# การสังเคราะห์ฟิล์มบางไฮโดรฟิลิกยิ่งยวดของซิงค์ออกไซด์/อะลูมินา และ ไทเทเนีย/อะลูมินา โดยวิธีโซลเจล

นางสาวปัทมา ภุมรินทร์



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551

# SYNTHESIS OF ZINC OXIDE/ALUMINA AND TITANIA/ ALUMINA SUPERHYDROPHILIC THIN FILM USING SOL-GEL METHOD

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A Thesis Submitted in Partial Fullfillment of the Requirments
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2008

| | |
|---|---|
| Thesis Title | SYNTHESIS OF ZINC OXIDE/ALUMINA AND TITANIA/ ALUMINA THIN FILM USING SOL-GEL METHOD |
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| Field of study | Chemical Engineering |
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ปัทมา ภุมรินทร์ : การสังเคราะห์ฟิล์มบางของซิงค์ออกไซด์/อะลูมินาและไทเทเนีย/อะลูมินา โดยวิธีโซลเจล (SYNTHESIS OF ZINC OXIDE/ALUMINA AND TITANIA/ ALUMINA THIN FILM USING SOL-GEL METHOD). อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร. ธวัชชัย ชรินพาณิชกุล, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร. เอกรัตน์ วงษ์แก้ว, 74 หน้า

การสังเคราะห์อนุภาคของอะลูมินาที่มีการเติมสังกะสีออกไซด์ลงไปและการสังเคราะห์อนุภาคของอะลูมินาที่มีการเติมไทเทเนียด้วยวิธีการสังเคราะห์ของโซลเจลในแอลกอฮอล์นั้นพบว่าอะลูมินัม เซค บิวทอกซ์ไซด์ เป็นวัสดุเริ่มต้นที่เหมาะสมสำหรับการสังเคราะห์อนุภาคของอะลูมินัมที่มีการเติมสังกะสีออกไซด์ลงไปและอนุภาคของอะลูมินัมที่มีการเติมไทเทเนียลงไป นอกจากนี้จึงได้ศึกษาถึงผลกระทบของเอทิลอะซีโตนอะซีเตรทและกรดไนตริกที่ทำให้ได้สารละลายของอะลูมินัมที่เป็นสารละลายใสได้ อนุภาคที่เป็นของแข็งของอะลูมินาที่มีการเติมสังกะสีออกไซด์และไทเทเนียมลงไปจะถูกวิเคราะห์ด้วยเครื่อง XRD, TEM และ SEM ตามลำดับ เพื่อหาโครงสร้างของสาร, ขนาดของอนุภาค และตำแหน่งของพีคของอะตอมที่เกิดขึ้นในการสังเคราะห์อนุภาคเหล่านี้

จากผลการทดลองพบว่าอนุภาคที่มีการเติมสังกะสีออกไซด์ลงไปที่อุณหภูมิ400องศาเซลเซียสจะทำให้อนุภาคนี้กลายเป็นอนุภาคชนิดใหม่คือซิงค์อะลูมิเนท ในขณะที่อนุภาคของอะลูมินาที่มีการเติมไทเทเนียลงไปจะมีโครงสร้างที่เป็นผลึกที่อุณหภูมิมากกว่า 800 องศาเซลเซียส อย่างไรก็ตามวัสดุที่สังเคราะห์ขึ้นนี้จะให้ค่ามุมของน้ำที่สัมผัสกับพื้นผิวของวัสดุที่สังเคราะห์ขึ้นอยู่ในช่วงของการเกิดคุณสมบัติไฮโดรฟิลิกเนื่องจากอะลูมินัมไฮดรอกไซด์สามารถที่จะรวมตัวกับไทเทเนียมไฮดรอกไซด์และซิงค์ไฮดรอกไซด์ในปฏิกิริยาไฮโดรไลซิสในการกลายเป็นวัสดุที่มีองค์ประกอบ 2 องค์ประกอบของอะลูมินากับซิงค์ออกไซด์และอะลูมินากับไทเทเนียในปฏิกิริยาการควบแน่นของการกลายเป็นซิงค์อะลูมิเนทและอะลูมินัมไทเทเนท



ภาควิชา.....วิศวกรรมเคมี.....ลายมือชื่อนิสิต.....ปัทมา ภุมรินทร์.....

สาขาวิชา.....วิศวกรรมเคมี.....ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์หลัก.....

ปีการศึกษา.....2551.....ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ร่วม.....

## 4970434121: MAJOR CHEMICAL ENGINEERING
KEY WORD: ALUMINA DOPED WITH ZINC OXIDE / ALUMINA DOPED WITH TITANIA / SOL-GEL / ALUMINUM PRECURSOR
PATTAMA POOMMARIN: SYNTHESIS OF ZINC XIDE/ALUMINA AND ITANIA/ ALUMINA THIN FILM USING SOL-GEL METHOD, THESIS PRINCIPAL ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng, AND THESIS CO-ADVISOR: ASST. PROF. AKKARAT WONGKAEW, Ph.D., 74 pp.

Alumina doped with zinc oxide and alumina doped with titania were synthesized by sol-gel method in alcohol solution. Aluminum sec butoxide were used as an aluminum precursor for synthesis of final product. Effect of molar ratio between ethylacetoacetate (EAC) and nitric acid were investigated for preparing clear homogeneous solution. All particulate powders were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to identify phases, particle size and chemical composition of their synthesize material.

It was experimentally found that a preparation of alumina doped with zinc oxide by calcination at temperature 400°C, resulting in a crystalline transformation of alumina doped with zinc oxide to zinc aluminate ($ZnAl_2O_4$). While, crystalline alumina doped with titania could be prepared by calcination at temperature over 800°C. These synthesized products exhibit hydrophilic property because aluminum hydroxide ($Al(OH)_3$) could be combined with zinc hydroxide ($Zn(OH)$) and titanium hydroxide ($Ti(OH)_4$) in hydrolysis reaction to become compounds of alumina and zinc as well as alumina and titania in condensation process. As a result, zinc aluminate ($ZnAl_2O_4$) and aluminum titanate ($Al_2TiO_5$) were obtained by sol-gel method.



Department .....Chemical Engineering ...Student's signature.....Pattama Poommarin.....

Field of study...Chemical Engineering....Principal Advisor's signature.....T. Charinpanitkul.....

Academic year.....2008.....Co-advisor's signature.....A. W.....

# ACKNOWLEDGEMENTS

The author would like to thank her advisor Assoc. Prof. Tawatchai Charinphanitkul and her co-advisor Asst. Prof. Akkarat Wongkaew for their introducing and comments in this thesis, deep discussion and constant encouragement throughout this project including the instructing for developing the author's self-learning capability.

The author gratefully acknowledges the financial support from NANOTEC, NSTDA and partial support from Chulalongkong University and Burapha University. In addition, the author would like to thank the Department of Chemical Engineering, Burapha University for experimental setting at chemical engineering laboratory.

Moreover, the author would like to thank Prof. Pichet Limsuwan and the two upper-class students at Burapha University (Pong& Aom) for their kind and helpful suggestion.

Furthermore, the author would like to thank all members of Center of Excellent in Particle Technology for their help, suggestion and warm collaborations.

Last but not least, the author would like to thank her family and her best friend for their love and encouragement.

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# NOMENCLATURES

| | | |
|---|---|---|
| CVD | = | Chemical vapor deposit |
| EAC | = | Ethylacetoacetate |
| SEM | = | Scanning electron microscopy |
| XRD | = | X-ray Diffraction |
| TEM | = | Transmisson electron microscopy |
| FT-IR | = | Fourier Transform Infrared Spectroscopy |
| EDX | = | Energy dispersive X-ray analysis |
| $Al(OH)_3$ | = | Aluminum hydroxide |
| $^oC$ | = | Degree celcious |
| HRTEM | = | High resolution transmisson electron microscopy |
| SAED | = | Selected area electron diffraction |

# CHAPTER I

# INTRODUCTION

## 1.1 Background

The preparation of metal oxide in nanometer scale has been synthesized by many methods because their properties can be improved selectively depending on their usage purposes. Furthermore, a various methods, such as CVD [1], sputtering method [2], microwave [3], and sol gel [4-5] and so on have been developed for preparing a variedly of materials in nanometer scale. Among them, sol gel is one of the most method for synthesizing material in nanometer scale because it easy to control. Additionally, such method could provide the film composition and in a large scale with low cost [4-7].

The semiconductor material of zinc oxide and titanium dioxide (or titania) have been wildly used in many fields because of their semiconductive behaviors with wild band gap 3.37 eV and 3.2 eV, respectively. Zinc oxide has been used as sensor, solar cell, electro-conductive material, and photo-induced surface of thin film, etc. [8-10] Another semiconductor, titania has been used as similar zinc oxide in many files [11-13]. In recent years, many researchers have been reported investigation results of $TiO_2$ or ZnO photo-induced surface property which could be stimulated after begin irradiated by ultraviolet ray (UV). It was found that angle of water on the coated surface decreased gradually, and finally, it became almost zero [9-11,14]. This phenomenon is called superhydrophilicity.

In this work, three types of aluminum compounds which are aluminum sec butoxide ($AlC_{12}H_{27}O_3$), aluminum isoproproxide ($AlC_9H_{21}O_3$) and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) were selected form the best suspension of aluminum compounds in alcohol solution. Then temperature was varied from 30 °C to 50 °C for investigating its effect. Quantity of ethylacetoacetate (EAC) and nitric acid were further investigated for preparing clear homogeneous solution of aluminum compounds. After that, zinc acetate ($(CH_3COO)_2$ $Zn{\cdot}2H_2O$) and titanium isoproproxide ($C_{12}H_{28}O_4Ti$) were added in aluminum solution to synthesize composite of alumina with zinc oxide and alumina with titania. These particulate products were characterized by SEM, XRD, TEM, respectively, for indicating morphology, the atom ratio of aluminum, zinc and titanium and crystalline structure of alumina doped with zinc oxide and alumina doped with titania. Furthermore, the optical properties of these synthetic materials were also investigated.

**1.2 Objective of this research**

To synthesize clear homogeneous solution of alumina doped with zinc oxide and alumina doped with titania by sol-gel method for investigating their microscopic and the optical properties.

**1.3 Scopes of research**

1. Investigation of parameters that have effect on the preparation of clear homogeneous solution of alumina doped with zinc oxide and titania using sol-gel process.

    1.1 Selection of the best aluminum precursor from 3 types of aluminum compounds, which were aluminum sec butoxide ($AlC_{12}H_{27}O_3$), aluminum isoproproxide ($AlC_9H_{21}O_3$) and aluminum

nitrate ($Al(NO_3)_3 \cdot 9H_2O$) which could provide homogeneous suspension. Moreover, the optimum temperatures for preparing clear homogeneous solution were varied from 30 to 50°C.

1.2 Selection of the optimum addition of EAC ($C_6H_{10}O_3$) which would provide stable aluminum sol in solution. Quantity of EAC were varied at 0.5, 1.0 and 1.5 ml.(9.8 mole%, 19.6 mole% and 29.9 mole%)

1.3 Selection of the optimum adddition of nitric acid ($HNO_3$) that could change sol solution to become gel. Quantity of nitric acid were varied at 0.124, 0.372 and 0.744 ml. (7.4 mole%, 22.3 mole% and 44.6 mole %)

2. Characterization of the particulate powder samples obtained from the sol gel process. The investigated parameters were related to

2.1 Investigation of the crystalline structure, shape, plane and ratio atom of aluminum (Al) and zinc (Zn) of alumina doped with zinc oxide using XRD, TEM and SEM, respectively.

2.2 Investigation of the crystalline structure, shape, plane and ratio atom of aluminum (Al) and titanium (Ti) of alumina doped with titania using XRD, TEM and SEM, respectively.

3 Application of alumina doped with zinc oxide and alumina doped with titania on glass substrate for investigating the photo-induced surface properties.

**1.4 Expected benefits**

1. Knowledge of mechanism of preparation of composite of alumina and zinc oxide as well as alumina and titania.

2. Knowledge of the mechanism of the photo-induced properties of thin film.

# CHAPERTER II

# FUNDAMENTAL THEORY AND LITERATURE REVIEW

## 2.1 Fundamental theory

### 2.1.1 sol-gel process

Sol is a colloidal suspension of solid particles in a liquid phase. The precursors (starting compounds) for preparing a colloid consist of metal or metalloid element which can be surrounded by various ligands (no including of metal or metalloid atom). The common precursors of alumina include inorganic salts such as Al $(NO_3)_3$ and organic compounds such as Al $(OC_4H_9)_3$, however organic compound of metal alkoxide is the most widely precursor for using as a raw material in sol-gel process.

**Mechanisms of reactions in sol-gel process**

The mechanisms of sol-gel process consist of two reactions for producing metal oxide are hydrolysis and condensation reactions. The reaction of hydrolysis is the reaction for producing molecule of metal hydroxide. After that, the molecule of metal hydroxide will combine to produce metal oxide in form of gel. Moreover, the mechanisms of sol-gel process can be shown chemical reaction as follow:

Hydrolysis reaction:

$$MOR + H_2O \longrightarrow MOH + ROH$$

The MOR represents metal alkoxide group. Which M is a metal, R is a proton or other ligand (if R is an alkyl, then OR alkoxy group), MOH is a metal hydroxide and ROH is an alcohol, the bar (-) is sometimes used to indicate a chemical bond. The

hydrolysis reaction occurs from the function of OR groups in metal alkoxide are replaced by OH. After that, the condensation reaction is occurred for producing metal oxide.

Condensation reaction:

$$MOH + MOH \longrightarrow MOM + H_2O$$

**Application of synthetic material from sol-gel process**

There are many applications of sol-gel materials in the form of thin films, composite material etc. In addition, the advantage of material from sol-gel process can be produced the high purity of synthetic material, homogeneity and controlling the porosity for protecting the casting of ceramic.

**Thin film** is one of the most successful commercial applications. The pattern of thin film is formed by dipping or spinning because it uses a little raw materials and quickly protection of cracking on surface area of thin film. Furthermore, the other method for preparing thin film includes spraying, inkjet printing or roll coating.

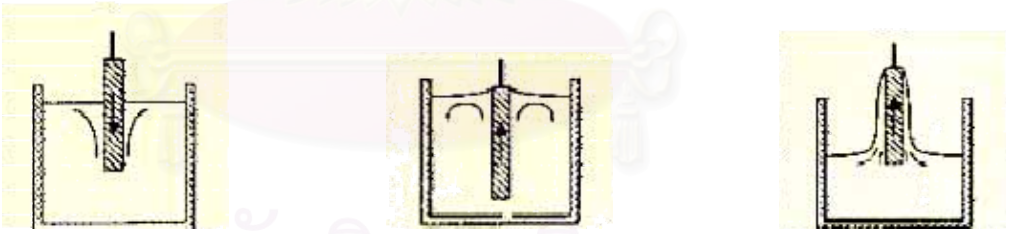
**Composite material** is a combination in the different type of materials. The sol- gel process can be produced material in the matrix phase of organic- inorganic and ceramic-metal composites. The sol particle of composite material of ceramic matrices has low viscosity of sols that it can be protected the abrasion of ceramic. In addition, the high surface area and small pore size of the gel matrix can be synthesized at high sintering force to protect the hot-pressing and the large shrinkage of the sol-gel matrix phase.

### 2.1.2 Film formation

One of the most important methods for preparing film formation is dipping, spinning, or spraying. The preparing film formation by dip coating is presented. The dip coating is the more important advantage of sol-gel processing than other method such as CVD, evaporation, or sputtering because this method can be controlled the microstructure of the deposition on thin film, the pore volume, pore size and surface area and saving money.

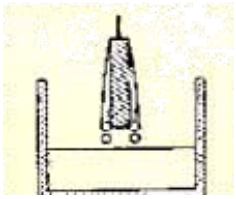
**Dip coating**

**Dip coating** is a method for immersing substrate into a tank which contains the coating material. After that, the substrate is removed the tank of containing coating material and evaporate the solution on substrate by force-drying or baking. The process of the dip coating process is shown in Fig.2.1.



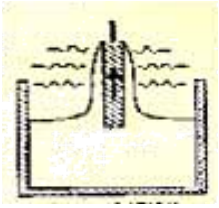
Immersion start-up Deposition & Drainage

(a) (b) (c)



Drainage

(d)



Evaporation

(e)

Fig.2.1 Stages of the dip coating process

(Ref. http://www.science.unitn.it/~gcsmfo/facilities/dip-coating.htm)

From Fig.2.1, this process can divide 5 steps for coating material on substrate as follow: immersion, star- up, deposition, drainage and evaporation. For coating material of volatile solvent of alcohol, we can divide 4 steps such as immersion, start-up, deposition and drainage steps. The step of evaporation is neglect because solution of alcohol is easy to evaporate by air.

**2.1.3 Photo- induced highly hydrophilicity**

There are two steps for occurring the photo-effects on a surface of semiconductor material. The first step, the surface of semiconductor is excited by UV in photocatalytic reaction. Next step, the highly hydrophilic property of surface is obtained by mechanism of excitable electron from valence band to conduction band in first step. In addition, $TiO_2$ and ZnO are the popular semiconductor material for applying in the field of the photo-induced highly hydrophilic on various substrates.

**What is hydrophilicity**

When UV irradiate on the surface of substrate which contain the semiconductor material, the contact angle of water will decrease to spread out (flat) on surface of substrate, leading to the contact angle reaches almost 0◦. At this case,

the surface becomes completely non-water repellant and is called “highly hydrophilic property”. The surface has a contact angle of a few degrees for a day or two without being exposed to UV light. After that, the contact angle slowly increases to become hydrophobic on surface of substrate. At this condition, the highly hydrophilic property can be simply recovered by exposing the surface again to UV light. Furthermore, the degree of the water on surface of coating material can be measured by contact angle equipment in unit degree. On glass or other substrate, water has a contact angle ranging from 20 to 30°.

Fig. 2.2 shows the contact angle on surface of substrate is irradiated by UV light. Before the surface is irradiated by UV light (Fig 2.2 (a)), the contact angle on the surface is more than 40°. After the UV light is irradiated on surface (Fig 2.2 (b)), the contact angle is less than 5°.

(a) (b)

Fig. 2.2 Appearance of contact angle of (a) before irradiation of UV light, (b) after irradiation of UV light (Ref. http://web.mit.edu/nnf/education/wettability/wetting.html)

**Mechanism of photo-induced highly hydrophilic process**

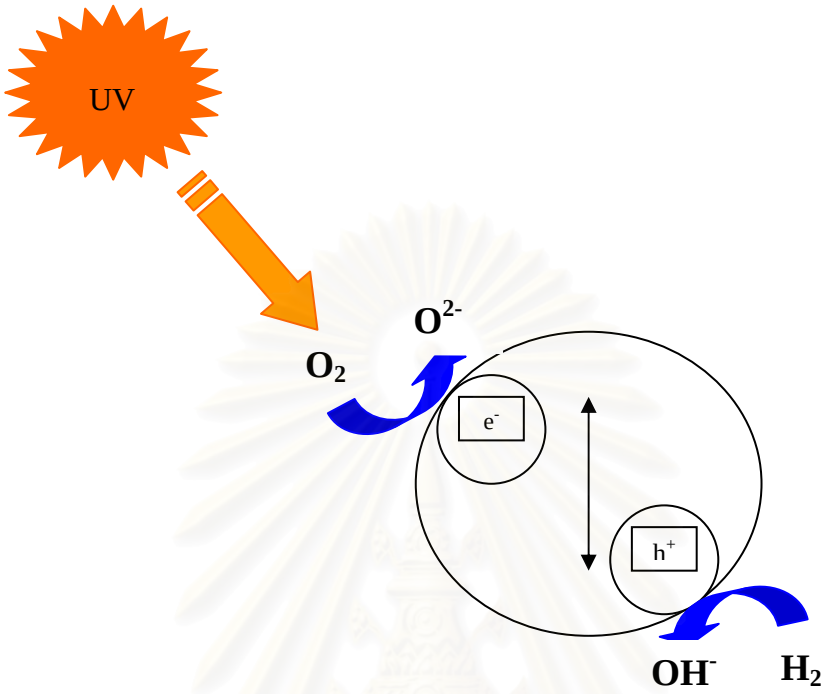



Fig.2.3 Mechanisms of photo-induced highly hydrophilic process

Fig.2.3 shows UV irradiates on surface of semiconductor material. In this Figure, UV light irradiate on surface of semiconductor material equal or higher than band gap energy of material. After that, the electron of semiconductor move from valence band to conduction band to become electrons and holes. In addition, $TiO_2$ is selected for exhibiting the mechanism of photo-induced highly hydrophilic process because $TiO_2$ is a popular material for applying in this field. The part of occurrence of $e^-$ , the molecule of oxygen ($O_2$) will react with electron to produce superoxide radical anions ($O^{2-}$). The part of holes will react with water to produce hydroxyl radicals ($OH^-$). This reaction will occur together to decompose organic compounds for applying in self cleaning glass. For the phenomenon of occurrence of superhydrophilicity has been studied in this work. When the surface of photocatalytic

film is irradiated by UV light from the sun and water is dropped on the photocatalytic film, molecule of water can occupy in hole that leading to the hydrophilic process on surface of thin film.

**Application of highly hydrophilic property**

There is an extremely wide range of applications of highly hydrophilic technology such as antifogging surfaces, and self-cleaning of building materials.

Fogging of the surface of mirrors and glass occurs when steam cools down on these surfaces to form water droplets. On a highly hydrophilic surface, no water droplets are formed. Instead, a uniform film of water is formed on the surface. This uniform can prevent fogging.

Strain-proofing and self-cleaning effects can be improved through the highly hydrophilic function. As an example, a plastic surface smeared with oil cannot be cleaned unless one uses detergent. A highly hydrophilic surface, however, has a higher affinity with water than oil. An oil smear on a plastic utensil is released from the plastic surface when the utensil is simply soaked in water. Based on this characteristic, a kitchen use fan which is likely to be covered with oil, could be easily cleaned by water if the fan blades were coated with a highly hydrophilic material.

Outdoor applications of this technique are also possible. Most of the exterior wall of buildings becomes soiled from automotive exhaust fumes, which contain oily components. If the building is coated with a highly hydrophilic material, the dirt on the walls can be washed away with rainfall, keeping the building exterior clean at all times.

Moreover, the applications of highly hydrophilic property are not limited to antifogging and self-cleaning. The highly hydrophilic surface can be extended in other fields.

**2.1.4 Zinc oxide (ZnO)**

Zinc oxide is a chemical compound with the formula ZnO. It is nearly insoluble in water but soluble in acids and alkalis. It has white powder. The crystal structure of ZnO has 2 structures. The structure is wurtzite and zincite structure. These both structures are hexagonal which is shown in Fig. 2.4

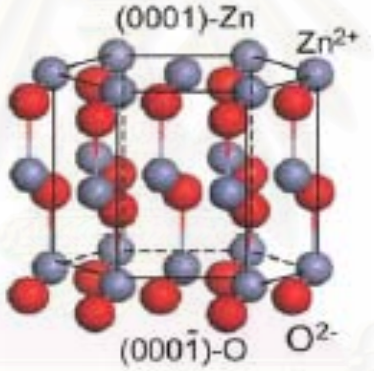



Fig.2.4 Crystalline structure of zinc oxide

(Ref. http://www.fhi-berlin.mpg.de/th/personal/hermann/ZnO.gif)

The property of zinc oxide

| | |
|---|---|
| Molecular weight | 81.38 |
| Density ($g/cm^3$) | 5.67 |
| Melting point (°C) | 1975 |

**Application of zinc oxide**

Zinc oxide can apply in many fields such as electrical material, pigment, chemical and biosensor etc.

**Cosmetic**

Zinc oxide can be used in ointments, creams, and lotions to protect sunburn of the body from ultraviolet light because zinc oxide can be wildly absorbed spectrum of UVA and UVB. In addition, zinc oxide has antimicrobial and antifungal activities that can be protected rash from diaper.

**Rubber manufacture**

Zinc oxide and stearic acid are compounds in the commercial manufacture of rubber goods because this mixture can be controlled the process of rubber cure. In addition, zinc oxide can also be used as filler in rubber mixtures

### 2.1.5 Titanium dioxide or Titania ($TiO_2$)

Titanium dioxide or titania is a chemical compound with the formula $TiO_2$. Titanium dioxide 3 structures of crystalline structure such as brookite , anatase and rutile. Moreover, the structure of anatase and rutile are the most popular structure for applying in many fields. Anatase and rutile structures have the same symmetry in pattern of tetragonal (Fig.2.5).

(a) (b)

Fig.2.5 Crystalline structure of Titanium dioxide which (a) anatase and (b) rutile

(Ref. http://ruby.colorado.edu/~smyth/min/tio$_2$.html)

The property of Titanium dioxide

| Property | Anatase | Rutile |
|---|---|---|
| Molecular weight(MW) | 79.890 | 79.890 |
| Crystal system | Tetragonal | Tetragonal |
| Density (g/cm$^3$) | 3.84 | 4.26 |

**Application of Titanium dioxide**

**Pigment**

Titanium dioxide is the most widely used in pigment because of its brightness and very high refractive index (n = 2.7). Approximately 4 million tons of $TiO_2$ pigments are consumed in world. Moreover, this $TiO_2$ pigment is extensively used in plastics and other applications for finding UV resistant properties because titanium

dioxides can behavior as UV absorber, efficiently destructive transformation of UV light energy in heat.

**Cosmetic**

In almost every sunscreen with a physical blocker, titanium dioxide is found because of its high refractive index, its strong UV light absorbing capabilities and its resistance to discoloration under ultraviolet light. This advantage enhances its stability and ability to protect the skin from ultraviolet light. Sunscreens designed for infants or people with sensitive skin are often based on titanium dioxide and/or zinc oxide, as these mineral UV blockers are less likely to cause skin irritation than chemical UV absorber ingredients, such as avobenzone.

**2.1.6 Alumina**

Alumina has been widely used as in oxide ceramic, catalysis, electronics, biomedicine, ceramic, pigment, and optical materials, either in pure form or as raw material to be mixed with other oxides. It can be found in the different degrees of purity and crystal structures. The composition of the alumina with other metal oxide can change to enhance particular desirable material characteristics. Example, addition alumina in zinc oxide can improve the conductivity of composite material.

**The property of alumina**

- Hard, wear- resistant
- Good thermal conductivity
- High strength and stiffness
- Excellent size and shape capability

**Application of alumina oxide**

**Catalysis**

Alumina always attract considerable attention because of their extensive applications in the fields of catalysis, electronics, biomedicine, ceramic, pigment, and optical materials, for their advantages of chemical and thermal stabilities. Particularly in the chemical industry, alumina can be used as catalytic support to disperse active components, including metals, metal oxides, acids, and bases, and so on. For example, they are usually utilized in some important industrial catalytic hydrogenation and oxygenation reactions because of their excellent stability and large specific surface area.

**Electrical insulation**

The high volume resistor and dielectric strength make alumina an excellent electrical insulator which leads to an application in electronics as substrates and connectors and in lower duty applications such as insulators for automotive spark plugs**.**

**Metal Cutting Tools**

The high “hot” hardness of alumina have led to an applications as tool tips for metal cutting (though in this instance alumina matrix composites with even higher properties are more common) and abrasive.

**2.2 Literature review**

***K. Tadanaga et.al*** (1994) investigated the precursor structure and hydrolysis gelation of aluminum sec butoxide Al (O-sec-Bu) $_3$ to modify with ethylacetoacetate(EAC) using IR, UV and high magnetic field $^{27}$Al NMR spectra. The $^{27}$Al NMR equipment showed the reaction of EAcAc with Al (O-sec-Bu)$_3$ led to the formation of six-

coordinated structure units and most of precursor could be present as linear trimer which contain a four and six coordinated of Al atoms. It was found that, the EAC was the formed of strong chelating bonds with Al (O-sec-Bu)$_3$ , led to the hardly attacked with molecule of water in gelation process of sol gel method.[15]

***C.B. Jing et.al*** (2006) investigated the stability of alumina with water was called alumina sol. The addition EAC could successfully extend time of occur alumina sol from seconds to four months because EAC could reacted with HO-Al groups on the surface of $Al_2O_3$ particle but it didn't directly react with ASB (alumina sec butoxide) molecule. The surface modification layer of EAC was formed around $Al_2O_3$ colloidal particle. As a result, the surface HO-Al groups of $Al_2O_3$ particle were sufficiently capped and the growth of colloidal particles was effectively prevented. Therefore, the alumina sol had the great potential of being used in practical applications because it could excellent stability and high $Al_2O_3$ content. From this research, the ratio of ASB: water at 1:30 gave the high alumina content in alumina sol.[16]

***R.S. Mane et.al*** (2006) investigated the super-hydrophilic in aqueous solution system of rutile phase ($TiO_2$) of violet color of nanocrystalline thin films growth on ITO substrate at room temperature. This method for preparing $TiO_2$ violet color nanocrystalline was simple, safe, cost effective and reproducible, respectively. From XRD,SEM and TEM was composed to densely packed nanometer-sized spherical grains of approximate diameter 3.15 $\pm$ 0.4 nm. Furthermore, the band gap energy 4.61 eV was obtained by absorption in visible region with excitonic maxima at 434 nm. The surface of film showed super-hydrophilic property in exhibition water contact angle at 7°C. Strong visible absorption (not due to chlorine) leaves future challenge to use these films in extremely thin absorber (ETA) solar cells.[17]

***A.A. Ashkarran et. al*** (2008) investigated $TiO_2$ thin films on soda lime glass using $TiCl_4$ as a precursor in sol-gel process. The synthesis $TiO_2$ surface was superhydrophilicity under UV irradiation. From this work, the contact angle of water on $TiO_2$ film was decreased to near zero after about 10 min of UV irradiation. The surface was obtained by this method could storage property of superhydrophilicity at least 24 hr. The ideal mechanisms of UV- induced wetting of $TiO_2$ surface was obtained by the removal hydrophobicity layers of hydrocarbon or other carbonaceous species using $TiO_2$ mediated photo-oxidation which could led to the attractive interaction between water and cleaning surface of $TiO_2$ [11]

***K. Katsumata et.al*** (2006) investigated photo-induced to change transparent of anatase polycrystalline thin films with large grain size about 200 nm. The film used vacuum ultraviolet (VUV) before heating at 500°C. Upon UV irradiation, the surface image was blurred with increasing apparent surface roughness, then, the image sharpened gradually as the surface returned to its initial level. This surface microstructure changed at the grain boundary.[18]

***T. Shibata et.al*** (2004) compared the photocatalytic oxidation and photo-induced hydrophilicity of brookite-rich $TiO_2$ to the anatase one. It was found that, the photocatalytic oxidation activities were evaluated by the initial photodegradation rates of methylene blue and cis-9-octadecenoic acid. The rates for the methylene blue bleaching were nearly identical ($-2.2\times10^{-3}$ Abs $min^{-1}$) for the brookite-rich and anatase films, and the rate for cis-9-octadecenoic acid decomposition on the brookite-rich film was slightly less than that on the anatase one ($-0.08 \pm 0.01$ mg $cm^{-2}$ $min^{-1}$ and $-0.10 \pm 0.01$ mg $cm^{-2}$ $min^{-1}$). The photo-induced hydrophilicity were evaluated by the changes in water contact angles ($\theta$) under rather weak UV light irradiation

(5 μW $cm^{-2}$), were better for the brookite surface than the anatase one. Moreover, the brookite-rich film became more hydrophilic (θ= 10°) than the anatase one (θ = 18°) after long time exposure to weak UV light irradiation and showed a good ability for the photo-induced hydrophilicity. [19]

***L. Huan et.al*** (2004) investigated the hierarchical structures similar with the lotus leaf created by nanostructures on sub-microstructures could give a constructing superhydrophobic surfaces. The CVD method was used to prepare superhydrophobicity Zno thin films, which proposes a very simple and relatively inexpensive method to produce a good quality film. The Zno thin film could show the contact angle 164.3° before UV irradiations and became superhydrophilic at contact angel less than 5° after irradiations. This result could extend a way alternate to improve Zno thin film in self-cleaning glasses process. [20]

***M. Miyauchi et.al*** (2005) investigated the photo-induced hydrophilic conversion on single crystalline ZnO films to depend on the crystal face of the surface by RF-magnetron sputtering. The ZnO films on sapphire A and C face were oriented along the (0001) direction, whereas the ZnO film on sapphire R face was oriented along the (11-20) direction. It was found that, the hydrophilic rate on the (11-20) face of ZnO was much higher than that on the (0001) face. Because at this face, the both oxygen and zinc ions were exposed on the (11-20) face, whereas zinc ions were terminated on the (0001) face. So, the highly hydrophilic property of (11-20) face was due to its terminated oxygen ions, which were reactive sites for hydrophilicity. This study showed that the photo-induced hydrophilicity could be controlled by the surface crystal faces.[10]

***G. Min et.al*** (2007) investigated the preparation single crystalline structure of ZnO-NAFs using hydrothermal method. From this research, the surface modification photo-induced hydrophilicity to superhydrophobicity transition on well-aligned single-crystalline ZnO nanorod array films (ZnO-NAFs), the surface of transparent ZnO-NAFs was highly hydrophilic with a water contact angle of 9.6±0.8°. However, after being exposed to octadecanethiol solution, the surfaces of the ZnO-NAFs became superhydrophobicity with a water contact angle of 156.2±1.8°. This technique could offer the great potentials for preparing two-dimensional micro-patterns with a high wettability contrast for water.[9]

***M.S. Kang*** (2005) compared superhydrophilicity of Al-$TiO_2$ and pure $TiO_2$ using solvothermal method. The result of XRD and FT-Raman spectra showed that Al ion well incorporated in $TiO_2$ structure and had size below 25 nanometer, exhibited spherical anatase structure. The Al-$TiO_2$ (195-299 $m^2/g$) exhibited surface area more than pure $TiO_2$ (45 $m^2/g$). In addition, the XPS spectra showed that the Al-$TiO_2$ have higher hydrophilic property than pure $TiO_2$. The superhydrophilicity was enhanced in Al-$TiO_2$ than pure $TiO_2$, this result of contact angle below 1° for water dropped under 365 radiations.[21]

***S.Ping et.al (2006)*** investigated the wettability of polycrystalline rutile $TiO_2$ by molten Al and factors influencing it such as atmosphere, temperature, and time and testing method. The contact angles measured in vacuum were smaller than those obtained in Ar, which, in turn, were smaller than in Ar–3% $H_2$. The influence of temperature with the initial contact angles showed a distinctive temperature dependent behavior; they were larger at higher temperatures. With regard to the contact angles obtained in vacuumand in Ar, which were generally smaller than 90°, Al–$TiO_2$ system

is a partial wetting nature. However, this system could easily be non-wetting due to a considerable increase in oxygen partial pressure around the Al was dropped as a result of $TiO_2$ reduction [22]

***R.D. Sun et.al*** (2001) investigated the photo-induced surface wettability conversion reactions of ZnO and $TiO_2$ films. Before UV irradiations, ZnO and $TiO_2$ film exhibited water contact angle of about 109 and 54°, respectively. UV irradiations turned both surfaces to highly hydrophilic with water contact angel less than 10°. The storage film in the dark could return from the highly hydrophilic to starting contact angle of their film. Reversible surface wettability conversion reactions were achieved by alternate UV irradiation and storage in the dark area of both films. The similar behaviors of wettability conversion observed on the ZnO and $TiO_2$ surfaces to followed a similar conversion mechanism. The adsorption of water with dissociation on the photo-induced surface defective sites contributes to the formation highly hydrophilic of ZnO and $TiO_2$ surfaces on films. The successes of preparation highly hydrophilic ZnO and $TiO_2$ surfaces on films by high-temperature annealing and $Ar^+$ sputtering were provided supporting evidence for explanation that surface defective sites play important roles in causing the surface wettability conversion reactions.[23]

***L. Huang et.al*** (2005) investigated the formation of a stable superhydrophobic surface of carbon nanotubes (CNTs) coated with zinc oxide (ZnO) thin film. The CNT template was synthesized by chemical vapor deposition on Fe-N catalyst layer and ZnO film was coated on the CNT template by the filtered cathode vacuum arc technique. It was found that, the contact angle measurement exposed that the surface of ZnO coated CNTs was superhydrophobic with water contact angle 159°. Unlike the uncoated CNTs surface, the ZnO-coated CNTs surface showed no sign of water

seepage even after a prolonged period of time. The wettability of the surface could be reversibly changed from superhydrophobicity to hydrophilicity by alternation of ultraviolet (UV) irradiation and dark storage.[24]

***M. Maeda et.al***.(2005) investigated effect of silicon dioxide (silica) addition into titanium oxide (titania) films on crystalline and photo-induced hydrophilicity. Titania films and titania–silica mixed films with 20% or 50% silica were prepared by spin-coating deposition. For the titania films, the photo-induced hydrophilicity was only observed in the films with anatase polycrystalline structure. For the titania–silica mixed films, these film didn't show the obvious anatase polycrystalline structure and the property of photo-induce hydrophilicity was observed. The super hydrophilicity of contact angle was showed at 0° in the titania–silica mixed films with 20% silica. The photo-induced hydrophilicity of the titania films closely connect with the anatase crystalline structure. In the titania–silica mixed films, the synergistic effects of anatase polycrystalline structure of titania and water-trapping effect of silica were important for their strong photo-induced hydrophilicity. [25]

From the mentioned literature review, they described the preparation alumina by sol gel method and occurrence of the photo-induced highly hydrophilic property of zinc oxide and titania. For this research, the preparation composite of alumina with zinc oxide and alumina with titania for investigating the photo-induced highly hydrophilic property are presented.

# CHAPER III

# EXPERIMENTAL

## 3.1 Materials

All chemical agents used in this work were imported from by Fluka, Ajax Finechem and Merck. The physical properties of each chemical agent were shown in table3.1

Table 3.1 Physical property data of each chemical agent

| Order no. | Name | Chemical formula | Density ($g/cm^3$) | appearance | manufacture |
|---|---|---|---|---|---|
| 1 | Aluminum sec butoxide | Al ($C_{12}H_{27}O_3$) | 0.96 | Slurry | Fluka |
| 2 | Aluminum isoproproxide | Al ($C_9H_{21}O_3$) | Not available | White powder | Fluka |
| 3 | Aluminum nitrate | $Al(NO_3)_3 \cdot 9H_2O$ | Not available | White powder | Fluka |
| 4 | Ethyacetoactate (EAC) | $C_6H_{10}O_3$ | 1.028 | Colorless liquid | Fluka |
| 5 | Nitric acid 65% | $HNO_3$ | 1.51 | Colorless liquid | Merck |
| 6 | Ethanol | $CH_3CH_2OH$ | 0.789 | Colorless liquid | Merck |

| Order no. | Name | Chemical formula | Density ($g/cm^3$) | appearance | manufacture |
|---|---|---|---|---|---|
| 7 | Zinc acetate | $(CH_3COO)_2Zn{\cdot}2H_2O$ | Not available | White powder | Ajax Finechem |
| 8 | Titanium isoproproxide | $C_{12}H_{28}O_4Ti$ | 0.96 | Colorless liquid | Fluka |

**3.2 Experimental procedure**

The experimental procedure was separated into 3 parts as follow:

*a) Selection the best aluminum compounds*

The first step, Alumina doped with zinc oxide and alumina doped with titania solution were prepared by following procedures. $9.8x10^{-3}$ moles of each aluminum compounds such as aluminum sec butoxide, aluminum isoproproxide and aluminum nitrate were dissolved in 40 ml of ethanol at temperature 30°C and 50°C, respectively. In addition, the aluminum precursor was selected from these aluminum compounds that could be well suspended in alcohol solution.

*b) Preparing clear homogeneous solution of alumina doped with zinc oxide and alumina doped with titania*

Based on the previous section, aluminum sec butoxide at 50°C was selected as aluminum precursor for synthesizing clear homogeneous solution. After that, quantity of EAC 0.5ml, 1.0 ml and 1.5 ml (9.8 mole%, 19.6 mol% and 29.9 mole%) was used as chelating agent by adding to the solution and waiting for 15 min., 0.53 ml of water was added for hydrolysis reaction with the best condition in aqueous solution. After having reaction for 15 min., quantity of nitric acid was varied at 0.124 ml, 0.372 ml.

and 0.744 ml. (7.4 mole%, 22.3 mole% and 44.6 mole%) to control the suspension of aluminum precursor in the gelation process. Next 15 min, 0.68 g and 0.89 g.of zinc acetate nonahydrate and titanium isoproproxide were added in clear homogeneous of aluminum solution. [Note: In the case of Titanium isoproproxide doping, it is recommended to close heater and wait until temperature decrease to room temperature]. Then, heater was closed and continuously stirred 30 min. Moreover, these solutions were coated on soda-lime glass substrates by dip coating process. The phase, shape and arrangement atom of their synthesis material were characterized by XRD, TEM and SEM respectively, for investigating their microscopic and the optical properties of synthetic material.

*c) Preparing soda-lime glass*

Soda-lime glass substrate was divided into 4 steps for cleaning. At first step, a soda-lime was cleaned by glass cleaner and rinsed with deionize water. Next, soda-lime glass was dried by tissue paper which had a little dust or small particle on paper tissue. Second step, the soda-lime glass was dipped about 5 min. in dilute nitric acid solution for eliminating ion charge on glass substrate and was dried by tissue paper again. Third step, soda-lime was dipped in isopropanol about 5 min. and was dried by tissue paper. Last step, the soda-lime glass was dipped in acetone for shaking by sonic batch about 1-2 min. These soda-lime glasses were kept in glass box for using in the next experiment.

**3.3 Analytical instruments**

The instruments used to characterize the property of alumina doped with zinc oxide and alumina doped with titania are UV-Vis spectrophotometer (Phamaspec UV-1700, Shimadzu), FT-IR (Jeol model JNM-A500), TEM (Jeol model JEM-2100),

XRD (Bruker AXS D8), and SEM (Jeol model JSM-6400 and JSM-5800LV) for finding transmittance of their synthetic material, shape, crystalline structure and chemical position, respectively. The instrument for measuring the photo-induced surface property on surface of thin film is contact angle equipment.

*UV-Visible spectrophotometer*

The instrument of UV-visible spectrophotometer (Phamaspec UV-1700, Shimadzu) was used to measure the transparent solution at wavelength 300-700 nm. Furthermore, this apparatus could be measured the transparent film coated on soda-lime glass substrate too. This instrument was shown in Fig.3.1

Fig. 3.1 UV-Visible spectrophotometer

*Fourier Transform Infrared Spectroscopy (FT-IR)*

FT-IR (Jeol model JNM-A500) was used to separate the function organic, inorganic compounds and chemical bonding of material in liquid phase and solid phase. This instrument was shown in Fig.3.2

Fig. 3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

*Transmission electron microscopy (TEM)*

TEM analysis was studied by Jeol model JEM-2100.(Fig.3.3) The particulate powder sample was prepared to suspend in alcohol before ultrasonic treatment with the sufficient time for ensuring its uniform dispersion. A drop of clearly solution was then dripped onto a carbon grid. The specimen was loaded into sample chamber and waiting for the vacuum condition and steady state inside the chamber about 30 min. This instrument was used to identify the shape and the type of plane in material.

Fig.3.3 Transmittance electron microscopy (TEM)

*X-Ray diffraction (XRD)*

The XRD (Bruker AXS D8) was used to analyze phase of alumina doped with zinc oxide and alumina doped with titania. These particulate powder samples were spread on the glass slide and then set in the equipment which provide x-ray beam for analyzing. This instrument was shown in Fig.3.4


Fig.3.4 X-Ray diffraction (XRD)

*Scanning electron microscopy (SEM)*

The SEM (Jeol model JSM-6400 and JSM-5800LV) was used to analyze the morphology of particulate powder sample. Furthermore, SEM could analyze the chemical position that related with percent mass of each element in the particulate powder. This instrument was shown in Fig.3.5

Fig. 3.5 Scanning electron microscopy (SEM)

*Contact angle*

Contact angle was the equipment for analyzing wettability on surface of material. This equipment was shown in Fig.3.6

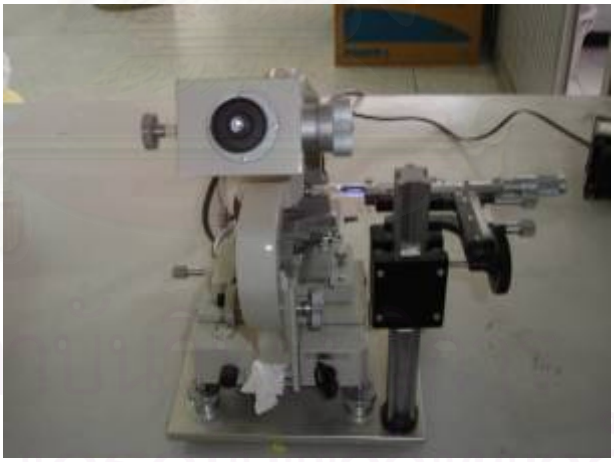


Fig. 3.6 Contact angle

# CHAPER IV

# RESULTS & DISCUSSION

This section dedicated to explanation and discussion of the experimental result of the preparation alumina doped with zinc oxide and alumina doped with titania for investigating the photo-induced surface property on glass substrate of their materials. Regarding to the objectives of this work, this chapter divided into 3 sections for discussing as follows:

## 4.1 Investigation of parameters that had effect on the preparation of alumina doped with zinc oxide and alumina doped with titania using sol-gel method

In this work, the suitable molar ratio for preparing clear homogeneous solution of aluminum precursor: EAC: nitric acids were selected by many considerations such as the selection aluminum compounds, optimum of EAC and nitric acid. Result of preparing clear homogeneous solution was presented in this section.

### 4.1.1 Selection of the best aluminum precursor

For selecting of the best aluminum precursor from aluminum sec butoxide, aluminum nitrate and aluminum isopropoxide were dissolved in ethanol (99.9%wt) at 40 ml. An aiming at preparation of nano-sized precursor it was expected that clear suspension would be obtained. Qualitative comparison of suspension prepared from each aluminum compound was shown in Fig. 4.1

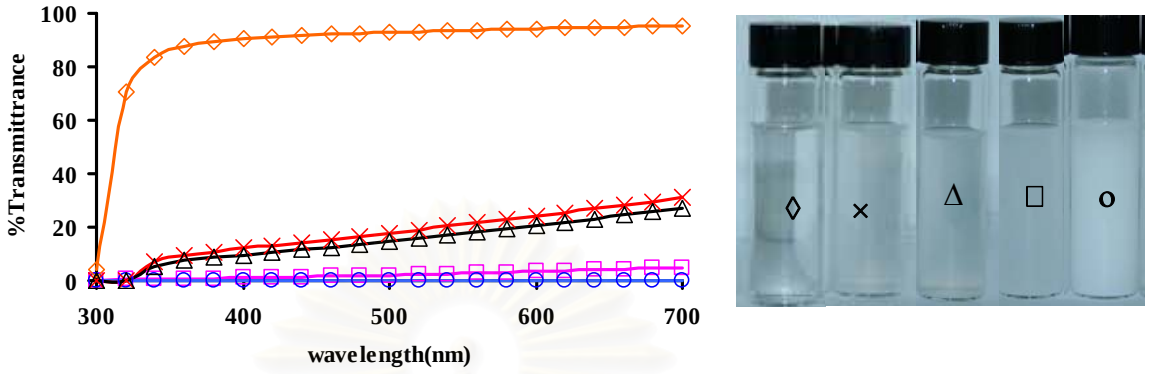



Fig.4.1 Comparison of UV transmittance of aluminum precursor prepared from each aluminum compound in ethanol: aluminum sec-butoxide at 50°C ( ◊),aluminium nitrate at 30°C (×), aluminum nitrate at 50°C(Δ), aluminum sec butoxide at 30°C (□) and aluminum isopropoxide at 30°C and 50°C (o)

Fig.4.1 shows UV transmittance spectra of aluminum precursor suspensions prepared from different aluminum compounds in ethanol at 30°C and 50°C in wavelength between 300-700 nm. At 30-50°C, aluminum isopropoxide provided the precursors which clearly precipitate, leading to the very low transmittance (Fig.4.1 (o)). Next aluminum compounds, aluminum nitrate could result in partial precipitation of alumina precursor at either 30°C or 50°C which was shown in Fig.4.1 (×) and Fig. 4.1(Δ), respectively. The last aluminum compounds, aluminum sec butoxide could lead to a very clear and homogeneous suspension of alumina precursor at 50°C (Fig.4.1 (◊)). However, at lower temperature, the precipitate of aluminum sec butoxide could be found in Fig.4.1 (□). Therefore, the preparation aluminum sec

butoxide in ethanol at 50°C was selected as the main constituent for preparing nano-sized aluminum precursor because this condition gave the highest transmittance.

**4.1.2 Selection of the optimum condition of EAC**

Base on the previous section (4.1.1), aluminum sec butoxide was selected as the aluminum precursor to produce aluminum sol solution. Aluminum sol was aluminum hydroxide (Al (OH) $_3$) obtained from hydrolysis reaction. However, this aluminum precursor could not directly react with water in hydrolysis reaction because it would precipitate immediately, leading to a requirement of addition of some chelating agent. Among various chelating agents, EAC exhibits a better performance in stabilizing suspension of aluminum precursor because EAC could combine aluminum precursor before being hydrolyzed by water to form aluminum hydroxide in solution. Fig. 4.2 shows that EAC could combine alumina precursor in FT-IR spectra.

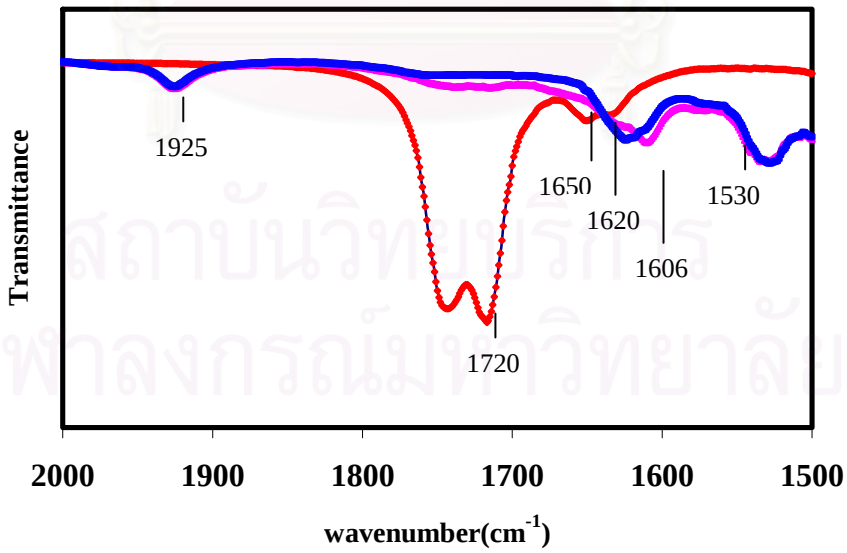



Fig. 4.2. FT-IR spectra of pure EAC represented in red line, Al-sec + EAC represented in blue line and Al-sec + EAC + $H_2O$ represented in pink line

Fig.4.2 shows IR transmission spectra of pure EAC represented in red line, Al-sec + EAC represented in blue line and Al-sec + EAC + $H_2O$ represented in pink line in wavenumber between 2000 and 1500 $cm^{-1}$. Based on IR spectra of pure EAC, there were two peak at wavenumber 1720 and 1650 $cm^{-1}$ which could be assigned to the C=O stretching vibration of the ketonic from and the enolic form, respectively. [15-16, 26] Next, EAC was added in solution, the peak of EAC at 1720 $cm^{-1}$ and 1650 $cm^{-1}$ disappeared almost completely which was shown in blue line and pink line. In contrast with these, two peaks at 1620 $cm^{-1}$ and 1530 $cm^{-1}$ were appeared. These two peaks could observe in blue line of Al-sec + EAC. After that, water was added in aqueous solution for producing aluminum hydroxide (Al $(OH)_3$), the peak of Al-sec+ EAC shifted from position 1620 $cm^{-1}$ to position 1606 $cm^{-1}$. It was expected that, at position 1606 $cm^{-1}$ was position of occurrence aluminum hydroxide from hydrolysis reaction because the peak of aluminum sec butoxide observe at position 992 $cm^{-1}$ and 912 $cm^{-1}$. Moreover, at position 1925 $cm^{-1}$ was the position of ethanol. The peak of aluminum sec butoxide and ethanol were shown in Fig. 4.3 Therefore, an addition of EAC played an important role in producing aluminum hydroxide (Al $(OH)_3$).

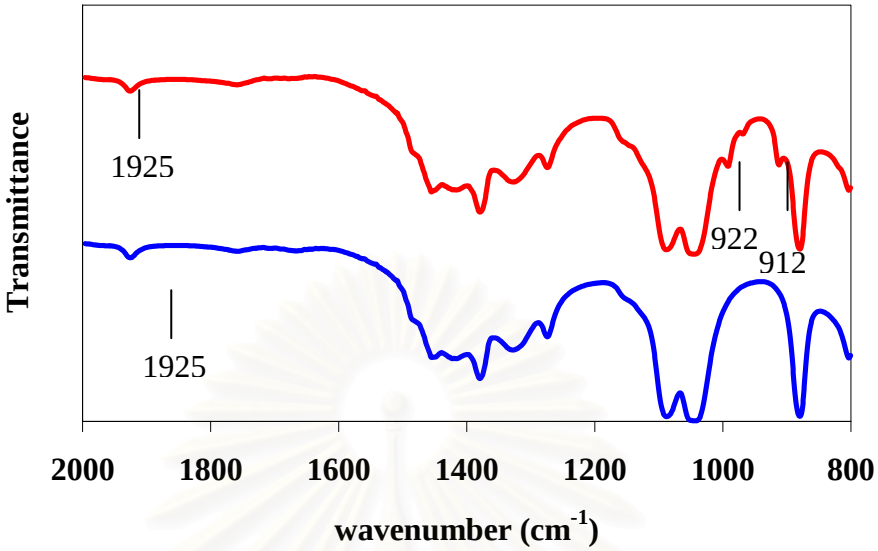



Fig. 4.3 FT-IR spectra of ethanol reprsented in blue line

and al-sec+ ethanol represented in red line

In Fig.4 .4 shows EAC with a concentration of 9.8 mol % could provide a clear and homogeneous suspension with the highest transmittance in the visual light spectra. The optimal molar ratio of aluminum sec butoxide to EAC was **1: 0.40.**

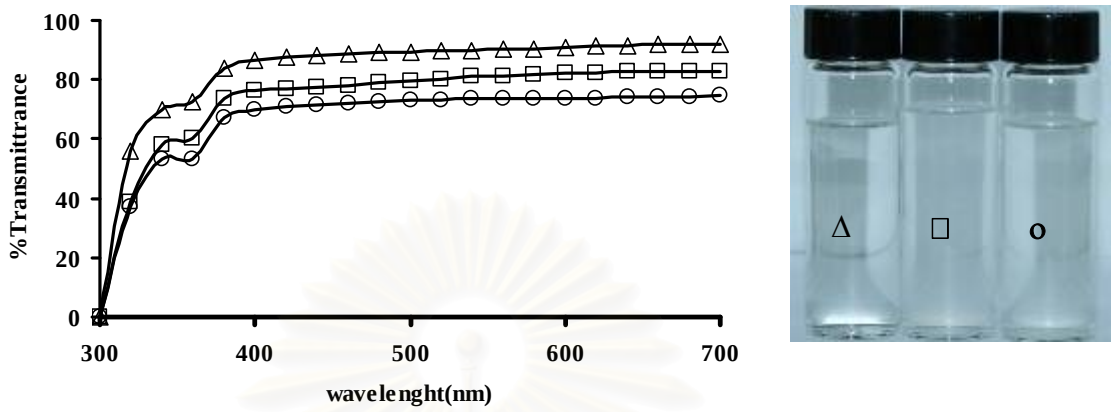



Fig.4.4 Effects of EAC on the transmittance and appearance of the prepared alumina precursor suspension: 9.8 mole %(Δ), 19.6 mole %(□) and 29.9 mole %(o)

**4.1.3 Selection of the optimum condition of nitric acid**

From section 4.1.2, an addition of EAC had effect with the longer the stability of alumina sol. [15-16, 26] For further improvement of the stability of sol suspension, nitric acid was selected because of its activity to help destruct bonding among sol particles in suspension and promote gelation. [27] The effect of quantity of nitric acid added to the sol suspension prepared from aluminum sec- butoxide in ethanol with EAC was further investigated. The optimal molar ratio of nitric acid was shown in Fig. 4.5

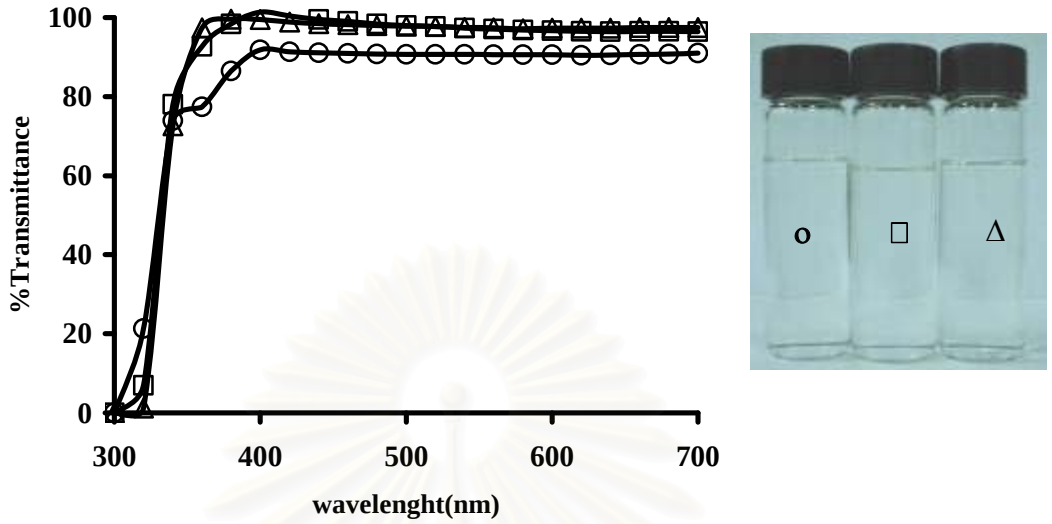



Fig.4.5 Effects of nitric acid on the transmittance and appearance of the prepared alumina precursor suspension: 7.4 mole %(o), 22.3 mole %(□) and 44.6 mole %(Δ)

From Fig.4.5, the concentration of 22.3 mole% and 44.6 mole% had closely transmittance spectra however an increasing of the quantity of nitric acid in the process had effect on the precipitation of sol solution after combined with zinc oxide or titania. Therefore, the concentration of nitric acid was provided the stable gel of alumina in this work was 22.3 mole %., the optimal molar ratio of aluminum sec-butoxide to nitric acid was **1: 0.9**.

For preparing composite of alumina with zinc oxide and alumina with titania, an amount of zinc acetate and titianium isoproproxide 0.68 g. and 0.89 g. were added into alumina clear homogeneous solution. The clear homogeneous solution image of alumina doped with zinc oxide and alumina doped with titania were shown in Fig. 4.6 (a) and Fig.4.6 (b), respectively,

(a) (b)

Fig. 4.6 Appearance solution of (a) alumina doped with zinc oxide and (b) alumina doped with titania

After that, clear homogeneous solution of alumina doped with zinc oxide and alumina doped with titania were placed at room temperature for becoming gel. The appearances of their gel were shown in Fig.4.7 (a) and Fig. 4.7 (b), respectively.

(a) (b)

Fig. 4.7 Appearance gel of (a) alumina doped with zinc oxide and (b) alumina doped with titania

**4.2 Characterization of the particulate powder samples**

After that, gel of alumina with zinc oxide and alumina with titania could be obtained in sol-gel process and taken to calcine at different calcination temperature. The calcination temperature of the particulate powder of alumina doped with zinc oxide and alumina doped with titania were characterized by XRD, TEM and SEM, respectively.

### 4.2.1 Investigation of the crystalline structure of alumina

From research of A. Vazquez et.al [28] found that, the crystalline structure of alumina provided by sol-gel method at calcination temperature over 1000 °C was α alumina and at lower 1000 °C, the crystalline structure of alumina was amorphous.

### 4.2.2 Investigation of the crystalline structure, shape, plane and ratio atom of aluminum (Al) and zinc (Zn) of alumina doped with zinc oxide

*Alumina doped with zinc oxide*

The particulate powders of alumina doped with zinc oxide at different calcination temperature (350-600 °C) were characterized by XRD. The spectra were shown in Fig. 4.8

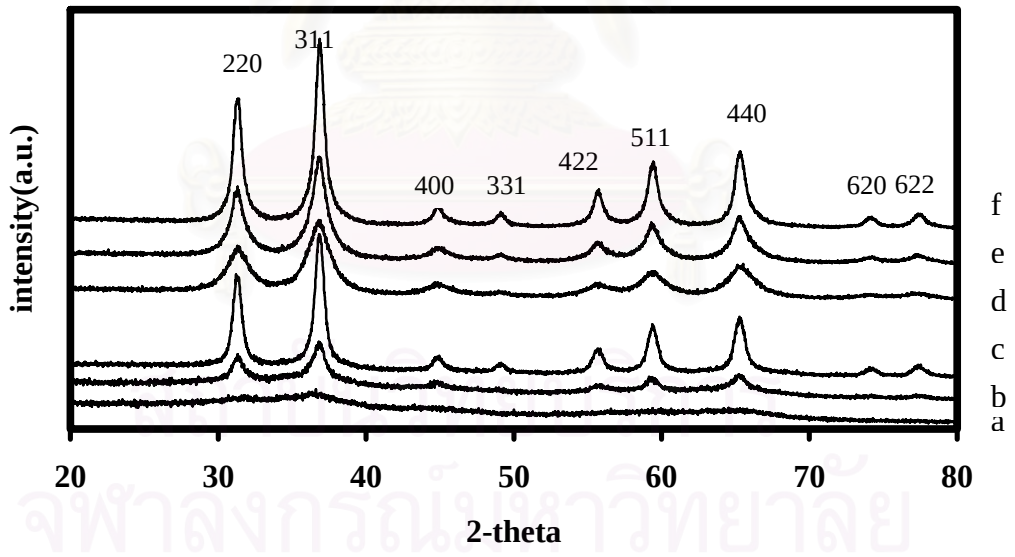
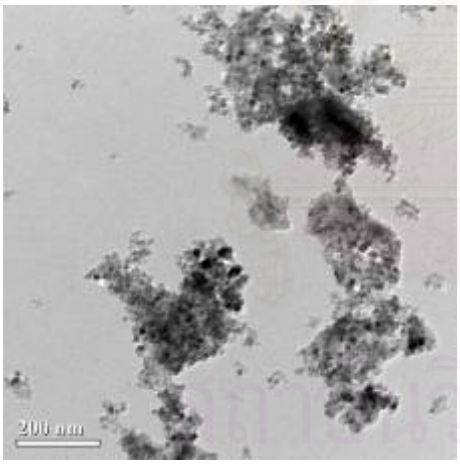
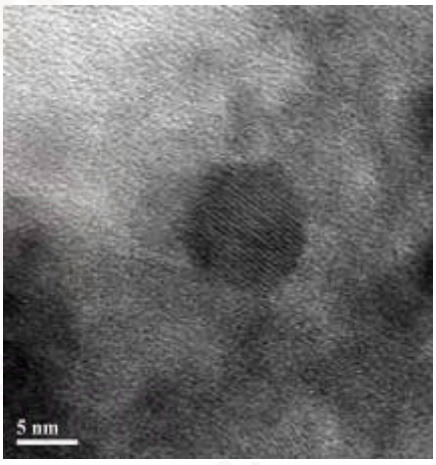



Fig. 4.8 XRD patterns of alumina doped with zinc oxide powder were calcined at different calcination temperatures (a) 350°C, (b) 400°C, (c) 450°C, (d) 500°C, (e) 550°C and (f) 600°C

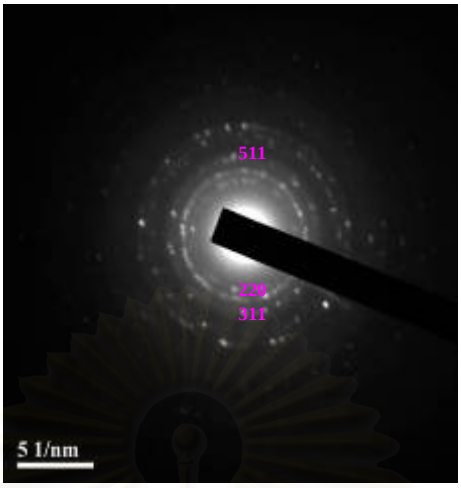
From Fig.4.8, All sample could observe diffraction peak of XRD pattern except that particulate powder which was calcined at 350°C. Peaks index as (220), (311), (400), (331), (422), (511), (440), (620) and (622) were corresponded with standard pattern of face center cubic of zinc aluminate ($ZnAl_2O_4$) which was referred from XRD instrument at spinel code 01-082-1534. No other phases could be detected in all calcinations temperature of their particulate powder samples. Moreover, an increasing of the heat-treatment temperature led to the increasing the intensity of the diffraction peaks which was associated with an increasing of crystalline [29-30]. To show that this particulate powders were zinc aluminate. TEM was used to confirm shape and plane of arrangement atom of zinc aluminate which corresponded with result of XRD.




(a)




(b)

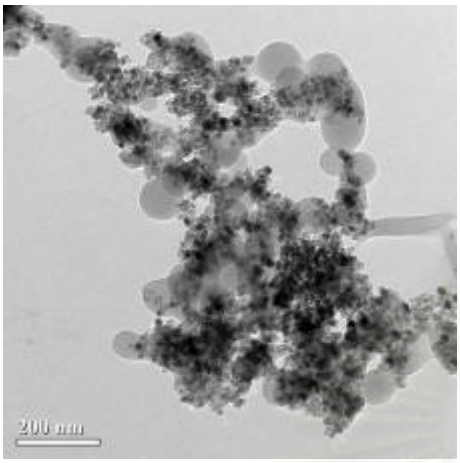



(c)

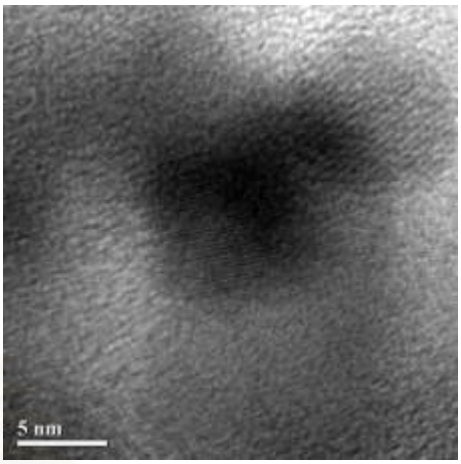
Fig. 4.9 (a) TEM image (b) HRTEM image and (c) SAED image of alumina doped with zinc oxide which was calcined at 400 ºC

Fig.4.9 shows image of alumina doped with zinc oxide which was calcined at 400 ºC. An average size of this particulate (Fig.4.8 (a)) was 10 nm. This particulate powder had the agglomeration of nano-sized primary particles with rather spherical morphology (Fig.4.8 (b)). The SAED image in Fig.4.8 (c) exhibits the similar plane with crystalline structure of zinc aluminate in XRD pattern.

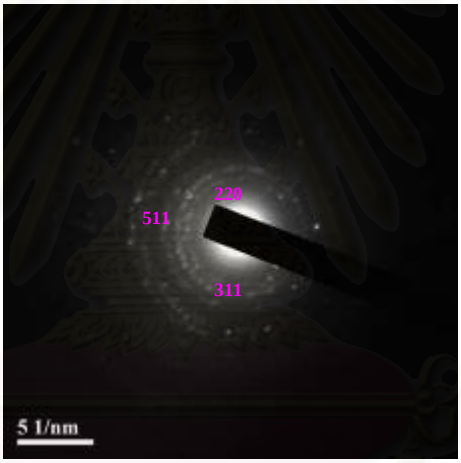
Moreover, TEM image of alumina doped with zinc oxide which was calcined at 600 ºC had an average size of this particulate approximation 20 nm.(Fig. 4.10(a)) Moreover, shape and plane were obtained at this condition exhibit the tendency as that of the previous section (Fig. 4.9). TEM image of alumina doped with zinc oxide at calcinations temperature 600 ºC was shown in Fig.4.10




(a)



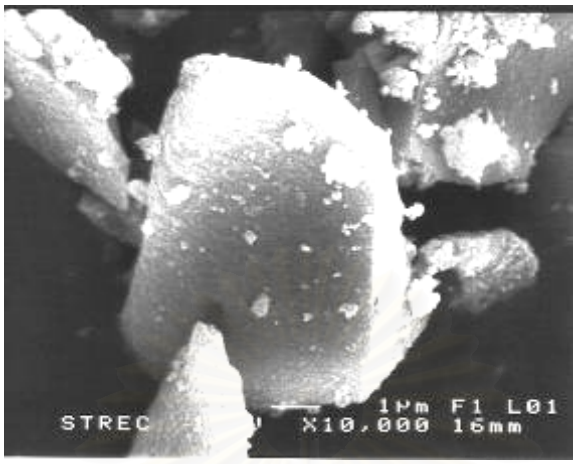

(b)



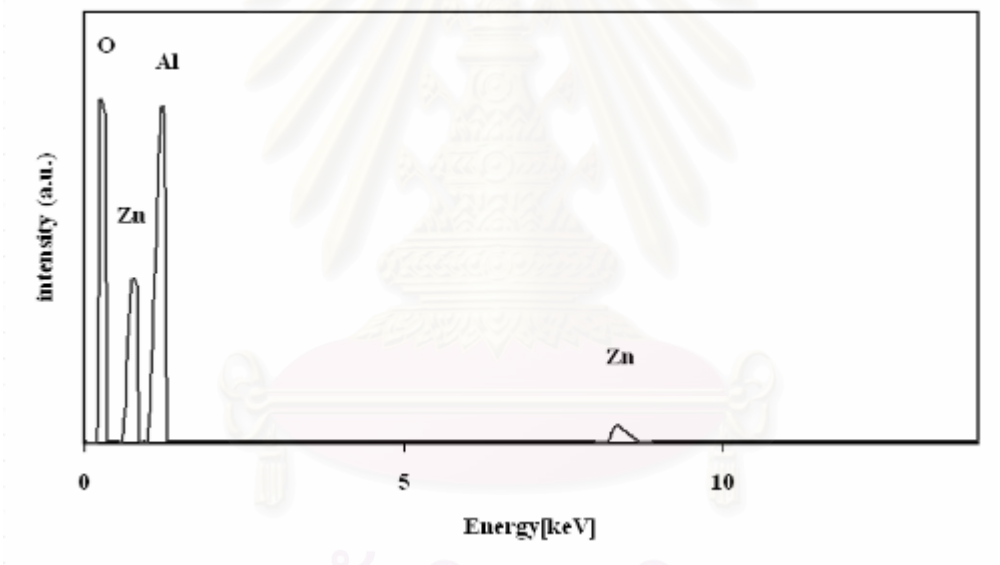

(c)

Fig. 4.10 (a) TEM image (b) HRTEM image and (c) SAED image of alumina doped with zinc oxide which was calcined at 600 ºC

The morphology image and chemical position of this particulate powder sample were shown in Fig.4.11




(a)




(b)

Fig.4. 11 (a) SEM image and (b) EDX of alumina doped with zinc oxide which was calcined at 400 ºC

Fig.4.11 (a) shows morphology image of alumina doped with zinc oxide which was calcined at 400 ºC. With further investigation by EDX, it could be confirmed that each sample was mainly composed of Al, Zn and O (See Fig. 4.10(b)). Comparing the ratio of aluminum and zinc atom was shown in Table 4.1 Moreover, amount of atoms of aluminum and titanium 8 positions in this particulate powder were measured by EDX.

Table 4.1 Comparing amount of Al: Zn

| Position | Amount of atom of Al: Zn | | | |
|---|---|---|---|---|
| | Synthesis | | EDX | |
| | Al | Zn | Al | Zn |
| 1 | $5.9\times10^{21}$ | $1.84\times10^{21}$ | 27.1 | 8.07 |
| 2 | | | 16.91 | 27.55 |
| 3 | | | 32.27 | 9.07 |
| 4 | | | 31.4 | 9.13 |
| 5 | | | 35.57 | 9.52 |
| 6 | | | 32.05 | 6.5 |
| 7 | | | 30.64 | 9.04 |
| 8 | | | 34.25 | 8.26 |
| Total | $5.9\times10^{21}$ | $1.84\times10^{21}$ | 30.02 | 10.89 |
| Ratio of Al: Zn | 3 | 1 | 3 | 1 |

From Table 4.2, the ratio of Al: Zn from alumina doped with zinc oxide synthesis by sol-gel process and EDX had a similar result. Therefore, the uniform texture of this particulate powder could be obtained in sol-gel process.

### 4.2.3 Investigation of the crystalline structure, shape, plane and ratio atom of alumina (Al), titanium (Ti) of alumina doped with titania

*Alumina doped with titania*

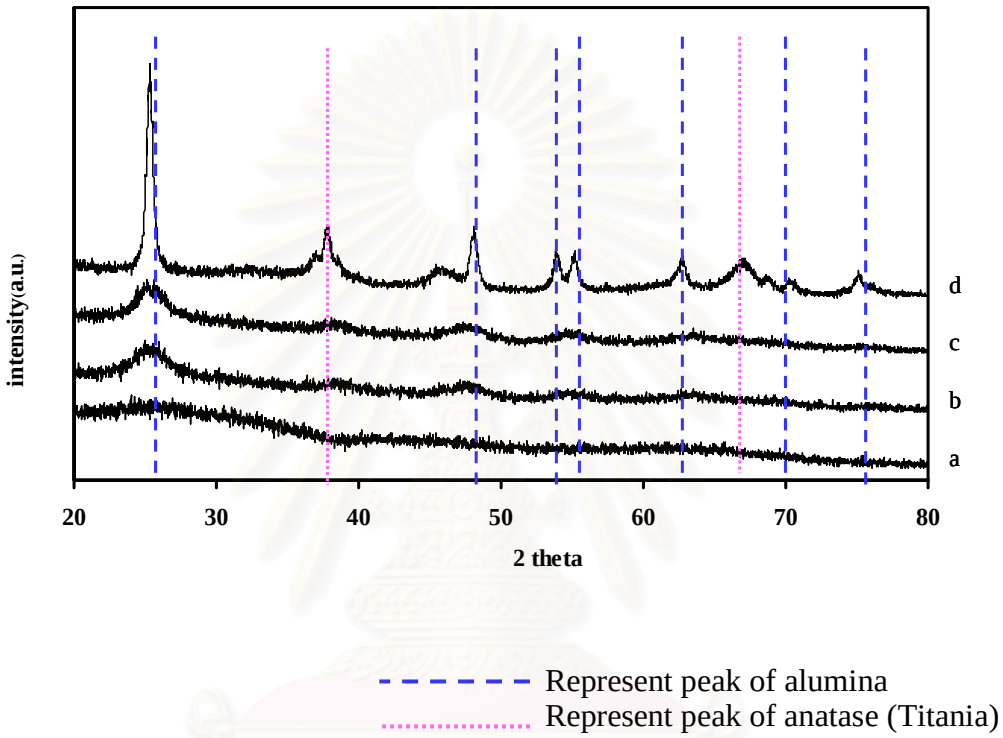
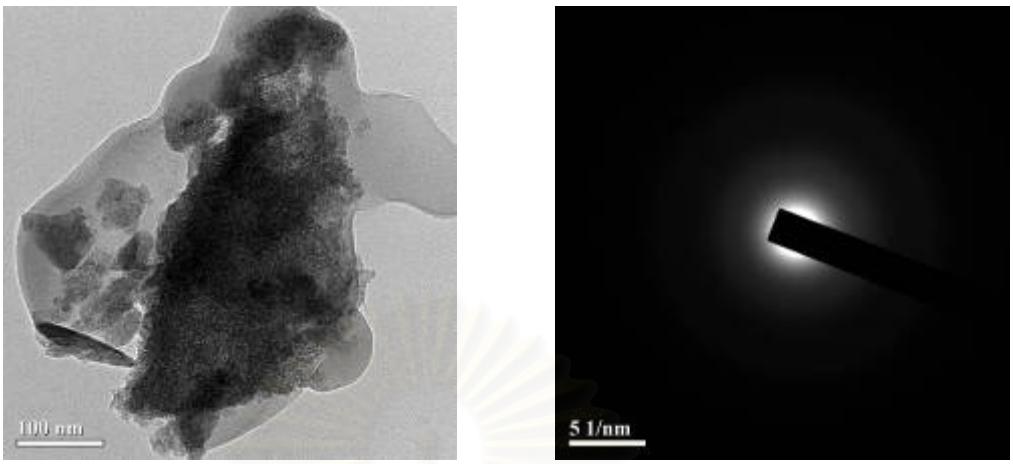



Fig. 4.12 XRD patterns of alumina doped with titania powder were calcined at different temperatures (a) 350°C, (b) 450°C,(c) 500°C and (d) 800°C

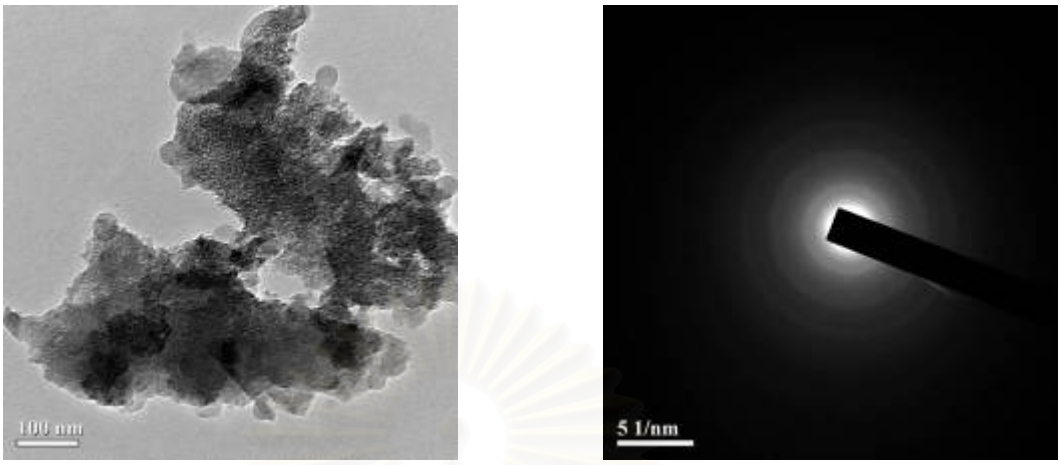
From Fig.4.12, peak of XRD patterns of alumina doped with titania could be observed peak of alumina and anatase at calcinations temperature of this particulate powder of 800°C, however, the calcination temperature of this particulate powders of 350°C, 450°C and 500°C could not be observed the structure with this instrument because these product were non crystalline structure. For this reason, TEM was used for observing the crystalline structure of alumina doped with titania.




(a) (b)

Fig.4.13 (a) TEM image and (b) SAED image of alumina doped with titania which was calcined at 350 ºC

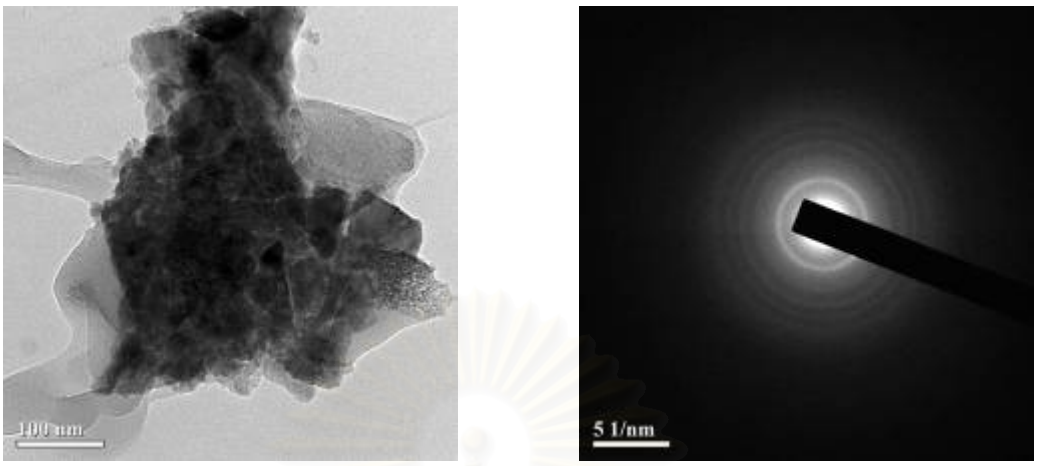
The particulate product of alumina doped with titania which was calcined at 350 ºC was characterized by TEM. The result was shown in Fig.4.13 (a). It was experimentally found that crystalline structure could not be synthesized at this condition. Beside, SEAD analysis in Fig. 4.13(b) of the arrangement atom of this particulate powder sample was amorphous structure which corresponding with XRD results in Fig. 4.12 (a).




(a) (b)

Fig.4.14 (a) TEM image and (b) SAED image of alumina doped with titania which was calcined at 450 ºC

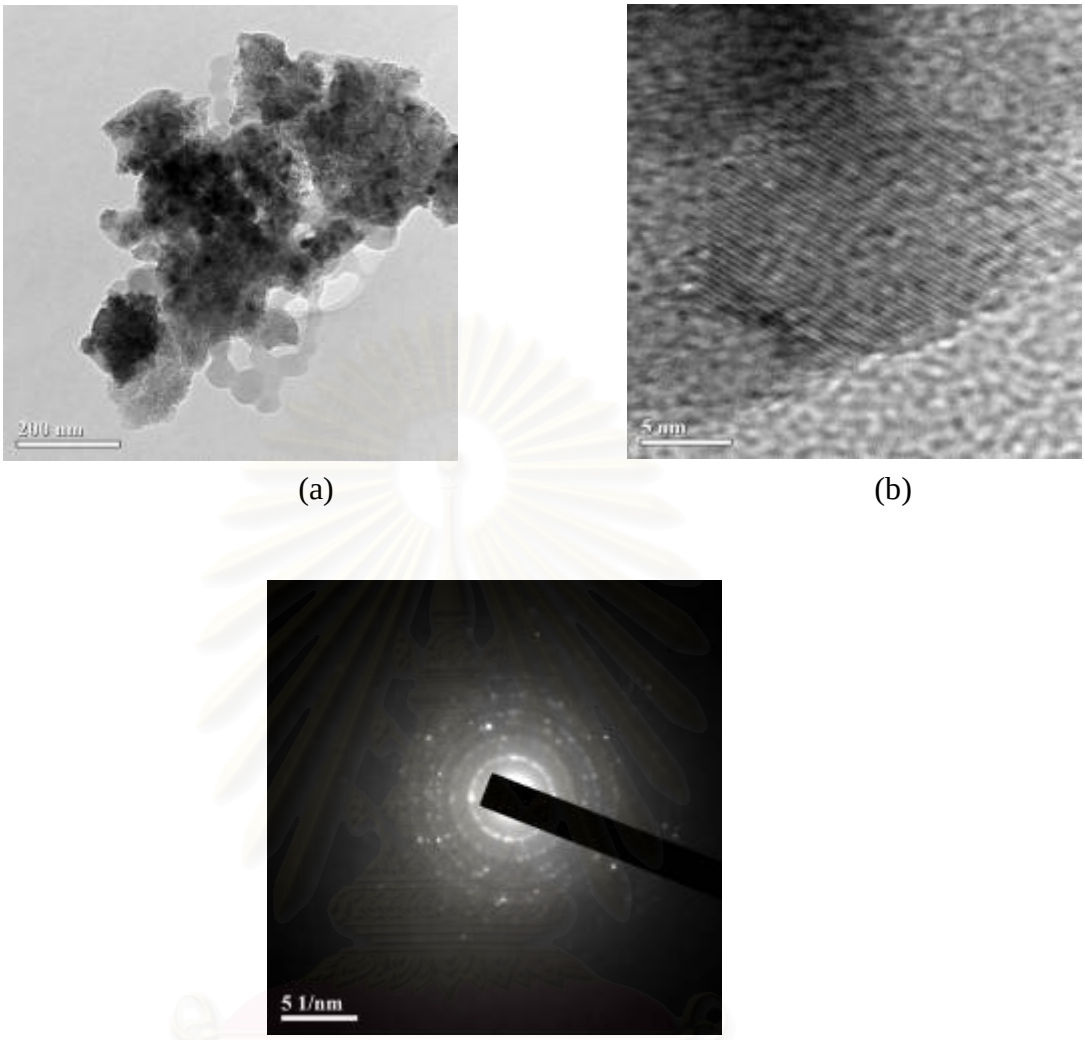
Next, TEM image of alumina doped with titania which was calcined at 450 ºC was shown in Fig. 4.14(a). It was found that, crystalline structure could not be synthesized by this calcination temperature. Moreover, SAED image obtained from TEM analysis in Fig.4.14 (b) indicated that the arrangement atom of this particulate powder was polycrystalline structure.




(a) (b)

Fig. 4.15 (a) TEM image and (b) SAED image of
alumina doped with titania which was calcined at 500°C

From Fig.4.15 (a) shows images of alumina doped with titania which was calcined at 500°C. It could not be obtained the crystalline structure of this calcination temperature. In addition, SAED image in Fig. 4.15(b) showed polycrystalline structure which corresponding with XRD result in Fig. 4.12 (c). Furthermore, it could be concluded that preparation of alumina doped with titania by sol-gel process which was calcined under 500 ºC could not be synthesized single crystalline structure. For confirmation that crystalline structure could be synthesized at higher temperature, the particulate powder of alumina doped with titania which was calcined at 800°C was characterized by TEM and SEAD analysis as show in Fig .4.16 (a), (b) and (c)



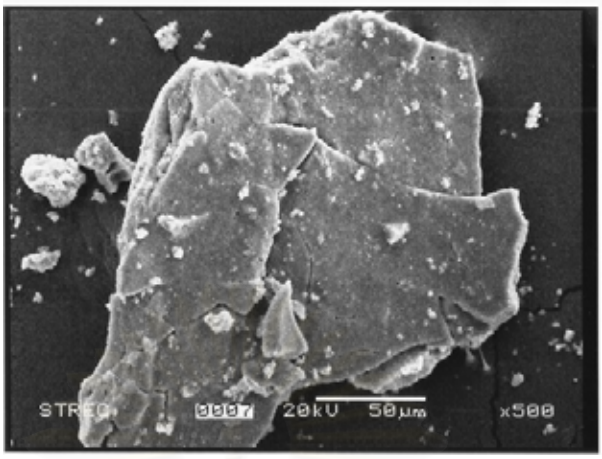

(a) (b)

(c)

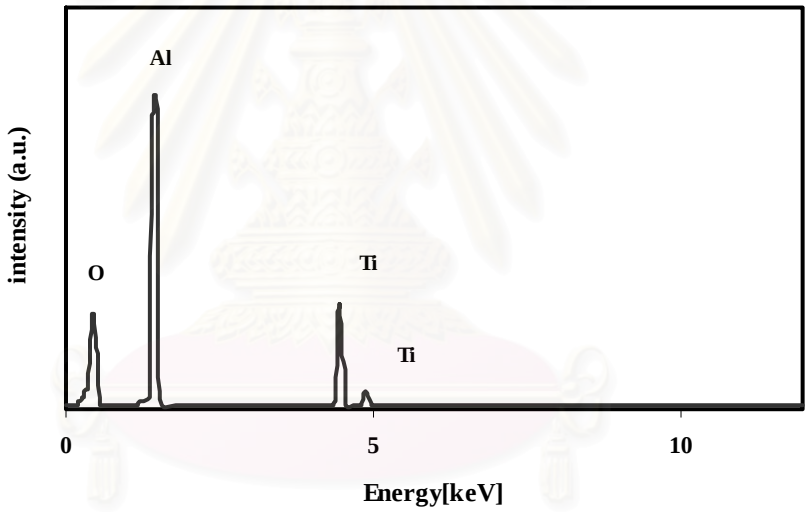
Fig. 4.16 (a) TEM image (b) HRTEM image and (c) SAED image of alumina doped with titania which was calcined at 800°C

The result showed that all parts of powder were well crystalline.(Fig.4.16(c)) Furthermore, the occurrences of crystal structure in this work corresponded with XRD patterns in Fig.4.12 (d) From this experiment, it could be concluded that crystalline structure could be synthesized when calcination temperature was over 800°C.

The morphology image and chemical position of this particulate powder sample was shown in Fig.4.17




(a)




(b)

Fig.4. 17 (a) SEM image and (b) EDX of alumina doped with titania which was calcined at 450 ºC

Fig.4.17 (a) illustrates morphology image of alumina doped with titania which was calcined at 450 ºC. With further investigation by EDX, it could be confirmed that each sample was mainly composed of Al, Ti and O (See Fig. 4.17 (b)). Comparing the ratio of aluminum and titanium atom was shown in Table 4.2 Moreover, amount of

atoms of aluminum and titanium 8 positions in this particulate powder were measured by EDX.

Table 4.2 Comparing amount of Al: Ti

| Position | Amount of Al: Ti | | | |
|---|---|---|---|---|
| | Synthesis | | EDX | |
| | Al | Ti | Al | Ti |
| 1 | $5.9\times10^{21}$ | $1.88\times10^{21}$ | 22.73 | 8.47 |
| 2 | | | 23.05 | 10.19 |
| 3 | | | 31.44 | 6.48 |
| 4 | | | 20.84 | 11.39 |
| 5 | | | 20.22 | 11.07 |
| 6 | | | 31.46 | 6.74 |
| 7 | | | 22.11 | 8.75 |
| 8 | | | 23.76 | 8.2 |
| Total | $5.9\times10^{21}$ | $1.88\times10^{21}$ | 24.45 | 8.91 |
| Ratio of Al: Ti | 3 | 1 | 3 | 1 |

From Table 4.2, the ratio of Al: Ti from alumina doped with titania synthesis in sol-gel process and EDX had a similar result. Therefore, the uniform texture of this particulate powder could be obtained in sol-gel process.

**4.3 Application of alumina doped with zinc oxide and alumina doped with titania on glass substrate for investigating the photo-induced surface property**

The solution of alumina doped with zinc oxide and alumina doped with titania were taken to coat on glass substrate by dip coating process. After that, their thin films were calcined at 400°C and 450 °C, respectively, at heating rate 5°C/min. for 2 hr. Moreover, the photo-induced surface property in range of superhydrophilicity could be obtained from measuring contact angle on the surface which is generally less than 5°[32], hydrophilicity is a contact angle on surface less than 90° [33] and superhydrophobicity is a contact angle on surface larger than 150°. [32] In this work,

the water was dropped at 3 positions on thin film for measuring contact angles between water droplet with surface of alumina doped with zinc oxide and alumina doped with titania. The results were shown in Fig.4.18

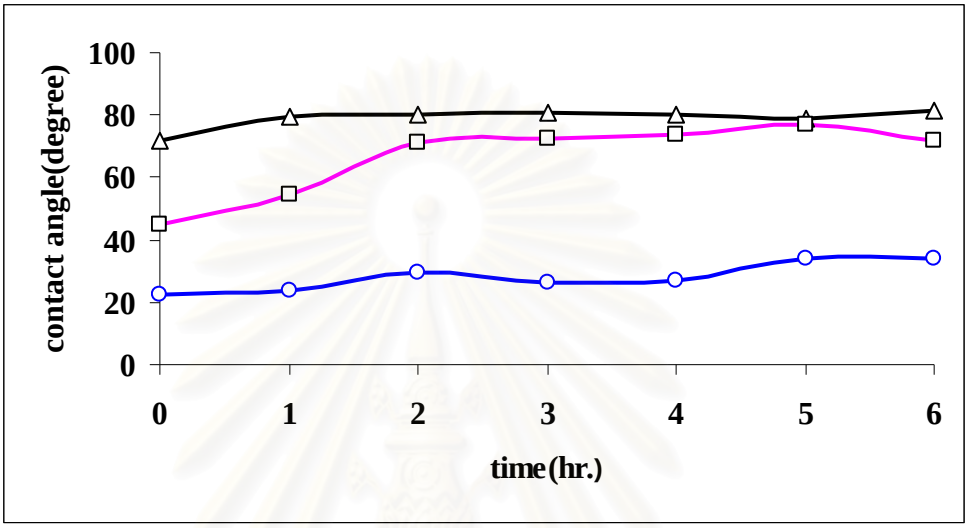



Fig.4.18 contact angle of: uncoated glass (O), alumina doped with titania (□) and alumina doped with zinc oxide (Δ) thin films

Fig.4.18 (O) shows that the contact angle of uncoated glass substrates was 30° while the contact angle of the glass substrate coated with alumina doped with titania and alumina doped with zinc oxide thin films were 70° and 80°, respectively. All glass substrate were irradiated by UV- spectra for 6 hr. From the result shows the photo-induced surface property in range of hydrophilicity. Because aluminum hydroxide (Al $(OH)_3$) could be combine with zinc hydroxide (Zn(OH)) or titanium hydroxide $(Ti(OH)_4)$ in hydrolysis reaction to become multi components of alumina with zinc oxide and alumina with titania in condensation process. The multi components were zinc aluminate ($ZnAl_2O_4$) and aluminum titanate ($Al_2TiO_5$). Furthermore, zinc aluminate has been widely used as catalyst, ceramic and electro-

conductive materials because of its high thermal stability, high mechanical resistance, low surface acidity, and excellent optical properties. [29-30] Aluminum titanate has been widely used as ceramic material due to good resistance against thermal shock. At this state, they found low thermal expansion coefficient. This property shows the performance of the protection of ceramic cracking. [31, 34-35]

# CHAPTER V

# CONCLUSION

## 5.1 CONCLUSION

This chapter divides into 3 sections for inferring in chapter IV as follow:

### 5.1.1 Investigation of parameters that had effect on the preparation of alumina doped with zinc oxide and alumina doped titania using sol-gel method

From this work, the best aluminum compound that could be a good suspension for aluminum precursor was aluminum sec butoxide which was dissolved in ethanol 40 ml. at 50°C. The optimum molar ratio for preparing clear homogeneous solution of alumina precursor was 1: 0.4: 0.9 (Aluminum sec butoxide: EAC: nitric acid). Furthermore, an addition of EAC played an important role in producing aluminum hydroxide ($Al(OH)_3$).

### 5.1.2 Characterization of the particulate powder samples.

***Alumina doped with zinc oxide***

The particulate product of alumina doped with zinc oxide was characterized by XRD, TEM and SEM, respectively. From XRD found that zinc aluminate ($ZnAl_2O_4$) was obtained by sol-gel method at different calcination temperature. (400-600°C) From TEM image showed plane of arrangement of zinc aluminate similar XRD pattern at calcination temperature of particulate product of 400°C and 600°C.

Zinc aluminate had a spherical shape and had average size of particulate powder approximation 10 nm and 20 nm at calcination temperature of 400°C and 600°C.

Moreover, the ratio of Al: Zn from synthesis in sol-gel process and EDX had similar result. These results showed the uniform texture of this particulate powder.

***Alumina doped with titania***

The particulate powder of alumina doped with titania was characterized by XRD, TEM and SEM, respectively. From XRD found that the crystalline structure of this particulate powder occurred at calcination temperature over 800°C. Furthermore, at calcination temperature of 350°C, 450 °C and 450°C could not be analyzed the crystalline structure by this equipment. Then TEM was used to analyze the crystalline structure of alumina doped with titania at these condition. At calcination temperature of 350°C found that the arrangement atom was amorphous structure and calcination temperature of 450°C and 500°C had polycrystalline structure. Moreover, the ratio of Al:Ti from synthesis in sol-gel process and EDX had similar result. These result showed the uniform texture of this particulate powder.

### 5.1.3 Application of alumina doped with zinc oxide and alumina doped with titania on glass substrate for investigating the photo-induced surface property

Photo-induced surface property of alumina doped with zinc oxide and alumina doped with titania exhibited hydrophilicity due to they became zinc aluminate ($ZnAl_2O_4$) and aluminum titanate ($Al_2TiO_5$).

## 5.2 Recommendation for future work

In this work, it was demonstrated that the preparation of alumina doped with zinc oxide and alumina doped with titania could not show the photo-induced surface in range of superhydrophilicity. Then, alumina is an improper material for using composite with semiconductor material of investigation this property.

Thus, in the future, other property of these synthetic materials of alumina doped with zinc oxide and alumina doped with titania will be investigated such as catalyst, ceramic and electro-conductive materials.

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# APPENDICES

# APPENDIX A

## Conference and Publications Resulting

## From This Research Work

# CONFERENCE

**International Proceedings**

Pattama Poommarin, Tawatchai Charinpanitkul and Akkarat Wongkaew.

"Effect of precursor ratio on synthesis of zinc oxide/alumina nanocomposite using sol-gel method" *Proceedings of international symposium on Pure and Applied Chemistry International Conference (PACCON 2008), January 30- Febuary1, 2008, Thailand.*

# PUBLICATION

This paper is published in journal of Kasertsart University Science Journal (KUSJ) Vol. 26 No. 1 Jan-Apr 2008

# EFFECT OF PRECURSOR RATIO ON SYNTHESIS OF ZINC OXIDE/ALUMINA NANOCOMPOSITE USING SOL-GEL METHOD

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**Abstract**

In this work, alumina doped with zinc oxide was synthesized by sol-gel method in alcohol solution. A thin film of mixed oxides was coated on a glass substrate for self-cleaning function of the glass surface using aluminum sec-butoxide, aluminum nitrate, and aluminum isopropoxide as precursors. The effect of alumina precursor molar ratio on the homogeneous of the solution was experimentally investigated. It was found that among various dispersants added during sol preparation step, ethylacetoacetate (EAC) and nitric acid could provide homogeneous reactive solutions. Additional experimental results also revealed that only aluminum sec-butoxide precursor could provide a very stable and clear suspension. Accordingly the ratios of the aluminum secbutoxide, ethylacetoacetate, water and nitric acid in alcohol solution were varied to investigate their effects on formation of alumina doped zinc oxide. The fabricated particulate thin films were then characterized by x-ray diffraction (XRD) and transmission electron microscope (TEM) to identify phases, particle size and chemical composition.

KEYWORD: sol-gel, alumina precursor, zinc, nanocomposite

**Introduction**

At present, there are various attentions on preparing alumina doped with zinc oxide for fabricate thin film coating on glass substrate for self cleaning glass by using various methods, such as sputtering, chemical bath deposition, sol-gel, etc [1-3]. Among them, sol-gel is one of the most promising methods because it could produce clearly homogeneous product with low synthesized temperature, and low investment [4].

There are several kinds of metal oxides used for the applications of optical electronics. In general, ZnO is the most popular due to its wide band gap characteristics. ZnO could also exhibit transparent conducting behavior, which is useful for various applications, such as solar cell electrode and varistor [5-6].

In this work, aluminum compound, ethylacetoacetate (EAC) and nitric acid are utilized for preparing clear homogeneous solution of alumina compound. Zinc acetate was then introduced to prepare composite of alumina and zinc compounds. The product sample obtained from the condensation process was analyzed for its morphology, chemical position, particle size and phases by SEM, TEM and XRD, respectively.

**Materials and Methods**

*Preparing alumina doped with zinc oxide solution*

Alumina doped with zinc oxide solution was prepared by following procedures. $9.8x10^{-3}$ mole of alumina alkoxide precursor was first dissolved in 40 ml of ethanol. After vigorous stirring for 20 min ethylacetoacetate with pre-calculated amount (0.5 – 1.5 ml) was introduced as the chelating agent to the solution. Typical solutions shown in **Figs. 1** and **2** were left still for 15 min and then 0.53 ml of water was added to hydrolyze the aqueous reactants. 0.36 ml of nitric acid was also added to the suspension of alumina precursor to control the gelation process. 0.68 g of zinc acetate was further introduced to the clear homogeneous solution to dope alumina precursor with zinc. All procedures were conducted in a refluxed flask with a controlled temperature ranged from room temperature to 50°C. Finally, samples of alumina doped zinc oxide gel were calcined at different temperature (350-600°C) for preparing calcined powder which was analyzed by TEM and XRD.

*Characterization of sample powders from sol-gel process*

The powder sample of alumina doped with zinc oxide was identified through powder X-ray diffraction analysis (XRD, Bruker AXS D8) with CuK radiation (40 kv, 40mA) and the scanning speed of 0.3 sec/step. The morphology and particle size of fine powder were observed by transmission electron microscope (TEM, JEM-2100).

**Results and Discussion**

Selected aluminum compounds such as, aluminum sec-butoxide, aluminum nitrate, and aluminum isopropoxide were dissolved in ethanol (99.9%wt). Aiming at preparation of nano-sized precursor it was expected that clear suspension would be obtained. Qualitative comparison of suspension prepared from each aluminum compound was shown in **Fig.1**

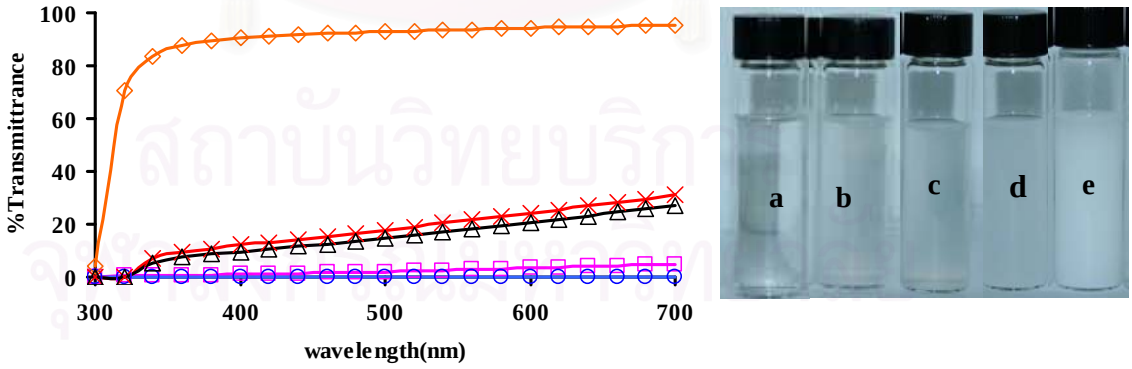



**Fig 1** Comparison of UV transmittance of alumina precursor prepared from each aluminum compound in ethanol: (a) aluminum sec-butoxide at 50°C ( ◊), (b) aluminium nitrate at 25°C (×), (c) aluminum nitrate at 50°C(Δ), (d) aluminum sec-butoxide at 25°C (□) and (e) aluminum isopropoxide at 25°C and 50°C (o)

**Fig.1** shows UV transmittance of alumina precursor suspensions prepared from different aluminum compounds in ethanol at 25°C and 50°C. It was found that aluminum isopropoxide at 25°C and 50°C provides the precursors which clearly precipitate, leading to the very low transmittance. Aluminum nitrate could result in partial precipitation of alumina precursor at either 25°C or 50°C. It should be noted that aluminum sec-butoxide could lead to a very clear and homogeneous suspension of alumina precursor ( ◊ in **Fig. 1**). Therefore, aluminum sec-butoxide in ethanol at 50°C has been selected as the main constituent for preparing nano-sized alumina precursor.

However, alumina precursor could not directly react with water in hydrolysis reaction because it would precipitate immediately, leading to a requirement of addition of some chelating agent [7,8]. Among various chelating agents, EAC exhibits a better performance in stabilizing suspension of alumina precursor because EAC could capture alumina precursor before being hydrolyzed by water to form alumina hydroxide in solution [9]. Therefore, in this work, EAC with varied quantity was introduced to the suspension of alumina precursor with gradual addition of water for controlled hydrolysis of alumina sol. **Fig. 2** reveals that EAC with a concentration of 9.8 mol % could provide a clear and homogeneous suspension with the highest transmittance in the visual light spectra. The optimal molar ratio of aluminum sec-butoxide to EAC is 1: 0.40.

For further improvement of the stability of sol suspension, nitric acid was selected because of its activity to help destruct bonding among sol particles in suspension and promote gelation [10]. The effect of quantity of nitric acid added to the sol suspension prepared from aluminum sec- butoxide in ethanol with EAC was further investigated. It was experimentally observed that an increase in nitric acid quantity added to the alumina sol suspension could result in longer gelation time. Concentration of nitric acid to provide stable gel of alumina in this work was 21.3 mol %. Similar to EAC, the optimal molar ratio of aluminum sec-butoxide to nitric acid is 1 : 0.86.

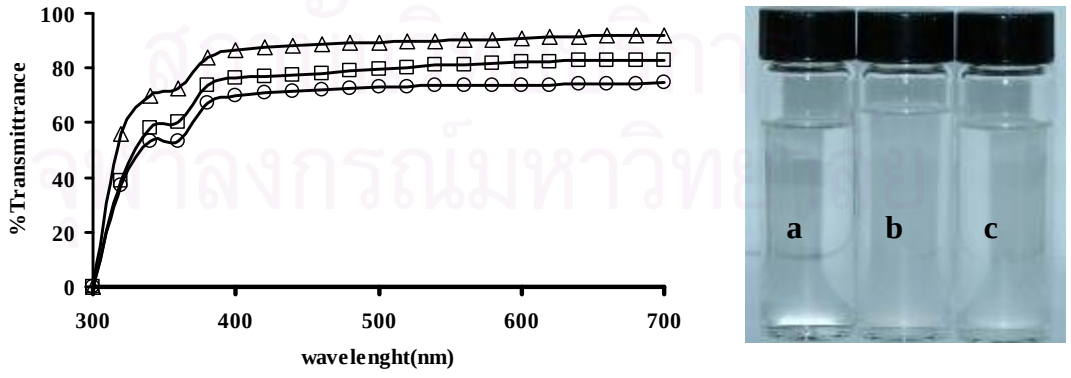



**Fig.2** Effects of ethylacetoacetate (EAC) on the transmittance and appearance of the prepared alumina precursor suspension: (a) 9.8 mole %(Δ), (b) 19.6 mole %(□) and (c) 29.9 mole %(o)

For preparing composite of alumina and zinc oxide, zinc acetate was added into the alumina precursor before the gelation process would terminate. As a result, gel of alumina and zinc compound could be obtained and taken to calcine at different temperature of 350 – 600 ºC. The calcined particulate sample of alumina and zinc compound were characterized by XRD of which spectrum is shown in **Fig. 3**. The observed diffraction peaks of all samples except that of 350 ºC are corresponding to the standard pattern of face center cubic $ZnAl_2O_4$. The peak of $ZnAl_2O_4$ at 31.3° with reference to the spinel code 01-082-1534 from XRD instrument. No other phases could be detected in all calcined samples. It should be noted that from XRD analyses, the increasing heat-treatment temperature could lead to the increasing intensity of the diffraction peaks, which could be attributed to the larger crystalline size [10]. The actual size of these particles would be further confirmed by TEM and SEM analyses.

**Fig. 4(a)** shows a typical TEM micrograph of particulate sample which was calcined at 600 °C. The composite particle is the agglomeration of nano-sized primary particles with rather spherical morphology. The average size of the primary crystalline was about 20 nm. With further investigation using EDX, it could be confirmed that each sample was mainly composed of Al, Zn and O (**Fig. 4(b)**). This is in good agreement with XRD result that atomic arrangement of this composite was $ZnAl_2O_4$ in cubic face center pattern. It is necessary to conduct further analyses of these composite samples to verify their characteristics as well as photo-induced properties.

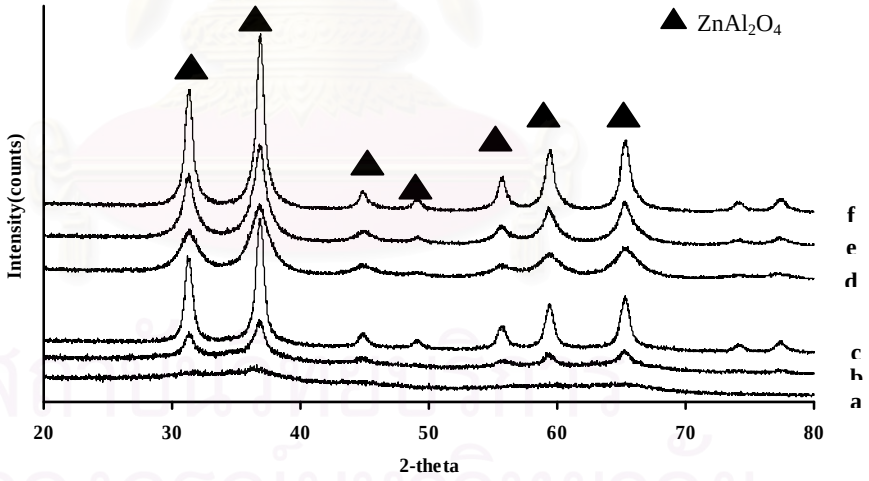
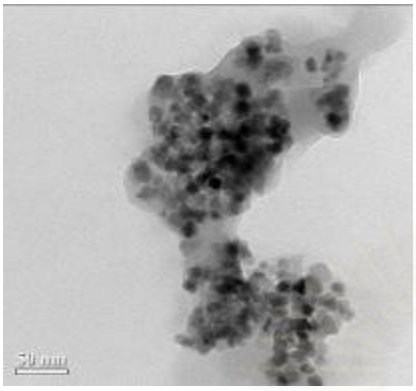
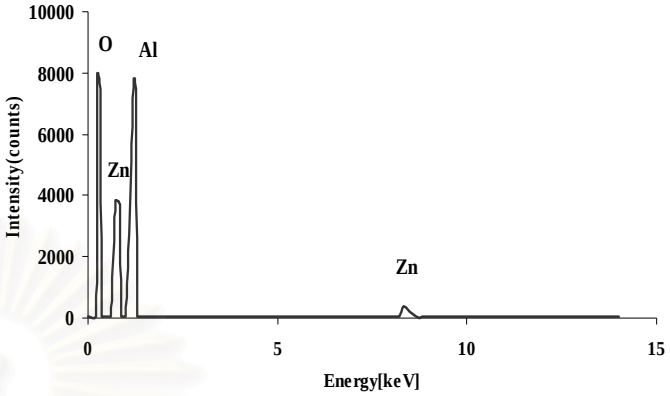



**Fig. 3** XRD patterns of particulate samples calcined at different temperatures (a) 350°C, (b) 400°C, (c) 450°C, (d) 500°C, (e) 550°C and (f) 600°C






(a) (b)

**Fig.4** (a) TEM and (b) XRD of alumina-zinc oxide composite calcined at 600°C

**Conclusion**

In this work, the preparation of alumina doped with zinc oxide using sol gel method was experimentally conducted. It was found that the suitable molar ratio of aluminum sec-butoxide to EAC to nitric acid for preparing the clear homogeneous sol was 1: 0.40: 0.86. After doping alumina precursor with zinc acetate solution the calcined particulate sample of alumina and zinc was analyzed by XRD and TEM. It could be confirmed that alumina doped with zinc oxide has a structure of single crystal $ZnAl_2O_4$ in cubic face center pattern of arrangement.

**Acknowledgement**

The authors gratefully acknowledge the financial support from NANOTEC, NSTDA and partial support from Chulalongkong University and Burapha University.

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# APPENDIX B

## Experimental Results

**1. The calculation of plane of zinc aluminate from SAED image in TEM**

Calculation of plane of particulate powder in this work is evaluated by Edward sphere equation:

$$R = \frac{1}{d} \qquad \ldots 1$$

Which: R is the distance of transmission bean to diffraction beam

d is d-spacing of particulate powder sample

From equation 1, the plane of zinc aluminate calculated from equation of cubic plane because zinc aluminate has a crystalline structure in cubic pattern from XRD result.

The equation of cubic plane pattern is

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2} \qquad \ldots 2$$

Which: a is a lattice parameter of $ZnAl_2O_4$ equal 0.81 nm.

$(h^2 + k^2 + l^2)$ is plan of particulate powder(zinc aluminate)

The value of $(h^2 + k^2 + l^2)$ from equation 2 compare with the value of $(h^2 + k^2 + l^2)$ in Table 1 for identifying the plane of this particulate powder.

Table 1 the possible value of $(h^2+k^2+l^2)$

Possible $(h^2+k^2+l^2)$ values

| $(h^2+k^2+l^2)$ =N | {h,k,l} |
|---|---|
| 1 | 100 |
| 2 | 110 |
| 3 | 111 |
| 4 | 200 |
| 5 | 210 |
| 6 | 211 |
| 7 | - |
| 8 | 220 |
| 9 | 221 or 300 |
| 10 | 310 |
| 11 | 311 |
| 12 | 222 |
| 13 | 320 |
| 14 | 321 |
| 15 | - |
| 16 | 400 |
| 17 | 410 |
| 18 | 411 or 330 |
| 19 | 331 |
| 20 | 420 |
| 21 | 421 |
| 22 | 332 |
| 23 | - |
| 24 | 422 |
| 25 | 500 |
| 26 | 510 |
| 27 | 511 or 333 |
| … | … |

**2. The calculation of the amount of atom in system**

**Alumina doped with zinc oxide and alumina doped with titania**

The mole of alumina is $9.8\times10^{-3}$ moles from the addition aluminum sec butoxide 2.42 grams in system. The molecular weight of aluminum sec butoxide is 246.32. Therefore, the total mole of alumina atom is

$$9.8\times10^{-3}\times6.02\times10^{23} = 5.9\times10^{21} \text{ atom.}$$

The mole of zinc is $6.14 \times 10^{-4}$ moles from the addition Zinc acetate 0.68 grams in system. The molecular weight of Zinc acetate is 219.49. Therefore, the total mole of zinc atom is

$$6.14 \times 10^{-4} \times 6.02 \times 10^{23} = 1.84 \times 10^{21} \text{ atom.}$$

The mole of titanium is $3.1 \times 10^{-5}$ moles from the addition Titanium isoproproxide 0.89 grams in system. The molecular weight of Titanium isoproproxide is 284.26. Therefore, the total mole of titanium atom is

$$3.1 \times 10^{-5} \times 6.02 \times 10^{23} = 1.88 \times 10^{21} \text{ atom.}$$

Therefore, the ratio of alumina, zinc atom can show in table 2

Table2 the ratio of alumina: zinc

| | The amount of each atom | |
|---|---|---|
| | Alumina | Zinc |
| | $5.9 \times 10^{21}$ | $1.84 \times 10^{21}$ |
| ratio | **3** | **1** |

The ratio of alumina, zinc atom can show in table 3

Table3 the ratio of alumina: titanium

| | The amount of each atom | |
|---|---|---|
| | Alumina | Titanium |
| | $5.9 \times 10^{21}$ | $1.88 \times 10^{21}$ |
| ratio | **3** | **1** |

# VITA

Miss. Pattama Poommarin was born on March 3, 1983 in Prachuapkhiri-khan, Thailand. She studied in primary Scholl at Darunsuksa Scholl and secondary Scholl at Benchamatheputit Petchaburi Scholl. In 2006, she received the Bachelor Degree of Engineering (Chemical Engineering) from Burapha University. After that, she gained admission to Graduate School of Chulalongkorn University.