ with 0.1 M KCl aqueous solution. The applied potential UME is -0.35 V. (b) Tip current recorded as linear scan voltammetry of copolymer (blue) and PEDOT:PSS (red) films from 0 V to -0.8 V at scan rate of 1 mV/s in 1 mM FcMeOH with 0.1 M KCl aqueous solution. The applied potential UME is -0.35 V.

The electrochromic properties of both films were characterized in terms of dynamic optical switching and coloration efficiency shown in Fig. 7.3. The self-doped copolymer films are expected to present improved charge transfer process, leading to fast switching and high coloration efficiency. As shown in Fig. 7.3a, both films exhibit the almost the same optical contrast of ~30%; and the copolymer films show fast coloration and bleaching speeds of 3 and 2 seconds, respectively, compared with PEDOT:PSS film. And it also present higher coloration efficiency (301 cm$^2$/C) than that of PEDOT:PSS films (266.9 cm$^2$/C).

Figure 7.3 (a) Dynamic optical transmittances of copolymer (blue) and PEDOT:PSS (red) films under square-wave potentials oscillating between +1 and -1 V at a time interval of 50 s in 1 M LiClO$_4$/PC. (b) Coloration efficiency of copolymer (blue...
squares refer to blue axis on top and right) and PEDOT:PSS (red squares refer to black axis on bottom and left) films. The reference electrode for the measurement is Ag/Ag$^+$. 

Based on the preliminary results, the self-doped copolymers exhibit improved properties in terms of electrochemical behaviours and electrochromic properties in comparison to the PEDOT:PSS films owing to the enhanced conductivity. Therefore, the EC properties of hybrid films based on this copolymers and WO$_3$ via one-pot sequential electrodeposition are expected to be improved as well. However, the copolymerization process cannot be well controlled in terms of sequence distribution, which may lead to insufficient dopants for the PEDOT segments in the copolymers. As a result, the electrochemical stability may be negatively affected. Therefore, the hybrid EC films based on PEDOT-PEDT$_S$ copolymers with well controlled structures and WO$_3$ through one-pot sequential electrodeposition can be an interesting topic in future research.

References

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### APPENDIX

**Table A.1 (a) XPS results of atomic concentration of elements (S/W/In/N) at different number of layers**

<table>
<thead>
<tr>
<th>Layers</th>
<th>Atomic Concentration</th>
<th>Ratio ((S/In))</th>
<th>Ratio ((W/In))</th>
<th>Ratio ((S/W))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S</td>
<td>W</td>
<td>N</td>
<td>In</td>
</tr>
<tr>
<td>P1</td>
<td>3.94</td>
<td>0</td>
<td>5.2</td>
<td>6.73</td>
</tr>
<tr>
<td>P2</td>
<td>5.28</td>
<td>0</td>
<td>6.4</td>
<td>1.28</td>
</tr>
<tr>
<td>P3</td>
<td>4.9</td>
<td>0</td>
<td>6.96</td>
<td>0.23</td>
</tr>
<tr>
<td>P4</td>
<td>4.62</td>
<td>0</td>
<td>8.36</td>
<td>0.11</td>
</tr>
<tr>
<td>P5</td>
<td>4.88</td>
<td>0</td>
<td>8.18</td>
<td>0</td>
</tr>
<tr>
<td>W1</td>
<td>0</td>
<td>3.81</td>
<td>5.33</td>
<td>10.38</td>
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<td>12.72</td>
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<td>W3</td>
<td>0</td>
<td>5.02</td>
<td>5.97</td>
<td>11.64</td>
</tr>
<tr>
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<td>7.79</td>
<td>4.52</td>
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<tr>
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<td>8.37</td>
<td>0.98</td>
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<tr>
<td>H3</td>
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<td>9.81</td>
<td>7.48</td>
<td>0.37</td>
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</table>

**Table A.1 (b) EDX results of atomic percentage of elements (S/W/In) at different number of layers**

<table>
<thead>
<tr>
<th>Layers</th>
<th>Atomic Percentage</th>
<th>Ratio ((S/In))</th>
<th>Ratio ((W/In))</th>
<th>Ratio ((S/W))</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>S</td>
<td>W</td>
<td>In</td>
<td></td>
</tr>
<tr>
<td>P1</td>
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<td>0</td>
<td>26.01</td>
<td>0</td>
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<tr>
<td>P2</td>
<td>0.68667</td>
<td>0</td>
<td>24.55667</td>
<td>0.00708</td>
</tr>
<tr>
<td>P3</td>
<td>0.85</td>
<td>0</td>
<td>21.75</td>
<td>0.00911</td>
</tr>
<tr>
<td>Layers</td>
<td>Atomic Percentage</td>
<td>Ratio (S/In)</td>
<td>Ratio (W/In)</td>
<td>Ratio (S/W)</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------</td>
<td>--------------</td>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>S</td>
<td>W</td>
<td>In</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>0</td>
<td>26.01</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>P2</td>
<td>0.68667</td>
<td>24.55667</td>
<td>0.00708</td>
<td>-</td>
</tr>
<tr>
<td>P3</td>
<td>0.85</td>
<td>21.75</td>
<td>0.00911</td>
<td>-</td>
</tr>
<tr>
<td>P4</td>
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<td>29.11</td>
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<td>-</td>
</tr>
<tr>
<td>P5</td>
<td>1.75333</td>
<td>27.35667</td>
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<td>0.06457</td>
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<td>25.58</td>
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<tr>
<td>H3</td>
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<td>2.0025</td>
<td>23.19</td>
<td>0.01916</td>
</tr>
<tr>
<td>H4</td>
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<td>3.60333</td>
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<td>3.96667</td>
<td>14.87</td>
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<td>12.53</td>
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</tr>
<tr>
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<td>3.96333</td>
<td>10.45667</td>
<td>0.23771</td>
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<tr>
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<td>4.3</td>
<td>2.91</td>
<td>4.33667</td>
<td>0.99566</td>
</tr>
</tbody>
</table>

**Appendix**
<table>
<thead>
<tr>
<th>Sample Films</th>
<th>Optical Contrast (%)</th>
<th>Switching Time (s)</th>
<th>Coloration Efficiency (cm²/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W10</td>
<td>7.3</td>
<td>6</td>
<td>58.6</td>
</tr>
<tr>
<td>P10</td>
<td>9.6</td>
<td>20</td>
<td>86.4</td>
</tr>
<tr>
<td>H5</td>
<td>20</td>
<td>8</td>
<td>117.7</td>
</tr>
</tbody>
</table>
Figure A.1. SEM images of WO$_3$-NPs drop-cast on glass slide at magnification of (a) 50000 and (b) 100000.

Figure A.2. XPS scan spectra of (a) ITO and ITO-PEI surfaces, one, two, and three layers of (b) PEDOT:PSS, (c) WO$_3$-NP, (d) hybrid films.
For conductive substrates, a typical positive feedback approach curve of ITO surface is recorded and fitted shown as Fig. A.3a. And for non-conductive substrate, a typical negative feedback approach curve of glass surface is recorded and fitted shown in Fig. A.3b. Thus, the approach curves of conductive or non-conductive surfaces can be fitted in a similar way as that of ITO or glass surfaces.

With applied potential of -300 mV, the WO$_3$ film exhibits a typical positive feedback as shown in Fig. A.3c. So it can be fitted to obtain the d value, which means the distance between substrate surface and microelectrode tip at its initial position. The conductivity of WO$_3$ decreases as applied potentials increase, namely -200, -100, and 0 mV, which leads to atypical approach curves. The microelectrode was withdrawn to the same initial position after each
measurement. Thus, the fitted d value can be used to plot the approaching curves under -200, -100, and 0 mV (Fig. 4.9b).

**Fitting Functions using Lefrou’s Model (ref.17-18 in Chapter 4):**

Negative feedback:

- **Number Of Parameters = 2**
- **Function Type = User-Defined**
- **Function Form = Equations**
- **Path =**
- **Number Of Independent Variables = 1**
- **Number Of Dependent Variables = 1**
- **FunctionPrev = NewFunction**

[Fitting Parameters]

- **Names = RG, L**
- **Initial Values = --(V)**
- **Meanings = ?**
- **Lower Bounds = --(X, OFF)**
- **Upper Bounds = --(X, OFF)**
- **Naming Method = User-Defined**
- **Number Of Significant Digits =**

[Independent Variables]

- **x =**

[Dependent Variables]

- **y =**

[Formula]

\[
y = \frac{2.08/(RG^{0.358})*((L-x)-0.145/RG)+1.585)}{150}
\]
(2.08/(RG^0.358)*((L-x)+0.0023*RG)+1.57+(\ln(RG))/(L-x)+2/(3.14*RG)*\ln(1+3.14*RG/(2*(L-x))))

y: Normalized current passing through the UME tip (i_t/i_{\infty}) (collected data)
L: The initial distance between UME tip and the substrate surface
x: The distance between the initial position and the current position of the UME tip during approaching process (collected data)
L-x: The distance between the UME tip and the substrate surface
RG: the radius of the insulating sheath over the radius of electrode (r_g/a)
(RG ~ 7 in this work)

Positive feedback

Number Of Parameters = 2
Function Type = User-Defined
Function Form = Equations
Path =
Number Of Independent Variables = 1
Number Of Dependent Variables = 1
FunctionPrev = NewFunction

[Fitting Parameters]
Names = RG,L
Initial Values = 7.000000(F),17.000000(V)
Meanings = ?,?
Lower Bounds = --(X, Off),16.000000(I, On)
Upper Bounds = --(X, Off),19.000000(I, Off)
Naming Method = User-Defined
Number Of Significant Digits = -1,-1
[Independent Variables]

x =

[Dependent Variables]

y =

[Formula]

\[
y = \ln(2) + \ln(2) \times (1 - 2/3.14 \times \cos(1/RG)) - \ln(2) \times (1 - (2/3.14 \times \cos(1/RG))^2) + 3.14/(4 \times (1 + 0.639 \times (1 - 2/3.14 \times \cos(1/RG)) - 0.186 \times (1 - (2/3.14 \times \cos(1/RG))^2)) \times \tan(L-x)) + (1 - ((\ln(2)) + (\ln(2) \times (1 - 2/3.14 \times \cos(1/RG)) - (\ln(2) \times (1 - (2/3.14 \times \cos(1/RG))^2) - 1/2 \times (1 + 0.639 \times (1 - 2/3.14 \times \cos(1/RG)) - 0.186 \times (1 - (2/3.14 \times \cos(1/RG))^2)))) \times 2/3.14 \times \tan(L-x))
\]

y: Normalized current passing through the UME tip \((i_t/i_{t,\infty})\) (collected data)
L: The initial distance between UME tip and the substrate surface
x: The distance between the initial position and the current position of the UME tip during approaching process (collected data)
L-x: The distance between the UME tip and the substrate surface
RG: the radius of the insulating sheath over the radius of electrode \((r_g/a)\)
(RG ~7 in this work)
Figure A.4 X-ray diffraction patterns of the electrodeposited WO\(_3\) and 5-bilayer hybrid thin films.