การยึดติดสังกะสีออกไซด์ระดับนาโนเมตรลงบนพอลิอิเล็กโทรไลต์ฟิล์ม
ด้วยเทคนิคเลเยอร์บายเลเยอร์

นางสาววลัยพร สุธาบัณฑิตพงศ์

DEPOSITION OF NANO-SCALED ZINC OXIDE ON POLYELECTROLYTE FILM
BY LAYER-BY-LAYER TECHNIQUE

Miss Walaiporn Suthabanditpong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2010

Thesis Title   DEPOSITION OF NANO-SCALED ZINC OXIDE ON POLYELECTROLYTE FILM BY LAYER-BY-LAYER TECHNIQUE

By   Miss Walaiporn Suthabanditpong

Field of Study   Chemical Engineering

Thesis Advisor   Associate Professor Tawatchai Charinpanitkul, D.Eng.

Thesis Co-Advisor   Kajornsak Faungnawakij, D.Eng.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.... Dean of the Faculty of Engineering

(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

.... Chairman

(Associate Professor Tharathon Mongkhonsi, Ph.D.)

.... Thesis Advisor

(Associate Professor Tawatchai Charinpanitkul, D.Eng.)

.... Thesis Co-advisor

(Kajornsak Faungnawakij, D.Eng.)

.... External Examiner

(Nawin Viriya-empikul, D.Eng.)

.... Examiner

(Apinan Soottitantawat, D.Eng.)

วลัยพร สุธาบัณฑิตพงศ์ : การยึดติดสังกะสีออกไซด์ระดับนาโนเมตรลงบนพอลิอิเล็กโทร
ไลต์ฟิล์มด้วยเทคนิคเลเยอร์บายเลเยอร์ (DEPOSITION OF NANO-SCALED ZINC
OXIDE ON POLYELECTROLYTE FILM BY LAYER-BY-LAYER TECHNIQUE)
อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ธวัชชัย ชรินพาณิชกุล, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม:
อ.ดร.ขจรศักดิ์ เฟื่องนวกิจ, 95 หน้า.

การยึดติดสังกะสีออกไซด์ระดับนาโนเมตรลงบนพอลิอิเล็กโทรไลต์ฟิล์ม   ด้วยเทคนิค
เลเยอร์บายเลเยอร์โดยให้กระจกมีความใส   และมีคุณสมบัติความชอบน้ำโดยการกระตุ้นด้วยแสง
ซึ่งการเคลือบพอลิอิเล็กโทรไลต์ฟิล์มของสังกะสีออกไซด์ลงบนกระจก สามารถเตรียมได้หลายวิธี
ด้วยกัน โดยในงานวิจัยนี้ทำการศึกษา 3 วิธีได้แก่ วิธีการตกผลึกสังกะสีออกไซด์ในพอลิอิเล็กโทร
ไลต์ฟิล์ม การเตรียมจากสารแขวนลอยของสังกะสีออกไซด์ในสารละลายพอลิอะคริลิคแอซิด และ
วิธีโซลเจล   ซึ่งตัวอย่างนั้นจะถูกเตรียมเป็นพอลิอิเล็กโทรไลต์ฟิล์ม   โดยอาศัยหลักการของ
เลเยอร์บายเลเยอร์   จากนั้นจะทำการเคลือบสังกะสีออกไซด์ที่เตรียมได้จากทั้ง 3 วิธีด้วยเทคนิค
การเคลือบแบบจุ่ม จากการทดลองพบว่า   พอลิอิเล็กโทรไลต์ฟิล์มที่มีความหนาและมีผิวที่เรียบ
เหมาะแก่การนำไปยึดติดสังกะสีออกไซด์นั้นควรเคลือบบนกระจกเพียง 1 ชั้นด้วยความเข้มข้นของ
พอลิอิเล็กโทรไลต์ 2 โมลต่อลิตร ด้วยอัตราการจุ่มและดึงขึ้น 3.0 เซนติเมตรต่อนาที   หลังจากนั้น
จะทำการยึดติดสังกะสีออกไซด์ระดับนาโนเมตรลงบนพอลิอิเล็กโทรไลต์ฟิล์มด้วยวิธี โซลเจลที่มี
ค่า pH ของสารละลายโซลเท่ากับ 1   ฟิล์มบางที่เตรียมได้มีค่าการส่องผ่านแสงมากกว่า 95
เปอร์เซ็นต์ ในช่วงแสงที่มองเห็น   และกระจกมีสมบัติความชอบน้ำอย่างมากแสดงด้วยค่ามุม
สัมผัสของน้ำมีค่าน้อยกว่า 5 องศา   หลังจากกระตุ้นด้วยแสงอัลตราไวโอเลตเป็นเวลา 15 นาที
ทั้งนี้ฟิล์มบางใสของสังกะสีออกไซด์ที่เตรียมได้จากทุกวิธีจะมีการวัดความหนาของฟิล์ม   และค่า
ความขรุขระของพื้นผิว

อย่างไรก็ตามวิธีการยึดติดสังกะสีออกไซด์ระดับนาโนเมตรลงบนพอลิอิเล็กโทรไลต์ฟิล์ม
ด้วยการเคลือบสารแขวนลอยของสังกะสีออกไซด์ในสารละลายพอลิอะคริลิคแอซิดนั้น สามารถ
นำมาปรับปรุงสมบัติความชอบน้ำของกระจกได้   แต่ต้องใช้เวลาในการกระตุ้นด้วยแสงมากเพื่อ
ทำให้กระจกมีความชอบน้ำ   เนื่องจากสังกะสีออกไซด์ที่ยึดติดบนฟิล์มนั้นเกิดการรวมตัวกันเป็น
ก้อนและกระจายตัวได้ไม่ดี

ภาควิชา.........วิศวกรรมเคมี..........ลายมือชื่อนิสิต...........วลัยพร สุธาบัณฑิตพงศ์.....................
สาขาวิชา.......วิศวกรรมเคมี..........ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก.............................
ปีการศึกษา.............2553............ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์ร่วม...ขจรศักดิ์ เฟื่องนวกิจ

5070435221: MAJOR CHEMICAL ENGINEERING

KEYWORDS: POLYELECTROLYTE FILM / PHOTOINDUCED HYDROPHILIC / ZINC OXIDE / SOL-GEL PROCESS / pH OF ZINC OXIDE SOL / DIP COATING

WALAIPORN SUTHABANDITPONG: DEPOSITION OF NANO-SCALED ZINC OXIDE ON POLYELECTROLYTE FILM BY LAYER-BY-LAYER TECHNIQUE. ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANIT-KUL, D.Eng., CO-ADVISOR: KAJORNSAK FAUNGNAWAKIJ, D.Eng., 95 pp.

Deposition of nano-scaled ZnO particles on polyelectrolyte film was conducted by 3 different methods which are precipitation of ZnO, suspension of ZnO in poly(acylic acid) (PAA) and sol-gel methods. Based on the experimental results, a suitable condition for preparation of polyelectrolyte film was dipping glass substrate into 2.0 M polyelectrolyte solution (poly(allylamine hydrochloride) and poly(acrylic acid) with a withdrawal speed at 3 cm/min. Deposition of ZnO particles onto a single bilayer polyelectrolyte film could be achieved by the sol-gel method with pH of sol precursor at 1. The incorporated polyelectrolyte film with ZnO exhibits transmittance of 95% in visible light range and highly hydrophilic property with the water contact angle of lower than 5 degrees after UV irradiation for 15 min.

The method of suspension of ZnO in poly(acrylic acid) (PAA) could also provide polyelectrolyte film containing ZnO which improve hydrophilic property of the coated substrates. However, activation UV with longer time compared with that of the sol-gel method would be required. This result is attributed to the agglomeration of ZnO in the polymer solution before coating, leading to lower hydrophilic property.

Department........Chemical Engineering.......Student's Signature...... W. Suthabanditpong .....
Field of study.....Chemical Engineering.....Advisor's Signature...
Academic year ....2010.....................Co-advisor's Signature... Kajornsak Faungnawakij

ACKNOWLEDGEMENTS

CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

Page

NOMENCLATURES

AFM	Atomic Force Microscopy
CLSM	Confocal Laser Scanning Microscope
EDX	Energy Dispersive Spectrometer X-ray
FESEM	Field Emission Scanning Electron Microscope
PAA	Poly (Acrylic Acid)
PAH	Poly (Allylamine Hydrochloride)
PET	polyelectrolyte film
R_{rms}	Root mean square roughness
UV-Vis	UV-Vis spectrophotometer
WS	Withdrawal Speed
XRD	X-Ray Diffraction
%T	Transmittance
θ	Water contact angle (°)

CHAPTER I

INTRODUCTION

1.1 Motivation

Glass has shown a great promise in the field of building decoration due to its optical property which can be widely used for increasing in coming light in work place, motor vehicle and other applications [1]. However, the important problem of glass is its cleanliness because dust, organic substances in the air, fog, fouling, and raindrops easily contaminate it. In general, we can solve this problem by cleaning the glass frequently. Nevertheless, it is quite difficult to clean a tall building's windows. Scientists have been searching and come up with a self-cleaning glass by using photocatalyst for eliminating contamination.

Hydrophilic/hydrophobic property is one of the key features essential for self cleaning property, which is required for various applications, such as cleanness of glass windows of any tall buildings. There are many attempts in search of hydrophilicity, which is obtained by using polarized molecules or some photocatalysts, while hydrophobicity is acquired from organic compounds. Meanwhile, it has been found that polyelectrolyte compounds, which contain an organic chain and the other end of polarized molecules, could hold strongly on glass surface. The polarized end of polyelectrolyte compound has hydrophilic property which can break down water droplets to spread over the coated surface and help rinse away loose dirt. The hydrophilic property of the coated surface containing photocatalyst is triggered by the ultraviolet (UV) irradiation. The hydrophilicity can simply be evaluated by mean of water contact angle measurement. With the contact angle less than 5°, the coated surface is recognized as superhydrophilic characteristics [1-9]. If water droplet contact angle is greater than 150°, the coated surface is classified as superhydrophobic one. The wettability is one of the important properties of solid surface from aspects of both fundamental research and practical applications. It is mainly controlled by the surface energy and the surface roughness. The surface

roughness is found to affect the hydrophilic property of the surface, while the hydrophobic surface becomes more hydrophobic. Among various semiconductor oxide materials, zinc oxide (ZnO) is a wide band gap (3.37eV) [10-15], which can be chemically activated by UV light to exhibit hydrophilicity. Regarding to previous work, ZnO thin film was prepared by sol-gel dip coating method using zinc acetate as a precursor and then photoinduced hydrophilic property of the coated glass substrate was investigated [2]. It was reported that the ZnO thin films prepared using 0.10 M zinc acetate and ethanol as the solvent with withdrawal speed of 3.0 cm/min at calcination temperature of 500°C, its transmittance above 90% in visible region. The film exhibits highly hydrophilic property because of it's the water contact angle of 5 degree after 30 min UV irradiation.

Recently, the semiconductive nanoparticles embedded in multilayer polymer film was studied by precipitation of ZnO into Poly(diallyldimethylammonium chloride) (PDDA) and poly(styrenesulfonate) sodium salt (PSS) with layer-by-layer self-assembly technique[10]. The results reveal that the repetitive adsorption of zinc nitrate and subsequent precipitation in ammonium hydroxide provided an effective method to fabricate multilayer film containing ZnO nanoparticle. The morphology of ZnO nanoparticles were controlled by the precipitation reaction cycles. Meanwhile, a variety of synthetic hydrophobic films has been studied to mimic the natural surface by enhancing the surface roughness of the underlying organic film (PAH/PAA) [3]. Chemical etching of glass substrate followed by deposition of silicon dioxide (SiO_2) nanoparticles and organic molecules has been employed for preparing the coated glass with finer-scaled roughness and lower surface energy. The fabricated films on glass substrate exhibits water contact angle higher than 150° as well as self-cleaning and anti–adhesion properties. However, information of incorporating the advantages of ZnO and polyelectrolyte layer for a control of hydrophilic and hydrophobic property of coated substrates is still limited. Such combination of ZnO and polyelectrolyte compounds would provide a promising alternative for substrate surface modification.

The main purpose of this work was to investigate the hydrophilic properties of the polyelectrolyte multilayer films incorporated with ZnO nanoparticles under the effect of UV irradiation. The ZnO thin film was fabricated to mimic the natural surface by controlling the dipping cycle, resulting in the varied surface roughness of

the underlying organic layer (PAH/PAA). The organic layers were prepared by the combination of electrochemical deposition and layer-by-layer technique and then followed by the deposition of ZnO nanoparticles using dip-coating method.

1.2 Objectives

Objective of this thesis was to investigate an effective method to deposit ZnO nanoparticles thin film on polyelectrolyte layer depositing on glass substrate using the dip coating technique and then examine the hydrophilic properties of the coated glass substrates after employing UV irradiation.

1.3 Scope of work

1.3.1 Determine the optimal condition for controlling the surface roughness by varying the following parameters :

1.3.1.1 Concentrations of polyelectrolytes: 0.02, 0.20, 0.50, 1.00, and 2.00 M

1.3.1.2 Withdrawal speeds: 3.0, 6.0, and 9.0 cm/min

1.3.1.3 Number of dipping cycle

1.3.2 Analysis the viscosity of polymer using Rheometer to investigate the effect of viscosity of polymer on the film thickness

1.3.2 Determine the suitable method for depositing ZnO nanoparticles on polyelectrolyte film

1.3.3 Study the effect of UV irradiation time: 15, 30, and 60 min (using the UV-A lamp (SAPHIT A.J.L. Supplies, Thailand) with emission wavelength in a range of 300-460 nm and output of 20 watts)

1.3.4 Characterize ZnO incorporated with PET film by UV-VIS (UV-Vis spectrophotometer), CLSM (confocal laser scanning microscope), FE-SEM (field emission scanning electron microscope), EDX (energy dispersive spectrometer x-ray), AFM (atomic force microscope), FTIR (fourier transform infrared) and Contact angle measurement

CHAPTER II

THEORY & LITERATURE SURVEY

2.1 Principle of polyelectrolyte film construction

2.1.1 Polyelectrolyte film (PET film)

Polyelectrolyte multilayer films offer new coating opportunities [16]. This technique has been described as being theoretically able to cover many kinds of surfaces. The mechanisms allowing film coating involve essentially electrostatic interactions, but the assembly of such multilayer structures has also been shown on non-ionic or non-polar substrates. Film is constructed by the alternate adsorption of oppositely charged polyelectrolytes at the surface of material, easily obtained when the material is dipped in polyelectrolyte solutions. The driving force for film construction is the charge excess (alternatively positive and negative) that appears after each new polyelectrolyte adsorption. A deposition cycle creates a bilayer, and this cycle can be repeated as often as necessary. The number of deposition cycles and the types of polyelectrolyte used in the construction control the thickness and roughness of the multilayered film. Recently, Callewaert et al. have employed surface morphology and wetting properties of surface coated with an amphilic diblock copolymer that were polystyrene-*b*-poly(acrylic acid) (PS-PAA) for modulatating hydrophobicity-hydrophilicity switching [17]. They reported that the surface roughness decreases with increasing the PAA/PS block length ratio and it was larger for dip-coated than for spin-coated layers. Moreover, dynamic wetting reveals that the reorganization of coated layer depends on the pH of the solutions due to the deprotonation and swelling of the PAA chains. A hydrophilic surface was obtained for the large PAA block after immersion at pH 11. Self-assembled polyelectrolyte film was studied on the effect of layer number and charge of the external layer using variety of electrochemical techniques such as cyclic voltammetry and linear sweep voltammetry with rotating disc electrode [18]. The research work demonstrated that the

electrochemical property of films relies on the deposition condition. It was also found that the increased number of layer films lowed to the film permeability. In application of superhydrophobic surface, a polyelectrolyte multilayer surface was used for construction of the lotus leaf structure as like the honeycomb [19]. And then, the polyelectrolyte was coated by SiO_2 nanoparticles. The surface of SiO_2 film has been hydrophobic character after modifying the surface by semifluorosilane. Moreover, the polyelectrolyte film formation plays role on the pH of polyelectrolyte solution when using ISA technique [20]. The ISA can be used to generate robust thin films in the large pH range. The 16 bilayers film exhibits transmittance of 51% at 643 nm. Zhu et al. developed smart surface using PS-PAA and characterized the film by AFM, FE-SEM and contact angle measurements to investigate the physiochemical features of the copolymer brushes [21]. The results show the surface wettability depends on PS/PAA mole ratio and the external solvent properties. Capability of hydrophilic surface can be maintained by basic solution treatment, as well as, polar solvent such as ethanol. However the surface can be reversed to hydrophobic by acidic solution or toluene because of the rearrangement or reorganization of polymer chain. In addition, surface roughness was improved by enhancing the tunable range of wettability which was done by coating with micro textured ZnO nanorods. During the past decade, the noionic and polymer type surfactant PEG has been used as templates to prepare several porous materials (TiO_2, SiO_2 and so on) due to its high chemical stability [22]. Especially, porous ZnO thin films on glass substrate was prepared by sol-gel method with PEG (Polyethylene glycol) as an organic template, zinc acetate as a precursor, ethanol as a solvent and diethnolamine as a chelating agent. Result reveals that structure of ZnO thin film exhibits hexagonal wurtzite structure. The transmittance in the visible region of the thin film was 80%. Consequently, it is interesting in both of scientific and technological standpoint for superhydrophobic surfaces and superhydrophilic surfaces. They would be applied to self-cleaning coatings. Latterly, the multilayer polymer films by LbL method (layer-by-layer self-assembly technique) was used to prepare ZnO nanoparticles embedded in multilayer polymer films [10]. The film was absorbed into zinc nitrate solutionwas absorbed and

then, precipitated using ammonium hydroxide. Transmission electron microscopy study reveals that the morphologies and growth of ZnO nanoparticles were restricted by number of precipitation cycle.

2.1.2 Layer-by-layer (LbL) coating technique

Based on a simple and environmentally friendly layer-by-layer (LbL) coating technique, it affords nanoscale control over the internal architecture and extends three-dimensional molecular in a direction perpendicular to the solid support [10]. To date, various semiconductors, metallic and magnetic nanoparticles have been directly incorporated with polyelectrolyte multilayer films. Especially, the in situ synthetic method based on LbL technique can achieve particle size control and good dispersion homogeneity over the entire matrix [18-19, 23-24]. It is well known that the LbL process of polyelectrolyte multilayers can be utilized to fabricate conformal thin film coatings with controlling molecular level over film thickness and chemistry. A coating of this type is capable of any surface amenable to the water-based LbL. The adsorption process is mainly used to assemble these polyelectrolyte multilayer, including to the inside surfaces of complex object.

2.1.3 Chemical etching (or wet etching) [25]

The roughness of generated surface can be an important issue for the wet polishing and deep wet etching of channels. Improving the etching surface quality can be performed by adding HCl to the HF solution. The role of HCl is to transform the insoluble products, such as CaF_2, MgF_2 and AlF_3, into soluble ones:

$$CaF_2 \rightarrow CaCl_2, \ MgF_2 \rightarrow MgCl_2, \ AlF_3 \rightarrow AlCl_3$$
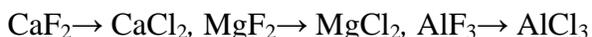
More experimental data are presented. The optimal HF (49%)/HCl (37%) ratio was found to be 10/1 for Corning 7740 as well as soda lime. Moreover, the etch rate was not much affected by the modification of the composition (a decrease of 5%). The

discoveries were used for the fabrication of dielectrophoretic devices packaged at wafer level, which are presented. In many case mentioned applications, a glass wafer, which was previously bonded on a silicon structure, was chemically thinned using a wet etching process in HF/HCl (10/1) from 500 to 100 μm. In this way, mechanical lapping and polishing were replaced by wet etching. The uniformity of the etching process was under 5% while the measured roughness of the surface was 10 nm. Moreover, via-holes for metallization were performed in the 100 μm-thick glass layer with a right selection of the material and good process design. Hydrophilicity or hydrophobicity of the surface, as we previously mentioned, also plays an important role. A small defect (micro-creep) on a hydrophobic surface will be very difficult to be filled with the etching solution. Silicon surface presents a hydrophobic characteristic, and for this reason, amorphous silicon or polysilicon masks, which generally give better results, are preferred over Cr/Au mask. The hydrophilicity of the surface can be changed by retaining and hard baking the photoresist mask.

2.2 Photoinduced hydrophilic property

2.2.1 Physicochemical property of Zinc oxide (ZnO)

Zinc oxide (ZnO), a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, has high transmittance and importance semiconductor material with excellent chemical and thermal stability [2, 6, 8, 13-14]. ZnO thin film is extensively used for various applications such as pH sensors, varistors, surface acoustic wave devices, optical waveguides, solar cells, biosensors and photoinduced hydrophilic glass [26-29]. Therefore many researchers in different fields have been all interested in ZnO thin film. The wetting properties of metal oxides thin films, mainly TiO_2 and ZnO, have been widely studied, since irradiation with UV light may significantly modify their wettability. This photoinduced transition can be reversed after storage in the dark place, indicating self-cleaning characteristics [29].

Several research works demonstrated that the ZnO films were polycrystalline with hexagonal wurtzite structure. The physicochemical property of ZnO was presented in Table 2.1

Table 2.1   Physicochemical property of ZnO [15, 30]

Other names	Zinc white
Molecular formula	ZnO
Molar mass	81.4084 g/mol
Crystal structure	Hexagonal wurtzite
Density and phase	5.606 g/cm^3, solid
Solution in water	Insoluble
Melting point	1975°C (decompose)
Boiling point	-
***a,c* Lattice constants**	3.249Å, 5.201Å
Refractive index	2.0

2.2.2 Principle of photoinduced hydrophilic property

The photoinduced hydrophilic property of semiconductor metals is obtained under irradiation with a certain wavelength. A semiconductor, which is theoretically described by valance band and conduction band, includes ZnO, TiO_2, ZrO_2, Fe_2O_3, WO_3 and so on. Band gap of a semiconductor is defined as a difference between its valence band and conduction band which could be related to the wavelength of photon. A photon having higher energy than or equal to the band gap is absorbed by the semiconductor, leading to the transition of electron from valence band to conduction band. Such irradiation excites electrons (ē) and holes (h$^+$) on the surface as shown in equation 2.1-2.2.

$$ZnO + 2h\nu \quad \rightarrow \quad ZnO^{*}(2\bar{e} + 2h^{+}) \qquad\qquad (2.1)$$

$$O^{2-} + h^{+} \quad \rightarrow \quad \tfrac{1}{2}\,O_1^{-} \qquad\qquad\qquad\qquad (2.2)$$

$$O_1^{-} + h^{+} \quad \rightarrow \quad 1/2O_2 + \text{oxygen vacancy} \qquad (2.3)$$

$$Zn^{2+} + \bar{e} \quad \rightarrow \quad Zn^{+}(\text{defective site}) \qquad\qquad (2.4)$$
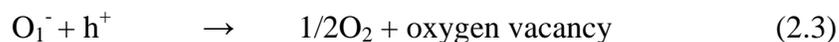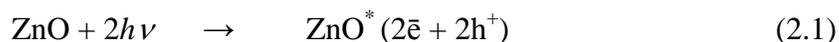
The holes can react with lattice oxygen leading to the formation of surface oxygen vacancies that represent in the equation 2.3 while some electrons can react with lattice metal ions to form defective sites as shown in equation 2.4. Water molecules can replace these oxygen vacancies producing chemisorbed hydroxyl groups. The photoinduced hydrophilic property ZnO is known as a photosensitive semiconductor due to its photoinduced hydrophilic property.

The scientists have been generally studied mainly of TiO_2 and ZnO, because their wettability may be significantly improved by the irradiation with UV light. This photoinduced transition can be reversed after storage in the dark, indicating self-cleaning characteristics [6]. Most recent, ZnO thin film was prepared by sol–gel dip coating method using zinc acetate as a precursor and then photoinduced hydrophilic property of the coated glass substrate was investigated [2]. It was reported the ZnO thin films, prepared using ethanol as the solvent, 0.10 M zinc acetate as a precursor, withdrawal speed of 3.0 cm/min, and calcination temperature of 500°C, can exhibit transmittance of above 90% in visible region and highly hydrophilic property with the water contact angle of 5 degree after 30 min UV irradiation. However, the pH value of sol-gel may affect the size of synthesized ZnO then, Rani et al. studied the influence of pH value of the sol on the crystallite size, morphology and structure of ZnO powder. The synthesized nanocrystalline ZnO powders were prepared via sol-gel route using zinc acetate and methanol as a precursor and then adjusting the pH value of the desired solution with sodium hydroxide for dye-sensitized solar cells [31]. The pH of sols was obtained in the range of 6 to 11 since the acidic nature of the solution ($\leq$6) prevents the gradually crystalline of ZnO powder at room temperature. It was found that the largest size nanocrystallite about 14 nm of ZnO powder was obtained at pH value of sol 9. And, the

XRD pattern exhibit the poor crystal quality was observed at pH value more than 9. The synthesized ZnO powders were successfully applied to be an electrode material for dye-sensitized solar cells. Li et al. studied about preparation of superhydrophobic of 2D ZnO having ordered pore arrays using solution-dipping template [8]. The morphology of the film was controlled by concentration of precursor. Hydrophilicity of the film also depends on concentration of precursor. The highest contact angle (165°) was exhibited at high precursor (1.0 M) and small sliding angle (less than 5°). It was also found that the modification of the ordered pore array film using micro or nanodevice film improved the resistance and self-cleaning properties. The surface transition from hydrophilicity to superhydrophobicity was induced by single crystalline ZnO nanorod array films (ZnO-NAFs) [8]. ZnO-NAFs were characterized by X-ray diffraction and scanning electron microscopy (SEM). The hydrophilic surface exhibited small water contact angle (9.6±0.8°) while the superhydrophobicity showed high water contact angle (156.2±1.8°). Many researchers are interested in preparation of nanocrystalline ZnO for superhydrophilic applications. The nanocrystalline ZnO thin films were fabricated by using zinc acetate as a precursor and cathodic electrodeposition as a deposition method [29]. The ZnO thin films were characterized by scanning electron microscopic (SEM), X-ray diffraction (XRD). However, the film was exposed to UV-light irradiation and keeping it in the dark storage, it was found that the surface wettability of the electrodeposited ZnO thin film reversed from hydrophobicity to super-hydrophilicity transition.

2.2.2.1 Wettability and contact angle

The wetting of rough surfaces is composed of two distinct wetting states. In the first state, water remains are suspended on the top of roughness surface while, air is enclosed underneath [4, 6, 19, 32-33]. Water drops in this *Cassie or composite* state of wetting are often easily displaced by slightly tilting substrates (superhydrophobic behavior). In the second state, liquid penetrates the surface. The consequential "penetrating" drops are less mobile due to a high contact angle (CA) hysteresis and they

remain strongly pinned to a specific position. The CA of drops in this state of wetting is described using Wenzel's equation (equation 2.5)

$$\cos\theta_r = r\cos\theta_s \qquad (2.5)$$

Where θ_s is the CA on the smooth material, θ_r is the CA on the rough surface, and r is the roughness factor, i.e., the factor by which the area of rough surface is enlarged compared to that of the smooth surface.

Wenzel's model is regarding only the behavior of drops in thermodynamic equilibrium; (equation 2.5) predicts the "most stable" (Marmur) equilibrium CA for a given surface. However, on rough surfaces, the actual CA may deviate from the value predicted by Wenzel wetting. As an outcome of CA hysteresis, it is often impossible to experimentally determine Wenzel's CA for a given surface. Qualitatively, Wenzel's model predicts the following trend: with an increasing roughness, a hydrophilic surface should become more hydrophilic.

Moreover, the contact angle can be related to Young's equation [34]. The Young's equation clarify that after a liquid droplet is applied on a solid surface, the balance between the cohesive force in the liquid and the adhesive force between the solid and the liquid control the contact angle of the droplet.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \qquad (2.6)$$

Where $\qquad \gamma_{SV}$ = the surface tension of solid-vapor surface

$\qquad\qquad \gamma_{SL}$ = the surface tension of solid-liquid surface

$\qquad\qquad \gamma_{LV}$ = the surface tension of liquid-vapor surface

$\qquad\qquad \theta$ = the contact angle (CA)
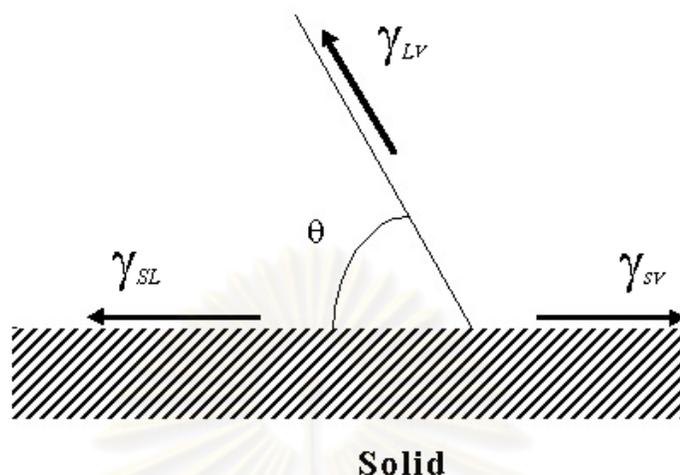
Figure 2.1   Schematic of a sessile drop on a surface [35].

2.2.2.2 Definition of hydrophilicity

In general, hydrophilic surface with a CA less than 5° can be realized through a three-dimensional or two-dimensional capillary effect on hydrophilic surface [33]. On the other hand, hydrophobic surfaces with a water contact angle (CA) greater than 150° can be obtained by controlling the topography of hydrophobic surface. In the Wenzel case, the liquid completely fills the grooves of the rough surface whereas they contact, the surface roughness dramatically enhances the CA on the hydrophobic surface but decrease the CA on the hydrophilic surface owing to the capillary effect.

2.3 Dip-coating technique for thin film fabrication

A batch dip coating process is generally divided into five steps: immersion, start-up, deposition, evaporation and drainage (See in figure 2.2) [36]. The process involves immersing a substrate into a reservoir of solution for some time thereby ensuring that the substrate is completely wetted and then withdrawing the substrate from the solution bath. After the solvent is evaporated, a uniform solid film is deposited upon the surface of the

substrate. The liquid film formation is achieved by 2 major forces, i.e. gravity draining of liquid solution and evaporation of solvent.

(a) immersion   (b) start-up   (c) deposition

(d) evaporation   (e) drainage
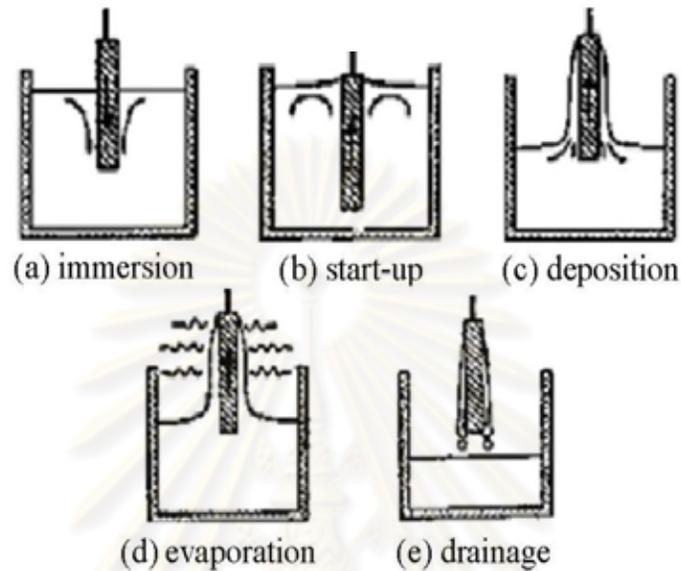
Figure 2.2   Fabrication stages of the dip coating process: (a) immersion,(b) start up, (c) deposition, (d) evaporation and (e) drainage [34]

A dip coating model was base purely on the hydrodynamics of a Newtonian fluid flow, ignoring solvent evaporation. This model considered a case of low viscosity of an infinite moving plate and relatively large liquid container. The liquid surface is divided into two independent regions.

(i) Surface situated high above the meniscus and directly dragged by the plate, where the surface of liquid may be taken to be nearly parallel to the plate surface.

(ii) The meniscus of liquid, which is slightly deformed by the motion of the plate. By using the classical lubrication equations, a matching condition for the film entrainment and used to obtain an expression for the film thickness as shown in equation.

$$h_0 = 0.944 \frac{(\eta u_0)^{(2/3)}}{\sigma^{(1/6)}(\rho g)^{(1/2)}} \quad\quad\quad (2.7)$$

Where
h_0 = the limiting film thickness

u_0 = the withdrawal speed (WS)

η = the solution viscosity

ρ = the solution density

σ = the solution surface tension

Dip coating process is a simple method for depositing a thin film of solution onto a plate, cylinder, or irregular shaped object, easy to maintain, low cost and uncomplicated equipment. On the other hand, the disadvantages of the dip coating are the difficult to prepare non-planar substrate because the film thickness will not be homogeneous. And, it has to use a long time for processing and requirement of treatment of waste coating solution [34]. The process of dip coater involves immersing and withdrawal speed of substrates into a reservoir of solution (Figure 2.3).

In this thesis, an originally made dip coating with adjustable withdrawal speed and immersed time is employed.

The technical data are as follow dimensions (W×L×H) = 15cm×15cm×25cm, withdrawal speed = 3.0-9.0 cm/min, immersed time = 0.5-90.0 min, power supply = 12V.

Figure 2.3   Dip coater machine (CEPT, CU)

2.4 Characterization of ZnO incorporated with PET films

PET films containing ZnO were characterized by UV-Vis spectrophotometer (UV-VIS-NIR; UV3150; SHIMADZU) using for optical transmittance of the films and investigation the element on the surface. The morphology of the films was also observed by Field Emission Scanning Electron Microscopy (FE-SEM; JSM7600F; JEOL). Atomic Force Microscopy (AFM; Veeco, Scanning Probe Microscopy Controller) was obtained grain size, morphology and surface roughness. And, the viscosity of polymer solutions for fabrication polyelectrolyte was measured by Rheometer (Rheostress 600; Haake). The reaction between polycation with polyanion and polymer with ZnO on the films by analyzing the chemical bonding and molecular structures were analyzed by Fourier transform infrared spectroscopy (FTIR; FT/IR6200 JASCO).   In addition, Energy

dispersive X-ray spectrometer (EDX-600HS; SHIMADZU) used for chemical characterization of the samples where as thickness and surface roughness were measured by confocal laser scanning microscope (CLSM; LEXT 3D MEASURING LASER MICROSCOPE CLS-4000; OLYMPUS). To characterization the hydrophilicity of the films, they were irradiated by a certain wavelength light before obtaining by water contact angle measurement.

2.4.1 Rheometer [36]

The viscosity of polymer concentrations was measured by rheometer. It was used for those fluids having a great value of viscosity and requires more parameters to be set and measure. The samples were placed on horizontal plate and a shallow cone placed into it. The gap between the surface of the cone and the plate is 1 mm. The cone and plate rheometer were also operated in an oscillating mode in combined rotational mode to measure viscosity of polymers that represent to Eta in the unit of Pa·s. In the case of the polymer occur crosslinking, the analyzed data could show the value of G''. On the other hand, the G' would be found if the sample is not crosslinked.
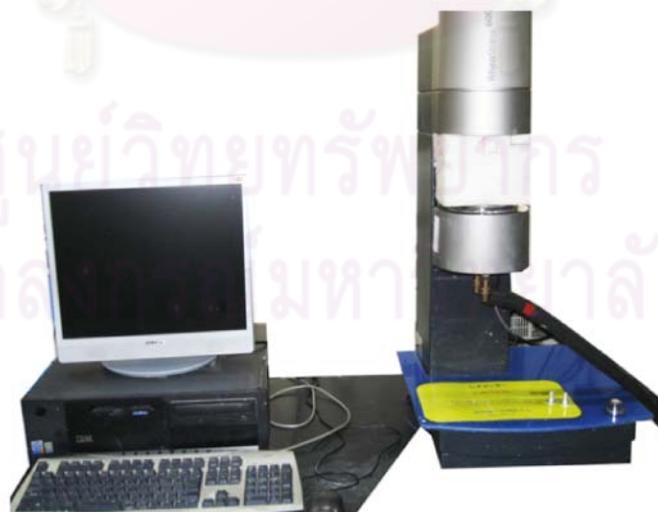
Figure 2.4   Rheometer (Rheostress 600; Haake)

2.4.2 UV - Vis spectrophotometer

The optical transmittance of PET films incorporated with ZnO was characterized by UV-Vis spectrophotometer which compared with the uncoated substrate that had already been cleaned. UV-Vis spectrophotometer measured the intensity of the light passing through a sample (I), and compared with the the incident light at a given wavelength (I_0) before it passed through the sample. The ratio of I/I0 is called the transmittance, and is usually expressed on % T. However, it relations with the absorbance that can be explained by the equation: $A = -\log(\frac{\%T}{100\%})$. The wavelengths of absorption peaks can be correlated with the optical band gap of element which is determined by the second derivative spectrum [37]. Therefore, the samples were also investigated the element on the surface by detecting the absorption band using UV-VIS spectrophotometer.
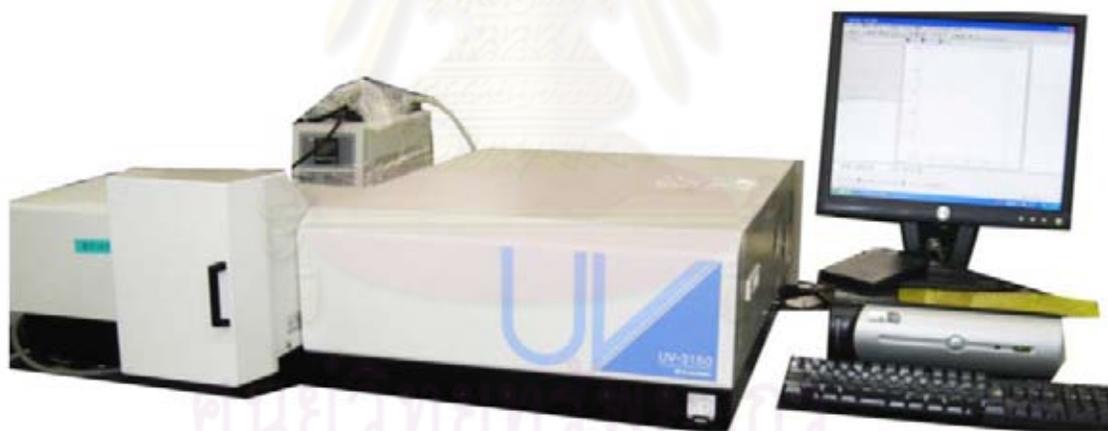
Figure 2.5   UV-Vis spectrophotometer (UV-VIS-NIR; UV3150; SHIMADZU)

2.4.3 Confocal Laser Scanning Microscope (CLSM or LSCM)

Film thicknesses were obtained by confocal laser scanning microscope with depth selectivity using the high resolution optical image [38]. The laser beam passed through a light source aperture and then was focused by an objective lens into a small area on the edge of film. Scattered and reflected laser light from the illuminated spot was then re-collected by the objective lens. After passing a pinhole, the light intensity was detected by a photodetection device, transforming the light signal into an electrical one that was recorded by a computer. The film thicknesses were evaluated by comparison between the light intensity of substrate and the coated area wherein, the surface roughness were considered the different of intensity of light in the each points on the surface of film.

Figure 2.6   Confocal Laser Microscope
(CLSM; LEXT 3D MEASURING LASER MICROSCOPE CLS-4000; OLYMPUS)

2.4.4 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to obtain the reaction between polycation with polyanion and polymer with ZnO on the films by analyzing the chemical bonding and molecular structures. The sample solutions were coated on the quartz SiO_2 as same as the condition to prepare the films on glass substrates. The coated

samples were set on the sample holder in the nitrogen atmosphere. The samples were exposed to infrared radiation and then, they absorbed the radiation at frequencies that match their vibration modes [39]. The detector was measured the radiation absorption as a function of frequency produces a spectrum which can be considered to indentify functional groups and compounds.

Figure 2.7   Fourier transform infrared spectroscopy (FTIR; FT/IR6200 JASCO)

2.4.5 Field Emission Scanning Electron Microscope (FE-SEM)

Field Emission Scanning Electron Microscope was used for observation morphology of ZnO embedded in PET films. And, it was also used for analyzation the chemical compositions on the surface. The samples were prepared by scratching and breaking in the appropriate size to fit in the specimen chamber. They were dried in the oven at 60°C for 1 day. And then, the dried samples were coated with an ultrathin coating osmium for 10 nm that is electrically-conducting material. After that, they were placed into the sample stub and scanning by the electron beam. The signal output was observed in the standard detection mode such as secondary electron imaging or SEI and back-scattered electrons BSE or COMPO mode [40]. The SEI mode is displayed as a two-dimensional intensity distribution that can be viewed and photographed on an analogue video display, or subjected to analog-to-digital conversion and saved as digital

image. BSE or COMPO mode consists of high-energy electrons originating in the electron beam, which are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms. Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image. BSE were used to detect contrast between areas with different chemical compositions.

Figure 2.8   Field Emission Scanning Electron Microscope
(FE-SEM; JSM7600F; JEOL)

2.4.6 Energy Dispersive X-ray spectroscopy (EDX) [41]

The elemental analysis or chemical characterization of the PET films containing ZnO was analyzed by energy dispersive X - ray spectrometer that connects with FE-SEM. The EDX systems are most typically observed on SEM image which exhibited characteristic of the particular element and indicated the element that presented under the electron probe.   This is achieved by creative index of X-rays that collected from a particular spot on the specimen surface which is known as a spectrum.

2.4.7 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) was used for observation the morphology, grain size and roughness of the ZnO embedded in the PET films. The samples were scratched and broken at the suitable area and then, placed on the stub. And then, the microscale cantilever with a sharp tip (probe) at its end used to scan the surface of sample. A tip was used for closeness of the surface; forces between the tip and the sample keep on a deflection of the cantilever.

Figure 2.9   Atomic Force Microscopy
(AFM; Veeco, Scanning Probe Microscopy Controller)

2.4.8 Contact angle measurement

The hydrophilic property of PET films containing ZnO was analyzed by water contact angle using water drop 2 μL on the different five points underlying coated substrate sample. The samples were irradiated by using the UV-A lamp (SAPHIT A.J.L. Supplies, Thailand) with emission wavelength in a range of 300-460 nm and output of 20 watts for a different certain time before classification their property by water contact angle measurement.

Figure 2.10   Contact angle measurement

CHAPTER III

EXPERIMENTAL

3.1 Raw materials

3.1.1 Poly (allylamine hydrochloride) (MW = 70,000, PAH, Aldrich) was used as a polycation to fabricate PET film

3.1.2 Poly (acrylic acid) (35 wt% in H_2O, MW = 100,000, PAA, Aldrich) was used as a polyaninon to fabricate PET film

3.1.3 Hydrochloric acid (35.0-37.0 wt%, cica-reagent, MW = 36.5, HCl, KANTO CHEMICAL CO., INC) was used for the creation of surface roughness.

3.1.4 Zinc oxide (95.0% purity, MW = 81.39, Particle size 0.02μm, ZnO, Wako Pure Chemical Industries, Ltd.) was used for preparation of suspension of ZnO in PAA.

3.1.5 Zinc acetate dihydrate (99.0% purity, cica-reagent, MW = 219.51, Zn $(CH_3COO)_2 \cdot 2H_2O$, KANTO CHEMICAL CO., INC) was used as a starting material in sol-gel method.

3.1.6 Absolute ethanol (99.99% purity, MW = 46.07, CH_3CH_2OH, Merck) was used as a solvent for preparation of sol-gel ZnO and using for cleaning glass substrates.

3.17 Acetone (MW=58.08, $(CH_3)_2CO$, KANTO CHEMICAL CO., INC) was used for cleaning glass substrates.

3.1.8 Acetic acid (99.7% purity, cica-reagent, MW = 60.05, CH_3COOH, KANTO CHEMICAL CO., INC) was used as a stabilizer for preparation of sol-gel ZnO method.

3.1.9 Zinc nitrate hexahydrate (99.0% purity, MW = 297.49, $Zn(NO_3)_2 \cdot 6H_2O$) was used as a material for precipitation method.

3.1.10 Ammonia water (25%, 25.0-27.9% purity, NH_3 = 17.03, Wako Pure Chemical Industries, Ltd.) was used for preparation of ammonium hydroxide as a solvent for precipitation ZnO method.

3.2 Experimental procedures

Deposition of polyelectrolyte (PET) film on glass substrate

Prior to PET film formation, all glass substrates (2.5cm×3.0cm×0.1cm) were ultrasonically cleaned in deionized water (DI-water), ethanol and acetone, respectively.

Fabrication of the PET film was prepared by using a dip coater and LbL technique which was modified from procedures of Nimittrakoolchai and Supothina [3].

3.2.1 The PET film was assembled by dipping the cleaned substrate in 0.02 M PAH aqueous solutions as a polycation with withdrawal speed (WS) 3.0 cm/min for 15 min.

3.2.2 Next layer was coated with polyanion solution as 0.02 M PAA using dip coating technique with WS 3.0 cm/min about 15 min. The polycation monolayer assembles with that of polyanion is called a bilayer coating film.

3.2.3 The same process was repeated by changing the concentration of PAH and PAA, withdrawal speed (WS) and the number of polyelectrolyte layers following to the conditions as shown in Table 3.1-3.3.

In this section, the experiment was investigate the optimal condition to prepare the sufficient PET film for coating ZnO which was selected as it gave the transparency, thickness and surface roughness of the samples. And then, the suitable PET film was coated ZnO by using different methods.

Part A: **Investigation effect of polymer concentration, withdrawal speed, and number of dipping cycle on the transparency and film thickness of the preparation of PET film**

Table 3.1 **Parameters for preparation of the 1st layer of PET film to study effect of polymer concentration**

Conditions	PAH and PAA concentration (M)	Number of coating bilayer	Properties
1	0.02	1	Transparency and Thickness
2	0.20	1	Transparency and Thickness
3	0.50	1	Transparency and Thickness
4	1.00	1	Transparency and Thickness
5	2.00	1	Transparency and Thickness

Table 3.2 Parameters for preparation of the bilayer PET film to study effect of withdrawal speed at the suitable concentration as as result from experiment in Table 3.1

Conditions	PAH and PAA concentration (M)	Withdrawal speed (WS) (cm/min)	Number of coating bilayer	Properties
1	X_1	3	1	Transparency and Thickness
		6		
		9		
2	X_2	3	1	Transparency and Thickness
		6		
		9		

Whereas, both of X_1 and X_2 were the suitable concentrations for fabrication the bilayer PET film as the result in part A. The appropriate concentrations were considered with transparency and thickness of the PET film.

Table 3.3 **Parameters for controlling surface roughness and thickness of PET film to study effect of the number of dipping on desired surface roughness and thickness of PET film**

Condition	PAH and PAA Concentration (M)	Number of coating bilayer	Properties
1	X	1	Thickness, Grain size and Roughness
		2	
		3	

Where X was the appropriate concentration for preparation polyelectrolyte film and gave higher thickness and smooth surface as a result from experimental in Table 3.2.

3.3 Analytical instruments used

3.3.1 The viscosity of polymer solutions for fabrication polyelectrolyte was measured by Rheometer (Rheostress 600; Haake)

3.3.2 The transmittance spectra of the PET films were analyzed by UV-Vis spectrophotometer (UV-VIS-NIR; UV3150; SHIMADZU).

3.3.3 The film thickness and surface roughness of PET films were measured by confocal laser scanning microscope (CLSM; LEXT 3D MEASURING LASER MICROSCOPE CLS-4000; OLYMPUS).

3.3.4 The grain size and surface roughness of PET films was observed by atomic force microscopy (AFM; Veeco, Scanning Probe Microscopy Controller).

Part B: **Investigation an appropriate methodology for deposition ZnO on photoinduced hydrophilic properties of ZnO incorporated with PET film**

PET film was deposited ZnO by using 3 methods to examine the method that exhibit the best hydrophilic property after UV irradiation at the certain time. The methods were suspension of ZnO in the polymer, sol-gel ZnO and precipitation method.

Method 1: **Preparation of ZnO on the PET film with precipitation method using a dip coater which was modified from technique of Wang [10]**

The PET film on glass substrate was respectively dipped in freshly prepared Zn $(NO_3)_2$ solution and NH_4OH solution (0.01 M) for 15 min which the schematic diagram of the formation of the ZnO nanocrystals was shown in Figure 3.1. This process was repeated every 20 min. Then, the modified film was dried at 180°C for 2 h. The procedure resulted in the fabrication of the multilayer films containing ZnO nanoparticles. There were various numbers of precipitation reaction cycles.
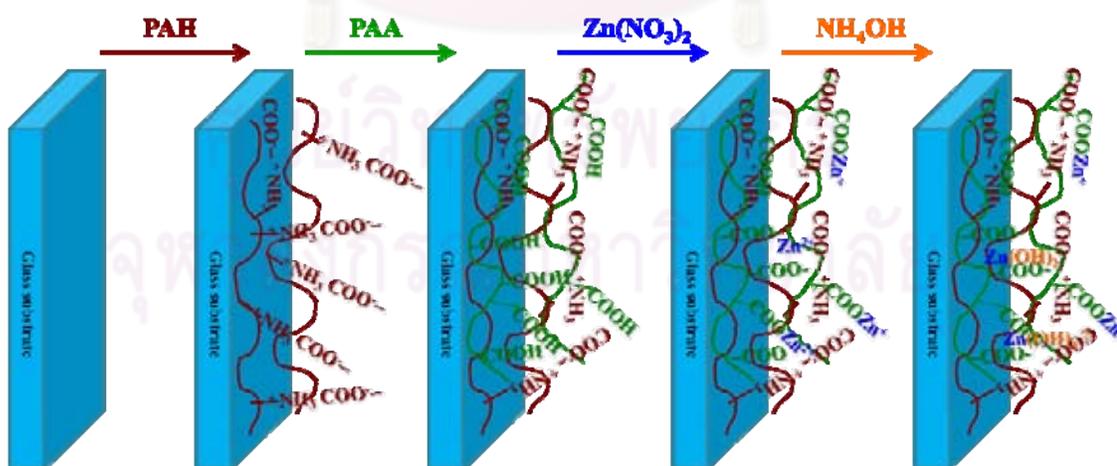
Figure 3.1 Schematic diagram of formation of ZnO nanocrystals.

Method 2: **Preparation of ZnO on the PET film by suspension of ZnO in polymer method using a dip coater which was modified from procedures of Nimittrakoolchai and Supothina [3].**

The PET film was modified surface roughness to create and open porosity or roughness on the surface. The sample was treated by a two-step chemical etching using HCl solutions having pH of 2.3 and 1.1, respectively for various immersion times (15, 30, 60 and 90 min). Then, ZnO nanoparticle having particle size of 20 nm were deposited on the dried PET film by dipping it into a suspension of ZnO in polymer as PAH or PAA. The ZnO suspensions were prepared by ultrasonically mixing ZnO in PAH or PAA with different content of ZnO in between 0.1-0.2 wt%. Finally, the ZnO incorporated with PET film was dried at 180°C for 2 h.

Method 3: **Preparation of ZnO on the PET film by sol-gel ZnO method using a dip coater which was modified from technique of Numpud [35]**

The step for deposition sol-gel ZnO on PET film was shown in Figure 3.2 which was prepared by dissolving zinc acetate in 50 mL ethanol at room temperature. The concentration of zinc acetate was studied at 0.1 M as the optimal condition in the Numpud research for preparing sol-gel ZnO. The solution was dried at 60 °C with magnetic stirring at 300 rpm for 30 min. Deionizied water and acetic acid were respectively added to the mixture solution. The acetic acid was used for adjusted pH of solution and stabilizer. The pH of solution was varied from 1 to 5 by adding acetic acid in between heat and stir until a transparent and homogeneous solution was obtained. After that, the PET films were immersed in the sol-gel solution with withdrawal speed 3 cm/min for 30 sec. The coated substrates were calcined at 500°C for 1 h with heating rate 1 °C/ min.

Figure 3.2   Preparation of sol-gel ZnO.

3.4 Characterization methods used

3.4.2 The viscosity of polymer solutions for fabrication polyelectrolyte was measured by Rheometer (Rheostress 600; Haake).

3.4.3 The optical transmittance spectra of the ZnO incorporated with PET films was analyzed by UV-Vis spectrophotometer (UV-VIS-NIR; UV3150; SHIMADZU) in the wavelength of 300-800 nm.

3.4.4 The film thickness and surface roughness of the ZnO incorporated with PET films were measured by confocal laser scanning microscope (CLSM; LEXT 3D MEASURING LASER MICROSCOPE CLS-4000; OLYMPUS).

3.4.5 The grain size of ZnO incorporated with PET films was observed by atomic force microscopy (AFM; Veeco, Scanning Probe Microscopy Controller).

3.4.6 The morphology and grain size of ZnO incorporated with PET films was obtained with field emission scanning electron microscope (FE-SEM; JSM5410V; JEOL).

3.4.7 The reaction between polycation with polyanion and polymer with ZnO on the films by analyzing the chemical bonding and molecular structures were investigated by Fourier transform infrared spectroscopy (FTIR; FT/IR6200 JASCO).

3.4.8 The elemental analysis of the ZnO incorporated with PET films was analyzed by energy dispersive X-ray spectrometer (EDX; EDX-600HS; SHIMADZU).

3.4.9 The hydrophilic property of ZnO incorporated with PET films was measured by water contact angle measurement.

CHAPTER IV

RESULTS AND DISCUSSION

Investigation on deposition of ZnO in polyelectrolyte (PET) film on glass substrates was divided into 2 steps, which were preparation of PET film on glass substrate and deposition ZnO in PET films by 3 different methods. The preparation of PET film by the dip coating technique was examined for the suitable conditions to fabricate stable film with smooth surface. Polymer concentration, withdrawal speed (WS) and number of dipping cycle was considered. Stable PET film was subjected to ZnO by the 3 different methods, namely precipitation method, suspension of ZnO in PAA, and sol-gel ZnO method for comparison of the most suitable alternative.

Part A: **Effect of polymer concentration, withdrawal speed (WS), and number of dipping cycle**

The fabrication of thickness behavior of weak polyelectrolyte was studied by Shiratori and Rubner [42]. They discussed about the effect of pH of polymer solution on thickness of polyelectrolyte film. The incremental thickness relates to the individual polycation (PAH) and polyanion (PAA) layers and highly sensitive to pH of dipping solution. Either an increase or a decrease in charge density of polyelectrolyte could affect the polycation or polyanion film thickness in a range of 5 to 80 Å regarding to the control of the pH of polyelectrolyte solution. For that reason, in this work, pH of polyelectrolyte solution was adjusted using 1.0 M HCl in order to control of charge density on each coating layer. pH of PAH and PAA was adjusted to find out a suitable condition to fabricate a bilayer PET film. Based on our preliminary experiments PAH layer was prepared in prior to dipping into PAH solution at pH 1.5 which could provide a stable bilayer film on glass substrate.

4.1 Effect of polymer concentration

Preparation of PET film was prepared using various concentration of PAH and PAA with the aim of investigation effect of polymer concentration on film characteristics. Both of PAH and PAA concentration was in the range of 0.02 to 2.00M. Confocal laser scanning microscope (CLSM) was employed to characterize thickness of fabricated film after drying operation at the temperature of 180°C. The films produced from various polymer concentrations show a considerable difference in the thickness as shown in Figure 4.1. The film thickness, represented by root mean square (RMS), was estimated to be 1.701, 1.916, 2.364, 2.698, and 2.897 μm for 0.02, 0.20, 0.50, 1.00, and 2.00 M, respectively. This indicates a strong influence of the polymer concentration on the film thickness because a higher concentration of polymer solution could provide the higher film thickness. It can be concluded that 2.0 M PAH/PAA at a constant withdrawal speed (WS) of 3 cm/min is suitable for fabricating PET film.
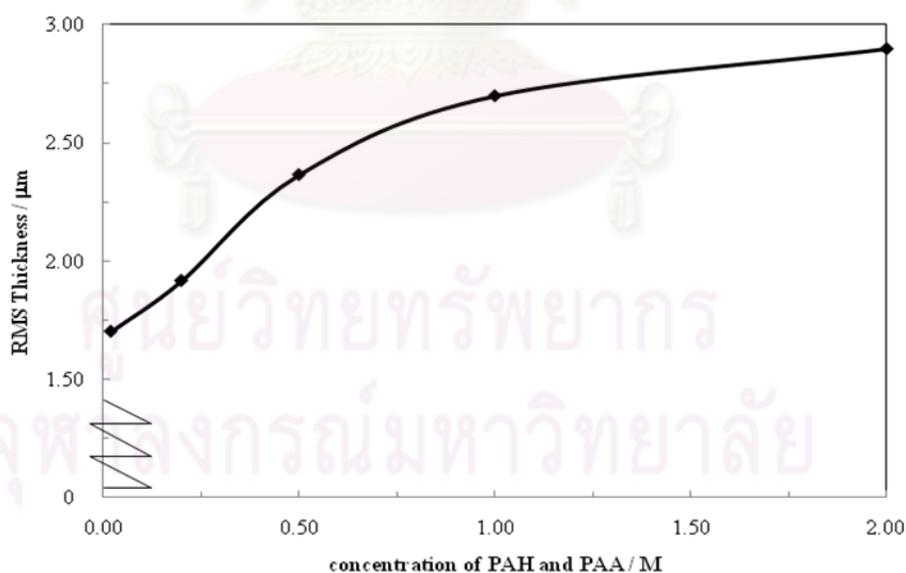
Figure 4.1   Film thicknesses as a function of polymer concentration of PAH and PAA in a range of 0.02-2.00 M

It would be noted that, the solution concentration is also related to the solution viscosity. The viscosity of PAH and PAA was characterized by a rheometer at room temperature. The incremental viscosity of the polymer solution depends on the increased polymer concentration as summarized in Table 4.1. The incremental film thickness as the solution concentration was increased; would be described to the increased amount of liquid attracting on the dipped glass substrate. The thickness dependency on the solution viscosity was also reported by Yimsiri and Mackley [35]. They discussed experimental observation on spin and dip coating of light-emitting polymer (LEP) solution. It was found that film thickness was essential dependent on the combined effect of viscosity and concentration. The amount of the liquid moving upwards with the substrate at the same withdrawal speed is larger for a more viscous liquid due to the drag force (ηu_0) is proportional to the effect of solution viscosity on the film thickness where η is a polymer solution viscosity and u_0 is the solvent evaporation rate.

Table 4.1   Viscosity of PAH and PAA at different concentration

Concentration of PAH (M)	Viscosity (cP)
0.02	1.16
0.20	3.71
0.50	10.57
1.00	10.93
2.00	35.23

Concentration of PAA (M)	Viscosity (cP)
0.02	0.95
0.20	1.18
0.50	1.80
1.00	1.90
2.00	11.33

In term of optical property, a transparent film prepared from polymer concentration in a range of 0.02-2.0 M was examined by UV-VIS in the wavelength of 300-800 nm as shown in Table 4.2. It was found that the average transmittances of the various polymer concentrations coated on glass substrates that prepared by WS 3 cm/min and dried temperature of 180 degree are higher than 95 %. However, the optical transmittances slightly decreased while the concentration increased.

Table 4.2   Summary of optical transmittance of PET film prepared with different concentration of PAH/PAA at withdrawal speed of 3.0 cm/min and dried temperature at 180°C

PAH/PAA concentration (M)	Average transmittance (%) (300-800 nm) (Ref. = glass)
0.02	99.9
0.20	99.6
0.50	98.8
1.00	98.9
2.00	95.8

4.2 Effect of withdrawal speed

From the previous experiment, it was found that the polymer concentrations insignificantly effect on the film transparency then, the withdrawal speed of dip coater was further investigated to expose whatever it was possible to improve the thin film transparency. The fabrication of PET films at the polymer concentration of 1.0 M and 2.0 M (as a result shown in the effect of polymer concentration on film thickness) and drying temperature at 180°C were fabricated with a various withdrawal speed in the range of 3.0-9.0 cm/min. Then, the roughness surface of the fabricated film was

observed by atomic force microscopic (AFM) as shown in Figure 4.2. It exhibits worm-like appearance.
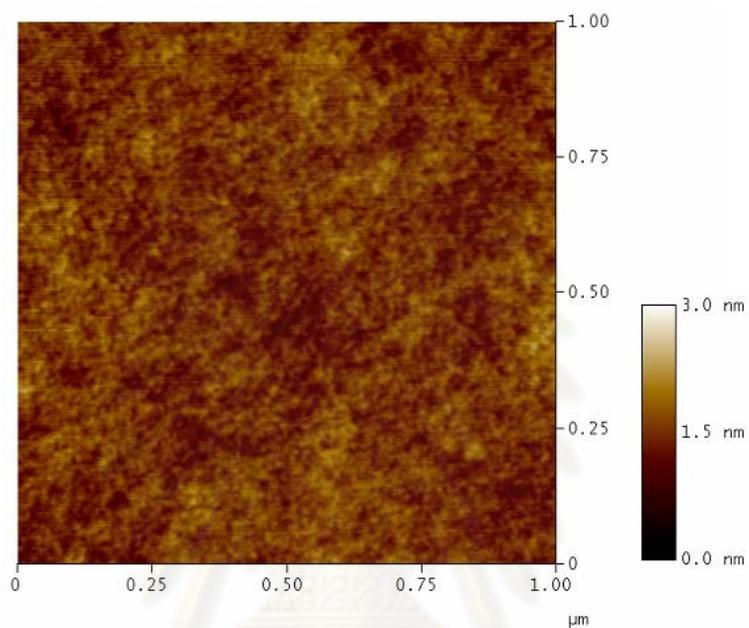
Figure 4.2   AFM topographical image of polyelectrolyte film as prepared by 2.0 M
PAH/PAA at withdrawal speed of 3 cm/min and drying temperature of
180°C

Table 4.3   Summary of optical transmittance of PET film prepared with 1.0 and
2.0 M PAH/ PAA coated at different withdrawal speed of 3.0-9.0 cm/min
and drying temperature of 180°C

PAH / PAA concentration (M)	Withdrawal speed (WS) (cm/min)	Average transmittance (%) (300-800 nm) (Ref. = glass)
1.00	3.0	99.2
	6.0	97.4
	9.0	96.8
2.00	3.0	92.1
	6.0	91.5
	9.0	90.9

Based on the analytical results of the optical transmittance, the polyelectrolyte
film prepared by a higher withdrawal speed has lower transparency as shown in Table
4.3. This is due to the fact that a high withdrawal speed yields a thicker film with opaque
appearance. Though, Numpud et al. reported that the optical property of the films
prepared from different withdrawal speeds was insignificantly different, the withdrawal
speed affected the thickness and surface roughness of films [34]. Based on experimental
results of Laudau and Levich, a higher withdrawal speed gives a larger force resulting in
great amount of liquid moving upwards toward the substrate surface and a thicker film is
obtained [43].   The relation between film thickness and withdrawal speed can be
described as a function of withdrawal speed (h), solvent evaporation rate (u_0), $h \propto u_0^x$ (x
as the exponent obtained from the experiment). Therefore, film thickness and surface
roughness of the polyelectrolyte film at different withdrawal speed was determined by
CLSM at the magnification of 20X.

Table 4.4   Film thickness and RMS roughness of PET films determined by CLSM

PAH and PAA concentration (M)	Withdrawal speed (WS) (cm/min)	Film thickness (μm)	RMS roughness (μm)
1.0	3	2.46	0.03
	6	2.46	0.04
	9	2.98	0.07
2.0	3	3.60	0.03
	6	3.64	0.04
	9	3.67	0.06

From the data in Table 4.4, the films prepared from 1.0 M and 2.0 M show the thickness ranging from 2.46-3.67 μm. And, the RMS roughness of the film prepared from both concentrations as the withdrawal speed was increased. This trend corresponds to the CLSM image show in Figure 4.3. It was found that the apparent film shows high surface roughness since the increased withdrawal speed. From this result, it can be concluded that at the same withdrawal speed, the polymer concentration affects only the film thickness but not the RMS roughness.

PAH/PAA 1.0 M WS 3 **PAH/PAA 1.0 M WS 6** **PAH/PAA 1.0 M WS 9**

PAH/PAA 2.0 M WS 3 **PAH/PAA 2.0 M WS 6** **PAH/PAA 2.0 M WS 9**
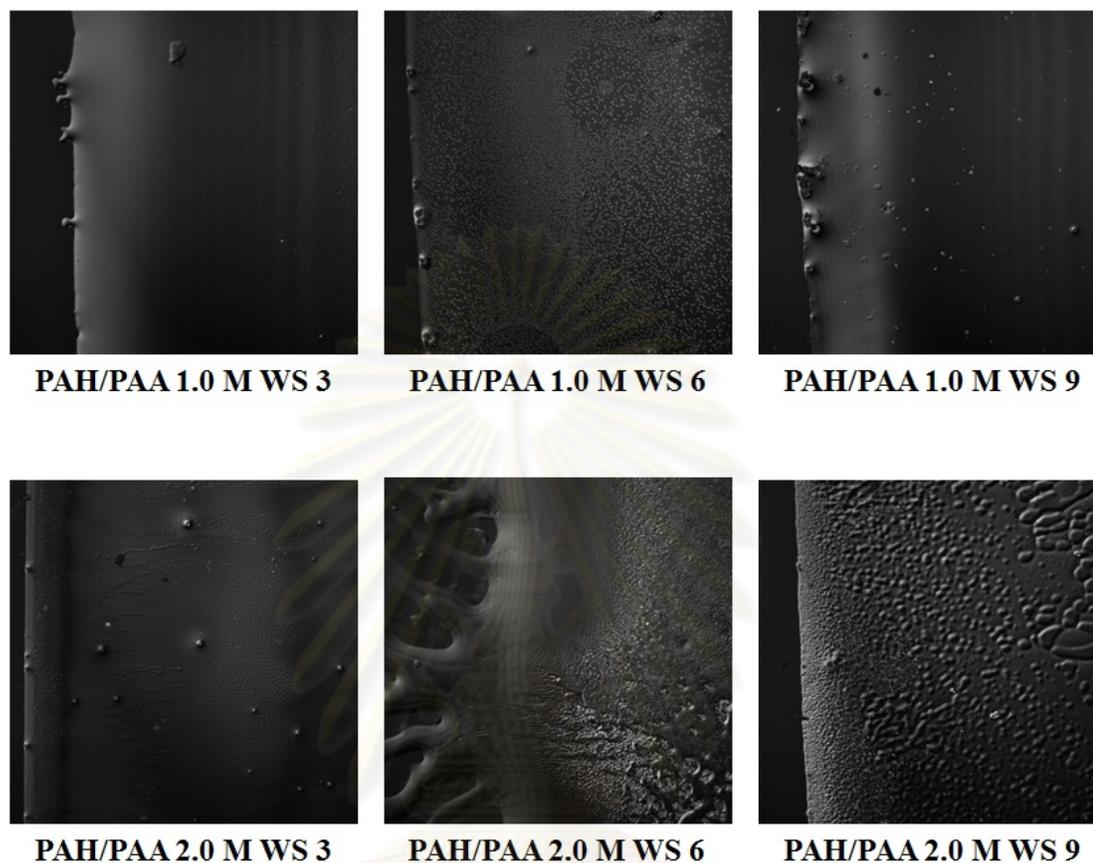
Figure 4.3 Apparent films obtained by confocal laser scanning microscopy (CLSM) observation through polyelectrolyte film on a glass substrate as prepared by different concentration with various withdrawal speeds in a range of 3.0-9.0 cm/min and drying temperature of 180°C

From these results, it was suggested that the film prepared from 2.0 M PAH/PAA with withdrawal speed 3 cm/min gives the proper thickness and fine surface. This concentration and withdrawal speed were chosen for further study affecting the film thickness, surface roughness and film transparency. However, polymer concentration and withdrawal speed of dip coater have exerted slight effects on the thickness and transparency of the film. Many studies have been investigated about the incremental number of dipping cycle influence the thickness and surface roughness of the PET film thickness [3, 44]. Then, the effect of number of layer on the thickness and surface roughness was further investigated.

4.3 Effect of number of dipping cycle on film thickness

Many studies have been investigated on the number of dipping cycles affect the thickness and surface roughness of the PET film thickness [3, 45]. The effect of number of layers on the thickness and surface roughness was investigated in this work. The thickness and surface roughness of polyelectrolyte films coating on glass substrates were analyzed using CLSM. It was found that the single bilayer film prepared by using 2.0 M and WS of 3.0 cm/min exhibited a similar thickness as compared to that of double and triple bilayer films according to the dissolution of the coated film into the dipping solution after repetitive cycles. All number of dipping cycles gives similar surface roughness as evidenced from RMS roughness of 0.03, 0.02 and 0.03 μm for single bilayer, double bilayer and triple bilayers, respectively.
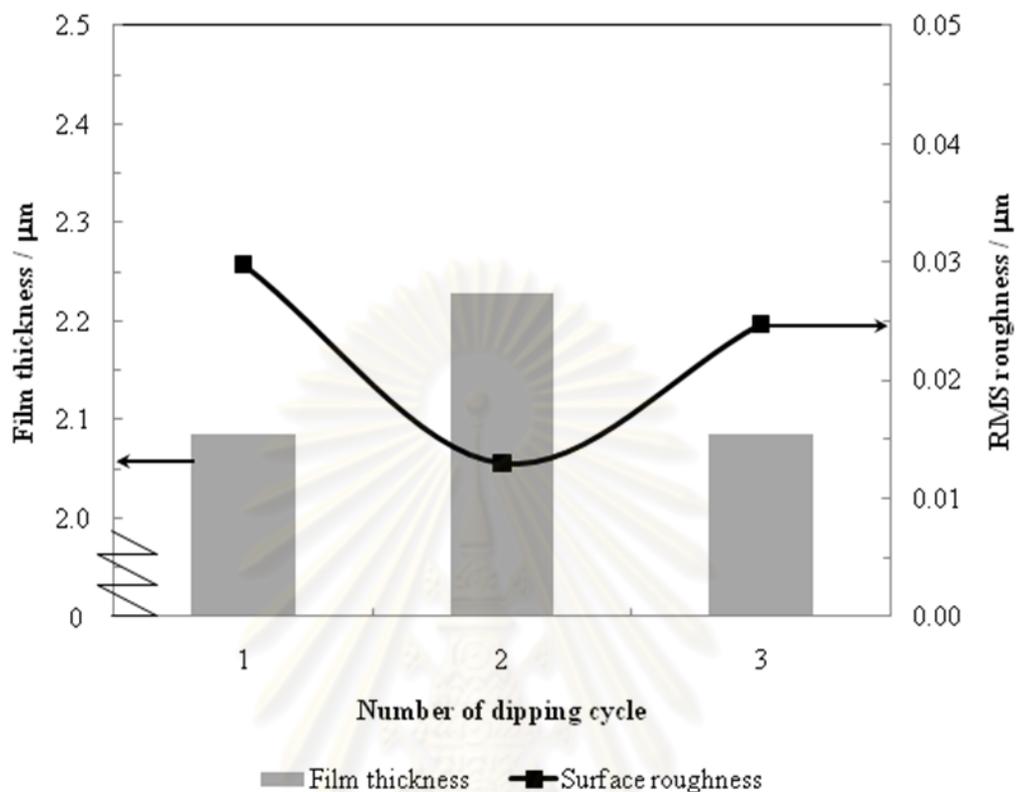
Figure 4.4   A plot of film thickness and surface roughness of PET films vs. number of dipping cycles

Figure 4.4 presents the effect of number of dipping cycle on the film thickness and RMS roughness. The film thickness of single, double, and triple bilayers coating films is 2.086, 2.227, and 2.085 μm, respectively. Interestingly, film thickness is independent to the number of dipping cycles since dipole force between polyelectrolyte film and glass substrate may be lower than viscous force of polymer solution in the step of drainage in the dip coating technique.
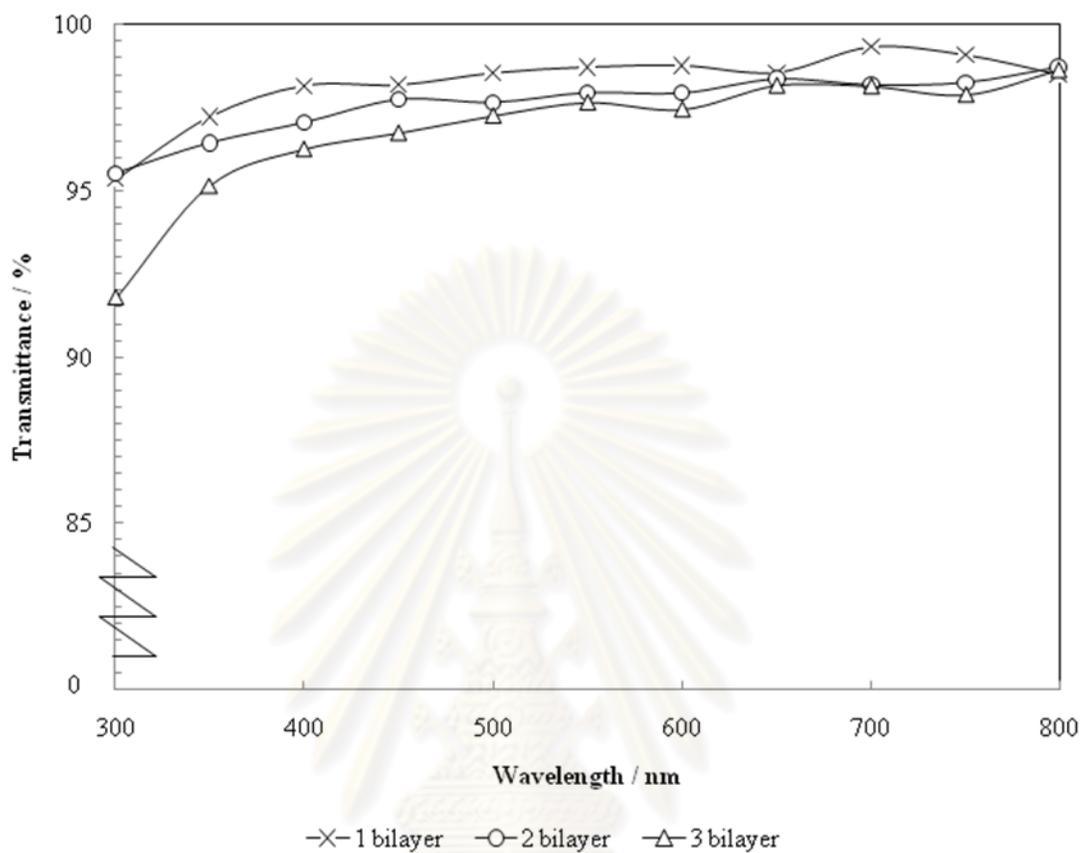
Figure 4.5 Optical transmittance of polyelectrolyte film at different number of dipping cycle such as 1 bilayer, 2 bilayer and 3 bilayer

The optical transmittance spectra of the various polyelectrolyte bilayer films were presented in Figure 4.5. The increased number of dipping cycles hence the lower transmittance of the polyelectrolyte film. These results implied that a single bilayer of polyelectrolyte film prepared by 2.0 M polymer solution with withdrawal speed of 3.0 cm/min was proper for our applications.

Part B: Effect of methodology for depositing ZnO onto the etched PET film

In general, superhydrophilicity of the film surface can be controlled by the surface roughness and surface energy by coating the metal oxides that aids the wetting property of the surface. Among numerous materials, ZnO can be chemically activated by UV light that significantly modified its wettability [7]. ZnO thin film can be deposited by several techniques such as pulsed laser deposition, sputtering, spray pyrolysis, electrodeposition, chemical vapor deposition, molecular beam epitaxy, pulsed laser deposition, metal-organic chemical vapor deposition and sol-gel dip coating technique [9-10, 12, 22, 26, 28, 46-50]. Recently, inorganic semiconductor nanoparticles embedded in polymer matrices have been investigated, since they can be used in optical, electrical, magnetic devices and surface wettability [3, 10, 17]. Moreover, a combination of ZnO and polyelectrolyte film can provide a promising alternative for substrate modification. However the information on the advantages of incorporating ZnO with polyelectrolyte films for a control hydrophilic and hydrophobic property of coated substrates is still limited. Then, ZnO incorporated with polyelectrolyte film was studied by using different method in order to improve transparency and hydrophilicity of the film.

4.4 Precipitation of ZnO into polyelectrolyte film

Wang et al. prepared polymer films by embedding ZnO nanocrystals in multilayer polymer films (PDDA and PSS) using $Zn(NO_3)_2$ and NH_4OH as precursor [9]. It was found that the morphologies of ZnO particles were controlled by a number of precipitation cycles. This approach provides an effective route for construct multilayer film containing ZnO nanoparticles. Modified from Wang et al., film was fabricated by immersing the appropriate polyelectrolyte film from part A into 0.01 M $Zn(NO_3)_2$ solution for 15 min, subsequently dipping into NH_4OH solution (0.01 M) for 30 sec. This process is accounted as one precipitation cycle. The number of cycles was varied in the

range of 1 to 5. The time between each cycle is 20 min. All films were dried at 180°C for 2 h.

Table 4.5   Summary of optical transmittance of ZnO thin films prepared with different number of precipitation cycle at withdrawal speed of 3.0cm/min and dried temperature at 180°C

Number of precipitation cycle	Average transmittance (%) (350-800 nm) (Ref. = glass)
1	99.4
2	99.5
3	95.4
4	86.1
5	97.8

Based on the analytical results of optical transmission, it was observed that the number of precipitation cycles could affect the film transparency as shown in Table 4.5. The decrease in transmittance indicates that more particles nucleate in the polyelectrolyte film with increasing precipitation cycles of Zn^{2+}. However, the film was more transparent when the number of precipitation cycle was increased to 5. This is attributed to the fact that at precipitation cycle higher than 4, Zn^{2+} was dissolved by the ammonium hydroxide in the previous layer. Moreover, the formation of tetrahydroxozincate might be increased as the hydroxyl group increased with an increasing number of precipitation cycle up to 5. These effect resulting in the translucency of the prepared film. However, the film with lower transmittance would contain more quantity of ZnO. The film with a precipitation cycle of 3 and 4 contained higher quantity of ZnO and was selected for further studies.

Table 4.6   Film thickness and RMS roughness of ZnO film at different number of precipitation cycle was observed by CLSM

Number of precipitation cycle	Film thickness (μm)	RMS roughness (μm)
1	2.03	0.048
2	2.39	0.058
3	4.27	0.062
4	4.50	0.076
5	4.57	0.080

The effect of precipitation cycles on the film thickness and surface roughness of ZnO thin film on glass substrates is shown in Table 4.6. The thickness of the prepared film slightly changes from 4.50 to 4.57 μm when the precipitation cycle is increased from 4 to 5. This indicated that the precipitation cycle higher than 4 would not provide a great amount of the deposited film on glass substrate. However, the surface roughness of the fabricated film dramatically increases from 0.048 to 0.080 μm as the number of precipitation increase. Regarding to confirm the surface roughness of the film as prepared by number of precipitation cycles of 3 and 4 (selected by a lower transmittance from previous experiment), the film was observed by AFM as shown in Figure 4.6 and 4.7, respectively.
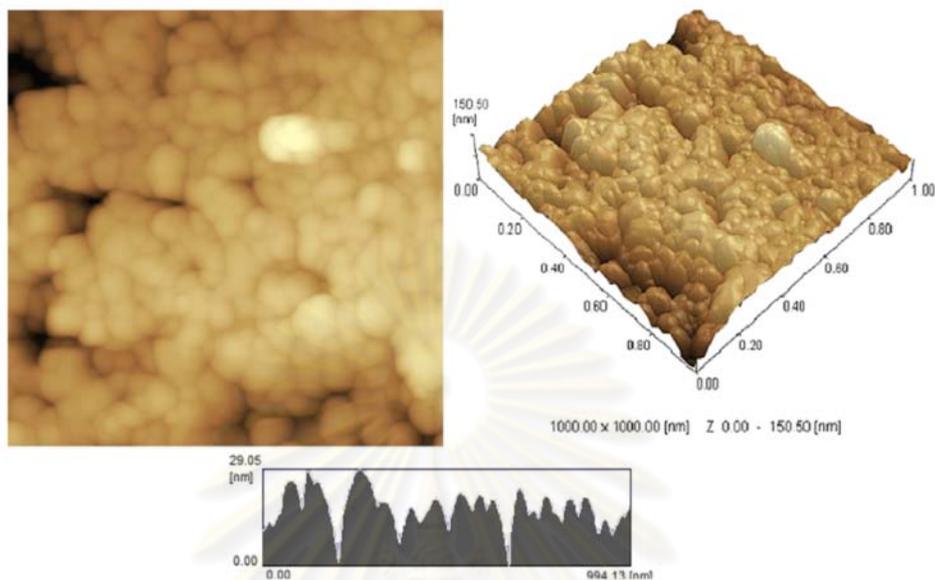
Figure 4.6   2D and 3D topographical (1μm×1μm) of ZnO in PET film prepared by 3
precipitation cycles
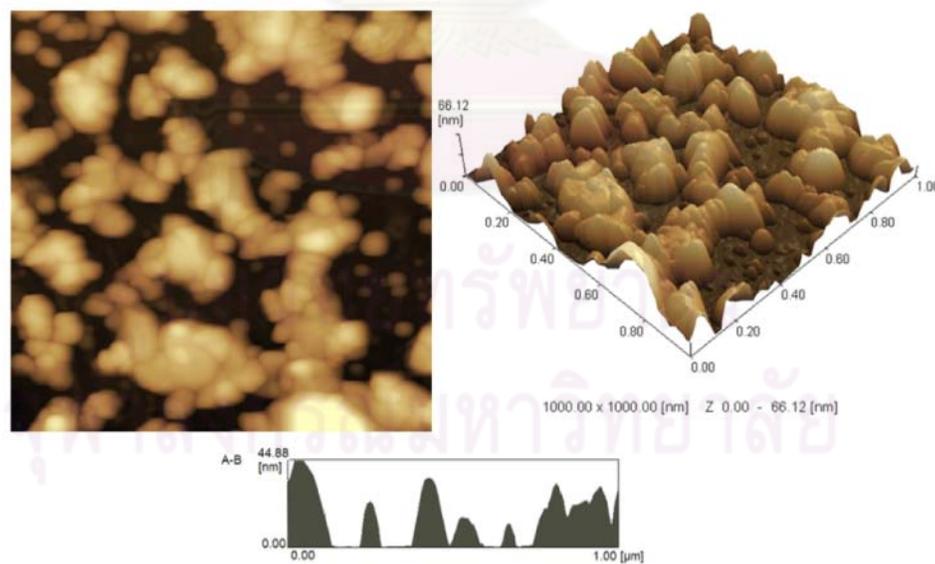
Figure 4.7   2D and 3D topographical (1μm×1μm) of ZnO in PET film prepared by 4
precipitation cycles

It was found that the number of precipitation changing from 3 to 4 cycles resulted in the average grain size increasing from 29.05 to 44.88 nm. The large grain size make possible the agglomeration; leading to high surface roughness. In order to confirm the chemical composition of the fabricated film, energy dispersive X-ray spectroscopic analysis was used for elemental analysis of the prepared films as shown in Figure 4.8.
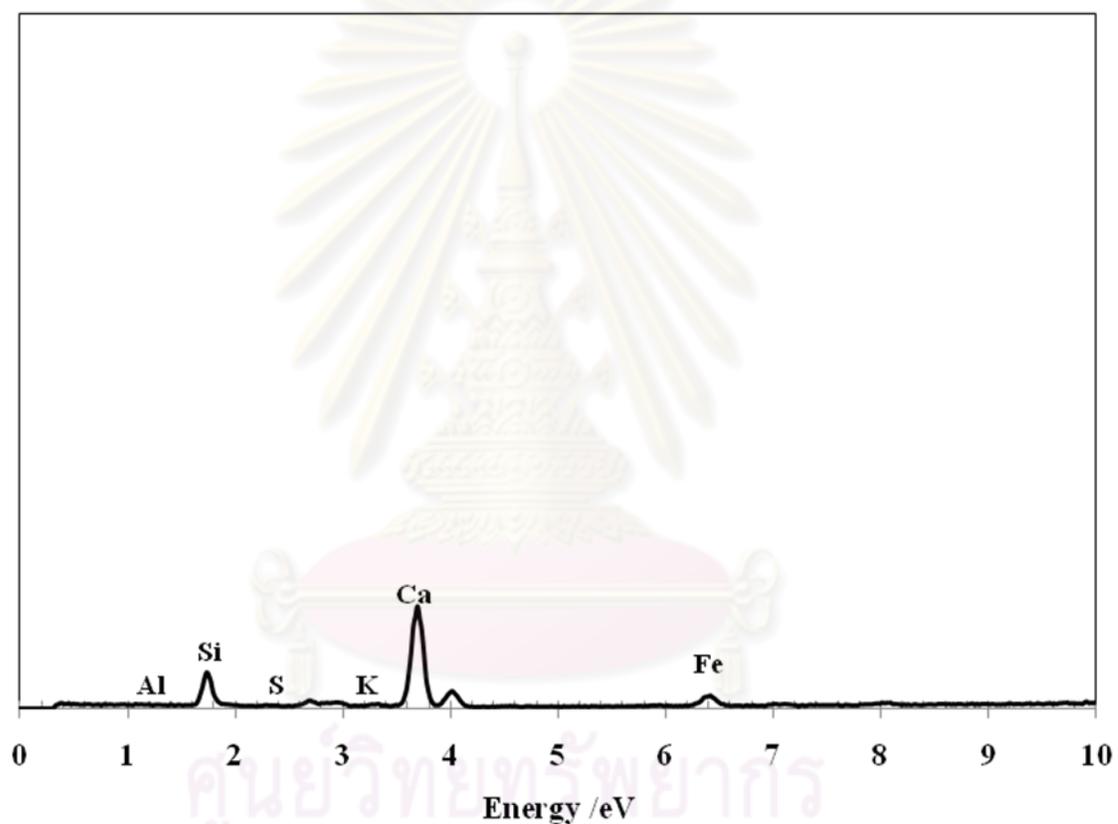
Figure 4.8   EDX analysis of ZnO thin film prepared with 3 precipitation cycles coated at withdrawal speed of 3.0 cm/min and drying temperature at 180°C for 2h

The EDX data of 3 precipitation cycles, ZnO in polyelectrolyte film shows no evidence of Zn, indicating that the film has very low content of Zn. Then, a higher concentration of $Zn(NO_3)_2$ (0.1 M) for precipitation ZnO thin film was used for prepared

ZnO in polyelectrolyte film. It was found that the prepared film exhibits transmittance lower than 60% and showing a peak of Zn in the EDX spectrum as shown in Appendix 1. Additionally, the film crystalline was also analyzed by XRD. The result gave no indication for the characteristic phase of the ZnO as shown in Appendix 3. Therefore, on the basis of EDX and XRD results, it may be concluded that the film was not crystalline and had a very low content of ZnO. As a consequence, there was no further study on the photoinduced hydrophilic properties of the film.

Accordingly, ZnO particles in polyelectrolyte film prepared from precipitation method cannot be obtained by the standard method. Then, we further studied on another method (suspension of ZnO in PAA and sol-gel ZnO) for depositing ZnO in polyelectrolyte film to improve their photoinduced hydrophilic property.
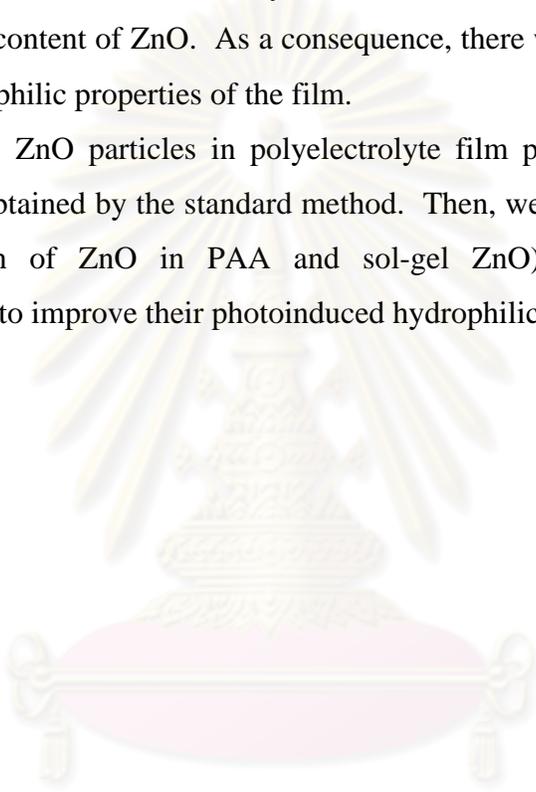
4.5 Suspension of ZnO in PAA

A schematic image of the PET coating film was depicted in Figure 4.9(a). The PAH/PAA coating layers were then subject to a chemical etching process using HCl solutions with pH of 2.3 and 1.1. The increased roughness of a surface can increase its hydrophilicity dramatically and the hydrophobic surface becomes more hydrophobic corresponding to Wenzel state [19, 44].
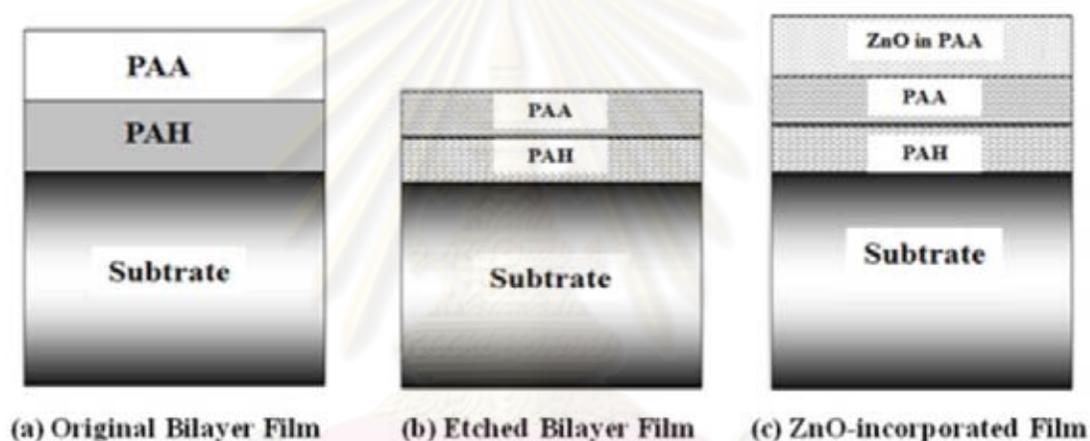
Figure 4.9   Schematic diagram of coating films

Nimitrakoolchai and Supothina studied the deposition of SiO_2 on the etched PAH/PAA (PET) for superhydrophobic films. The desired surface roughness was obtained by acid etching using HCl with pH 2.3 and 1.1 for various immersion times [3]. The results showed that the opposite trend that probably affected the surface chemistry modified after chemical etching. The increased etching time gave the RMS roughness lower than the as-prepared film but the water contact angle was much higher. Therefore, etching time was further investigated to find out whether it was possible improve the hydrophilic property of the surface. Etching time was varied in a range of 15 to 90 min and drying temperature would be set at 180°C for 2 hrs to manipulate the surface

roughness of polyelectrolyte film. The modified surface was coated with suspension of ZnO in PAA. The contents of ZnO in the polymer solution was also investigated to study the effect of the quantity of ZnO on its hydrophilic property

4.5.1 Effect of etching time on the hydrophilicity of the PET film

Comparison of surface roughness of the etched PET film against etching time was shown in Figure 4.10. A different degree of surface roughness of PET film strongly depends on etching time. The etched PET films were subjected to water contact angle analysis. The film thickness and surface roughness in each layer was also measured by CLSM.
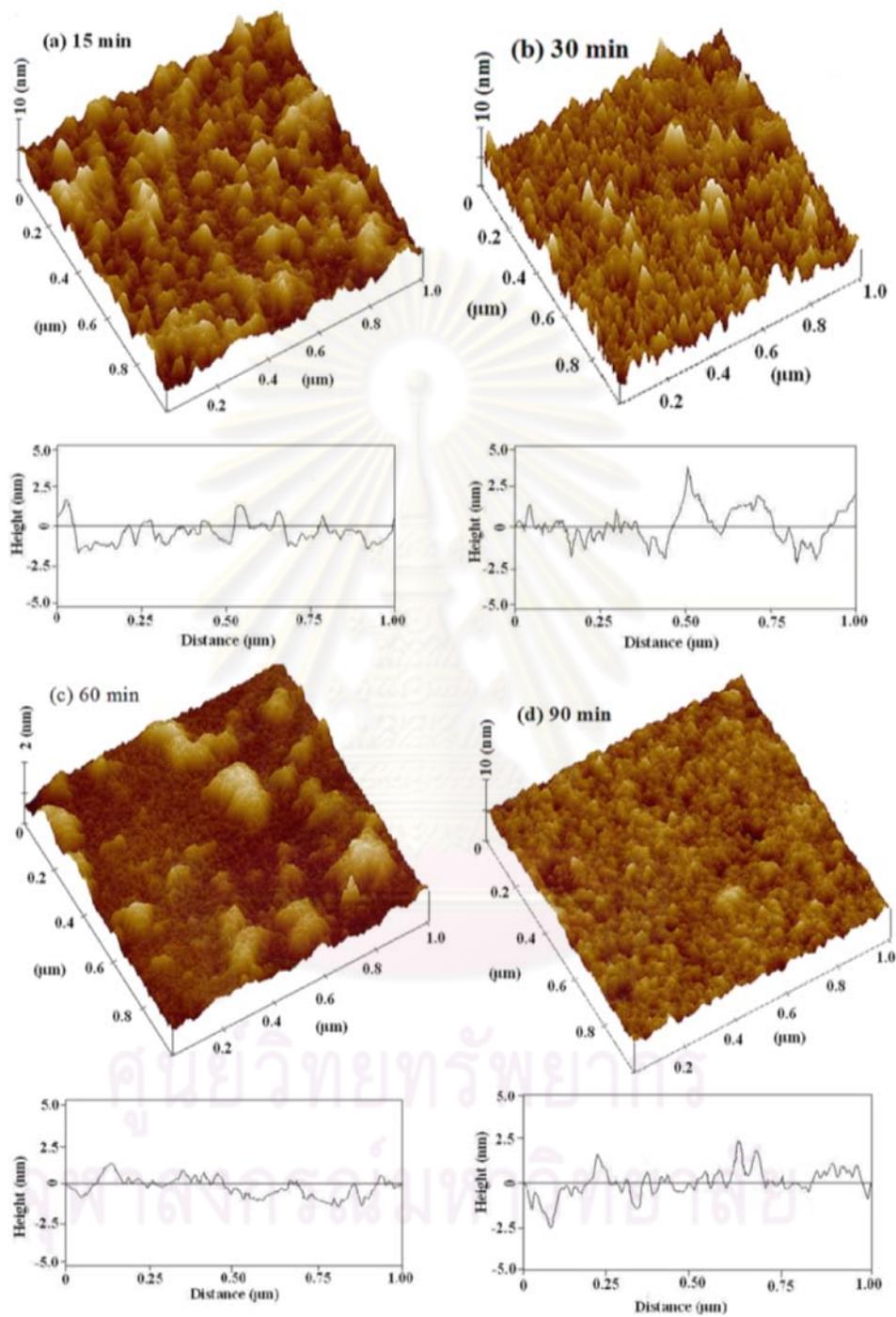
Figure 4.10   2D and 3D topographical images of the PET film etched at different times (a) 15 min, (b) 30 min, (c) 60 min, and (d) 90 min.

Table 4.7   Summary of the water contact angle and surface roughness of each layer

Sample	Contact angle (°)	RMS roughness (nm)
PAH	n/e[*]	0.714
PAA	69.57	0.187
PAH/PAA (PET)	49.47	0.200
Etch PAH/PAA (PET)_15 min	27.16	1.789
Etch PAH/PAA (PET)_30 min	22.38	1.980
Etch PAH/PAA (PET)_60 min	29.67	1.619
Etch PAH/PAA (PET)_90 min	33.08	0.715

[*] n/e = not examined according to dissolution of PAH in water

The water contact angle and surface roughness of PAH, PAA, non-etched bilayer PET film and the etched bilyayer PET films were shown in Table 4.7. The bilayer PET film etched for 30 min gave the lowest contact angle and the highest surface roughness. It is clearly shown that the contact angle is decreased when the RMS roughness is increased.   This is attributed to the fact that the surface with higher roughness can accommodate the spreading water better. The existence of deeper grooves on the surface with higher roughness will try lower volume of air leading to a better water spreading process and lower water contact angle [46].

4.5.2 Investigation of the ZnO-incorporated PET films

ZnO incorporated with PET film was prepared by immersing the etched PET film into a ZnO suspension in PAA for 15 min (purpose: deposition of ZnO onto the base electrolytic film) which was schematically shown in Fig. 4.9(b). The PAA solution was selected for ZnO suspension due to its stability. PAH cannot be employed for delivering ZnO onto the coated surface because it rapidly dissolves in water. Distribution of ZnO on the PET film was observed by FESEM in the function of COMPO mode and SEI mode as shown in Figure 4.11. The COMPO mode used the back-scattered electrons; a reflection from the sample by elastic scattering [40]. The intensity of back-scattered electrons signal strongly relates to the atomic number (Z) of the specimen. Then, COMPO images provide information about the distribution of different elements in the sample. The element with higher atomic number emits brighter light from Figure 4.11 (b) and (c), the brighter particles shown on the surface are supported to be ZnO. In addition the sizes of ZnO particles as shown in Figure 4.11 (b) and (c) are longer than the ZnO particle used for preparing the film. This may be due to the agglomeration of ZnO particle in PAA.
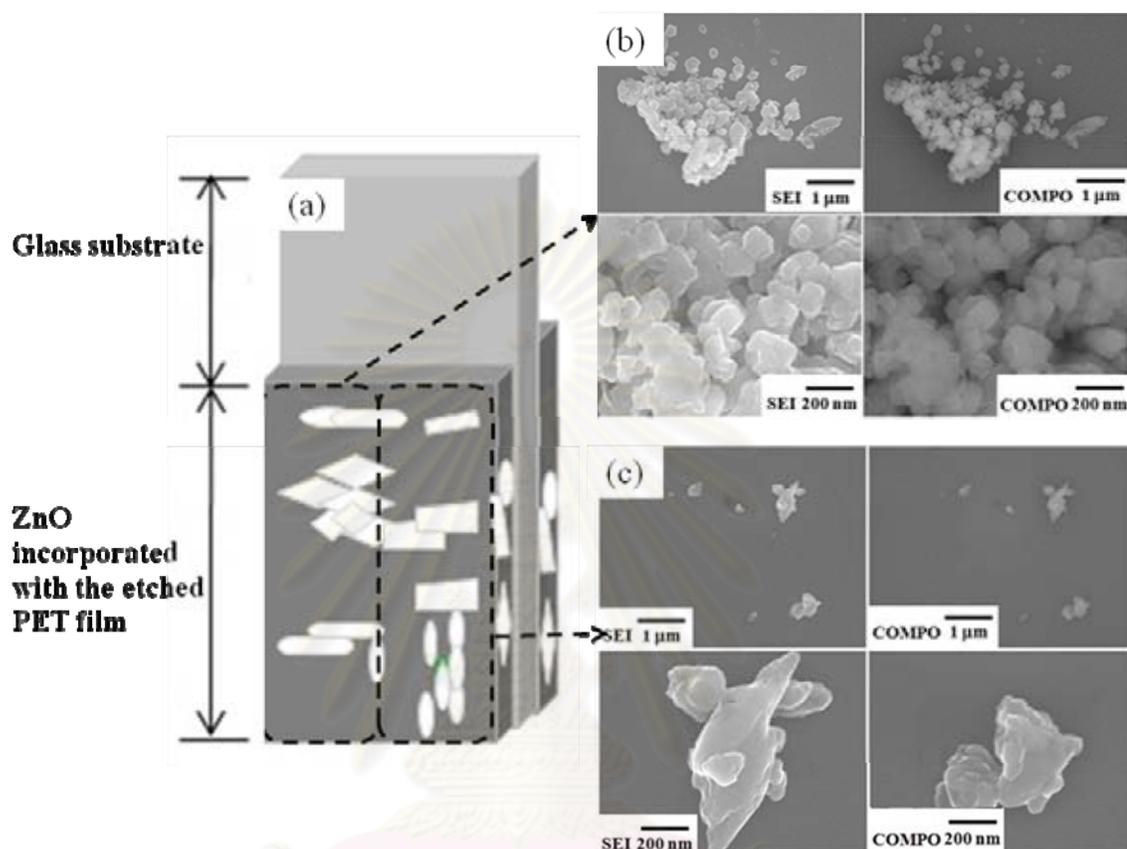
Figure 4.11   (a) Schematic diagram of ZnO distribution on PET film; (b) and (c) FESEM images in SEI and COMPO modes of the ZnO incorporated PET film for the left and right side of the film
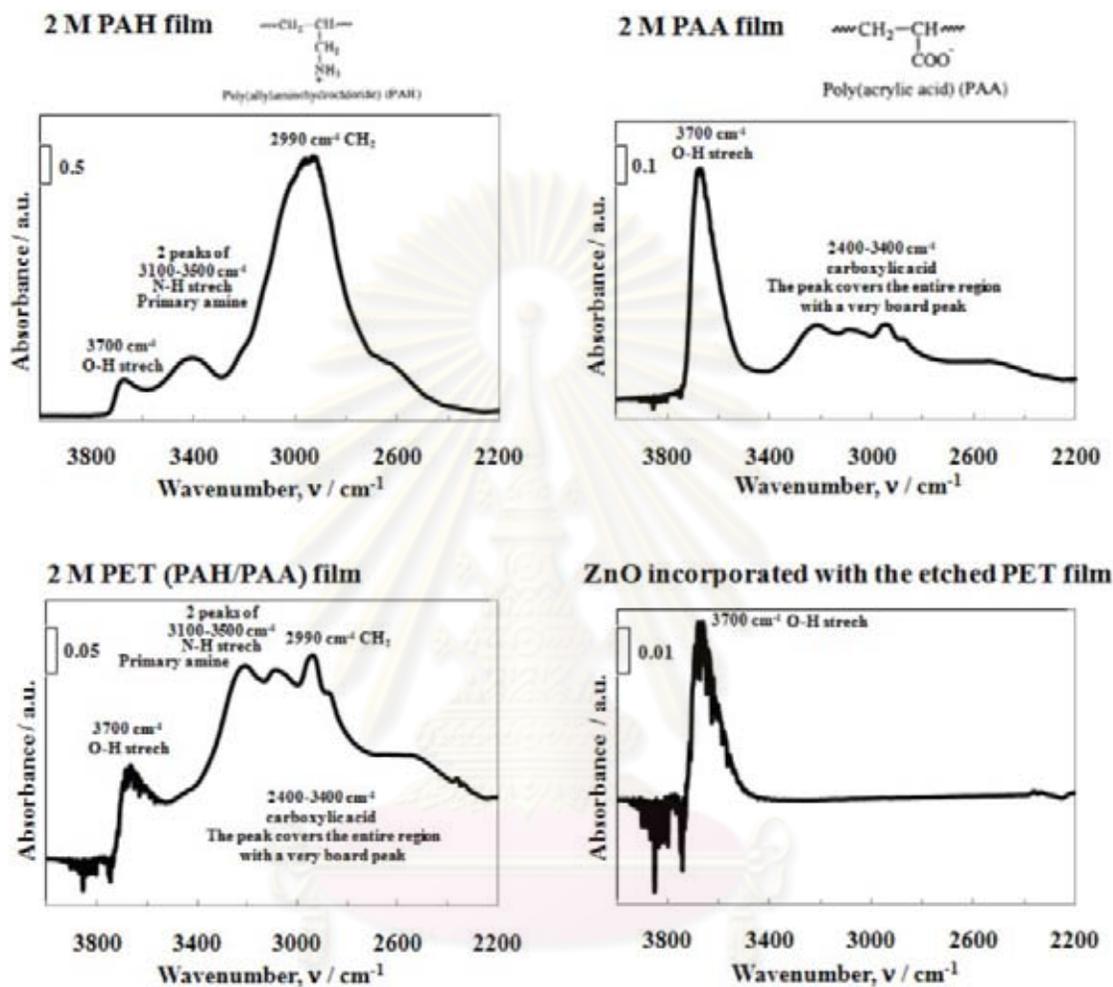
Figure 4.12   FTIR spectra of PAH film, PAA film, PAH/PAA (PET) film and ZnO incorporated with PET film; dried at temperature of 180°C for 2 h.

Figure 4.12 shows infrared spectra of PAH and PAA films deposited onto the glass substrate. The top spectrum was obtained from the film fabricated with a PAH and PAA dipping solution of pH of 1.0 and drying operation at 180°C for 2 h. Wherein, the bottom spectrum was obtained the polyelectrolyte film (PAH/PAA, PET) and the fabricated film with ZnO in PAA deposited onto the PET film which was dried at the

same process of PAH and PAA film. The O-H stretch in both of PAH and PAA film had on absorption band of 3700 cm^{-1} [45]. Hence, the water was used as solvent to prepare polymer solution although the films were dried. The films would have a little water content.

The PAH film exhibits the peak of CH_2 at the absorption band of 2990 cm^{-1}. It was observed that the two peaks of N-H stretch of primary amine about 3100-3500 cm^{-1}. The results corresponded to structural of PAH as well as in the same case of PAA. The peak of interest in the spectra of PAA is carboxylic acid at 2400-3400 cm^{-1}. This peak always covers the entire region with a very broad peak. The alternate functional group of PAA deposited on PAH film was reaction between PAH and PAA film (investigated by FTIR). It is clearly represented the PAH bond with PAA since the absorption bands of PAH near 2990 cm^{-1} (CH_2) and the two peaks of 3100-3500 cm^{-1} (primary amine) merge with the carboxylic acid absorption band of PAA. In addition, the peak intensity of carboxylic acid was increased when the ZnO was added into the suspension of ZnO in PAA. The ZnO deposited on the etched PET was studied the changeable functional group on the surface. Results showed that the absorption band of PAH and PAA was removed, but the O-H stretch band arising. Then, the ZnO would bond with the etched PET film so the larger particle of ZnO (observed by FESEM). This occurs when the polymer covers the ZnO powder that corresponding to result in size distribution as obtained by Zeta-sizer.

Comparison the particle size distributions of ZnO particle in PAA solution at different concentration showed in Figure 4.13 and 4.14. It was found that the precursor solution of 0.1 wt% ZnO in PAA for fabricating ZnO thin film showed size distribution about 5.6 μm. It was larger than the size distribution of 0.2 wt% ZnO in PAA. This evidence confirms that ZnO will bond with water in polymer aqueous solution after mixing between ZnO and PAA solution. Therefore, high content of water in the polymer solution should provide a greater size of ZnO.
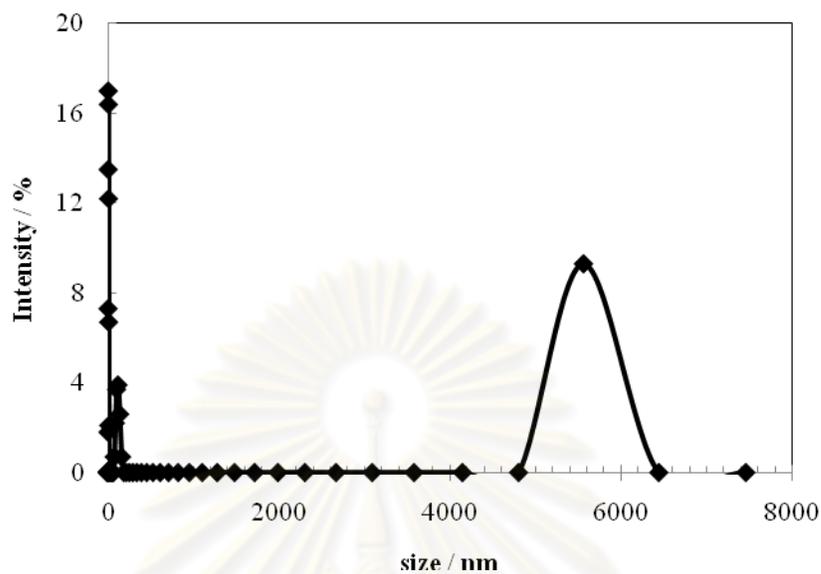
Figure 4.13 Particle size distribution of ZnO in poly(acrylic acid) (PAA) solution at concentration of 0.1 wt % ZnO in PAA for depositing ZnO into etched polyelectrolyte film
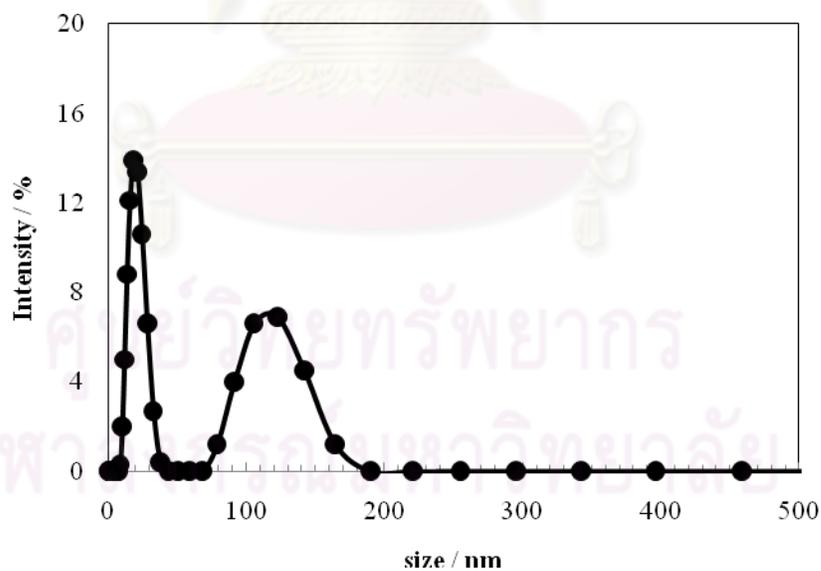
Figure 4.14 Particle size distribution of ZnO in poly(acrylic acid) (PAA) solution at concentration of 0.2 wt % ZnO in PAA for depositing ZnO into etched polyelectrolyte film

Based on the water contact angle, the hydrophilicity of ZnO/PAA films were significantly improved after the UV irradiation of 0 to 60 min as shown in Figure 4.15. Before irradiation, the coating film prepared from 0.2 wt% ZnO suspension exhibited a contact angle of 36.91 degree. The contact angle significantly decreased to 13.74 and 11.11 degree after irradiation time was increased from 1800 and 3600 sec. In addition, it was found that the water contact angle of the coating film prepared from 0.2%wt ZnO suspension was lower than that of film prepared from 0.1 wt% ZnO suspension. In addition, the contact angle of ZnO/PAA film is significantly lower than that of original PET film due to the photosensitive behavior of ZnO that (semiconductor) with band gap energy of ~3.37 eV [51]. The UV illumination onto ZnO nanoparticles enhanced water adsorption on their surface according to the photo-generated surface defective site.
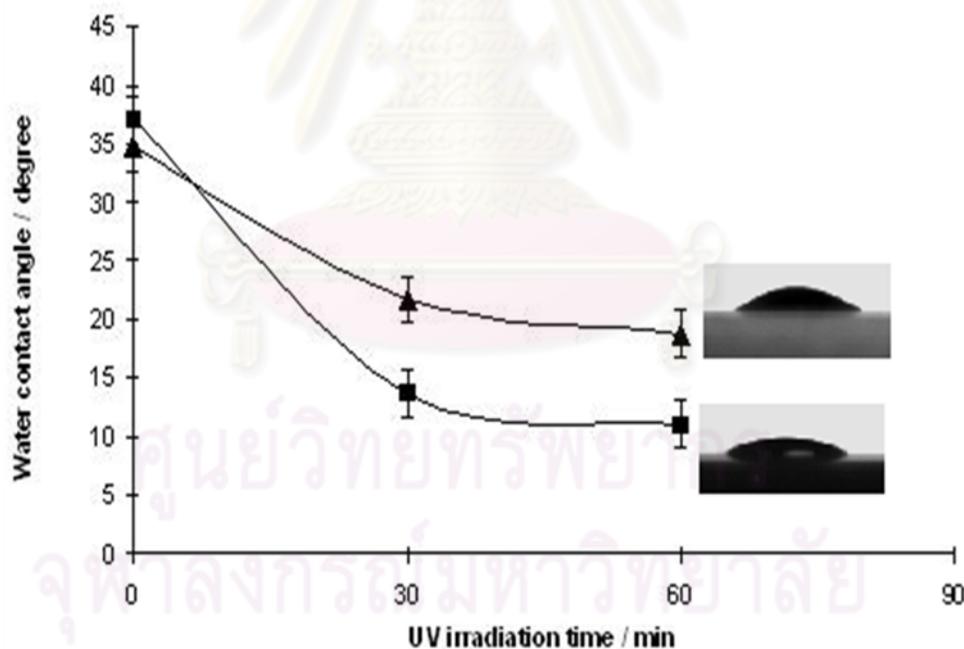
Figure 4.15   Water contact angle vs UV irradiation time of ZnO in PAA on etched PET film (▲ = 0.1 wt% ZnO in PAA on etched PET film, ■ = 0.2 wt% ZnO in PAA on etched PET film)

Such difference in the content of ZnO in suspension provided a hint in their constituent difference. Therefore, energy dispersive X-ray spectroscopic analysis has been achieved for elemental analysis of the coated film as shown in Figures 4.16-4.20.
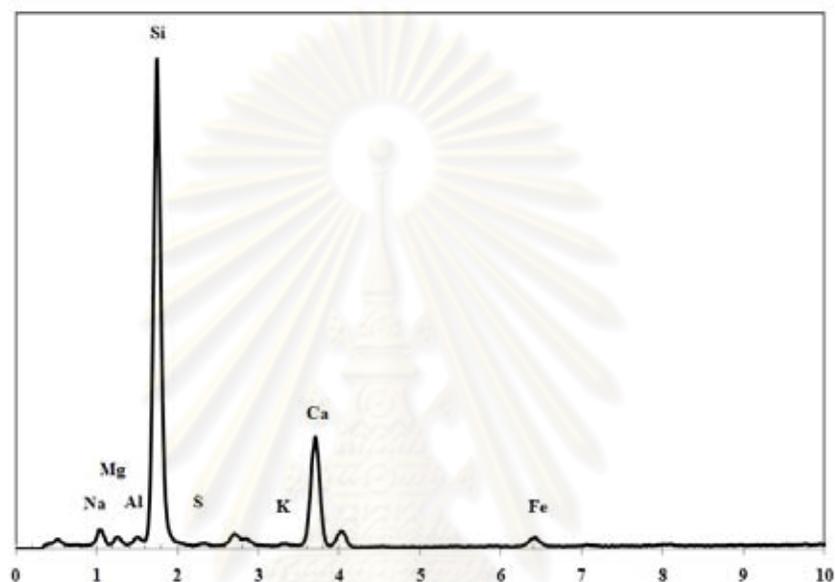
Figure 4.16　EDX analysis of glass substrate

Table 4.8　　Summary of the oxide compounds on glass substrate observed by EDX

Oxide compound	Weight percent
Na_2O	13.81
MgO	3.75
Al_2O_3	2.28
SiO_2	72.61
SO_3	0.31
K_2O	0.20
CaO	6.94
Fe_2O_3	0.10
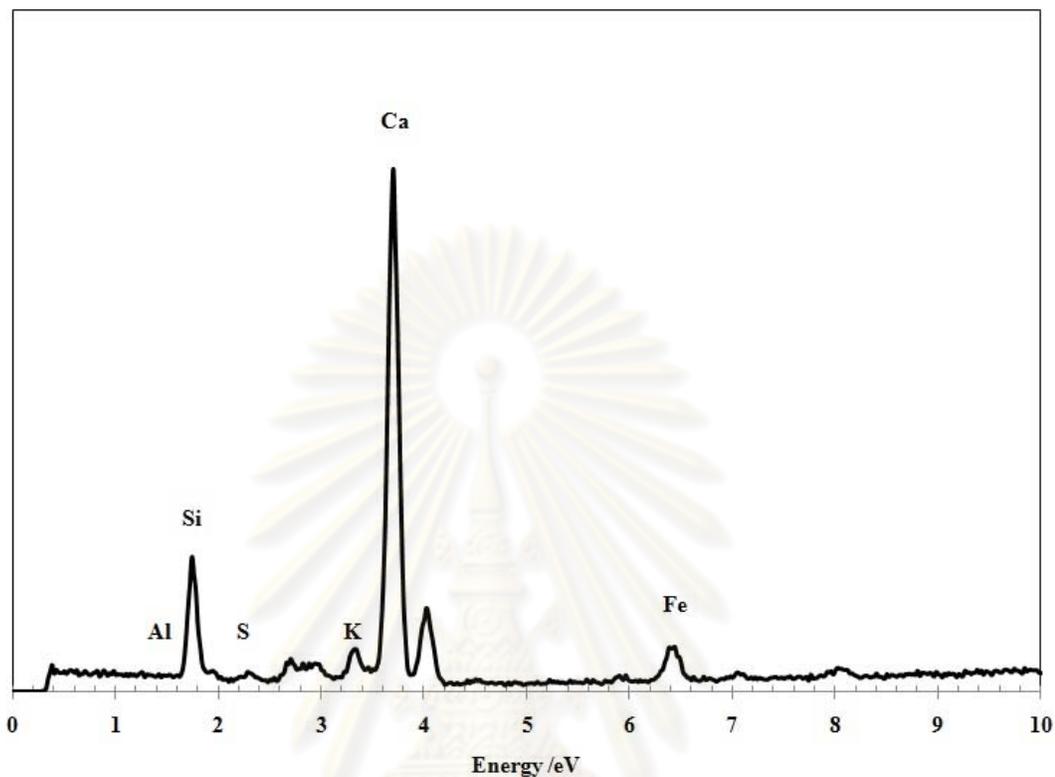
Figure 4.17   EDX analysis of polyelectrolyte film prepared with PAH/PAA concentration of 2.0 M coated at withdrawal speed of 3.0 cm/min and drying temperature at 180°C for 2 h

Table 4.9   Summary of the oxide compounds on polyelectrolyte film observed by EDX

Oxide compound	Weight percent
Al_2O_3	3.30
SiO_2	80.70
SO_3	1.27
K_2O	1.31
CaO	13.26
Fe_2O_3	0.16
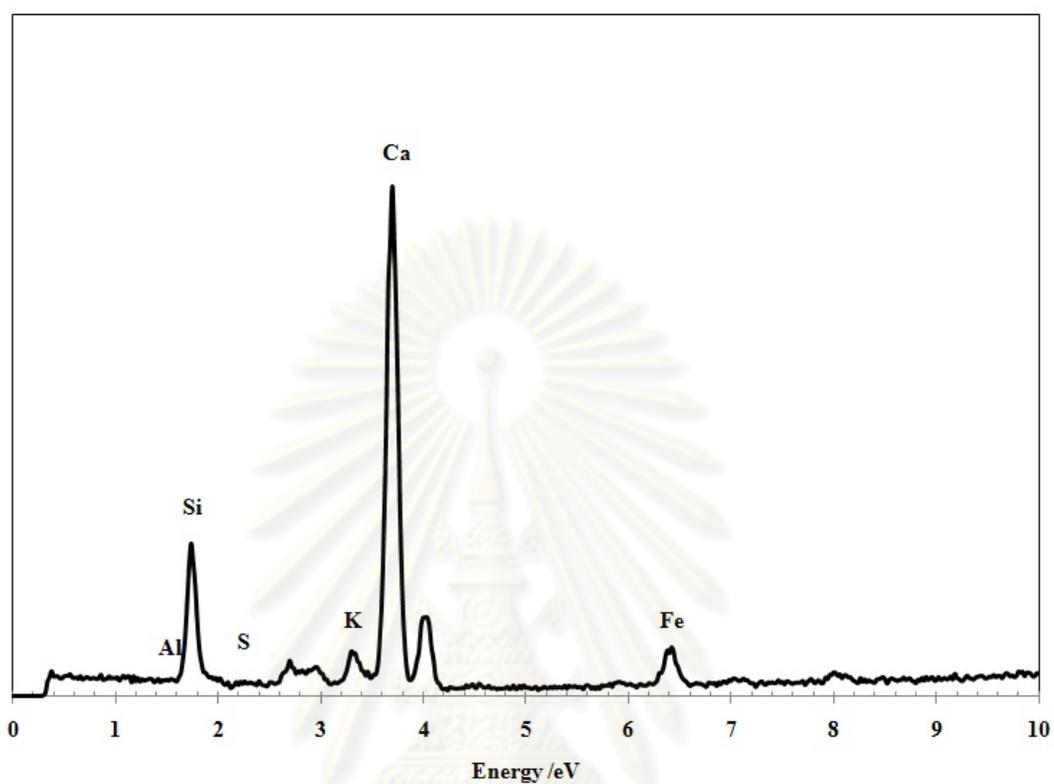
Figure 4.18   EDX analysis of an etched polyelectrolyte film for 30 min and drying temperature of 180°C for 2 h

Table 4.10   Summary of the oxide compounds on the etched polyelectrolyte film for 30 min observed by EDX

Oxide compound	Weight percent
Al_2O_3	2.73
SiO_2	83.98
SO_3	0.26
K_2O	1.16
CaO	11.87

A typical EDX spectrum as shown in Figure 4.7 exhibits that the PET (PAH/PAA) film coated on glass substrate using PAH/PAA concentration of 2.0 M with withdrawal speed of 3.0 cm/min and drying at 180°C was composed of Al, Si, S, K, Ca and Fe. Meanwhile, EDX spectrum of the glass substrate as shown in Figure 4.14 consisted of Na, Mg, Al, Si, S, K, Ca and Fe. It is clearly observed that the coated PET film may prevent diffusion of Na^+ and Mg^+ from glass to the surface since the dried substrate at the high temperature. Moreover, the EDX spectrum of the etched PET film still shows the element of Al, Si, S, K and Ca as well as the result of PET film. Consequently, compound oxide in the each layer that observed by EDX, it can be calculated that shown in the Table 4.8-4.10.
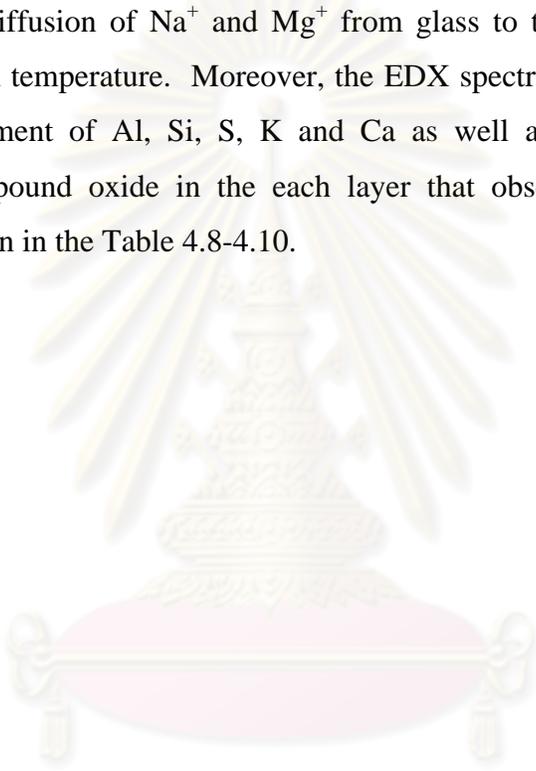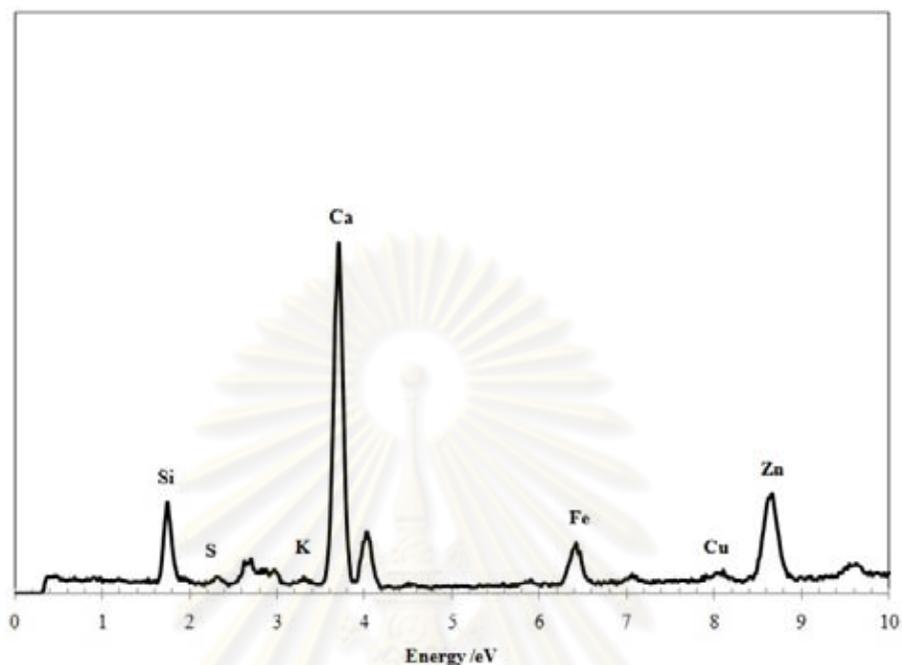
Figure 4.19   EDX analysis of ZnO film prepared by dipping the etched polyelectrolyte
film in 0.1 wt% ZnO in PAA solution for 15 min and drying temperature
of 180°C for   2 h

Table 4.11   Summary of the oxide compounds on the ZnO film (prepared by dipping
the etched polyelectrolyte film in 0.1 wt% ZnO in PAA solution) observed
by EDX

Oxide compound	Weight percent
SiO_2	82.82
SO_3	2.14
K_2O	0.39
CaO	14.10
Fe_2O_3	0.30
CuO	0.03
ZnO	0.22
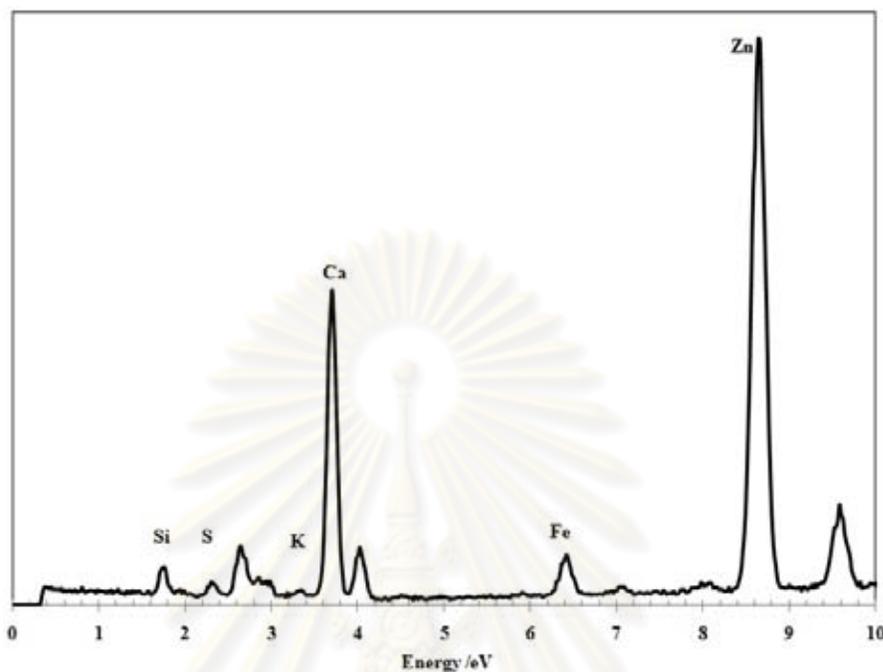
Figure 4.20 EDX analysis of ZnO film prepared by dipping the etched polyelectrolyte film in 0.2 wt% ZnO in PAA solution for 15 min and drying temperature of 180°C for 2 h

Table 4.12 Summary of the oxide compounds on the ZnO film (prepared by dipping the etched polyelectrolyte film in 0.2 wt% ZnO in PAA solution) observed by EDX

Oxide compound	Weight percent
SiO_2	62.10
SO_3	7.09
K_2O	0.61
CaO	25.80
Fe_2O_3	0.70
ZnO	3.70

Comparison of the Figure 4.19 and 4.20 as shown the EDX analysis of ZnO film were prepared by varying the content of ZnO in PAA from 0.1 to 0.2 wt% and both specimens were also dried at 180°C for 2 h. It was found that with the 0.2 wt% ZnO in PAA the highest Zn was obtained. Consequently, the oxide compound film prepared by 0.1 and 0.2 wt% ZnO in PAA show different quantity of ZnO in their layer which exhibit in Table 4.11 and 4.12, respectively. This is evidence to confirm that the higher concentration of ZnO in PAA provides a higher possibility of ZnO deposition within the coating PAA film. Moreover, the ZnO film was also obtained the phase of ZnO in the film by XRD which shown in the appendix B2-B3. However, this characterization may not be suitable for observing the low content of ZnO on the coated film in this experiment because it cannot found the peaks at 31.72°, 34.4° and 36.2° within the X-ray diffratograms assigns to the (100), (002) and (101) planes of ZnO [8].

Regarding to this experimental results, the ZnO suspension in PAA can provide ZnO incorporated with polyelectrolyte films that can improve their hydrophilic property after UV illumination. Nevertheless, this method may occur the agglomeration of ZnO in polymer solution as a result in a larger size of ZnO so it would be irradiated by UV light for long time to be a superhydrophilic surface. Thus, we were also selected as another alternative method for decreasing the irradiation time to progress the hydrophilic property of ZnO thin film.

4.6 ZnO embedded in PET film by sol-gel dip coating method

Currently, the various semiconductors, metallic and magnetic nanoparticles have studied incorporated with polyelectrolyte multilayer films [10]. This method produces by construction the polyelectrolyte (PET) film via the interaction between polycation and polyanion in order to form nanoreactor. Then, the nucleation of metal ion in precursor adsorb into the cavities of the polymers. Most recently, the ZnO nanocrystals were embedded in multilayers polymer films (PDDA and PSS) by using Zn $(NO_3)_2$ and NH_4OH as a precursor. It was found that the morphologies of ZnO particles

were controlled by the nucleation and growth from precipitation of reaction cycles. This approach provides an effective route to construct multilayer film containing ZnO nanoparticles. Most results about effects of ZnO sol concentration, ZnO sol aging time and annealing treatment on ZnO thin films have been reported but the effect of pH of ZnO sol on the optical property and hydrophilic property of ZnO thin films is seldom studied. Then, the method of ZnO embedded in PET film by sol-gel dip coating method was investigated the effect of pH of precursor sol on the optical property and morphology of the ZnO before analyzing the hydrophilic property of the film.

4.6.1 Effect of pH of sol on the optical property and morphology of the ZnO embedded in PET film

The ZnO embedded in PET film was observed (the film thickness and surface roughness) by CLSM at the magnification of 20X. It was found that an increased pH the precursor ZnO sol gave thicker film because a large amount of ZnO adsorbed in the cavities of PET film. Then, excess ZnO particle cannot be penetrated into the hole of the polymer, hence may occur (growth grain size on the coated surface) as agglomerate to be a larger size then it exhibits thicker film as shown in Figure 4.21. In addition, the several quantity of ZnO particle on the film was quantitatively correlated with the solvent evaporation, the higher thickness film affects the drying of the solvent. This result was supported by research work of Brinker et al.. Wherein, thicker film gave a longer time to dry the solvent, this eventually increasing the aging time to dry up the outer surface of the entrained sol [52].
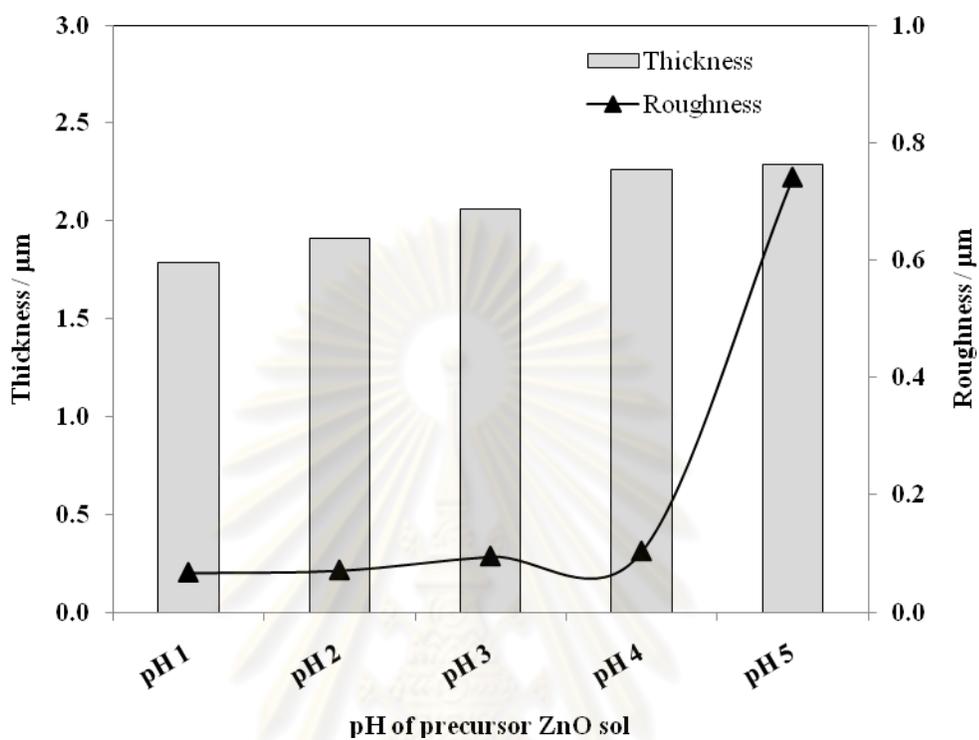
Figure 4.21   Film thickness and surface roughness as a function of pH of precursor ZnO sol
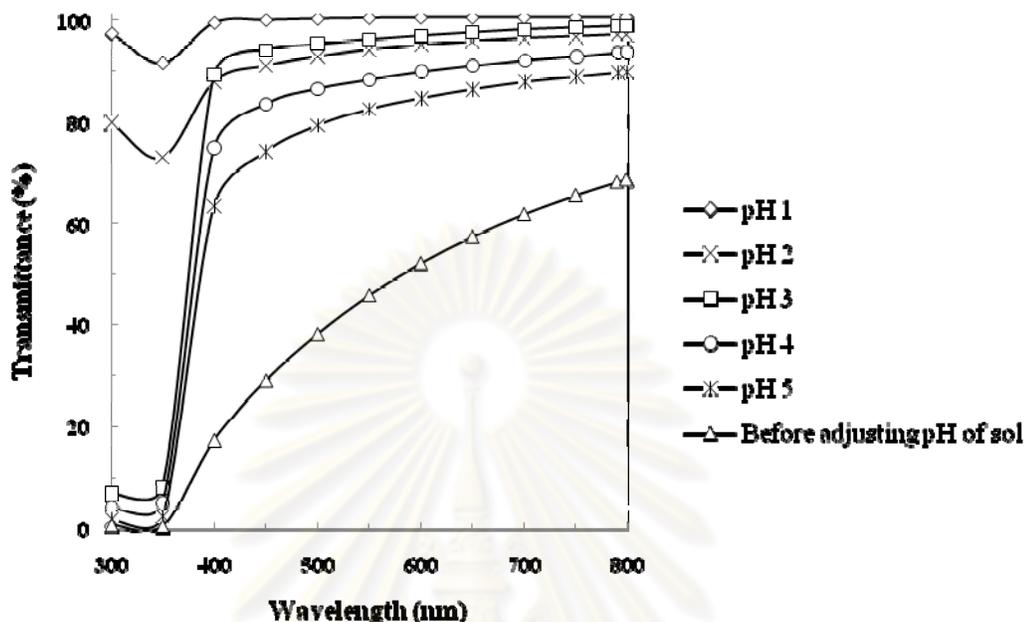
Figure 4.22   Optical transmittance spectra of ZnO embedded in PET film from different pH of precursor sol

Figure 4.22 shows the effect of pH of precursor ZnO sol on the optical properties of the ZnO embedded in PET film.   Results showed that most the film have a transmittance over than 70 % in the visible range.   Especially for the ZnO film as prepared by precursor ZnO sol at pH 1 exhibited an average transmittance in the visible range is above 99%.   With the increase pH of sol, the transmittance of ZnO thin film in the visible range is gradually decreased.   Nevertheless the pH of sol does not affect the strong absorption property of ZnO thin film in the ultraviolet range and the absorption edges of the samples all lay at ~370 nm.
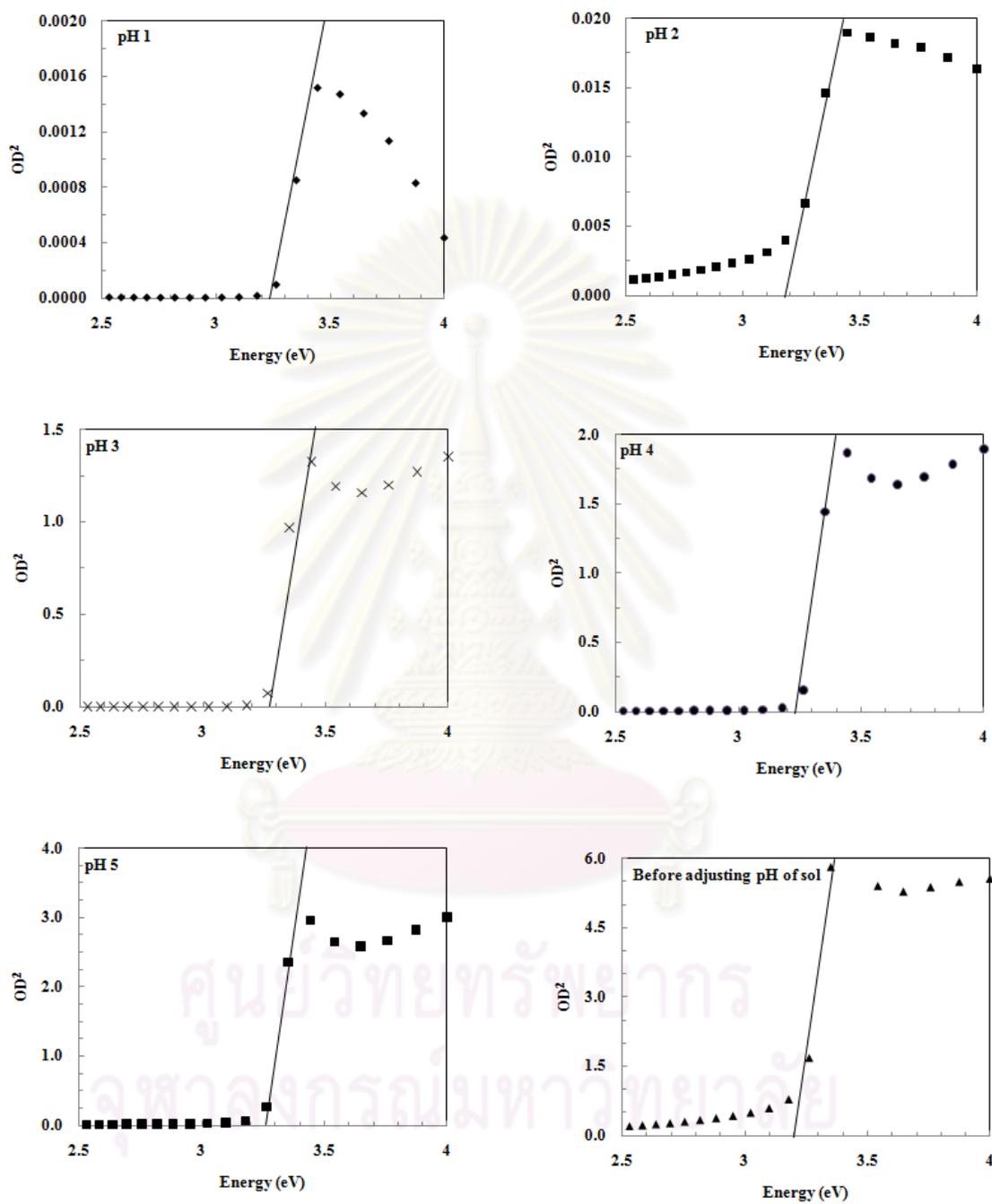
Figure 4.23 A plot of OD^2 vs energy for finding intercept on x axis that represents the gap width of ZnO embedded in PET film

The fundamental absorption corresponds to electron excitation from the valence band to the conduction band can be used to calculate the value of the optical band gap that relates to the characteristic of the material [53]. These relation evaluated by plot of the square of the optical density (OD, OD = log (100/T) as a function of hv in Figure 4.23 gives the gap width for films with various pH of sol. The h is a Planck's constant as 6.620×10^{-34} J·s. The number of carrier v can be deduced from c/λ with c as a speed of light where λ is a wavelength of photon. Curves are limited at the high photon energies by the absorption of the substrate. The value of the gap width of all the samples were around 3.2-3.4 eV which is quite nearly the band gap energy of ZnO (3.37 eV). The evidence reveals that the surface of the film has ZnO filler on the surface. Wherein, the two major factors effect on the transmittance were surface roughness and grain size of the film. Therefore, the surface morphology of the high transparent ZnO embedded in PET film was observed by FESEM which was chosen the pH of the precursor ZnO sol of 1 and 2 due to their optical properties (see in Figure 4.22).
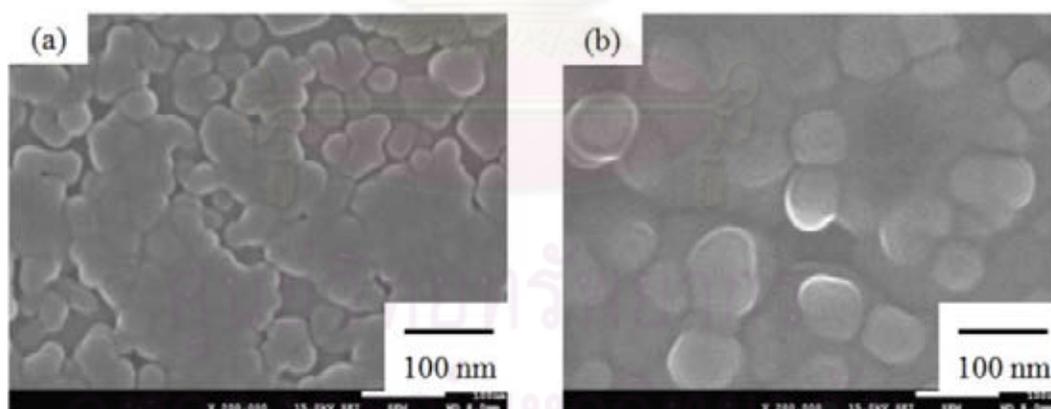
Figure 4.24   FE-SEM images of ZnO embedded in PET film as prepared at
(a) pH = 1.0 and (b) pH = 2.0

Figure 4.24 shows the surface morphology images of ZnO embedded in PET film prepared by precursor of ZnO sol with pH 1 and pH 2. It was found that the grain size of

the films depend on pH of the sol with the pH 1 estimated the average grain size about 20 nm and increased to 50 nm as the increased pH of sol to 2. The increased pH of sol also relates to the surface roughness of the film. Consequently, the optical transmittance of the film as the prepared with the higher pH of ZnO sol exhibited the decreased transmittance of the film at the larger grain size and higher surface roughness of the film. Base on our experiment, the morphology of ZnO thin film is determined mainly by the competition between the polycondensation of hydrolyzed zinc acetate and the zinc oligomers adsorbed by PET film. The large amount of H^+ ions in the low pH of sol inhibited hydrolysis and condensation process of the sol through polymerization of the metal-oxygen bonds leads to the smaller grain size of the film in low pH. This evidence tend to support the experimental of Houng et al., reported at higher pH accelerates the rate of hydrolysis and polycondensation that affects the highly branched metal-oxygen polymeric network resulted in a larger grain microstructure in the film [26]. On the other hand, the competitive of zinc oligomers adsorbed in the cavities of the PET film probably occurs randomly so the grain-boundary of the film is not so clear in both of the FE-SEM image of the film prepared with pH 1 and 2.

4.6.2 Investigation of the hydrophilic property of the ZnO embedded in PET film

The hydrophilic of the ZnO embedded in PET film was investigated by measuring the water contact angle. It's well known that the wettability of the surface depends on two main factors, i.e. surface roughness and UV light irraditation time were studied in these factors. Therefore, the surface roughness of the ZnO embedded in PET film observed by SPM was shown in Figure 4.25. It was found that the pH 1 of precursor of ZnO sol embedded in PET film showed the flattest surface among the film. The smaller size of ZnO oligomer adsorbed in the cavities of the PET film then it can be obtained in smaller particles embedded in the surface as shown in Figure 4.25(a). On the other hand the ZnO thin film from ZnO sol pH 2 exhibited the greater size of particle agglomerate on the surface (Figure 4.25(b)) due to the effect of pH of sol precursor. The decreased H^+

ions at the higher pH of sol probably affect the lower rate of polycondensation of the metal oxide as a result in the bigger particle growth on the film. Therefore, the higher surface roughness of the ZnO film from pH 1 gave the lower contact angle than the film as prepared by the ZnO sol-gel at pH 2. Result showed that the wettability of a surface may depends on their surface roughness. The relationship between the roughness surface and the hydrophilic property of the film was explained by Wenzel's model that described the water contact angle on rough and solid surfaces [19, 44, 47]. The model illustrates that the hydrophilic surface becomes more hydrophilic surface when the surface roughness enhances. The increased surface roughness also provides the highly hydrophobic in the case of hydrophobic surface. Miyauchi et al. reported that the water contact angle of the flat TiO_2 surface less than 90°, as with most inorganic substances [47]. Then, the surface of TiO_2 become more hydrophilic when roughness is provided that corresponded to Wenzel's model.
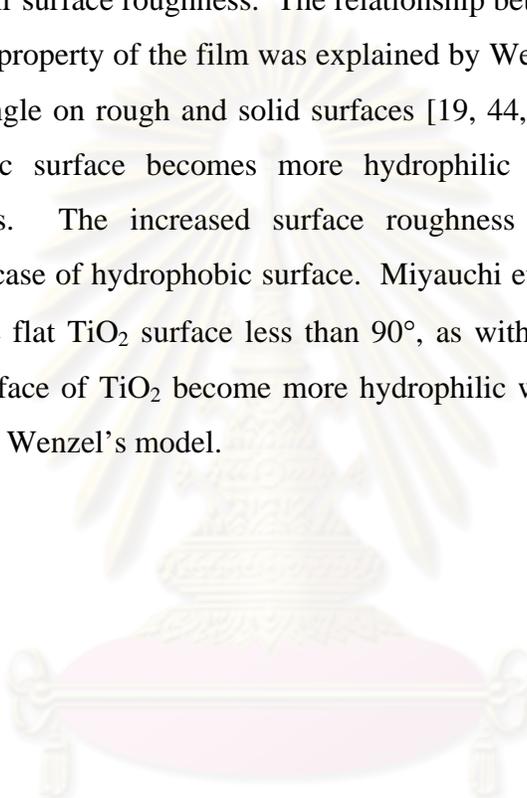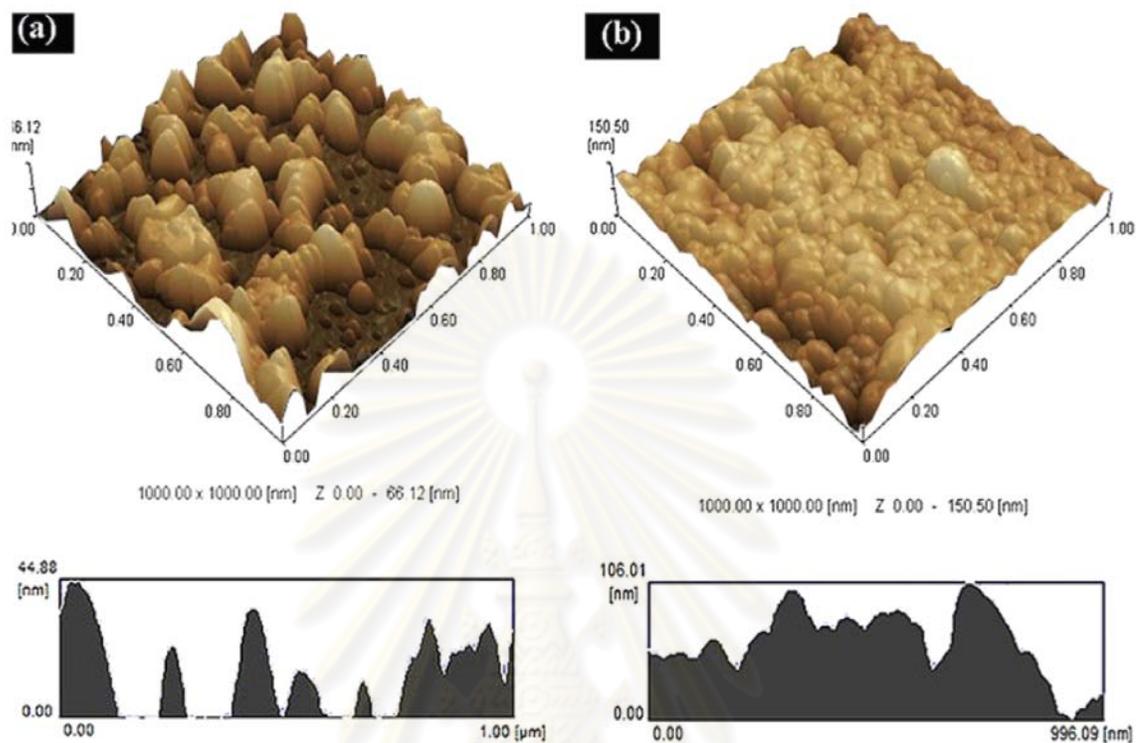
Figure 4.25   2D and 3D topographical (1μm×1μm) of the ZnO embedded in PET film prepared by the different pH of precursor of ZnO sol (a) pH 1 and (b) pH 2

In order to investigate the effect of the UV irradiation time on the hydrophilic property of the ZnO embedded in PET film, the film exposure to the light irradiation in the atmospheric air at different five areas. It can be seen from Figure 4.26 that the changeable water contact angle of the films after UV irradiation time.
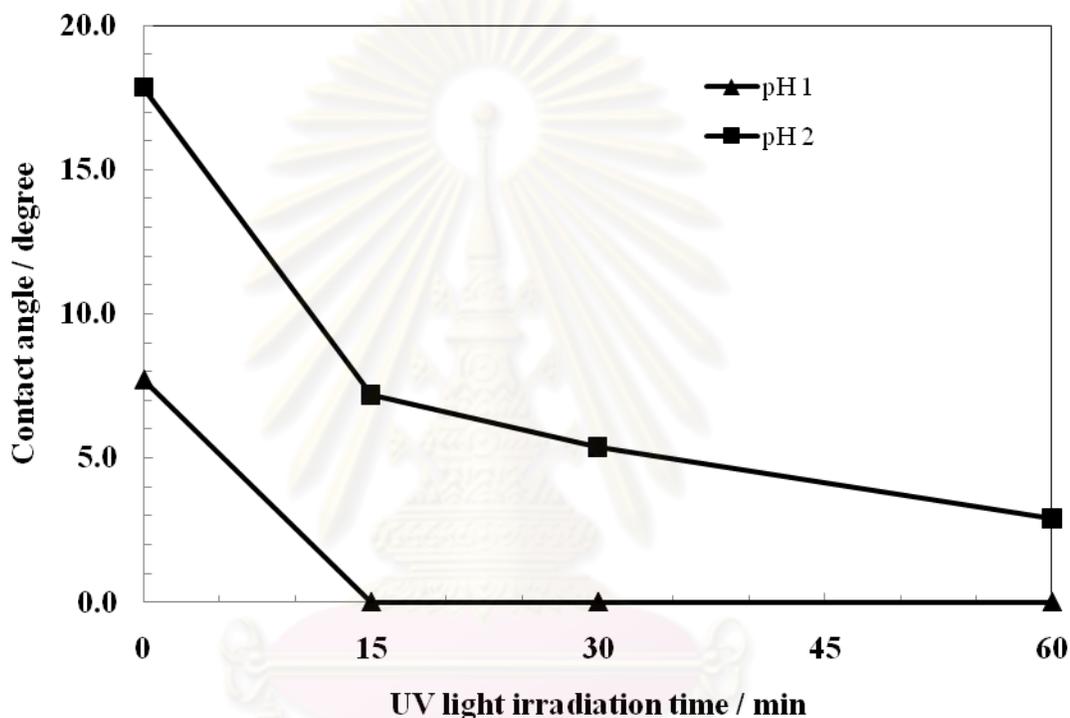
Figure 4.26 Water contact angle as induced by the UV light irradiation of the ZnO embedded in PET film as prepared by the various pH of precursor of ZnO sol

Prior to light illumination, the film as prepared by pH 1 and pH 2 of precursor of ZnO sol were water contact angles around 8° and 18°, respectively. Upon UV light illumination, the water contact angle for the both of the film from pH of ZnO precursor sol as 1 and 2, dramatically decreased to 0° and 7° after 15 min UV exposed time. In addition, after 30 min UV irradiation time, the films achieved again a low water contact

angle values of 0 and 5 degree for the film as prepared at pH 1 and 2, respectively. However, the contact angle of zero still exhibited after the UV illumination of 15 to 60 min in the case of the pH 1 ZnO sol embedded in PET film. During the UV irradiation is attributed to structural changes at the surface. The electron and hole generated by ZnO under band gap illumination diffuse to the surface to react with lattice metal ions Zn^{2+} to form Zn^{2+} defective sites and the lattice oxygen resulting in the formation of surface oxygen vacancies, respectively. The oxygen vacancies are apparently favorable coordinate to water molecules, leading to the increasing water adsorption as a cause in the highly hydrophilic surface were formed. Based on results, the surface roughness of ZnO embedded in the PET film affects the wettability of the surface of the film. Even at longer irradiation time, pH 1 (rougher surface, low ZnO) produced lower contact angle compare to pH 2 (smooth surface, high ZnO). Hence, surface roughness provides more than defective sites (produced by UV irradiation) in ZnO in terms of wettability of the surface film. In addition at lower pH, produced lower concentration of OH^- which eventually formed to less a $Zn(OH)_2$ in the sol. To confirm these results, the quantity of ZnO embedding in polyelectrolyte film with prepared at pH 1 and 2, were analyzed by energy dispersive X-ray spectroscopic which present in Table 4.13 and 4.14, respectively. Results reveal that a lower pH of precursor sol could afford low content of ZnO in film due to adjusting the pH of the precursor sol by acetic acid. Therfore, the formation ZnO through sol-gel process at lower OH^- (low pH) to react with Zn^{2+} and then easily to form ZnO, it would be difficult. This result also supports the research work of Rani et al.. They studied the larger pH (6-11) on the growth of ZnO nanoparticles in zinc acetate solution. The sol having pH<7 could have insufficient OH^- that affects the growth of ZnO paricle as a cause lack of $Zn(OH)_2$ to become ZnO after calcinations [31]. Thus, the threshold of pH level may control sol-gel process in nanostructure to formation.
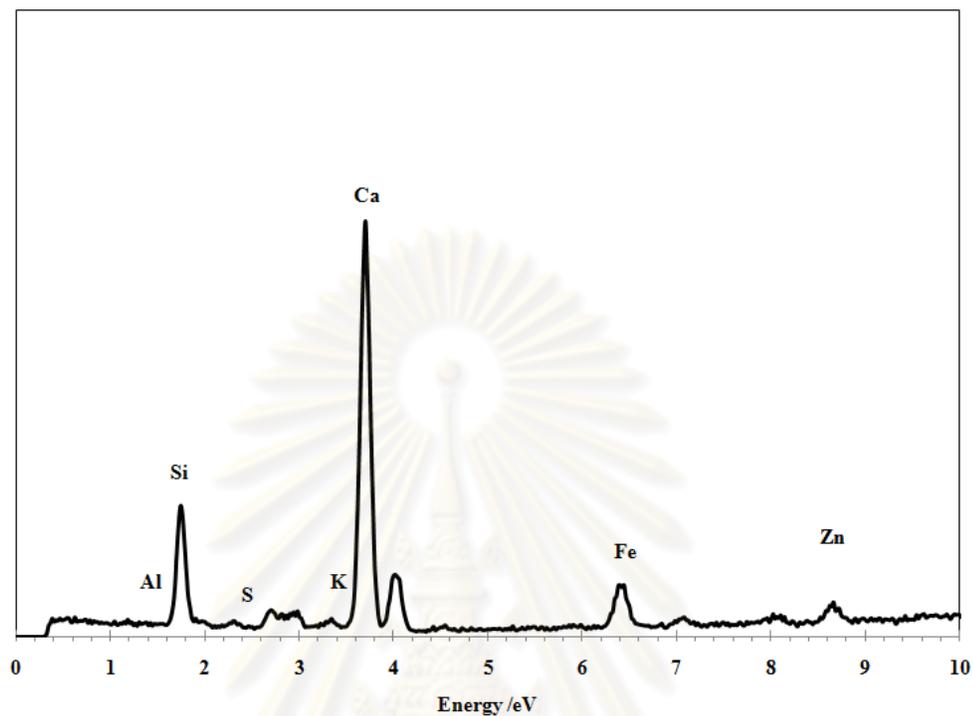
Figure 4.27 EDX analysis of ZnO film prepared by sol-gel precursor pH 1 at withdrawal speed 3 cm/min and calcination temperature of 500°C for 1 h

Table 4.13 Summary of the oxide compounds on the ZnO film (by sol-gel precursor pH 1 at withdrawal speed 3 cm/min and calcination temperature of 500°C for 1 h) observed by EDX

Oxide compound	Weight percent
Al_2O_3	2.63
SiO_2	85.40
SO_3	0.94
K_2O	0.31
CaO	10.51
Fe_2O_3	0.18
ZnO	0.03
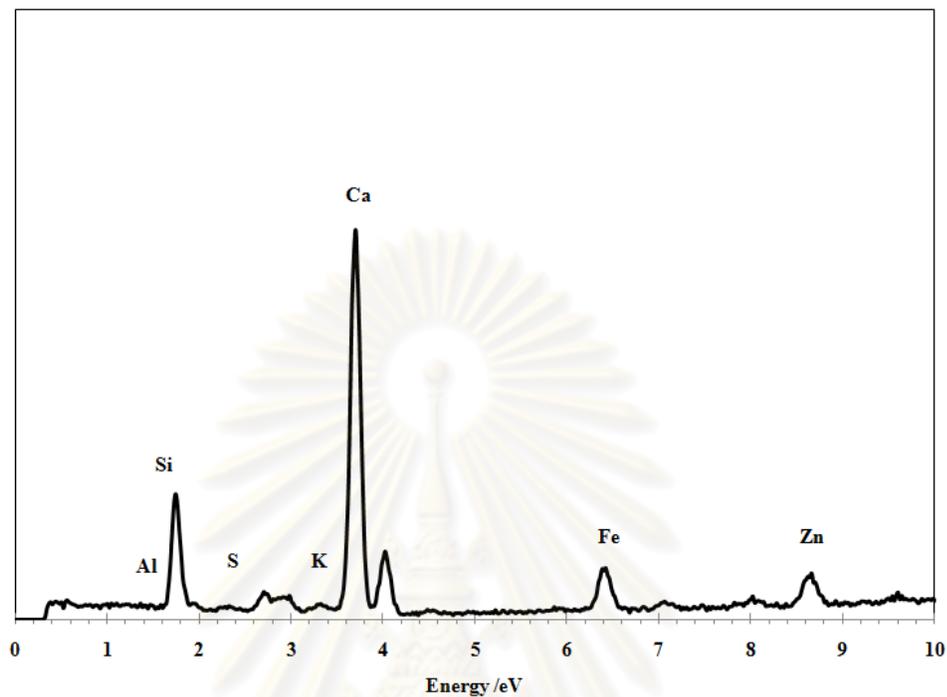
Figure 4.28   EDX analysis of ZnO film prepared by sol-gel precursor pH 2 at withdrawal speed 3 cm/min and calcination temperature of 500°C for 1 h

Table 4.14   Summary of the oxide compounds on the ZnO film (by sol-gel precursor pH 2 at withdrawal speed 3 cm/min and calcination temperature of 500°C for 1 h) observed by EDX

Oxide compound	Weight percent
Al_2O_3	2.40
SiO_2	85.63
SO_3	0.74
K_2O	0.30
CaO	10.70
Fe_2O_3	0.18
ZnO	0.05

As the results, these experiments suggest that transparent film of ZnO incorporated with polyelectrolyte film coated on glass substrate using layer-by-layer and dip coating technique should prepare by sol-gel which exhibit good photoinduced hydrophilic property in a short time (15 min). Although, this method would decompose polyelectrolyte film since the film prepared by sol-gel would be calcined at the high temperature of 500°C to formation ZnO in the film. In summary based on all experimental results conducted in this work, the hydrophilic property of the fabricated ZnO incorporated with polyelectrolyte films are attributed to their surface roughness, grain size, distribution and quantity of ZnO which are in turn affected by the number of coating layer (precipitation method), precursor concentration (suspension of ZnO in PAA) and pH of precursor solution (sol-gel method).
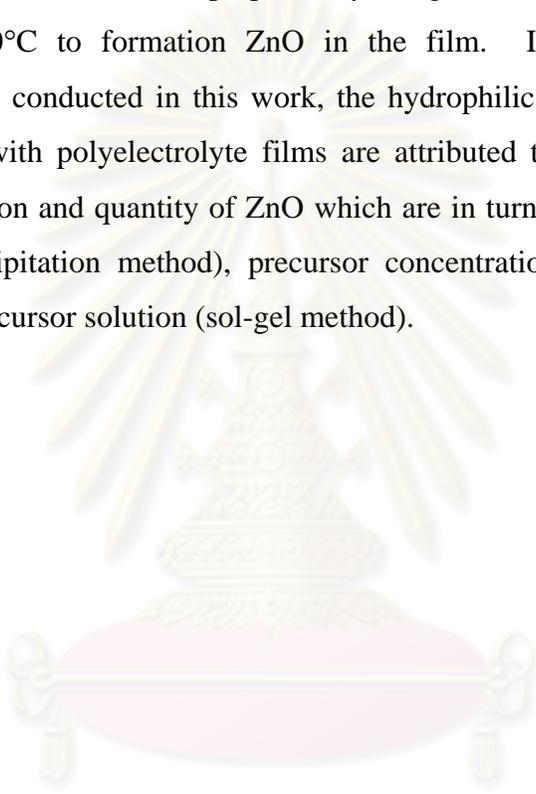
CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In this thesis, it was demonstrated that the transparent zinc oxide incorporated with polyelectrolyte films were fabricated from dipping a glass substrate coated with a single bilayer polyelectrolyte film into ZnO precursor solution with layer-by-layer dip coating technique. The pH of the ZnO precursor solution for preparation ZnO thin film is adjusted to be 1. The photoinduced hydrophilic property of the fabricated films were investigated, its dependence on pH of precursor sol. However, the suspension of ZnO in PAA would be used for preparation of the transparent ZnO incorporated with polyelectrolyte film. This method could be agglomeration of ZnO. Its problem to using a long time period to activate surface defective site leading to the most water contact angle that mean the lower hydrophilic property.

In part A, effect of polymer concentration, withdrawal speed (WS) and number of dipping cycle were explore to find out the appropriate condition to prepare the sufficient film thickness with smooth surface. It was found that the number of bilayer polyelectrolyte film that suitable for deposition ZnO into the film was 1 bilayer which was prepared from 2.0 M PAH/PAA (as poly(allylamine hydrochloride), PAH and poly(acrylic acid), PAA) with withdrawal speed 3 cm/min and drying at the temperature of 180°C.

Regarding to improve the photoinduced hydrophilic property of ZnO incorporated with polyelectrolyte film coated on glass substrate, influence of the methodology for depositing ZnO were experimentally investigated in Part B. As experimental results, the ZnO incorporated with polyelectolyte film prepared by sol-gel method at pH of precursor about 1 exhibited the water contact angle lower than 5 degree after UV irradiation for 15 min. It still exposed to be lower than 5 degree as the increased UV irradiation time from

15 to 60 min. Although, the suspension of ZnO in PAA was easily to deposit ZnO into the etched polyelectrolyte film but it was not suitable for improving the hydrophilic property of the film. This method would not provide the distribution of ZnO into the film due to the ZnO agglomeration through reaction between ZnO and poly(acrylic acid) solution. Moreover, the precipitation method could not be a suitable method for improving the photoinduced hydrophilic property of ZnO incorporated with polyelectrolyte film.

5.2 Recommendation for future work

5.2.1 To investigate effect of number of sol-gel ZnO coating layer on
improvement photoinduced hydrophilic property.

5.2.2 To investigate ZnO thin film durability after being kept in dark storage.
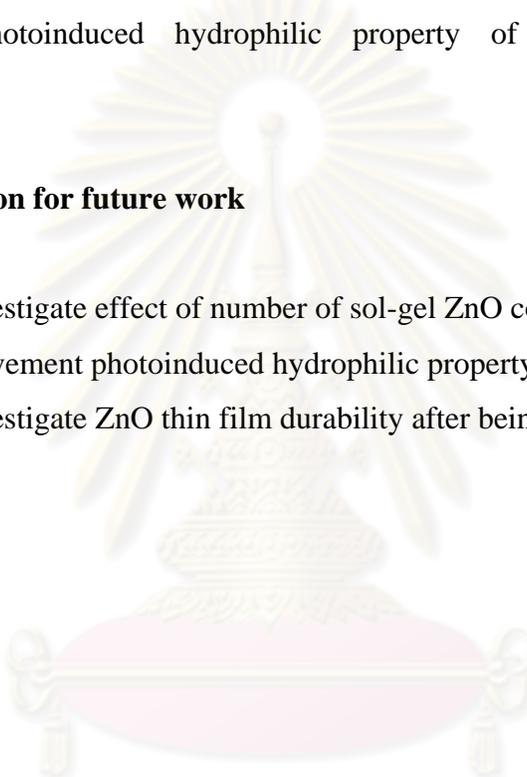
REFERENCES

[1] Euvananont, C., Junin, C., Inpor, K., Limthongkul, P., and Thanachayanont, C. TiO$_2$ optical coating layers for self-cleaning applications. Ceram. Inter. 34 (2008): 1067-1071.

[2] Numpud, P., Charinpanitkul, T., and Tanthapanichakoon, W. Photoinduced hydrophilic property of zinc oxide thin films prepared by sol-gel dip coating method. J. Ceram. Soc. Japan. 116 (2008): 414-417.

[3] Nimittrakoolchai, O-U., and Supothina, S. Deposition of organic-based superhydrophobic films for anti-adhesion and self-cleaning applications. J. Eur. Ceram. Soc. 28 (2008): 947-952.

[4] Li, Y., et al. Superhydrophobicity of 2D ZnO ordered pore arrays formed by solution-dipping template method. J. Colloid Interf. Sci. 287 (2005): 634-639.

[5] Ma, M., and Hill, R.M. Superhydrophobic surfaces. Curr. Opin. Colloid In. 11 (2006): 193-202.

[6] Kenanakis, G., et al. Light-induced reversible hydrophilicity of ZnO structures grown by aqueous chemical growth. Appl. Surf. Sci. 254 (2008): 5695-5699.

[7] Watanabe, T., et al. Photocatalytic activity and photoinduced hydrophilicity of titanium dioxide coated glass. Thin Solid Films. 351 (1999): 260-263.

[8] Guo, M., Diao, P., and Cai. S. Highly hydrophilic and superhydrophobic ZnO nanorod array films. Thin Solid Films. 515 (2007): 7162-7166.

[9] Ding, B., Ogawa, T., Kim, J., Fujimoto, K., and Shiratori, S. Fabrication of a super-hydrophobic nanofibrous zinc oxide film surface by electrospinning. Thin Solid Films. 516 (2008): 2495-2501.

[10] Wang, C., et al. Nucleation and growth of ZnO nanocrystals in polymer films. Thin Solid Films. 516 (2008): 6058-6062.

[11] Kenanakis, G., Vernardou, D., Koudoumas, E., and Katsarakis, N. Growth of *c*-axis oriented ZnO nanowires from aqueous solution: The decisive role of a seed layer for controlling the wires' diameter. J. Cryst. Growth. 311 (2009): 4799-4804.

[12] Zhang, J., Feng, H., Hao, W., and Wang, T. Blue-emitting ZnO sol and film obtained by sol-gel process. J. Sol-Gel Sci. Technol. 39 (2006): 37-39.

[13] Li, P., Wei, Y., Liu, H., and Wang, X. Growth of well-defined ZnO microparticles with additives from aqueous solution. J. Solid State Chem. 178 (2005): 855-860.

[14] Zhao, J., Jin, Z.-G., Liu, X.-X., and Jin, Z.-G. Growth and morphology of ZnO nanorods prepared from $Zn(NO_3)_2$/NaOH solutions. J. Eur. Ceram. Soc. 26 (2006): 3745-3752.

[15] Vernardou, D., et al. The effect of growth time on the morphology of ZnO structures deposited on Si (100) by the aqueous chemical growth technique. J. Cryst. Growth. 308 (2007): 105-109.

[16] Etienne, O., et al. Polyelectrolyte multilayer film coating and stability at the surfaces of oral prosthesis base polymers: an *in vitro* and *in vivo* study. J Dent Res. 85 (2006): 44-48.

[17] Callewaert, M., Gohy, J.-F., Dupont-Gillain, C.C., Boulangé-Petermann, L., and Rouxhet, P.G. Surface morphology and wetting properties of surfaces coated with an amphiphilic diblock copolymer. Surf. Sci. 575 (2005): 125-135.

[18] Silva, T.H., Barreira, S.V.P., Moura, C., and Silva, F. Electrochemical characterization of a self-assembled polyelectrolyte film. Portugaliae electrochemica acta. 21 (2003): 281-292.

[19] Zhai, L., Cebeci, F.Ç, Cohen, R.E., and Rubner, M.F. Stable superhydrophobic coatings from polyelectrolyte multilayers. <u>Nano Lett</u>. 4 (2004): 1349-1353.

[20] Tang, Z., Donohoe, S.T., Robinson, J.M., Chiarelli, P.A., and Wang, H.L. Film formation, surface character, and relative density for electrochromic PEI/(PSS:PEDOT) Multilayered thin films. <u>Polymer</u>. 46 (2005): 9043-9052.

[21] Zhu, Y., Shi, M., Wu, X., and Yang, S. Amphilic copolymer grafted "smart surface" enhanced by surface roughness. <u>J. Colloid Interf. Sci</u>. 315 (2007): 580-587.

[22] Liu, Z., Li, J., Ya, J., Xin, Y., and Jin, Z. Mechanism and characteristic of porous ZnO films by sol-gel method with PEG template. <u>Mater. Lett</u>. 62 (2008): 1190-1193.

[23] Dai, X., Zhang, Y., Guan, Y., Yang, S., and Xu, J. Mechanical properties of polyelectrolyte multilayer self-assembled films. <u>Thin Solid Films</u>. 474 (2005): 159-164.

[24] Shao, L., and Lutkenhaus, J.L. Thermochemical properties of free-standing electrostatic layer-by-layer assemblies containing poly(allylamine hydrochloride) and poly(acrylic acid). <u>Soft matter</u>. 6 (2010): 3363-3369.

[25] Iliescu, C., Chen, B., and Miao, J. On the wet etching of Pyrex glass. <u>Sens. Actuator A</u>. 143 (2008): 154-161.

[26] Houng, B., Huang, C.-L., and Tsai, S.-Y. Effect of the pH on the growth and properties of sol-gel derived boron-doped ZnO transparent conducting thin film. <u>J. Cryst. Growth</u>. 307 (2007): 328-333.

[27] Ayouchi, R., Martin, F., Leinen, D., and Ramos-Barrado, J.R. Growth of pure ZnO thin films prepared by chemical spray pyrolysis on silicon. <u>J. Cryst. Growth</u>. 247 (2003): 497-504.

[28] Li, Y., Xu, L., Li, X., Shen, X., and Wang, A. Effect of aging time of ZnO sol on the structural and optical properties of ZnO thin films prepared by sol-gel method. Appl. Surf. Sci.. 256 (2010): 4543-4547.

[29] Karuppuchamy, S., and Ito, S. Cathodic electrodeposition of nanoporous ZnO thin films from new electrochemical bath and their photoinduced hydrophilic properties. Vacuum. 82 (2008): 547-550.

[30] ZnO [Online]. Available from: http://en.wikipedia.org/wiki/Zinc_oxide. [2008, September 30].

[31] Rani, S., Suri, P., Shishodia, P.K., and Mehra, R.M. Synthesis of nanocrystalline ZnO powder via sol-gel route for dye-sensitized solar cells. Solar Energy Mater Solar Cells. 92 (2008): 1639-1645.

[32] Zhou, X., Guo, X., Ding, W., and Chen, Y. Superhydrophobic or superhydrophilic surfaces regulated by micro-nano structured ZnO powders. Appl. Surf. Sci. 255 (2008): 3371-3374.

[33] Berg, J.C. Wettability. Washington: Washington University Press. 1993.

[34] Numpud, P. Photoinduced Hydrophilic property of zinc oxide thin films prepared by sol-gel dip coating method. Master's Thesis. Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, 2008.

[35] Yimsiri, P., and Mackley, M.R. Spin and dip coating of light-emitting polymer solutions: matching experiment with modelling. Chem. Eng. Sci. 61 (2006): 3496-3505.

[36] Rheometer [Online]. Available from: http://en.wikipedia.org/wiki/Rheometer. [2010, August 18].

[37] Djouadi, D., Chelouche, A., Aksas, A., and Sebais, M. Optical properties of ZnO/silica nanocomposites prepared by sol-gel method and deposited by dip-coating technique. Physics procedia. 2 (2009): 701-705.

[38] Confocal laser scanning microscopy (CLSM) [Online]. Available from: http://en.wikipedia.org/wiki/Confocal_laser_scanning_microscope. [2010, June 7].

[39] Evans Analytical Group (EAG). Fourier transform infrared spectroscopy (FTIR) [Online].Available from: http://www.eaglabs.com/techniques/analytical _techniques/ftir.php. [2010, June 7].

[40] Scanning electron microscope (SEM) [Online]. Available from: http://en.wikipedia.org/wiki/Scanning_electron_microscope. [2010, June 7].

[41] Energy-dispersive X-ray spectroscopy (EDX) [Online]. Available from: http://en.wikipedia.org/wiki/Energy-dispersive_X-ray_spectroscopy. [2010, June 7].

[42] Shiratori, S.S., and Rubner, M.F. pH-Dependent thickness behavior of sequentially adsorbed layers of weak polyelectrolytes. Macromolecules. 33 (2000): 4213-4219.

[43] Landau, L., and Levich, B. Dragging of a liquid by a moving plate. Acta Physicochimica U.R.S.S. 17 (1-2) (1942): 42-54.

[44] Dorrer, C., and Ruhe, J. Drops on Microstructured surfaces coated with hydrophilic polymer: Wenzel's model and Beyond. Langmuir. 24 (2008): 1959-1964.

[45] Wu, H.-S., Jone, H.-C., and Hwang, J.-W. Reaction of polyacrylic acid and metal oxides: Infrared spectroscopic kinetic study and solvent effect. J. Appl. Polym. Sci. 63(1997): 89-101.

[46] Liu, H., Feng, L., Zhai, J., Jiang, L., and Zhu, D. Reversible wettability of a chemical vapor deposition prepared ZnO film between superhydrophobicity and superhydrophilicity. Langmuir. 20 (2004): 5659-5661.

[47] Miyauchi, M., et al. Reversible wettability control TiO_2 surface by light irradiation. Surf. Sci. 511 (2002): 401-407.

[48] Liu, Z., Jin, Z., Li, W., and Qiu, J. Preparation of ZnO porous thin films by sol-gel method using PEG template. Mater. Lett. 59 (2005): 3620-3625.

[49] Oyama, M., Kozuka, H. and Yoko, T. Sol-gel preparation of ZnO films with extremely preferred orientation along (002) plane from zinc acetate solution. Thin Solid Films. 306 (1997): 78-85.

[50] Znaidi, L., et al. Oriented ZnO thin films synthesis by sol-gel process for laser application. Thin Solid Films. 428 (2003): 257-262.

[51] Sun, R.-D., Nakajima, A., Fujishima, A., Watanabe, T., and Hashimoto, K. Photoinduced surface wettability conversion of ZnO and TiO_2 thin films. J. Phys. Chem. B.105 (2001): 1984-1990.

[52] Brinker, C.J., Frye, G.C., Hurd, A.J., and Ashley, C.S. Fundamentals of sol-gel dip coating. Thin Solid Films. 201 (1991): 97-108.

[53] Terrier, C., Chatelon, J.P., and Roger, J.A. Electrical and optical properties of Sb: SnO_2 thin films obtained by the sol-gel method. Thin Solid Films. 295 (1997): 95-100.

APPENDICE

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Appendix 1   EDX analysis of ZnO film prepared by 0.1 M Zn(NO$_3$)$_2$ with 3 precipitation cycles coated at withdrawal speed of 3.0 cm/min and drying temperature of 180°C for 2 h

Appendix 2   Summary of the oxide compounds on the ZnO film (prepared by 0.1 M Zn(NO$_3$)$_2$ with 3 precipitation cycles coated at withdrawal speed of 3.0 cm/min and drying temperature at 180°C for 2 h) observed by EDX

Oxide compound	Weight percent
SiO$_2$	71.21
SO$_3$	0.80
K$_2$O	0.20
CaO	7.11
Na$_2$O	14.84
MgO	2.28
ZnO	0.02

Appendix 3   X-ray diffractograms of ZnO incorporated with polyelectrolyte film
prepared by precipitation method with 3 precipitation cycles and drying
temperature of 180°C

Appendix 4   X-ray diffractograms of ZnO incorporated with polyelectrolyte film
prepared by 0.1 wt% ZnO in poly(acrylic acid) (PAA) solution with
drying temperature of 180°C

Appendix 5   X-ray diffractograms of ZnO incorporated with polyelectrolyte film prepared by 0.2 wt% ZnO in poly(acrylic acid) (PAA) solution with drying temperature of 180°C

Appendix 6   X-ray diffractograms of ZnO incorporated with polyelectrolyte film prepared by sol-gel method as prepared by pH of precursor sol of 1 with calcination temperature of 500°C

Appendix 7 X-ray diffractograms of ZnO incorporated with polyelectrolyte film prepared by sol-gel method as prepared by pH of precursor sol of 2 with calcination temperature of 500°C

VITA

Miss Walaiporn Suthabanditpong was born on April 23, 1984 in Bangkok, Thailand. She graduated from a secondary school of Mahidolwittayanusorn School in 2001. In 2006, she received a Bachelor degree in Chemical Engineering from King Mongkut's University of Technology Thonburi and continued her study in Chemical Engineering for the Master degree at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. During the master program, she conducted a research entitled "Deposition of nano-scaled zinc oxide on polyelectrolyte film by layer-by-layer technique" under supervision of Assoc. Prof. Tawatchai Charinpanitkul, the head of Center of Excellence in Particle Technology (CEPT). As a part of her master program, she received financial support from Japan Student Service Oganization (JASSO, Japan) to work as a research student at Nagoya Institute of Technology (NIT, Japan) for 10 months. She received the Master degree of Chemical Engineering in 2010.

International Proceeding

1. W. Suthabanditpong, K. Faungnawakij, N. Viriya-empikul, A. Sootitantawat and T. Charinpanitkul. "Deposition of nano-scaled zinc oxide on polyelectrolyte film by layer-by-layer technique" *Proceedings of International Conference on 6th Asian Aerosol Conference (AAC09)*, November 24-27, 2009, Bangkok, Thailand, p.69.

2. W. Suthabanditpong, H. Watanabe, T. Shirai, K. Faungnawakij, N. Viriya-empikul, A. Sootitantawat, T. Charinpanitkul and M. Fuji. "Deposition of nano-scaled zinc oxide on polyelectrolyte film by layer-by-layer technique" *Proceedings of International Conference on 3rd Thailand-Japan international Conference (TJIA2010)*, November 19, 2010, Nagoya, Japan, p.72-73.