

奈米晶寬能隙半導體薄膜製備與應用

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摘要

本研究係以溶膠-凝膠(sol-gel)法，製備透明導電的AZO薄膜。首先將氯化鋁添加於醋酸鋅水溶液中，經旋轉塗佈 (spin-on-deposition)於玻璃基板上。其中調控Al之濃度、熱處理、二次熱處理添加還原氣體，依此，分析AZO薄膜之結構、電性及其光學特性。本研究經SEM分析發現AZO薄膜之晶粒小於10nm，係屬同質性，緻密細微構造。又摻雜濃度之調控可提升光學特性及電性，常壓下熱處理、二次熱處理添加還原氣體，促使薄膜有良好結晶性。本研究最理想的摻雜濃度為 Al/Zn=2.25 at.%，最小電阻率為 9.90×10^{-3} 歐姆-cm， n 濃度和遷移率分別是 $1.25 \times 10^{20} \text{cm}^{-3}$ and $5.04 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ ，可見光區之透光率可達90%以上。接下來本研究分別以紫外光和可見光照射於塗有二氧化鈦光觸媒之管狀反應裝置中，分析光催化分解低濃度甲苯之特性。本研究所使用之二氧化鈦光觸媒有，SG-TiO₂和P25-TiO₂二種型式。全部的光觸媒以浸鍍法塗佈在玻璃管內部表面，接下來作熱處理。另使用二氧化鈦及TCPP分別調製出TCPP/SG-TiO₂與TCPP/P25-TiO₂之二氧化鈦光觸媒，使其具光敏性，再以可見光方式進行照射。進行4種光觸媒對於低濃度甲苯進行光催化分解分析。經紫外光方式進行照射之兩種TiO₂光觸媒薄膜皆能有效分解低濃度甲苯[To]，然而當甲苯濃度分別從原始狀態增加至6.5 ppm及4.0ppm時，SG-TiO₂及P25-TiO₂光觸媒對甲苯分解力明顯下降。甲苯EC圖顯示SG-TiO₂及P25-TiO₂之EC分別為4.9和2.7 mg hr⁻¹ m⁻²。在相同的條件比較下可見光及紫外光對染料敏化TiO₂光觸媒照射下，可見光對甲苯分解力低於紫外光。在相同的條件下，TCPP/P25-TiO₂光觸媒經HCl溶液浸泡酸處理後，對甲苯分解力有進一步的改善。在我們的研究光觸媒分解低濃度甲苯之動力學時，一般應符合Langmuir-Hinshelwood (L-H)模式， k 為L-H模式之比例常數，而 K 為吸收常數兩者成反比趨勢，SG-TiO₂分解甲苯能力比P25-TiO₂大，因此，SG-TiO₂光觸媒對甲苯有較高的分解力，經XRD分析銳鈦礦之結晶，歸因於有較小的grain size (4.6~8.1 nm)。

關鍵詞：鋁雜氧化鋅 (AZO)、薄膜、化學先驅物、水相沉積、室內空氣、光觸媒、染料敏化二氧化鈦、甲苯、可見光。

目錄

AUTHORIZED LETTER.....	iii
中文摘要.....	iv
Abstract.....	iv
ACKNOWLEDGMENTS.....	iv
LIST OF CONTENTS.....	ix
LIST OF FIGURES.....	xii
LIST OF TABLES.....	xvi
Chapter 1 INTRODUCTION.....	1
1.1 Introduction.....	1
Chapter 2 LITERATURE REVIEW.....	7
2.1 Transparent conducting oxide (TCO).....	7
2.2 Structure and properties of ZnO.....	7
2.3 Characteristics of AZO.....	8
2.4 Sol gel method.....	9
2.4.1 The advantages of sol-gel method to prepare thin films are.....	9
2.4.2 The disadvantages of sol-gel method to prepare thin films are.....	9
2.4.3 The sol-gel process is a method of preparing inorganic materials via chemical routes. In general, this process involves the following steps.....	9
2.4.4 This process is controlled by parameters such as.....	10
2.4.5 Applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms.....	10
2.4.6 Sol and Gel.....	11
2.4.7 The reactions are as followed.....	12
2.4.8 The pH value of sol-gel as shown in Figure 2.4.....	13
2.5 Crystal structures and properties of titanium dioxide.....	13
2.5.1 Crystal structures of titanium dioxide.....	13
2.5.2 A simplified reaction scheme of photocatalysis is shown in Figure 2.7.....	16
2.5.3 One of the reasons lies in the differences in their.....	16
2.5.4 The band gap diagrams of some semiconductors are shown in Figure 2.9.....	17
2.5.5 Photocatalytic oxidation mechanism of TiO ₂ with UV-light.....	17
2.5.6 Sensitized TiO ₂ photocatalyst.....	18
Chapter 3 Experimental Procedure.....	21
3.1 Introduction of AZO Experimental Procedure.....	21
3.1.1 Materials.....	21
3.1.2 The experimental procedures will be described as shown Figure 3.1、3.2、3.3、3.4. These processes include.....	22
3.2 Experimental equipment.....	27
3.2.1 Heat-treatment system.....	27
3.3 Characterization Techniques.....	27
3.3.1 Structural analysis.....	28
3.3.1.1 Thermogravimetry – differential thermal analyzer (TG – DTA).....	28
3.3.1.2 Fourier Transform Infrared transmittance measurements.....	29
3.3.1.3 X-ray diffraction (XRD).....	29
3.3.1.4 Atomic force microscope (AFM, Veeco Vip-II).....	30
3.3.1.5 Field emission scanning-electron microscope (FE-SEM).....	30
3.3.2 Compositional analysis.....	30
3.3.2.1 X-ray Photoelectron Spectroscopy (XPS).....	30
3.3.3 Optical analysis.....	31
3.3.3.1 UV-VIS -NIR spectrophotometer.....	31

Photoluminescence (PL)	31	3.3.4 Electrical analysis.....	32	3.3.4.1 Alpha-Step.....	32	3.3.4.2
Four-point probe.....	32	3.3.4.3 Hall Effect measurements.....	33	3.4. Introduction of photocatalysts Experimental Procedure.....	33	3.4. 1 Materials.....
3.4. 1 Materials.....	33	3.4.2 Experiments setup and procedure.....	35	Chapter 4 Results and discussion.....	38	4.1 Optical and electrical characteristics of Al-doped ZnO thin films prepared by aqueous phase depositio.....
3.4.2 Experiments setup and procedure.....	35	4.1.1 Structural properties.....	38	4.1.1 Structural properties.....	38	4.1.2 Electrical properties.....
Chapter 4 Results and discussion.....	38	4.1.2 Electrical properties.....	52	4.1.3 Optical properties.....	54	4.2 Photocatalytic Destruction of Gaseous Toluene by Porphyrin-sensitized TiO ₂ Thin Films.....
4.1 Optical and electrical characteristics of Al-doped ZnO thin films prepared by aqueous phase depositio.....	38	4.2 Photocatalytic Destruction of Gaseous Toluene by Porphyrin-sensitized TiO ₂ Thin Films.....	59	4.2.1 Structure, Morphology and optical properties of TiO ₂ thin films.....	59	4.2.2 Performance of TiO ₂ photocatalysts.....
4.1.1 Structural properties.....	38	4.2.1 Structure, Morphology and optical properties of TiO ₂ thin films.....	59	4.2.2 Performance of TiO ₂ photocatalysts.....	64	4.2.3 Performance of dye-sensitized SG-TiO ₂ photocatalysts.....
4.1.2 Electrical properties.....	52	4.2.2 Performance of TiO ₂ photocatalysts.....	64	4.2.4 Effects of acid treatment on photocatalytic activity of thin films.....	77	4.2.5 Kinetics of photocatalytic oxidation by using TiO ₂ -coated tubular reactors.....
4.1.3 Optical properties.....	54	4.2.3 Performance of dye-sensitized SG-TiO ₂ photocatalysts.....	72	4.2.5 Kinetics of photocatalytic oxidation by using TiO ₂ -coated tubular reactors.....	80	Chapter 5 Conclusions and Outlook.....
4.2 Photocatalytic Destruction of Gaseous Toluene by Porphyrin-sensitized TiO ₂ Thin Films.....	59	4.2.4 Effects of acid treatment on photocatalytic activity of thin films.....	77	Chapter 5 Conclusions and Outlook.....	84	5. 1 Optical and electrical characteristics of Al-doped ZnO thin films prepared by aqueous phase deposition.....
4.2.1 Structure, Morphology and optical properties of TiO ₂ thin films.....	59	Chapter 5 Conclusions and Outlook.....	84	5. 1 Optical and electrical characteristics of Al-doped ZnO thin films prepared by aqueous phase deposition.....	84	5.2 Photocatalytic Destruction of Gaseous Toluene by Porphyrin-sensitized TiO ₂ Thin Films.....
4.2.2 Performance of TiO ₂ photocatalysts.....	64	5. 1 Optical and electrical characteristics of Al-doped ZnO thin films prepared by aqueous phase deposition.....	84	5.2 Photocatalytic Destruction of Gaseous Toluene by Porphyrin-sensitized TiO ₂ Thin Films.....	84	References.....
4.2.3 Performance of dye-sensitized SG-TiO ₂ photocatalysts.....	72	5.2 Photocatalytic Destruction of Gaseous Toluene by Porphyrin-sensitized TiO ₂ Thin Films.....	84	References.....	86	List of Figures
4.2.4 Effects of acid treatment on photocatalytic activity of thin films.....	77	References.....	86	List of Figures		Figure 2.1 Crystal structure of the zinc oxide (ZnO) in which small circles represent zinc atoms, seeing that large circles depict oxygen atoms.....
4.2.5 Kinetics of photocatalytic oxidation by using TiO ₂ -coated tubular reactors.....	80	List of Figures		Figure 2.1 Crystal structure of the zinc oxide (ZnO) in which small circles represent zinc atoms, seeing that large circles depict oxygen atoms.....	7	Figure 2.2 Sol-Gel Technologies and their applications.....
Chapter 5 Conclusions and Outlook.....	84	Figure 2.1 Crystal structure of the zinc oxide (ZnO) in which small circles represent zinc atoms, seeing that large circles depict oxygen atoms.....	7	Figure 2.2 Sol-Gel Technologies and their applications.....	11	Figure 2.3 Sol-gel technologies and their products.....
5. 1 Optical and electrical characteristics of Al-doped ZnO thin films prepared by aqueous phase deposition.....	84	Figure 2.2 Sol-Gel Technologies and their applications.....	11	Figure 2.3 Sol-gel technologies and their products.....	12	Figure 2.4 pH value of Sel-Gel.....
5.2 Photocatalytic Destruction of Gaseous Toluene by Porphyrin-sensitized TiO ₂ Thin Films.....	84	Figure 2.3 Sol-gel technologies and their products.....	12	Figure 2.4 pH value of Sel-Gel.....	13	Figure 2.5 Crystal structure of anatase.....
References.....	86	Figure 2.4 pH value of Sel-Gel.....	13	Figure 2.5 Crystal structure of anatase.....	15	Figure 2.6 Crystal structure of rutile.....
List of Figures		Figure 2.5 Crystal structure of anatase.....	15	Figure 2.6 Crystal structure of rutile.....	15	Figure 2.7 Mechanism of photo-excited reaction.....
Figure 2.1 Crystal structure of the zinc oxide (ZnO) in which small circles represent zinc atoms, seeing that large circles depict oxygen atoms.....	7	Figure 2.6 Crystal structure of rutile.....	15	Figure 2.7 Mechanism of photo-excited reaction.....	16	Figure 2.8 Energy diagram for TiO ₂ and relevant redox potentials.....
Figure 2.2 Sol-Gel Technologies and their applications.....	11	Figure 2.7 Mechanism of photo-excited reaction.....	16	Figure 2.8 Energy diagram for TiO ₂ and relevant redox potentials.....	16	Figure 2.9 Band gap place of several semiconductors: The lower edge of the conduction band (red) and upper edge of the valence band (green) are presented.....
Figure 2.3 Sol-gel technologies and their products.....	12	Figure 2.8 Energy diagram for TiO ₂ and relevant redox potentials.....	16	Figure 2.9 Band gap place of several semiconductors: The lower edge of the conduction band (red) and upper edge of the valence band (green) are presented.....	17	Figure 2.10 Schematic photoexcitation of TiO ₂
Figure 2.4 pH value of Sel-Gel.....	13	Figure 2.9 Band gap place of several semiconductors: The lower edge of the conduction band (red) and upper edge of the valence band (green) are presented.....	17	Figure 2.10 Schematic photoexcitation of TiO ₂	18	Figure 2.11. Principle of photosensitized degradation reaction on sensitized TiO ₂ particle.....
Figure 2.5 Crystal structure of anatase.....	15	Figure 2.10 Schematic photoexcitation of TiO ₂	18	Figure 2.11. Principle of photosensitized degradation reaction on sensitized TiO ₂ particle.....	19	Figure 2.12 Excitation step using dye molecule sensitizer.....
Figure 2.6 Crystal structure of rutile.....	15	Figure 2.11. Principle of photosensitized degradation reaction on sensitized TiO ₂ particle.....	19	Figure 2.12 Excitation step using dye molecule sensitizer.....	20	Figure 2.13 Molecular formula of Tetrakis (4-carboxyphenyl) porphine.....
Figure 2.7 Mechanism of photo-excited reaction.....	16	Figure 2.12 Excitation step using dye molecule sensitizer.....	20	Figure 2.13 Molecular formula of Tetrakis (4-carboxyphenyl) porphine.....	20	Figure 3.1 experimental procedures setup chart.....
Figure 2.8 Energy diagram for TiO ₂ and relevant redox potentials.....	16	Figure 2.13 Molecular formula of Tetrakis (4-carboxyphenyl) porphine.....	20	Figure 3.1 experimental procedures setup chart.....	23	Figure 3.2 Substrate cleaning setup chart.....
Figure 2.9 Band gap place of several semiconductors: The lower edge of the conduction band (red) and upper edge of the valence band (green) are presented.....	17	Figure 3.1 experimental procedures setup chart.....	23	Figure 3.2 Substrate cleaning setup chart.....	24	Figure 3.3 Prepare of the aqueous gel route setup chart.....
Figure 2.10 Schematic photoexcitation of TiO ₂	18	Figure 3.2 Substrate cleaning setup chart.....	24	Figure 3.3 Prepare of the aqueous gel route setup chart.....	25	Figure 3.4 Coating of AZO films and annealing of AZO films setup chart.....
Figure 2.11. Principle of photosensitized degradation reaction on sensitized TiO ₂ particle.....	19	Figure 3.3 Prepare of the aqueous gel route setup chart.....	25	Figure 3.4 Coating of AZO films and annealing of AZO films setup chart.....	26	Figure 3.5 Heat-treatment system setup chart.....
Figure 2.12 Excitation step using dye molecule sensitizer.....	20	Figure 3.4 Coating of AZO films and annealing of AZO films setup chart.....	26	Figure 3.5 Heat-treatment system setup chart.....	27	Figure 3.6 TG – DTA, SDT Q600.....
Figure 2.13 Molecular formula of Tetrakis (4-carboxyphenyl) porphine.....	20	Figure 3.5 Heat-treatment system setup chart.....	27	Figure 3.6 TG – DTA, SDT Q600.....	28	Figure 3.7 XRD, Shimadzu XRD-6000, CuK , =1.5405A.....
Figure 3.1 experimental procedures setup chart.....	23	Figure 3.6 TG – DTA, SDT Q600.....	28	Figure 3.7 XRD, Shimadzu XRD-6000, CuK , =1.5405A.....	29	Figure 3.8 FE-SEM, JEOL, JSM-7401F.....
Figure 3.2 Substrate cleaning setup chart.....	24	Figure 3.7 XRD, Shimadzu XRD-6000, CuK , =1.5405A.....	29	Figure 3.8 FE-SEM, JEOL, JSM-7401F.....	30	Figure 3.9 UV/VIS/NIR spectrophotometer ,Shimadzu, UV-1700.....
Figure 3.3 Prepare of the aqueous gel route setup chart.....	25	Figure 3.8 FE-SEM, JEOL, JSM-7401F.....	30	Figure 3.9 UV/VIS/NIR spectrophotometer ,Shimadzu, UV-1700.....	31	Figure 3.10 Tencor Alpha-Step 500 setup chart.....
Figure 3.4 Coating of AZO films and annealing of AZO films setup chart.....	26	Figure 3.9 UV/VIS/NIR spectrophotometer ,Shimadzu, UV-1700.....	31	Figure 3.10 Tencor Alpha-Step 500 setup chart.....	32	Figure 3.11 Hall Effect measurements ,ECOPIA ,HMS-2000.....
Figure 3.5 Heat-treatment system setup chart.....	27	Figure 3.10 Tencor Alpha-Step 500 setup chart.....	32	Figure 3.11 Hall Effect measurements ,ECOPIA ,HMS-2000.....	33	Figure 3.12 Schematic of the tubular photoreactor and experimental setup.....
Figure 3.6 TG – DTA, SDT Q600.....	28	Figure 3.11 Hall Effect measurements ,ECOPIA ,HMS-2000.....	33	Figure 3.12 Schematic of the tubular photoreactor and experimental setup.....	36	Figure 3.13 The absorption of gaseous toluene without illumination of UV light by: (a)P25-TiO ₂ (b)SG-TiO ₂
Figure 3.7 XRD, Shimadzu XRD-6000, CuK , =1.5405A.....	29	Figure 3.12 Schematic of the tubular photoreactor and experimental setup.....	36	Figure 3.13 The absorption of gaseous toluene without illumination of UV light by: (a)P25-TiO ₂ (b)SG-TiO ₂	37	Figure 4.1 TG-DTA curve of the dried ZnO precursor gel in N ₂ flow at a heat rate
Figure 3.8 FE-SEM, JEOL, JSM-7401F.....	30	Figure 3.13 The absorption of gaseous toluene without illumination of UV light by: (a)P25-TiO ₂ (b)SG-TiO ₂	37	Figure 4.1 TG-DTA curve of the dried ZnO precursor gel in N ₂ flow at a heat rate	39	Figure 4.2 FTIR spectra of the precursor gel at (a).25 and by a two-step heat treatment to (b).300 , (c).500 , (d).700
Figure 3.9 UV/VIS/NIR spectrophotometer ,Shimadzu, UV-1700.....	31	Figure 4.1 TG-DTA curve of the dried ZnO precursor gel in N ₂ flow at a heat rate	39	Figure 4.2 FTIR spectra of the precursor gel at (a).25 and by a two-step heat treatment to (b).300 , (c).500 , (d).700	41	Figure 4.3A XRD patterns of 2.0 at.% Al-doped ZnO films annealed at 650 under different ambient atmospheres: 5% O ₂ in argon (a), argon (b), 5% H ₂ in argon (c).....
Figure 3.10 Tencor Alpha-Step 500 setup chart.....	32	Figure 4.2 FTIR spectra of the precursor gel at (a).25 and by a two-step heat treatment to (b).300 , (c).500 , (d).700	41	Figure 4.3A XRD patterns of 2.0 at.% Al-doped ZnO films annealed at 650 under different ambient atmospheres: 5% O ₂ in argon (a), argon (b), 5% H ₂ in argon (c).....	43	Figure 4.3B XRD patterns of the thin films annealed at 700oC under 5% H ₂ in argon: (a).undoped, (b).2.0 at.% Al-doped, (c).2.25at.% Al-doped, (d).2.5at.% Al-doped and (e).2.75at.% Al-doped ZnO.....
Figure 3.11 Hall Effect measurements ,ECOPIA ,HMS-2000.....	33	Figure 4.3A XRD patterns of 2.0 at.% Al-doped ZnO films annealed at 650 under different ambient atmospheres: 5% O ₂ in argon (a), argon (b), 5% H ₂ in argon (c).....	43	Figure 4.3B XRD patterns of the thin films annealed at 700oC under 5% H ₂ in argon: (a).undoped, (b).2.0 at.% Al-doped, (c).2.25at.% Al-doped, (d).2.5at.% Al-doped and (e).2.75at.% Al-doped ZnO.....	44	Figure 4.4 AFM micrographs of: (a). undoped, (b).2.0 at.% Al-doped, (c).2.25at.% Al-doped, (d).2.5at.% Al-doped and (e).2.75at.% Al-doped ZnO films;(f).RMS roughness at various doping concentration.....
Figure 3.12 Schematic of the tubular photoreactor and experimental setup.....	36	Figure 4.3B XRD patterns of the thin films annealed at 700oC under 5% H ₂ in argon: (a).undoped, (b).2.0 at.% Al-doped, (c).2.25at.% Al-doped, (d).2.5at.% Al-doped and (e).2.75at.% Al-doped ZnO.....	44	Figure 4.4 AFM micrographs of: (a). undoped, (b).2.0 at.% Al-doped, (c).2.25at.% Al-doped, (d).2.5at.% Al-doped and (e).2.75at.% Al-doped ZnO films;(f).RMS roughness at various doping concentration.....	46	Figure 4.5 SEM micrographs of (a). undoped, (b).2.0 at.% Al-doped, (c).2.25at.%.....
Figure 3.13 The absorption of gaseous toluene without illumination of UV light by: (a)P25-TiO ₂ (b)SG-TiO ₂	37	Figure 4.4 AFM micrographs of: (a). undoped, (b).2.0 at.% Al-doped, (c).2.25at.% Al-doped, (d).2.5at.% Al-doped and (e).2.75at.% Al-doped ZnO films;(f).RMS roughness at various doping concentration.....	46	Figure 4.5 SEM micrographs of (a). undoped, (b).2.0 at.% Al-doped, (c).2.25at.%.....	48	Figure 4.6 XPS spectra of AZO films (a).wide scan spectra, 2.25 at.% Al-doped; (b).Zn LMM spectra, (c).Zn 2p spectra and (d).Al 2p spectra. curve a:2.0at.% Al-doped, curve b:2.25at.% Al-doped, curve c:2.5at.% Al-doped, curve d:2.75at.% Al-doped.....
Figure 4.1 TG-DTA curve of the dried ZnO precursor gel in N ₂ flow at a heat rate	39	Figure 4.5 SEM micrographs of (a). undoped, (b).2.0 at.% Al-doped, (c).2.25at.%.....	48	Figure 4.6 XPS spectra of AZO films (a).wide scan spectra, 2.25 at.% Al-doped; (b).Zn LMM spectra, (c).Zn 2p spectra and (d).Al 2p spectra. curve a:2.0at.% Al-doped, curve b:2.25at.% Al-doped, curve c:2.5at.% Al-doped, curve d:2.75at.% Al-doped.....	49	Figure 4.7 (a).XPS spectra of O1s and (b).relative strength of resolved OI/(OI+OII).....
Figure 4.2 FTIR spectra of the precursor gel at (a).25 and by a two-step heat treatment to (b).300 , (c).500 , (d).700	41	Figure 4.6 XPS spectra of AZO films (a).wide scan spectra, 2.25 at.% Al-doped; (b).Zn LMM spectra, (c).Zn 2p spectra and (d).Al 2p spectra. curve a:2.0at.% Al-doped, curve b:2.25at.% Al-doped, curve c:2.5at.% Al-doped, curve d:2.75at.% Al-doped.....	49	Figure 4.7 (a).XPS spectra of O1s and (b).relative strength of resolved OI/(OI+OII).....	51	Figure 4.8 Resistivity of the AZO films (2.0at.% Al-doped) as a function of annealing temperature.....
Figure 4.3A XRD patterns of 2.0 at.% Al-doped ZnO films annealed at 650 under different ambient atmospheres: 5% O ₂ in argon (a), argon (b), 5% H ₂ in argon (c).....	43	Figure 4.7 (a).XPS spectra of O1s and (b).relative strength of resolved OI/(OI+OII).....	51	Figure 4.8 Resistivity of the AZO films (2.0at.% Al-doped) as a function of annealing temperature.....	52	Figure 4.9 Resistivity, Hall mobility and carrier concentration of AZO films as a function of doping concentration.....
Figure 4.3B XRD patterns of the thin films annealed at 700oC under 5% H ₂ in argon: (a).undoped, (b).2.0 at.% Al-doped, (c).2.25at.% Al-doped, (d).2.5at.% Al-doped and (e).2.75at.% Al-doped ZnO.....	44	Figure 4.8 Resistivity of the AZO films (2.0at.% Al-doped) as a function of annealing temperature.....	52	Figure 4.9 Resistivity, Hall mobility and carrier concentration of AZO films as a function of doping concentration.....	54	Figure 4.10 Optical transmittance spectra of AZO films.....
Figure 4.4 AFM micrographs of: (a). undoped, (b).2.0 at.% Al-doped, (c).2.25at.% Al-doped, (d).2.5at.% Al-doped and (e).2.75at.% Al-doped ZnO films;(f).RMS roughness at various doping concentration.....	46	Figure 4.9 Resistivity, Hall mobility and carrier concentration of AZO films as a function of doping concentration.....	54	Figure 4.10 Optical transmittance spectra of AZO films.....	55	Figure 4.11 Optical band gaps of AZO films.....
Figure 4.5 SEM micrographs of (a). undoped, (b).2.0 at.% Al-doped, (c).2.25at.%.....	48	Figure 4.10 Optical transmittance spectra of AZO films.....	55	Figure 4.11 Optical band gaps of AZO films.....	57	Figure 4.12 PL spectra of AZO films: (a).2.0at.% Al-doped, (b).2.25at.% Al-doped,(c).2.5at.% Al-doped and (d).2.75at.% Al-doped.....
Figure 4.6 XPS spectra of AZO films (a).wide scan spectra, 2.25 at.% Al-doped; (b).Zn LMM spectra, (c).Zn 2p spectra and (d).Al 2p spectra. curve a:2.0at.% Al-doped, curve b:2.25at.% Al-doped, curve c:2.5at.% Al-doped, curve d:2.75at.% Al-doped.....	49	Figure 4.11 Optical band gaps of AZO films.....	57	Figure 4.12 PL spectra of AZO films: (a).2.0at.% Al-doped, (b).2.25at.% Al-doped,(c).2.5at.% Al-doped and (d).2.75at.% Al-doped.....	59	Figure 4.13 SEM photograph of: (a).P25-TiO ₂ films and (b).SG-TiO ₂ films.....
Figure 4.7 (a).XPS spectra of O1s and (b).relative strength of resolved OI/(OI+OII).....	51	Figure 4.12 PL spectra of AZO films: (a).2.0at.% Al-doped, (b).2.25at.% Al-doped,(c).2.5at.% Al-doped and (d).2.75at.% Al-doped.....	59	Figure 4.13 SEM photograph of: (a).P25-TiO ₂ films and (b).SG-TiO ₂ films.....	60	Figure 4.14 XRD pattern of: (a). the as-deposited SG-TiO ₂ film, and films annealed at (b).150 ; (c).300 ; (d).450 , respectively and (e). a commercial P25-TiO ₂ (used as recived.....
Figure 4.8 Resistivity of the AZO films (2.0at.% Al-doped) as a function of annealing temperature.....	52	Figure 4.13 SEM photograph of: (a).P25-TiO ₂ films and (b).SG-TiO ₂ films.....	60	Figure 4.14 XRD pattern of: (a). the as-deposited SG-TiO ₂ film, and films annealed at (b).150 ; (c).300 ; (d).450 , respectively and (e). a commercial P25-TiO ₂ (used as recived.....	62	Figure 4.15. Absorption spectrum of 0.5mM porphyrin (TCPP) in ethanol (dash line) and TCPP absorbed on TiO ₂ films (solid line). The molecule structure was depicted in the inset derived from Cherian and Wamser
Figure 4.9 Resistivity, Hall mobility and carrier concentration of AZO films as a function of doping concentration.....	54	Figure 4.14 XRD pattern of: (a). the as-deposited SG-TiO ₂ film, and films annealed at (b).150 ; (c).300 ; (d).450 , respectively and (e). a commercial P25-TiO ₂ (used as recived.....	62	Figure 4.15. Absorption spectrum of 0.5mM porphyrin (TCPP) in ethanol (dash line) and TCPP absorbed on TiO ₂ films (solid line). The molecule structure was depicted in the inset derived from Cherian and Wamser	63	Figure 4.16. Time courses of toluene removal efficiency by P25-TiO ₂ under the illumination of UV light (10W black light blue lamp, =365nm) with an air flow rate of 200mL/min
Figure 4.10 Optical transmittance spectra of AZO films.....	55	Figure 4.15. Absorption spectrum of 0.5mM porphyrin (TCPP) in ethanol (dash line) and TCPP absorbed on TiO ₂ films (solid line). The molecule structure was depicted in the inset derived from Cherian and Wamser	63	Figure 4.16. Time courses of toluene removal efficiency by P25-TiO ₂ under the illumination of UV light (10W black light blue lamp, =365nm) with an air flow rate of 200mL/min	66	Figure 4.17. Elimination capacity and removal efficiency of P25-TiO ₂ at various toluene loading
Figure 4.11 Optical band gaps of AZO films.....	57	Figure 4.16. Time courses of toluene removal efficiency by P25-TiO ₂ under the illumination of UV light (10W black light blue lamp, =365nm) with an air flow rate of 200mL/min	66	Figure 4.17. Elimination capacity and removal efficiency of P25-TiO ₂ at various toluene loading	68	Figure 4.18. Time courses of toluene removal efficiency by SG-TiO ₂ under the illumination of UV light (10W black light blue lamp, =365nm) with an air flow rate of 200 mL/min.....
Figure 4.12 PL spectra of AZO films: (a).2.0at.% Al-doped, (b).2.25at.% Al-doped,(c).2.5at.% Al-doped and (d).2.75at.% Al-doped.....	59	Figure 4.17. Elimination capacity and removal efficiency of P25-TiO ₂ at various toluene loading	68	Figure 4.18. Time courses of toluene removal efficiency by SG-TiO ₂ under the illumination of UV light (10W black light blue lamp, =365nm) with an air flow rate of 200 mL/min.....	69	Figure 4.19. Elimination capacity and removal efficiency of SG-TiO ₂ at various toluene loading
Figure 4.13 SEM photograph of: (a).P25-TiO ₂ films and (b).SG-TiO ₂ films.....	60	Figure 4.18. Time courses of toluene removal efficiency by SG-TiO ₂ under the illumination of UV light (10W black light blue lamp, =365nm) with an air flow rate of 200 mL/min.....	69	Figure 4.19. Elimination capacity and removal efficiency of SG-TiO ₂ at various toluene loading	71	Figure 4.20. Time courses of toluene removal efficiency by TCPP/SG-TiO ₂ under the illumination of visible light (10W fluorescent lamp) with an air flow rate of 200 mL/min.....
Figure 4.14 XRD pattern of: (a). the as-deposited SG-TiO ₂ film, and films annealed at (b).150 ; (c).300 ; (d).450 , respectively and (e). a commercial P25-TiO ₂ (used as recived.....	62	Figure 4.19. Elimination capacity and removal efficiency of SG-TiO ₂ at various toluene loading	71	Figure 4.20. Time courses of toluene removal efficiency by TCPP/SG-TiO ₂ under the illumination of visible light (10W fluorescent lamp) with an air flow rate of 200 mL/min.....	72	Figure 4.21. Elimination capacity and removal efficiency of TCPP/SG-TiO ₂ at various toluene loading.....
Figure 4.15. Absorption spectrum of 0.5mM porphyrin (TCPP) in ethanol (dash line) and TCPP absorbed on TiO ₂ films (solid line). The molecule structure was depicted in the inset derived from Cherian and Wamser	63	Figure 4.20. Time courses of toluene removal efficiency by TCPP/SG-TiO ₂ under the illumination of visible light (10W fluorescent lamp) with an air flow rate of 200 mL/min.....	72	Figure 4.21. Elimination capacity and removal efficiency of TCPP/SG-TiO ₂ at various toluene loading.....	74	Figure 4.22. A schematic representation of the different reactions occurring at the sensitized TiO ₂ photocatalysts surface, where kinj is the rate of the photoinduced electron transfer from the porphyrin excited state; kfluor stands for the rate of the fluorescence deactivation
Figure 4.16. Time courses of toluene removal efficiency by P25-TiO ₂ under the illumination of UV light (10W black light blue lamp, =365nm) with an air flow rate of 200mL/min	66	Figure 4.21. Elimination capacity and removal efficiency of TCPP/SG-TiO ₂ at various toluene loading.....	74	Figure 4.22. A schematic representation of the different reactions occurring at the sensitized TiO ₂ photocatalysts surface, where kinj is the rate of the photoinduced electron transfer from the porphyrin excited state; kfluor stands for the rate of the fluorescence deactivation		
Figure 4.17. Elimination capacity and removal efficiency of P25-TiO ₂ at various toluene loading	68	Figure 4.22. A schematic representation of the different reactions occurring at the sensitized TiO ₂ photocatalysts surface, where kinj is the rate of the photoinduced electron transfer from the porphyrin excited state; kfluor stands for the rate of the fluorescence deactivation				

of the porphyrin excited state; k_{CR} represents the rate of the charge recombination between the oxidized porphyrin and electrons in the conduction band of TiO_2 and k_{reg} is the rate of the electron-transfer reaction between the oxidized porphyrin and the redox mediator in the environment76 Figure 4.23. Effects of acid pretreatment on the toluene removal efficiency by TCPP/P25- TiO_2 at $[T]_0 = 0.5\text{ppm}$ and 1.5ppm , respectively under the illumination of visible light (10W fluorescent lamp) with an air flow rate of 200 mL/min.....78 Figure 4.24 Comparison of three kinds of visible light photocatalysts at (a). $[T]_0 = 0.5\text{ppm}$ and (b). $[T]_0 = 1.5\text{ppm}$ under the illumination of visible light (10W fluorescent lamp) with an air flow rate 200 mL/min.....79 Figure 4.25 Plot of $(V/Q)(C_0 - C)^{-1}$ versus $\ln(C_0/C)(C_0 - C)^{-1}$ for decomposition of toluene by (a). SG- TiO_2 ; (b). P25- TiO_2 ; (c). TCPP/SG- TiO_2 ; (d). TCPP/P25- TiO_2 (ACT).....81.. List of Tables Table 2.1 Fundamental properties of ZnO.....8 Table 2.2 Properties of anatase TiO_2 and rutile TiO_214 Table 2.3. Chemical identity of Tetrakis (4-carbonoxyphenyl) porphine.....20

參考文獻

- [1] S. Major, S. Kumar, M. Bhatnagar, K.L. Chopra, *Appl. Phys. Lett.* 49 (1986) 394.
- [2] W.T. Yen, Y. C. Lin, P.C. Yao, J.H. Ke, Y.L. Chen, *Thin Solid Films* 518 (2010) 3882.
- [3] T. Minami, H. Nanto, S. Takata, *Jpn. J. Appl. Sci.* 23 (1984) L280.
- [4] D.R. Sahu, S.Y. Lin, J.L. Huang, *Appl. Surf. Sci.* 253 (2007) 4886.
- [5] H. Kim, A. Pique, J.S. Horwitz, H. Murata, Z.H. Kafafi, C.M. Gilmore, D.B. Chrisey, *Thin Solid Films* 377-378 (2009) 798.
- [6] M A Kaid, A. Ashour, *Appl. Surf. Sci.* 253 (2007) 3029.
- [7] A.F. Aktaruzzaman, G.L. Sharma, L.K. Malhotra, *Thin Solid Films* 198 (1991) 647.
- [8] T. Minami, H. Sonohara, S. Takata, H. Sato, *Jpn. J. Appl. Sci.* 33 (1994) L743.
- [9] W. Tang, D.C. Cameron, *Thin Solid Films* 238 (1994) 83.
- [10] T. Tsuchiya, T. Emoto, T. Sei, *J. Non-Crystal. Solids* 178 (1994) 327.
- [11] M. Ohyama, H. Kozuka, T. Yoko, *J. Am. Ceram. Soc.* 81 (1998) 1622.
- [12] A.E. Jimenez-Gonzalez, J.A.S. Urueta, R. Suarez-Parra, *J. Cryst. Growth* 192 (1998) 430.
- [13] P. Sagar, M. Kumar, R.M. Mehra, *Thin Solid Films* 489 (2005) 94.
- [14] T. Schuler, M.A. Aegerter, *Thin Solid Films* 351 (1999) 125 [15] S.Y. Kuo, W.C. Chen, F.I. Lai, C.P. Cheng, H.C. Kuo, S.C. Wang, W.F. Hsieh, *J. Crystal Growth* 287 (2006) 78.
- [16] J.H. Lee, K.H. Ko, B.O. Park, *J. Crystal Growth* 247 (2003) 119.
- [17] Y.S. Kim, W.P. Tai, *Appl. Surf. Sci.* 253 (2007) 4911 [18] V. Musat, B. Teixeira, E. Fortunato, R.C.C. Monteiro, P. Vilarinho, *Surf. Coat. Technol.* 180-181 (2004) 659.
- [19] Z. Xu, H. Deng, J. Xie, Y. Li, Y. Li, *J. Sol-Gel Sci.* 36 (2005) 223.
- [20] H. Van den Rul, D. Mondelaers, M.K. Van Bael, J. Mullens, *J. Sol-Gel Sci.* 39 (2006) 41.
- [21] D. Mondelaers, G. Vanholyland, H.V. Rul, J. D' Haen, M.K. Van Bael, J. Mullens, *MRS Bull.* 37 (2002) 901.
- [22] K. Van Werde, D. Mondelaers, G. Vanholyland, D. Nelis, M.K. Van Bael, J. Mullens, L.C. Van Poucke, *J. Mater. Sci.* 37 (2002) 81.
- [23] D. Mondelaers, G. Vanholyland, H. Van den Rul, J. D' Haen, M.K. Van Bael, J. Mullens, L.C. Van Poucke, *J. Sol-Gel Sci.* 26 (2003) 523.
- [24] Y.G. Wang, S.P. Lau, X.H. Zhang, H.H. Hng, H.W. Lee, S.F. Yu, B.K. Tay, *J. Non-Crystal. Solids* 259 (2003) 335.
- [25] S.W. Xue, X.T. Zu, W.G. Zheng, M.Y. Chen, X. Xiang, *Physica B* 382 (2006) 201.
- [26] K.E. Lee, M.S. Wang, E.J. Kim, S.H. Hahn, *Current Appl. Phys.* 9 (2009) 683.
- [27] S. Cho, J. Ma, Y. Kim, Y. Sun, G.K.L. Wong, J.B. Ketterson, *Appl. Phys. Lett.* 75 (1999) 2761.
- [28] Y. Igasaki, H. Saito, *Thin Solid Films* 199 (1991) 223.
- [29] A.A. Ogwu, E Bouquerel, O Ademosu, S Moh, E Crossan, F Placido, *J. Phys. D: Appl. Phys.* 38 (2005) 266.
- [30] M. Hilgendorff, L Spanhel, Ch. Rothenhousler, G. Muller, *J. Electrochem. Soc.* 145 (1998) 3632.
- [31] K.H. Kim, K.C. Park, D.Y. Ma, *J. Appl. Phys.* 81 (1997) 7764.
- [32] M. Berber, V. Bulto, R. Klis, H. Hahn, *Scripta Materialia* 53 (2005) 547.
- [33] R.F. Silva, E.D. M.E.D. Zaniquelli, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 198 – 200 (2002) 551.
- [34] K.N.P. Kumar, K. Keizer, A.J. Burggraaf, T. Okubo, H. Nagamoto, S. Morooka, *Nature* 358 (1992) 48.
- [35] A.Y. Oral, Z.B. Bahsi, M.H. Aslan, *Appl. Surf. Sci.* 253 (2007) 4593.
- [36] D. Bao, H. Gu, A. Kuang, *Thin Solid Films* 312 (1998) 37.
- [37] P.B. Barna, M. Adamik, *Thin Solid Films* 317 (1998) 27.
- [38] Y.F. Sun, W.F. Liu, Z.D. He, S.L. Liu, Z.Z. Yia, G.T. Du, *Vacuum* 80 (2006) 981.
- [39] Abe R., K. Sayam, and H. Arakaw, " Efficient Hydrogen Evolution from Aqueous Mixture of I- and Acetonitrile Using a Merocyanine Dye-sensitized Pt/ TiO_2 Photocatalyst under Visible Light Irradiation, " *Chem. Phys. Lett.*, 362, 441 (2002).
- [40] Alberici, R. and W. Jardim, " Photocatalytic Destruction of VOCs in the Gas-phase Using Titanium Dioxide, " *Appl. Catal. B: Environ.*, 14,

55 (1997).

- [41]Anderson, C. and A. J. Bard, "An Improved Photocatalyst of TiO₂ /SiO₂ Prepared by a Sol-Gel Synthesis," *J. Phys. Chem.*, 99, 9882 (1995).
- [42]Andersen, I., G. R. Lundqvist, and L. Molhave, "Human Response to Controlled Levels of Toluene in Six-hour Exposures," *Scandinavian J. Work, Envir. & Health.*, 9, 405 (1983).
- [43]Anpo, M. and M. Takeuchi, "The Design and Development of Highly Reactive Titanium Oxide Photocatalysts Operating under Visible Light Irradiation," *J. Catal.*, 216, 505 (2003).
- [44]Argazzi, R., N.Y.M. Iha, H. Zabri, F. Odobel, and C. A. Bignozzi, "Design of Molecular Dyes for Application in Photoelectrochemical and Electrochromic Devices Based on Nanocrystalline Metal Oxide Semiconductors," *Coord. Chem. Rev.*, 248, 1299 (2004).
- [45]Barraud, E., F. Bosc, D. Edwards, N. Keller, and V. Keller, "Gas Phase Photocatalytic Removal of Toluene Effluents on Sulfated Titania," *J. Catal.*, 235, 318 (2005).
- [46]Bischoff, B.L. and M. A. Anderson, "Peptization Process in the Sol-Gel Preparation of Porous Anatase (TiO₂)," *Chem. Mater.*, 7, 1772 (1995).
- [47]Bouzaza, A. and A. Laplanche, "Photocatalytic Degradation of Toluene in the Gas Phase: Comparative Study of Some TiO₂ Supports," *J. Photochem. Photobiol. A: Chem.*, 150, 207 (2002).
- [48]Bouzaza, A., C. Vallet, and A. Laplanche, "Photocatalytic Degradation of Some VOCs in the Gas Phase using an Annular Flow Reactor: Determination of the Contribution of Mass Transfer and Chemical Reaction Steps in the Photodegradation Process," *J. Photochem. Photobiol. A: Chem.*, 177, 212 (2006).
- [49]Campbell, W.M., A. K. Burrell, D. L. Officer, and K. W. Jolley, "Porphyrins as Light Harvesters in the Dye-sensitized TiO₂ Solar Cell," *Coord. Chem. Rev.*, 248, 1363 (2004).
- [50]Carp, O., C. L. Huisman, and A. Reller, "Photoinduced Reactivity of Titanium Dioxide," *Prog. in Solid State Chem.* 32, 33 (2004).
- [51]Chao, C.Y.H., C. W. Kwong, and K. S. Hui, "Potential Use of a Combined Ozone and Zeolite System for Gaseous Toluene Elimination," *J. Hazardous Mater.*, 143, 118 (2007).
- [52]Chatterjee, D. and A. Mahata, "Photoassisted Detoxification of Organic Pollutants on the Surface Modified TiO₂ Semiconductor Particulate System," *Catal. Commun.*, 2, 1 (2001).
- [53]Cherian, S. and C. C. Wamser, "Adsorption and Photoactivity of Tetra(4-carboxyphenyl) Porphyrin (TCPP) on Nanoparticulate TiO₂," *J. Phys. Chem. B*, 104, 3624 (2000).
- [54]Cho, Y., W. Choi, C. H. Lee, T. Hyeon and H. I. Lee, "Visible Light-induced Degradation of Carbon Tetrachloride on Dye-sensitized TiO₂," *Environ. Sci. Technol.*, 35, 966 (2001).
- [55]Cho, Y. and W. Choi, "Visible Light-induced Reactions of Humic Acids on TiO₂," *J. Photochem. Photobiol. A: Chem.*, 148, 129 (2002).
- [56]d'Henezela, O., P. Pichat, and D. F. Ollis, "Benzene and Toluene Gas-phase Photocatalytic Degradation over H₂O and HCl Pretreated TiO₂: By-products and Mechanisms," *J. Photochem. Photobiol. A: Chem.*, 118, 197 (1998).
- [57]De Rivas, B., J. I. Gutierrez-Ortiz, R. Lopez-Fonseca, and J. R. Gonzalez-Velasco, "Analysis of the Simultaneous Catalytic Combustion of Chlorinated Aliphatic Pollutants and Toluene over Ceria-zirconia Mixed Oxides," *Appl. Catal. A: General*, 314, 54 (2006).
- [58]Domingueza, C., J. Garcia, M. A. Pedraz, A. Torres, and M. A. Galan, "Photocatalytic Oxidation of Organic Pollutants in Water," *Catal. Today*, 40, 85 (1998).
- [59]Einag, H., S. Futamura, and T. Ibusuki, "Heterogeneous Photocatalytic Oxidation of Benzene, Toluene, Cyclohexene and Cyclohexane in Humidified Air: Comparison of Decomposition Behavior on Photoirradiated TiO₂ Catalyst," *Appl. Catal. B: Environ.*, 38, 215 (2002).
- [60]Fujii, Y., Y. Tsukahara, and Y. Wada, "pH-dependent Reversible Switching of Fluorescence of Water-soluble Porphyrin Adsorbed on Mesoporous TiO₂ Film," *Bull. Chem. Soc. Jpn.*, 79, 561 (2006).
- [61]Fujishima, A., T. N. Rao, and D. A. Tryk, "Titanium Dioxide Photocatalysis," *J. Photochem. Photobiol. C: Photochem. Rev.*, 1, 1 (2000).
- [62]Gratzel, M., "Photoelectrochemical Cells," *Nature*, 414, 338 (2001) [63]Hagfeldt, A. and M. Gratzel, "Molecular Photovoltaics," *Acc. Chem. Res.*, 33, 269 (2000) [64]Houlding, V.H. and M. Gratzel, "Photochemical H₂ Generation by Visible Light. Sensitization of TiO₂ Particles by Surface Complexation with 8-Hydroxyquinoline," *J. Am. Chem. Soc.*, 105, 5695 (1983).
- [65]Huijser, A., T. Savenije, A. Kotlewski, S. Picken, and L. Siebbeles, "Efficient Light-harvesting Layers of Homeotropically Aligned Porphyrin Derivatives," *Adv. Mater.*, 18, 2234 (2006).
- [66]Hoffmann, M., S. Martin, W. Choi, and D. Bahnemann, "Environmental Applications of Semiconductor Photocatalysis," *Chem. Rev.*, 95, 69 (1995).
- [67]Iliev, V. and D. Tomova, "Photocatalytic Oxidation of Sulfide ion Catalyzed by Phthalocyanine Modified Titania," *Catal. Commun.*, 3, 287 (2002).
- [68]Iliev, V., "Phthalocyanine-modified Titania - Catalyst for Photooxidation of Phenols by Irradiation with Visible Light," *J. Photochem. Photobiol. A: Chem.*, 151, 195 (2002).
- [69]Jeong, J., K. Sekiguchi, and K. Sakamoto, "Photochemical and Photocatalytic Degradation of Gaseous Toluene Using Short-wavelength UV

Irradiation with TiO₂ Catalyst: Comparison of Three UV Sources, " *Chemosphere*, 57, 663 (2004).

[70]Jin, Z., X. Zhang, Y. Li, S. Li, and G. Lu, " 5.1% Apparent Quantum Efficiency for Stable Hydrogen Generation over Eosin-sensitized CuO/TiO₂ Photocatalyst under Visible Light Irradiation, " *Catal. Commun.*, 8, 1267 (2007).

[71]Kalyanasundaram, K. and M. Gratzel, " Applications of Functionalized Transition Metal Complexes in Photonic and Optoelectronic Devices, " *Coord. Chem. Rev.*, 77, 347 (1998).

[72]Keller, N., E. Barraud, F. Bosc, D. Edwards, and V. Keller, " On the Modification of Photocatalysts for Improving Visible Light and UV Degradation of Gas-phase Toluene over TiO₂, " *Appl. Catal. B: Environ.*, 70, 423 (2007).

[73]Kim, S.B. and S. C. Hong, " Kinetic Study for Photocatalytic Degradation of Volatile Organic Compounds in Air Using Thin Film TiO₂ Photocatalyst, " *Appl. Catal. B: Environ.*, 35, 305 (2002).

[74]Lewandowski, M. and D. F. Ollis, " Halide Acid Pretreatments of Photocatalysts for Oxidation of Aromatic Air Contaminants: Rate Enhancement, Rate Inhibition, and a Thermodynamic Rationale, " *J. Catal.*, 217, 38 (2003).

[75]Linsebigler, A., G. Lu, and J. Yates, " Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results, " *Chem. Rev.*, 95, 735 (1995).

[76]Maira; A.J., K. L. Yeung, J. Soria, J. M. Coronado, C. Belver, C. Y. Lee, and V. Augugliaro, " Gas-phase Photo-oxidation of Toluene Using Nanometer-size TiO₂ Catalysts, " *Appl. Catal. B: Environ.*, 29, 327 (2001).

[77]Marci, G., M. Addamo, V. Augugliaro, S. Coluccia, E. Garcia-Lopez, V. Loddo, G. Martra, L. Palmisano, and M. Schiavello, " Photocatalytic Oxidation of Toluene on Irradiated TiO₂: Comparison of Degradation Performance in Humidified Air Water and in Water Containing a Zwitterionic Surfactant, " *J. Photochem. Photobiol. A: Chem.*, 160, 105 (2003).

[78]Mo, J., Y. Zhang, Q. Xu, and R. Yang, " Effect of TiO₂ /Adsorbent Hybrid Photocatalysts for Toluene Decomposition in Gas Phase, " *J. of Hazardous Mater.*, 168, 276 (2009).

[79]Moon, J., C. Y. Yun, K. W. Chung, M. S. Kang, and J. Yi, " Photocatalytic Activation of TiO₂ under Visible Light Using Acid Red 44, " *Catal. Today*, 87, 77 (2003).

[80]Nakajima, A., H. Obata, Y. Kameshima, and K. Okada, " Photocatalytic Destruction of Gaseous Toluene by Sulfated TiO₂ Powder. " *Catal. Commun.*, 6, 716 (2005).

[81]Nasr, C., K. Vinodgopal, L. Fisher, S. Hotchandani, A. K. Chattopadhyay, and P. Kamat, " Environmental Photochemistry on Semiconductor Surfaces. Visible Light Induced Degradation of a Textile Diazo Dye, Naphthol Blue Black, on TiO₂ Nanoparticles, " *J. Phys. Chem.*, 100, 8436 (1996).

[82]Obee, T. and R. Brown, " TiO₂ Photocatalysis for Indoor Air Applications: Effects of Humidity and Trace Contaminant Levels on the Oxidation Rates of Formaldehyde, Toluene, and 1% Butadiene, " *Environ. Sci. Technol.*, 29, 1223 (1995).

[83]Obee, T., " Photooxidation of Sub-Parts-Per-Million Toluene and Formaldehyde Levels on Titania Using a Glass-Plate Reactor. " *Environ. Sci. Technol.*, 30, 3578 (1996).

[84]Odobel, F., E. Blart, M. Lagre ' e, M. Villieras, H. Boujtita, N. Murr, S. Caramoric, and C. A. Bignozzi, " Porphyrin Dyes for TiO₂ Sensitization, " *J. Mater. Chem.*, 13, 502 (2003) [85]Ozcan, O., F. Yukruk, E. U. Akkaya, and D. Uner, " Dye Sensitized Artificial Photosynthesis in the Gas Phase over Thin and Thick TiO₂ Films under UV and Visible Light Irradiation, " *Appl. Catal. B: Environ.*, 71, 291 (2007).

[86]Robertson, N., " Optimizing Dyes for Dye-sensitized Solar Cells, " *Angew. Chem. Int. Ed.*, 45, 2338 (2006).

[87]Ross, H., J. Bendig, and S. Hecht, " Sensitized Photocatalytical Oxidation of Terbutylazine, " *Solar Energy Mater. Solar Cells*, 33, 475 (1994).

[88]M. Voinov and J. Augustynski in Schiravello, M.(Editor), *Heterogeneous Photocatalysis*, p.8, John-Wiley and Sons, Inc., New York, U.S.A. (1997)

[89]Sekiguchi, K., A. Sanada, and K. Sakamoto, " Degradation of Toluene with an Ozone-Decomposition Catalyst in the Presence of Ozone, and the Combined Effect of TiO₂ Addition, " *Catal. Commun.*, 4, 247 (2003).

[90]Sekiguchi, K., K. Yamamoto, and K. Sakamoto, " Photocatalytic Degradation of Gaseous Toluene in an Ultrasonic Mist Containing TiO₂ Particles, " *Catal. Commun.*, 9, 281 (2008).

[91]Shiraishi, F. and T. Ishimatsu, " Toluene Removal from Indoor Air Using a Miniaturized Photocatalytic Air Purifier Including a Preceding Adsorption/Desorption Unit, " *Chem. Eng. Sci.*, 64, 2466 (2009).

[92]Smestad, G.P., " Education and Solar Conversion: Demonstrating Electron Transfer, " *Solar Energy Mater. Solar Cells*, 55, 157 (1998).

[93]Strini, A., S. Cassese, and L. Schiavi, " Measurement of Benzene, Toluene, Ethylbenzene and o-Xylene Gas Phase Photodegradation by Titanium Dioxide Dispersed in Cementitious Materials Using a Mixed Flow Reactor, " *Appl. Catal. B: Environ.*, 61, 90 (2005).

[94]Subrahmanyam, Ch., A. Renken, and L. Kiwi-Minsker, " Catalytic Abatement of Volatile Organic Compounds Assisted by Non-Thermal Plasma, Part II. Optimized Catalytic Electrode and Operating Conditions, " *Appl. Catal. B: Environ.*, 65, 157 (2006).

[95]Vinodgopal, K. and D. Wynkoop, " Environmental Photochemistry on Semiconductor Surfaces: Photosensitized Degradation of a Textile Azo Dye, Acid Orange 7, on TiO₂ Particles Using Visible Light, " *Environ. Sci. Technol.*, 30, 1660 (1996).

[96]Wang R. C., K. S. Fan, and J. S. Chang, " Removal of Acid Dye by ZnFe₂O₄/TiO₂ -immobilized Granular Activated Carbon under Visible Light Irradiation in a Recycle Liquid – Solid Fluidized Bed, " *J. Taiwan Inst. Chem. Eng.*, 40, 533(2009) [97]Watson, D.F. and G. J. Meyer,

- “ Electron Injection at Dye-sensitized Semiconductor Electrodes, ” *Annu. Rev. Phys. Chem.*, 56, 119 (2005).
- [98]Yen, W. T., Y. C. Lin, P. C. Yao, J.H. Ke, and Y.L. Chen, “ Growth Characteristics and Properties of ZnO:Ga Thin Films Prepared by Pulsed DC Magnetron Sputtering, ” *Appl. Surf. Sci.*, 256, 3432 (2010).
- [99]Yu, J. and X. Zhao, “ Effect of Surface Treatment on the Photocatalytic Activity and Hydrophilic Property of the Sol-Gel Derived TiO₂ Thin Films, ” *Mater. Res. Bull.*, 36, 97 (2001).
- [100]Yu, J.C, J. Yu, and J. Zhao, “ Enhanced Photocatalytic Activity of Mesoporous and Ordinary TiO₂ Thin Films by Sulfuric Acid Treatment, ” *Appl. Catal. B: Environ.*, 36, 31 (2002).
- [101]Zhang, P. F. Liang, G. Yu, Q. Chen, and W. Zhu, “ A Comparative Study on Decomposition of Gaseous Toluene, ” *J. Photochem. Photobiol. A: Chem.*, 156, 189 (2003).
- [102]Zhang, Y., J. C. Crittenden, D. W. Hand, and D. L. Perram, “ Fixed-bed Photocatalysts for Solar Decontamination of Water, ” *Environ. Sci. Technol.*, 28, 435 (1994).
- [103] H. L. Hartnagel, A. K. Jain and C. Tagadish, “ Semiconducting Transparent Thin Films ” ,published by Institute of Physics Publication, 1995, P. 17.
- [104]K. Ellmer, A. Klein, B. Rech, “ Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells ” , Springer, illustrated edition (2007)
- [105] P. Nunes, E. Fortunato, P. Tonello, F.B. Fernandes, P. Vilarinho, R. Martins, *Vacuum* 64 (2002) 281.
- [106] R.J. Hong, X. Jiang, B. Szyszka, V. Sittinger, A. Pflug, *Appl. Surf. Sci.* 207 (2003) 341.
- [107] M. de la L. Olvera, A. Maldonado, R. Asomoza, *Sol. Energy Mater. Sol. Cells* 73 (2002) 425.
- [108] C.H. Lee, L.Y. Lin, *Appl. Surf. Sci.* 92 (1996) 163.
- [109] Y. Natsume, H. Sakata, *Mater. Chem. Phys.* 78 (2002) 170.
- [110] C.H. Lee, K.S. Lim, Jinsoo Song, *Jpn. J. Appl. Phys.* 36 (1997) 4418.
- [111] H. Mondragon Suarez, A. Maldonado, M. de la L. Olvera, A. Reyes, R. Castanedo Perez, G. Torres Delgado, R. Asomoza, *Appl. Surf. Sci.* 193 (2002) 52.
- [112] A. Suzuki, T. Matsushita, N. Wada, Y. Sakamoto, M. Okuda, *Jpn. J. Appl. Phys.* 35 (1996) L56.
- [113] J.-H. Lee, B.-O. Park, *Thin Solid Films* 426 (2003) 94.
- [114] J. D. Mackenzie, in “ Ultrastructure Processing of Ceramics, Glass and Composites ” , eds. L. L. Hench and D. R. Ulrich, p15 wiley , New York, 1984.
- [115]謝曙旭, “ 以溶凝膠法在低溫下製備奈米級PTO 及PZT粉末及其相變化與低溫燒結之研究 ” , 國立清華大學材料科學與工程研究所, 民國93年6月.
- [116] Calzada, M. L.; Sirela, R.; Carmona, F.; Jimenez, B. Investigations of a diol based sol-gel process for the preparation of lead titanate materials. *J. Am. Ceram. Soc.* 1995, 77, 1802-1808.
- [117]Ulrich, S.; Nicola, H.; Lorenz, A. Hybrid inorganic-organic materials by sol-gel processing of organofunctional metal alkoxides. *Chem. Mater.* 1995, 7, 2010-2017.
- [118] R. R. Bhave, *Inorganic membranes synthesis, characteristics and applications*, Van Nostrand Reinhold, 1991.
- [119] 謝坤龍, “ 鈹銀合金/氧化鋁複合膜之特性研究:以溶凝膠法修飾基材孔徑之探討 ” , 國立成功大學化學工程研究所碩士論文 (2000)
- [120] R. J. Gonzalez, R. Zallen, and H. Beger, *Phys. Rev. B*, 55, 7014 (1997).
- [121] J. S. Kasper and K. D. Lomdale, “ International tables of X-ray crystallography ” , 2nd edition (1959).
- [122] T. E. Weirich, M. Winterer, S. Seifried, H. Hahn, and H. Fuess, *Ultramicroscopy*, 81, 263, (2000).
- [123] Powder Diffraction File, Card No. 21-1272, Joint committee on powder diffraction standards, Swarthmore, PA.
- [124] Powder Diffraction File, Card No. 21-1276, Joint committee on powder diffraction standards, Swarthmore, PA.
- [125] J. Muscat, N. M. Harrison, and G. Thornton, *Phys. Rev. B*, 59, 2320 (1999).
- [126]A. Fujishima, K. Hashimoto, and T. Watanabe, “ TiO₂ Photocatalysis Fundamentals and Applications ” , 1st edition, BKC Inc. (1999).
- [127] R. Benedix, F. Dehn, J. Quaas, and M. Orgass, *LACER*, 5, 157 (2000).
- [128] A. Fujishima, K. Hashimoto, and T. Watanabe, “ TiO₂ Photocatalysis Fundamentals and Applications ” , 1st edition, BKC Inc. (1999).
- [129]Gratzel, M., 2001. Photoelectrochemical cells. *Nature* 414, 338 – 344.
- [130]Lee, S.Y., Park, J., Joo, H., 2006. Visible light-sensitized photocatalyst immobilized on beads by CVD in a fluidizing bed. *Solar Energy Material & Solar Cells* 90, 1905 – 1914.
- [131]Srinivasan, S.S., Wade, J., Stefanakos, E.K., 2005. Visible light photocatalysis via nano-composite CdS-TiO₂ materials. *Material Research Society Symposium Proceeding* 876E, R5.2.1 – R5.2.8.
- [132] Cheng, P., Li, W., Zhou, T., Jin, Y., Gu, M., 2004. Physical and photocatalytic properties of zinc ferrite doped titania under visible light irradiation. *Journal of Photochemistry and Photobiology A: Chemistry* 168, 97 – 101.
- [133] Ding, H., Sun, H., Shan, Y., 2005. Preparation and characterization of mesoporous SBA-15 supported dye-sensitized TiO₂ photocatalyst. *Journal of Photochemistry and Photobiology A: Chemistry* 169, 101 – 107.
- [134] Kamat, P.V., Fox, M.A., 1983. Photosensitization of TiO₂ colloids Erythrosine B in acetonitrile. *Chemical Physics Letters* 102(4), 379 –

- [135] Patrick, B., Kamat, P.V., 1992. Photoelectrochemistry in semiconductor particulate systems. 17. Photosensitization of large-bandgap semiconductor: charge injection from triplet excited thionine into zinc oxide colloids. *The Journal of Physical Chemistry* 96(3), 1423 – 1428.
- [136] Vlachopoulos, N., Liska, P., Augustynski, J., Graetzel, M., 1988. Very efficient visible light energy harvesting and conversion by spectral sensitization of high surface area polycrystalline titanium dioxide films. *Journal of the American Chemical Society* 110(4), 1216 – 1220.