

# **STUDY OF LOW DIMENSIONAL TUNGSTEN OXIDE BY ANODIZATION AND SOL-GEL METHODS**

by

**CHAI YINGQI**

**Thesis submitted in fulfillment of the requirements  
for the degree of  
Doctor of Philosophy**

**June 2018**

## **ACKNOWLEDGEMENT**

First of all, I would like to thank my supervisor, Dr. Yam Fong Kwong, and my co-supervisor, Prof. Zainuriah Hassan, for their easygoing supervision and guidance throughout this project. Their advice, dedication and energy to me are appreciated.

I would also like to show my gratitude to the lab assistants of Institute of Nano-Optoelectronics Research and Technology as well as the School of Physics of University Sains of Malaysia (USM). Their help in providing a convenient working environment and experimental equipments allowed me to run my experiments smoothly. Besides, I would also like to thank my colleagues and other researchers from NOR lab for the great discussions and suggestions.

Finally and mostly, I would also like to thank my family and friends for their support and motivation.

## TABLE OF CONTENTS

<b>ACKNOWLEDGEMENT</b>	<b>ii</b>
<b>TABLE OF CONTENTS</b>	<b>iii</b>
<b>LIST OF TABLES</b>	<b>vii</b>
<b>LIST OF FIGURES</b>	<b>viii</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xiv</b>
<b>ABSTRAK</b>	<b>xvi</b>
<b>ABSTRACT</b>	<b>xviii</b>
<b>CHAPTER 1: INTRODUCTION</b>	<b>1</b>
1.1 Introduction	1
1.2 Why Tungsten Oxide	1
1.3 Fabrication methods of nanostructured tungsten oxide	3
1.3.1 Anodization	4
1.3.2 Sol gel	6
1.4 Current research and problem statements	7
1.5 Research Objectives	10
1.6 Research Novelities	10
1.7 Outline of Thesis	10
<b>CHAPTER 2: LITERATURE REVIEW AND RESEARCH                     BACKGROUND</b>	<b>12</b>
2.1 Introduction	12
2.2 Fundamental properties of tungsten oxide	12
2.3 Anodic growth mechanism of nanostructured WO <sub>3</sub>	15

2.4	Fabrication of WO <sub>3</sub> by sol-gel method	19
2.4.1	Type of precursors	19
2.4.2	Sol-gel process	20
2.5	Photoelectrochemical water splitting	22
2.5.1	Principle and efficiency of photo-electrode water splitting	23
2.5.2	Requirement of the Photo-electrode for Water Splitting	25
2.5.3	Challenge of the Photo-electrode for Water Splitting	26
2.6	Humidity Sensor	28
2.6.1	Humidity sensing mechanism	30
2.6.2	Current research on humidity sensor	33
	<b>CHAPTER 3: EXPERIMENTAL PROCEDURE</b>	<b>37</b>
3.1	Introduction	37
3.2	Growth and characterization of WO <sub>3</sub> by anodization method	37
3.2.1	Growth of WO <sub>3</sub> by anodization method	37
3.2.2	Characterization of the anodic growth WO <sub>3</sub>	41
3.3	Growth and characterization of WO <sub>3</sub> by sol-gel method	43
3.3.1	Growth of WO <sub>3</sub> by sol-gel method	43
3.3.2	Fabrication of WO <sub>3</sub> humidity sensor	45
3.3.3	Characterization of the sol-gel-made WO <sub>3</sub>	47
	<b>CHAPTER 4: TUNGSTEN OXIDE GROWN BY ANODIZATION METHOD</b>	<b>49</b>
4.1	Introduction	49
4.2	Anodization in oxalic acid electrolyte	49
4.2.1	Effect of voltage on the WO <sub>3</sub> formed in oxalic acid	49

4.2.2	Effect of duration on the WO <sub>3</sub> formed in oxalic acid	52
4.2.3	Formation mechanism of nanopores	54
4.2.4	Effect of post-annealing on the WO <sub>3</sub> formed in oxalic acid	56
4.3	Anodization in HCl electrolyte	61
4.3.1	Effect of voltage on WO <sub>3</sub> formed in HCl	61
4.3.2	Effect of anodization duration on WO <sub>3</sub> formed in HCl	63
4.3.3	Effect of anodization temperature on WO <sub>3</sub> formed in HCl	64
4.3.4	Formation mechanism of nanoplates	67
4.4	Anodization in H <sub>2</sub> SO <sub>4</sub> electrolyte	69
4.4.1	Effect of concentration on WO <sub>3</sub> formed in H <sub>2</sub> SO <sub>4</sub>	69
4.4.2	Effect of voltage on WO <sub>3</sub> formed in H <sub>2</sub> SO <sub>4</sub>	70
4.4.3	Effect of anodization duration on WO <sub>3</sub> formed in H <sub>2</sub> SO <sub>4</sub>	72
4.4.4	Effect of anodization temperature on WO <sub>3</sub> formed in H <sub>2</sub> SO <sub>4</sub>	73
4.5	Photoelectrochemical measurement	76
4.5.1	Photoelectrochemical measurement of WO <sub>3</sub> formed in oxalic acid	76
4.5.2	Photoelectrochemical measurement of WO <sub>3</sub> formed in HCl	77
4.5.3	Photoelectrochemical measurement of WO <sub>3</sub> formed in H <sub>2</sub> SO <sub>4</sub>	79
4.5.4	Comparison of the photoelectrochemical measurement of WO <sub>3</sub> formed with different methods and their efficiency	80
4.6	Summary	83
<b>CHAPTER 5: TUNGSTEN OXIDE GROWN BY SOL-GEL METHOD</b>		<b>84</b>
5.1	Introduction	84
5.2	Visual inspection of the sol-gel-made tungsten oxide	84
5.2.1	Visual inspection of the sol-gel-made tungsten oxide with different acid volumes and ageing durations	85

5.2.2	Visual inspection of the sol-gel-made of tungsten oxide with different mixing rates	88
5.3	Morphological property of the sol-gel-made tungsten oxide	89
5.3.1	Effect of the acid concentration on the morphological property	90
5.3.2	Effect of the ageing duration on the morphological property	93
5.3.3	Effect of the mixing flow rate on the morphological property	94
5.4	Structural and vibrational properties of the sol-gel-made tungsten oxide	96
5.4.1	Effect of the acid volume on the structural and vibrational properties of tungsten oxide	96
5.4.2	Effect of the ageing durations on the structural and vibrational properties of tungsten oxide	100
5.4.3	Effect of the mixing rate on the structural and vibrational properties of tungsten oxide	103
5.5	Humidity sensing properties of the sol-gel-made tungsten oxide	105
5.5.1	Effect of acid concentration on the sensitivity of tungsten oxide humidity sensor	105
5.5.2	Effect of ageing duration on the sensitivity of tungsten oxide humidity sensor	107
5.5.3	Effect of flow rates on the sensitivity of tungsten oxide humidity sensor	107
5.5.4	Comparison of the humidity sensing property of the samples	108
5.6	Summary	109
<b>CHAPTER 6: CONCLUSION AND FUTURE WORK</b>		<b>111</b>
6.1	Conclusion	111
6.2	Proposed future works	112
<b>REFERENCES</b>		<b>113</b>
<b>APPENDICES</b>		
<b>LIST OF PUBLICATIONS</b>		

## LIST OF TABLES

		<b>Page</b>
Table 2.1	Recent works on humidity sensors since 2003	35
Table 3.1	Anodization parameters for the samples prepared in 0.3 M oxalic acid.	39
Table 3.2	Anodization parameters for the samples prepared in 1 M HCl.	40
Table 3.3	Anodization parameters for the samples prepared in H <sub>2</sub> SO <sub>4</sub> .	41
Table 3.4	Experimental parameters for WO <sub>3</sub> fabricated by sol-gel technique.	44
Table 5.1	Calculated lateral and crystallite size for the samples prepared with different sol-gel parameters.	92

## LIST OF FIGURES

	<b>Page</b>	
Figure 2.1	Stability of polymorphs of $\text{WO}_3$ at different temperatures. Source: Ref. [82].	13
Figure 2.2	(a) Crystalline $\text{WO}_3$ structure with corner-sharing $\text{WO}_6$ octahedra layers. (b) $\text{W}_{18}\text{O}_{49}$ structure with both corner- and edge- sharing $\text{WO}_6$ octahedra layers. Source: Ref. [89].	14
Figure 2.3	(a) Plane view and (b) cross section view of SEM images of anodic growth alumina in 0.5 M oxalic acid at 15 °C for 1h. Source: Ref. [99].	17
Figure 2.4	Cross sectional view of SEM image of titanium oxide nanotubes formed in mixture of glycerol and water (50:50 vol. %) + 0.5 wt. % $\text{NH}_4\text{F}$ . Inset shows the corresponding plane view image. Source: Ref. [100].	18
Figure 2.5	(a) Plane view and (b) cross sectional view SEM images of $\text{WO}_3$ grown in 0.5 wt % $\text{NaF}$ + 1 M $\text{H}_2\text{SO}_4$ . Source: Ref. [15].	18
Figure 2.6	SEM image of $\text{WO}_3$ formed in $\text{H}_3\text{PO}_4$ + 8 M $\text{HF}$ . Inset depicts the cross sectional image of the corresponding image. Source: Ref. [58].	18
Figure 2.7	Photoelectrochemical water splitting systems using n-type semiconductor photoanode. C.B., B.G., and V.B. represent energy level of the conductor band, band gap and valence band respectively. Source: Ref. [109].	23
Figure 2.8	Illustration of the energetic criteria for water splitting. Source: Ref. [109].	25
Figure 2.9	The bandgap positions for various semiconductors relative to the redox potential of water. NHE stands for normal hydrogen electrode. Source: Ref. [115]	27
Figure 2.10	Adsorption process of water molecules on sensing materials in different stages: (a) metal oxide surface (b) chemisorbed water (c) physisorbed water (d) multi-layer structure of condense water. Source: Ref. [144, 145].	31
Figure 2.11	Illustration of the Grotthuss mechanism. The arrows indicate hopping of protons. Source: Ref. [142].	31



Figure 2.12	Illustration of the electronic conduction mechanism. $E_c$ , $E_F$ , and $E_v$ represent lowest energy of conduction band, Fermi energy level, and highest energy of valence band respectively. Source: Ref. [142]	32
Figure 2.13	Requirements of the humidity sensor. Source: Ref. [138].	34
Figure 3.1	Process flow for the growth of $WO_3$ by anodization method.	37
Figure 3.2	Schematic diagram of the experimental setup for anodization.	38
Figure 3.3	Experimental setup for the photoelectrochemical measurement.	42
Figure 3.4	Process flow for the fabrication of $WO_3$ by sol-gel method.	43
Figure 3.5	Schematic diagram of the experimental setup to grow $WO_3$ by sol-gel method.	44
Figure 3.6	Process flow for the fabrication of tin plated IDE on PCB.	46
Figure 3.7	Design of the IDE pattern.	46
Figure 3.8	(a)Plane view and (b) cross-sectional view of the humidity sensor.	47
Figure 3.9	Experimental setup for the characterization of humidity sensor.	48
Figure 4.1	FESEM images of the films which are grown in 0.3 M oxalic acid for 30 min at (a) 20, (b) 40, (c) 60, (d) 80, (e) 100 V and (f) 110 V respectively. The insets show the cross sectional view of the respective images.	50
Figure 4.2	Pore layer thickness and pore diameter as a function of anodization voltage.	51
Figure 4.3	Current transients during anodization at different voltages. The inset shows the detail of the curve patterns in the low current density range.	51
Figure 4.4	FESEM top-view images of porous tungsten oxide films which are anodized in 0.3 M oxalic acid at 40 V for different durations. The inset in (e)-(i) shows the cross-sectional view images.	54
Figure 4.5	Schematic diagram of the porous tungsten oxide formation: (a) compact oxide layer formation, (b) growth of the pits, (c) growth of the pore, (d) precipitation of the soluble tungsten species and nucleation of small pore in the existing pore, (e) voids formation beneath the surface, (f) regular porous $WO_3$ structure.	55

- Figure 4.6 FESEM top view images of (a) as-grown and post-annealed films at (b) 400 °C, (c) 500 °C and (d) 600 °C for 2 hrs. Cross sectional view of film (e) without annealing and (f) film annealed at 600 °C. 57
- Figure 4.7 (a) XRD patterns of WO<sub>3</sub> films post-annealed at different temperatures. (b) Magnified patterns in the range of 22.5°-25°. (c) XRD patterns for compact and porous films annealed at 400 °C for 2 h. Symbol ‘ε’ indicates monoclinic phase of WO<sub>3</sub> while ‘ω’ indicates tungsten substrate. 58
- Figure 4.8 (a) Raman spectra of films annealed at different temperatures. (b) Magnified spectra of (a) in the range of 800 -1000 cm<sup>-1</sup>. (c) Changes of intensity and FWHM of peak at 807 cm<sup>-1</sup> as the function of annealing temperature. 60
- Figure 4.9 Current transients of the samples anodized in 1 M HCl at different potentials for 4 h. The inset shows the shift of the peak positions with the variation of applied potentials. 62
- Figure 4.10 Selected FESEM top-view images of nanostructured film anodized at (a) 2 V, (b) 10 V and (c) 15 V in HCl for 4 h. Insets (a) and (b) are the cross-sectional images of the respective films. Inset (c) is the magnified view of the samples. 62
- Figure 4.11 Current transients of the sample anodized in 1 M HCl at 10 V for 15 h. 63
- Figure 4.12 Selected FESEM top-view images of samples anodized at 10 V in 1 M HCl for (a) 1 h, (b) 2 h and (c) 15 h which correspond to point I-III as labeled in figure 4.11. The insets are the cross-sectional images of the respective samples. 64
- Figure 4.13 Current transients of the samples anodized in 1 M HCl at different temperatures for 4 h. The inset shows the local maximum of current density and shifting of the peak positions as a function of anodization temperature. 65
- Figure 4.14 FESEM top-view images of samples anodized at (a) 25°C (b) 40 °C, (c) 60 °C and (d) 80 °C at 10 V in 1 M HCl for 4 h. The insets are the cross-sectional images of the respective films. 65
- Figure 4.15 XRD patterns of WO<sub>3</sub> films anodized at different temperatures in 1 M HCl. Symbols ‘\*\*’, ‘\*’, ‘τ’ and ‘ω’ refer to WO<sub>3</sub>·2H<sub>2</sub>O, WO<sub>3</sub>·H<sub>2</sub>O, WO<sub>3</sub>·<sup>1</sup>/<sub>3</sub>H<sub>2</sub>O and W peaks. 66
- Figure 4.16 Schematic diagram of the formation mechanism of nanostructured WO<sub>3</sub> film (not in scale): (a) formation of the oxide layer by field-assisted oxidation, (b) formation of WO<sub>2</sub><sup>2+</sup> by field-assisted dissolution, (c) formation of WO<sub>2</sub><sup>2+</sup> by chemical dissolution, (d)

	precipitation of saturated $\text{WO}_2^{2+}$ , (e) formation of closely packed flower-like structure (f) corresponding FESEM image of the closely packed flower-like structure.	68
Figure 4.17	FESEM top-view images of films anodized at 50 V for 1 h in (a) 0.5 M, (b) 1 M, (c) 3 M $\text{H}_2\text{SO}_4$ .	70
Figure 4.18	Current transients of the selected samples anodized in 1 M $\text{H}_2\text{SO}_4$ at different potentials for 4 h.	71
Figure 4.19	Selected FESEM top-view images of the samples anodized in 1 M $\text{H}_2\text{SO}_4$ for 4 h at (a) 5 V, (b) 40 V, (c) 60 V. The insets are the cross-sectional images of the respective films.	72
Figure 4.20	FESEM top-view images of samples anodized at 20 V in 1 M $\text{H}_2\text{SO}_4$ for (a) 4 h, (b) 8 h, (c) 23 h.	73
Figure 4.21	Current transients of the samples anodized in 1 M $\text{H}_2\text{SO}_4$ at 20 V for 4 h at different temperatures. The inset shows the local maximum of current density and shifting of the peak positions as a function of anodization temperature.	74
Figure 4.22	FESEM images of the samples anodized at 20 V for 4 h at (a) 40 °C, (b) 60 °C and (c) 80 °C.	75
Figure 4.23	XRD patterns of $\text{WO}_3$ films anodized at different temperatures in 1 M $\text{H}_2\text{SO}_4$ . Symbols ‘**’, ‘*’ and ‘ω’ refer to $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , $\text{WO}_3 \cdot \text{H}_2\text{O}$ and W peaks respectively.	75
Figure 4.24	Photoresponse measurement with 40 s light on/off interval time with 1 V applied potential in 0.1 M $\text{Na}_2\text{SO}_4$ for the samples annealed at different temperatures.	76
Figure 4.25	Photocurrent responses of the selected samples under AM 1.5 light source at (a) 1 V and (b) 0 V biased voltage in 0.1 M $\text{Na}_2\text{SO}_4$ . The switch on/off interval duration is 40s.	78
Figure 4.26	Photocurrent responses of the selected samples under AM 1.5 light source at 1 v biased voltage in 0.1 M $\text{Na}_2\text{SO}_4$ . The switch on/off period is 40s.	80
Figure 4.27	Linear sweep voltammograms of the selected samples. Oxalic, 25°C (400 °C) is the sample anodized at 25 °C and annealed at 400 °C. HCl, 40 °C (400 °C) and $\text{H}_2\text{SO}_4$ , 80 °C (400 °C) are the samples anodized at 40 and 80 °C respectively and annealed at 400 °C.	81

Figure 4.28	Efficiency of the selected samples. Oxalic, 25 °C (400 °C) is the sample anodized at 25 °C and annealed at 400 °C. HCl, 40 °C (400 °C) and H <sub>2</sub> SO <sub>4</sub> , 80 °C (400 °C) are the samples anodized at 40 and 80 °C respectively and annealed at 400 °C.	82
Figure 5.1	Images of the sample prepared with 120 ml acid during mixing of HNO <sub>3</sub> into Na <sub>2</sub> WO <sub>4</sub> where the sample changed gradually from (a) transparent, (b) yellowish transparent, to (c) milky yellow color.	84
Figure 5.2	Images of the samples prepared with normal flow rate (~2.3 ml/min) at different volumes of nitric acid (a) right after mixing process, (b) after 1-day ageing and (c) after 10-day ageing.	85
Figure 5.3	Sol-gel condensation polymerization reaction and cluster condensation. Source: Ref. [39].	87
Figure 5.4	Images of the samples prepared with different mixing rates (a) right after the experiment and (b) after 1 day.	89
Figure 5.5	FESEM plane view images for samples prepared with different volumes of nitric acid (40, 80, 120, 160 ml) after 1-day ageing.	91
Figure 5.6	(a) Lateral size distributions of the nanoplates over various acid volumes. (b) Plot of the mean size of nanoplates as a function of acid volume.	92
Figure 5.7	FESEM plane view images for samples prepared with different volumes of nitric acid ((a)40, (b)80, (c)120, (d)160 ml) after 10-day ageing.	93
Figure 5.8	(a) Lateral size distributions of the nanoplates over various acid volumes after 10-day ageing. (b) Plot of the mean size of nanoplate as a function of acid volume.	94
Figure 5.9	FESEM plane view images for the samples prepared with 120 ml acid using (a) slow, (b) normal and (c) fast mixing rate after 1-day ageing.	95
Figure 5.10	(a) Lateral size distributions of the nanoplates over different flow rates after 1-day ageing. (b) Plot of the mean size of nanoplate as a function of flow rate.	96
Figure 5.11	XRD patterns of (a) the as-grown samples prepared with different acid volumes. (b) Magnified patterns in the range of 22- 28°. Symbols ‘**’, ‘*’ and ‘ε’ represent WO <sub>3</sub> •2H <sub>2</sub> O, WO <sub>3</sub> •H <sub>2</sub> O and WO <sub>3</sub> respectively.	97

Figure 5.12	Raman spectra of the as-grown samples prepared with different acid volumes.	98
Figure 5.13	XRD patterns of the samples prepared with 40 ml acid for different ageing durations from 1 to 20 days. Symbols ‘**’, ‘*’ and ‘ε’ represent $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , $\text{WO}_3 \cdot \text{H}_2\text{O}$ and $\text{WO}_3$ respectively.	101
Figure 5.14	XRD patterns of the samples prepared with 40-160 ml acid after 10-day ageing. Symbols ‘**’, ‘*’ and ‘ε’ represent $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , $\text{WO}_3 \cdot \text{H}_2\text{O}$ and $\text{WO}_3$ respectively.	102
Figure 5.15	Raman spectra of the samples prepared with 40-160 ml acid after 10-day ageing.	102
Figure 5.16	XRD patterns of the samples prepared with different flow rates. (b) Magnified patterns in the range of $22^\circ$ - $28^\circ$ . Symbols ‘**’, ‘*’ and ‘ε’ represent $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , $\text{WO}_3 \cdot \text{H}_2\text{O}$ and $\text{WO}_3$ respectively.	103
Figure 5.17	Raman spectra of the samples prepared with different flow rates.	104
Figure 5.18	(a) Resistance and (b) sensitivity versus relative humidity for the samples prepared with different acid volumes after 1-day ageing.	106
Figure 5.19	(a) Resistance and (b) sensitivity versus relative humidity for the samples prepared with different acid volumes after 10-day ageing.	107
Figure 5.20	(a) Resistance and (b) sensitivity versus relative humidity for the samples prepared with different flow rates after 1-day ageing.	108

## LIST OF ABBREVIATIONS

CVD	Chemical vapour deposition
EC	Electrochromic
FTO	Fluorine doped tin oxide
GPTS	2-(2,3 epoxypropoxy)propyl-trimethoxysilane
HFCVD	Hot filament chemical vapour deposition
IDE	Interdigitated electrode
IPA	Isopropanol
IPCE	Incident photon to electron conversion efficiency
ITO	Indium tin oxide
IUPAC	International Union of Pure and Applied Chemistry
MPECVD	Microwave plasma-enhanced chemical vapour deposition
NPs	Nanoparticles
OLED	Organic light emitting diodes
PA	Polyacrylic acid
PAA	Porous anodic alumina
PCB	Printed circuit board
PEC	Photoelectrochemical

PET	Polyester
POA	Poly(o-anisidine)
PMAPTAC	Poly-[3-(methacrylamino)propyl]trimethyl ammonium chloride
PPy	Polypyrrole
PTA	Peroxopolytungstic acid
PTN	2,4-pentanedione
PVA	Poly(vinylalcohol)
RH	Relative humidity
RTP	Room temperature (~25°C)
SMOLED	Small molecule organic light emitting diodes
SMU	Source measure unit
TCTA	4,4',4''-tris(carbazol-9yl)-triphenylamine
TEG	Tetraethyleneglycol
TEOS	Tetraethoxysilane
TiO <sub>2</sub>	titanium dioxide
Vol.	Volume
WO <sub>3</sub>	Tungsten trioxide
WO <sub>≤3</sub>	Tungsten oxide
Wt.	Weight

# **PENGAJIAN TUNGSTEN OKSIDA DIMENSI RENDAH DENGAN KAEDAH PENGANODAN DAN SOL-GEL**

## **ABSTRAK**

Low dimensi tungsten oksida ( $WO_{\leq 3}$ ) dapat menarik perhatian penyelidikan sebab aplikasi ia sebagai peranti elektrokromik, sensor gas, peranti fotokatalis untuk pembahagian molekul air, sel solar secara pencilupan dan sensor kelembapan. Penggunaan tungsten oksida sebagai peranti permukaan-sensitif memerlukan fabrikasi tungsten oksida yang berkost efektif dan berkawalan morfologi. Kaedah penganodan dan sol-gel menawarkan cara-cara sintesis nanostruktur tungsten trioksida ( $WO_3$ ) yang mudah. Akan tetapi, pengajian tentang penggunaan kaedah penganodan dan sol-gel untuk mengfabrikasi nanostruktur  $WO_3$  adalah tidak mencukupi. Tesis ini mengkaji penggunaan kaedah penganodan dan sol-gel untuk pembentukan nanostruktur  $WO_3$ . Kesan-kesan parameter penganodan (elektrolit, voltan, tempoh, dan suhu) dan parameter sol-gel (isipadu asid, tempoh penuaan, dan kadar pencampuran asid) pada ciri-ciri  $WO_3$  disamping ciri-ciri sensor fotoelektrokimia dan kelembapannya juga diperiksa masing-masing. Penganodan dalam electrolit yang berbeza menghasilkan nanostruktur yang berbeza. Lapisan nanoliang ( $\sim 400$  nm) dapat dibentuk dalam asid oksalik sementara lapisan nanopiring ( $>1$   $\mu$ m) telah ditunjukkan oleh penganodan dalam HCl dan  $H_2SO_4$ . Daripada keputusan eksperimen, mekanisme penumbuhan nanoliang dan nanopiring telah dicadangkan. Pengukuran arus foto menunjukkan bahawa struktur nanoliang mempunyai keputusan pengukuran arus foto yang lebih baik berbanding dengan struktur nanopiring. Dalam penumbuhan  $WO_3$  dengan sol-gel teknik, nanopiring



dapat dibentuk. Penggunaan isipadu asid yang lebih tinggi, tempoh penuaan yang lebih pendek, dan kadar pencampuran asid yang lebih lambat didapati akan mengecilkan saiz nanopiring. Sampel yang ditumbuhkan dengan isipadu acid yang tinggi (>40 ml) menunjukkan struktur kristal tungsten trioksida terhidrat ( $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{WO}_3 \cdot \text{H}_2\text{O}$ ) dan  $\text{WO}_3$ . Sensor kelembapan jenis rintangan yang sangat sensitif dapat difabrikasikan dengan penyalutan sampel  $\text{WO}_3$  ke atas interdigital elektrod yang diperbuat sendiri. Kepekaan sensor kelembapan yang tinggi ( $\sim 190000$ ) telah diperolehi oleh sampel yang mempunyai dimensi nanopiring yang kecil, susunan krystal yang bagus dan permukaan kumpulan-oxo.

# STUDY OF LOW DIMENSIONAL TUNGSTEN OXIDE BY ANODIZATION AND SOL-GEL METHODS

## ABSTRACT

Low dimensional tungsten oxides ( $\text{WO}_3$ ) have attracted considerable research attention due to potential applications such as electrochromic devices, gas sensors, photocatalysts for water splitting, dye-sensitized solar cells and humidity sensors. The use of tungsten oxide for surface-sensitive device applications requires cost-effective fabrication of tungsten oxide with controllable morphological property. Both anodization and sol-gel methods offer facile ways to synthesize nanostructured tungsten trioxide ( $\text{WO}_3$ ). However, inadequate works have been done to employ anodization and sol-gel techniques for the fabrication of nanostructured  $\text{WO}_3$ . In this thesis, investigations of the use of anodization and sol-gel methods for the formation of nanostructured  $\text{WO}_3$  are presented. The effects of anodization parameters (electrolyte, voltage, duration, and temperature) and sol-gel parameters (acid volume, ageing duration, and mixing rate) on the properties of the  $\text{WO}_3$  as well as their photoelectrochemical and humidity sensing properties were also examined respectively. Anodization in different electrolytes resulted in different nanostructures. Nanoporous layer of  $\sim 400$  nm could be formed in oxalic acid while nanoplates layer of  $>1$   $\mu\text{m}$  were demonstrated by anodization in HCl and  $\text{H}_2\text{SO}_4$ . From our experimental results, growth mechanisms of nanopores and nanoplates were both proposed. Photocurrent measurements revealed that nanoporous structure had better photoelectrochemical response as compared to the nanoplate structure. For the fabrication of  $\text{WO}_3$  by sol-gel method, nanoplates could be formed. Higher

volume of acid, shorter ageing duration and slower mixing rate were found to decrease the size of nanoplates. As-grown sample in high acidic volume (>40 ml) could exist in crystalline structure of hydrated tungsten trioxide ( $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{WO}_3 \cdot \text{H}_2\text{O}$ ) and  $\text{WO}_3$ . Resistive type humidity sensors with high sensitivity were successfully fabricated by coating  $\text{WO}_3$  samples on the self-synthesized interdigitated electrode. High humidity sensitivity of  $\sim 190000$  was achieved by the sample with smaller nanoplates, good crystallinity and surface oxo-group.

## CHAPTER 1: INTRODUCTION

### 1.1 Introduction

This chapter gives a general overview of tungsten oxide by briefly introducing the potential applications of tungsten oxide as well as various fabrication methods. Fabrication techniques based on anodization and sol-gel methods will be discussed, followed by review of the fields and problem statements. In addition, the objectives and the novelties of the project are presented.

### 1.2 Why Tungsten Oxide

Tungsten oxide ( $\text{WO}_{\leq 3}$ ) is an n-type semiconductor with the indirect bandgap of (2.60 – 3.25 eV) [1, 2]. Apart from the stable and popular tungsten trioxide ( $\text{WO}_3$ ), tungsten oxides could exist as oxygen deficient oxides as  $\text{WO}_{2.92}$ ,  $\text{WO}_{2.9}$ ,  $\text{WO}_{2.83}$ ,  $\text{WO}_{2.77}$ ,  $\text{WO}_{2.72}$ ,  $\text{WO}_{2.67}$  and  $\text{WO}_{2.63}$  due to the non-stoichiometric property of  $\text{WO}_3$  [1]. It has been reported that tungsten oxide has high chemical stability at appropriate pH value, good electric conductivity ranging from 10 to  $10^{-4} \text{ Scm}^{-1}$  depending on the stoichiometry, modulated optical property where the physical color can change from yellow to dark blue with the presence of external stimuli (applied voltage and reducing gases) and charge-storage/delivery properties due to the valence change between  $\text{W}^{6+}$  and  $\text{W}^{5+}$  [1-4]. Owing to these properties, tungsten oxide has attracted considerable research attention particular for the green and renewable energy related applications (e.g. electrochromic window [5], dye-sensitized solar cell [6], photocatalyst for water splitting [7]) and other applicants (e.g. gas sensor [8] and humidity sensor [9]).

Since the invention of electrochromic device by Deb in 1969 [10], tungsten oxide has become one of the most promising materials for the study of electrochromic property which can change the transparency of windows by applying voltage [11]. Electrochromic windows could help save energy consumption in buildings by controlling the transparency of the windows. According to the research, > 1 % of the United States annual energy consumption, or more than \$10 billion energy waste could be saved by using electrochromic windows [12].

From the literature, Zheng and co-authors have demonstrated the fabrication of dye-sensitized solar cell based on  $\text{WO}_3$  [6]. At the forefront of research on photovoltaic devices, dye-sensitized solar cell has the advantage of low level requirement of material processing and the simplicity of cell assembly. Dye-sensitized solar cells based on titanium dioxide could achieve efficiency approaching 12 % [13]. Tungsten oxide, a more stable material in the exposure of strong acids and carrier mobility ( $10.2 - 2.8 \text{ cm}^2/\text{Vs}$ ) with the range of titanium dioxide, is believed to have potential to act as photoanode for electron transport material in dye sensitized solar cells with acceptable efficiency [6].

Yafeng et al. [14] and Berger et al. [15] have demonstrated the photoelectrochemical water splitting property of  $\text{WO}_3$  for hydrogen production. This application allows the conversion of solar energy directly to the hydrogen gas which could be used as renewable energy with zero pollution in the process of energy generation.

### 1.3 Fabrication methods of nanostructured tungsten oxide

Considering the applications of tungsten oxide, fabrications of low dimensional tungsten oxide have been attracting great scientific interests. Compared with their bulk tungsten oxide counterparts, nanostructured tungsten oxide has high surface aspect ratio which could significantly enhance their sensitivity. For example, with the estimated porosity of 65 %, Berger et al. demonstrated that four-fold increase of the photocurrent was achieved by the nanoporous film compared to the thick film [15]. Besides, nanomaterials could have different physical, chemical and electronic properties from the thick film due to quantum confinement effect. For instance, increase of the band gap energy was detected with the reduction of the grain size [16]. Owing to these advantages, various techniques used for the fabrication of nanostructured tungsten oxide have been developed to improve the performance of their applications. Appendix A shows the table of the various techniques used for fabrication of nanostructured tungsten oxides.

Nguyen et al. fabricated tungsten oxides nanowires with the length of a few micrometers and diameters of 90-1000 nm using thermal evaporation technique where the pressure and temperature were controlled at  $10^{-2}$  -10 Torr and 950 - 1050 °C [17]. The improvement of NO<sub>2</sub> gas sensing performance was demonstrated and they pointed out that this could be due to the formation of nanowires structure. Zhang et al. grew platinum-activated tungsten oxides with the grain sizes of ~30 nm using radio frequency sputtering in 0.2 Pascal [18]. Their results showed high gas sensor response of 4 s in 200 ppm H<sub>2</sub> at 220 °C. Tesfamichael et al. synthesized tungsten oxide nanoparticles with the diameters of 2.6 -12 nm using electron beam evaporation technique operating at 4 kV in the pressure of  $10^{-5}$  - $10^{-4}$  Pa and tested for

the gas sensing response [19]. They attributed the high sensitivity (450) of the gas sensor in 5 ppm NO<sub>2</sub> to the small grain sizes and high porosity of the film.

These fabrication methods of low-dimensional tungsten oxides require sophisticated machines like sputtering machine, electron gun, and thermal evaporation system with the vacuum system and often operating at high temperature condition which will increase the production cost for the device applications. Electrochromic device has been synthesized using sputtering machine and commercialized for the automobile window, however, it can't be utilized for the window of the building because of the the limitation of the sputtering system to fabricate the film in large size. As a result of these, attempts to fabricate nanostructured tungsten oxide have been made by other methods, such as sol-gel and anodization which are able to grow nanostructure in large scale and size with only simple experiment tools and setups such as chemical, electrolyte, power supply and glassware. This motivates our present work to synthesize nanostructured tungsten oxide by anodization and sol-gel techniques.

### **1.3.1 Anodization**

Anodization is a very simple and cheap process employed in fabricating nanostructure which requires only electrochemical cell consisting of power supply, electrolyte, target sample as anode and cathode. When the power is turned on in the electrochemical cell, oxygen ions from the electrolyte will react with anode to form metal oxide while hydrogen ions will receive the electrons from the inert cathode to form hydrogen gas. Anodization process has been first employed as a method to grow thick protective oxide layer on the metal to prevent it from corrosion. It was then used as a process to grow nanostructure for porous anodic alumina by using

suitable parameters [20]. After research for 5 decades, anodic growth of alumina could achieve tunable size (pore diameter: 25 -420 nm; cell size: 25 -42 nm; thickness of the porous layer: 350 nm -80  $\mu$ m) and shape (close-packed array of hexagonal cells with a cylindrical central) [21-25]. Owing to the abundance of alumina and well control of the porous structure, anodic growth alumina has been widely used as a template to assist the growth of nanostructure of other materials [26, 27].

Following the successful to grow porous alumina, huge efforts have been exerted to study fabrication of nanostructure by anodization method on other valve metals, especially on titanium [28-31]. Grimes et al. synthesized titanium dioxide nanotube using hydrofluoric acid [32]. However, they failed to control the size of nanotubes where only tube lengths of  $\sim$ 250 nm were achieved which were too short for applications as the photoelectrochemical device and dyed-sensitized cell. After enormous efforts were devoted, significant improvements have been made. By using different electrolytes such as mixing of fluoride based electrolytes with buffer electrolytes (sodium fluoride), polar organic electrolytes (ethylene glycol) or using non-fluoride based electrolytes (hydrochloric acid, hydrogen peroxide and perchloric acid) to control the pH, water content of the solution and concentration of the acid, precisely controllable and self-ordered nanoscale could be achieved [33-36]. Anodization has a huge advantage for the fabrication of nanostructure where desired dimension of nanotubes of titanium dioxide or nanopores of alumina could be obtained by tuning the anodization parameters (e.g. applied source, type of electrolyte, electrolyte concentration/temperature, and duration). Great achievements to form self-ordered nanostructure on alumina and titanium dioxide have given



researcher confidence and driven them to explore the formation of nanostructured  $\text{WO}_3$  using anodization method.

### **1.3.2 Sol gel**

Sol-gel process is a wet chemical method for the fabrication of solid inorganic polymers/ceramic (silicon oxide[37], titanium oxide[38], tungsten oxide[39] and etc[40, 41]) from the transformation of liquid precursors to a sol and gel through hydrolysis and condensation processes. Sol-gel method requires only chemicals reactants and glass wares which are free of any sophisticated and high cost machine. This offers a low cost and simple technique to produce ceramic and complex inorganic materials at low temperatures while the conventional way to produce ceramic requires high temperature condition at their melting point.

Sol-gel method was first introduced in 1845 for the synthesis of hydrous silica which could be used to produce fibers and optical lenses [42]. In spite of early discovery, sol-gel chemistry only attracted interest in 20 century because of the deficiency of the sol-gel technology at that moment where long drying period of 1 year was required to avoid fracture of silica gels [43, 44]. As time goes by, knowledge and technologies on the sol-gel science were gained and improved gradually where ultralight aerogels had been invented in 1932 [45] while homogeneous powders of aluminum oxide, silicon oxide, titanium oxide, zirconium oxide were successfully prepared in 1950 [44]. It was until 1960, sol-gel science has attracted great interest of studies [44, 46, 47]. With the ability to control the size and morphology, sol-gel technology was extended into many other materials like oxide, hydroxides, sulfides to prepare glass, ceramic fibers, ITO coating and etc [48-52]. Owing to the nature of sol-gel technique where sols are made from the

interconnected small molecules starting from precursors, the homogeneity of the solution could be achieved at molecular level. In addition, the purity and properties (crystal phase and refractive index) can also be controlled by choosing refined precursors and types of ligands of the precursors [53].

#### **1.4 Current research and problem statements**

Fabrication by anodization and sol-gel methods are both facile and inexpensive techniques to fabricate nanostructured  $\text{WO}_3$ . As the material properties are dependent on the synthesis condition, as-grown  $\text{WO}_3$  samples with these different techniques have different properties and particular interest of applications.

Development of the formation of  $\text{WO}_3$  by anodization method is shown in Appendix B. Fabricating on the conductive tungsten metal contact, anodic growth of  $\text{WO}_3$  is widely studied for their application as photoelectrochemical response [14, 15, 54] but not for gas sensing and electrochromic applications which require non-conductive or transparent substrate. As the photoelectrochemical device requires illumination of sun light on the film to function, control of the morphological property of the sample plays a crucial role. Majority of the anodic growth of  $\text{WO}_3$  films used fluoride based electrolytes and result in thin porous layer ( $< 500$  nm) [14, 15, 28, 55, 56]. To improve the performance of the device application, control of the thickness of the nanostructured layer is essential. As shown by Shankar et al., increase of the thickness of nanotube array of titanium dioxide from  $8.2 \mu\text{m}$  to  $14.4 \mu\text{m}$  increase the photoconversion efficiency from 9.88 to 14.42% [57]. However, further increase the length of the nanotubes will decrease the photoconversion efficiency due to the recombination of the photogenerated charges. In the attempt to increase the thickness of nanostructured layer of  $\text{WO}_3$ , Watcharenwong et al.

employed viscous solutions as electrolyte in the anodization [54]. While this method was found to be workable for the anodization of titanium to control the thickness and length of the tubes, they reported no significant improvement of the thickness in the case of  $\text{WO}_3$ .

Yang et al. successfully synthesized  $\text{WO}_3$  with the nanostructured layer thickness of  $\sim 2 \mu\text{m}$  by anodization [58]. However, concentrated hydrofluoric acid (40%) and phosphoric acid (85%) were utilized in order to form the thick nanostructured layer. Lee et al. fabricated nanoporous  $\text{WO}_3$  with the thickness of the porous layer up to  $9 \mu\text{m}$  using potassium hydrogen phosphate in glycerol at  $80 - 100 \text{ }^\circ\text{C}$  [59]. Although they successfully grew thick porous layer, they still failed to control the size of the pores and erosion of the wall of the pores. No notable improvement of the morphological properties of the anodic growth of  $\text{WO}_3$  was reported in recent year. We suggest that this is due to the inadequate understanding of the mechanism of the anodic growth of  $\text{WO}_3$ . Further work is necessary to control the morphological property of the nanostructured  $\text{WO}_3$  for device applications. Exploration on the formation of nanostructured  $\text{WO}_3$  using non-fluoride based electrolyte could be beneficial to control the morphological property of the  $\text{WO}_3$  as the formation of nanostructures utilizing fluoride based electrolytes have yet to achieve the goal while attempts to use non-fluoride based electrolytes for the formation of self-ordered titanium dioxide nanotubes have been proven to be successful.

Fabrication of  $\text{WO}_3$  by sol-gel method on the other hand, often studies for their electrochromic properties [60-64]. (Appendix C shows the development of the growth of  $\text{WO}_3$  by sol-gel method.) For example, Soliman et al. improved the electrochromic properties by obtaining a stable solution with the addition of oxalic acid,  $\text{H}_2\text{O}_2$  [65] or using different precursors ( $\text{WOCl}_4$ ) [61]. In addition, lithium

based compound was added to improve the bleaching process while polystyrene microspheres template was used to produce high density pores [66]. Apart from that, gold particle was incorporated to improve faster diffusion and charge transfer rates [64].

The study of the formation of nanostructure  $\text{WO}_3$  using sol-gel method or exploration of the sol-gel synthesized  $\text{WO}_3$  for the other applications such as photoelectrochemical (PEC) water splitting device [67], gas sensor [68], gasochromic device [69], OLED [70] and humidity sensor [71] has not been emphasized. In the research on the formation of nanostructure by sol-gel method, effects of different acids, pHs, mixing rates on the spin coater, and humidity of the drying environments on the morphological properties of the  $\text{WO}_3$  have been studied and examined for their  $\text{NO}_2$  gas sensing properties [39, 68]. However, the research on the formation of nanostructured  $\text{WO}_3$  from sol-gel method is still inadequate where the detail study of the effects of the sol-gel parameters such as type of the precursor, concentration of the precursor, mixing rate, ageing duration, additive and temperature of synthesis on the formation of nanostructure are remain unclear. To the best of our knowledge, only Dai et al. utilized sol-gel-made  $\text{WO}_3$  to synthesize humidity sensor [71]. However, their research focused on the architecture of the humidity sensor which was integrated with micro-heater and inverting amplifier circuit on chip manufactured using complementary metal oxide semiconductor and micro-electromechanical systems (CMOS-MEM) while no study was made on the effect of the nanostructure on the sensing properties. Sundaram et al. and Patil et al. fabricated humidity sensor based on  $\text{WO}_3$  but their research focused on the compositions of lead, zinc or poly(*o*-anisidine) to the purchased  $\text{WO}_3$  to improve the

sensitivity of the sensor [72, 73]. None of them has investigated the effect of the properties of the nanostructured  $\text{WO}_3$  on the humidity sensor.

### **1.5 Research Objectives**

1. To study the effect of anodization parameters using non-fluoride based electrolytes on the morphological property of  $\text{WO}_3$  and their photoelectrochemical property.
2. To investigate and examine the effect of sol-gel parameters on the growth of low-dimensional  $\text{WO}_3$ .
3. To explore and develop the application of sol-gel fabricated  $\text{WO}_3$  as humidity sensor.

### **1.6 Research Novelties**

1. Fabrication of thick nanoplate structure by anodization method using  $\text{H}_2\text{SO}_4$  and HCl.
2. Proposed growth mechanisms of the  $\text{WO}_3$  nanopores and nanoplates formed by anodization method.
3. Dimensionality control of nanostructured  $\text{WO}_3$  by tuning sol-gel parameters.
4. Development of extremely high sensitivity humidity sensor based on pristine  $\text{WO}_3$  grown by sol-gel method.

### **1.7 Outline of Thesis**

Chapter 1 shows applications of tungsten oxide, fabrication methods of nanostructured tungsten oxide including anodization and sol-gel methods, review of

the fields, problem statements, research objectives and the novelties of the research works.

Chapter 2 describes the fundamental properties of tungsten oxide, the theories of the growth of tungsten oxide by anodization and sol-gel methods. In addition, theories and overview of their applications as photoelectrochemical cell and humidity sensor are also presented.

Chapter 3 presents the experimental procedure to grow  $\text{WO}_3$  by both anodization and sol-gel methods. Experimental procedures to fabricate photocatalytic water splitting device and humidity sensor are also described.

Chapter 4 discusses the fabrication and characterization of the  $\text{WO}_3$  samples grown by anodization method. Their photocatalytic properties are also examined.

Chapter 5 covers the results and discussion of the sol-gel-made  $\text{WO}_3$  and their humidity sensing property.

Finally, chapter 6 provides a summary of the current research and suggestion for future research.

## CHAPTER 2: LITERATURE REVIEW AND RESEARCH BACKGROUND

### 2.1 Introduction

This chapter provides information of the fundamental properties of tungsten oxide. Literature reviews and theories of the fabrication of tungsten oxide by anodization and sol-gel techniques are discussed. Apart from these, theories and background of the applications of tungsten oxide as photoelectrochemical water splitting and humidity sensor are also presented.

### 2.2 Fundamental properties of tungsten oxide

Tungsten oxide is an n-type semiconductor which has a 2.60- 3.25 eV indirect bandgap [1, 2] and  $10$  to  $10^{-4}$   $\text{Scm}^{-1}$  electrical conductivity where their bandgap and electrical conductivity could be largely varied by crystallinity, grain size, grain boundary, stoichiometry/oxygen vacancy and film thickness [1, 2, 74-80]. For example, the large bandgap of 3.25 eV reported for the  $\text{WO}_3$  in the amorphous stage with large grain size can be reduced to 2.62 eV in the crystalline structure [81]. Besides the bandgap of  $\text{WO}_3$  can also be decreased with an increase of oxygen vacancy [1] or a decrease in grain size [79]. On the other hand, electron mobility of  $\text{WO}_3$  was reported to be  $6.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  [77], which has significantly improved to  $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for the case of  $\text{W}_{18}\text{O}_{49}$  with the oxygen vacancies acting as the donors [80].

$\text{WO}_3$  is formed by corner-sharing of  $\text{WO}_6$  octahedra which could be arranged in the crystalline form with different tilting angles and rotation order as triclinic, monoclinic, orthorhombic, tetragonal, cubic and hexagonal phase, as shown in figure 2.1 [82]. Each of these phases is stable at the specific temperatures as shown in figure 2.1 which are partially reversible [83]. It should be noted that the change of

the phase does not suddenly happen at the distinct temperature [84] and the stability of the phase in the temperature as shown in figure 2.1 is reported for bulk  $\text{WO}_3$ , which could be varied for low dimensional  $\text{WO}_3$  and fabrication techniques [85].

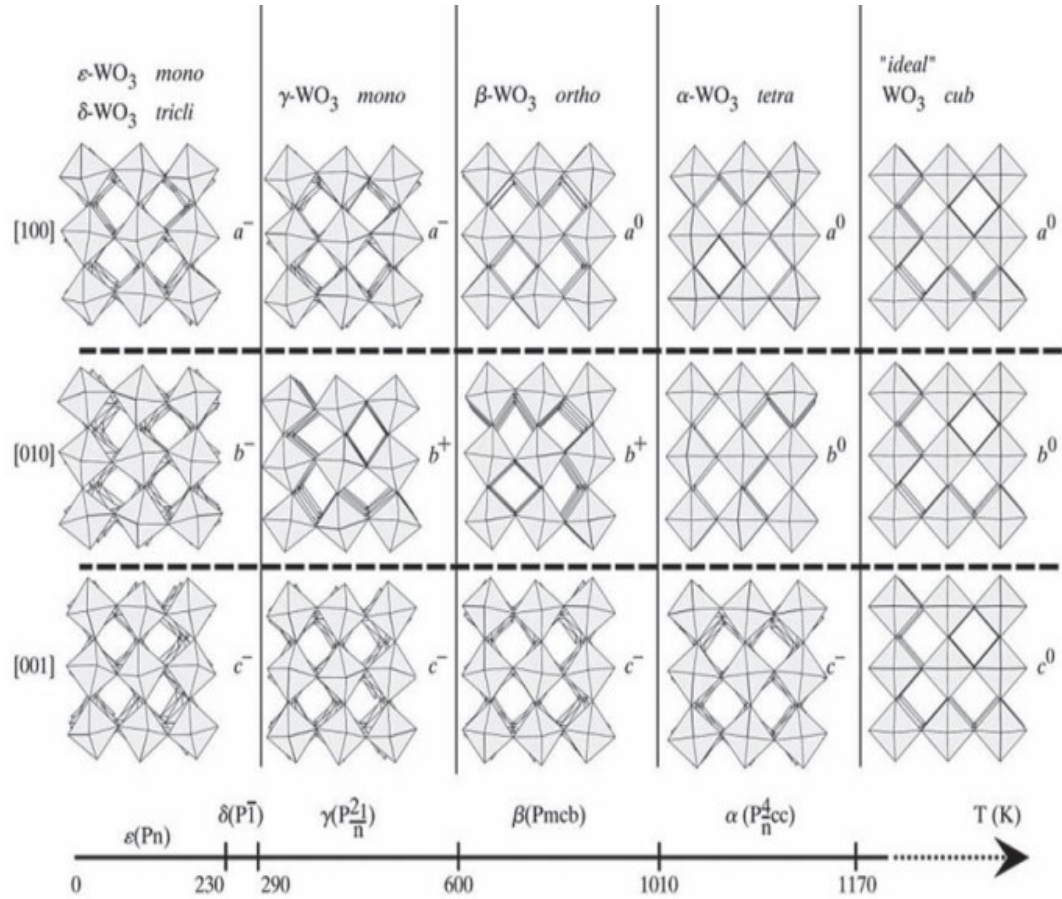


Figure 2.1 Stability of polymorphs of  $\text{WO}_3$  at different temperatures. Source: Ref. [82].

Fabrications of tungsten oxides could result in  $\text{WO}_3$ ,  $\text{WO}_{x<3}$  ( $x = 2.92, 2.9, 2.83, 2.77, 2.72, 2.67$  and  $2.63$ ) with oxygen vacancies and  $\text{WO}_3 \cdot x\text{H}_2\text{O}$  (i.e.  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{WO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$ ) [1].  $\text{WO}_{x<3}$  are usually obtained by fabrication using thermal evaporation techniques or annealing of any form of tungsten oxide in oxygen deficient environment at high temperature [17, 86] while annealing in oxygen environment would result in  $\text{WO}_3$  [87]. The presence of  $\text{WO}_x$  with oxygen vacancies could be attributed to the removal of oxygen from  $\text{WO}_3$  by transforming the corner-



sharing  $\text{WO}_6$  (figure 2.2(a)) to both corner- and edge-sharing structure (figure 2.2(b)), according to crystal-shear mechanism [88, 89]. These  $\text{WO}_x$  with the oxygen vacancies as a shallow donor have different properties as compared to  $\text{WO}_3$  as discussed earlier.

$\text{WO}_3 \cdot x\text{H}_2\text{O}$  or hydrated tungsten oxides are usually formed by liquid related synthesis method (hydrothermal, sol-gel) which could transform to  $\text{WO}_3$  by annealing [39, 90].  $\text{WO}_3 \cdot \text{H}_2\text{O}$  could be formed by substitution of one oxygen from the  $\text{WO}_6$  octahedra by  $\text{H}_2\text{O}$  or by intercalation of  $\text{H}_2\text{O}$  between the sheets of the layered structure and not bonded to  $\text{W}^{6+}$  [91].  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  consists layers of octahedra similar to  $\text{WO}_3 \cdot \text{H}_2\text{O}$ . The intercalation of the second water molecule between the layers was found to increase the layer distance by  $\sim 23\%$  [92].  $\text{WO}_3 \cdot 0.33\text{H}_2\text{O}$  is formed by stacking layers of  $\text{WO}_6$  octahedra where part of the oxygen atoms from  $\text{WO}_6$  are replaced by  $\text{W}=\text{O}$  and  $\text{W}-(\text{OH})_2$  bonding [93].  $\text{WO}_3 \cdot x\text{H}_2\text{O}$  could be found in both amorphous and crystal phases [39].

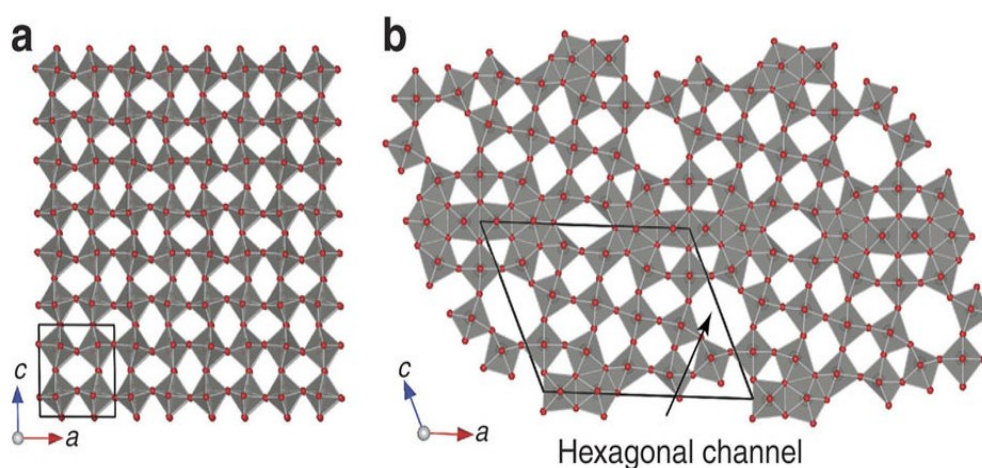


Figure 2.2 (a) Crystalline  $\text{WO}_3$  structure with corner-sharing  $\text{WO}_6$  octahedra layers. (b)  $\text{W}_{18}\text{O}_{49}$  structure with both corner- and edge-sharing  $\text{WO}_6$  octahedra layers. Source: Ref. [89].

### 2.3 Anodic growth mechanism of nanostructured WO<sub>3</sub>

Formation of nanostructure through anodization method was first started on porous alumina and then applied to other valve metals such as titanium. After the research groups working on anodization of titanium have successfully grown titanium dioxide nanotubes, they applied this anodization technology on tungsten to form nanostructured tungsten oxide. The presence anodization technology for the formation of nanostructured WO<sub>3</sub> is still in the process of development and yet to be well documented. However, well studied anodization processes of WO<sub>3</sub> in different pHs were provided by Johnson et al. [45] and Anik et al.[94]. In this section, mechanism of the formation of nanostructured WO<sub>3</sub> are proposed by combining the general information of the formations of nanostructures by anodization from other valve metals (Al, Ti) and chemical dissolution mechanisms of WO<sub>3</sub> in the anodization process.

Generally, nanostructure formation from the anodization technique is usually driven by 3 processes: electrochemical oxidation, electrochemical dissolution and chemical dissolution [32]. When the power supply is turned on, both electrochemical oxidation (equation 2.1 and 2.2) and dissolution processes (equation 2.3) begin simultaneously in acidic condition [45, 95].



The strength of the electrochemical dissolution is affected by both the applied potential and the oxide barrier layer. Considering this, etching rate at the thin oxide

layer of the pit/holes is much higher than the the bulk oxide surface, resulting of the growth of the thickness of the porous layer [32]. The initial formation of small pits could be explained by the localized dissolution of the oxide layer [96].

After the formation of oxide layer, chemical dissolution also takes part to etch away the oxide layer other than electrochemical dissolution [97]. Unlike anodization of other metals (Al, Ti), chemical dissolution process of  $WO_3$  is very complex due to the stoichiometry of  $WO_3$  and various tungstate ions [94]. Chemical dissolution of  $WO_3$  could be classified in three catagories:  $H^+$  assisted, water molecules assisted and  $OH^-$  assisted chemical dissolution [94]. While all three types of chemical dissolutions could happen simultaneously, each of the processes is dominant in a specific pH value. Under high acidic condition,  $H^+$  assisted chemical dissolution as shown in equation 2.4 is dominant while in less acidic condition, water molecules assisted dissolution is the main process as shown in equation 2.5 [94]. On the other hand, under high pH condition,  $OH^-$  assisted chemical process as shown in equation 2.6 is more dominant [94].



It is believed that the complicated chemical dissolution of  $WO_3$  is the reason of the poor control of the morphology of anodic growth  $WO_3$ . In order to control the morphology of nanostructure, the electrochemical oxidation and dissolution as well as the chemical dissolution have to be well controlled. In the case of porous anodic growth alumina, electrochemical dissolution is dominant compared to chemical

dissolution where the effect of chemical dissolution could be ignored [32]. Rate of the field assisted dissolution at the pits is much higher than the bulk oxide layer due to the high field effect at thin oxide layer of the pit [98, 99]. This results in the continuous growth of the pit/pores, leading to the self-organized PAA with controllable thickness by tuning the potential, as shown in figure 2.3 [99].

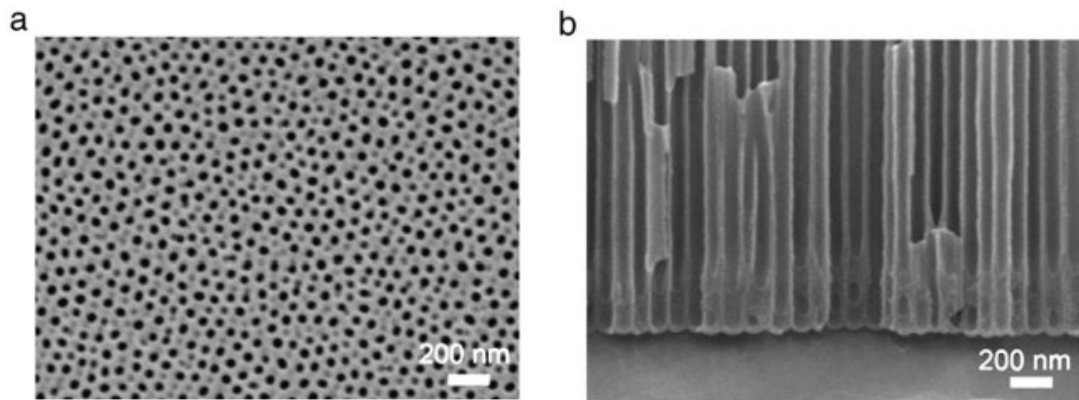


Figure 2.3 (a) Plane view and (b) cross section view of SEM images of anodic growth alumina in 0.5 M oxalic acid at 15 °C for 1h. Source: Ref. [99].

In the case of the anodic growth titanium dioxide nanotubes, the rate of chemical dissolution is comparable or even higher than the rate of electrochemical dissolution where chemical dissolution etches both the porous oxide layer and oxide barrier on the the film surface, hindering the growth of the porous layer thickness [97]. To control the chemical dissolution, high viscosity electrolytes like ethylene glycol and glycerol are employed to restrict the chemical dissolution at the oxide barrier on the film surface while allows the chemical dissolution at the pores, resulting in the self-organized nanotubes, as shown in figure 2.4 [100]. Considering the formation of thin porous layer (figure 2.5(b)) and the uncontrolled etching of the porous wall (figure 2.5, figure 2.6), it is believe that anodic growth  $\text{WO}_3$  has higher chemical dissolution rate than the electrochemical dissolution rate [15, 58].

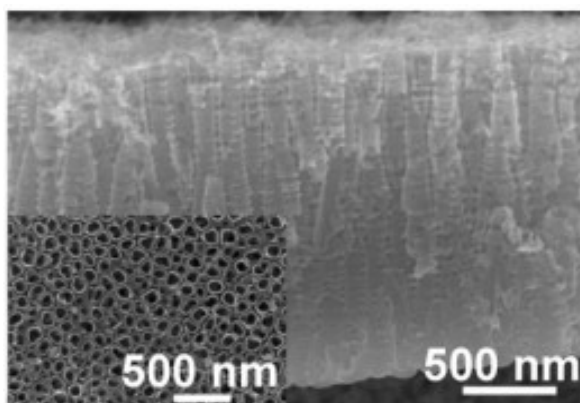


Figure 2.4 Cross sectional view of SEM image of titanium oxide nanotubes formed in mixture of glycerol and water (50:50 vol. %) + 0.5 wt. %  $\text{NH}_4\text{F}$ . Inset shows the corresponding plane view image. Source: Ref. [100].

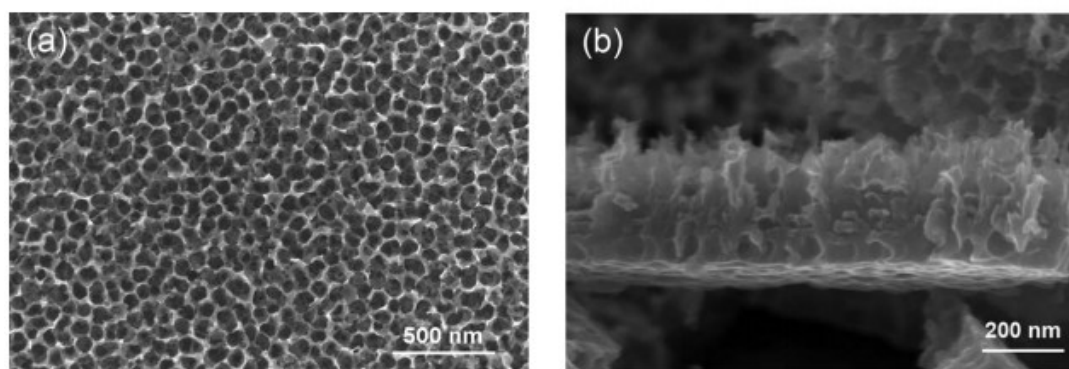


Figure 2.5 (a) Plane view and (b) cross sectional view SEM images of  $\text{WO}_3$  grown in 0.5 wt %  $\text{NaF}$  + 1 M  $\text{H}_2\text{SO}_4$ . Source: Ref.[15].

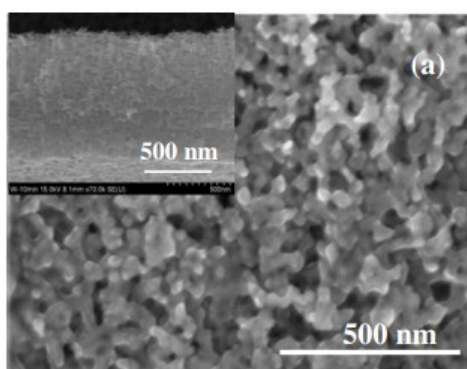


Figure 2.6 SEM image of  $\text{WO}_3$  formed in  $\text{H}_3\text{PO}_4$  + 8 M  $\text{HF}$ . Inset depicts the cross sectional image of the corresponding image. Source: Ref. [58].

Apart than the porous structure, platelet structure could also be attained due to the precipitation of the soluble tungstate charge ( $\text{WO}_2^{2+}$ ). As described by Ng et al., with

the assistance of electric field and presence of water molecules, the saturated  $WO_2^{2+}$  in the suitable pH could precipitate on the W surface as shown in equation 2.7, 2.8 and 2.9 [95]. Formation of nanoplates by precipitation is also demonstrated by Widenkvist et al., in the chemical bath method [101].



## 2.4 Fabrication of $WO_3$ by sol-gel method

### 2.4.1 Type of precursors

Sol-gel-made  $WO_3$  can be formed by five different types of precursors which are: 1) colloidal tungstic solutions ( $Na_2WO_4$ ) [60, 102], 2) Peroxotungstic acid (PPTA/PTA) [103, 104], 3) tungsten hexachlorides ( $WCl_6$ ) [53], 4) tungsten oxychloride ( $WOCl_4$ ) [61], and 5) tungsten alkoxides [70].

Colloidal tungstic solution is usually formed by acidification of  $Na_2WO_4$  (mixing with acid or passing through ion exchange resin). This precursor was firstly used in 1983 by Chemseddin to test for electrochromic property [60]. It is the most frequently used precursors to synthesize  $WO_3$  by sol-gel method, however, formation of sol-gel using  $Na_2WO_4$  precursor is not stable [102]. Unstable sol will transform to gel and precipitate very fast which is not suitable for electrochromic device [102]. To overcome this, stabilizing agents like oxalic acid,  $H_2O_2$ , acetic acid and alcohol are added into the solution [65, 102]. Owing to this deficiency, this precursor is replaced by  $WCl_6$  and PPTA. Both  $WCl_6$  and PPTA are inexpensive starting materials (PPTA could be formed by mixing of W powder with  $H_2O_2$ ) which could form stable sol-gel

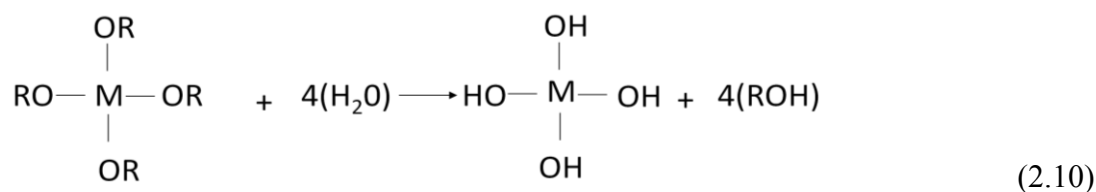
compared to  $\text{Na}_2\text{WO}_4$  precursor. Fabrication of  $\text{WO}_3$  from  $\text{WOCl}_4$  is stable and shows good electrochromic properties [61]. However, it requires dry atmosphere and suffers from long term stability problem. Among all the precursors, tungsten alkoxide is the least studied precursor due to the high material cost and fast reaction with moisture [103].

### 2.4.2 Sol-gel process

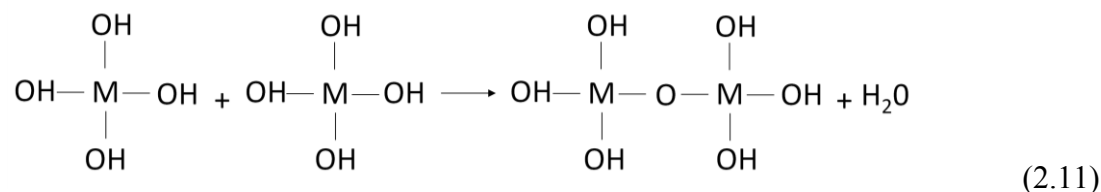
There are 5 sol-gel processes, which are: 1) Mixing of precursors and formation of sol; 2) gelation; 3) ageing; 4) drying/syneresis; 5) dehydration and densification [44, 105]. The product of the sol-gel is highly dependent on the sol-gel process parameters, for example: selection of the type of precursors, ligands of the precursors, types of additive used, duration and condition of ageing and heat treatment temperature [44].

#### 1) Mixing of precursors and formation of sol:

In sol-gel chemistry, precursor is the starting compound which comprises of two components (metal or metalloid bonds with number of ligands). At the first step, precursor is mixed with water at certain pH. This step leads to hydrolysis and condensation of the precursor, resulting in the formation of sol. Hydrolysis is a reaction involving the breaking of a bond in a molecule using water. For an example, hydrolysis of metal alkoxides is shown in equation 2.10 [105]:



where M and R could be any metal/metalloid and ligand respectively. Hydrolyzed molecules can connect to each other in condensation reaction to liberate small molecules, as shown in equation 2.11 [105]:



Through continuous hydrolysis and polycondensation reactions, M-O-M bonds interconnect with each other forming larger particles. As the particles size reach submicrometer size, sol is formed. According to IUPAC, sol is a colloidal suspension (solid particles with diameters of 1-1000 nm) in a liquid. Considering the small size of the sol, gravitational forces are negligible and the sols could move randomly in the solution according to Brownian motion.

## 2) Gelation:

Gel is a single giant cluster network which is formed from further condensation of several sols or polymers [105]. No change of bonding and latent heat is involved in gelation process. However, formation of gel could be easily recognized as the viscosity of the gel increase significantly from sol due to the large cluster network of gel, as shown in Appendix D. The structure of gel is determined by the hydrolysis and condensation processes [106].

## 3) Ageing:

Ageing allows the gel or the sample immerses in liquid for a time span, allowing further polycondensation and precipitation of the gel network which increases the thickness of interparticle necks and decreases the porosity [105].



#### **4) Drying/Syneresis**

Drying process expel the liquid from the gel/ precipitate. Drying process has to be controlled to prevent cracking due to the capillary stress[105].

#### **5) Dehydration and densification**

Dehydration process removes the hydroxyl bonds from the pore network by heat treatment [105].

### **2.5 Photoelectrochemical water splitting**

Water splitting is the process to split water molecule to obtain both hydrogen and oxygen gases. It is currently received tremendous research focus because hydrogen is considered as unlimited source from water or renewable energy, which can replace our current fossil fuel to provide zero pollution fuel with high thermodynamic conversion efficiency. This solves the two of the main problems of our curent living issues: pollution and depletion of the fossil fuel.

Currently, hydrogen energy is mostly provided by coal gasification and biomass materials [107]. However, both of these methods produce byproducts of pollutant gases ( $\text{CO}_2$ ,  $\text{CH}_4$ ) [107] which is not desirable. Therefore, there is an urgent need to develop photoelectrochemical water splitting which is still in the research stage. Photoelectrochemical water splitting was first reported by Fujishima and Honda in 1972, which employs solar energy to split the water molecules in order to obtain hydrogen gas [108].

### 2.5.1 Principle and efficiency of photo-electrode water splitting

Figure 2.7 shows the experimental setup of the photoelectrochemical water splitting system based on n-type semiconductor photoelectrode [109]. The mechanisms of the photoelectrochemical water splitting process are also illustrated in the figure 2.7. There are three main steps for the photo-electrode water splitting to occur in photoelectrochemical cell (PEC) [109, 110]:

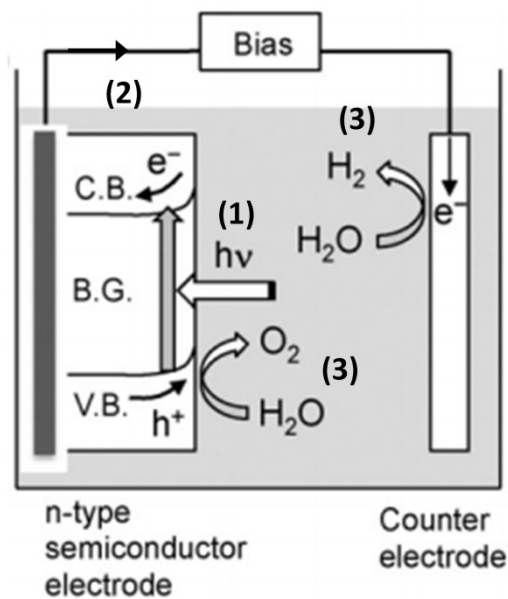
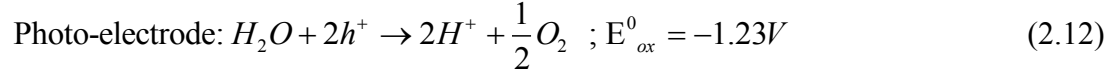


Figure 2.7 Photoelectrochemical water splitting systems using n-type semiconductor photoanode. C.B., B.G. and V.B. represent of the conductor band, band gap and valence band respectively. Source: Ref. [109].

- 1<sup>st</sup>: generation of electron hole pair after absorption of photons by photo-electrode.
- 2<sup>nd</sup>: transportation of these photo-generated carriers to the interface of photo-electrode/electrolyte and counter electrode/electrolyte interface

3<sup>rd</sup>: Catalytic reaction with water molecules where holes ( $h^+$ ) oxidize water to form  $O_2$  at photo-electrode (equation 2.12) while electrons reduce  $H^+$  to generate  $H_2$  at Pt cathode (equation 2.13).



The performance of the water photoelectrolysis cell can be determined by the photoconversion efficiency ( $n$ ) which is the efficiency to convert light energy to chemical energy with the applied potential. The photoconversion efficiency is defined as [111, 112]:

$$n = \frac{J_{photo} (1.23 - V_{bias})}{P_{light}} \times 100\% \quad (2.14)$$

where  $J_{photo}$ ,  $V_{bias}$ , and  $P_{light}$  represent photocurrent density, applied potential and intensity of the light respectively.

Apart from photoconversion efficiency, the performance of the photoelectrolysis cell could also be evaluated by photon to current conversion efficiency (IPCE) which measures the efficiency to convert photon's incident on the cell to photocurrent flowing between the working and counter electrodes. The IPCE is defined as [113]:

$$IPCE = \frac{I_{ph}(\lambda)}{qP(\lambda)} \times 100\% \quad (2.15)$$

where  $I_{ph}(\lambda)$  is the photocurrent density at wavelength  $\lambda$ ;  $q$  is the electronic charge;  $P(\lambda)$  is the incident photon flux density of certain wavelength at the photoelectrode.