UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Effect of Mixed and Non-mixed Solvent on the Coating Properties of Sol Gel TiO_2 Thin Films

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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DECLARATION

I hereby, declared this report entitled "Effect of Mixed and Non-mixed Solvent on the Coating Properties of Sol Gel TiO_2 Thin Films" is the results of my own study except as cited in references.

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Date : 2 July 2015

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment to the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

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(Prof Madya Dr. Zulkifli Bin Mohd Rosli)

ABSTRAK

Pada masa kini seramik atau kaca biasanya digunakan untuk banyak aplikasi sama ada dalam industri, semikonduktor atau dalam kehidupan seharian. Sebaliknya, kita perlu mengekalkan tahap kebersihan kaca. Tambahan pula, bakteria juga hanya boleh tumbuh di permukaan kaca. Oleh itu, untuk mencegah pertumbuhan bakteria, salutan TiO_2 digunakan untuk substrat kaca dan Titanium Tetra isopropoxide sebagai pendahulu. Dari kajian yang lepas, mereka menggunakan beberapa teknik untuk menyalut kaca seperti teknik semburan, lapisan spin dan juga sol-gel. Dalam kaedah sol-gel, pelarut adalah satu bahagian penting untuk mewujudkan sol-gel. Pilihan tepat pelarut adalah penting dan kritikal kerana kebanyakannya sol-gel adalah perlu pelarut. Dari pelarut, kita boleh menentukan perbezaan kesan mereka kepada saiz kristal, fasa, dan juga pada kesan morfologi. Daripada tindak balas dengan TiO_2, kita boleh membezakan kualiti salutan untuk substrat dan kesannya kepada sifat penyelesaian. Walau bagaimanapun, kita juga perlu mengambil berat tentang ketepatan pelarut ditambah kerana apabila pelarut tidak tepat, kita tidak boleh membezakan kesannya kepada pendahulu. Dengan menggunakan pelarut, kita tahu bahawa kita boleh mendapatkan pelbagai jenis mikro dan kesan morfologi, contohnya dengan menambah metanol; kita boleh mendapatkan kehadiran fasa anatase dan rutil serta mempunyai saiz hablur yang kecil. Walau bagaimanapun, ia jarang digunakan dengan mencampurkan pelarut di mana dengan mencampurkan perbezaan pelarut boleh memberi kesan yang berbeza. Terdapat satu inovasi yang menarik untuk mengkaji kesan pelarut dengan sifat-sifat lapisan. Terdapat banyak kajian yang menggunakan pelarut akan mendapatkan hasil yang menarik sebagai kesan kepada salutan pada substrat. Jumlah TiO_2 yang tinggi kandungan propanol dengan mencampurkan pelarut etanol akan menunjukkan morfologi permukaan yang baik dan retak telah dikurangkan jika berbanding dengan jumlah yang kurang kandungan propanol.

ABSTRACT

Nowadays ceramics or glass is commonly used for many applications either in industrial, semiconductor or in daily life. On the other hand, we need to maintain the level of cleanliness of the glass. Furthermore, bacteria also can simply grow on the glass surface. Thus, to prevent the bacteria growth, TiO_2 coating is being used for glass substrate and Titanium Tetra isopropoxide as the precursor. From the previous research, they are using several techniques for coating the glass such as spray technique, spin coating and also sol-gel. In the sol-gel method, solvent is an important part to create sol-gel. The right choice of solvent is a critical important because mostly the sol-gel is need the solvent. From the solvent, we can determine the difference of their effect to the crystal size, phases, and also on the effect of morphological. From the reaction with the TiO_2, we can distinguish the quality of the coating to the substrates and their effect to the solution properties. However, we also need to care about the accuracy of the solvent added because when the solvent are not accurate, we cannot differentiate their effect to the precursor accurately. By using the solvent, we know that we can get various types of microstructure and morphological effect, for example by adding the methanol; we can get the presence of anatase and rutile phases and have the small crystallite size. However, it was rarely used is by mixing the solvent where by mixing the difference solvent can give the difference effect. There is an interesting innovation to study the effect of the solvent to the coating properties. By study a lot of solvent used as a solvent will get the interesting result as an effect to the coating and substrates. TiO_2 coating solution with appear of high amount of propanol with mixing solvent with ethanol shows good surface morphology which is the crack were reduced compared to the less amount of propanol.

DEDICATION

I dedicate to everyone that involves to this research, which is my supervisor, my family and my friend that has been supporting during conducting the study.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURES

3D	-	Three dimensional
%	-	Percentage
TiO_2	-	Titanium Dioxide
CO_2	-	Carbon Dioxide
SiO_2	-	Silicon Dioxide
ZnO	-	Zinc Oxide
TTIP	-	Titanium tetraisopropoxide
HCL	-	Hydrochloric Acid
H_2O	-	Water
TiCl4	-	Titanium tetrachloride
TBOT	-	Tetrabutyl orthotitanate
XRD	-	X-Ray Diffraction
SEM	-	Scanning Electron Microscope
FESEM	-	Field Emission Scanning Electron Microscope
EtOH	-	Ethanol
MeOH	-	Methanol
PrOH	-	Propanol
BuOH	-	Butanol
CMC	-	Carboxy methy cellulose
PVP	-	polyvinyl pyrrolidon
HPC	-	Hydroxylpropy cellulose
PEG	-	polyethylene glycol
DSSC	-	dye-sensitized solar cells
TEM	-	Transmission electron microscope
μm	-	Micrometer
nm	-	Nanometer

ml	-	milliliter
^{o}C	-	Degree Celcius
SE	-	Secondary electron
BSE	-	Back-scattered electrons
CL	-	Athodoluminescence
CRT	-	Cathode Ray Tube
EDX	-	Energy-dispersive X-ray spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background Study

Sol-Gel method is a process for producing solid materials from small molecules. The process are refers to where the solid nanoparticles isolated in a liquid which is called sol agglomerate to produce a 3D network extending through the sol liquid where called a gel. On the other hand, Sol-gel method also is widely used for technique to coat glasses, ceramic and metals where it has an excellent mechanical and chemical stability (A. Shokuhfar, 2012). In addition, sol gel method also have their advantages where it was required lower operating temperature, easiness of controlling composition, uniformity, good optical properties, and also reasonable equipment cost (Sung Min Lee, 2010). Thus, sol-gel usages can be classified for the controlling composition, microstructure, and consistency of the method at low temperatures.

Solvent is an important part to create sol-gel. The right choice of solvent is a critical important because by using different solvent will create different coating properties. From the solvent, we can determine the difference of their effect to the crystal size, phases, and also on the effect of morphological. By choosing the different solvent, cannot be denied, we can get various types of microstructure and morphological effect, for example by adding the methanol; we can get the presence of anatase and rutile phases and have the small crystallite size (D. Robert, 2003). Therefore, solvent is one of parameter that needs to be concerned for control to get the different coating properties.

However, it was rarely used is by mixing the solvent where by mixing the difference solvent can give the difference effect. There is an interesting innovation to study the effect of the solvent to the coating properties. According to Y. Bessekhouad ET. Al. had found that for non-mixing solvent by using ethanol, the occurrence of anatase and rutile phases was near to that experimental which is 23 % of rutile phases, but by mixing the solvent, there are any possibility can occur depends on the type of solvent used where their coating properties it can be closed to the non-mixing solvent and it also can be totally different from the non-mixing solvent.

1.2 Problem Statement

Solvent plays an important role in a sol-gel method especially in determining films quality such as their effect on crystal size, phases, and morphology. For examples, M.A. Behnajady and his co-worker have shown that the used of different solvents like methanol, ethanol, and isopropanol that can give the different effect in morphology and microstructure. Leeyih et. Al. had found that the nature of chemicals for solvents like tetrahydrofuran, acetone, toluene, chloroform, and hexane can influenced the particle size and combination occurrence of titania considerably. Therefore, understanding the right solvents for right applications are crucial as it we can make lead to undesired properties of particular thin films if wrongly chosen.

Moreover, mixing and non-mixing solvent to TiO_2 also can give the different effect for crystal size, phases and morphology. From previous research, by adding the methanol; we can get the presence of anatase and rutile phases and have the small crystallite size. However, it was rarely used is by mixing the solvent where by mixing the difference solvent can give the difference effect where it was strongly reduces the rutile formation (Golobostanfard 2012). Besides, according to Sumio Sakka et. Al. there are difference effect of the solvent on properties of sol-gel coatings by using ethanol, mixing the ethanol with isopropyl and also mixing the ethanol with 2-ethoxyethanol where it was found that by adding of 2-ethoxyethanol or isopropyl to ethanol solutions of titanium tetra isopropoxide were effects the microstructure, performance of crystallization, and

also the photo electrochemical properties of the TiO2 thin film. In short, although using the same solvent, but by mixing with the different solvent, the coating properties can be different behavior.

By using the different solvent and solvent parameter like mixed and non-mixed solvent, we know that we can get various types of microstructure and morphological effect. On the other hand, by study a lot of solvent used and control their mixing ratio, it will get the interesting result as an effect to the coating and substrates. The need to understand the use of solvent systematically is worth it to study.

1.3 Objectives

The objectives in this study are:

I. To characterize the TiO_2 coatings properties such as elemental analysis deposited from mixed and non-mixed solvent.
II. To analyze the effect of mixing and non-mixing solvent on the morphological of TiO_2 coating.

1.4 Scope

This project will focus mainly on the experimental effort on producing sol-gel derived Titanium oxide coating on glass substrate. Moreover, there are also several variables to be assessed when preparing the sample and the coating solution which are renovation coating solution which is using different solvent and mix and non-mix solvent. After completing the coating process, the characterization headed for the Titanium oxide coating on the glass substrates will be completed to achieve the coating characteristics.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter will discuss about the theory of TiO_2 coatings, sol-gel technique, coating properties and also will lead to solvent used in the TiO_2 coating. In addition, this chapter will highlight about the effect of mixing and non-mixing solvent used for TiO_2 coating. Even though the effect of solvent on TiO_2 coatings has been performed before, however the effect of mixing solvent and by controlling their mixing ratio was never performed before. So, this chapter will include the effect of ethanol and propanol, on structure and morphology properties.

2.2 TiO_2 coating

Titanium dioxide is an inorganic substance that is stable in thermal condition, less solubility, nonflammable, and not categorized as hazard chemicals. For TiO_2, the oxide of titanium metal was occurs naturally in some types of rock and also sands. Titanium is a part of most common element in the earth's layer and it is normally thought of as being inert chemicals. TiO_2 coating thin film was widely used for elimination of air pollutants. Titanium dioxide also has their advantages compared to other precursor in the features of chemical stability, low cost, non-toxicity, and high oxidation rate (Hung-Jen Chen, 2007). This TiO_2 coating has been commonly used in ceramic applications for coating.

2.2.1 Advantages of TiO_2 coating

There are a lot of advantages when using TiO_2 coating which is as the photocatalyst, it is a low cost material used. In applications today, they will be looking towards at low cost material first but it is effective to use. In addition, according to Marius Stamate ET, Al. when using TiO_2, the reaction is quite fast at room temperature and atmospheric pressure operating conditions. It is become more attractive for the sol-gel method because when the reaction is fast, no chemical reactants must be used and no side reactions are produced. Besides, the TiO_2 become more interesting because it has a nature where a wide spectrum of organic contaminants can be converted to water and CO_2. TiO_2 coating can kill the cancer cells, bacteria and viruses under mild UV illumination. Other than that, it is also easily to oxidize non-toxicity and also have the chemical and physical stability. That's make it as a good antimicrobial material. Figure 2.1 below is the illustration of how the TiO_2 coating works on the substrates surface.

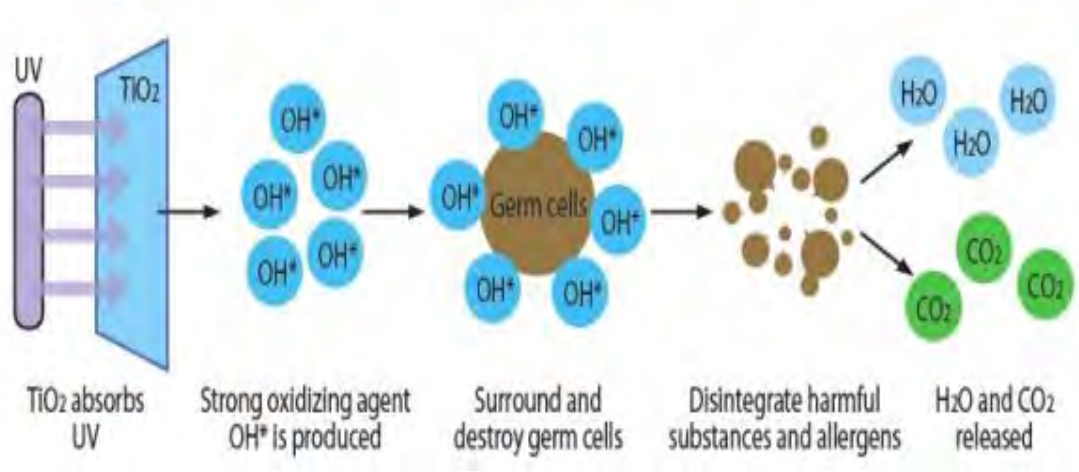

Figure 2.1: Reaction process of the TiO_2 coating with bacteria.

2.2.2 Comparison with other materials

TiO_2 coatings are commonly used for ceramic coating because of their behavior which is easily to oxidize non-toxicity and also have the chemical and physical stability. TiO_2, together with SiO_2 and also ZnO are most usual additives that used with developed applications in the nanoscale fields. The TiO2 antimicrobial activity which are giving the significant ecosystem for health precautions. However, there are rarely giving the consideration to the antibacterial activity of SiO2 and ZnO while they also creating reactive oxygen classes. These three reactive nanomaterials were hazardous to all organisms, with increasing of and also particle concentration. In addition, toxicity of these three compounds decreasing from ZnO to TiO_2 to SiO_2. However, the small particle size did not affect the toxicity of these compounds. Besides that, the antibacterial activity was well-known under both either dark or light conditions specifying that mechanisms. These results focus the need for cautiousness during the use and removal of such manufactured nanomaterial to prevent chance to the environmental impacts.

2.3 Sol Gel Techniques

Sol-gel technique is a simplest technique to making thin films. The sol-gel technique is a multipurpose solution technique for producing the materials such advance ceramics and organic or inorganic materials. Commonly, the sol-gel techniques includes the evolution of a solution from a liquid that was call a sol and mostly are colloidal into a solid state or gel phases. Quality of the prepared films is influenced by the parameters of the sol-gel process and the used technique for deposition. By developing the sol-gel technique, it is probable to produce the advanced materials in a comprehensive variety of forms thin film coatings, fibers, dense materials, and porous aerogel materials. There are a lot of the sol-gel derived films have been prepared for different applications. From the previous research, it shows a lot of people found the advantages of sol gel method.

Table 2.1: Previous Research about Sol Gel

	Journal	Definition	Advantage	Disadvantage
1	Materials Science and Engineering B 174 (2010) 18–30	Soft chemistry allows expanding solid material from solution by using a sol or a gel as an transitional step.	-	-
2	Journal of Non-Crystalline Solids 100 (1988) 162-168	Use of low viscosity liquid solutions as mixture of raw materials, able to achieved homogenazation at a molecular level in a short time.	Require lower temperatures, lower vaporization losses and minimize reactions with containers and the environment	Large shrinkage associated with the gelation process and the drying of gels, Presence of high cost of raw material, long processing time
3	Nanoscience and Nanotechnology 2012, 2(1): 22-25	Sol gel SiO_2, technique to coat glasses, ceramic and metals	Excellent mechanical and chemical stability	-
4	Thin Solid Films, 201 (1991) 97 108	-	Able to tailor the microstructure of the deposited film, require less equipment.	-
5	Journal of the University of Chemical Technology and Metallurgy, 43, 2, 2008, 181-192	-	Require lower temperature, possible to produce material with high purity, high homogeneity, and able to control particle size distributions in nano-scale.	-
6	Progress in NaturalScience:Materials International2013; 23(1):77–84	-	Required lower temperature, uniformity, easiness of control composition, good equipment cost and good optical properties.	-

2.3.1 Process of Sol Gel

The sol-gel process comprises solution, gelation, drying, and densification. The preparation of a TiO_2 sol gel begins with an appropriate Titanium tetraisopropoxide precursor which is mixed with deionized water and a common solvent to form a solution. Then, the hydrolysis process leads to the formation of mixing the element. Subsequent condensation of reactions producing the bonding. TiO_2 gel was formed by this process leads to a rigid, and the interconnected of 3D network containing of polymeric chains and sub micrometer pores. For the drying process, it is at ambient pressure, then, the solvent liquid was removed and significant shrinkage were occurs. The final material was known as a xerogel.

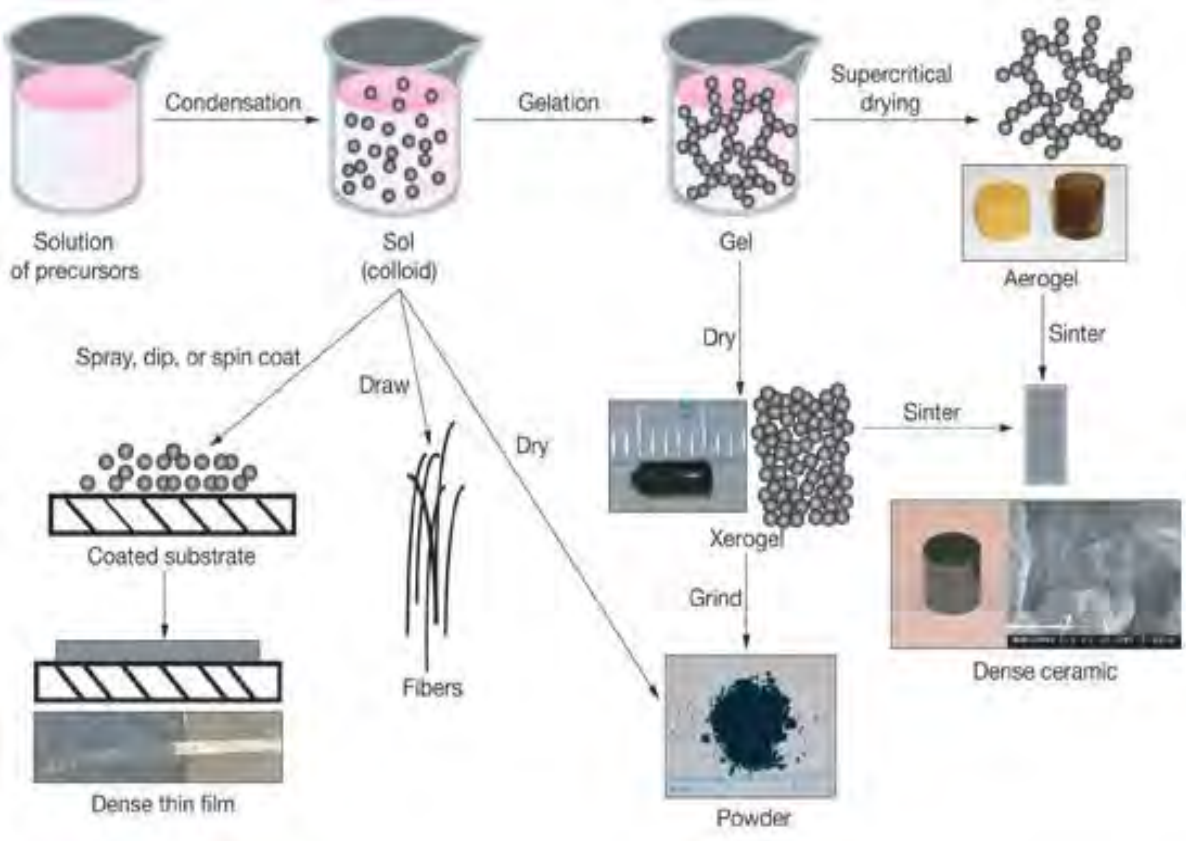

Figure 2.2: A Review for Sol Gel Preparation

2.3.2 Precursors for TiO_2 Sol Gel

Precursor is a compound that contributes in the reaction of chemical that produces other compound. Term "precursor" was used more definitely to refer as a chemical compound prior another in a metabolic path. Precursors were used for the synthesis of oxide systems by the sol-gel method that plays important role in various stages of the process is discussed. Highlighting is given to titanium tetraisopropoxide precursors and to their physical and chemical properties. Different precursor used, it will give the different effect to the sol gel.

Table 2.2: Previous Research about Precursor used for TiO_2 Sol Gel

	Journal	Precursor	Solvent	Remarks
1.	Preparation of TiO_2 Sol Using $TiCl_4$ as a precursor	$TiCl_4$	HCl	-
2.	Pressureless nanoimprinting of anatase TiO_2 precursor films	Titanium butoxide	Methoxy ethanol	-
3.	Atomic Layer Deposition of TiO_2 Thin Films from Ti(Oi Pr)2(dmae)2 and H_2O	[Ti(OPri)2(dmae)2]	-	-
4.	Deposition of TiO_2 and Ag:TiO_2 thin films by the polymeric precursor method and their application in the photodegradation of textile dyes	Titanium tetraisopropoxide (Aldrich)	aqueous solution of citric acid	-
5	The synthesis of nanosized TiO_2 powder using a sol-gel method with $TiCl_4$ as a precursor	$TiCl_4$ ethanol solution	-	When mixed with ethanol, TiCl4 reacted with ethanol to form TiClx(OCH2CH3)4−x species and HCl gas
6	TiO_2 thin films prepared by sol gel method	Titanium tetra isopropoxide (TTIP, Fluka)	1-butanol	-
7	Sol–gel reactions of titanium alkoxides and water: influence	Titanium tetra isopropoxide (TTIP)	Isopropyl (99.5% anhydrous,	-

	of pH and alkoxy group on cluster formation and properties of the resulting products		Aldrich)	
8	Photocatalytic degradation of Lissamine Green B dye by using nanostructured sol–gel TiO_2 films	titanium (IV) isopropoxide ($Ti(C_3H_5O_{12})_4$) – TIP	i-propanol (C_3H_7OH) – PrOH	-
9	Photocatalytic investigations of TiO_2 nanocomposite thin films prepared by peroxotitanic acid modified sol–gel method	tetra isopropyl orthotitanate (TTIP, 98% Merck)	Isopropanol (Merck)	-
10	Solar Photo catalytic activity of anatase TiO_2 Nano crystals synthesized by non-hydrolytic sol–gel method	Titanium (IV) chloride (99.9%)	benzyl alcohol (99.8%, anhydrous)	-
11	Semiconductor TiO_2 and Al_2O_3 thin film gas sensors derived from aqueous particulate sol gel process	Titanium tetraisopropoxide (TTIP) with a normal purity of 97% (Aldrich, UK)	-	-
12	Preparation of continuous TiO_2 fibers by sol–gel method and its photocatalytic degradation on formaldehyde	tetrabutyl orthotitanate (TBOT)	anhydrous alcohol (Ethanol)	-
13	Preparation and visible light induced photocatalytic activity of H-PVA derived TiO_2 composite loaded on glass via sol gel method	Tetrabutyl titanate (TBOT)	absolute ethanol	-

2.3.3 Solvent

In sol gel method, solvent is important because from the solvent, we can determine the quality of the coating properties. From previous research, by using different solvent, we can get different effect on their crystal structure, phases and also morphology. The important thing here is we need to understand about the applications used to choose the right solvent because there are different properties for different applications. Besides, we also need to know the ratio of the solvent that need to mix with the precursor, time taken for stirring, aging time and also the molarity of the chemicals. All of these factors are important to get the proper sol gel with good surface morphology and microstructure. By observing how the rate of a reaction was affected with the changing conditions, sometimes, we also can learn specifically of what is happening at the molecular level. However, a little modification in the parameters conditions of the mixture, such as solvent, temperature, catalyst, concentration or time, it can produce large adjustments in the final properties of the material.

Table 2.3: Previous Research about Solvent used for TiO_2 Sol Gel

Journal	Solvent	Microstructure	Crystal Size	Characterization
Tio_2 Powder Photocatalyst From Sol Gel Route And Its Immobilization With Cement For Photocatalytic Phenol Removal	Methanol	TiO_2 powder 1 has small particle size than powder 2. Then, the formation of small particles of powder 1 is due to its less advanced hydrolysis rate and during the synthesis. So that, the powder particles form slowly in the solution and producing small size particles.	TiO_2 Powder 2 high crystallinity	From XRD results, it shows both of TiO_2 powders are mostly crystalline anatase structure which is TiO_2 powder 2 has higher crystalline phases than powder 1.