Nanostructured electrochromic and photoelectrochemical materials and devices

Jiao, Zhihui

2014

Jiao, Z. (2013). Nanostructured electrochromic and photoelectrochemical materials and devices. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/61039>

<https://doi.org/10.32657/10356/61039>

**Nanostructured Electrochromic and
Photoelectrochemical Materials and Devices**

Jiao Zhi Hui

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2013

ACKNOWLEDGMENTS

I would like to take this opportunity to express my sincerest gratitude towards my supervisor, Prof. Sun Xiao Wei. He inspired me to do research in this direction and always provided various support along my research in the past four years. He always shared his valuable knowledge and experience and always encouraged me to open up and be resourceful in my research. I appreciate his guidance and various constructive suggestions on both my research and life. I would like to thank my co-supervisor Dr. Ke Lin profusely for her guidance, advices and assistance on the experimental support.

I would like to thank all the staff and students at the Nanoelectronics Lab 1 and 2 and Institute of Materials and Research Engineering (IMRE). Special thanks to Prof. Hilmi Volkan Demir and Prof. Liu Xuewei for their insight views and fruitful discussions; I would also like to thank Dr. Zhao Dewei, Dr. Liu Jiehua, Dr. Wang Jianxiong, Dr. Yang Yi, Dr. Divayana Yoga, Dr. Zhao Junliang, Luo Dan, Wang Ye, Ling Bo, Aung Ko Ko Kyaw, Du Qingguo, Yang Mingfei, Zheng Ke, Wei Yuefan and all the friends from the Nanoelectronics Lab for their friendship, encouragement, inspirational discussions, and various assistance they provided me.

Finally, I would like to express my utmost gratitude to my family for their continuous encouragement and support during my studies. I want to thank my wife, Jiao Nana, who companied me and gave me love during my PHD research. I also want to thank my parents for their love, understanding and support.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	III
TABLE OF CONTENTS.....	IV
ABSTRACT	VII
LIST OF FIGURES	X
LIST OF TABLES	XVI
CHAPTER 1 ELECTROCHROMIC DEVICES	1
1.1 INTRODUCTION	1
1.1.1 Electrochromic materials	4
1.1.2 Transparent conductors	11
1.1.3 Electrolyte layers	12
1.1.4 Device structure and operation principles.....	12
1.2 WO ₃ FILM ASSEMBLING TECHNIQUES.....	16
1.3 SUMMARY	18
CHAPTER 2 PHOTOELECTROCHROMIC DEVICES.....	19
2.1 INTRODUCTION	19
2.2 DEVICE STRUCTURE AND OPERATION MECHANISM.....	19
2.3 ELECTROCHROMIC MATERIALS IN PEC DEVICES.....	22
2.4 SUMMARY	22
CHAPTER 3 PHOTOELECTROCHEMICAL DEVICES	24
3.1 INTRODUCTION	24
3.2 BASIC PRINCIPLES	25
3.2.1 Prototype of the photoelectrochemical cell.....	25
3.2.2 Semiconductor electrolyte interfaces	26
3.3 BAND ENERGY REQUIREMENTS FOR AN EFFICIENT PHOTO WATER SPLITTING.....	28
3.4 PHOTOELECTROCHEMICAL PERFORMANCES BASED ON WO ₃ PHOTOANODE	30
3.5 SUMMARY	31
CHAPTER 4 SINGLE LAYER ELECTROCHROMIC DEVICES	33
4.1 INTRODUCTION	33
4.2 FABRICATION AND CHARACTERIZATION OF THE WO ₃ AND HYDRATED WO ₃ FILMS.....	36
4.2.1 Synthesis of brick-like WO ₃ films	36
4.2.2 Synthesis of plate-like hydrated WO ₃ films.....	37
4.2.3 Characterization	38
4.3 STRUCTURES, MORPHOLOGIES AND ELECTROCHROMIC PROPERTIES	39
4.3.1 Brick-like WO ₃ films	39
4.3.2 Plate-like hydrated WO ₃ films	49
4.4 SUMMARY	59

CHAPTER 5 COMPLEMENTARY LAYER ELECTROCHROMIC DEVICES.....	61
5.1 INTRODUCTION	61
5.2 SYNTHESIS AND CHARACTERIZATION OF THE HYDRATED WO ₃ FILMS.....	63
5.2.1 Synthesis of stick/particle-like hydrated WO ₃ films.....	63
5.2.2 Synthesis of brick-like hydrated WO ₃ films	64
5.2.3 Characterization	64
5.3 ASSEMBLING AND TEST OF THE COMPLEMENTARY DEVICES.....	65
5.4 STRUCTURES, MORPHOLOGIES AND GROWTH MECHANISMS	66
5.4.1 Stick/particle like hydrated WO ₃ films	66
5.4.2 Brick-like hydrated WO ₃ films	70
5.5 ELECTROCHEMICAL AND ELECTROCHROMIC PROPERTIES	77
5.5.1 Nanostick/particle hydrated WO ₃ films and the complementary EC devices	77
5.5.2 Brick-like hydrated WO ₃ films and the complementary EC devices	87
5.6 SUMMARY	93
CHAPTER 6 PRUSIAN BLUE BASED PHOTOELECTROCHROMIC DEVICES.....	95
6.1 INTRODUCTION	95
6.2 FABRICATION AND CHARACTERIZATION OF THE PEC DEVICE	97
6.2.1 Electrodeposition and characterization of PB films.....	95
6.2.2 Preparation of dye-sensitized TiO ₂ nanocrystalline photoanode	98
6.2.3 Assembly of the photoelectrochromic cell	98
6.2.4 Characterization	99
6.3 MORPHOLOGY AND CYCLIC VOLTAMMETRY OF THE PB FILM	99
6.4 WORKING PRINCIPLES OF THE PHOTOELECTROCHROMIC CELL	100
6.5 OPTICAL-ELECTRO CHARACTERIZATIONS OF THE PEC CELL	105
6.6 SUMMARY	114
CHAPTER 7 NANOSTRUCTURED TUNGSTEN OXIDE BASED PHOTOELECTROCHEMICAL DEVICES	116
7.1 INTRODUCTION	116
7.2 SYNTHESIS AND CHARACTERIZATION OF THE NANOSTRUCTURED WO ₃ FILMS	117
7.2.1 Preparation of crystal seeds	117
7.2.2 Preparation of substrates	118
7.2.3 Preparation of precursors and hydrothermal synthesis	118
7.2.4 Characterizations.....	119
7.3 STRUCTURES AND MORPHOLOGIES OF THE WO ₃ FILMS	120
7.4 OPTICAL AND PHOTOELECTROCHEMICAL PROPERTIES OF THE WO ₃ FILMS	132
7.5 SUMMARY	137
CHAPTER 8 CONCLUSION AND FUTURE WORKS	139
8.1 CONCLUSION.....	139
8.2 FUTURE WORKS.....	142

JOURNAL PUBLICATIONS	144
CONFERENCE PRESENTATIONS	146
BIBLIOGRAPHY	147

ABSTRACT

Nanostructured tungsten oxide (WO_3) and hydrated tungsten oxide ($\text{WO}_3 \cdot \text{H}_2\text{O}$) films were assembled on fluorine doped tin oxide (FTO) coated glass substrates by seed-assisted hydrothermal methods. Plate-like, brick-like and stick-like nanostructured WO_3 or hydrated WO_3 films were obtained by using sodium sulfate (Na_2SO_4), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium acetate ($\text{CH}_3\text{COONH}_4$) as capping agents, respectively. The electrochromic (EC) characteristics of the as-prepared films were investigated in single EC layer devices and complementary EC devices with Prussian blue (PB) as the counter electrode.

Compared to the films without capping agent, the plate-like nanostructured $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film grown with Na_2SO_4 shows significantly improved EC performance. A high coloration efficiency value of $112.7 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm is obtained, and the response time for 90% transmittance changes is found to be 4.3 s for coloration and 1.4 s for bleaching for a sample size $\sim 2 \text{ cm}^2$ (FTO sheet resistance: $15 \text{ } \Omega/\square$), respectively, while the brick-like monoclinic WO_3 film displays a comparable switching response of $t_{c, 90\%} = 272 \text{ s}$ and $t_{b, 90\%} = 364 \text{ s}$ (sample size $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15 \text{ } \Omega/\square$) and a coloration efficiency of $38.2 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm. Both films show adjustable transmittance modulation under different voltages and a good reversible coloration/bleaching stability. The single layer EC devices based on these films demonstrate promising applications in smart windows and large-area information displays.

Complementary EC devices based on nanostick/nanoparticle and nanobrick $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film and PB film were also fabricated. The orthorhombic nanostick/nanoparticle $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film grown with $\text{CH}_3\text{COONH}_4$ as the capping agent shows better EC performances than the nanobrick film without capping agent. A complementary EC device based on the nanostick/nanoparticle $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film and PB was assembled and shows higher optical modulation (54% at 754 nm), a larger coloration efficiency ($151.9 \text{ cm}^2 \text{ C}^{-1}$ at 754 nm) and faster switching responses with a bleaching time of 5.7 s and a coloring time of 1.3 s (sample size $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) than a single $3\text{WO}_3 \cdot \text{H}_2\text{O}$ layer device. Orthorhombic nanobrick $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films were obtained by using $(\text{NH}_4)_2\text{SO}_4$ as the capping agent, and a complementary device made up of the nanobrick $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film and PB film was also fabricated and demonstrates much faster coloration/bleaching response ($t_{\text{c}, 90\%} = 1.8 \text{ s}$, $t_{\text{b}, 90\%} = 3.7 \text{ s}$ for a sample size $\sim 1.7 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$), larger coloration efficiency value ($164.6 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm) and increased color contrast.

Moreover, a fast-switching negative photoelectrochromic (PEC) cell composed of dye-sensitized nanocrystalline TiO_2 and PB electrodes was fabricated. Adjustable grayscales were obtained by illuminating the cell with different light intensity and time. The photo bleaching response of the cell at 100 mW cm^{-2} is 6.2 s, and the EC response with a 2 V bias is about 600 ms for 70% transmittance change at 780 nm with coloration efficiency of $103.4 \text{ cm}^2 \text{ C}^{-1}$ (sample size $\sim 1.5 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$). This hybrid PEC cell shows good stability and can be potentially applied in erasable displays.

The photoelectrochemical (PE) properties of the porous WO_3 thin films consisted of sheet-like, wedge-like and plate-like nanostructures with the capping agents of $\text{CH}_3\text{COONH}_4$, $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 were also investigated. The sheet-like film grown using $\text{CH}_3\text{COONH}_4$ could generate anodic photocurrents of 1.15 mA cm^{-2} for oxidization of methanol and 0.5 mA cm^{-2} for water splitting, the highest photo conversion efficiency of about 0.3% can be obtained for water splitting under simulated solar illumination.

In summary, this dissertation addresses the fabrication and characterization of WO_3 or $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films grown with various capping agents using the hydrothermal methods. Single layer EC devices and complementary layer EC devices based on these films were assembled and their EC performances were investigated. The photoelectrochemical properties of the porous WO_3 films were also studied. And a PEC cell based on PB electrodes was fabricated and investigated. The work done demonstrates the promising applications of the nanostructured WO_3 or $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films and PB films in EC and photoelectrochemical devices.

LIST OF FIGURES

FIGURE 1-1 SWITCHING SEQUENCE OF AN EC LAMINATED GLASS.[6]	2
FIGURE 1-2. BASIC CONFIGURE OF SINGLE LAYER EC DEVICE. (A) WITH BARE ITO OR FTO AS A COUNTER ELECTRODE, (B) WITH AN IONS STORAGE LAYER AS A COUNTER ELECTRODE.	13
FIGURE 1-3. CONFIGURE OF A COMPLEMENTARY EC LAYERS DEVICES.....	14
FIGURE 3-1. SCHEMATIC CONFIGURATION OF THE PE CELL WITH A N-TYPE PHOTOANODE.	26
FIGURE 3-2. ENERGY LEVEL DIAGRAMS FOR A SEMICONDUCTOR METAL PE CELL. (A) NO CONTACT FROM THE INITIAL CONDITION; (B) EQUILIBRIUM IN DARK; (C) ILLUMINATED CONDITION AND (D) ILLUMINATED CONDITION WITH A BIAS VOLTAGE.[99]	27
FIGURE 3-3. ENERGY DIAGRAM OF A PE CELL FOR THE PHOTO-ELECTROLYSIS OF WATER. THE CELL IS BASED ON AN N-TYPE SEMICONDUCTING PHOTOANODE.[100].....	29
FIGURE 4-1. XRD PATTERNS OF BARE FTO AND AS-PREPARED WO ₃ THIN FILMS.	39
FIGURE 4-2. SEM IMAGES OF (A) WO ₃ MICRO-PARTICLES GROWN WITHOUT A SEED LAYER, (B) AND (C) THE AS-PREPARED WO ₃ THIN FILM. INSET OF FIGURE 4-2 (C) IS THE CROSS SECTIONAL SEM IMAGE. (D) HRTEM IMAGE OF A SINGLE WO ₃ BRICK-LIKE NANOSTRUCTURE.	40
FIGURE 4-3. TRANSMITTANCE SPECTRA OF THE EC DEVICE MEASURED AT 0 V, -1.0 V, -2.0 V, AND -3.0 V, RESPECTIVELY.	42
FIGURE 4-4. (A) CYCLIC VOLTAMMETRY (CV) CURVES OF THE WO ₃ THIN FILM AT THE 1ST AND 3000TH CYCLE. THE MEASUREMENT WAS PERFORMED IN 0.2 M LiClO ₄ / γ - BUTYROLACTONE WITH A SWEEP RATE OF 0.1 V/s. (B) CV CURVES RECORDED AT 5, 10, 25, 50, AND 100 mV/s, RESPECTIVELY. INSET OF FIGURE 4-4 (B) SHOWS THE CATHODIC/ANODIC PEAK CURRENT DENSITY AS A FUNCTION OF THE SQUARE ROOT OF THE SCAN RATES.....	43
FIGURE 4-5. CHRONOAMPEROMETRY (CA) OF THE WO ₃ THIN FILM, RECORDED WITH A POTENTIAL STEP OF ± 0.5 V FOR 50 s.	45
FIGURE 4-6. (A) OPTICAL DENSITY VARIATION WITH RESPECT TO THE CHARGE DENSITY (MEASURED AT 632.8 NM, -3 V BIAS). (B) SWITCHING TIME CHARACTERISTICS BETWEEN THE COLORED AND BLEACHED STATES FOR EC DEVICE MEASURED AT ± 3 V. (C) SWITCHING TIME CHARACTERISTICS FOR THE DEVICE MEASURED AT ± 1 V, ± 2 V AND ± 3 V, RESPECTIVELY.....	46

FIGURE 4-7. A WO ₃ -BASED EC DISPLAY AFTER BIASING AT +3 V (A) AND (B) -3V.	48
FIGURE 4-8. (A) XRD PATTERNS OF THE BARE FTO SUBSTRATE AND, THE AS-SYNTHESIZED FILMS GROWN WITH AND WITHOUT Na ₂ SO ₄ . (B) SCHEMATIC ILLUSTRATION OF THE 3WO ₃ H ₂ O STRUCTURE. (C) RAMAN SPECTRA OF THE FILMS. A: WITHOUT Na ₂ SO ₄ . B: WITH Na ₂ SO ₄ . (D) WIDE SCANNING XPS SPECTRA OF THE AS-FABRICATED NANOPLATE FILMS.....	49
FIGURE 4-9. (A) AND (B) FESEM IMAGES OF THE 3WO ₃ H ₂ O THIN FILMS GROWN WITH Na ₂ SO ₄ GIVEN UNDER DIFFERENT MAGNIFICATIONS. INSET OF (B): CROSS-SECTIONAL VIEW IMAGE. (C) TEM IMAGE OF THE NANOPLATE SCRATCHED FROM THE FILM. INSET: SAED PATTERN. (D) HRTEM IMAGE. (E) AND (F) FESEM IMAGES OF THE 3WO ₃ H ₂ O THIN FILMS GROWN WITHOUT Na ₂ SO ₄ GIVEN UNDER DIFFERENT MAGNIFICATIONS.....	51
FIGURE 4-10. A SCHEMATIC ILLUSTRATION OF THE FORMATION PROCESS FOR 3WO ₃ H ₂ O FILMS GROWN WITH AND WITHOUT Na ₂ SO ₄	53
FIGURE 4-11. (A) CV CURVES OF THE 3WO ₃ H ₂ O FILMS GROWN WITHOUT AND WITH Na ₂ SO ₄ IN 0.5M H ₂ SO ₄ SOLUTION, AT A SCAN RATE OF 0.1 V/S. (B) CHRONOAMPEROMETRY CURVES BY APPLYING PULSED POTENTIAL OF ±0.3 V, 30 s FOR EACH STATE. (C) CV CURVES OF THE FILM WITH Na ₂ SO ₄ AFTER THE 1ST, 1500TH AND 3000TH CYCLES. (D) UV-VIS TRANSMITTANCE SPECTRA OF THE PLATE-LIKE 3WO ₃ H ₂ O FILM BASED EC DEVICE UNDER 0, -0.1, -0.2 AND -0.3 V, RESPECTIVELY.	54
FIGURE 4-12. PHOTOGRAPHS OF THE EC DEVICE MADE UP OF THE NANOPLATE 3WO ₃ H ₂ O FILM UNDER 0, -0.1, -0.2 AND -0.3 V, RESPECTIVELY.	56
FIGURE 4-13. (A) SWITCHING TIME CHARACTERISTICS FOR BOTH FILMS MEASURED AT ±0.3 V AT 632.8 NM. (B) OPTICAL DENSITY VARIATION WITH RESPECT TO THE CHARGE DENSITY RECORDED AT 632.8 NM. (C) SWITCHING PROPERTIES OF THE NANOPLATE FILM UNDER ±0.1 V AND ±0.2 V AT 632.8 NM.	57
FIGURE 5-1. SCHEMATIC OF THE CONFIGURATION OF COMPLEMENTARY DEVICE.....	66
FIGURE 5-2. XRD PATTERNS (A) AND (B) TUNGSTEN 4F REGION XPS SPECTRA OF THE AS-SYNTHESIZED THIN FILMS GROWN WITH AND WITHOUT CH ₃ COONH ₄	67
FIGURE 5-3. FESEM IMAGES OF (A) AND (B) THE NANOBRICK 3WO ₃ H ₂ O THIN FILM GROWN WITHOUT CH ₃ COONH ₄ ; AND (C) AND (D) NANOSTICK/NANOPARTICLE FILM WITH CH ₃ COONH ₄ . INSETS: CROSS-SECTIONAL AND HRTEM IMAGE.	69
FIGURE 5-4. SCHEMATIC ILLUSTRATION OF THE FORMATION PROCESS OF THE AS-GROWN THIN FILMS.....	69
FIGURE 5-5. (A) XRD PATTERNS OF THE BARE FTO SUBSTRATE AND THE AS-SYNTHESIZED THIN FILMS. (B) WIDE SCANNING XPS SPECTRA OF THE AS-PREPARED NANOBRICK	

FILM. (C) RAMAN SPECTRA OF THE FILM. (D) SCHEMATIC ILLUSTRATION OF THE ORTHORHOMBIC $3\text{WO}_3 \cdot \text{H}_2\text{O}$ STRUCTURE.....	71
FIGURE 5-6. (A) AND (B) FESEM IMAGES OF THE H-WO_3 THIN FILMS UNDER DIFFERENT MAGNIFICATIONS. (C) TEM IMAGE OF THE NANOBRICK SCRATCHED FROM THE FILM. (D) SAED PATTERN OF THE NANOBRICK. (E) HRTEM IMAGE OF THE NANOBRICK.	72
FIGURE 5-7. (A) AND (B) SEM IMAGES OF THE PRODUCT GROWN WITHOUT SEED LAYER UNDER DIFFERENT MAGNIFICATIONS. (C) AND (D) THE PRODUCT GROWN WITHOUT ADDITION OF $(\text{NH}_4)_2\text{SO}_4$. (E) AND (F) THE PRODUCT GROWN WITHOUT ADDITION OF H_2O_2	74
FIGURE 5-8. A SCHEMATIC ILLUSTRATION OF THE FORMATION PROCESS FOR THE PRODUCTS.	77
FIGURE 5-9. SEM IMAGES OF THE PRODUCTS UNDER DIFFERENT MAGNIFICATIONS. (A) AND (B) 0.1 G $(\text{NH}_4)_2\text{SO}_4$; (C) AND (D) 0.4 G H_2O_2	77
FIGURE 5-10. (A) CYCLIC VOLTAMMOGRAMS (CVS) OF THE NANOSTICK/NANOPARTICLE AND NANOBRICK $3\text{WO}_3 \cdot \text{H}_2\text{O}$ FILMS IN γ -BUTYROLACTONE WITH 0.2 MOL LiClO_4 ; (B) AND (C) CVS OF THE NANOSTICK/NANOPARTICLE AND NANOBRICK FILM AT THE SCAN RATES OF 5, 10, 25, 50 AND 100 mV/s, RESPECTIVELY. INSETS: THE CATHODIC/ANODIC PEAK CURRENT DENSITY AS A FUNCTION OF THE SQUARE ROOT OF THE SCAN RATES; (D) CVS OF THE NANOSTICK/NANOPARTICLE FILM AFTER 1ST, 1000TH, AND 2000TH CYCLES, AND (E) CHRONOAMPEROMETRY (CA) CURVE OF THE AS-SYNTHESIZED FILMS RECORDED AT ± 0.5 V FOR 40S.	78
FIGURE 5-11. IN-SITU TRANSMITTANCE RESPONSE AND COLORATION EFFICIENCY AT 754 NM FOR THE NANOBRICK FILM (A AND B) AND THE NANOSTICK/NANOPARTICLE FILM (C AND D).....	82
FIGURE 5-12. FESEM IMAGES OF ELECTRODEPOSITED PB FILM.	84
FIGURE 5-13. CYCLIC VOLTAMMETRY (CV) CURVE OF PB FILM AT A SCAN RATE OF 50 mV s^{-1} WITH 0.2 M LiClO_4 IN γ -BUTYROLACTONE ELECTROLYTE.	84
FIGURE 5-14. OPTICAL ABSORPTION SPECTRA OF A COMPLEMENTARY EC DEVICE AND A SINGLE PB LAYER DEVICE AT THE COLORED AND BLEACHED STATE UNDER $\pm 0.8\text{V}$, RESPECTIVELY.....	85
FIGURE 5-15. (A) SWITCHING TIME CHARACTERISTICS BETWEEN THE COLORED AND BLEACHED STATES FOR THE COMPLEMENTARY EC DEVICE MEASURED AT ± 0.8 V FOR 30S AND (B) OPTICAL DENSITY VARIATION WITH RESPECT TO THE CHARGE DENSITY RECORDED AT 754 NM.	86
FIGURE 5-16. PHOTOGRAPHS OF A COMPLEMENTARY EC DEVICE AT THE BLEACHED STATE (A) AND (B) THE COLORED STATE UNDER $\pm 0.8\text{V}$, RESPECTIVELY.....	87

FIGURE 5-17. (A) CV CURVES OF AS-PREPARED H-WO ₃ FILM AND ELECTRODEPOSITED PB FILM, MEASURED IN 0.3 M LiClO ₄ Γ-BL ELECTROLYTE AT A SCAN RATE OF 0.1 V S ⁻¹ , AND (B) CV CURVES OF THE H-WO ₃ FILM AFTER 1ST, 1000TH AND 2000TH CYCLES.....	88
FIGURE 5-18. UV-VIS TRANSMITTANCE SPECTRA OF THE (A) COMPLEMENTARY EC DEVICE AND SINGLE PB LAYER DEVICE AND (B) THE SINGLE NANOBRICK FILM DEVICE AT BLEACHED AND COLORED STATE UNDER ±0.8 V, RESPECTIVELY.....	89
FIGURE 5-19. (A) SWITCHING TIME CHARACTERISTICS BETWEEN THE COLORED AND BLEACHED STATES FOR THE COMPLEMENTARY EC DEVICE AND (B) THE SINGLE H-WO ₃ FILM DEVICE UNDER ± 0.8 V AT 632.8 NM, RESPECTIVELY. (C) OPTICAL DENSITY VARIATION WITH RESPECT TO THE CHARGE DENSITY RECORDED AT 632.8 NM FOR THE COMPLEMENTARY DEVICE AND (D) SINGLE H-WO ₃ FILM DEVICE AT 632.8 NM.	91
FIGURE 5-20. PHOTOGRAPHS OF THE COMPLEMENTARY DEVICE AT BLEACHED STATE (A) AND (B) COLORED STATE. SINGLE H-WO ₃ LAYER DEVICE AT BLEACHED (C) AND (D) COLORED STATE UNDER ±0.8 V, RESPECTIVELY.	93
FIGURE 6-1. SCHEMATIC OF THE PROPOSED HYBRID PHOTOELECTROCHROMIC CELL.	99
FIGURE 6-2. (A) SEM IMAGES OF THE ELECTRODEPOSITED PB FILM. (B) CYCLIC VOLTAMMETRY CURVE OF PB FILM MEASURED WITH 0.2 M LiClO ₄ IN Γ-BUTYROLACTONE AS ELECTROLYTE AT ROOM TEMPERATURE WITH A SCAN RATE OF 100 mV/S FROM -1.2 TO 1.7 V.	100
FIGURE 6-3. SCHEMATICS AND PHOTOGRAPHS OF A PEC CELL WITH A 1.5 cm ² ACTIVE AREA. THE DURATION FOR ELECTRODEPOSITION OF PB FILM IS 300 s. (A) SCHEMATIC OF THE SHORT CIRCUIT CELL UNDER ILLUMINATION FOR BLEACHING. (B) THE BLEACHED CELL ACHIEVED BY ILLUMINATION OF 100 mW cm ⁻² FOR 1 MIN IN SHORT CIRCUIT CONFIGURATION. (C) SCHEMATIC OF THE CELL UNDER EXTERNAL VOLTAGE FOR COLORING. (D) PHOTOGRAPH OF THE CELL AT COLORED STATE AFTER APPLYING A 2 V BIAS AT PB ELECTRODE FOR 30 s. (E) AND (F) SPATIALLY RESOLVED BLEACHING STATES ACHIEVED BY ILLUMINATING THE CELL WITH MASKS.	104
FIGURE 6-4. ABSORBANCE SPECTRA OF THE PEC CELL AT BLEACHED STATE BY ILLUMINATION WITH A SIMULATED SOLAR INTENSITY OF 100 mW cm ⁻² FOR 1 MIN AND COLORED STATE BY APPLYING A 2 V BIAS AT THE PB ELECTRODE FOR 30 s. THE PB FILMS ASSEMBLED IN THESE CELLS WERE ELECTRODEPOSITED FOR (A) 100 s, (B) 300 s, (C) 500 s AND (D) 700 s, RESPECTIVELY.....	107
FIGURE 6-5. TRANSMITTANCE SPECTRA OF THE CELL BETWEEN BLEACHED AND COLORED STATE.	108

FIGURE 6-6. THE HAZE NUMBER OF THE PEC CELL AT BLEACHED STATE.....	109
FIGURE 6-7. (A) ABSORBANCE SPECTRA OF THE AS-PREPARED CELL AND ILLUMINATED WITH SIMULATED LIGHT INTENSITY LEVELS OF 5, 10, 20, 30, 40, 50, AND 100 MW CM ⁻² FOR 3 S IN SHORT CIRCUIT CONFIGURATION. (B) ABSORBANCE SPECTRA OF THE AS- PREPARED CELL AND ILLUMINATED WITH 5 MW CM ⁻² FOR 5, 10, 15, 20, 25, 30, AND 60 S RESPECTIVELY.	110
FIGURE 6-8. (A) IN-SITU TRANSMITTANCE RESPONSE OF THE CELL UNDER 100 MW CM ⁻² ILLUMINATION IN SHORT CIRCUIT CONFIGURATION AT 780 NM. INSET: TRANSIENT CURRENT CHANGES. (B) TRANSMITTANCE RESPONSE AT 780 NM UNDER 2 V BIAS. (C) CORRESPONDING CURRENT CHANGES OF THE COLORATION PROCESS. INSET: INTEGRATED CHARGE FOR COLORATION. (D) COLORATION EFFICIENCY CURVE OF THE PEC CELL RECORDED AT 780 NM WITH 2 V BIAS.....	112
FIGURE 6-9. OPTICAL TRANSMITTANCE CHANGE VERSUS TIME OF THE PEC CELL IN SHORT CIRCUIT UNDER DARK AND OPEN CIRCUIT UNDER ILLUMINATION, RESPECTIVELY. THE CELL WAS BLEACHED UNDER 100 MW CM ⁻² ILLUMINATION IN SHORT CIRCUIT CONFIGURATION FOR 100 S.	113
FIGURE 6-10. THE TRANSMITTANCE CHANGE (ΔT) AT 700 NM AS A FUNCTION OF CYCLE NUMBER OF THE PEC CELL, BLEACHED UNDER 100 MW CM ⁻² ILLUMINATION FOR 60 S AND COLORED BY ADDING A 2 V BIAS FOR 30 S.	114
FIGURE 7-1. SCHEMATIC ILLUSTRATION OF THE FILM FABRICATION PROCESS.....	118
FIGURE 7-2. XRD PATTERNS OF THE AS-SYNTHESIZED THIN FILMS PREPARED (A) WITHOUT ANY SALT ADDED, (B) WITH Na ₂ SO ₄ , (C) WITH (NH ₄) ₂ SO ₄ , AND (D) WITH CH ₃ COONH ₄ ADDED.....	120
FIGURE 7-3. (A) SEM IMAGE OF AS-SYNTHESIZED TUNGSTEN OXIDE HYDRATE FILM COMPOSED OF PLATE-LIKE NANOSTRUCTURES WITH Na ₂ SO ₄ AS CAPPING AGENT, (B) HIGHER- MAGNIFICATION SEM IMAGE (TOP VIEW), (C) CROSS SECTIONAL IMAGE OF THE FILM, AND (D) HRTEM IMAGE OF A SINGLE NANOPATE.	122
FIGURE 7-4. (A) AND (B) SEM IMAGES OF AS-SYNTHESIZED FLOWER-LIKE TUNGSTEN OXIDE HYDRATE PARTICLES WITHOUT SEED LAYER, (C) AND (D) AS-SYNTHESIZED TUNGSTEN OXIDE HYDRATE THIN FILM GROWN WITHOUT ANY SALT.	124
FIGURE 7-5. (A) SEM IMAGE OF AS-SYNTHESIZED TUNGSTEN OXIDE HYDRATE FILM COMPOSED OF WEDGE-LIKE NANOSTRUCTURES GROWN WITH (NH ₄) ₂ SO ₄ AS CAPPING AGENT. THE INSET SHOWS CROSS SECTIONAL IMAGE OF THE FILM. (B) HRTEM IMAGE OF A SINGLE NANOWEDGE. THE INSET OF FIGURE (B) SHOWS THE SAED PATTERN FROM A NANOWEDGE.	125

FIGURE 7-6. (A) AND (B) SEM IMAGE OF AS-SYNTHESIZED TUNGSTEN OXIDE HYDRATE FILM WITH SHEET-LIKE NANOSTRUCTURES GROWN WITH $\text{CH}_3\text{COONH}_4$ AS CAPPING AGENT AND (C) TEM IMAGES OF A SINGLE NANOSHEET. THE INSET OF FIGURE (C) SHOWS THE SAED PATTERN FROM A NANOSHEET. (D) HRTEM IAMGE.	126
FIGURE 7-7. SCHEMATIC OF THE SOL-GEL CONDENSATION POLYMERIZATION REACTION, CLUSTER CONDENSATION AND FORMATION PROCESS OF THE AS-SYNTHESIZED NANOSTRUCTURES.	129
FIGURE 7-8. XRD PATTERNS OF THE AS-SYNTHESIZED THIN FILMS WITH Na_2SO_4 AS THE CAPPING AGENT. (A) THE AS-PREPARED TUNGSTEN OXIDE HYDRATE THIN FILM, AFTER ANNEALING AT (B) 300, (C) 400 AND (D) 500 $^{\circ}\text{C}$ FOR 30 MIN, RESPECTIVELY	130
FIGURE 7-9. SEM IMAGES OF AS-SYNTHESIZED FILMS AFTER ANNEALING AT 500 $^{\circ}\text{C}$ FOR 30 MIN. (A) GROWN WITHOUT ANY SALT, (B) WITH Na_2SO_4 , (C) WITH $(\text{NH}_4)_2\text{SO}_4$ AND (D) WITH $\text{CH}_3\text{COONH}_4$	130
FIGURE 7-10. THE UV-VIS ABSORPTION SPECTRA OF THE AS-SYNTHESIZED FILMS GROWN (A) WITHOUT ANY SALT, WITH Na_2SO_4 (B), (C) $(\text{NH}_4)_2\text{SO}_4$ AND (D) $\text{CH}_3\text{COONH}_4$ AS CAPPING AGENTS, RESPECTIVELY.	132
FIGURE 7-11. CURRENT-POTENTIAL SCANS OF AS-SYNTHESIZED FILMS MEASURED IN DARKNESS AND UNDER SIMULATED SOLAR SPECTRUM IN A 1M H_2SO_4 SOLUTION CONTAINING 0.1M METHANOL.	133
FIGURE 7-12. (A) CURRENT-POTENTIAL SCANS OF FILMS GROWN WITH $\text{CH}_3\text{COONH}_4$ AS CAPPING AGENT MEASURED IN DARKNESS AND UNDER SIMULATED SOLAR SPECTRUM IN A 1M H_2SO_4 SOLUTION AND (B) PHOTOCONVERSION EFFICIENCY.	135
FIGURE 7-13. SCHEMATIC OF THE BAND DIAGRAM OF WO_3 PHOTO-ANODE AND OPERATION OF THE PHOTOELECTROCHEMICAL CELL. THE ELECTROLYTE IS 1 M H_2SO_4 SOLUTION.	137

LIST OF TABLES

TABLE 1. PHOTOELECTROCHROMIC CELLS WITH DIFFERENT THICKNESSES OF PB FILMS AND CORRESPONDING ABSORBANCE MODULATION AT 700 NM	105
--	-----

CHAPTER 1 ELECTROCHROMIC DEVICES

1.1 Introduction

The depletion of fossil energy and climate change due to global warming nowadays has attracted intensive attention that numerous efforts have been focused on combating these urgent issues. The development of nanotechnology brings human beings new opportunities to resolve the above problems. Various green energy techniques are being developed to enrich the energy contribution besides fossil energy, such as the utilizations of solar energy, wind energy, tide energy and so on.[1,2] And some energy efficient techniques based on nanotechnologies have been carried out to save more energy. According to the study by the United Nations Environment Program, around 30 to 40% primary energy is consumed in a conventional building,[3] mainly for temperature regulation, ventilation and lighting. In particular, the energy demand for air conditioning is still increasing, which has accounted for the peak power demand in the summer.[4]

Utilization of EC technique-based ‘smart windows’ could significantly save energy by reducing the cooling loads in buildings. Moreover, the EC smart windows could also provide more comfort by decreasing the glare and more safety for people in the interior building.[5]

Figure 1-1 Switching sequence of an EC laminated glass.[6]

Electrochromics refers to the effect that certain materials undergo reversible variations in their optical spectra upon electron-transfer or redox reactions when an external voltage is applied with varying polarities.[7-12] Materials with this property are called ‘EC materials’. Intense interests have been attracted since the discovery of EC effects in some materials, resulting in various developments in the theory and technology of this field.[13] Various promising applications have been proposed, such as architectural ‘smart windows’, antiglare rear-view mirrors, protective eyewear, controllable aircraft canopies, optical iris for a camera lens and some display devices and so on.[14-19] In the future, more applications may appear with the improvement of device performance.

Up to now, a lot of materials with EC properties have been reported. According to the intrinsic composition properties, these materials can be mainly divided into two categories: inorganic EC materials and organic EC materials. The inorganic EC materials are mainly composed of transition metal oxides and metal hexacyanometallates (Prussian blue, et.al), while the organic EC materials mainly include viologens, conjugated conducting polymers (such as polypyrrole, polythiophene, polyaniline and their derivatives), metallopolymers and metal

phthalocynines.[19-24] In general, the organic EC materials show faster response time, multiple colorism and higher coloration efficiency (CE) than the inorganic ones, but with poorer anti-ultra violet (UV) degradation ability. As a result, the organic EC materials based devices are more promising for application in electronic non-emissive displays. On the other hand, devices based on the inorganic EC materials are more durable and stable for thousands repetitions of coloration/bleaching under various environments, making them suitable for applications in large area architectural windows and information displays for which response time up to several minutes are endurable. Although a lot of materials exhibiting the EC characteristics, only those with beneficial properties are promising in real applications.

A simple classification system of the EC materials is also reported by Chang in 1975. In this classification system, according to the solubility of redox state during operation, the EC materials can also be divided into three types.[19,25] For type I and type II, EC materials are both or either soluble in the redox states, such as prototype viologen, heptyl viologen, et.al. Type III EC materials are solid for both redox states, such as WO_3 , conjugated conducting polymers, Prussian blue and metallopolymers. Fabrication of thin films of such kind of materials in EC devices makes it possible to regulate the optical properties such as transmittance (T), reflectance (R), absorbance (A) and heat through reversible color changes when an external potential is added. This work will focus on fabrication of thin films of this kind of EC materials and investigate their EC properties, such as WO_3 and Prussian blue.

1.1.1 Electrochromic materials

Since the report of electrochromism of WO_3 in the late 60s, more and more materials have been investigated and shown EC properties, such as transition metal oxides, Prussian blue, viologen, conjugated conducting polymers and metallopolymers, et.al.[19,21] Although their EC mechanisms are different, all of these materials can regulate the optical spectrum. And the device performance is highly related to the structures, morphologies, film assembling techniques of the EC materials.

1.1.1.1 Transition metal oxides

Transition metal oxides are a large class of materials showing EC property, including tungsten oxides, iridium oxides, vanadium oxides, molybdenum oxides, rhodium oxides, manganese oxides, cobalt oxides, et.al.[26] Most of the EC colors of these materials derive from optical absorption transitions due to the intervalence charge-transfer during the redox reactions. To establish the applications, these EC materials have to be deposited into thin films by various techniques such as thermal evaporation,[27] sputtering,[28] electroplating,[29] chemical vapor deposition (CVD),[30] sol-gel,[31] spray deposition,[32] et.al. Using the vacuum deposition methods, the thickness and composition of the as-prepared films can be precisely controlled in a large scale and the films show good uniformity and stability. However, particular costly equipment is needed to realize the fabrication process. In this regard, wet chemistry methods are more cost effective for large scale deposition of the EC films. Moreover, the density, thickness, composition, crystal

and structure feature sizes can be tailored as required by varying the experimental parameters.

(1) Tungsten oxide

Among all the EC materials, WO_3 is mostly studied for its excellent EC properties, such as the high optical contrast, coloration efficiency and good memory effect.[33] And it remains until now the most promising EC material for applications in smart windows. At normal state, stoichiometric WO_3 thin films are almost transparent with all W sites in W^{6+} oxidation state. When a cathodic voltage is applied, it will be reduced to non-stoichiometric W^{5+} state by insertion of small ions (H^+ , Li^+ , etc). This electronic intervalence charge transfer causes intense optical absorption and the film displays deep blue color.[33] And its ‘empty-perovskite’ type cubic structure provides the interstitial sites for the inserted guest ions.[34] Although detailed EC mechanism of the WO_3 is still controversial, it is generally thought that this effect is related to the redox reactions, caused by the injection and extraction of electrons and cations (H^+ , Li^+ , etc) and shown as the following equation:

The intercalation of cations into the film is carried out by a diffusion process. The film reversibly shows blue and transparent during this process due to the transition between W^{6+} to W^{5+} states.[34]

Recently, a major application of WO_3 EC device is in the ‘smart windows’ for control of the heat gains within the building through reversible color changes. Thereby, more energy will be saved for the buildings due to the reduction of air

conditioners used for cooling loads. Many glass manufacturers have recognized this opportunity of EC windows for vast market need, and great efforts have been carried out to fabricate large scale, reliable and cost-effective products. For example, SAGE Electrochromics uses WO_3 film as the EC materials and has produced EC windows suitable for building application.[26] These EC windows have a size up to $108 \times 150 \text{ cm}^2$ and durability more than 100,000 cycles. The WO_3 EC films are deposited on transparent conductive glasses using sputtering technique.

With the development of the nanotechnology, a lot of research works on fabricating a reliable and cost-effective WO_3 EC film are ongoing at many research groups and various new developments are reported. Santato et al. described the synthesis and characterization of WO_3 nanoparticles.[35] Modified electrodes by using these nanoparticles obtained coloration efficiencies of $40 \text{ cm}^2 \text{ C}^{-1}$ and high durability of more than 10,000 cycles. Deepa et al. reported the formation of mesoporous WO_3 electrodes (5-10 nm) with response times of 2-3 s and coloration efficiency of $90 \text{ cm}^2 \text{ C}^{-1}$. [9] Lee et al. reported crystalline WO_3 nanoparticles that prepared by a hot-wire chemical-vapor-deposition method, and the WO_3 nanoparticles were assembled into porous nanoparticle film by an electrophoresis technique.[36] It is found that the inserted cathodic charge for WO_3 nanoparticles was about $32 \text{ mC cm}^{-2} \text{ mg}^{-1}$, compared with $3 \text{ mC cm}^{-2} \text{ mg}^{-1}$ and $9 \text{ mC cm}^{-2} \text{ mg}^{-1}$ for crystalline and amorphous films, respectively. The cycling stability of the WO_3 nanoparticle film in $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ shows no obvious degradation even after 3000 cycles, indicating good stability of this film. Although great achievement of

WO₃ in EC devices has been obtained, more work still need to be done to reduce the cost and improve the performance.

(2) Nickel oxide

Nickel oxide (NiO) is an anodically colored EC material with the color changing between transparent and brown upon charge insertion/extraction according to the following reactions:

The electrochromism of NiO is believed to be a surface effect due to the surface oxygen excess. During the redox reactions, the coloration results from the transformation of the over-stoichiometric hydrated Ni oxide to hydroxide and oxy-hydroxide.[5] The NiO usually acted as a complementary electrode with a cathodically colored WO₃ electrode in EC devices. The brown color of NiO is complementary to the blue color of WO₃, both together yielding a neutral (grey) color in the dark state, and both electrodes are transparent at bleached state. Moreover, its EC properties can be further improved by mixing with other wide bandgap metal oxides such as MgO or Al₂O₃. [37,38]

(3) Other metal oxides

Many other transition metal oxides also show EC properties, such as iridium oxide (IrO₂ and Ir₂O₃), [39,40] molybdenum oxide (MoO₃), [41] vanadium oxide (V₂O₅) [42] and niobium oxide (Nb₂O₅). [43] For the MoO₃, V₂O₅ and Nb₂O₅, a more intensely absorbing state is obtained on reduction, combining the cathodic ions insertion according to the following equations:

In contrast, iridium oxide becomes colored on electrochemical oxidation with anodic ion-insertion.

1.1.1.2 Metal hexacyanometallates

Transition metal hexacyanometallates are also an important class of EC materials including Prussian blue (PB) and its derivatives. They are mixed-valence compounds with a general formula $\text{M}'_z[\text{M}''(\text{CN})_6]_n$ (z, n integral), where M' and M'' are transition metals with different oxidation states that result in charge/electron transfer between them, leading to the optical absorption differences.[34] For PB, the transition metal M is iron (Fe), and it is ferric ferrocyanide. The two states of Fe^{2+} and Fe^{3+} are coupled by a cyanide bridge: $\text{Fe(III)}-\text{N}\equiv\text{C}\equiv\text{Fe(II)}$. The electrochromism of PB may be described as the following equation:

The electrochemical reduction and oxidation of PB can lead to the ‘Prussian white’ and ‘Prussian green’, respectively.[34] Over oxidation will lead to the formation of “Prussian yellow”, which shows poor reversibility. To get a good stability, proper voltage range should be adopted to switch the film from PW and PB.

To date, two kinds of methods are used to deposit PB film on electrode. Electrodeposition has proved to be the most efficient way to fabricate PB film on

electrode.[44,45] The electrochemical deposition reaction of PB film can be shown by below equation:

The as-deposited PB film shows a color changing from blue to transparent when reduced by a proper voltage.

Apart from the electrodeposition method, water or organic solvent-dispersible PB nanoparticle ink was synthesized by wet chemical process and reported by Hara and Sakamoto.[46] By surface modification with $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ anions and oleylamine molecules, water dispersible and organic solvent dispersible PB nanoparticle ink can be prepared, respectively. This technology has the advantages of low cost and easiness to scaling up by conventional coating and printing methods, such as spin coating and dip coating. The obvious color changes from blue to transparent of the PB thin film fabricated by spin coating method is obviously observed at potentials between +0.6 to -0.4 V. The response time and optical contrast depend on the film thickness and can be improved by optimization of configurations of the actual devices. The film's thickness can be controlled by varying the ink concentration and spinning rate. It is observed that such PB film endures at least beyond 10000 repetitions, indicating an excellent cyclic stability.[46] Moreover, various patterns of PB film could be achieved by photolithography, indicating potential application in information displays and smart windows. Since PB is a cathodically colored EC material, it is a suitable complementary EC electrode to WO_3 film. This complementary device shows improved optical contrast, switching stability and coloration efficiency.

1.1.1.3 Polymer electrochromics

Besides the inorganic EC materials there are also organic polymers with EC properties, and these EC polymers normally possess much faster response time and multiple colorism.[19,21,22,34,47] These polymers can be assembled into thin film on the electrode by various facile and cost effective coating methods. However, most of these EC polymers show poor UV degradation stability and are hence less likely for energy-related applications in EC windows. Due to their fast switching response and high coloration efficiency, they are promising in electronic display applications. Many different polymers have been investigated on their electrochromism, including viologens,[17,48] polyaniline (PANI),[49,50] poly (3, 4-ethylene-dioxythiophene) (PEDOT),[51] etc.

➤ Viologen

Viologen belongs to the family of 4, 4'-dipyridinium compounds that can have one electron or two electron reduction states. In recent years, the viologens or their derivatives are modified with an anchoring group (usually phosphate) and one monolayer is absorbed on nanocrystalline titanium oxide (TiO_2) particle electrode.[17] The viologen is colorless after oxidation, while the radical cation can display blue, violet, purple or green. The redox potential of multicolor electrochromophore lies above the conduction band edge of the semiconductor so that electrons can be transferred from the conduction band to the molecule reversibly. The semi-conductor behaves like a conductor for the adsorbed electroactive species. It is reported that the EC devices composed of viologen can

be switched from white to dark blue in less than 1 s,[17] and the work on this topic is still in progress.

➤ Conjugated conducting polymers

Conducting polymers can be prepared through chemical or electrochemical polymerization of various aromatic molecules such as aniline, pyrrole, furan, thiophene, etc.[22] They can be oxidized and “doped” with counter anions, possessing a delocalized π -electron band structure, and the intrinsic optical and electrical properties of these materials are determined by the energy gap (E_g). Hence, the optical properties can be turned by the introduction of new states in the band gap by doping. The widely known examples are polypyrrole, polyaniline and polythiophene.[34]

1.1.2 Transparent conductors

All EC devices require at least one optically transparent conductive electrode which is normally composed of an optically transparent and electrically conducting film deposited onto glass or polyethylene terephthalate (PET).[19] To date, the most widely used transparent conductors are tin doped indium oxide ($\text{In}_2\text{O}_3:\text{Sn}$, ITO) and fluorine doped tin oxide ($\text{SnO}_2:\text{F}$, FTO), which are generally doped semiconductor oxides. Recently, the metal nanowire mesh transparent electrode has attracted intense interests.[52] The electrode made up of random meshes of metal nanowires exhibits an optical transparency equivalent to or better than ITO electrode for the same sheet resistance, which already has been applied in organic solar cells. Moreover, more and more alternatives are proposed, such as PEDOT,[53] carbon nanotubes (CNTs)[54] and grapheme.[55]

1.1.3 Electrolyte layers

The electrolyte layer in an EC device must be an ionically conductive layer to support the ions transportation process. And it also should be highly transparent and low volatile.[19] A lot of reported EC devices use inorganic solid compound or semisolid organic polymers as electrolyte. Various solid inorganic materials are investigated, such as Lithium Niobate (LiNbO_3)[56]; Magnesium Fluoride (MgF_2)[57] and hydrogen uranyl phosphate tetrahydrate[58]. For the semisolid organic electrolytes, they can be divided into two categories: polyelectrolytes and polymer electrolytes.[59,60] Polyelectrolytes molecules contain ion-labile moieties periodically along their backbone that determines their ionic conductivity. Polymer electrolytes are normally a mixture solution of ions conducting salts usually Li^+ ion salts (LiClO_4 , LiPF_6 , etc) and polymer molecules such as poly (ethylene oxide) and poly (propylene glycol), etc. The viscosity of such polymers increases with molecular weight. For research purpose, some liquid form electrolytes are used to investigate the performances of the EC materials. These electrolytes are mixture solutions of some organic molecular solvent (propylene carbonate, γ -butyrolactone) and Li^+ containing salts.

1.1.4 Device structure and operation principles

The EC devices is a multi-layer structure, containing two transparent conductive layers as electrodes (mostly ITO or FTO), one or two EC layers and one electrolyte layer filled between the two electrodes. They can be mainly divided into two configures, single EC layer configure and complementary EC layers configure.

(1) Single EC layer device

Most EC devices includes one single EC layer, such as WO_3 , PB, et al. The counter electrode is used either bare ITO or FTO layer or one ion storage layer.[46,61,62] The device structures are shown as below:

Figure 1-2. Basic configure of single layer EC device. (a) With bare ITO or FTO as a counter electrode, (b) with an ions storage layer as a counter electrode.

The EC layers change their optical properties reversibly when an external bias voltage is added with changing polarities, during which process redox reactions and electron injection/extraction are undergoing. The electrolyte used maybe varied case by case. For the liquid form electrolytes, they usually consist of polymer solution containing ions salt (Li^+ , H^+). However, due to the leakage problem and evaporation of liquid electrolyte during device sealing, solid electrolyte have attracted more and more efforts.[63,64] For the EC devices with bare ITO or FTO counter electrode, the electrolyte layers serves as both the ionic conductive layer and storage layer. To improve the stability and lifetime of the device, ions storage layer (CeO_2 coating TiO_2) has been reported for counter electrode.[62]

(2) Complementary EC layers device

The complementary EC devices are normally composed of two EC layers, one anodically colored and one cathodically colored that undergo a simultaneous coloring or bleaching process.[15,64,65] Compared to the single EC layer device, a complementary EC device has the advantages of increased coloration efficiency, optical contrast and cycling stability. For this dual-layer device, the effective range of voltages for the anodically colored material must have overlap with the cathodically colored material to realize the complementary coloring/bleaching process. The device configure is shown in Figure 1-3:

Figure 1-3. Configure of a complementary EC layers devices.

Up to date, there have been various reports on complementary EC devices such as $\text{WO}_3\|\text{PB}$, [15,65] $\text{WO}_3\|\text{NiO}$, [66] $\text{WO}_3\|\text{Polyaniline}$, [67] $\text{PB}\|\text{poly(ProDOT-Et-2)}$, [68] etc.

When an external voltage applied to the electrodes, the ions in the electrolyte will be driven to insert into/extract from the EC layers, to keep electronic neutrality, electrons are moving to the EC layers through the external circuit which leads to redox reactions at the EC layers. Electrochromism of the EC devices will be observed during this process. And the process is reversible when the polarity of the external voltage is changed reversibly.

Main parameters to evaluate the EC performance:

There are several critical parameters to evaluate the performances of the as-prepared EC films, including cyclic or switching stability, response time, transmittance regulation and CE.

(I) The cyclic or switching stability indicates the long term stability of the EC layers which is critical to evaluate the lifetime of the EC devices. For the commercial applications, the EC devices should have the switching times as long as possible to compensate its cost.

(II) The response time is used to evaluate the switching response of the EC devices, which is largely dependent on the intrinsic materials properties and EC mechanisms. For example, the organic polymer EC materials commonly have faster responses than the inorganic transition metal oxides. Hence, they are more suitable for electronic display applications, while the transition metal oxides (WO_3 , NiO) are preferred to be applied in large area “smart windows” on which several minutes can be tolerated for the switching. For the same EC material, the layer with a higher porosity processes a faster response because of the reduced diffusion length of the ions.

(III) The optical contrast of the EC devices can be assessed by the transmittance regulation between the colored and bleached state, mostly refers to the visible range. This performance is related to the EC layers’ thickness and external bias voltage. The EC layer with larger thickness has low transmittance at bleached state, and a larger bias voltage may lead to deeper colored state but may deteriorate the reversible stability.

(IV) The coloration efficiency (CE) is a critical parameter to evaluate the EC performance of the materials. It represents the change in the optical density (OD) per unit charge density (Q/A , where Q is the charge and A is the film area) and can be calculated according to the formula: $CE = \Delta OD / (Q/A)$, where $\Delta OD = \log(T_{\text{color}}/T_{\text{bleach}})$. A high CE indicates a larger optical contrast can be obtained for specific amount of charge. It is highly related to the crystal size and porosity of the EC layers.

In conclusion, all the parameters are highly related to the intrinsic materials properties, morphologies, porosity, crystal sizes and defects of the EC layers, which depend largely on the film assembling techniques.

1.2 WO_3 film assembling techniques

To date, various WO_3 film assembling methods have been reported including vacuum methods (sputtering, thermal evaporation), CVD, electrodeposition, anodization, spray pyrolysis and wet chemistry methods (sol-gel, hydrothermal, dip coating), etc. Vacuum deposition technologies can deposit dense WO_3 films with flat surface on substrate in a large scale.[69,70] The as-deposited films are normally amorphous, and crystalline structure could be obtained after annealing. The thickness and the composition of the as-prepared films can be precisely controlled. However, these technologies are usually costly due to the expensive equipment. In spite of their high cost, the vacuum techniques are still preferred to deposit WO_3 films by many glass companies because the films as-prepared are stable, reliable and controllable. CVD can also be used to deposit

WO₃ films on various substrates.[71,72] However, during the deposition, substrates are heated to a high temperature, which may lead to increased resistance of the conductive layer. Electrodeposition methods have been reported to fabricate WO₃ films on conductive substrate in a large scale.[15,65] However, specific facility for the deposition process is needed. Sol-gel processing following dip-coating or screen-printing can deposit thin film coatings on large areas with lower cost than conventional vacuum methods, and hence offers a possible solution for reducing the cost of these devices.[73] Moreover, they also offers advantages in controlling the microstructures, crystal sizes, porosity and composition of depositing films, which may influence the kinetics, durability and coloration efficiency of the EC electrode.[74,75] However, much attention has to be paid on the stability of the precursor solution and it still remains a big challenge to deposit crack-free uniform coatings on large-area with good adhesion and desired thickness. Spray-pyrolysis is another cost-effective method to deposit uniform WO₃ films with various microstructures and good adhesion. Suvarna and Pail reported a fibrous reticulated WO₃ film prepared by pulsed spray-pyrolysis method, the CE is found to be 34 cm² C⁻¹ at 630 nm.[76] Besides the methods mentioned above, hydrothermal approach is another promising and cost-effective way to fabricate uniform WO₃ films with tailored microstructures and good adhesion.[77] Moreover, this method has the merits of low reaction temperature, flexible substrate selection, and easiness to scale-up. Recently, to directly assemble uniform and well adhesive WO₃ films on ITO/FTO still remains a challenge and there have been few reports on the EC characteristics of hydrothermally grown WO₃ films.

1.3 Summary

EC devices can regulate the optical properties through reversible color changes, which can be applied in smart windows, anti-reflection mirrors, protective eyewear, etc. Moreover, the heat indoors can also be tuned, which can reduce the energy consumption by air-conditioners. As a well-known and most studied EC material, WO_3 has shown EC properties such as high color contrast, good memory effect and high CE value. And the EC properties are highly related to the film properties such as structure sizes, film morphologies and porosity, which are determined by the assembling techniques. Among various reported methods, hydrothermal has the merits of low cost, simple and easy to scale-up. To directly grow uniform and good adhesive nanostructured WO_3 films on conductive substrates still remains a challenge. Moreover, there are few reports on the EC properties of hydrothermally grown WO_3 films. Hence, we set out goal to assemble WO_3 films on FTO substrate using the hydrothermal methods in this dissertation. The structures, morphologies and EC performances of as-grown WO_3 films will be investigated by various characterizations and discussions will be carried out.

CHAPTER 2 PHOTOELECTROCHROMIC DEVICES

2.1 Introduction

To date, technologies regarding renewable energy and energy saving have become significantly important due to the depletion of fossil fuels and the climate change from global warming. Smart windows that can control the light transmittance and heat gain of the interior buildings have received intensive attention because of their energy saving functions such as reduction in cooling loads.[16,26,78] With these windows, the number of air-conditioners can be significantly reduced. This important characteristic makes them ideally suitable for applications in buildings, automobiles, sunglasses and aircrafts. Electrochromic or photochromic devices that can reversibly regulate light transmittance in response to an external bias voltage or illumination are commonly used in smart windows.[79] Besides these two kinds of devices, photoelectrochromic (PEC) devices can modulate the optical properties by reversible color changes utilizing photo energy, in which process redox reactions are taking place by the insertion/extraction of ions and electrons. In 1996, PEC cell was firstly reported and demonstrated by Bechinger and Gregg.[80] Since then, this technology has attracted more and more interests.

2.2 Device structure and operation mechanism

Since the first report of PEC device by Bechinger in 1996, various efforts have been executed to improve the device performances, including the application of new materials and developments on the device structures. Compared with the

EC techniques, the PEC devices are more energy efficient since the light energy (including the solar energy) can be used to generate color changes.

Up to date, the structures of the PEC devices can be divided into two main categories according to whether the EC layer and light active layer are at one side or separated by the electrolyte layer. For the mostly reported PEC devices, the EC layer is separated from the light sensitive layer, and ionic conductive electrolyte is filled between the two electrodes.[80,81] The light active layer is commonly composed of nanocrystalline TiO_2 layer decorated with a layer of the light sensitive dyes, and the EC layer is at the counter electrode and electrolyte layer containing ionic conducting salts is filled in between the two electrodes. It is a combination of a Grätzel photovoltaic cell and an EC electrode separated by a conductive electrolyte. In the electrolyte, the cation species (Li^+ , for example) is used for charge compensation in the EC material, and the anion species (a redox couple I^-/I_3^-) is used for dye regeneration. Under illumination, the dyes molecules absorb the photon energy and get excited, the electrons at the lowest unoccupied molecular orbital (LUMO) of dyes can inject to the conduction band of the semiconductors (usually TiO_2). In short circuit configuration, the electrons will transport to the counter EC layer electrode through the external circuit, and the cations in the electrolyte will be driven to insert into the EC layer to maintain its electric neutrality. The electrons injected to EC layers cause change in color and regenerate I^- .

Under illumination, photoelectrons generated by the dye molecules migrate through the TiO_2 nanoparticle layer to the WO_3 counter electrode via an external

circuit, and the Li^+ ions in the electrolyte insert into WO_3 EC layer to form dark blue $\text{Li}_x\text{WO}_{3-x}$. The colored cell can be bleached in dark state in a short circuit configuration, but the bleaching rate is very slow.

The reactions during the above processes are:

1) dye excitation (S) by photons and generation of electrons:

2) dye regeneration:

3) iodide regeneration:

4) reduction of tungsten oxide

5) balance

Recently, Wu's group improved the cell performance by modifying the cathode using a patterned WO_3/Pt EC electrode, showing both photoelectrochromic and photovoltaic characteristics.[12] Under illumination, the cell can be colored in short circuit configuration with tunable transmittance and it can be bleached much faster when the circuit is opened (~ 60 s). The fast bleaching process is attributed to charge transfer pathways provided by the patterned WO_3/Pt EC electrode. For above cases, WO_3 is adopted as EC electrode, the coloration is attained by the photo-electron conversion and bleaching by self-discharging; there is no need for external power sources.

Different device configurations have also been proposed to accelerate the bleaching process.[82,83] In one of them, the WO_3 layer was placed between the transparent conducting oxide FTO and the dye-sensitized TiO_2 photoanode, with a layer structure of FTO/ WO_3 / TiO_2 -dye/electrolyte/Pt/FTO. It is reported that the bleaching process can be accelerated from one day to 10 min.

2.3 Electrochromic materials in PEC devices

To date, a lot of EC materials have been reported for applications in PEC devices. WO_3 has been the most studied EC materials in applications of PEC devices due to its good stability, large optical contrast and high coloration efficiency.[12,14,80-83] Other materials such as $\text{TiO}_2-x\text{N}_x/\text{NiO}$,[84] or poly(3,4-alkylenedioxythiophene) (PEDOT)[85] in PEC devices have also been reported. Prussian blue (PB) is another well-known material with excellent EC properties such as fast switching response and good cyclic stability. However, there have been few reports about PB in applications of PEC devices.

2.4 Summary

PEC devices are the combination of photovoltaic and EC devices that can provide better efficiency in energy saving, for PEC device can achieve color change by application of the light energy. In short circuit configuration, the PEC device under illumination by suitable light wavelength and intensity can generate color changes. The reversible process can be performed by either self-discharging in open circuit or adding an external bias voltage. Due to their energy saving properties, the PEC devices may find application in smart windows on buildings to

regulate the light and heat gain. To date, various EC materials, device configurations and electrolytes have been reported. However, there have been few reports on using PB as the EC layer in PEC devices. PB is an anodically colored EC material, hence the PEC device based on PB will be bleached under illumination, rather than WO_3 ones that getting colored by illumination.

CHAPTER 3 PHOTOELECTROCHEMICAL DEVICES

3.1 Introduction

Since the first report of photo water splitting to produce hydrogen and oxygen using titanium oxide (TiO_2) by Fujishima and Honda in 1972,[86] intensive efforts have been focused on improving the efficiency in a photoelectrochemical (PE) cell for an inexpensive way to produce clean energy.[87] The major attention in photo water splitting research have been put on developing a robust, efficient, cost effective and stable PE system. The photo corrosion stability, optical wavelength response, electronic properties (conductance, carrier mobility and life time) are the key characteristics for evaluating the photo electrode materials. Among various photo active electrode materials, metal oxides are cost effective and stable photoanode materials. The most widely studied metal oxide photoanode materials are TiO_2 , SrTiO_3 , WO_3 , SnO_2 , ZnO , BiVO_4 and Fe_2O_3 , etc.[87-95] However, no semiconductors have been reported to realize the photo water splitting process efficiently without external bias voltage assistance, although they may have theoretically suitable bandgaps that larger than 1.23 eV, which is the minimum potential energy for the photo water splitting reaction. It is found that the narrower band gap photo sensitive materials can absorb most of the visible spectrum but have poorer photo corrosion stability than the wider band gap materials. Various efforts including the bandgap modifications by doping with various foreign elements have been addressed to resolve the problems.[88,96-98]

3.2 Basic principles

3.2.1 Prototype of the photoelectrochemical cell

The function of PE cell is to produce clean energy in the form of hydrogen and oxygen by transferring the absorbed solar light energy to chemical energy through water splitting. To realize this process, the photo active metal oxide materials are usually deposited onto the conductive substrates as thin films, so called photoanode. The counter cathode is either a metal sheet (usually Pt) or a complementary photocathode, and electrolyte is filled between these two electrodes. The device structure is schematically shown in Figure 3-1. When the cell is under illumination, solar light energy is harvested by the semiconductor photoanode, and electrons can be pumped from the valence band to conduction band by utilization of the photo energy to generate hole and electron pair (e^-h^+), which are delivered to the electrolyte to reduce or oxidize the water or some sacrificial agents in the electrolyte. The photons causing such a transition have a specific wavelength with energy equal to or greater than the bandgap of the photoelectrode. The generated e^-h^+ pair then get separated due to the built-in electrical field and move to the interface and counter electrode, respectively. However, the life time of the excited carriers is quite short (from nanoseconds to milliseconds) in liquids and the e^-h^+ may recombine very quickly with the emission of heat or photon. To avoid this problem, the separation of the e^-h^+ pair must be efficiently achieved before they get recombined.

The overall reaction for water splitting is:

Figure 3-1. Schematic configuration of the PE cell with a n-type photoanode.

3.2.2 Semiconductor electrolyte interfaces

In this dissertation, the semiconductor-electrolyte interface discussed will refer to a n-type semiconducting photoanode immersed in an electrolyte with a metal electrode as the counter cathode.

Figure 3-2 shows the semiconductor-electrolyte interface under various conditions.

Figure 3-2. Energy level diagrams for a semiconductor metal PE cell. (a) No contact from the initial condition; (b) equilibrium in dark; (c) illuminated condition and (d) illuminated condition with a bias voltage.[99]

In a PE cell, the photoelectrode is in direct contact with the electrolyte, where a depletion region near the semiconductor surface is formed. The metal cathode is connected through an external circuit. Figure 3-2 E_g corresponds to the bandgap of the photoanode, E_F corresponds to the fermi level and V_B refers to the band bending at the interface. The flat band potential, U_{fb} is the potential of the semiconductor at equilibrium. V_{bias} is the bias voltage applied to the cell. When the photoanode and the metal cathode are not connected, equilibrium between the metal cathode and the electrolyte will be established. At this state, the E_F of the electrolyte and metal are the same (shown in Figure 3-2(a)). When the connection is established, to reach E_F equilibrium between the photoanode semiconductor and

the electrolyte (the same with the metal cathode), electrons will flow from the semiconductor to the electrolyte. This process will create a depletion layer and a band bending of V_B is formed (Figure 3-2(b)). A very thin (< 1 nm) so called Helmholtz layer will be formed between the photoelectrode and electrolyte. The potential drop across the Helmholtz layer $V_{\text{Helmholtz}}$, is determined by the interaction between the semiconductor and the electrolyte. When the photoanode is illuminated (Figure 3-2(c)), charge carriers (e^-h^+ pairs) are generated and then separated by the built-in electric field in the depletion layer. A photovoltage is generated, leading to E_F move upwards. As a result, the band bending is reduced. To raise the metal electrode E_F above the H^+/H_2 potential and make the water splitting reaction happen, an external bias voltage V_{bias} is applied (Figure 3-2(d)), However, the efficiency of the water splitting is reduced when a bias voltage is applied.

3.3 Band energy requirements for an efficient photo water splitting

Figure 3-3. Energy diagram of a PE cell for the photo-electrolysis of water. The cell is based on an n-type semiconducting photoanode.[100]

The energy diagram for a n-type photoanode PE cell for water splitting is presented in Figure 3-3. Under illumination, electrons of the photoanode are excited from the valence band into the conduction band upon absorption of photons with energy equal to or larger than the bandgap. After the electron-hole carrier pair separated, the electrons travel to the counter electrode through external circuit where they reduce water to produce hydrogen gas, while the holes migrate to the surface, where they oxidize water to produce oxygen gas.

According to the calculation of Gibbs free energy change of water splitting reaction (237 KJ mol^{-1}), the decomposition of water is possible when the electromotive force of the cell is equal to or larger than 1.23 V, corresponding to a minimum bandgap requirement for the semiconductors of 1.23 eV. In real applications, over potential for providing additional energy is usually required to drive the reaction.

In conclusion, the following conditions should be satisfied to efficiently carry out the photo water splitting:

1. The photon energy of incident light should be equal or larger than the bandgap of the semiconductor, so as to pump the electrons from the valance band to the conduction band after being absorbed by the photoanode.

2. The bandgap of the semiconductor should be larger than 1.23 eV, the Gibbs free energy water splitting.

3. The bandgap of the semiconductors should straddle the water decomposition redox reactions, which means the conduction band position should be more positive than the reversible potential of the hydrogen electrode reaction and the valence band edge should be more negative than the reversible potential of oxygen electrode reaction.

4. The semiconductor photoanode should have good anti-photocorrosion stability.

However, no such materials can satisfy all the requirements to date. The researchers now focus on developing promising materials using various techniques such as the bandgap engineering, surface modifications, and building heterojunctions, etc. [93,96,98,101-103]

3.4 Photoelectrochemical performances based on WO_3

photoanode

WO_3 is a n-type indirect bandgap semiconductor with bandgap energy of ~ 2.6 eV that it mainly absorbs the blue part of the solar spectrum. Compared to other

wide bandgap semiconductors such as TiO_2 , SnO_2 , ZnO , WO_3 could harvest more light due to its narrower bandgap. As one of the few semiconductors that are chemically inert and photostable in acidic pH, it has demonstrated excellent photoelectrochemical performances. For example, Su reported vertically aligned WO_3 nanowire arrays on FTO substrate. The films show incident photo-to-current conversion efficiencies higher than 60 % at 400 nm and a photocurrent of 1.43 mA cm^{-2} . [104] Qin reported dense layers of vertically oriented WO_3 photoanode by a surfactant-free hydrothermal method. [105] A largest photocurrent density of 2.3 mA cm^{-2} at 1.2 V vs Ag/AgCl was obtained for the 17 h films with a thickness of $3.6 \text{ }\mu\text{m}$. And the incident photo-to-current conversion efficiencies were found to be 40 % at 400 nm. Wang reported the hydrogen-treated WO_3 nanoflakes films with enhanced photostability and photoelectrochemical performances. The hydrogen treated films at $350 \text{ }^\circ\text{C}$ achieved a maximum photocurrent density of 0.88 mA cm^{-2} at 1.0 V vs Ag/AgCl, which is about an order of magnitude enhancement compared to pristine WO_3 film. [106] Santato reported the WO_3 nanoparticle films by a layer by layer screen printing method with a thickness of $2 \text{ }\mu\text{m}$. The WO_3 nanoparticles have diameters ranging from 20 to 50 nm. The films show a maximum incident photo-to-current conversion efficiency about 77% and a photocurrent density of 2.4 mA cm^{-2} . [107]

3.5 Summary

PE cells are capable to produce clean energy through water splitting by harvesting solar light energy. WO_3 is a promising photoanode material because of

its proper bandgap (2.6 eV) and excellent stability. For applications in PE cells, WO_3 needs to be assembled into a thin film on conductive substrates (FTO or ITO) serving as the photoanode. It is well known that the photoelectrochemical performances of the WO_3 films are highly related to their properties such as characteristic feature sizes, porosity, and defect density. Although there have been various reports on the photoelectrochemical performances of WO_3 photoanodes, to directly grow porous WO_3 films on FTO substrate with good adhesion and uniformity using cost effective wet chemistry method still remains a big challenge. And there have been few reports on the investigation of photoelectrochemical properties of the hydrothermally grown WO_3 films.

CHAPTER 4 SINGLE LAYER ELECTROCHROMIC DEVICES¹

4.1 Introduction

EC devices are capable of reversibly changing their optical properties upon charge injection and extraction induced by the external voltage, which makes them suitable for various of applications including EC displays,[17,108-110] smart windows,[15,111-114] self-dimming rear mirrors, [115] and sensors.[116] Tungsten trioxide (WO_3) has attracted intensive attention due to its distinctive physical and chemical properties that makes it suitable for extensive applications in EC device,[10,13,20,36,66,112,117-123] gas sensor,[116,124] dye sensitized solar cell[125] and photoelectrochemical device.[96,126,127] As a well-known inorganic EC material, WO_3 can display blue color and become colorless by alternating polarity of the applied voltage, which induces the migration of cations such as proton and lithium to insert into or extract from the host material at the same time. It has been extensively studied as an EC material because it exhibits high coloration efficiency and a high cyclic stability compared to other transition metal oxides.[9,24,128,129] EC devices made of WO_3 films have evoked considerable interests during the last few years, because of their promising applications in energy-efficient windows that can control the solar light

¹ The main results of this Chapter have been published as: Z. Jiao, X.W. Sun, J.M. Wang, L. Ke and H.V. Demir, *Journal of Physics D-Applied Physics*, 2010, 43 (28) 285501; Z. Jiao, X. Wang, J.M. Wang, L. Ke, H.V. Demir, T.W. Koh and X.W. Sun, *Chemical Communications*, 2012, 3 (48), 365.

transmission indoors through reversible color changes, contributing therefore not only significantly to energy saving in buildings (as a result of curtailing of air conditioning) but also comfortable esthetics (thermal discomfort and less glare).[5]

Compared to the amorphous structure, crystalline WO_3 demonstrates better durability due to the denser structure and slower dissolution rate in electrolytes, especially in acidic ones.[36,130] However, bulk crystalline WO_3 particles usually lead to slower switching responses and smaller coloration efficiency. Thus, nanostructured WO_3 with large specific area has been expected to obtain fast switching response and good durability. There have been recent reports on the applications of nanosized or nanoporous crystalline WO_3 materials for improvement of response time and coloration efficiency. For example, Lee reported 10-20 nm diameter nanocrystalline WO_3 with improved EC behavior.[36] This nanocrystalline WO_3 film deposited by an electrophoresis process showed a $42 \text{ cm}^2 \text{ C}^{-1}$ (at 670 nm) coloration efficiency and unfortunately, response time was not reported. Wang reported crystalline WO_3 nanorods synthesized by a hydrothermal method.[130,131] EC films based on these nanorods show a CE value of $37.6 \text{ cm}^2 \text{ C}^{-1}$, but with 25.2 s for coloration and 18.0 s for bleaching for 70% transmittance changes. The Son's group reported ultrafine WO_3 nanorods ($2.90 \pm 0.57 \text{ nm}$) fabricated by a colloidal approach under assistance of surfactant oleylamine, in which EC system a fast bleaching response (6.4 s for coloration and 3 s for bleaching) and a high coloration efficiency ($132 \text{ cm}^2 \text{ C}^{-1}$ at 700 nm) were obtained.[132] Although the response time and coloration efficiencies of WO_3

systems have been significantly improved by nanotechnology, more effort needs to be made.

Traditionally, WO_3 is assembled as a thin film on a conductive substrate that serves as the working electrode. To date, a lot of methods have been put forward to assemble WO_3 films on various substrates, such as sputtering,[28,133-135] chemical vapor deposition,[136,137] electrodeposition,[117,138,139] spray pyrolysis,[140,141] sol-gel[142,143] and hydrothermal.[120,122,127] The EC performance of as-obtained film is highly related to its porosity, crystallinity and crystal size, which largely depends on the assembling methods. Large area uniformity, low production cost and excellent durability of WO_3 are highly desired in the fabrication of EC devices. Generally, vacuum techniques are expensive and their as-prepared film is denser. For electrosynthesis, high energy input (high voltage or current) is needed. Sol-gel process followed dip-coating method provides a low-cost and high-efficiency fabrication of WO_3 film over large areas. However, particular attention must be paid to the chemistry of solutions and the annealing conditions to get stable, uniform and good-adhesion WO_3 films with desired microstructures and thicknesses. In comparison, the hydrothermal approach is promising for fabricating WO_3 films because of its merits of low reaction temperature, flexible substrate selection and easiness for scaling up. Recently, there have been reports on the synthesis of many one-dimensional WO_3 nanostructures, such as nanorods[130] and nanobelts.[144] However, directly growing a uniform nanostructured WO_3 thin film with good adhesion on a substrate still remains as a

challenge. Moreover, little attention has been paid on the study of EC characteristics of hydrothermally grown WO_3 films.

Herein, we present directly grown nanostructured uniform WO_3 and hydrated WO_3 films with good adhesion to substrates using facile and efficient crystal-seed-assisted hydrothermal approaches and demonstrate their good EC characteristics.

4.2 Fabrication and characterization of the WO_3 and hydrated WO_3 films

4.2.1 Synthesis of brick-like WO_3 films

The typical synthesis procedure of the brick-like WO_3 films is described as follows. Firstly, 1 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved into 15 mL de-ionized water, and then HCl solution was added until no precipitate was formed. The precipitate was washed using de-ionized water in ice bath for many times. Then 2 mL H_2O_2 was added into the precipitate under intense stirring and its temperature was raised to obtain a WO_3 seed solution. The mixture was then spin coated onto FTO glasses that were previously cleaned by acetone, isopropanol, and de-ionized water in sequence. Subsequently, the substrates were heated to 400 °C in atmosphere for 40 minutes. Meanwhile, the as-prepared WO_3 seed solution was diluted using de-ionized water and transferred into an autoclave as the hydrothermal reaction precursor. The prepared FTO glass substrates with WO_3 seed layer were put into autoclave for the hydrothermal growth where the reaction was kept at 180 °C for 12 h. In comparison, a bare FTO glass substrate was also used as the reference.

4.2.2 Synthesis of plate-like hydrated WO₃ films

(1) Preparation of Crystal Seeds Layers: The typical synthesis procedure of crystal seed solution is described as follows. Firstly, 1.5 mL HCl solution was added into 15 mL 0.03 g/L Na₂WO₄·2H₂O solution. The formed yellowish precipitate was washed using de-ionized water in ice bath for many times and finally 50 mL mixture was obtained. Then 2 mL H₂O₂ was added into the heated precipitate under intense stirring to obtain a WO₃ seed solution. The mixture was then spin coated onto FTO glasses that were previously cleaned by acetone, isopropanol, and de-ionized water in sequence. Subsequently, the substrates were heated to 400 °C in atmosphere for 40 minutes.

(2) Preparation of Precursor and Hydrothermal Treatment: In a typical experiment for preparing the precursor, Na₂WO₄·2H₂O (1 g) was dissolved into 15 mL of de-ionized water and then HCl (7 mL) was added into the solution. The precipitate was washed using de-ionized water in ice bath for several times and finally 100 mL mixture was obtained. Then H₂O₂ (3 mL) was added into the above suspension under intense stirring and heating. The white precipitate was dissolved and a transparent solution was obtained. The solution was diluted to half concentration by de-ionized water and Na₂SO₄ (5×10^{-4} g/L) was added as the capping agent. For comparison, a solution without adding Na₂SO₄ was also used. The as-prepared solutions were transferred into autoclaves as precursors for hydrothermal treatments. The FTO glasses coated by WO₃ seed layers were put into autoclaves and the hydrothermal reactions were kept at 180 °C for 2 h. The as-prepared films were washed by di-water and dried in atmosphere.

4.2.3 Characterization

The phases of the products were characterized by X-ray powder diffraction (XRD, Siemens), using Cu K $_{\alpha 1}$ ($\lambda = 0.15406$ nm) radiation. Morphologies of the as-prepared thin films were observed by field-emission scanning electron microscopy (FESEM, JSM-6340). High-resolution transmission electron microscope (HRTEM) images were obtained by a JEM-2010 microscope with an accelerating voltage of 200 kV. Cyclic voltammetry of the films was measured by a three-electrode system (VersaSTAT 3F Potentiostat/Galvanostat) with Pt as the counter electrode and Ag/AgCl/1M KCl as the reference electrode. The electrolyte for brick-like WO $_3$ film is 0.5 M H $_2$ SO $_4$, while for plate-like WO $_3$ film is 0.2 M lithium perchlorate (LiClO $_4$) in γ -butyrolactone. The transmittance spectra were measured by a UV-Vis spectrophotometer (JESCO V670).

The electrochromic measurement was performed by a three electrode system with WO $_3$ film coated substrate as the working electrode, Pt wire as the counter electrode and Ag/AgCl/1M KCl as the reference electrode. All the three electrodes were partially immersed into a container with quartz window and filled with 0.2 M lithium perchlorate (LiClO $_4$) in γ -butyrolactone as electrolyte. The electrode bias voltage was controlled by a potentiostat during which the charge amount was recorded. During the process, the in-situ transmittance change of the WO $_3$ film was recorded by a UV-Vis spectrophotometer. In this way, the response time and coloration efficiency data could be obtained.

4.3 Structures, morphologies and electrochromic properties

The structures, morphologies, growth mechanisms, optical and EC properties of the as-grown brick-like WO_3 and plate-like hydrated WO_3 films were investigated, and discussions were also carried out.

4.3.1 Brick-like WO_3 films

Figure 4-1 shows XRD patterns of the bare FTO substrate and the as-prepared products grown by the hydrothermal method. The XRD pattern of the substrate can be indexed to F doped SnO_2 . For the hydrothermally grown product, different peaks can be seen. All the peaks can be indexed to the monoclinic phase of WO_3 (JCPDS 83-0950) with lattice constants of $a=7.301 \text{ \AA}$, $b = 7.539 \text{ \AA}$ and $c = 7.690 \text{ \AA}$. The sharp peaks indicate the as-synthesized thin film is of high crystal quality.

Figure 4-1. XRD patterns of bare FTO and as-prepared WO_3 thin films.

Figure 4-2. SEM images of (a) WO_3 micro-particles grown without a seed layer, (b) and (c) the as-prepared WO_3 thin film. Inset of Figure 4-2 (c) is the cross sectional SEM image. (d) HRTEM image of a single WO_3 brick-like nanostructure.

The morphologies of as-synthesized products on bare FTO and seeded FTO substrates are shown in Figure 4-2. It can be seen that sparsely distributed WO_3 particles with a size of $\sim 2 \mu\text{m}$ are present for the reference sample without a seed layer [Figure 4-2(a)]. These particles show weak adhesion to the FTO substrate and could be easily dislodged by the de-ionized water. Moreover, there are a lot of empty surface regions without WO_3 growth and the coverage uniformity of these aggregated particles is inferior. In this process, bare FTO substrate served as aggregation sites for the WO_3 particles. As a comparison, using the seed layer

coated on the surface of FTO, a uniform WO₃ thin film composed of brick-like nanostructures is grown on the surface [Figure 4-2(b) and 2(c)].

The growth mechanism of the brick-like nanostructured WO₃ film can be explained according to the following reactions:

H₂WO₄ precipitate was formed after HCl solution was added into Na₂WO₄ solution. Then it was dissolved by adding hydrogen peroxide (H₂O₂) and Peroxopolytungstic acid (PTA) was formed. WO₃ crystal nucleus was obtained when the reaction temperature exceeded the decomposition temperature of PTA, and the seed-coating substrate acted as nucleation and growth sites. Finally the WO₃ nucleus grew into brick-like nanostructures. It can be seen that there are some pores existing between the plates. These pores are formed from stacking of the nanoplates. The calculated porosity of the WO₃ film using Brunauer-Emmett-Teller (BET) method is about 5.4% with average pore size of 63.7 nm, in agreement with the Figure 4-2(b) and 2(c). The pores between the nanoplates can increase the interface area between WO₃ and electrolyte, and the diffusing ions in the electrolyte can transport through these pores to the inner WO₃ interface easily. Porous WO₃ films contributing to fast ions diffusing kinetics can result in better EC performances compared to the solid film. It can be seen from the cross sectional SEM image in the inset of Figure 4-2(c) that the thickness of the as-synthesized film is ~ 1.5 μm. Figure 4-2(d)

shows the HRTEM image of a single brick-like WO_3 piece. Clear lattice fringes corresponding to the (200) plane can be identified, indicating the single crystal quality of the WO_3 nanostructure. It is well known that the EC performance of WO_3 is closely related to its crystallization level.[70] Generally, amorphous WO_3 shows faster EC switching response than crystalline WO_3 arising from its large specific surface area. However, the cyclic stability of amorphous WO_3 is worse than crystalline WO_3 due to the W-O-H and W=O defect sites, which may act as intercalated ion trapping sites.[130] And the amorphous WO_3 can only be used in lithium-based electrolytes since its incompact structure has a high dissolution rate in acidic electrolyte, while the crystalline WO_3 can endure acidic electrolyte without degradation for a long cyclic time. Moreover, EC devices based on crystalline WO_3 show more energy-efficient glazing than amorphous WO_3 . [70]

Figure 4-3. Transmittance spectra of the EC device measured at 0 V, -1.0 V, -2.0 V, and -3.0 V, respectively.

Figure 4-3 shows the transmittance spectra of the WO_3 film recorded at -1.0 V, -2.0 V and -3.0 V. With increasing negative bias, the WO_3 EC film changes from semi-transparent colorless to deep blue gradually. The peak transmittance wavelengths measured at -1.0, -2.0 and -3.0 V are 597, 492 and 427 nm, respectively, showing an obvious blue-shift.

Figure 4-4. (a) Cyclic Voltammetry (CV) curves of the WO_3 thin film at the 1st and 3000th cycle. The measurement was performed in 0.2 M LiClO_4 / γ -butyrolactone with a sweep rate of 0.1 V/s. (b) CV curves recorded at 5, 10, 25, 50, and 100 mV/s, respectively. Inset of Figure 4-4 (b) shows the cathodic/anodic peak current density as a function of the square root of the scan rates.

To investigate the stability of ion intercalation/deintercalation, cyclic voltammetry (CV) curves were recorded for the 1st and 3000th cycles at room temperature (Figure 4-4). The test was performed at a 100 mV/s sweep speed between -1.0 V to 1.0 V. The recorded current is due to cation intercalation/deintercalation according to the following reaction. During each run, the color of the film is observed to change from blue to semi-transparent colorless reversibly.

From Figure 4-4, it can be seen there is no obvious change of the current densities after 3000 cycles; only a slight reduction at the oxidization end is observed. This indicates that the high stability of the as-prepared WO₃ film. CV curves of the WO₃ film recorded between ± 0.8 V at scan rates varied from 5 mV/s to 100 mV/s are shown in Figure 4-4(b). As the increase of scan rates, the anodic peaks corresponding to the Li⁺ deintercalation shift toward positive potential gradually. Moreover, the ratio between the cathodic peak current and anodic peak current density is less than unity. All these characteristics are similar to the spray-pyrolysis synthesized WO₃ films.[141] It is well known that the switching response is largely dependent on the diffusion coefficient of diffusion species, large diffusion coefficient will result in fast response. The inset of Figure 4-4 (b) shows the cathodic and anodic peak current density values (j_{pa} and j_{pc}) as a function of square root of the scan rate ($v^{1/2}$), approximate linear dependence is obtained indicating the cyclic process is diffusion controlled. The effective diffusion coefficient D of Li⁺ ions during intercalation and deintercalation can be calculated from the cathodic and anodic peak current (j_{pc} and j_{pa}) dependence on square root of potential scan rate ($v^{1/2}$) assuming simple solid state diffusion controlled process:[145]

$$\delta i_p / \delta \sqrt{v} = 2.69 \times 10^5 n^{3/2} A C \sqrt{D} \quad (20)$$

$$D = 0.1382 \times 10^{-10} n^{-3} A^{-2} C^{-2} (\delta i_p / \delta \sqrt{v})^2 \quad (21)$$

where n is the number of electrons transferred in unit reaction, A is the effective geometric surface area of the WO₃ electrode, and C is the concentration of the

diffusion species (Li^+). The effective diffusion coefficient D_{Li^+} has been calculated to be 2.73×10^{-11} and $1.44 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for the intercalation and deintercalation process, respectively. The D_{Li^+} values are in qualitative agreement with data calculated by Bathe and Patil.[146]

Figure 4-5. Chronoamperometry (CA) of the WO_3 thin film, recorded with a potential step of $\pm 0.5 \text{ V}$ for 50 s.

Chronoamperometry (CA) data were recorded for the WO_3 thin film with the potential being stepped from -0.5 V to $+0.5 \text{ V}$ for 50 s, as shown in Figure 4-5. The current-time transient curves under different applied voltages show typical characteristics of WO_3 as reported.[146] The peak bleaching current is higher than coloration, arising from the better conductivity of tungsten bronze (H_xWO_3) than WO_3 . And the bleaching current decays faster than the coloration due to the conductor-to-insulator transition. The response times for coloration (t_c) and bleaching (t_b) were obtained from Figure 4-5 and recorded for 70% current-time transient change. The calculated color-bleach response are $t_{c,0.7} = 4 \text{ s}$ and $t_{b,0.7} = 3 \text{ s}$, respectively. Due to the well-defined different mechanisms controlling the two

processes, the bleaching kinetics is always faster than the coloring rate for WO_3 film.

Figure 4-6. (a) Optical density variation with respect to the charge density (measured at 632.8 nm, -3 V bias). (b) Switching time characteristics between the colored and bleached states for EC device measured at ± 3 V. (c) Switching time characteristics for the device measured at ± 1 V, ± 2 V and ± 3 V, respectively.

The coloration efficiency (CE) represents the change in the optical density (OD) per unit charge density (Q/A , where Q is the charge and A is the area) during switching and can be calculated according to the formula: $\text{CE} = \Delta \text{OD} / (Q/A)$, where $\Delta \text{OD} = \log(T_{\text{color}}/T_{\text{bleach}})$. Figure 4-6(a) shows OD versus the intercalation charge density at -3 V of coloration potential and at the wavelength of 632.8 nm. The CE

was extracted as the slope of the line fitted to the linear region of the curve. The calculated CE value is $38.2 \text{ cm}^2 \text{ C}^{-1}$, which is comparable to the other reported crystalline WO_3 structures.[36] A square wave voltage was applied (between -3.0 V and 3.0 V) to investigate the transition response time between coloration and bleaching, and color switching stability. Figure 4-6(b) shows the dynamic coloration/bleaching characteristics of the EC device composed of WO_3 thin film (sample size $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15\Omega/\square$) recorded at the wavelength of 632.8 nm for the 1st, 500th and 1000th cycles. The coloration and bleaching time can be defined as the time required for 50%, 70% and 90% changes in the whole transmittance modulation, respectively. The coloration time of 50% changes $t_{c(50\%)}$ is found to be 22 s while the bleaching time $t_{b(50\%)}$ is 23 s. For 70% modulation, $t_{c(70\%)} = 51 \text{ s}$ and $t_{b(70\%)} = 36 \text{ s}$, which are comparable to amorphous structures. However, the crystalline WO_3 is more stable than the amorphous one.[9] The switching time further increases to $t_{c(90\%)} = 236 \text{ s}$ and $t_{b(90\%)} = 95 \text{ s}$ for 90% modulation. Compared to WO_3 nanorods fabricated by hydrothermal method and assembled on conductive substrate by dip-coating ($t_{c(90\%)} = 272 \text{ s}$ and $t_{b(90\%)} = 364 \text{ s}$),[131] the coloration and bleaching time for 90% modulation is 36 s and 269 s shorter, respectively. Moreover, considering that the as-prepared WO_3 EC film ($\sim 1.5 \mu\text{m}$) is much thicker than the film assembled by dip-coating[131] or Langmuir-Boldget approach,[147] the fast switching time is further more appreciated. It is also worth mentioning that there is no observable degradation after 500 cycles in our experiment, which indicates a good switching stability of the WO_3 film. The

switching response time for the EC device based on WO_3 film measured at ± 1 V and ± 2 V were also investigated and shown in Figure 4-6(c). The obtained responses for 70% transmittance change are $t_{c(70\%)} = 110$ s, $t_{b(70\%)} = 54$ s for ± 1 V, and $t_{c(70\%)} = 234$ s, $t_{b(70\%)} = 17$ s for ± 2 V, respectively. The applied small bias voltage on the EC device cannot result in a clear coloration/bleaching switching.

Figure 4-7. A WO_3 -based EC display after biasing at +3 V (a) and (b) -3V.

Figure 4-7 shows an EC display based on this patterned film with another bare FTO substrate used as the counter electrode. Lithium perchlorate (LiClO_4) in γ -butyrolactone (0.2 M) was filled in between the two electrodes as the electrolyte. At biases of ± 3 V (Figure 4-7), a good contrast can be seen for a wide range of viewing angles. The color can be retained for several hours after removal of the external voltage for our unsealed devices.

In summary, uniform WO_3 thin films with brick-like nanostructures on FTO glass substrate were synthesized via a simple low-cost hydrothermal approach. EC display based on this film showed good coloration/bleaching switching

characteristics. There is a good prospect in applying these hydrothermal WO_3 thin films in smart windows and electronic papers.

4.3.2 Plate-like hydrated WO_3 films

Figure 4-8. (a) XRD patterns of the bare FTO substrate and, the as-synthesized films grown with and without Na_2SO_4 . (b) Schematic illustration of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ structure. (c) Raman spectra of the films. a: without Na_2SO_4 . b: with Na_2SO_4 . (d) Wide scanning XPS spectra of the as-fabricated nanoplate films.

Figure 4-8(a) shows the X-ray powder diffraction (XRD) patterns of the bare FTO substrate and the as-prepared thin films grown with and without Na_2SO_4 . The XRD pattern of the substrate can be clearly indexed to tin oxide (JCPDF 70-

4176). The hydrothermally grown films have the same crystalline structure since all diffraction peaks appear at the same position, and no other impurity peaks are observed. The sharp peaks indicate the good crystalline quality of the as-fabricated films. All peaks can be well indexed to the orthorhombic phase of $3\text{WO}_3 \cdot \text{H}_2\text{O}$ (JCPDF 87-1203). However, the relative peak intensity for crystalline planes of (002) and (200) of the film grown with Na_2SO_4 is different from the one without Na_2SO_4 , indicating different preferred growing direction due to the capping effect of Na_2SO_4 . The orthorhombic $3\text{WO}_3 \cdot \text{H}_2\text{O}$ contains two type of corner-sharing WO_6 octahedrons. One type is conducted by a central tungsten atom that is surrounded by six oxygen atoms, while in the second type, two of the oxygen atoms are replaced by a shorter terminal $\text{W}=\text{O}$ bond and a longer $\text{W}-(\text{OH})_2$ bond, respectively.[148] The relatively weaker interaction between adjacent layers may restrict the stacking to prevent the bulk formation. Finally, the two dimensional plate-like $3\text{WO}_3 \cdot \text{H}_2\text{O}$ nanostructure is formed under the capping effect of Na_2SO_4 by stacking up layers consisting of these two structural units as shown in Figure 4-8(b). Figure 4-8(c) displays a Raman spectrum of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films. The bands at 680 and 807 cm^{-1} arise from the O-W-O stretching vibrations of the bridging oxygen atoms, the band at 260 cm^{-1} belongs to W-O-W bending mode and the bands at 330 cm^{-1} and 924 cm^{-1} can be assigned to the stretching of W-OH₂ and W=O, respectively.[149,150] The wide scanning x-ray photoelectron spectroscopy (XPS) of the nanoplate film was also investigated and shown in Figure 4-8(d). The binding energies of the sample were corrected using a value of 284.6 eV for the C 1s peak of carbon. All the peaks appeared in the spectra can be well indexed to be

W and O elements. There is no contaminated element except C in the film. And it is well known that such adventitious carbon layer is usually formed for the samples exposed in the air. The above result indicates that these as-prepared films are orthorhombic $3\text{WO}_3 \cdot \text{H}_2\text{O}$ with high purity.

Figure 4-9. (a) and (b) FESEM images of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ thin films grown with Na_2SO_4 given under different magnifications. Inset of (b): cross-sectional view image. (c) TEM image of the nanoplate scratched from the film. Inset: SAED pattern. (d) HRTEM image. (e) and (f) FESEM images of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ thin films grown without Na_2SO_4 given under different magnifications.

The morphologies of the as-synthesized films are shown in Figure 4-9. The film grown with Na_2SO_4 is composed of plate-like nanostructures, forming a rough surface (Figure 4-9(a) and 9(b)). These uniform nanoplates grow nearly vertically on the substrate. Numerous pores are formed among them so that the contact area between the film and electrolyte can be largely increased. Through these pores, ions in the electrolyte can diffuse more easily and efficiently. The cross-sectional view image (inset of Figure 4-9(b)) shows that the film of ~ 700 nm in thickness has a good adhesion to the substrate. Figure 4-9(c) shows the transmission electron microscopy (TEM) image of the nanoplates. The biggest “rectangular block” with a size of ~ 200 nm has vertical joint angles. The inset of Figure 4-9(c) depicts the selected area electron diffraction (SAED) pattern of this nanoplate. Regular diffraction spots indicate that it is single crystalline with preferential growing directions along crystal planes of (200) and (002). The high-resolution TEM (HRTEM) image from the edge of a single nanoplate in Figure 4-9(d) shows a crystal lattice of 0.36 nm, corresponding to the d-spacing of (200) planes. Clear lattice fringes also support its single crystal quality. Figure 4-9(e) and 9(f) present top view images of the film grown without Na_2SO_4 under different magnifications. The film is composed of stacking brick-like nanostructures with much bigger sizes. The surface area of the brick-like film is much smaller compared to the plate-like one. Consistent with the SEM studies, the mass density of the nanoplate film has been found to be approximately 3.2 g/cm^3 , estimated from mass and thickness data. Since the bulk density of orthorhombic $3\text{WO}_3 \cdot \text{H}_2\text{O}$ is 6.6 g/cm^3 , the pore volume of the film was calculated to be $0.16 \text{ cm}^3/\text{g}$, which is slightly smaller than the

nanoparticle films.[151] On the other hand, the mass density of the brick-like film grown without Na_2SO_4 is 5.4 g/cm^3 , yields a pore volume of $0.03 \text{ cm}^3/\text{g}$, which is much smaller than the nanoplate film. The formation process of plate-like and stacked brick-like $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films was schematically illustrated in Figure 4-10.

Figure 4-10. A schematic illustration of the formation process for $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films grown with and without Na_2SO_4 .

The precipitation of WO_3 from the WO_4^{2-} containing solution and the growth mechanism of the plate-like nanostructured film can be explained according to the following well known reactions:

H_2WO_4 precipitate was formed after addition of HCl solution. Then it was dissolved by adding hydrogen peroxide (H_2O_2) and peroxopolytungstic acid (PTA) was obtained. A layer of $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$ crystal nucleus was formed from the decomposition temperature of PTA at high temperature, and the seed-coating substrate acted as nucleation and growth sites. The plate-like nanostructures were

grown eventually from the $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$ nucleus under the capping agent of Na_2SO_4 , while stacked brick-like films were obtained.

Figure 4-11. (a) CV curves of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films grown without and with Na_2SO_4 in 0.5M H_2SO_4 solution, at a scan rate of 0.1 V/s. (b) Chronoamperometry curves by applying pulsed potential of ± 0.3 V, 30 s for each state. (c) CV curves of the film with Na_2SO_4 after the 1st, 1500th and 3000th cycles. (d) UV-vis transmittance spectra of the plate-like $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film based EC device under 0, -0.1, -0.2 and -0.3 V, respectively.

The cyclic voltammograms (CVs) normalized to the geometric area of the electrode and to the weight of film within that area is compared in Figure 4-11(a), measured in 0.5 M H_2SO_4 with a scan rate of 0.1 V/s. During each scan, both films

will reversibly change their colors from colorless to blue, resulting from H^+ intercalation/deintercalation and electron transfer between W^{6+} and W^{5+} according to the following reaction:

The integrated cathodic/anodic current over time equates to the amount of H^+ intercalation/deintercalation. The nanoplate film leads to a much higher current density for both intercalation/deintercalation processes over the same time period than the nanobrick one, indicating a faster H^+ intercalation/deintercalation kinetics. The total cathodic charge for the nanoplate film was about $0.67 \text{ mC cm}^{-2} \text{ mg}^{-1}$, compared to only about $0.19 \text{ mC cm}^{-2} \text{ mg}^{-1}$ for the nanobrick one. Moreover, the onset of the cathodic current for the nanoplate (0.27 V) is more positive compared with the nanobrick one (0.15 V), while the oxidation peak of the nanoplate film (-0.17 V) shows a negative shift compared to the nanobrick one (-0.03 V). These results imply that the nanoplate film has reduced interfacial charge-transfer resistance, providing another reason for the improved electrochemical response. The faster ion intercalation/deintercalation kinetics of the nanoplate film was further confirmed by the chronoamperometry result (Figure 4-11(b)). The chronoamperometry test was conducted by applying pulsed potential of $\pm 0.3 \text{ V}$ for 30 s in each state. The nanoplate film reaches a higher transient current peak density and exhibits faster current decays than the nanobrick one, agreeing well with Figure 4-11(a). Moreover, the nanoplate film also shows good cyclic stability (Figure 4-11c) even in the acidic solution, since there is no significant change in the shape of the CVs, only a small reduction was observed after 3000 cycles.

Tunable transmittance could be obtained for the nanoplate film under -0.1, -0.2 and -0.3 V in 0.5 M H_2SO_4 solution (Figure 4-11(d)). With increased negative bias voltage, more H^+ will be inserted into the film and the color of the film will become deeper, leading to the decrease of optical transmittance above 460 nm and a blue shift of the peak transmittance from 884 to 802, 703 and 675 nm, respectively.

Figure 4-12. Photographs of the EC device made up of the nanoplate $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film under 0, -0.1, -0.2 and -0.3 V, respectively.

Photographs of the EC device made of the plate-like film are shown in Figure 4-12, depicting a high contrast between the bleached and colored states which leads to the obvious transparency changes. With increased negative bias, the device shows a deeper blue color, leading to a larger optical regulation between bleached and colored state.

Figure 4-13. (a) Switching time characteristics for both films measured at ± 0.3 V at 632.8 nm. (b) Optical density variation with respect to the charge density recorded at 632.8 nm. (c) Switching properties of the nanoplate film under ± 0.1 V and ± 0.2 V at 632.8 nm.

Figure 4-13(a) shows the in-situ coloration/bleaching transmittance response of the nanoplate and nanobrick films measured at 632.8 nm. Obvious color changes can be observed during the switching. The nanoplate film shows a fast response and the switching time extracted for a 90% transmittance change are found to be 4.3 s for coloration (t_c) and 1.4 s for bleaching (t_b) for a sample size ~ 2 cm² (FTO sheet resistance: 15 $\Omega/\square$). However, for the nanobrick film, t_c and t_b are increased to 9.2 and 1.7 s, respectively. Moreover, the film grown with Na₂SO₄

depicts an enhanced optical modulation of 38 %, which is larger than 5% of the nanobrick one. The fast coloration/bleaching kinetics are mainly attributed to the small mass density and large surface area of the porous morphology, which facilitates the ions intercalation/deintercalation by reducing their diffusion path lengths. The switching speed of the film for both the coloration and bleaching is faster than previously reported micro-brick films and nanowire array films.[152,153]

Figure 4-13 (b) shows the optical density (OD) plots at $\lambda = 632.8$ nm versus the inserted charge density (Q) under -0.3 V. The CE was extracted as the slope of the line fitted to the linear region of the curve. The calculated CE value of the nanoplate film is $112.7 \text{ cm}^2 \text{ C}^{-1}$, which is improved by about 422% compared with the nanobrick film ($\text{CE} = 21.6 \text{ cm}^2 \text{ C}^{-1}$). The CE value is also largely increased compared with the reported ones of the nanoparticle film and micro-brick film.[36,152] The hydrothermally grown nanoplate WO_3 (hydrate) film herein depicts some improvement in either response time or coloration efficiency. Moreover, the switching responses of the nanoplate film under ± 0.1 V and ± 0.2 V were also further investigated (Figure 4-13(c)). When ± 0.1 V was applied, coloration time t_c and bleaching time t_b are found to be 9.2 s and 1.3 s respectively, while they are 18 s and 1 s respectively under ± 0.2 V bias. Reverse trend for coloration and bleaching speed is obtained when increasing the bias from ± 0.1 V to ± 0.3 V. And smaller optical modulations were found under these biases.

In conclusion, nanostructured $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films were assembled on FTO glass substrate by an efficient and facile crystal-seed-assisted hydrothermal method. Plate-like nanostructured film was synthesized with Na_2SO_4 as the capping agent. Compared with the one without adding Na_2SO_4 , the nanoplate film showed significantly improved EC performance, thanks to a smaller mass density (3.2 g/cm^3) and larger surface area. The CE value for the nanoplate film was calculated to be $112.7 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm , while the nanobrick film only exhibited a CE of $21.6 \text{ cm}^2 \text{ C}^{-1}$. The nanoplate film also depicted a fast switching response, with 90% transmittance changes found to be 4.3 and 1.4 s for coloration and bleaching, respectively. Such $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films with improved EC behavior hold great promise for energy-efficient smart windows and large-area information displays.

4.4 Summary

Brick-like WO_3 and plate-like $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films on FTO substrates have been prepared by crystal-seed-assisted hydrothermal methods. The brick-like monoclinic WO_3 nanostructures were grown directly on FTO substrate without any capping agents. EC measurements show the film displays tunable transmittance modulation under different voltages and a good reversible coloration/bleaching stability after 3000 cycles. The EC device composed of the WO_3 film (sample size $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) has a comparable switching response of $t_{c(90\%)} = 272 \text{ s}$ and $t_{b(90\%)} = 364 \text{ s}$ and a CE of $38.2 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm . The plate-like nanostructured $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film was synthesized with Na_2SO_4 as the capping agent. Due to the larger surface area, the nanoplate film grown with Na_2SO_4 shows

significantly improved EC performance. A high CE value of $112.7 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm is obtained, and the response time for 90% transmittance changes (sample size $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) is found to be 4.3 and 1.4 s for coloration and bleaching, respectively. These films demonstrate promising applications in smart windows and large-area information displays.

CHAPTER 5 COMPLEMENTARY LAYER ELECTROCHROMIC DEVICES¹

5.1 Introduction

Electrochromism is the phenomenon of reversible changes in the optical properties of a material during electrochemical redox processes, which can be applied in energy-efficient smart windows, antiglare rear-view mirrors and displays.[10,23,26,66,112,119,154-157] Compared with a single EC layer device, a complementary device depicts improved optical regulation, coloration efficiency and cyclic stability.[158,159] By properly chose of the EC materials on their working voltage, an anodically colored and cathodically colored material can be assembled in one EC device, which can be colored or bleached simultaneously.

Among various EC materials, WO₃ has attracted intensive attention due to its distinguished EC properties such as high coloration efficiency, good color-memory effect, large color contrast and good cyclic stability.[10,36,160] Although considerable achievements have been made, the performances of WO₃ films-based EC devices can be further improved by incorporating with another complementary EC layer. Compared with a single layer EC device, it is well known that a complementary device containing two proper EC layers could further improve the

¹ The main results of this Chapter have been published as: Z. Jiao, J.M. Wang, L. Ke, X.W. Liu, H.V. Demir, M.F. Yang and X. W. Sun, *Electrochimica Acta*, 2012, 63, 153.; Z. Jiao, J.M. Wang, L. Ke, X.W. Sun and H.V. Demir, *Journal of Nanoscience and Nanotechnology*, 2012, 12, 1.

performance, such as the optical modulation, cyclic stability and coloration efficiency.[159,161]

Prussian blue is a well-known anodically colored EC material. It is reported that an electrodeposited PB film exhibits electrochromism between blue and colorless with a fast response ($\sim$ less than 100 ms) and a high durability after 5×10^6 cycles.[162] However, the PB film shows little absorption in the IR region which hinders its applications in energy efficient smart windows. The combination of WO_3 and PB in a complementary device has demonstrates improved optical modulation, response speed and coloration efficiency. For example, Kraft and Rottmann reported large-area laminated EC glass composed of electrodeposited WO_3 and PB films.[15,65] The device shows a coloration efficiency of $\sim 140 \text{ cm}^2 \text{ C}^{-1}$ and transmittance modulation T% of $\sim 70\%$ at 630 nm, both are higher than that of single component EC devices.[152,153] However, the WO_3 film adopted by Kraft et al. is a relatively smooth and dense thin film prepared by an electrodeposition process, for which specific and costly facilities are required. Hence, more efforts need to be done to explore a cost effective method to assemble porous and highly adhesive nanostructured WO_3 films. To the best of our knowledge, little work has been done on applying the hydrothermally grown nanostructured hydrated tungsten oxide films in such kind of devices.

In this dissertation, we make an attempt to grow nanostructured WO_3 films directly on FTO-coated glass by facile and low cost crystal-seed-assisted hydrothermal approaches using various capping agents. The structures, morphologies and EC properties of the resulting nanostructured hydrated WO_3

films were investigated. The results show that as-prepared hydrated WO_3 films are uniform with good adhesion. And good cyclic stability, comparable coloration efficiency and fast switching response are exhibited. Moreover, their performances could be further improved by incorporating a PB layer in a complementary EC device. The devices demonstrate increased color contrast, switching speed and coloration efficiency, which can be applied in energy-efficient smart windows and large area information displays.

5.2 Synthesis and characterization of the hydrated WO_3 films

5.2.1 Synthesis of stick/particle-like hydrated WO_3 films

Preparation of crystal seeds layers, precursor and hydrothermal treatment: the procedures for preparing crystal seeds layers are similar to our previous report, which can be found elsewhere.[152] In a typical experiment for preparing the precursor, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.0655 g) was dissolved into 20 mL of de-ionized water and then 4 mL of HCl was added into the solution until no more precipitate was formed. The above suspension was kept in ice bath for about 10 min, then the top liquid part was removed and de-ionized water was added to obtain a 20 mL suspension. Subsequently, H_2O_2 (0.2 g) was added into the above suspension under intensely stirring and heating. The white precipitate was dissolved and a transparent solution was obtained. After stirring for 5 min, $\text{CH}_3\text{COONH}_4$ (0.1 g) was added as the capping agent. Then NaOH (1 mol) solution was slowly mixed into this solution while rigorously stirring until the pH value of the solution

reached 1.5. For the purpose of comparison, a solution without adding capping agent was also used. The as-prepared solutions were transferred into autoclaves as precursors for hydrothermal treatments. The FTO glasses coated by WO_3 seed layers were put into autoclaves and the hydrothermal process was kept at 180°C for 18 h.

5.2.2 Synthesis of brick-like hydrated WO_3 films

In a typical experiment for preparing the precursor, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.065g) was dissolved into 20 mL of de-ionized water and then H_2O_2 (0.2g) and $(\text{NH}_4)_2\text{SO}_4$ (0.045 g) was added into the solution under intense stirring. Pure HCl was dropped into the above solution until the pH value reaches 1.5. For the purpose of comparison, solutions without adding H_2O_2 , $(\text{NH}_4)_2\text{SO}_4$ or both were also prepared. The as-prepared solutions were transferred into autoclaves as hydrothermal precursors. The seed coated FTO glasses were lie at the bottom of the autoclaves and the hydrothermal growth was performed at 180°C for 18 h. High transparent films were grown on the substrate after washing away the adhered precipitate by di-water. Then the films were dried in atmosphere.

5.2.3 Characterization

The phases of the as-grown films were identified by x-ray powder diffraction (XRD, Siemens), using $\text{Cu K}\alpha_1$ ($\lambda = 0.15406 \text{ nm}$) radiation. The phase structures were characterized by Raman spectroscopy (Renishaw inVia). X-ray photoelectron spectroscopy (XPS) data were obtained on a Kratos AXIS spectrometer with monochromatic $\text{Al-K}\alpha$ (1486.71 eV) X-ray radiation. The

morphologies of the as-prepared thin films were observed by field emission scanning electron microscope (FESEM, JSM 6340). High-resolution transmission electron microscopy (HRTEM) image was obtained by a JEM-2100 microscope using an accelerating voltage of 200 kV. Thicknesses of the films were measured by a TENCOR P-10 Surface Profiler.

5.3 Assembling and test of the complementary devices

Electrodeposition of PB and preparation of EC device: the electrodeposition of PB film was carried out by a conventional three-electrode system, where a clean FTO glass ($1.5 \times 2 \text{ cm}^2$) served as the working electrode, a platinum sheet as the counter electrode, and a Ag/AgCl/1M KCl as the reference electrode. The electrodeposition bath contained 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 10 mM FeCl_3 and 0.1 M KCl and the electrodeposition was carried out by applying a constant cathodic current density of $50 \text{ } \mu\text{A cm}^{-2}$ for 130 s and 300 s, respectively. Then the WO_3 (hydrated) working electrode and PB counter electrode were sandwiched together with hot-melt Surlyn spacers. A liquid electrolyte composed of 0.3 M or 0.2 M LiClO_4 in γ -butyrolactone (γ -BL) was introduced between the two electrodes by capillary action. Finally the cells were sealed by epoxy with a structure of FTO || hydrated (WO_3) || γ -BL (LiClO_4) || PB || FTO, which is schematically shown in Figure 5-1.

Figure 5-1. Schematic of the configuration of complementary device.

The optical absorbance and transmittance spectra of the devices were measured using a UV/Vis spectrophotometer (JESCO V670). Electrochemical measurements were performed by a three-electrode system (VersaSTAT 3F Potentiostat/Galvanostat) with LiClO_4 in γ -BL as the electrolyte, Pt sheet as the counter electrode and Ag/AgCl/sat'd KCl as the reference electrode.

The electrochromic measurement of the complementary device was performed similarly with the single EC layer device, but with the counter Pt wire replaced by PB as counter electrode. Detailed measurement introduction could be found in Chapter 4.

5.4 Structures, morphologies and growth mechanisms

5.4.1 Stick/particle like hydrated WO_3 films

Figure 5-2(a) shows the x-ray diffraction (XRD) patterns of the as-prepared thin films grown with and without $\text{CH}_3\text{COONH}_4$. Both films show the same crystalline structure and all peaks can be well indexed to the orthorhombic phase of $3\text{WO}_3 \cdot \text{H}_2\text{O}$ (JCPDF 87-1203) with the corresponding lattice constants of $a = 7.345$, $b = 12.547$ and $c = 7.737$ Å. The sharp peaks indicate the good crystalline quality of the as-fabricated films. The EC performance of WO_3 is closely related to

its crystallinity. Crystalline WO_3 has a better stability to endure acidic electrolyte without degradation for a longer cyclic time compared to amorphous one, but at the cost of slower response time and smaller coloration efficiency arising from its smaller specific surface area.[151] By increasing the porosity and precisely controlling the crystal size, crystalline WO_3 films with good stability and fast response can simultaneously be achieved. Figure 5-2 (b) shows the x-ray photoelectron spectroscopy (XPS) data of the as-synthesized films. The binding energies of the samples were corrected using a value of 284.5 eV for the C 1s peak of carbon. For both films, two well-resolved peaks at about 35.5 and 37.6 eV in the spectra are attributed to the spin orbit split doublet peaks of $\text{W } 4f_{7/2}$ and $\text{W } 4f_{5/2}$, respectively. These two peaks are well separated without any shoulders, indicating that all W atoms are in the +6 oxidation states.

Figure 5-2. XRD patterns (a) and (b) Tungsten 4f region XPS spectra of the as-synthesized thin films grown with and without $\text{CH}_3\text{COONH}_4$.

Figure 5-3 shows the morphologies of the as-synthesized films. It can be seen that the film grown without $\text{CH}_3\text{COONH}_4$ consists of irregular aggregated nanobricks with sizes ranging from tens to hundreds of nanometers (see Figure 5-3 (a) and (b)), while thin film made up of stacked nanosticks and nanoparticles is obtained by adding $\text{CH}_3\text{COONH}_4$ as the capping agent (Figure 5-3(c) and (d)). The nanosticks with an average length of ~ 50 nm are horizontally stacked together, leading to a coarse surface. A lot of small nanoparticles with sizes of tens of nanometers are accumulated underneath these sticks. Clear lattice fringes of the high-resolution transmission electron microscopy (HRTEM) image from a nanostick (inset of Figure 5-3(d)) indicate its single crystalline quality. The inset cross-sectional image shows that the film with a thickness of ~ 560 nm has a good adherence to the substrate. According to the recent report,[148] orthorhombic $3\text{WO}_3 \cdot \text{H}_2\text{O}$ actually contains two type of corner-sharing WO_6 octahedras. One type is conducted by a central tungsten atom that is surrounded by six oxygen atoms, while in the second type, two of the oxygen atoms are replaced by a shorter terminal $\text{W}=\text{O}$ bond and longer $\text{W}-(\text{OH})_2$ bond, respectively. Finally, the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ lattice is formed by stacking up layers consisting of these two structural units. Herein, the $\text{CH}_3\text{COONH}_4$ has a capping effect on the stacking of these two structural units, resulting in the formation of nanosticks.

Figure 5-3. FESEM images of (a) and (b) the nanobrick 3WO₃·H₂O thin film grown without CH₃COONH₄; and (c) and (d) nanostick/nanoparticle film with CH₃COONH₄.

Insets: cross-sectional and HRTEM image.

Figure 5-4 schematically illustrates the formation process of the films grown with and without CH₃COONH₄.

Figure 5-4. Schematic illustration of the formation process of the as-grown thin films.

5.4.2 Brick-like hydrated WO_3 films

The x-ray powder diffraction patterns of the bare FTO substrate and the as-prepared thin film are illustrated in Figure 5-5(a). The pattern of the substrate is indexed to tin oxide layer. For the hydrothermally grown film, characteristic peaks of hydrated WO_3 were obtained. All the diffraction peaks can be well indexed to orthorhombic hydrated $3\text{WO}_3 \cdot \text{H}_2\text{O}$ (H- WO_3) phase with lattice constants of $a = 7.345$, $b = 12.547$ and $c = 7.737$ Å, agreeing well with the standard diffraction pattern (JCPDF 87-1203). And no impurity peaks were observed on the pattern, implying high purity of the H- WO_3 film. The sharp peaks indicate the good crystalline quality of the as-fabricated film. The x-ray photoelectron spectroscopy (XPS) and Raman spectra of the nanobrick H- WO_3 film were also investigated and shown in Figure 5-5(b) and (c), respectively. All the peaks appeared on the spectra can be well assigned to be H- WO_3 and no other impurities were detected, coincide with the XRD result. The orthorhombic $3\text{WO}_3 \cdot \text{H}_2\text{O}$ phase contains two type of structure units: one is conducted by six oxygen atoms surrounded one centered W atom that shares the six corner oxygen atoms with adjacent octahedra, and the other is containing a coordinative water molecule with a prolonged W-OH₂ bond and a shorted W=O bond (shown in Figure 5-5(d)). It is clear that the EC performance of WO_3 is closely related to its level of crystallization.[36] Crystalline WO_3 films with large surface area and porous morphologies are expected to achieve a good stability, high coloration efficiency values and fast response.[150,153]

Figure 5-5. (a) XRD patterns of the bare FTO substrate and the as-synthesized thin films. (b) Wide scanning XPS spectra of the as-prepared nanobrick film. (c) Raman spectra of the film. (d) Schematic illustration of the orthorhombic $3\text{WO}_3 \cdot \text{H}_2\text{O}$ structure.

Figure 5-6. (a) and (b) FESEM images of the H-WO₃ thin films under different magnifications. (c) TEM image of the nanobrick scratched from the film. (d) SAED pattern of the nanobrick. (e) HRTEM image of the nanobrick.

Figure 5-6(a) and (b) show the top-view SEM images of the as-synthesized H-WO₃ film under different magnifications. It can be seen that the film is composed of brick-like nanostructures with average size of ~ 100 nm, forming a rough surface. These nanobricks gather together and grow along various directions, leading to the formation of a lot of pores which could increase the surface area of film. Through these pores, ions in the electrolyte can insert into or extract from the film more easily and efficiently, resulting from the reduced length of ion diffusion path. The cross-sectional view image (inset of Figure 5-6 (b)) shows that the film

with a thickness of ~ 320 nm has a good adhesion to the substrate. Figure 5-6(c) shows the TEM image of the nanobricks scratched away from the substrate. One nanobrick with integral shape (length: ~ 320 nm) shows vertically joint angles. Figure 5-6(d) depicts the selected area electron diffraction (SAED) pattern of this nanobrick. Regular diffraction spots are obtained, proving it is single crystalline. The nanobrick has preferential growing direction along c axis, corresponding to crystal planes of (002). The HRTEM image in Figure 5-6(e) from the edge of this nanobrick shows its crystal lattices of 0.38 nm, corresponding to the d-spacing of (002) planes, in good agreement with Figure 5-6(d). Clear lattice fringes also indicate its single crystal quality.

To investigate the growth mechanism of the H-WO_3 films, the effects of seed layer, H_2O_2 and $(\text{NH}_4)_2\text{SO}_4$ on the products were also studied. Figure 5-7(a) and (b) show the SEM images of products grown without seed layer under different magnifications, while other conditions remain the same with Figure 5-6. Irregular bricks with different sizes rather than a film are obtained. These bricks are stacked disorderly and adhered to the substrate surface. This result indicates that crystal-seed-layer offers the nucleation sites for the growth of bricks, which is crucial on organizing these bricks into an ordered film system on the substrate. Figure 5-7(c) and (d) depict the SEM images of film grown without addition of $(\text{NH}_4)_2\text{SO}_4$. Thick yellowish film composed of gathered blocks with irregular shape and sizes are prepared. The nanoblock film shows a good adhesion to the substrate. The above result implies that $(\text{NH}_4)_2\text{SO}_4$ has a capping effect on the product.

Figure 5-7. (a) and (b) SEM images of the product grown without seed layer under different magnifications. (c) and (d) The product grown without addition of $(\text{NH}_4)_2\text{SO}_4$. (e) and (f) The product grown without addition of H_2O_2 .

Figure 5-7(e) and (f) show the morphologies of products grown without addition of H_2O_2 . Accumulated nanospheres with uniform sizes (~ 80 nm) were synthesized. These nanospheres stacked intricately on the substrate are easily washed away by di-water. It seems that H_2O_2 has some chelating effect on directing the condensation of the $[\text{WO}_6]$ and $[\text{WO}_5\text{-H}_2\text{O}]$ octahedrons through the peroxo group. Moreover, it plays a role in linking the nucleus to the seed-layer coated surface. From the above result, it can be seen that H- WO_3 films can only be obtained on seed-layer-coated substrate with the addition of H_2O_2 . The growth mechanism of the brick-like nanostructured film can be explained according to the following reactions:

H_2WO_4 precipitate was formed immediately after addition of HCl solution. Then it was rapidly dissolved by the existing hydrogen peroxide (H_2O_2) in the precursor and peroxopolytungstic acid ($\text{WO}_3 \cdot x\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$, PTA) was obtained. The peroxo group of the H_2O_2 behaves as a chelating agent on directing the condensation of the $[\text{WO}_6]$ and $[\text{WO}_5\text{-H}_2\text{O}]$ octahedrons.[163,164] It decreases the functionality of aqueous precursors toward condensation and prevents precipitation. Without the addition of H_2O_2 , H_2WO_4 precipitate composed of numerous small clusters were formed and these clusters were further developed into nanospheres after

hydrothermal process under high temperature. PTA can be easily decomposed at high temperature and a layer of $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$ crystal nucleus was formed from the decomposition of PTA, and the seed-coating substrate acted as nucleation and growth sites. Without seed layer, irregular bricks attaching on the substrate surface rather than a film are obtained. Although there is no chemical reaction between the $(\text{NH}_4)_2\text{SO}_4$ and tungstic acid, the $(\text{NH}_4)_2\text{SO}_4$ will act as structure-directing and dispersing agents through both the anions (SO_4^{2-}) and cations (NH_4^+) on the condensation of $[\text{WO}_6]$ and $[\text{WO}_5\text{-H}_2\text{O}]$ octahedrons. The brick-like nanostructures were grown eventually from the $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$ nucleus under the capping effect of $(\text{NH}_4)_2\text{SO}_4$, while block-like films were obtained without $(\text{NH}_4)_2\text{SO}_4$. Figure 5-8 schematically summarizes the formation process of as-prepared products under different hydrothermal conditions.

The thicknesses of the as-grown nanobrick films can be controlled by altering the concentration of precursor solution. A thicker film can be obtained under higher concentration. Moreover, the effects of the amount of $(\text{NH}_4)_2\text{SO}_4$ and H_2O_2 on the products were also investigated and shown in Figure 5-9. When the amount of $(\text{NH}_4)_2\text{SO}_4$ increased to 0.1 g, some irregular particles were obtained and attached on the surface of substrate (shown in Figure 5-9(a) and (b)), which may be due to the high ionic strength of the solution. While thin film made up of irregular microbricks was obtained when the amount of H_2O_2 was increased from 0.2 to 0.4 g (shown in Figure 5-9(c) and (d)), with similar morphology to the previous reports.[152]

Figure 5-8. A schematic illustration of the formation process for the products.

Figure 5-9. SEM images of the products under different magnifications. (a) and (b) 0.1 g (NH₄)₂SO₄; (c) and (d) 0.4 g H₂O₂.

5.5 Electrochemical and electrochromic properties

5.5.1 Nanostick/particle hydrated WO₃ films and the complementary EC devices

Figure 5-10. (a) Cyclic voltammograms (CVs) of the nanostick/nanoparticle and nanobrick $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films in γ -butyrolactone with 0.2 mol LiClO_4 ; (b) and (c) CVs of the nanostick/nanoparticle and nanobrick film at the scan rates of 5, 10, 25, 50 and 100 mV/s , respectively. Insets: the cathodic/anodic peak current density as a function of the square root of the scan rates; (d) CVs of the nanostick/nanoparticle film after 1st, 1000th, and 2000th cycles, and (e) Chronoamperometry (CA) curve of the as-synthesized films recorded at ± 0.5 V for 40s.

Cyclic voltammograms (CVs) were investigated for both films and shown in Figure 5-10(a). These CVs were normalized with respect to the geometric area and to the weight of $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film within that area. During each scan, the films undergo typical reversible color changes from blue to colorless. The integrated cathodic/anodic current equates to the amount of Li^+ intercalation/deintercalation. It can be clearly seen that the nanostick/nanoparticle film grown with $\text{CH}_3\text{COONH}_4$ shows a higher current density for both intercalation and deintercalation processes over the same time period than the nanobrick one, indicating faster Li^+ intercalation/deintercalation kinetics. The total cathodic charge for the nanostick/nanoparticle film is about $4.2 \text{ mC cm}^{-2} \text{ mg}^{-1}$, compared to only about $2.0 \text{ mC cm}^{-2} \text{ mg}^{-1}$ for nanobrick films.

The CVs of nanostick/nanoparticle and nanobrick films recorded between -1.0 and 1.2 V at various scan speeds are shown in Figure 5-10(b) and (c), respectively. It can be seen from Figure 5-10(b) that when the scan speed is 5 mV/s, there are two oxidation peaks that appear at about -0.83 and -0.56 V, and two reduction peaks that appear at -0.45 and -0.85 V. With the increased scan speed, the first oxidation peaks disappear, while the second peaks get broader and higher, and the peak positions shift to a higher oxidation potential. The reduction peaks show a similar trend. When the second anodic peak current densities are plotted against the square root of scan rates, $v^{1/2}$, approximately a linear relationship is obtained (inset of Figure 5-10(b)), which signifies a diffusion-controlled process.[165] The effective diffusion coefficient D for the diffusing species Li^+ can be estimated from the peak current density (j_p) dependence on the square root of

the potential scan rate ($v^{1/2}$) assuming a simple solid state diffusion controlled process:[145]

$$\delta_{ip} / \delta \sqrt{v} = 2.69 \times 10^5 n^{3/2} A C \sqrt{D} \quad (31)$$

$$D = 0.1382 \times 10^{-10} n^{-3} A^{-2} C^{-2} (\delta_{ip} / \delta \sqrt{v})^2 \quad (32)$$

where n is the number of electrons transferred in unit reaction, A is the effective geometric surface area of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ electrode, and C is the concentration of the diffusion species (Li^+). The effective diffusion coefficients D_{Li^+} have been calculated from equation (33) to be 2.19×10^{-11} and $1.39 \times 10^{-11} \text{ cm}^2/\text{s}$ for the intercalation and deintercalation process, respectively, comparable to the reported values.[146] Figure 5-10(c) shows the CVs of the nanobrick film recorded at different scan rates, showing a similar profile but smaller current density. The calculated diffusion coefficients D_{Li^+} are 9.60×10^{-12} and $6.101 \times 10^{-12} \text{ cm}^2/\text{s}$ for the intercalation process and deintercalation process, respectively, which are smaller than those of the nanostick/nanoparticle film. The faster ion diffusion kinetics of the nanostick/nanoparticle film arises from its much rougher surface, which increases its surface area and reduces the ions diffusion path length. The cyclic stability of the nanostick/nanoparticle film was also measured for the 1st, 1000th, and 2000th cycle at room temperature and the results are shown in Figure 5-10(d). The current density increases slightly within 2000 cycles, without a clear change in the shape of CV curve, indicating excellent cyclic stability of the film, which is similar to the reported crystalline WO_3 nanoparticles.[36] Chronoamperometry (CA) data were recorded for both films with the potential being stepped from -0.5

V to +0.5 V for 40 s, as shown in Figure 5-10(e). During each cycle, the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films change from bleached state to colored state reversibly. For both films, the peak current density of bleaching is much higher than that of coloration, and the current density during bleaching decays faster than coloration. This characteristic is typical for WO_3 with small ion intercalation/deintercalation. The higher bleaching current arises from the good conductivity of tungsten bronze (Li_xWO_3), and the rapid current decay is due to the conductor (Li_xWO_3)-to-semiconductor (WO_3) transition, while the coloring kinetics is always slower than the bleaching one for WO_3 films owing to the higher resistance during WO_3 to Li_xWO_3 transition. Moreover, the peak current densities of coloration/bleaching (-4.9 and 14.1 mA cm^{-2}) of the nanostick/nanoparticle film are higher than those (-2.4 and 7.5 mA cm^{-2}) of the nanobrick film. The response time (defined as 70% decrease of current density) for coloration (t_c) and bleaching (t_b) are calculated from current-time transient data from Figure 5-10(e). The nanostick/nanoparticle film shows faster coloration/bleaching responses ($t_c \sim 7.0 \text{ s}$ and $t_b \sim 3.0 \text{ s}$) than those ($t_c \sim 9.0 \text{ s}$ and $t_b \sim 3.5 \text{ s}$) of the nanobrick film, in well agreement with the results in Figure 5-10(a-c). The fast responses for both films are comparable to the spray-pyrolysis deposited amorphous WO_3 film.[141]

Figure 5-11. In-situ transmittance response and coloration efficiency at 754 nm for the nanobrick film (a and b) and the nanostick/nanoparticle film (c and d).

The in-situ transmittance responses of the nanostick/nanoparticle and nanobrick film (sample sizes $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) for a 90% transmittance change were also investigated at 754 nm by a $\pm 0.8 \text{ V}$ bias (see Figure 5-11(a) and (c)). For the nanostick/nanoparticle film, the coloration time t_c is found to be 7.9 s, and the bleaching time t_b is 4.8 s. However, for the nanobrick film, the coloration time t_c is found to be 7.3 s, and the bleaching time t_b is 7.1 s. The bleaching speed of the nanostick/nanoparticle film is much faster than the nanobrick film, but the coloration speed is a little slower. It is worth to mention that a larger optical modulation of $\sim 45\%$ of the nanostick/nanoparticle film is

achieved, compared to that only 38% of the nanobrick film. Coloration efficiency (CE) values of both films were also studied and shown in Figure 5-11(b) and (d), respectively. The CE is extracted as the slope of the line fits to the linear region of the curve. It can be seen that the calculated CE of the nanostick/nanoparticle film is $45.5 \text{ cm}^2 \text{ C}^{-1}$, larger than that of the nanobrick film ($36.8 \text{ cm}^2 \text{ C}^{-1}$). The improved EC performance of the nanostick/nanoparticle film is due to its large surface area.

To further improve the optical contrast, coloration efficiency and switching stability, the nanostick/nanoparticle film is incorporated in an EC device with an anodically colored PB film as a complementary EC layer. The morphology and CV curve of the as-deposited PB film were also investigated and shown in Figure 5-12 and Figure 5-13, respectively. It can be seen that the PB film is composed of a large scale of aggregated nanoparticles with sizes of $\sim 20\text{-}50 \text{ nm}$. There are cracks in the film formed due to stress. The CV of the PB film was also taken with 0.2 M LiClO_4 in γ -butyrolactone electrolyte at a scan rate of 50 mV s^{-1} . The redox reaction for the PB film in the presence of Li^+ ions is proposed as follows:

The typical voltammogram is similar to the reported one measured on electrodeposited PB films.[162] During each cycle, the film is observed to change its color from blue to colorless reversibly.

Figure 5-12. FESEM images of electrodeposited PB film.

Figure 5-13. Cyclic voltammetry (CV) curve of PB film at a scan rate of 50 mV s^{-1} with 0.2 M LiClO_4 in γ -butyrolactone electrolyte.

Figure 5-14. Optical absorption spectra of a complementary EC device and a single PB layer device at the colored and bleached state under $\pm 0.8V$, respectively.

Figure 5-14 shows optical absorption spectra of the complementary EC device and a single PB layer device at the bleached and colored state under a ± 0.8 V bias. Compared with the single PB layer device, the complementary device shows a larger optical modulation above 410 nm, especially in the near IR region, indicating a higher color contrast and larger heat regulation. Moreover, the complementary device depicts a higher absorption in the near UV region at both colored and bleached states due to the absorption of $3WO_3 \cdot H_2O$ films. The above result is highly desired in smart window applications since more heat can be prohibited from entering the interior buildings, resulting in a reduction of cooling loads.

Figure 5-15. (a) Switching time characteristics between the colored and bleached states for the complementary EC device measured at ± 0.8 V for 30s and (b) optical density variation with respect to the charge density recorded at 754 nm.

Figure 5-15(a) shows the in-situ coloration/bleaching transmittance response of the complementary device (sample size ~ 2 cm², FTO sheet resistance: $15\Omega/\square$) measured at 754 nm. The maximum transmittance modulation (ΔT) of coloration/bleaching was found to be about 54% after applying a ± 0.8 V voltage for 30 s, agreeing well with the absorbance spectra shown in Figure 5-14. Obvious color changes can be observed during the switching. The coloration and bleaching time extracted as 90% transmittance changes are found to be 1.3 and 5.7 s, respectively. The switching responses of the complementary device for both the coloration and bleaching processes are much faster than those reported values.[65] For this complementary EC device, limitations of switching response are mainly due to $3\text{WO}_3 \cdot \text{H}_2\text{O}$ electrode. The fast coloration/bleaching kinetics may be attributed to the large active specific area of the rough surface, which facilitates the ions intercalation/deintercalation by reducing their diffusion lengths. CE of the

complementary cell was also investigated at its peak absorbance ($\lambda = 754$ nm) and shown in Figure 5-15(b). The calculated CE value is $151.9 \text{ cm}^2/\text{C}$, comparable to that of the reported $\text{WO}_3||\text{PB}$ complementary device.[65] And the CE of the complementary device is improved by about 234% compared with a single $3\text{WO}_3 \text{ H}_2\text{O}$ EC layer ($\text{CE} = 45.5 \text{ cm}^2/\text{C}$).

Figure 5-16. Photographs of a complementary EC device at the bleached state (a) and (b) the colored state under $\pm 0.8\text{V}$, respectively.

Photographs of the complementary device are shown in Figure 5-16, depicting a high contrast between the bleached and colored states, which leads to the obvious transparency changes. The device shows promising applications in energy-saving smart windows.

5.5.2 Brick-like hydrated WO_3 films and the complementary EC devices

CVs normalized to the geometric area of the H- WO_3 film and PB film electrodes are shown in Figure 5-17(a), measured in 0.3 M LiClO_4 in $\gamma\text{-BL}$ as the electrolyte with a scan rate of 0.1 V/s . The PB film shows typical oxidation and reduction peaks at 0.23 V and -0.37 V , respectively. The H- WO_3 film shows oxidation peak at -0.34 V . Compared with the H- WO_3 film, the PB film has a higher current density, implying faster ions intercalation/deintercalation kinetics.

During each scan, both films will reversibly change their colors from colorless to blue. For H-WO_3 , this behavior is resulting from Li^+ and electron transfer between W^{6+} and W^{5+} .

The cyclic stability of the H-WO_3 film was also investigated by multiple cycles and shown in Figure 5-17(b). No significant shape change was observed, and only a small current reduction was found after 2000 cycles, indicating an excellent cyclic stability. The long term cyclic stability is crucial for applications in energy efficient smart windows to compensate its relatively high cost.

Figure 5-17. (a) CV curves of as-prepared H-WO_3 film and electrodeposited PB film, measured in 0.3 M LiClO_4 γ -BL electrolyte at a scan rate of 0.1 V s $^{-1}$, and (b) CV curves of the H-WO_3 film after 1st, 1000th and 2000th cycles.

Figure 5-18. UV-vis transmittance spectra of the (a) complementary EC device and single PB layer device and (b) the single nanobrick film device at bleached and colored state under ± 0.8 V, respectively.

Transmittance spectra of the complementary device and single PB layer device at bleached and colored state were compared (shown in Figure 5-18(a)), operated under ± 0.8 V in γ -BL electrolyte (0.3 M LiClO_4). The single PB layer device shows obvious broad optical modulation between bleached and colored states, especially in the range of 470 nm to 850 nm, similar to the reports.[46,166] The complementary device depicts a comparable high transmittance level at bleached state, indicating a highly transparent state of as-grown H-WO_3 films. When the device is colored, lower transmittance in the whole range is achieved, resulting from the complementary color contrast of H-WO_3 films. As a result, the complementary device demonstrates an improved optical regulation and an increased color contrast. Moreover, the complementary device shows a larger modulation in the infrared light due to a high absorbance and reflectance of crystalline H-WO_3 films,[73] which property is highly desired in energy saving

windows applications since a large amount of heat energy in infrared light is blocked from entering into the interior building. Transmittance spectra of the as prepared H-WO₃ film and the film at colored/bleached states were investigated and shown in Figure 5-18(b). The transmittance decreases obviously at the colored state above 400 nm compared to the bleached state. And a larger modulation in the infrared light region was observed compared with the single PB layer device. Moreover, the transmittance at bleached state is very close to the as-prepared state, indicating good reversibility of the film. Compared with the complementary device, the single H-WO₃ film device shows smaller transmittance regulation, resulting in the indistinctive optical contrast between colored complementary device and single PB layer device.

Figure 5-19(a) shows the in-situ switching transmittance response of the complementary device at 632.8 nm, conducted by ± 0.8 V for 30 s. Obvious color changes between transparent and blue can be seen during the switching. A maximum transmittance modulation (ΔT) of $\sim 30\%$ between coloration and bleaching is achieved at this wavelength, agreeing well with the transmittance spectra shown in Figure 5-18. The response time is extracted as the time for 90% transmittance change. The coloration time ($t_{c,90\%}$) is found to be 1.8 s and bleaching time ($t_{b,90\%}$) is 3.7 s, respectively, both are much faster than the previous reported values.[15,65] It is clear that the fast switching speed of the complementary device is mainly due to the fast switching kinetics of PB film, which account for the primary optical regulation. Although H-WO₃ films contribute a small complementary color contrast, it is crucial in regulating infrared light.

Figure 5-19. (a) Switching time characteristics between the colored and bleached states for the complementary EC device and (b) the single H-WO₃ film device under ± 0.8 V at 632.8 nm, respectively. (c) Optical density variation with respect to the charge density recorded at 632.8 nm for the complementary device and (d) single H-WO₃ film device at 632.8 nm.

The coloration/bleaching responses of the H-WO₃ films (sample size ~ 1.7 cm², FTO sheet resistance: $15\Omega/\square$) were also investigated and shown in Figure 5-19(b). A slower response of $t_{c,90\%} = 51.5$ s, $t_{b,90\%} = 11.5$ s and a smaller transmittance modulation ($\sim 13\%$) is found. However, the switching response is much faster than the reported nanorods and microbrick WO₃ films.[131,152] Fast

switching speed is due to the small thickness and large surface area that resulting in a short diffusion path for ions.

CE of the complementary device and single WO₃ film device was also investigated and compared at $\lambda = 632.8$ nm (shown in Figure 5-18(c)). CE, a crucial characteristic parameter for evaluating EC materials, a high value of CE indicates that the EC film exhibits a large optical modulation with a small charge inserted (or extracted), which is related the porosity, crystal sizes and phase structures of the film. For the complementary device, the CE value is calculated to be $164.6 \text{ cm}^2 \text{ C}^{-1}$, which is larger than the reported value ($\sim 140 \text{ cm}^2 \text{ C}^{-1}$). [15,65] The OD variation is dramatic initially with the insertion of ions, then it gets smaller and smaller and finally gets stabilized after more ions inserted into the films. An inflection point at $\sim 0.008 \text{ C cm}^{-2}$ is observed, and the OD quickly gets stabilized after it. For the single H-WO₃ film Figure 5-19(d)), a CE value of $30.1 \text{ cm}^2 \text{ C}^{-1}$ is obtained, which is comparable to the reported value. [152]

Photographs of the complementary EC device and the single H-WO₃ film device are shown in Figure 5-20. The complementary device depicts a higher contrast between bleached and colored state than the single H-WO₃ film one. The device is promisingly applied in energy efficient smart windows and large area information displays.

Figure 5-20. Photographs of the complementary device at bleached state (a) and (b) colored state. Single H-WO₃ layer device at bleached (c) and (d) colored state under ± 0.8 V, respectively.

5.6 Summary

Orthorhombic hydrated tungsten trioxide ($3\text{WO}_3 \cdot \text{H}_2\text{O}$) films consisted of nanosticks and nanoparticles were successfully prepared on FTO-coated substrate by a facile and template-free hydrothermal method using $\text{CH}_3\text{COONH}_4$ as the capping agent. Irregular nanobrick films were obtained without $\text{CH}_3\text{COONH}_4$. Due to the highly rough surface, the nanostick/nanoparticle film depicts faster ion intercalation/deintercalation kinetics and a larger CE value ($45.5 \text{ cm}^2 \text{ C}^{-1}$) than the nanobrick film. A complementary electrochromic device based on the nanostick/nanoparticle $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film and Prussian blue (PB) was assembled. As a result, the complementary device (sample size $\sim 2.0 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) shows a higher optical modulation (54% at 754 nm), a larger coloration efficiency ($151.9 \text{ cm}^2 \text{ C}^{-1}$ at 754 nm) and faster switching responses with a

bleaching time of 5.7 s and a coloring time of 1.3 s than a single $3\text{WO}_3 \cdot \text{H}_2\text{O}$ layer device, making it attractive for a practical application.

By using $(\text{NH}_4)_2\text{SO}_4$ as the capping agent, uniform, highly adhesive and transparent nanobrick hydrated WO_3 (H- WO_3) films were assembled on FTO glass substrate. The effects of seed-layer, $(\text{NH}_4)_2\text{SO}_4$ and H_2O_2 on the products are studied. The seed-layer and H_2O_2 are vital in assembling the nanostructures into a thin film on the substrate, and both $(\text{NH}_4)_2\text{SO}_4$ and H_2O_2 have influences on the products' morphologies. The as-synthesized orthorhombic H- WO_3 films show good cyclic stability, comparable switching response ($t_{c,90\%} = 51.5$ s, $t_{b,90\%} = 11.5$ s) and CE value ($30.1 \text{ cm}^2 \text{ C}^{-1}$). A complementary device made up of H- WO_3 and PB film is also fabricated and demonstrates highly improved EC performance. This device (sample size $\sim 1.7 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) shows much faster coloration/bleaching response ($t_{c,90\%} = 1.8$ s, $t_{b,90\%} = 3.7$ s), larger CE value ($164.6 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm) and increased color contrast. The complementary device is prospectively applied in smart windows and displays, and the as-synthesized H- WO_3 films may find more applications in gas sensors and electronic devices.

CHAPTER 6 PRUSSIAN BLUE BASED PHOTOELECTROCHROMIC DEVICES¹

6.1 Introduction

In recent years, the growing interest in low-power systems has led to the development of various energy-efficient chromic technologies including electrochromism, photochromism, gaschromism, thermalchromism and photoelectrochromism.[78,80,167-169] Among them, photoelectrochromic (PEC) devices have attracted significant attention because of their unique function of dynamically controlled solar energy gain and optical properties through switchable glazing in response to illumination, with promising applications in smart windows, sunglasses and light-writable low-information content displays.[16,81,85] Although various device configurations and working mechanisms have been reported in recent years,[80,170-172] most of the reported PEC devices are composed of a light-sensitive photovoltaic layer and an EC layer. A dye-sensitized TiO₂ nanoparticle (NP) photoanode has been most commonly adopted as the photovoltaic layer, and various EC materials (inorganic or organic) have been assembled as the EC electrode including WO₃ or polyaniline.[12,80,173] Under illumination, photoelectrons generated by the dye molecule inject into the conduction band of TiO₂ and then transport through the external circuit to the counter EC electrode, driving the ions in the electrolyte to intercalate into the EC

¹ The main results of this Chapter have been published as: Z. Jiao, J.L. Song, X.W. Sun, X.W. Liu, J.M. Wang, L. Ke and H.V. Demir, *Solar Energy Materials and Solar Cells*, 2012, 98, 154.

layer at the same time. Correspondingly, the transmittance of the PEC device will be decreased as a result of the darkened EC layer. The bleaching state can be achieved by either short circuit or open circuit configuration with light blocked. The switching response is mainly dependent on the EC material and electrode adopted. Recently, Chen's group improved the bleaching rate of a WO_3 -based PEC device using a patterned WO_3/Pt electrode, providing the charge transfer pathways to accelerate the bleaching process.[12] Under illumination, the cell can be colored in a short circuit configuration with tunable transmittance and bleached more quickly when the circuit is opened (~ 60 s).

Prussian blue [PB, iron (III) hexacyanoferrate (II)] is a well-known synthetic coordination-compounded transition metal hexacyanometallate, which has attracted considerable attention owing to its various applications in electrochromic,[46,174] sensors,[175] catalysts,[45] and batteries.[176] Different from WO_3 , PB is an anodically coloring EC material with promising EC properties. It is reported that an electrodeposited PB film exhibits electrochromism between blue and colorless state with a fast response (≤ 100 ms) and a high durability for 5×10^6 cycles.[162] The excellent EC performance makes it an ideal candidate for applications in smart windows and electronic paper displays. Although there have been numerous reports regarding EC applications of PB, to our knowledge, such a PB film has not been incorporated in a device to enable fast-switching light-writable and electric-erasable photoelectrochromic operation to date.

In this dissertation, we propose and demonstrate a negative PEC cell, composed of an electrodeposited PB EC electrode and a dye-sensitized TiO₂ NP photoanode. The cell can be bleached in short circuit configuration under illumination and re-coloration can be achieved through applying a proper external voltage with fast switching response, providing a negative mode to the existing photoelectrochromic technology. The PEC cell is promising for light-writable and electric-erasable information display applications.

6.2 Fabrication and characterization of the PEC device

6.2.1 Electrodeposition and characterization of PB films

Fluorine doped tin oxide (SnO₂:F, FTO) glasses (NSG Group, $R_s=15\ \Omega/\square$ and 2.2 mm thick) washed by acetone, isopropanol, and de-ionized water in sequence were used as substrates. The electrodeposition of PB films was carried out in a standard three-electrode system (VersaSTAT 3F Potentiostat/Galvanostat) with a clean FTO glass (2 cm × 3 cm) as the working electrode, a platinum sheet as the counter electrode, and a Ag/AgCl/sat'd KCl as the reference electrode. The electrodeposition bath of PB contained 10 mM K₃Fe(CN)₆ (Aldrich), 10 mM FeCl₃ (Aldrich), and 0.1 M KCl (Aldrich). The PB films were prepared by applying a constant cathodic current density of 50 $\mu\text{A cm}^{-2}$ for 100, 300, 500 and 700 s, respectively. Then the as-deposited blue PB films were rinsed by de-ionized water gently and dried at room temperature in atmosphere.

6.2.2 Preparation of dye-sensitized TiO₂ nanocrystalline photoanode

To fabricate the photoanode, TiO₂ NP paint (Solaronix, Ti-Nanoxide T20/SP) was first screen-printed on a piece of FTO glass which was ultrasonically cleaned sequentially by acetone, isopropanol and de-ionized water. After calcination at 450 °C for 1 h, a transparent and well adhesive TiO₂ film with a thickness of ~ 4 μm was obtained. Dye absorption was carried out by immersing the TiO₂ electrode into a Z907 solution [(cis-bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II) in dilute (8 μM) ethanol solution containing 60 mM chenodeoxycholic acid] for 110 mins. The electrode was then washed with acetonitrile for 3 times to remove the unanchored dye molecules. The dye coverage was kept low to make the cells semi-transparent in the “off” state.

6.2.3 Assembly of the photoelectrochromic cell

The dye-sensitized TiO₂ nanocrystalline photoanode and PB electrode was bonded together with hot-melt Surlyn spacers. Then a liquid electrolyte solution composed of 0.1 M LiI and 0.01 M 4-t-butylpyridine in γ-butyrolactone was introduced between the two electrodes by capillary action. Finally the cell was sealed with epoxy. The final cell has a configuration of:

which is schematically shown in Figure 6-1.

Figure 6-1. Schematic of the proposed hybrid photoelectrochromic cell.

6.2.4 Characterization

The morphologies of electrodeposited PB films were characterized by field emission scanning electron microscopy (FESEM JSM 6340F). Cyclic voltammogram (CV) of the PB film was performed with 0.2 M LiClO_4 in γ -butyrolactone as the electrolyte, a platinum sheet as the counter electrode and $\text{Ag}/\text{AgCl}/\text{sat. KCl}$ as the reference electrode. Thicknesses of the PB films were measured by a Tencor P-10 surface profiler. The transmittance was measured by a JASCO V670 UV-VIS-NIR spectrophotometer. A 150 W Xe lamp with optical filter (>300 nm) was used as the light source and the light intensity was calibrated by a pyranometer (PMA 2144 from Solar Light)

6.3 Morphology and cyclic voltammetry of the PB film

The morphologies of electrodeposited PB films were investigated (see Figure 6-2(a)). It can be clearly seen from Figure 6-2(a) that the film is composed

of accumulated nanoparticles with sizes of 20-50 nm. There are a lot of cracks with an average gap dimension of ~ 20 nm among the film, formed due to stress. The cyclic voltammetry (CV) curve of the PB film was measured with 0.2 M LiClO₄ in γ -butyrolactone as electrolyte at a scan rate of 100 mV/s (Figure 6-2(b)). The broad oxidation and reduction peaks appear at 0.84 and -0.8 V, respectively. During the cycling, the color of the PB film was observed to change between blue and colorless.

Figure 6-2. (a) SEM images of the electrodeposited PB film. (b) Cyclic voltammetry curve of PB film measured with 0.2 M LiClO₄ in γ -butyrolactone as electrolyte at room temperature with a scan rate of 100 mV/s from -1.2 to 1.7 V.

6.4 Working principles of the photoelectrochromic cell

It is well known that PB is an anodically EC material, opposite to WO₃ which is colored cathodically. Due to the opposite EC behaviors of PB and WO₃, the as-prepared cell is bleached rather than colored under illumination in short circuit configuration, providing a negative mode of the existing photoelectrochromic technology.[80,81] Under illumination, light absorption by the sensitizing dye leads to electron injection into the conduction band of TiO₂ and

then transport through external circuit to the counter PB electrode, driving the insertion of Li^+ from the electrolyte into the PB film at the same time. Accordingly, the color of the PB film changes from blue to colorless, which can be described by the following reaction:

At the same time, the excited dye molecules are reduced by iodide ion (I^-) present in the electrolyte according to the reaction: [1]

where S^0 and S^+ are the ground and ionized state of the dye molecule, respectively. The photo-bleaching process terminates when all I^- in the electrolyte are transformed to triiodide (I_3^-) or until the generated photovoltage equals the electromotive force of the formed $\text{Li}_4\text{Fe(II)}_4[\text{Fe(II)(CN)}_6]_3$ film, preventing the further diffusion of the electrons into the EC layer. Figure 6-3(a) schematically depicts the photo-bleaching process of the short circuit photoelectrochromic cell under illumination from the side of dye-sensitized TiO_2 NP photoanode. The color of PB film changes from original blue to colorless, resulting from the insertion of Li^+ and electrons, while the iodide ions are oxidized to triiodide by the excited dye molecules at the electrolyte\|dye interface. Figure 6-3(b) shows the photograph of a bleached photoelectrochromic cell (1.5 cm^2) after illumination of 100 mW cm^{-2} for 1 min in short circuit configuration. The PB film assembled in the cell is electrodeposited for 300 s and its thickness is measured to be 452 nm. It can be

seen that the original blue color of the PB film changes to colorless and the bleached cell displays pale yellow arising from the dye molecules absorbing on the surface of TiO₂ electrode.

The re-coloration process was carried out by applying a positive 2 V bias on PB electrode (while TiO₂ side is grounded) until the current density was stabilized, during which Li⁺ was driven out from PB film to the electrolyte, leaving PB in blue. At the same time, triiodide ions at the counter electrode were reduced to iodide ions by the electrons injected from the external bias:

In this way, triiodide ions are produced during the photo-bleaching process and are reduced back to iodide ions during the re-coloration process at the dye/electrolyte interface.

In fact, the re-coloration of the cell can also be achieved in either short circuit under dark or open circuit with or without illumination. The charged Li₄Fe(II)₄[Fe(II)(CN)₆]₃ electrode possesses a negative potential, which causes the cell to discharge spontaneously back to its colored state. However, the re-coloration without external bias shows a much slower speed. It needs about ~2 h to complete the re-coloration process of the open-circuited cell under illumination. The short-circuited cell shows a faster re-coloration speed than the open-circuited one, since the electrons can transport to the counter electrode through external circuit more efficiently, while the electrons in open circuit configuration are extracted from the EC layer and undergo a diffusion process to counter electrode.

However, it still needs more than one hour for the re-coloration in short circuit configuration. To reach a fast and efficient re-coloration, a proper external bias is adopted to overcome this problem.

To obtain good reversible stability, charges and ions involved in the two processes should be balanced. Correspondingly, an optimum bias voltage should be adopted since a too large bias will lead to over oxidization of PB to Prussian White (PW), while a too small bias results in insufficient re-coloration and slow response. For our cells, 2 V bias was adopted for re-coloration and, as a result, a fast response and good stability were achieved. Figure 6-3(c) shows the schematic of the re-coloration process and Figure 6-3(d) depicts the photograph of the cell after applying a positive 2 V bias on PB electrode for 30 s. It can be seen that the PB film changes to its original blue color reversibly after applying an electric stimuli. Moreover, spatially resolved bleaching was achieved when the cell was partially illuminated (Figure 6-3(e) and (f)). The spatially resolved bleaching occurs because the electric field is created spatially in the illuminated region; i.e., the electric field is concentrated between the oxidized dye and reduced PB counter electrode. However, the resolution of such spatially resolved bleaching is limited as such the electric field is maintained by ion diffusions. The above results indicate the prepared PEC cells can be potentially applied in negative mode light-writable and electric-erasable information displays.

Figure 6-3. Schematics and photographs of a PEC cell with a 1.5 cm² active area. The duration for electrodeposition of PB film is 300 s. (a) Schematic of the short circuit cell under illumination for bleaching. (b) The bleached cell achieved by illumination of 100 mW cm⁻² for 1 min in short circuit configuration. (c) Schematic of the cell under external voltage for coloring. (d) Photograph of the cell at colored state after applying a 2 V bias at PB electrode for 30 s. (e) and (f) spatially resolved bleaching states achieved by illuminating the cell with masks.

6.5 Optical-electro characterizations of the PEC cell

It is clear that longer duration of electrodeposition will lead to thicker PB films with a deeper blue color. Since the bleached PB films remain highly transparent, for single PB EC layer device, larger optical modulation (absorbance or transmittance) could be obtained using a thicker film. However, for thicker films, a larger operating voltage is needed for complete coloration/bleaching processes. To investigate the thickness effect on the optical modulation between bleached and colored states of the PEC cells, PB films with electrodeposition durations of 100, 300, 500 and 700 s were assembled as EC layers into the cells, respectively. The thicknesses of all the electrodeposited PB films were measured and tabulated in Table 1.

Table 1. Photoelectrochromic cells with different thicknesses of PB films and corresponding absorbance modulation at 700 nm

Type	Duration (s)	Thickness (nm)	Absorbance Modulation
A	100	123	0.20
B	300	452	0.44
C	500	785	0.24
D	700	1106	0.13

For all the cells, the conditions of dye-sensitized TiO₂ nanocrystalline photoanode and electrolyte were fixed. Subsequently, all the cells were bleached by illumination at 100 mW cm⁻² for 1 min in short circuit configuration and re-

colored by a positive 2 V bias on the PB electrode for 30 s. Optical absorbance spectra were investigated for all cells at the two states (Figure 6-4). It can be seen from Figure 6-4 that with increased PB film thickness, the absorbance of all cells at the colored state is enhanced from 470 to 840 nm. Also, the absorbance of all cells at the bleached state is obviously decreased compared to its colored state. Moreover, with PB film thickness increased from 123 to 452 nm, the absorbance modulations recorded at 700 nm between the two states are increased from 0.2 to 0.44. However, the modulation was decreased to 0.24 and 0.13 when the film thickness was further increased to 785 and 1106 nm, respectively, resulting from the insufficient bleaching. For our PEC cells, the photogenerated voltage (~ 0.4 V) is fixed under the same light intensity, and a too thick film will result in shallow bleaching level of PB film due to insufficient operating voltage and increased resistance. As shown in Figure 6-4(b), the largest absorbance modulation (0.44) recorded at 700 nm was obtained when the PB film thickness is set to 452 nm. The corresponding transmittance of the cell under this optimum condition is shown in Figure 6-5 for reference.

Figure 6-4. Absorbance spectra of the PEC cell at bleached state by illumination with a simulated solar intensity of 100 mW cm^{-2} for 1 min and colored state by applying a 2 V bias at the PB electrode for 30 s. The PB films assembled in these cells were electrodeposited for (a) 100 s, (b) 300 s, (c) 500 s and (d) 700 s, respectively.

Figure 6-5. Transmittance spectra of the cell between bleached and colored state.

Compared with the colored states, the absorbance of all cells at the bleached states are increased in the spectral range of 400 to 470 nm, which may be attributed to the absorption of triiodide ions formed at the dye\electrolyte interface. In the following part, we fix the thickness of PB film at the optimal value (452 nm). Following the standard test method of ASTM D1003A,[83,177] the haze numbers of the cell at bleached state were investigated and shown in Figure 6-6. It can be seen that the haze number increases with decreasing wavelength, which is due to the scattering losses caused by the TiO_2 nanoparticle becomes increasingly pronounced.[83] The luminous transmittance (T_{lum}) of the bleached device recorded from 400 to 850 nm is calculated to be 42%, and the luminous transmittance (T_{lum}) of the colored device is 18%, which corresponds to a contrast ratio of 2.3. More work is being done now to further decrease the thickness of the TiO_2 nanoparticle electrode to improve the contrast ratio between bleached and colored state of the device.

Figure 6-6. The haze number of the PEC cell at bleached state.

To further investigate the impact of light intensity on its absorbance, the cell was illuminated with simulated solar illumination of 5, 10, 20, 30, 40, 50, and 100 mW cm^{-2} , respectively for a fixed duration (3 s) in short circuit configuration (Fig. 7a). It can be seen that with increased light intensity, the absorbance decreases gradually from 470 to 840 nm. Moreover, the absorbance decreases significantly in 3 s between 10 and 50 mW cm^{-2} , and from 50 to 100 mW cm^{-2} , the decrease is comparatively less, indicating adjustable absorption of the cell under different levels of light intensity (grayscale is obtainable). Fig. 7b shows the absorbance spectra after 5, 10, 15, 20, 25, 30, and 60 s of illumination with a fixed simulated solar intensity of 5 mW cm^{-2} . It can be seen that the absorbance decreases with prolonged illumination time from 470 to 840 nm, and the decrease is mostly completed in 25 s, after which the decrease is not obvious. For both cases, there is not much difference of absorbance below 470 nm, indicating the cell

mainly regulates the absorbance in the visible range. Thus the absorbance of the cell in the visible light range can be adjusted with either light intensity or illumination time.

Figure 6-7. (a) Absorbance spectra of the as-prepared cell and illuminated with simulated light intensity levels of 5, 10, 20, 30, 40, 50, and 100 mW cm⁻² for 3 s in short circuit configuration. (b) Absorbance spectra of the as-prepared cell and illuminated with 5 mW cm⁻² for 5, 10, 15, 20, 25, 30, and 60 s respectively.

The photo-bleaching response of the cell (sample size ~ 1.5 cm², FTO sheet resistance: 15Ω/□) was investigated at a wavelength of 780 nm by 100 mW cm⁻² illumination in short circuit configuration (shown in Figure 6-8(a)). The response for 70% change is found to be 6.2 s. Inset of Figure 6-8(a) depicts the corresponding transient current change of the cell from the colored to bleached state under illumination. It can be seen that a clear current impulse was obtained upon illumination. The current shoots up from near zero to 1.4 mA in 0.4 s, then decays quickly in several seconds before getting stabilized. The time for 70% decrease ($t_{70\%}$) of the highest peak current is 6.4 s, very closed to the response of transmittance change. Figure 6-8(b) shows the in-situ transmittance response

recorded at 780 nm from the bleached to colored state by applying a positive 2 V bias on PB electrode. The transmittance shows a fast decrease from 95% to 14% in less than one second. Figure 6-8(c) shows the corresponding transient current change of this process, displaying a fast current decay. It can be seen that $t_{70\%}$ of both the in-situ transmittance and transient current are ~ 600 ms, implying a fast EC coloration response. The inset of Figure 6-8(c) shows the charge involved during the coloration process by chronocoulometry. Corresponding to the current-time plot, charges are increased significantly in the first 10 s, and then a linear increase with time is found for the following process. The EC performance of the PEC cell was also investigated by measuring its coloration efficiency (CE, η) according to Figure 6-8(b) and (c). As it is known, CE represents the change in the optical density (ΔOD) per unit charge density change ($\Delta Q/A$) during coloration or bleaching and can be calculated by equations (4) and (5):

$$\Delta OD = \log (T_{bleach}(\lambda) / T_{color}(\lambda)), \quad (38)$$

$$\text{and } \eta = \Delta OD / \Delta Q/A, \quad (39)$$

where $T_{bleach}(\lambda)$ is the transmittance of the bleached state and $T_{color}(\lambda)$ is the transmittance of the colored state. ΔQ is the change of the charge consumed for the change in the optical density. The CE of the PEC cell recorded at 780 nm after adding a 2 V bias voltage is shown in Figure 6-8(d). The CE was extracted as the slope of the line fitted to the linear region of the curve. The calculated CE value is $103.4 \text{ cm}^2/\text{C}$ for our cell, which is comparable to the reported values.[178]

The cell at colored state shows good stability in open circuit. While the photo-bleached cell gradually returns to colored state in either short circuit under dark state or open circuit with or without illumination, since the charged $\text{Li}_4\text{Fe(II)}_4[\text{Fe(II)(CN)}_6]_3$ electrode possesses a negative potential that causes the cell to discharge spontaneously back to its colored state.

Figure 6-8. (a) In-situ transmittance response of the cell under 100 mW cm^{-2} illumination in short circuit configuration at 780 nm. Inset: Transient current changes. (b) Transmittance response at 780 nm under 2 V bias. (c) Corresponding current changes of the coloration process. Inset: Integrated charge for coloration. (d) Coloration efficiency curve of the PEC cell recorded at 780 nm with 2 V bias.

Figure 6-9. Optical transmittance change versus time of the PEC cell in short circuit under dark and open circuit under illumination, respectively. The cell was bleached under 100 mW cm^{-2} illumination in short circuit configuration for 100 s.

Figure 6-9 shows the transmittance change of the cell in short circuit under dark and open circuit under illumination recorded at 780 nm, respectively. The cell was photo-bleached under 100 mW cm^{-2} illumination in short circuit configuration for 100 s. It can be seen that the transmittance gradually decrease in either short or open circuit. Moreover, the short-circuited cell shows a faster decrease rate than that of the open-circuited one. The time for 30% transmittance decrease are found to be 806 s and 505 s for open-circuited and short-circuited case, respectively.

The stability of the PEC cell was also investigated by measuring the transmittance changes recorded at 700 nm between the bleached and colored states (Figure 6-10). The photo-bleaching process of the cell was conducted under 100 mW cm^{-2} illumination in short circuit configuration for 60 s and the re-coloration was obtained by adding a 2 V bias on PB electrode for 30 s. After 1000 cycles of

operation, the performance of the cell is still quite stable. The transmittance attenuation was about 57.8 % (from 90.6% to 32.8%) of the first cycle, and after 1000 cycles, it had decreased to ca. 55.7% (from 88.9% to 33.2%); only 2.1% optical degradation was found, indicating a good stability.

Figure 6-10. The transmittance change (ΔT) at 700 nm as a function of cycle number of the PEC cell, bleached under 100 mW cm^{-2} illumination for 60 s and colored by adding a 2 V bias for 30 s.

6.6 Summary

A fast-switching negative PEC cell composed of dye-sensitized nanocrystalline TiO_2 and PB electrodes was studied. Adjustable grayscales were obtained by illuminating the cell with different light intensity and time. The photo bleaching response of the cell (sample size $\sim 1.5 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) at 100 mW cm^{-2} is 6.2 s, and the EC response with a 2 V bias is about 600 ms for 70% transmittance change at 780 nm with an EC CE value of $103.4 \text{ cm}^2 \text{ C}^{-1}$. This

hybrid PEC cell shows good stability and can be potentially applied in erasable displays.

CHAPTER 7 NANOSTRUCTURED TUNGSTEN OXIDE BASED PHOTOELECTROCHEMICAL DEVICES¹

7.1 Introduction

Assembly of functional nanoscale building blocks in thin film form for example with large surface area and desired morphologies is an important prerequisite for large scale electronic and optoelectronic applications with improved performance.[179-181] As one of few n-type semiconductors, WO₃ has also been considered to be an interesting photocatalytic material, due to its high resistance against photocorrosion, good stability in acidic solution (below ca. pH 4) and a suitable band gap for visible light absorption (~2.6 eV).[107,182]

Thus far, thin films of WO₃ have been grown by various techniques including physical vapor deposition (thermal evaporation and sputtering),[158,183] and chemical methods (sol-gel and hydrothermal approach).[31,77,143,184] Hydrothermal approach stands out to be a very promising route featuring low reaction temperature, flexible substrate selection and easiness for scaling-up. A number of hydrothermal methods have been used for the preparation of 1D WO₃ nanostructures with various characteristic sizes and morphologies by adding different kinds of inorganic salts or surfactants.[90,131,185,186] Some of the nanostructures with large surface area are assembled into thin film on conductive

¹ The main results of this Chapter have been published as: Z. Jiao, J.M. Wang, L. Ke, X. W. Sun and H.V. Demir, *ACS Applied Materials & Interfaces*, 2011, 3 (2), 229.

substrate, showing promising photocatalytic characteristics. For example, Hong investigated the size effect of hydrothermally grown WO_3 nanoparticles for photooxidation of water and achieved a maximum photocurrent density of 0.6 mA cm^{-2} for the sample calcined at 600°C . [90] Although the photocatalytic characteristics of hydrothermally grown WO_3 nanostructures have been reported, there have been few works focusing on photocatalytic behavior of hydrothermally grown WO_3 films. [187] Moreover, to directly grow WO_3 thin film with controllable morphology and good adhesion on substrates using the hydrothermal methods are much harder to realize.

Herein, we report a simple hydrothermal approach to realize the morphology-controllable synthesis of tungsten oxide hydrate ($3\text{WO}_3 \cdot \text{H}_2\text{O}$) thin film on FTO glasses. Under the assistance of seed layers, $3\text{WO}_3 \cdot \text{H}_2\text{O}$ thin films composed of plate-like, wedge-like and sheet-like nanostructures could be selectively prepared by adding Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and $\text{CH}_3\text{COONH}_4$ as capping agents, respectively. The photocatalytic activities of the as-prepared thin films for oxidization of methanol and splitting water were studied.

7.2 Synthesis and characterization of the nanostructured WO_3 films

7.2.1 Preparation of crystal seeds

1 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved into 15 mL of de-ionized water and then HCl was added until no more precipitate was formed. The precipitate was washed using de-ionized water in ice bath for 6 times to obtain 50 mL of

precipitate-containing suspension. Then, 0.9 g of oxalic acid was added into the suspension under intense stir at $\sim 50^\circ\text{C}$. The precipitate was dissolved and the suspension was changed to transparent sol which was used as WO_3 seed precursor. The pH of the above precursor was 1.7.

7.2.2 Preparation of substrates

The as-prepared transparent WO_3 seed precursor was spun coated onto FTO glasses which were ultrasonic cleaned beforehand by acetone, isopropanol, ethanol and de-ionized water in sequence. The spin coating processes were performed at 3000 rpm for 30 s and repeated for 4 times, during each process the coated substrates were heated at 300°C for ~ 10 min. Then all the substrates were heated to 400°C in atmosphere for 40 min.

7.2.3 Preparation of precursors and hydrothermal synthesis

Figure 7-1. Schematic illustration of the film fabrication process.

0.0655 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved into 20 mL of de-ionized water and then ~ 4 mL of HCl was added into the solution until no more precipitate was formed. The above suspension was kept in an ice bath for 10 min and then the upper liquid was removed. De-ionized water was added into it to obtain a final 20 mL suspension. Then 0.14 g of oxalic acid was added into the above suspension under intensely stir at ~50 °C. After stirring for 5 min, 0.04 g of capping agent Na_2SO_4 was added. For the cases using other capping agents, 0.04 g of $(\text{NH}_4)_2\text{SO}_4$ or 0.1 g of $\text{CH}_3\text{COONH}_4$ was added, accordingly. Then 1 M NaOH solution was slowly added into the above solution with stirring until the pH value of the solution reached 1.5. For the purpose of comparison, a solution without any capping agent was also prepared. The as-prepared solutions were transferred into autoclaves as precursors for hydrothermal growth. The FTO glasses coated by WO_3 seed layers were put into autoclaves and the reaction were kept at 180 °C for 20 h. For comparison, bare FTO glass (without crystal seeds) was also used as a reference substrate. The as-prepared thin films were washed using de-ionized water. To test their photocatalytic activities for oxidization of methanol and water, the as-prepared thin films were calcined in air at 500 °C for 30 min. The experimental process is schematically illustrated in Figure 7-1.

7.2.4 Characterizations

The crystal structure of the products was identified by x-ray powder diffraction (XRD, Siemens) using $\text{Cu K}\alpha_1$ ($\lambda = 0.15406$ nm) radiation. The morphologies of the as-prepared thin films were observed by scanning electron

microscopy (SEM, JSM 5910LV). High-resolution transmission electron microscopy (HRTEM) images were obtained by a JEM-2010 microscope using an accelerating voltage of 200 kV. The UV-vis absorption spectra were measured using a UV-vis spectrophotometer (Lambda 950). Photocatalytic activity was measured in a typical three-electrode configuration in 1 M H_2SO_4 and 1 M H_2SO_4 containing 0.1 M methanol as electrolyte, respectively. Ag/AgCl was used as reference electrode and a Pt foil as counter electrode. A 200 W xenon lamp (Oriel, 66011) with a filter (>300 nm) was placed near the photoelectrode to simulate solar irradiation (the light intensity was adjusted to 100 mW cm^{-2}). The photocurrent measurements were conducted using a computer controlled potentiostat (VersaSTAT 3F Potentiostat/Galvanostat, Princeton Applied Research).

7.3 Structures and morphologies of the WO_3 films

Figure 7-2. XRD patterns of the as-synthesized thin films prepared (a) without any salt added, (b) with Na_2SO_4 , (c) with $(\text{NH}_4)_2\text{SO}_4$, and (d) with $\text{CH}_3\text{COONH}_4$ added.

The XRD patterns of the as-synthesized films grown without and with addition of different capping agents were shown in Figure 7-2. Intense and sharp diffraction peaks are observed, indicative of a high degree of crystallinity. The diffraction peaks of the as-prepared films appear at the same positions. It is also observed that there are no other impurity phase peaks. All the peaks can be indexed to the orthorhombic phase of $3\text{WO}_3 \cdot \text{H}_2\text{O}$ (JCPDF 87-1203) with constants of $a = 7.345$, $b = 12.547$ and $c = 7.737$ Å. Moreover, the full width at half-maximum of the (222) crystal planes of all orthorhombic $3\text{WO}_3 \cdot \text{H}_2\text{O}$ patterns can be used to estimate the average crystalline size of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$, using the Debye-Scherrer equation:

$$D = K\lambda / (\beta \cos \theta), \quad (40)$$

where D is the average crystalline size, β is the corrected band broadening (full width at half-maximum), K is a constant taken as 0.89 here, λ is the wavelength of the x-ray radiation ($\text{Cu K}_{\alpha 1} = 0.15406$ nm) and θ is the diffraction angle. The average crystalline size for nanostructures of $3\text{WO}_3 \cdot \text{H}_2\text{O}$ films synthesized without capping salt is estimated at 24.0 nm. The sizes of nanostructures for adding Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and $\text{CH}_3\text{COONH}_4$ are 21.4, 27.3 and 24.5 nm, respectively.

However, the diffraction patterns of these films show some differences in the intensities. The films grown with Na_2SO_4 or $\text{CH}_3\text{COONH}_4$ show a highest peak intensity of (220), suggesting that most of the (220) planes are parallel to the substrate (22). In the patterns of the films grown without salt or with $(\text{NH}_4)_2\text{SO}_4$, a peak attributable to the (222) diffraction exhibits high intensity, indicating selective

orientation of (222) planes parallel to the substrate. The various selective orientations can be attributed to the different capping effect of salts in the condensation and polymerization of WO_6 octahedral clusters.

Figure 7-3. (a) SEM image of as-synthesized tungsten oxide hydrate film composed of plate-like nanostructures with Na_2SO_4 as capping agent, (b) Higher-magnification SEM image (top view), (c) cross sectional image of the film, and (d) HRTEM image of a single nanoplate.

According to previous reports,[185] 1D WO_3 nanostructures could be controllably synthesized by addition of sulfate as the capping agent by a hydrothermal approach. Inspired by these results, morphology-controllable synthesis of WO_3 film may be realized by adding sulfate or other capping agents into the precursor to direct the nanostructures' growth. Hence Na_2SO_4 was

introduced in our synthesis. Morphologies of the as-synthesized film are shown in Figure 7-3. It can be seen that a film consisting of plate-like nanostructure is assembled on the surface of FTO (Figure 7-3(a) and (b)). These nanoplates with clear crystal facets gathered together and a lot of pores were formed among these accumulated nanoplates, leading to a coarse surface. Cross-sectional image of the film (Figure 7-3(c)) shows its thickness is about 2 μm , and the as-synthesized film has a good adhesion to the substrate. Figure 7-3(d) shows the HRTEM image of a single nanoplate. Clear lattice fringes corresponding to the (220) plane with d-spacing of 0.32 nm can be seen, indicating single crystal quality of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ nanoplate, which is in good agreement with the XRD result.

To investigate the influence of the seed layer on the morphology of as-synthesized film, bare FTO substrate without any seed layer was compared. It can be seen that flower-like particles spreading on the surface of FTO with diameter of $\sim 8\text{-}10 \mu\text{m}$ and height of $\sim 2\text{-}4 \mu\text{m}$ were synthesized (Figure 7-4(a) and (b)). Some particles are not completely developed which may be due to the randomness of self-assembly process. The higher-magnification image of a single particle (Figure 7-4(b)) shows that the center of particle is made up of lamina layers and many small nanoplates grow along the center. From this result, we can get a conclusion that the seed layer does play a key role in assembling the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ thin film and offers the nucleation and growing sites for the film. These flower-like particles can be easily removed from the substrate. However, the film grown with seed layers shows good adhesion to the substrate, which further verifies the crucial impact of seed layer on assembling of the $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film. For comparison, precursor

solution without any salt (with seed layer and other conditions remain the same as in Figure 7-3) was compared as well. It can be seen from Figure 7-4(c) and (d) that dense thin film made up of irregular particles with different sizes was prepared, which is quite different from those films grew using capping salts. Hence, the morphologies of nanostructures are determined by the capping agents, similar to the hydrothermally grown 1D WO_3 nanostructures grown with capping agent.[77,185,186]

Figure 7-4. (a) and (b) SEM images of as-synthesized flower-like tungsten oxide hydrate particles without seed layer, (c) and (d) as-synthesized tungsten oxide hydrate thin film grown without any salt.

Figure 7-5. (a) SEM image of as-synthesized tungsten oxide hydrate film composed of wedge-like nanostructures grown with $(\text{NH}_4)_2\text{SO}_4$ as capping agent. The inset shows cross sectional image of the film. (b) HRTEM image of a single nanowedge. The inset of Figure (b) shows the SAED pattern from a nanowedge.

To further investigate the influence of cations on the morphology of the as-synthesized thin film, $(\text{NH}_4)_2\text{SO}_4$ was added into the precursor instead of Na_2SO_4 . Figure 7-5(a) shows the top-view images of the resultant film. It can be seen that a film composed of uniform wedge-like nanostructures was synthesized. These wedge-like nanostructures with size of $\sim 2 \mu\text{m}$ gathered together and a lot of pores can be obviously observed among them. These pores are formed due to the accumulation of the nanowedges. It is obvious that the obtained nanostructures grown with $(\text{NH}_4)_2\text{SO}_4$ have sharp edges and smaller characteristic size compared with the nanostructures grown with Na_2SO_4 . The cross sectional image (inset of Figure 7-5(a)) shows that the thickness of the as prepared film is $\sim 2 \mu\text{m}$. The HRTEM image of the edge of a single “wedge” in Figure 7-5(b) shows its crystal lattices of 0.38 nm corresponding to the d-spacing of (002) planes. Clear lattice fringes indicate its single crystal quality. The inset of Figure 7-5(b) depicts the

SAED image of the single “wedge”. Regular diffraction spots also prove the wedge is single crystalline.

Figure 7-6. (a) and (b) SEM image of as-synthesized tungsten oxide hydrate film with sheet-like nanostructures grown with $\text{CH}_3\text{COONH}_4$ as capping agent and (c) TEM images of a single nanosheet. The inset of Figure (c) shows the SAED pattern from a nanosheet. (d) HRTEM image.

The above result indicates that besides sodium ions, ammonium ions also has some effect in directing the crystal growth of $3\text{WO}_3 \cdot \text{H}_2\text{O}$ nanostructures and determining the final morphologies of the as-synthesized films. Up to now, controllable synthesis of WO_3 nanostructures has been achieved by adding various salts as capping agents, such as RbSO_4 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and NaCl . [77,186]

However, to the best of our knowledge, acetate is rarely reported. As acetate has been widely used for ZnO nanostructure synthesis,[188] we studied the influence of $\text{CH}_3\text{COONH}_4$ as a capping agent on the as-synthesized film. SEM images of the as-obtained film are shown in Figure 7-6(a) and (b).

It can be seen that the thin film consists of sheet-like nanostructures. The “nanosheet” with a thickness of ~ 50 nm grew disorderly on the substrate, forming a quite rough surface. It can be further seen from the higher magnification (Figure 7-6(b)) that some edges of the nanosheets are not smooth, showing a zig-zag shape. Numerous pores are existed among these nanosheets. These nanostructures should be more beneficial for accelerating the interface electron kinetics between the sheet and electrolyte for its larger active surface area. Figure 7-6(c) shows the TEM image of a nanosheet and its ragged edge can be clearly discerned. The inset shows the SAED pattern of the nanosheet and its single crystal quality could be proved by the regular diffraction spots. Clear lattice fringes correspond to the d-spacing of (002) planes with lattice spacing of 0.38 nm which was taken from the corner area of the nanosheet are shown in of Figure 7-6(d), further indicating its single-crystal quality, which is in good agreement with Figure 7-6(c). The above results indicate that acetate do have a capping effect on the crystal growth of $3\text{WO}_3 \cdot \text{H}_2\text{O}$ nanostructures. Moreover, it can be seen that the HRTEM image and SAED pattern of the selected area from the film grown with $\text{CH}_3\text{COONH}_4$ is quite similar to that grown with $(\text{NH}_4)_2\text{SO}_4$ due to their same crystalline structure (orthorhombic phase of $3\text{WO}_3 \cdot \text{H}_2\text{O}$). And the similar HRTEM images and SAED patterns imply that the as-synthesized nanostructures with $(\text{NH}_4)_2\text{SO}_4$ and $\text{CH}_3\text{COONH}_4$ may have the

same growth direction. However, it can be seen that the morphologies, sizes, thickness of the nanostructures synthesized using different salts are different; moreover, the arrangement of these different nanostructures in the grown films are also different. These factors significantly affect the intensities of diffraction peaks of the films grown using different salts.

Tungstate ions exhibit a lot of species in an aqueous solution at different pH values, such as WO_4^{2-} , HWO_4^- , H_2WO_4 , $\text{HW}_6\text{O}_{21}^-$, and $\text{W}_6\text{O}_{21}^{6-}$. [189] The major species is WO_4^{2-} with $\text{pH} > 7$. The dropping of concentrated HCl (37%) will force the WO_4^{2-} to precipitate from solution and H_2WO_4 will be formed, as shown in reaction (41).

With the increase of H^+ concentration, the intermediate H_2WO_4 shows high condensation polymerization tendency where two hydroxyl ligands combine to eliminate water and form a shared oxygen bond between the two tungsten centers. Further addition of acid will result in the formation of dihydroxy ligands $\text{W}-(\text{OH})_2$ by progressively hydrated tungsten oxo ligands ($\text{W}=\text{O}$). After further condensation and increase of the cross-linking degree of these ligands, a final 3-dimensional octahedral WO_6 structure in which tungsten centers are cross-linked to adjacent tungsten centers via four or six shared oxygen bonds, forming structures similar to those found in polyoxo-tungstates. [190] Then the oxalic acid is added into the complex coordination system and a transparent colloidal is obtained. It is believed that the oxalic acid will tailor the long coordination complex through hydroxyl groups, since the colloidal particle size is largely dependent on the concentration of

oxalic acid.[168] Finally, induced by various salts, these short coordinated clusters undergo further condensation and polymerization by hydrothermal reactions under elevated temperature and high pressure, forming plate-like, wedge-like and sheet-like nanostructures on the surface of seed-layer coated substrate. The seeds coated on substrate act as nucleation and growth sites. The whole process in detail is schematically illustrated in Figure 7-7.

Figure 7-7. Schematic of the sol-gel condensation polymerization reaction, cluster condensation and formation process of the as-synthesized nanostructures.

Figure 7-8. XRD patterns of the as-synthesized thin films with Na_2SO_4 as the capping agent. (a) The as-prepared tungsten oxide hydrate thin film, after annealing at (b) 300, (c) 400 and (d) 500 °C for 30 min, respectively

Figure 7-9. SEM images of as-synthesized films after annealing at 500 °C for 30 min. (a) Grown without any salt, (b) with Na_2SO_4 , (c) with $(\text{NH}_4)_2\text{SO}_4$ and (d) with $\text{CH}_3\text{COONH}_4$.

WO₃ is an n-type semiconductor with a band gap ~ 2.6 eV which can utilize ~ 12% of solar spectrum.[191] Moreover, it shows a high stability in acid bath. These advantages make it a promising candidate in photocatalytic degradation of organic compounds and water splitting to produce hydrogen.[107,126,192] To investigate their photocatalytic performances, all the films were calcined in atmosphere at 500 °C for 30 min. As previously reported,[31] WO₃ film prepared by a sol-gel method shows the highest photocatalytic activity after being calcined at 500 °C. The crystal structure evolution as a function of temperature is also investigated on the film synthesized with Na₂SO₄ as capping agent. It can be seen from Figure 7-8 that there is no obvious differences in the diffraction pattern of as-prepared film for a calcination temperature up to 300 °C. Due to the dehydration, some peaks' relative intensities get changed. After calcination at 400 °C, the XRD pattern gets obviously changed, showing some characteristic diffraction peaks of monoclinic WO₃ (PDF 24-0747). It is believed that this is a mixture of both orthorhombic and monoclinic structure. For calcination temperature of 500 °C, the structure changes to monoclinic WO₃ (JCPDF 24-0747) with lattice constants of $a=7.297 \text{ \AA}$, $b = 7.539 \text{ \AA}$ and $c = 7.688 \text{ \AA}$. Our experiment results show that the other two films prepared using (NH₄)₂SO₄ and CH₃COONH₄ as capping agents follow the same crystal structure change after calcination. The morphologies of the films after calcination are shown in Figure 7-9 and no obvious changes were observed, indicating good stability.

7.4 Optical and photoelectrochemical properties of the WO_3 films

Figure 7-10 shows the UV-vis absorption spectra of the films after calcination. It can be seen that all the films show high UV light absorption. Moreover, the absorption band edge for films prepared with $\text{CH}_3\text{COONH}_4$, $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 as capping agents show obviously red shifts. The broadened light absorption is much desired for photocatalytic applications, because more photo excited electrons will be generated contributing a higher photocatalytic efficiency.

Figure 7-10. The UV-vis absorption spectra of the as-synthesized films grown (a) without any salt, with Na_2SO_4 (b), (c) $(\text{NH}_4)_2\text{SO}_4$ and (d) $\text{CH}_3\text{COONH}_4$ as capping agents, respectively.

To investigate the photocatalytic properties of as-prepared films, the photocurrent densities were measured in a 1 M H_2SO_4 solution containing 0.1 M methanol under illumination (100 mW cm^{-2}) (Figure 7-11).

Figure 7-11. Current-potential scans of as-synthesized films measured in darkness and under simulated solar spectrum in a 1M H_2SO_4 solution containing 0.1M methanol.

It can be seen that the current densities in dark are small (typically $<100 \mu\text{A cm}^{-2}$) for all calcined films in the effective range of applied potentials. Compared to the film synthesized without capping agent (0.40 mA cm^{-2}), the photocurrent densities of the films with Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and $\text{CH}_3\text{COONH}_4$ capping agents show an obviously increase of 112%, 140% and 180% to 0.85, 0.96 and 1.12 mA cm^{-2} at 1.4 V vs Ag/AgCl, respectively. The photocatalytic performances of the films are in good agreement with the optical absorption. Moreover, the open-circuit voltages (V_{OCV}) are negatively shifted from 0.42V of the one without salt to 0.31 V, 0.29 V and 0.32 V for WO_3 films obtained with Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and $\text{CH}_3\text{COONH}_4$ capping agents, respectively, which are attributed to the numerous

pores existing among the nanostructures assembled in films that could increase the interface between the photoanode and electrolyte, facilitating the hole transfer to methanol more efficiently. The WO_3 nanostructures absorb effective photons that caused the generation of valance band holes (h_{vb}^+) and conduction band electrons (e_{cb}^-). These photon-generated holes serve as oxidation sites for the absorbed methanol molecules, i.e.

The best film prepared with $\text{CH}_3\text{COONH}_4$ renders the highest photocurrent density of about 1.16 mA cm^{-2} (at 1.45 V). However, this value is smaller compared to the reported porous sol-gel WO_3 films (4.1 mA cm^{-2} , AM 1.5, film thickness $2.8 \mu\text{m}$). [143] The inferior catalytic performance for photodegradation of methanol maybe due to the less optimum film thicknesses and slow carrier transporting kinetics. Further study is required to optimize the parameters.

Figure 7-12. (a) Current-potential scans of films grown with $\text{CH}_3\text{COONH}_4$ as capping agent measured in darkness and under simulated solar spectrum in a 1M H_2SO_4 solution and (b) photoconversion efficiency.

The photoelectrochemical performance of film synthesized with $\text{CH}_3\text{COONH}_4$ capping agent for hydrogen production through water splitting was also investigated in 1 M H_2SO_4 and shown in Figure 7-12(a). The highest photocurrent density of about 0.5 mA cm^{-2} can be obtained under illumination, which is comparable to other reported values.[90,193] The photoconversion efficiency (PCE) of light to hydrogen energy is calculated according to the following equation:[194]

$$\text{PCE (\%)} = [J_p \cdot (E_{\text{WS}} - |E_{\text{app}}|) / I_0] \times 100, \quad (46)$$

where J_p is the photocurrent density (mA cm^{-2}), I_0 is the incident light intensity (100 mW cm^{-2}), E_{WS} is the standard reversible potential for water splitting reaction (1.23 V for the water-splitting reaction at $\text{pH}=0$), and $|E_{\text{app}}|$ refers to the absolute value of the applied potential E_{app} , which is obtained as

$$E_{\text{app}} = (E_{\text{meas}} - E_{\text{ocp}}), \quad (47)$$

where E_{meas} is the electrode potential at which the photocurrent density J_p is measured, and E_{ocp} is the electrode potential at open circuit condition under the same illumination intensity. It can be seen from Figure 7-12(b) that a highest PCE value of about 0.3% is obtained at 0.65 V bias for our experiment. More work is underway to improve the photoconversion efficiency by optimizing the electrolyte, film thickness and annealing conditions.

The band diagram of the WO_3 photo-anode and operation of the photoelectrochemical cell was schematically shown in Figure 7-13. When the WO_3 photo-anode is placed in contact with the electrolyte, a depletion layer at the interface will be formed resulting from the move of electrons from WO_3 to electrolyte, producing an upward bending of the band.[87] Upon illumination, photo generated electrons will be excited and injected into the conduction band, leaving the holes in the valence band. An external bias is required to pump the electrons to the cathode and elevate the cathode (Pt) Fermi level E_F above the H^+/H_2 energy level, thus making the process of water decomposition possible.[195] The hydrogen ions will be reduced by electrons, and hydrogen will be formed at the side of Pt. At the same time, the holes in the valence band will transfer to the electrolyte to oxidize water and oxygen will be generated on the surface of WO_3 . The efficiency of the cell could be further improved by preciously tailoring the WO_3 nanostructures and increasing its surface area.

Figure 7-13. Schematic of the band diagram of WO₃ photo-anode and operation of the photoelectrochemical cell. The electrolyte is 1 M H₂SO₄ solution.

7.5 Summary

Porous tungsten trioxide hydrate (3WO₃ · H₂O) thin films with different morphologies were directly grown on transparent conductive glasses in a large scale by a hydrothermal approach. Systematic investigations of the influence of seed layer and different capping agents on the morphologies and structures of the as-synthesized films have been carried out. It was found that flower-like particles with sizes of ~8-10 μm were synthesized and spread on the substrate without seed layers. Under the assistance of seed layer, dense thin film was formed without capping agent. After adding suitable amount of CH₃COONH₄, (NH₄)₂SO₄ and Na₂SO₄ into the precursor, thin films consisted of sheet-like, wedge-like and plate-like nanostructures could be synthesized, respectively. The dehydrated porous films showed high photocatalytic activities for photodegradation of methanol. The

film grown using $\text{CH}_3\text{COONH}_4$ as the capping agent could generate anodic photocurrents of 1.15 mA cm^{-2} for oxidization of methanol and 0.5 mA cm^{-2} for water splitting, the highest photoconversion efficiency of about 0.3% can be obtained for water splitting under simulated solar illumination.

CHAPTER 8 CONCLUSION AND FUTURE WORKS

8.1 Conclusion

In this dissertation, we report the synthesis of the nanostructured WO_3 and hydrated WO_3 films with various morphologies on FTO substrates by facile and crystal-seed-assisted hydrothermal methods with addition of various capping agents. It is found that the capping agents, seed layer, precursor concentration and reaction time play an important role in determining the structures, characteristic feature sizes and morphologies of the as-prepared films. EC properties of the as-prepared films were investigated in single and complementary EC layer devices.

Brick-like monoclinic WO_3 films were obtained and the films display tunable transmittance modulation under different voltages and a good reversible coloration/bleaching stability after 3000 cycles. A single EC layer device composed of this film shows a comparable switching response of $t_{c(90\%)} = 272$ s, $t_{b(90\%)} = 364$ s and a CE value of $38.2 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm (sample size $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$). By modifying the precursor composition and concentration, plate-like nanostructured $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film was synthesized with Na_2SO_4 as the capping agent, while nanobrick film was obtained without capping agent. The nanoplate film grown with Na_2SO_4 shows significantly improved EC performance. A high CE value of $112.7 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm is obtained, and the response time for 90% transmittance changes is found to be 4.3 s for coloration and 1.4 s for bleaching (sample size $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$), respectively.

Both films have been assembled in single layer EC devices and demonstrate promising applications in smart windows and large-area information displays.

Moreover, orthorhombic nanostick/nanoparticle hydrated WO_3 films grown with $\text{CH}_3\text{COONH}_4$ as the capping agent were obtained, while irregular nanobrick films were obtained without $\text{CH}_3\text{COONH}_4$. The nanostick/nanoparticle film depicts faster ion intercalation/deintercalation kinetics and a greater CE value ($45.5 \text{ cm}^2 \text{ C}^{-1}$ at 754 nm, sample size $\sim 2 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) than the nanobrick film. A complementary EC device based on the nanostick/nanoparticle $3\text{WO}_3 \cdot \text{H}_2\text{O}$ film and Prussian blue (PB) was assembled. The device shows higher optical modulation (54% at 754 nm), a larger CE value ($151.9 \text{ cm}^2 \text{ C}^{-1}$ at 754 nm) and faster switching responses with a bleaching time of 5.7 s and a coloring time of 1.3 s than a single $3\text{WO}_3 \cdot \text{H}_2\text{O}$ layer device.

By using $(\text{NH}_4)_2\text{SO}_4$ as the capping agent, highly adhesive and uniform nanobrick hydrated WO_3 films were assembled on FTO glass substrate. It is found the seed-layer and H_2O_2 are vital in assembling the nanostructures into a thin film on the substrate, and both $(\text{NH}_4)_2\text{SO}_4$ and H_2O_2 influence the products' morphologies. The as-synthesized orthorhombic hydrated WO_3 films show good cyclic stability, comparable switching response ($t_{\text{c},90\%} = 51.5 \text{ s}$, $t_{\text{b},90\%} = 11.5 \text{ s}$) and CE value ($30.1 \text{ cm}^2 \text{ C}^{-1}$). The complementary device (sample size $\sim 1.7 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) made up of hydrated WO_3 film and PB film was also fabricated and demonstrates highly improved EC performance. This device shows much faster coloration/bleaching response ($t_{\text{c},90\%} = 1.8 \text{ s}$, $t_{\text{b},90\%} = 3.7 \text{ s}$), larger CE value ($164.6 \text{ cm}^2 \text{ C}^{-1}$ at 632.8 nm) and increased color contrast. These

complementary devices are prospectively applied in smart windows and displays, and the as-synthesized hydrated WO_3 films may find more applications in gas sensors and electronic devices.

A fast-switching negative PEC cell composed of dye-sensitized nanocrystalline TiO_2 and PB electrodes was fabricated and its PEC properties were studied. Adjustable grayscales were obtained by illuminating the cell with different light intensity and time. The photo bleaching response of the cell (sample size $\sim 1.5 \text{ cm}^2$, FTO sheet resistance: $15 \Omega/\square$) at 100 mW cm^{-2} is 6.2 s, and the EC response with a 2 V bias is about 600 ms for 70% transmittance change at 780 nm with a CE value of $103.4 \text{ cm}^2 \text{ C}^{-1}$. This hybrid PEC cell shows good stability and can be potentially applied in erasable displays.

As a well-known n type semiconductor, WO_3 has a band gap $\sim 2.6 \text{ eV}$. Recently, the photoelectrochemical performance of WO_3 has attracted intense interest for its good optical absorption and photo oxidation stability. Herein we report porous hydrate WO_3 ($3\text{WO}_3 \cdot \text{H}_2\text{O}$) thin films consisted of sheet-like, wedge-like and plate-like nanostructures grown on FTO substrate by a hydrothermal approach by adding suitable amount of $\text{CH}_3\text{COONH}_4$, $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 as capping agents, respectively. The influences of seed layer and different capping agents on the morphologies and structures of the as-synthesized films were investigated. It was found that flower-like particles with sizes of $\sim 8\text{-}10 \mu\text{m}$ were synthesized and spread on the substrate without seed layers. Under the assistance of seed layer, dense thin film was formed without capping agent. The dehydrated porous films showed high photocatalytic activities for photodegradation of

methanol. The film grown using $\text{CH}_3\text{COONH}_4$ as the capping agent could generate anodic photocurrents of 1.15 mA cm^{-2} for oxidization of methanol and 0.5 mA cm^{-2} for water splitting, a highest photoconversion efficiency of about 0.3% can be obtained for water splitting under simulated solar illumination. The above result shows that as-prepared porous WO_3 films may find potential applications in PEC cells and organic pollutant photocatalytic degradation.

8.2 Future works

Although great development have been achieved on application of WO_3 films in EC devices, the overall performance of this technique also needs to further improved and the cost needs be reduced for massively commercial applications. Solution based chemical fabrication methods have lower cost merits than the physical deposition approaches. To further reduce the cost, sol-gel techniques should be developed since it is easy to fabricate large size EC layer on conductive substrate. And the mature films assembling techniques such as spin coating, dip coating and inject printing can be applied. In this way, the cost of device fabrication process is largely reduced compared with the vacuum techniques such as sputtering, physical vapor deposition and thermal evaporation. But the stability, adhesion, feature size and porosity of the sol-gel deposited WO_3 films should be further improved for achieving a good EC performance.

Hydrothermal method is also a good approach to reduce the cost, but the as grown WO_3 or hydrate WO_3 films should be more stable, transparent, cost-effective and easy to be scaled-up. The films should have a higher porosity to

possess a faster switching response by reducing the ions diffusion length, while low haze level should be controlled for maintaining highly transparency at bleached state. To meet these requirements, the hydrothermal method should be further optimized, such as the preparation of the seed layer, application of capping agents, precursor composition and concentration and reaction duration and temperature.

For photoelectrochemical applications, the WO_3 photoanode should have higher porosity to increase the effective contact area between the electrolyte and active sites. The morphologies and feature size of nanostructures should be further optimized to efficiently separate the photo generated holes and electrons. More strategies should also be adopted to enhance the solar light harvest by bandgap engineering, such as the doping various elements to introduce intermediate states or design of heterojunctions by modification of narrow bandgap semiconductor with proper band edge positions including CdS, CdSe, BiVO_4 , etc. Moreover, the efficiency may be further improved by decoration of oxygen evolution catalyst such as Pi-Co , IrO_2 , etc.

JOURNAL PUBLICATIONS

- (1) **Z. Jiao**, X. Wang, J.M. Wang, L. Ke, H.V. Demir, T.W. Koh and X.W. Sun, Efficient synthesis of plate-like crystalline hydrated tungsten trioxide thin films with highly improved electrochromic performance, *Chemical Communications*, 2012, 3 (48), 365.
- (2) **Z. Jiao**, J.M. Wang, L. Ke, X. W. Sun and H.V. Demir, "Morphology-Tailored Synthesis of Tungsten Trioxide (Hydrate) Thin Films and Their Photocatalytic Properties," *ACS Applied Materials & Interfaces*, 2011, 3 (2), 229.
- (3) **Z. Jiao**, X.W. Sun, J.M. Wang, L Ke and H.V. Demir, "Hydrothermally grown nanostructured WO₃ films and their electrochromic characteristics," *Journal of Physics D-Applied Physics*, 2010, 43 (28) 285501.
- (4) **Z. Jiao**, J.L. Song, X.W. Sun, X.W. Liu, J.M. Wang, L. Ke and H.V. Demir, A fast-switching light-writable and electric-erasable negative photoelectrochromic cell based on Prussian blue films, *Solar Energy Materials and Solar Cells*, 2012, 98, 154.
- (5) **Z. Jiao**, J.M. Wang, L. Ke, X.W. Liu, H.V. Demir, M.F. Yang and X. W. Sun, Electrochromic properties of nanostructured tungsten trioxide (hydrate) films and their applications in a complementary electrochromic device, *Electrochimica Acta*, 2012, 63, 153.
- (6) **Z. Jiao**, J.M. Wang, L. Ke, X.W. Sun and H.V. Demir, A complementary electrochromic device with highly improved performance based on brick-like

hydrated tungsten trioxide film, *Journal of Nanoscience and Nanotechnology*, 2012, 12, 1.

(7) **Z. Jiao**, J.S. Luo, L. Ke, H.V. Demir, X.W. Sun and H.J. Fan, CdS-CdSe co-sensitized tungsten oxide film with highly improved photoelectrochemical performance. (in process)

(8) J.M. Wang, X.W. Sun, **Z. Jiao**, E. Khoo, P.S. Lee, J. Ma and H.V. Demir, Tailoring insoluble nanobelts into soluble anti-UV nanopotpourris, *Nanoscale*, 2011, 3(11), 4742.

(9) J.M. Wang, X.W. Sun, **Z. Jiao**, Application of Nanostructures in electrochromic materials and devices: recent progress, *Materials*, 2010, 3(12), 5029.

(10) S. B. Dolmanan, S. C. Lai, L. Ke, W. W. Loh, **Z. H. Jiao** and X. W. Sun, Improved Photoelectrochemical Cell With Carbon Nanotubes, *IEEE Electron Dev. Lett.* 2010, 31, 734.

(11) Y. Wei, L. Ke, J. Kong, H. Liu, **Z. Jiao**, X. Lu, H. Du and X. W. Sun, Enhanced photoelectrochemical water-splitting effect with a bent ZnO nanorod photoanode decorated with Ag nanoparticles, *Nanotechnology*, 2012, 23, 235401.

CONFERENCE PRESENTATIONS

(1) **Z. Jiao** and X.W. Sun, Hydrothermally Grown Nanostructured Tungsten Trioxide (hydrate) Films and their Photocatalytic Properties, MRS Fall Meeting proceedings, 2011.

(2) **Z. Jiao**, X.W. Sun and J.M. Wang, Nanostructured tungsten oxide thin films and their electrochromic characteristics, East Asian Postgraduate Workshop on Nanoscience and Technology proceedings, Hong Kong, 2011.

BIBLIOGRAPHY

- [1] B. Oregan and M. Gratzel, "A low-cost, high-efficiency solar-cell based on dye-sensitized colloidal TiO_2 films," *Nature* 353 (6346), 737-740 (1991).
- [2] A. Hepbasli, "A key review on exergetic analysis and assessment of renewable energy resources for a sustainable future," *Renewable & Sustainable Energy Reviews* 12 (3), 593-661 (2008).
- [3] UNEP, in United Nations Environment Programme (Paris, Franch, 2007).
- [4] A. Jäger-Waldau, Ref-syst status report 2004. (EUR 21297 EN, Joint Research Center, Ispra, Italy, 2004).
- [5] C. G. Granqvist, G. A. Niklasson, and A. Azens, "Electrochromics: Fundamentals and energy-related applications of oxide-based devices," *Applied Physics a-Materials Science & Processing* 89 (1), 29-35 (2007).
- [6] 2009 Gesimat, retrieved April 14, (2009) <www.gesimat.de>.
- [7] S. A. Agnihotry, P. Singh, A. G. Joshi, D. P. Singh, K. N. Sood, and S. M. Shivaprasad, "Electrodeposited prussian blue films: Annealing effect," *Electrochimica Acta* 51 (20), 4291-4301 (2006).
- [8] E. Avendano, A. Azens, G. A. Niklasson, and C. G. Granqvist, "Electrochromism in nickel oxide films containing Mg, Al, Si, V, Zr, Nb, Ag, or Ta," *Solar Energy Materials and Solar Cells* 84 (1-4), 337-350 (2004).
- [9] M. Deepa, A. K. Srivastava, K. N. Sood, and S. A. Agnihotry, "Nanostructured mesoporous tungsten oxide films with fast kinetics for electrochromic smart windows," *Nanotechnology* 17 (10), 2625-2630 (2006).
- [10] C. G. Granqvist, "Electrochromic tungsten oxide films: Review of progress 1993-1998," *Solar Energy Materials and Solar Cells* 60 (3), 201-262 (2000).
- [11] H. C. Ko, M. Kang, B. Moon, and H. Lee, "Enhancement of electrochromic contrast of poly(3,4-ethylenedioxythiophene) by incorporating a pendent viologen," *Advanced Materials* 16 (19), 1712-1716 (2004).
- [12] J. J. Wu, M. D. Hsieh, W. P. Liao, W. T. Wu, and J. S. Chen, "Fast-switching photovoltachromic cells with tunable transmittance," *Acs Nano* 3 (8), 2297-2303 (2009).
- [13] S. K. Deb, "Opportunities and challenges in science and technology of WO_3 for electrochromic and related applications," *Solar Energy Materials and Solar Cells* 92 (2), 245-258 (2008).
- [14] A. Georg, W. Graf, and V. Wittwer, "Switchable windows with tungsten oxide," *Vacuum* 82 (7), 730-735 (2008).

- [15] A. Kraft, M. Rottmann, and K. H. Heckner, "Large-area electrochromic glazing with ion-conducting PVB interlayer and two complementary electrodeposited electrochromic layers," *Solar Energy Materials and Solar Cells* 90 (4), 469-476 (2006).
- [16] C. M. Lampert, in *Solar and switching materials*, edited by C. M. Lampert, C. G. Granqvist, and K. L. Lewis (Spie-Int Soc Optical Engineering, Bellingham, 2001), Vol. 4458, pp. 95-103.
- [17] P. Bonhote, E. Gogniat, F. Campus, L. Walder, and M. Gratzel, "Nanocrystalline electrochromic displays," *Displays* 20 (3), 137-144 (1999).
- [18] X. W. Sun and J. X. Wang, "Fast switching electrochromic display using a viologen-modified ZnO nanowire array electrode," *Nano Letters* 8 (7), 1884-1889 (2008).
- [19] R. J. Mortimer, "Electrochromic materials," *Annual Review of Materials Research*, Vol 41, 241-268 (2011).
- [20] C. R. Granqvist, "Electrochromic materials: Out of a niche," *Nature Materials* 5 (2), 89-90 (2006).
- [21] R. J. Mortimer, "Electrochromic materials," *Chemical Society Reviews* 26 (3), 147-156 (1997).
- [22] R. J. Mortimer, "Organic electrochromic materials," *Electrochimica Acta* 44 (18), 2971-2981 (1999).
- [23] R. J. Mortimer, A. L. Dyer, and J. R. Reynolds, "Electrochromic organic and polymeric materials for display applications," *Displays* 27 (1), 2-18 (2006).
- [24] M. Vidotti and S. I. C. de Torresi, "Nanochromics: Old materials, new structures and architectures for high performance devices," *Journal of the Brazilian Chemical Society* 19 (7), 1248-1257 (2008).
- [25] I. F. Chang, B. L. Gilbert, and T. I. Sun, "Electrochromic systems for display applications," *Journal of electrochemical society* 122, 955-962 (1975).
- [26] R. Baetens, B. P. Jelle, and A. Gustavsen, "Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: A state-of-the-art review," *Solar Energy Materials and Solar Cells* 94 (2), 87-105 (2010).
- [27] D. Gogova, L. K. Thomas, and B. Camin, "Comparative study of gasochromic and electrochromic effect in thermally evaporated tungsten oxide thin films," *Thin Solid Films* 517 (11), 3326-3331 (2009).
- [28] Y. Yamada, K. Tabata, and T. Yashima, "The character of WO₃ film prepared with RF sputtering," *Solar Energy Materials and Solar Cells* 91 (1), 29-37 (2007).
- [29] M. Deepa, A. K. Srivastava, S. Singh, and S. A. Agnihotry, "Structure-property correlation of nanostructured WO₃ thin films produced by electrodeposition," *Journal of Materials Research* 19 (9), 2576-2585 (2004).

- [30] W. B. Henley and G. J. Sacks, "Deposition of electrochromic tungsten oxide thin films by plasma-enhanced chemical vapor deposition," *Journal of the Electrochemical Society* 144 (3), 1045-1050 (1997).
- [31] S. Badilescu and P. V. Ashrit, "Study of sol-gel prepared nanostructured WO₃ thin films and composites for electrochromic applications," *Solid State Ionics* 158 (1-2), 187-197 (2003).
- [32] C. P. Li, C. A. Wolden, A. C. Dillon, and R. C. Tenent, "Electrochromic films produced by ultrasonic spray deposition of tungsten oxide nanoparticles," *Solar Energy Materials and Solar Cells* 99, 50-55 (2012).
- [33] C. G. Granqvist, *Handbook of inorganic electrochromic materials*. (Elsevier, Amsterdam, 1995).
- [34] P. R. Somani and S. Radhakrishnan, "Electrochromic materials and devices: Present and future," *Materials Chemistry and Physics* 77 (1), 117-133 (2003).
- [35] C. Santato, M. Odziemkowski, M. Ulmann, and J. Augustynski, "Crystallographically oriented mesoporous WO₃ films: Synthesis, characterization, and applications," *Journal of the American Chemical Society* 123 (43), 10639-10649 (2001).
- [36] S. H. Lee, R. Deshpande, P. A. Parilla, K. M. Jones, B. To, A. H. Mahan, and A. C. Dillon, "Crystalline WO₃ nanoparticles for highly improved electrochromic applications," *Advanced Materials* 18 (6), 763-766 (2006).
- [37] A. Avendano, A. Azens, G. A. Niklasson, and C. G. Granqvist, "Sputter deposited electrochromic films and devices based on these: Progress on nickel-oxide-based films," *Materials Science and Engineering B-Solid State Materials for Advanced Technology* 138 (2), 112-117 (2007).
- [38] E. Avendano, A. Azens, G. A. Niklasson, and C. G. Granqvist, "Electrochromism in nickel oxide films containing Mg, Al, Si, V, Zr, Nb, Ag, or Ta," *Solar Energy Materials and Solar Cells* 84 (84), 337-350 (2004).
- [39] J. Backholm, A. Azens, and G. A. Niklasson, "Electrochemical and optical properties of sputter deposited Ir-Ta and Ir oxide thin films," *Solar Energy Materials and Solar Cells* 90 (4), 414-421 (2006).
- [40] K. Nishio, Y. Watanabe, and T. Tsuchiya, "Preparation and properties of electrochromic iridium oxide thin film by sol-gel process," *Thin Solid Films* 350 (1-2), 96-100 (1999).
- [41] C. S. Hsu, C. C. Chan, H. T. Huang, C. H. Peng, and W. C. Hsu, "Electrochromic properties of nanocrystalline MoO₃ thin films," *Thin Solid Films* 516 (15), 4839-4844 (2008).
- [42] K. Takahashi, Y. Wang, and G. Z. Cao, "Growth and electrochromic properties of single-crystal V₂O₅ nanorod arrays," *Applied Physics Letters* 86 (5) (2005).

- [43] M. Schmitt, S. Heusing, M. A. Aegerter, A. Pawlicka, and C. Avellaneda, "Electrochromic properties of Nb₂O₅ sol-gel coatings," *Solar Energy Materials and Solar Cells* 54 (1-4), 9-17 (1998).
- [44] A. Hamnett, S. Higgins, R. S. Mortimer, and D. R. Rosseinsky, "A study of the electrodeposition and subsequent potential cycling of prussian blue films using ellipsometry," *Journal of Electroanalytical Chemistry* 255 (1-2), 315-324 (1988).
- [45] U. Scharf and E. W. Grabner, "Electrocatalytic oxidation of hydrazine at a prussian blue-modified glassy carbon electrode," *Electrochimica Acta* 41 (2), 233-239 (1996).
- [46] S. Hara, H. Tanaka, T. Kawamoto, M. Tokumoto, M. Yamada, A. Gotoh, H. Uchida, M. Kurihara, and M. Sakamoto, "Electrochromic thin film of prussian blue nanoparticles fabricated using wet process," *Japanese Journal of Applied Physics Part 2-Letters & Express Letters* 46 (36-40), L945-L947 (2007).
- [47] Thomas Gambke Klaus Bange, "Electrochromic materials for optical switching devices," *Advanced Materials* 2 (1), 10-16 (1990).
- [48] R. Cinnsealach, G. Boschloo, S. N. Rao, and D. Fitzmaurice, "Coloured electrochromic windows based on nanostructured TiO₂ films modified by adsorbed redox chromophores," *Solar Energy Materials and Solar Cells* 57 (2), 107-125 (1999).
- [49] A. A. Argun, P. H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid, and J. R. Reynolds, "Multicolored electrochromism polymers: Structures and devices," *Chemistry of Materials* 16 (23), 4401-4412 (2004).
- [50] T. Kobayashi, H. Yoneyama, and H. Tamura, "Polyaniline film-coated electrodes as electrochromic display devices," *Journal of Electroanalytical Chemistry* 161 (2), 419-423 (1984).
- [51] S. Kirchmeyer and K. Reuter, "Scientific importance, properties and growing applications of poly(3,4-ethylenedioxythiophene)," *Journal of Materials Chemistry* 15 (21), 2077-2088 (2005).
- [52] J. Y. Lee, S. T. Connor, Y. Cui, and P. Peumans, "Solution-processed metal nanowire mesh transparent electrodes," *Nano Letters* 8 (2), 689-692 (2008).
- [53] W. Y. Chou, S. T. Lin, H. L. Cheng, M. H. Chang, H. R. Guo, T. C. Wen, Y. S. Mai, J. B. Horng, C. W. Kuo, F. C. Tang, C. C. Liao, and C. L. Chiu, "Polymer light-emitting diodes with thermal inkjet printed poly(3,4-ethylenedioxythiophene): Polystyrenesulfonate as transparent anode," *Thin Solid Films* 515 (7-8), 3718-3723 (2007).
- [54] C. M. Trottier, P. Glatkowski, P. Wallis, and J. Luo, "Properties and characterization of carbon-nanotube-based transparent conductive coating," *Journal of the Society for Information Display* 13 (9), 759-763 (2005).

- [55] H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, and Y. Chen, "Evaluation of solution-processed reduced graphene oxide films as transparent conductors," *Acs Nano* 2 (3), 463-470 (2008).
- [56] R. B. Goldner, G. Seward, K. Wong, T. Haas, G. H. Foley, R. Chapman, and S. Schulz, "Completely solid lithiated smart windows," *Solar Energy Materials* 19 (1-2), 17-26 (1989).
- [57] A. Deneuve, P. Gerard, and R. Billat, "Principles and operation of an all solid-state electrochromic display based on α - WO_3 ," *Thin Solid Films* 70 (2), 203-223 (1980).
- [58] A. T. Howe, S. H. Sheffield, P. E. Childs, and M. G. Shilton, "Fabrication of films of hydrogen uranyl phosphate tetrahydrate and their use as solid electrolytes in electrochromic displays," *Thin Solid Films* 67 (2), 365-370 (1980).
- [59] J. P. Randin, "Ion-containing polymers as semisolid electrolytes in WO_3 -based electrochromic devices," *Journal of the Electrochemical Society* 129 (6), 1215-1220 (1982).
- [60] G. Casalbore-Miceli, M. J. Yang, N. Camaioni, C. M. Mari, Y. Li, H. Sun, and M. Ling, "Investigations on the ion transport mechanism in conducting polymer films," *Solid State Ionics* 131 (3-4), 311-321 (2000).
- [61] C. C. Liao, F. R. Chen, and J. J. Kai, "Electrochromic properties of nanocomposite WO_3 films," *Solar Energy Materials and Solar Cells* 91 (14), 1282-1288 (2007).
- [62] B. Munro, P. Conrad, S. Kramer, H. Schmidt, and P. Zapp, "Development of electrochromic cells by the sol-gel process," *Solar Energy Materials and Solar Cells* 54 (1-4), 131-137 (1998).
- [63] J. Nagai, G. D. McMeeking, and Y. Saitoh, "Durability of electrochromic glazing," *Solar Energy Materials and Solar Cells* 56 (3-4), 309-319 (1999).
- [64] T. H. Kuo, C. Y. Hsu, K. M. Lee, and K. C. Ho, "All-solid-state electrochromic device based on poly(butyl viologen), prussian blue, and succinonitrile," *Solar Energy Materials and Solar Cells* 93 (10), 1755-1760 (2009).
- [65] A. Kraft and M. Rottmann, "Properties, performance and current status of the laminated electrochromic glass of gesimat," *Solar Energy Materials and Solar Cells* 93 (12), 2088-2092 (2009).
- [66] G. A. Niklasson and C. G. Granqvist, "Electrochromics for smart windows: Thin films of tungsten oxide and nickel oxide, and devices based on these," *Journal of Materials Chemistry* 17 (2), 127-156 (2007).
- [67] F. Michalak and P. Aldebert, "A flexible electrochromic device based on colloidal tungsten oxide and polyaniline," *Solid State Ionics* 85 (1-4), 265-272 (1996).
- [68] K. C. Chen, C. Y. Hsu, C. W. Hu, and K. C. Ho, "A complementary electrochromic device based on prussian blue and poly(prod-ot-et-2) with high contrast and high coloration efficiency," *Solar Energy Materials and Solar Cells* 95 (8), 2238-2245 (2011).

- [69] A. Rougier, F. Portemer, A. Quede, and M. El Marssi, "Characterization of pulsed laser deposited WO_3 thin films for electrochromic devices," *Applied Surface Science* 153 (1), 1-9 (1999).
- [70] A. Subrahmanyam and A. Karuppasamy, "Optical and electrochromic properties of oxygen sputtered tungsten oxide (WO_3) thin films," *Solar Energy Materials and Solar Cells* 91 (4), 266-274 (2007).
- [71] K. A. Gesheva and T. Ivanova, "A low-temperature atmospheric pressure CVD process for growing thin films of MoO_3 and $\text{MoO}_3\text{-WO}_3$ for electrochromic device applications," *Chemical Vapor Deposition* 12 (4), 231-238 (2006).
- [72] B. Yous, S. Robin, A. Donnadieu, G. Dufour, C. Maillot, H. Roulet, and C. Senemaud, "Chemical vapor-deposition of tungsten-oxides-a comparative-study by x-ray photoelectron-spectroscopy, x-ray-diffraction and reflection high-energy electron-diffraction," *Materials Research Bulletin* 19 (10), 1349-1354 (1984).
- [73] A. Agrawal, J. P. Cronin, and R. Zhang, "Review of solid-state electrochromic coatings produced using sol-gel techniques," *Solar Energy Materials and Solar Cells* 31 (1), 9-21 (1993).
- [74] J. P. Cronin, D. J. Tarico, J. C. L. Tonazzi, A. Agrawal, and S. R. Kennedy, "Microstructure and properties of sol-gel deposited WO_3 coatings for large-area electrochromic windows," *Solar Energy Materials and Solar Cells* 29 (4), 371-386 (1993).
- [75] K. Machida and M. Enyo, "Structural and electrochromic properties of tungsten and molybdenum trioxide electrodes in acidic media," *Journal of the Electrochemical Society* 137 (4), 1169-1175 (1990).
- [76] S. R. Bathe and P. S. Patil, "Electrochromic characteristics of pulsed spray pyrolyzed polycrystalline WO_3 thin films," *Smart Materials & Structures* 18 (2) (2009).
- [77] J. M. Wang, P. S. Lee, and J. Ma, "One-pot synthesis of hierarchically assembled tungsten oxide (hydrates) nano/microstructures by a crystal-seed-assisted hydrothermal process," *Crystal Growth & Design* 9 (5), 2293-2299 (2009).
- [78] C. M. Lampert, "Smart switchable glazing for solar energy and daylight control," *Solar Energy Materials and Solar Cells* 52 (3-4), 207-221 (1998).
- [79] Y. G. Mo, R. O. Dillon, and P. G. Snyder, "Visible and infrared photochromic properties of amorphous WO_{3-x} films," *Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films* 17 (5), 2933-2938 (1999).
- [80] C. Bechinger, S. Ferrer, A. Zaban, J. Sprague, and B. A. Gregg, "Photoelectrochromic windows and displays," *Nature* 383 (6601), 608-610 (1996).
- [81] B. A. Gregg, "Photoelectrochromic cells and their applications," *Endeavour* 21 (2), 52-55 (1997).

- [82] G. De Filpo, S. Mormile, F. P. Nicoletta, and G. Chidichimo, "Fast, self-supplied, all-solid photoelectrochromic film," *Journal of Power Sources* 195 (13), 4365-4369 (2010).
- [83] G. Leftheriotis, G. Syrokostas, and P. Yianoulis, "Development of photoelectrochromic devices for dynamic solar control in buildings," *Solar Energy Materials and Solar Cells* 94 (12), 2304-2313 (2010).
- [84] H. Huang, S. X. Lu, W. K. Zhang, Y. P. Gan, C. T. Wang, L. Yu, and X. Y. Tao, "Photoelectrochromic properties of NiO film deposited on an n-doped TiO₂ photocatalytical layer," *Journal of Physics and Chemistry of Solids* 70 (3-4), 745-749 (2009).
- [85] J. Y. Liao and K. C. Ho, "A photoelectrochromic device using a PEDOT thin film," *Journal of New Materials for Electrochemical Systems* 8 (1), 37-47 (2005).
- [86] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature* 238 (5358), 37-38 (1972).
- [87] M. Gratzel, "Photoelectrochemical cells," *Nature* 414 (6861), 338-344 (2001).
- [88] T. Lindgren, J. M. Mwabora, E. Avendano, J. Jonsson, A. Hoel, C. G. Granqvist, and S. E. Lindquist, "Photoelectrochemical and optical properties of nitrogen doped titanium dioxide films prepared by reactive dc magnetron sputtering," *Journal of Physical Chemistry B* 107 (24), 5709-5716 (2003).
- [89] J. Zhang, J. H. Bang, C. C. Tang, and P. V. Kamat, "Tailored TiO₂-SrTiO₃ heterostructure nanotube arrays for improved photoelectrochemical performance," *Acs Nano* 4 (1), 387-395 (2012).
- [90] S. J. Hong, H. Jun, P. H. Borse, and J. S. Lee, "Size effects of WO₃ nanocrystals for photooxidation of water in particulate suspension and photoelectrochemical film systems," *International Journal of Hydrogen Energy* 34 (8), 3234-3242 (2009).
- [91] J. Z. Su, X. J. Feng, J. D. Sloppy, L. J. Guo, and C. A. Grimes, "Vertically aligned WO₃ nanowire arrays grown directly on transparent conducting oxide coated glass: Synthesis and photoelectrochemical properties," *Nano Letters* 11 (1), 203-208 (2012).
- [92] K. Vinodgopal, I. Bedja, and P. V. Kamat, "Nanostructured semiconductor films for photocatalysis. Photoelectrochemical behavior of SnO₂/TiO₂ composite systems and its role in photocatalytic degradation of a textile azo dye," *Chemistry of Materials* 8 (8), 2180-2187 (1996).
- [93] K. Kakiuchi, E. Hosono, and S. Fujihara, "Enhanced photoelectrochemical performance of ZnO electrodes sensitized with n-719," *Journal of Photochemistry and Photobiology a-Chemistry* 179 (1-2), 81-86 (2006).
- [94] K. Sayama, A. Nomura, Z. G. Zou, R. Abe, Y. Abe, and H. Arakawa, "Photoelectrochemical decomposition of water on nanocrystalline

- BiVO₄ film electrodes under visible light," *Chemical Communications* (23), 2908-2909 (2003).
- [95] A. Kay, I. Cesar, and M. Gratzel, "New benchmark for water photooxidation by nanostructured α -Fe₂O₃ films," *Journal of the American Chemical Society* 128 (49), 15714-15721 (2006).
- [96] B. Cole, B. Marsen, E. Miller, Y. F. Yan, B. To, K. Jones, and M. Al-Jassim, "Evaluation of nitrogen doping of tungsten oxide for photoelectrochemical water splitting," *Journal of Physical Chemistry C* 112 (13), 5213-5220 (2008).
- [97] A. Ghicov, J. M. Macak, H. Tsuchiya, J. Kunze, V. Haeublein, L. Frey, and P. Schmuki, "Ion implantation and annealing for an efficient n-doping of TiO₂ nanotubes," *Nano Letters* 6 (5), 1080-1082 (2006).
- [98] S. Sakthivel, M. Janczarek, and H. Kisch, "Visible light activity and photoelectrochemical properties of nitrogen-doped TiO₂," *Journal of Physical Chemistry B* 108 (50), 19384-19387 (2004).
- [99] A. J. Nozik and R. Memming, "Physical chemistry of semiconductor-liquid interfaces," *Journal of Physical Chemistry* 100 (31), 13061-13078 (1996).
- [100] R. van de Krol, Y. Q. Liang, and J. Schoonman, "Solar hydrogen production with nanostructured metal oxides," *Journal of Materials Chemistry* 18 (20), 2311-2320 (2008).
- [101] G. M. Wang, X. Y. Yang, F. Qian, J. Z. Zhang, and Y. Li, "Double-sided CdS and CdSe quantum dot co-sensitized ZnO nanowire arrays for photoelectrochemical hydrogen generation," *Nano Letters* 10 (3), 1088-1092 (2010).
- [102] J. W. Sun, D. K. Zhong, and D. R. Gamelin, "Composite photoanodes for photoelectrochemical solar water splitting," *Energy & Environmental Science* 3 (9), 1252-1261 (2010).
- [103] K. Maeda, M. Higashi, B. Siritanaratkul, R. Abe, and K. Domen, "SrNbO_{2n} as a water-splitting photoanode with a wide visible-light absorption band," *Journal of the American Chemical Society* 133 (32), 12334-12337 (2011).
- [104] J. Z. Su, L. J. Guo, N. Z. Bao, and C. A. Grimes, "Nanostructured WO₃/BiVO₄ heterojunction films for efficient photoelectrochemical water splitting," *Nano Letters* 11 (5), 1928-1933 (2011).
- [105] D. D. Qin, C. L. Tao, S. A. Friesen, T. H. Wang, O. K. Varghese, N. Z. Bao, Z. Y. Yang, T. E. Mallouk, and C. A. Grimes, "Dense layers of vertically oriented WO₃ crystals as anodes for photoelectrochemical water oxidation," *Chemical Communications* 48 (5), 729-731 (2012).
- [106] G. M. Wang, Y. C. Ling, H. Y. Wang, X. Y. Yang, C. C. Wang, J. Z. Zhang, and Y. Li, "Hydrogen-treated WO₃ nanoflakes show enhanced photostability," *Energy & Environmental Science* 5 (3), 6180-6187 (2012).

- [107] C. Santato, M. Ulmann, and J. Augustynski, "Photoelectrochemical properties of nanostructured tungsten trioxide films," *Journal of Physical Chemistry B* 105 (5), 936-940 (2001).
- [108] C. J. Schoot, J. J. Ponjee, H. T. Vandam, R. A. Vandoorn, and P. T. Bolwijn, "New electrochromic memory display," *Applied Physics Letters* 23 (2), 64-65 (1973).
- [109] K. Yamanaka, "Electrodeposited films from aqueous tungstic acid-hydrogen peroxide solutions for electrochromic display devices," *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers* 26 (11), 1884-1890 (1987).
- [110] M. J. Wang, G. J. Fang, L. Y. Yuan, H. H. Huang, Z. H. Sun, N. S. Liu, S. H. Xia, and X. Z. Zhao, "High optical switching speed and flexible electrochromic display based on WO₃ nanoparticles with ZnO nanorod arrays' supported electrode," *Nanotechnology* 20 (18) (2009).
- [111] C. M. Lampert, "Towards large-area photovoltaic nanocells - experiences learned from smart window technology," *Solar Energy Materials and Solar Cells* 32 (3), 307-321 (1994).
- [112] R. D. Rau, "Electrochromic windows: An overview," *Electrochimica Acta* 44 (18), 3165-3176 (1999).
- [113] C. G. Granqvist, "Electrochromic oxides-systematics, materials, and applications to smart windows," *Renewable Energy* 5 (1-4), 141-153 (1994).
- [114] H. Yoshimura and N. Koshida, "Fast electrochromic effect obtained from solid-state inorganic thin-film configuration with a carrier accumulation structure," *Applied Physics Letters* 88 (9) (2006).
- [115] F. G. Baucke, K. Bange, and T. Gambke, "Reflecting electrochromic devices," *Displays* 9 (4), 179-187 (1988).
- [116] C. Cantalini, H. T. Sun, M. Faccio, M. Pelino, S. Santucci, L. Lozzi, and M. Passacantando, "NO₂ sensitivity of WO₃ thin film obtained by high vacuum thermal evaporation," *Sensors and Actuators B-Chemical* 31 (1-2), 81-87 (1996).
- [117] S. H. Baeck, K. S. Choi, T. F. Jaramillo, G. D. Stucky, and E. W. McFarland, "Enhancement of photocatalytic and electrochromic properties of electrochemically fabricated mesoporous WO₃ thin films," *Advanced Materials* 15 (15), 1269-1273 (2003).
- [118] W. Cheng, E. Baudrin, B. Dunn, and J. I. Zink, "Synthesis and electrochromic properties of mesoporous tungsten oxide," *Journal of Materials Chemistry* 11 (1), 92-97 (2001).
- [119] C. G. Granqvist, "Progress in electrochromics: Tungsten oxide revisited," *Electrochimica Acta* 44 (18), 3005-3015 (1999).
- [120] Z. H. Jiao, X. W. Sun, J. M. Wang, L. Ke, and H. V. Demir, "Hydrothermally grown nanostructured WO₃ films and their electrochromic characteristics," *Journal of Physics D-Applied Physics* 43 (28).

- [121] J. Zhang, J. P. Tu, X. H. Xia, Y. Qiao, and Y. Lu, "An all-solid-state electrochromic device based on NiO/WO₃ complementary structure and solid hybrid polyelectrolyte," *Solar Energy Materials and Solar Cells* 93 (10), 1840-1845 (2009).
- [122] J. Zhang, J. P. Tu, X. H. Xia, X. L. Wang, and C. D. Gu, "Hydrothermally synthesized WO₃ nanowire arrays with highly improved electrochromic performance," *Journal of Materials Chemistry* 21 (14), 5492-5498.
- [123] J. Zhang, X. L. Wang, X. H. Xia, C. D. Gu, Z. J. Zhao, and J. P. Tu, "Enhanced electrochromic performance of macroporous WO₃ films formed by anodic oxidation of dc-sputtered tungsten layers," *Electrochimica Acta* 55 (23), 6953-6958.
- [124] J. L. Solis, S. Saukko, L. Kish, C. G. Granqvist, and V. Lantto, "Semiconductor gas sensors based on nanostructured tungsten oxide," *Thin Solid Films* 391 (2), 255-260 (2001).
- [125] Y. Saito, S. Uchida, T. Kubo, and H. Segawa, "Surface-oxidized tungsten for energy-storable dye-sensitized solar cells," *Thin Solid Films* 518 (11), 3033-3036.
- [126] B. D. Alexander, P. J. Kulesza, L. Rutkowska, R. Solarska, and J. Augustynski, "Metal oxide photoanodes for solar hydrogen production," *Journal of Materials Chemistry* 18 (20), 2298-2303 (2008).
- [127] Z. H. Jiao, J. M. Wang, L. Ke, X. W. Sun, and H. V. Demir, "Morphology-tailored synthesis of tungsten trioxide (hydrate) thin films and their photocatalytic properties," *Acs Applied Materials & Interfaces* 3 (2), 229-236.
- [128] K. Nishio, K. Iwata, and H. Masuda, "Fabrication of nanoporous WO₃ membranes and their electrochromic properties," *Electrochemical and Solid State Letters* 6 (10), H21-H23 (2003).
- [129] S. H. Lee, H. M. Cheong, C. E. Tracy, A. Mascarenhas, A. W. Czanderna, and S. K. Deb, "Electrochromic coloration efficiency of a-WO_{3-y} thin films as a function of oxygen deficiency," *Applied Physics Letters* 75 (11), 1541-1543 (1999).
- [130] J. M. Wang, E. Khoo, P. S. Lee, and J. Ma, "Controlled synthesis of WO₃ nanorods and their electrochromic properties in H₂SO₄ electrolyte," *Journal of Physical Chemistry C* 113 (22), 9655-9658 (2009).
- [131] J. M. Wang, E. Khoo, P. S. Lee, and J. Ma, "Synthesis, assembly, and electrochromic properties of uniform crystalline WO₃ nanorods," *Journal of Physical Chemistry C* 112 (37), 14306-14312 (2008).
- [132] S. Y. Park, J. M. Lee, C. Noh, and S. U. Son, "Colloidal approach for tungsten oxide nanorod-based electrochromic systems with highly improved response times and color efficiencies," *Journal of Materials Chemistry* 19 (42), 7959-7964 (2009).

- [133] C. H. Chen, S. J. Wang, R. M. Ko, Y. C. Kuo, K. M. Uang, T. M. Chen, B. W. Liou, and H. Y. Tsai, "The influence of oxygen content in the sputtering gas on the self-synthesis of tungsten oxide nanowires on sputter-deposited tungsten films," *Nanotechnology* 17 (1), 217-223 (2006).
- [134] E. B. Franke, C. L. Trimble, M. Schubert, J. A. Woollam, and J. S. Hale, "All-solid-state electrochromic reflectance device for emittance modulation in the far-infrared spectral region," *Applied Physics Letters* 77 (7), 930-932 (2000).
- [135] I. Valyukh, S. Green, H. Arwin, G. A. Niklasson, E. Wackelgard, and C. G. Granqvist, "Spectroscopic ellipsometry characterization of electrochromic tungsten oxide and nickel oxide thin films made by sputter deposition," *Solar Energy Materials and Solar Cells* 94 (5), 724-732.
- [136] P. X. Feng, X. P. Wang, H. X. Zhang, B. Q. Yang, Z. B. Wang, A. Gonzalez-Berrios, G. Morell, and B. Weiner, "Study of the structural evolutions of crystalline tungsten oxide films prepared using hot-filament CVD," *Journal of Physics D-Applied Physics* 40 (17), 5239-5245 (2007).
- [137] K. Sivula, F. Le Formal, and M. Gratzel, "WO₃-Fe₂O₃ photoanodes for water splitting: A host scaffold, guest absorber approach," *Chemistry of Materials* 21 (13), 2862-2867 (2009).
- [138] S. H. Baeck, T. Jaramillo, G. D. Stucky, and E. W. McFarland, "Controlled electrodeposition of nanoparticulate tungsten oxide," *Nano Letters* 2 (8), 831-834 (2002).
- [139] N. R. de Tacconi, C. R. Chenthamarakshan, K. Rajeshwar, T. Pauporte, and D. Lincot, "Pulsed electrodeposition of WO₃-TiO₂ composite films," *Electrochemistry Communications* 5 (3), 220-224 (2003).
- [140] S. R. Bathe and P. S. Patil, "Influence of Nb doping on the electrochromic properties of WO₃ films," *Journal of Physics D-Applied Physics* 40 (23), 7423-7431 (2007).
- [141] S. R. Bathe and P. S. Patil, "Electrochromic characteristics of fibrous reticulated WO₃ thin films prepared by pulsed spray pyrolysis technique," *Solar Energy Materials and Solar Cells* 91 (12), 1097-1101 (2007).
- [142] B. Yang, P. R. F. Barnes, W. Bertram, and V. Luca, "Strong photoresponse of nanostructured tungsten trioxide films prepared via a sol-gel route," *Journal of Materials Chemistry* 17 (26), 2722-2729 (2007).
- [143] B. Yang, Y. J. Zhang, E. Drabarek, P. R. F. Barnes, and V. Luca, "Enhanced photoelectrochemical activity of sol-gel tungsten trioxide films through textural control," *Chemistry of Materials* 19 (23), 5664-5672 (2007).

- [144] Y. B. Li, Y. Bando, D. Golberg, and K. Kurashima, "WO₃ nanorods/nanobelts synthesized via physical vapor deposition process," *Chemical Physics Letters* 367 (1-2), 214-218 (2003).
- [145] I. Shiyankovskaya, M. Hepel, and E. Tewksbury, "Electrochromism in electrodeposited nanocrystalline WO₃ films i. Electrochemical and optical properties," *Journal of New Materials for Electrochemical Systems* 3 (3), 241-247 (2000).
- [146] S. J. Yoo, J. W. Lim, Y. E. Sung, Y. H. Jung, H. G. Choi, and D. K. Kim, "Fast switchable electrochromic properties of tungsten oxide nanowire bundles," *Applied Physics Letters* 90 (17) (2007).
- [147] L. Zhou, J. Zou, M. M. Yu, P. Lu, J. Wei, Y. Q. Qian, Y. H. Wang, and C. Z. Yu, "Green synthesis of hexagonal-shaped WO₃·0.33H₂O nanodiscs composed of nanosheets," *Crystal Growth & Design* 8 (11), 3993-3998 (2008).
- [148] X. H. Zhang, X. H. Lu, Y. Q. Shen, J. B. Han, L. Y. Yuan, L. Gong, Z. Xu, X. D. Bai, M. Wei, Y. X. Tong, Y. H. Gao, J. Chen, J. Zhou, and Z. L. Wang, "Three-dimensional WO₃ nanostructures on carbon paper: Photoelectrochemical property and visible light driven photocatalysis," *Chemical Communications* 47 (20), 5804-5806 (2011).
- [149] M. F. Daniel, B. Desbat, J. C. Lassegues, B. Gerand, and M. Figlarz, "Infrared and raman-study of WO₃ tungsten trioxides and WO₃·xH₂O tungsten trioxide hydrates," *Journal of Solid State Chemistry* 67 (2), 5235-247 (1987).
- [150] M. Deepa, T. K. Saxena, D. P. Singh, K. N. Sood, and S. A. Agnihotry, "Spin coated versus dip coated electrochromic tungsten oxide films: Structure, morphology, optical and electrochemical properties," *Electrochimica Acta* 51 (10), 1974-1989 (2006).
- [151] Z. H. Jiao, X. W. Sun, J. M. Wang, L. Ke, and H. V. Demir, "Hydrothermally grown nanostructured WO₃ films and their electrochromic characteristics," *Journal of Physics D-Applied Physics* 43 (28) (2010).
- [152] J. Zhang, J. P. Tu, X. H. Xia, X. L. Wang, and C. D. Gu, "Hydrothermally synthesized WO₃ nanowire arrays with highly improved electrochromic performance," *Journal of Materials Chemistry* 21 (14), 5492-5498 (2011).
- [153] S. I. Cho, W. J. Kwon, S. J. Choi, P. Kim, S. A. Park, J. Kim, S. J. Son, R. Xiao, S. H. Kim, and S. B. Lee, "Nanotube-based ultrafast electrochromic display," *Advanced Materials* 17 (2), 171-+ (2005).
- [154] S. I. Cho, R. Xiao, and S. B. Lee, "Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) nanotubes towards fast window-type electrochromic devices," *Nanotechnology* 18 (40) (2007).
- [155] D. T. Gillaspie, R. C. Tenent, and A. C. Dillon, "Metal-oxide films for electrochromic applications: Present technology and future directions," *Journal of Materials Chemistry* 20 (43), 9585-9592 (2010).

- [156] T. J. Richardson, J. L. Slack, R. D. Armitage, R. Kostecki, B. Farangis, and M. D. Rubin, "Switchable mirrors based on nickel-magnesium films," *Applied Physics Letters* 78 (20), 3047-3049 (2001).
- [157] H. T. Sun, C. Cantalini, L. Lozzi, M. Passacantando, S. Santucci, and M. Pelino, "Microstructural effect on NO₂ sensitivity of WO₃ thin film gas sensors .1. Thin film devices, sensors and actuators," *Thin Solid Films* 287 (1-2), 258-265 (1996).
- [158] J. Zhang, J. P. Tu, X. H. Xia, Y. Qiao, and Y. Lu, "An all-solid-state electrochromic device based on NiO/WO₃ complementary structure and solid hybrid polyelectrolyte," *Solar Energy Materials and Solar Cells* 93 (10), 1840-1845 (2009).
- [159] C. G. Granqvist, "Solar energy materials," *Advanced Materials* 15 (21), 1789-1803 (2003).
- [160] H. Huang, J. Tian, W. K. Zhang, Y. P. Gan, X. Y. Tao, X. H. Xia, and J. P. Tu, "Electrochromic properties of porous nio thin film as a counter electrode for NiO/WO₃ complementary electrochromic window," *Electrochimica Acta* 56 (11), 4281-4286.
- [161] K. Itaya, K. Shibayama, H. Akahoshi, and S. Toshima, "Prussian-blue-modified electrodes - an application for a stable electrochromic display device," *Journal of Applied Physics* 53 (1), 804-805 (1982).
- [162] J. Livage and D. Ganguli, "Sol-gel electrochromic coatings and devices: A review," *Solar Energy Materials and Solar Cells* 68 (3-4), 365-381 (2001).
- [163] J. Livage and G. Guzman, "Aqueous precursors for electrochromic tungsten oxide hydrates," *Solid State Ionics* 84 (3-4), 205-211 (1996).
- [164] A. J. Bard and L. R. Faulkner, (Wiley, New York, 2001).
- [165] S. Hara, H. Shiozaki, A. Omura, H. Tanaka, T. Kawamoto, M. Tokumoto, M. Yamada, A. Gotoh, M. Kurihara, and M. Sakamoto, "Color-switchable glass and display devices fabricated by liquid processes with electrochromic nanoparticle "Ink"," *Applied Physics Express* 1 (10) (2008).
- [166] C. G. Granqvist, P. C. Lansaker, N. R. Mlyuka, G. A. Niklasson, and E. Avendano, "Progress in chromogenics: New results for electrochromic and thermochromic materials and devices," *Solar Energy Materials and Solar Cells* 93 (12), 2032-2039 (2009).
- [167] M. Sun, N. Xu, Y. W. Cao, J. N. Yao, and E. G. Wang, "Nanocrystalline tungsten oxide thin film: Preparation, microstructure, and photochromic behavior," *Journal of Materials Research* 15 (4), 927-933 (2000).
- [168] V. Wittwer, M. Datz, I. Ell, A. Georg, W. Graf, and G. Walze, "Gasochromic windows," *Solar Energy Materials and Solar Cells* 84 (1-4), 305-314 (2004).
- [169] U. O. Krasovec, A. Georg, V. Wittwer, J. Luther, and M. Topic, "Performance of a solid-state photoelectrochromic device," *Solar Energy Materials and Solar Cells* 84 (1-4), 369-380 (2004).

- [170] Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota, and A. Fujishima, "Multicolour photochromism of TiO_2 films loaded with silver nanoparticles," *Nature Materials* 2 (1), 29-31 (2003).
- [171] T. Tatsuma and K. Suzuki, "Photoelectrochromic cell with a Ag- TiO_2 nanocomposite: Concepts of drawing and display modes," *Electrochemistry Communications* 9 (4), 574-576 (2007).
- [172] X. F. Yu, Y. X. Li, N. F. Zhu, Q. B. Yang, and K. Kalantar-zadeh, "A polyaniline nanofibre electrode and its application in a self-powered photoelectrochromic cell," *Nanotechnology* 18 (1), 8 (2007).
- [173] D. M. DeLongchamp and P. T. Hammond, "High-contrast electrochromism and controllable dissolution of assembled prussian blue/polymer nanocomposites," *Advanced Functional Materials* 14 (3), 224-232 (2004).
- [174] A. A. Karyakin, "Prussian blue and its analogues: Electrochemistry and analytical applications," *Electroanalysis* 13 (10), 813-819 (2001).
- [175] A. Eftekhari, "Potassium secondary cell based on prussian blue cathode," *Journal of Power Sources* 126 (1-2), 221-228 (2004).
- [176] H. L. Yu, C. C. Hsiao, and W. C. Liu, "New apparatus for haze measurement for transparent media," *Measurement Science & Technology* 17 (8), N29-N36 (2006).
- [177] L. C. Chen, Y. H. Huang, and K. C. Ho, "A complementary electrochromic system based on prussian blue and indium hexacyanoferrate," *Journal of Solid State Electrochemistry* 7 (1), 6-10 (2002).
- [178] A. Z. Sadek, H. D. Zheng, K. Latham, W. Wlodarski, and K. Kalantar-Zadeh, "Anodization of ti thin film deposited on ITO," *Langmuir* 25 (1), 509-514 (2009).
- [179] L. Vayssieres and M. Graetzel, "Highly ordered SnO_2 nanorod arrays from controlled aqueous growth," *Angewandte Chemie-International Edition* 43 (28), 3666-3670 (2004).
- [180] J. X. Wang, X. W. Sun, Y. Yang, H. Huang, Y. C. Lee, O. K. Tan, and L. Vayssieres, "Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications," *Nanotechnology* 17 (19), 4995-4998 (2006).
- [181] M. A. Butler, "Photoelectrolysis and physical-properties of semiconducting electrode WO_3 ," *Journal of Applied Physics* 48 (5), 1914-1920 (1977).
- [182] B. Marsen, E. L. Miller, D. Paluselli, and R. E. Rocheleau, "Progress in sputtered tungsten trioxide for photoelectrode applications," *International Journal of Hydrogen Energy* 32 (15), 3110-3115 (2007).
- [183] E. Widenkvist, R. A. Quinlan, B. C. Holloway, H. Grennberg, and U. Jansson, "Synthesis of nanostructured tungsten oxide thin films," *Crystal Growth & Design* 8 (10), 3750-3753 (2008).
- [184] Z. J. Gu, T. Y. Zhai, B. F. Gao, X. H. Sheng, Y. B. Wang, H. B. Fu, Y. Ma, and J. N. Yao, "Controllable assembly of WO_3

- nanorods/nanowires into hierarchical nanostructures," *Journal of Physical Chemistry B* 110 (47), 23829-23836 (2006).
- [185] J. H. Ha, P. Muralidharan, and D. K. Kim, "Hydrothermal synthesis and characterization of self-assembled h-WO₃ nanowires/nanorods using edta salts," *Journal of Alloys and Compounds* 475 (1-2), 446-451 (2009).
- [186] F. Amano, D. Li, and B. Ohtani, "Fabrication and photoelectrochemical property of tungsten(vi) oxide films with a flake-wall structure," *Chemical Communications* 46 (16), 2769-2771 (2010).
- [187] J. Chen, D. W. Zhao, W. Lei, X. W. Sun, J. L. Song, and W. Q. Deng, "A highly effective method for synthesizing hybrid Pt-CdSe nanocomposite," *Applied Surface Science* 256 (5), 1526-1529 (2009).
- [188] F. Di Natale and A. Lancia, "Recovery of tungstate from aqueous solutions by ion exchange," *Industrial & Engineering Chemistry Research* 46 (21), 6777-6782 (2007).
- [189] A. Chemseddine and U. Bloeck, "How isopolyanions self-assemble and condense into a 2d tungsten oxide crystal: Hrtem imaging of atomic arrangement in an intermediate new hexagonal phase," *Journal of Solid State Chemistry* 181 (10), 2731-2736 (2008).
- [190] N. S. Gaikwad, G. Waldner, A. Bruger, A. Belaidi, S. M. Chaqour, and M. Neumann-Spallart, "Photoelectrochemical characterization of semitransparent wo₃ films," *Journal of the Electrochemical Society* 152 (5), G411-G416 (2005).
- [191] R. Solarska, C. Santato, C. Jorand-Sartoretti, M. Ulmann, and J. Augustynski, "Photoelectrolytic oxidation of organic species at mesoporous tungsten trioxide film electrodes under visible light illumination," *Journal of Applied Electrochemistry* 35 (7-8), 715-721 (2005).
- [192] K. S. Ahn, S. H. Lee, A. C. Dillon, C. E. Tracy, and R. Pitts, "The effect of thermal annealing on photoelectrochemical responses of WO₃ thin films," *Journal of Applied Physics* 101 (9) (2007).
- [193] H. Wang, X. Quan, Y. Zhang, and S. Chen, "Direct growth and photoelectrochemical properties of tungsten oxide nanobelt arrays," *Nanotechnology* 19 (6) (2008).
- [194] T. Bak, J. Nowotny, M. Rekas, and C. C. Sorrell, "Photoelectrochemical hydrogen generation from water using solar energy. Materials-related aspects," *International Journal of Hydrogen Energy* 27 (10), 991-1022 (2002).