

Preparation and Characterization of Titanium Dioxide Nanoparticles and Thin Films

LIEW SIENG LING

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DECLARATION

No portion of the work referred to in this description has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

Liew Sieng Ling (12240)

Programme of Resource Chemistry

Faculty of Resource Science and Technology

University Malaysia Sarawak

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Liew Sieng Ling

Resource Chemistry Programme
Faculty of Resource Science and Technology
University Malaysia Sarawak

ABSTRACT

Titanium dioxide (TiO_2) nanoparticles in the form of colloidal suspension were prepared by three different synthesis approaches. These TiO_2 sols were characterized using Scanning Ultraviolet-Visible Spectrophotometer to investigate their stability and relative aggregate sizes upon aging. TiO_2 sol synthesized by method 1, (sol-gel method) was comparatively more stable than that of the other two methods. TiO_2 thin films prepared under ambient temperature and after annealed at 400°C were porous and nanoparticulate in nature, with TiO_2 nanoparticles of spherical shape. TiO_2 films showed high hydrophilicity when the film was being exposed to sunlight. Ceramic tiles coated with TiO_2 thin film were evaluated for their photocatalytic activities. However, no conclusive result was obtained in this study due to too short experimental duration.

Keywords: Titanium Dioxide, Thin Films, Photocatalytic Activity.

ABSTRAK

Butiran halus titanium dioksida dalam bentuk nanosaiz telah disediakan dengan tiga kaedah penyediaan yang berlainan. Ketiga-tiga larutan TiO_2 telah dianalisis dengan menggunakan imbasan spektrofotometer UV-Vis untuk menyelidik kestabilan serta saiz relatif kepada penuaan. Larutan TiO_2 daripada kaedah 1 (kaedah sol-gel), adalah lebih stabil berbanding dengan dua kaedah yang lain. Tipisan halus TiO_2 yang disediakan pada suhu bilik serta selepas dikalsinkan pada suhu 400°C adalah zarah-zarah nanosaiz dan berliang-liang kecil, yang berbentuk sfera. Tipisan TiO_2 menunjukkan sifat hidrofilik apabila disinari bawah matahari. Aktiviti pemangkinan telah dikaji pada seramik yang dikot dengan TiO_2 . Tiada perubahan atas seramik diperhati disebabkan tempoh eksperimen yang terlalu pendek.

Kata kunci: Titanium Dioksida, Tipisan Halus, Aktiviti Pemangkinan.

CHAPTER 1

INTRODUCTION

Titanium dioxide (TiO_2) is a transition metal oxide which is white in colour, inexpensive, and nontoxic in nature. TiO_2 exists in different forms such as anatase ($\beta\text{-TiO}_2$), rutile ($\alpha\text{-TiO}_2$), brookite ($\gamma\text{-TiO}_2$), pyrite (Pa3), $\alpha\text{-PbO}_2$ type, baddeleyite (ZrO_2) type, fluorite, etc. (Habib *et al.*, 2005). Anatase is not as thermodynamically stable as rutile. Rutile TiO_2 has been proven to be comparable to anatase TiO_2 in the application of dye sensitized solar cells. Besides, rutile TiO_2 has dominated anatase TiO_2 in the case of high refractive index. Brookite appears to exist only as a meta-stable phase, while the $\alpha\text{-PbO}_2$ type phase is quenched, high pressure polymorph, which is formed at a pressure between 0.8 and 10.0 GPa depending upon starting materials (Haines and Leger, 1993). At 12 GPa, rutile TiO_2 transforms to a phase with baddeleyite (ZrO_2) structure. Upon decompression, this phase transforms at 7 GPa to another phase with $\alpha\text{-PbO}_2$ structure. The baddeleyite type phase is denser than rutile.

Of all the compounds of the transition metals, titanium dioxide is being produced in the largest quantity (approximately 2 billion lb/yr) because of its extensive use in paint (James and Kathleen, 2001). Different kinds of precursor materials have been employed for TiO_2 nanoparticles production. Titanium alkoxide, a highly stable, environmentally friendly, non-toxic, low-cost precursor material, has been widely exploited to produce TiO_2 nanoparticles because of their extended application in photocatalysis for wastewater treatment, in solar cells and electronic devices and, more recently, also in sensors (Andrea *et al.*, 2006). Titanium dioxide films are also

being widely used as biomaterial due to their good biocompatibility with the human body (Wu *et al.*, 2005).

Photocatalytic processes are rapidly developing as potential techniques for the purification of wastewaters. TiO₂ is excellent for photocatalytically breaking down organic compounds. For example, if one puts catalytically active TiO₂ powder into a shallow pool of polluted water and allows it to be illuminated with sunlight, the water will gradually become purified (Fujishima *et al.*, 2000b). One of the most important aspects of TiO₂ is that, like the photoelectric effect, it depends upon the energy of the incident photons, but to a first approximation, not on their intensity. Thus, ordinary room light may be sufficient to help to purify the air or to keep the walls clean in the indoor environment, because the amount of pollutants is typically small. There have been significant developments in photocatalytic technology in the US. For example, TiO₂-coated glass microbubbles have been developed for the specific application of cleanup of oil films on water, particularly after the major portion of oil spills has been removed. Self-cleaning window glass has been developed, as well as TiO₂-containing, self-cleaning paint (Fujishima *et al.*, 2000b). However, most of the TiO₂ powders show low values of quantum efficiency (Maurizio *et al.*, 2005). The photoactivity strongly depends on several variables such as preparation method, particle size, reactive surface area, and ratio between anatase and rutile phases. A way to improve the activity of a photocatalyst is to increase its specific surface area and to decrease the size of the particles.

In efforts to extend the utility and value of paper and nonwoven cellulosic products, Japanese and European companies have recently announced products with photocatalytic activity

that can decompose organic pollutants and kill bacteria. These advances reflect the convergence of two technologies—the use of TiO₂ as an opacifying filler for paper and the discovery by Fujishima and Honda that TiO₂ photocatalyzes the decomposition of water. In spite of many recent patents and few scientific studies, photocatalytic paper has only been reviewed in the Japanese literature (Robert *et al.*, 2006). Robert *et al* (2006) have provided an overview of the developing field of photocatalytic paper. TiO₂ is being used in paper products usually to improve opacity and whiteness. However, its high cost, compared to clay and calcium carbonate, limits conventional TiO₂ usage to high value- added printing papers. Current applications of TiO₂ have been restricted to mineralization and disinfection. One could imagine photoinitiation of polymerization perhaps for self-repairing materials, sensing UV light exposure, or photo-release of paper supported agricultural chemicals. A particularly attractive application would be as part of a simple, disposable, very low power, paper-based fuel cell for powering printed electronic applications.

The second unique aspect of TiO₂ is its high wettability or being termed as superhydrophilicity. There is an extremely wide range of applications for superhydrophilic technology. Fogging of the surface of mirrors and glass occurs when humid air condenses, with the formation of many small water droplets, which scatter light. On a superhydrophilic surface coated with TiO₂, no water droplets are formed. Mirrors with superhydrophilic coatings retain their capacity for photoinduced wetting semipermanently, at least for several years. Various glass products such as mirrors and eyeglasses can now be imparted with antifogging functions using this new technology, with simple processing and at low cost (Fujishima *et al.*, 2000b).

TiO₂-based photocatalytic technology is making inroads in such diverse applications as environmental remediation, organic compound transformation and self-cleaning materials, for instance, TiO₂-coated windows and bathroom tiles (Sawunyama *et al.*, 1998). Except for the latter applications, TiO₂ is normally used in the form of particulate suspensions. In recent years, however, interest has shifted toward nanometer-sized particles with crystalline dimension $\leq 10\text{nm}$ in the form of colloids or film networks on supports. An attractive property of nanometer-sized photocatalytic films or systems is the ability to alter the electrochemical potentials of the photogenerated charge carriers by simply modifying the size of the particles.

TiO₂ thin films have been made by a variety of techniques such as e-beam evaporation, magnetron sputtering technique, anodization, chemical vapour deposition (CVD) and the sol-gel technique. Among the different methods for the preparation of thin TiO₂ electrochromic layer, the sol-gel method has many advantages, particularly the possibility of producing large surfaces (Mansor and Ismail, 2003).

According to Liufu *et al.* (2005), control of the colloidal properties and stability of titanium dioxide suspensions is of significant importance in the manufacture of high-quality products such as paints, cosmetics, and ceramics. The stability of colloidal systems is the result of an extremely slow aggregation process. The main reasons for such a slow aggregation process are the high electrostatic repulsion and the repulsion due to adsorbed polymer layers, called steric repulsion. When polyelectrolyte adsorbs flatly on the surface then steric effects make a small contribution and the stabilization mechanism originates mainly from electrostatic interaction. This situation happens when the polyelectrolyte is highly charged and in consequence adsorbed

onto the surface with opposite charge, forming mainly a train-type structure. With the increase of the adsorption layer thickness of the polymer the contribution of steric repulsion is bigger and this effect is responsible for stabilization of the suspension.

In this research, we aim to prepare TiO₂ nanocrystalline particles using different synthesis approaches such as the sol-gel technique and hydrolysis method. The main focus was to prepare TiO₂ nanoparticles of controllable sizes by varying the synthesis parameters such as concentration, temperature, addition of appropriate additives and pH of the reaction mechanism.

The objectives of the research are:

1. To synthesize TiO₂ nanoparticles with controllable sizes using different synthesis approaches.
2. To characterize the physical and chemical properties of these nanoparticles prepared.
3. To prepare and characterize TiO₂ thin films prepared from nanoparticles of various sizes.
4. To evaluate the potential applications of nanostructured TiO₂ thin films.

CHAPTER 2

LITERATURE REVIEW

Since the introduction of nanostructured materials by Gleiter (Gleiter, 1989), many researchers have paid attention to the preparation methods and properties of these materials. Many physical and chemical methods have been utilized to prepare nanostructured materials with desirable characteristics. The ideal preparation route of any material is one that is convenient and economical and does not lose desirable properties.

The design, synthesis, and characterization of nanoscale materials characterized by a grain size of < 100 nm have been the subject of much recent research. Experiments have shown that the properties of nanoscale materials are significantly different and improved compared to their coarse-grained (micron-sized) counterparts (Lin *et al.*, 1997b). Successful synthesis of nanoscale materials of powders has utilized inert gas condensation (Birringer *et al.*, 1984), hydrothermal method (Dawson, 1988), and sol-gel method (Roy *et al.*, 1993), among others. Despite considerable success of these methods, there are some problems and limitations as reported by Lin *et al.* (1997a), such as complex technique, possible reaction between metal vapor and oven material, limited success with refractory metals for gas condensation, high temperature and high pressure required for the hydrothermal method.

The sol-gel method is widely employed for the preparation of nanoparticles, due to the inexpensive equipment required and the low temperatures involved. The properties of the sol-gel derived samples are strongly dependent not only on the composition, but also on the preparation

conditions including the starting materials and solvents, the solution preparation sequence and various other processing conditions such as [precursor]/[solvent] ratio, temperature, stirring and aging time. The TiO₂ particles obtained by this method are amorphous in nature and require temperatures higher than 623K to realize the transition from amorphous to anatase phase (Maurizio *et al.*, 2005). Unfortunately, the high calcination temperatures give rise to an increase of the size of the nanoparticles and to a decrease of their specific surface areas.

Recently, various nanostructured TiO₂ catalysts have been prepared by hydrolysis of titanium isopropoxide or titanium tetrachloride. The samples derived from TiCl₄ were the most photoactive and neither filtration nor calcination was needed to obtain a highly efficient anatase phase. The preparation of nanostructured TiO₂ photocatalysts using TiCl₄ as the precursor appears worthy of attention since this compound does not give rise to formation of organic impurities in the final products. It should be noticed, however, that carbon modified TiO₂ samples prepared by hydrolysis of TiCl₄ with tetrabutylammonium hydroxide have demonstrated a superior photocatalytic activity under direct artificial and diffused natural light (Maurizio *et al.*, 2005).

Numerous literatures have reported on the fabrication of TiO₂ thin films by the sol-gel dip coating technique using many types of titanium alkoxides as precursors. Chrysicopoulou *et al.* (1998) used titanium tetraethoxide as a precursor, ethanol as a solvent and HNO₃ as a catalyst in the presence of a small amount of water. Harizanov (2000) and Nilgun *et al.* (1995) used titanium ethoxide dissolved in butanol or ethanol and glacial acetate acid as modifier. Bell *et al.* (1994) reported that TiO₂ can be produced by hydrolyzing titanium propoxide in ethanol. The use of

tetraisopropylorthotitanate as precursor was also reported (Su and Lu, 1998). Titanium butoxide and H_2O_2 as starting materials for making TiO_2 thin films had also been used.

Maurizio *et al.* (2005) reported the preparation of efficient nanostructured TiO_2 particles obtained by controlling the hydrolysis of TiCl_4 in pure water in very mild conditions. Several samples were prepared as suspensions or colloidal dispersions by using $\text{TiCl}_4/\text{H}_2\text{O}$ volume ratios ranging between 1:1 and 1:100. A dialysis process was performed in some cases to reduce the amount of chloride ions present in the system. The samples were characterised by X-ray diffraction analysis, specific surface area determination, diffuse reflectance spectroscopy and scanning electron microscopy. The X-ray diffractograms indicated always the presence of a badly crystallised anatase phase although small amount of rutile can be noticed in samples prepared by using high $\text{TiCl}_4/\text{H}_2\text{O}$ volume ratios. The comparison of the XRD patterns reveals that a better crystallinity was obtained when the $\text{TiCl}_4/\text{H}_2\text{O}$ ratio was 1:50. The diameter of the crystallites, estimated by means of the Scherrer equation, was in the range 10–50 nm. SEM observations revealed that all the samples presented irregular shapes and consisted of aggregates of particles whose sizes appeared generally bigger (30–60 nm) than those calculated by the Scherrer equation. This may be due probably to the difficulty to obtain good micrographs at high resolution. EDX analysis indicated a significant presence of Cl^- ions (ca. 5% w/w) in the samples obtained by hydrolysis. The dialysed samples at pH= 5 contained, instead, only small traces of Cl^- (< 0.2%).

In the work of Zhang *et al.* (1999), a stable aqueous TiCl_4 solution made from TiCl_4 that vigorously reacts with water in an ice-water bath is used as the starting material to obtain an

ultrafine TiO₂ powder with uniform size. Because crystalline TiO₂ precipitates formed homogeneously at room temperature to 100°C with a productivity >90% by just heating, stirring and neutralizing the TiCl₄ solution, which is diluted with an appropriate amount of water, neither high temperature nor oxygen gas is needed for oxidation and calcination to take place during this process. Thus process simplification leads to lower production costs and makes a continuous process possible. Moreover, in an optimum process, titania powder of anatase phase was prepared without calcination, which primary particle size was 4nm and its BET surface area was 290m²/g. This TiO₂ powder is finer than that of alkoxide-derived powders.

According to Mansor and Ismail (2003), tetraisopropyl-orthotitanate (TIP, Ti(O-*i*-C₃H₇)₄) was used as a precursor and ethanol as a solvent to form thin films onto indium tin oxide (ITO) coated glass by the sol-gel dipping technique. Acetate modification was performed in order to stabilize the sol by introducing glacial acetic acid. The chemical composition of the starting alkoxide solution was Ti(O-*i*-C₃H₇)₄ : C₂H₅OH : CH₃COOH = 1 : 45 : 0.3 in molar ratio, was able to produce a good coating based on morphology, homogeneity and transparency of TiO₂ thin films. The process was exothermic and the pH of the solution was about 4 to 5. The equivalent diameter of the grain size was about 20nm and the solution was found to be stable over 7 days when glacial acetic acid was used. The glacial acetic acid acts as an acid catalyst and also as a ligand that changes the alkoxide precursor at the molecular level, therefore modifying the whole hydrolysis and condensation process resulting in a more stable sol.

The manufacture of nano-TiO₂ whiskers was performed via the hydrolysis of titanium butoxide at room temperature (Ying and Chuan, 1999). It was found that acetic acid could

restrain the hydrolysis of alkoxides by coordinating to titanium. Without acetic acid in reaction solution, aggregated nano-TiO₂ spherical particles were obtained under similar experimental condition. Once the concentration of reactants had been reduced to large extent, the size of particles could remain constant. With a high water: alkoxide molar ratio, anatase nanocrystalline TiO₂ was obtained and subsequent ethanol rinsing could reverse the condensation reaction and caused the anatase crystallites to form an amorphous phase. Amorphous TiO₂ gel was obtained by hydrolysis-condensation reactions of titanium butoxide which was refluxed in ethanol with 2,4-pentanedione being added to the alkoxide solution. Hexadecyltrimethylammonium bromide and tetramethylammonium hydroxide were employed to arrest the hydrolysis of titanium tetraisopropoxide and thus form a nanocrystalline TiO₂. Monosized spherical titania fine particles were synthesized by controlled hydrolysis of titanium tetraethoxide in ethanol at low temperature. TiO₂ nanoparticles with a diameter of about 40 nm and a length of about 35 nm had been synthesized. After the heat treatment, the diameter of nano-TiO₂ has been reduced to 8 nm and a length of about 40 nm.

In the investigation of Habib *et al.* (2005), chemical bath deposition (CBD) was utilized for the synthesis of nanocrystalline TiO₂ thin films at room temperature from highly acidic bath (pH 1-2). The chemical such as TiCl₃ solution and NH₃ were used for the solution preparation. The film was scratched from substrate for TEM analysis. TEM images indicated that the particles (size ~ 2 nm) consist of agglomeration of small particles. This method affords flexibility in the choice of non-heat resistance substrates such as plastic film, polyester, etc., which should be beneficial not only for the dye sensitized solar cells but also for photocatalytic applications.

Techniques have been developed to treat various types of surfaces with TiO_2 to make them self-cleaning. Fujushima *et al.* (2000a) have developed highly transparent, photoactive TiO_2 thin films as coatings for glass substrates, using the sol-gel technique. The research also successful in coating films on glass, quartz, soda-lime glass (SLG) and SiO_2 -precoated SLG (SiO_2/SLG) substrates using the spray-pyrolysis technique, with titanium tetraisopropoxide as the titanium source. The films coated by this technique showed a transparency of 80% in the visible region. The photocatalytic activity of TiO_2 -coated quartz was found to be much higher than that of TiO_2 -coated SLG. However, the TiO_2 coated SiO_2/SLG showed much higher catalytic activity than that of films deposited directly on SLG, the catalytic activity being similar to that of TiO_2 -coated quartz. In collaboration with Nippon Soda Co., Fujushima *et al.* (2000a) have developed similar transparent TiO_2 films that consist of particles in the 10-20 nm range on SLG and SiO_2/SLG substrates, specifically for studying the catalytic activity for the decomposition of oily materials.

The TiO_2 nanocrystals have been prepared by a gas-evaporation method based on Hwu *et al.* (1997). Similar method is also being used by Lin *et al.* (1997a). A preparation vacuum chamber was backfilled with mixed helium and oxygen, and titanium was evaporated from a tantalum boat. The TiO_2 particles condensed in the mixed gases were transported via convection and deposited on the surface of a liquid nitrogen cooled cold trap. The samples were collected in vacuum and transferred to the main ultrahigh vacuum (UHV) chamber for measurements. This method produces very fine TiO_2 particles with rather uniform size distribution (~20nm) which was checked by transmission electron microscopy (TEM). The research also reported that whether rutile or anatase TiO_2 formed depends on the preparation method. Anatase will transform

to rutile at high temperature (700°C). But for very small particle size (< 50 nm), anatase seems more stable.

Cathodic electrosynthesis is evolving as an important method in ceramic processing. This technique enables formation of ceramic oxide materials in the form of thin films or powders. Zhitomirsky (1997) has performed electrosynthesis of titania films and powders via hydrolysis by electrogenerated base of TiCl_4 salt dissolved in water or mixed water-methyl alcohol solvent in the presence of hydrogen peroxide. The use of peroxocomplex $[\text{Ti}(\text{O}_2)(\text{OH})_{n-2}]^{(4-n)+}$ can solve the problem associated with handling titanium salts in aqueous solutions. The method of cathodic electrosynthesis does not require expensive materials or equipment and can easily be transformed from laboratory to manufacturing scale. The rate of deposition decreases with increase of H_2O_2 concentration. The crystallization of anatase was observed to occur at 300°C.

The microemulsion approach is a promising method to prepare nanometer-sized particles. An inverse microemulsion system, which consists of an oil phase, a surfactant phase, and an aqueous phase, is a thermodynamically stable isotropic dispersion of the aqueous phase in the continuous oil phase. The size of the droplets was ranged from 5 to 20 nm in diameter. Chemical reactions will take place when droplets containing the desirable reactant collide with each other and therefore nanometer-sized particles form. Microemulsion processing techniques have been employed to synthesize nanometer-sized particles of a variety of materials, such as Ag, ZrO_2 , and BaTiO_3 etc. Recently, a microemulsion method was successfully applied to synthesize TiO_2 nanometer-sized particles in various microemulsion systems with titanium alkoxide as the starting material (Li and Wang, 1999). TiO_2 particles prepared in these systems have average size of

about 5 nm and a narrow size distribution. However, this method is expensive, because the ratio of aqueous phase to oil phase and surfactant in these microemulsion systems is too small and therefore only a small amount of TiO₂ nanometer-sized particles can be obtained at the cost of a large amount of oil and surfactant.

The size, the phase and the composition of the nanocrystalline TiO₂ particles, the structure and the degree of defects in the prepared films are expected to have a decisive influence on the usefulness of nanocrystalline TiO₂ films in the applications (Bernd *et al.*, 2005). Therefore, the study of Bernd *et al.* (2005) was to prepare nanocrystalline films of the anatase phase of TiO₂ using nanoparticles of different sizes and to investigate the size dependent properties of these films; in particular, the structure of the films and of individual particles within them, the chemical composition and the possible presence of impurities, and some pertinent electrical properties such as the DC conductivity and the impedance of the films under various conditions (varying sample temperature or ambient oxygen partial pressure). Nanocrystalline anatase TiO₂ particles with three different nominal sizes (6, 12, and 20 nm, respectively) were used. Nanocrystalline thin films were deposited by painting the colloidal suspensions of nanocrystalline TiO₂ particles either onto glass, sapphire, or silicon substrates. The films were then dried in air at room temperature for 24 h and subsequently annealed at 720 K in air for 1 h. XRD and TEM analyses indicate that the films are composed solely of anatase TiO₂ nanoparticles; their average size agrees very closely with the nominal size of the primary particles. The electrical conductivity was observed to exhibit, as a function of oxygen pressure, a power-law dependence, $\sigma \propto p(\text{O}_2)^{-n}$, with the exponent n showing a distinct size dependence.

Apart from the synthesis approaches mentioned above, there were still some new methods reported for the synthesis of titanium dioxide nanoparticles films with different structures. Miao et al. (2006) reported a new method by synthesizing mesoporous TiO₂ films in ionic liquid dissolving cellulose. Mesoporous TiO₂ films were successfully prepared via calcining ionic liquid (1-allyl-3-methylimidazolium chloride, AMIMCl) solution containing titanium tetrabutoxide and cellulose. Cellulose was first dissolved in ionic liquid, and then titanium tetrabutoxide (TTBO) was added into the solution to form a homogeneous solution, followed by calcining the TTBO / cellulose / IL solution, resulting in TiO₂ films. The as-prepared TiO₂ films were characterized by different techniques including X-ray diffraction, transmission electron microscopy, scanning electron microscopy and nitrogen sorption analysis. It was indicated that the resulting nanofilms were composed of anatase nanoparticles with size of about 14 nm. The pore size of the films could be adjusted by changing the cellulose concentration in the ionic liquid. The resulting TiO₂ films can be used to photoreduce Ag(I) and Au(III) into Ag(0) and Au(0), respectively.

CHAPTER 3

METHODOLOGY

3.1 Preparation of titanium dioxide sol.

3.1.1 Method 1 (sol-gel method):

4.30 mL of concentrated nitric acid was added to 600 mL of distilled water at room temperature. 50 mL Titanium isopropoxide was added to the acid solution slowly in about 20 minutes, while stirring vigorously so that the precipitates were as small as possible. The resulting precipitate was then peptized by vigorous stirring at room temperature for 3 to 4 days. The resulted sol was transparent, slightly milky and bluish. The sol was then undergo dialysis using Spectra Por 3500 m.w. Cutoff tubing against ultrapure water for 3 to 4 days, until the sol pH was about 3.5. Dialysate of 100 mL sol / 1 L H₂O are used and water was changed everyday.

Dialysis tube was first prepared by submerging a 20cm length tubing in the wash solution prepared from 1 L of 1 mM EDTA and 2 % sodium bicarbonate. The solution with tubing was heated to 80°C while stirred for 30 minutes, cooled and rinsed. The process of heating and stirring was repeated several times with ultrapure water.

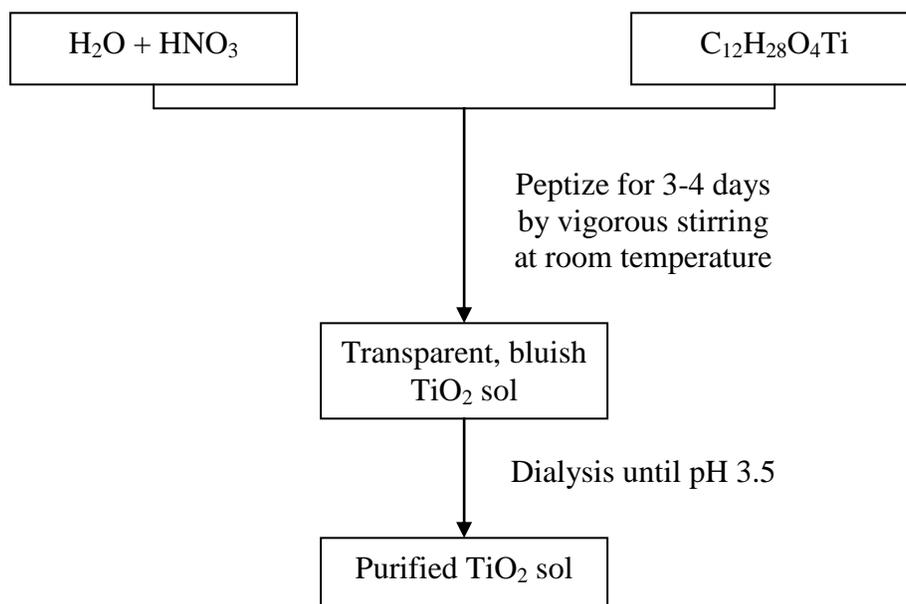


Figure 3.1: Flow chart of the steps involved in the preparation of TiO_2 sol – Method 1 (Xu and Anderson, 1994).

3.1.2 Method 2 (hydrolysis method):

In this method, TiO_2 sol was through the hydrolysis of titanium isopropoxide at room temperature. Firstly, solution (A) was prepared by diluting 5 mL of titanium isopropoxide with 45 mL anhydrous ethanol (volume ratio of 1:9). Secondly, solution (B) was prepared by mixing 150 mL deionized water with 50 mL anhydrous ethanol and acetic acid. Then solution (A) was dropped into solution (B) with vigorous stirring. The resulting mixture was then stirred for few days until an opalescent sol was obtained.