

Effect of pH on TiO₂ nanoparticles via sol gel method

Siti Aida Ibrahim, and Srimala Sreekantan

Abstract—A series of titania nanoparticles was successfully synthesized via sol gel method using titanium tetraisopropoxide as a precursor. In this paper, data concerning the effect of pH towards the development of TiO₂ nanoparticles is reported. The samples were characterised by x-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD results showed the existence of nanocrystalline anatase phases with crystallite size ranging from 7-14 nm. Surface morphological studies obtain from SEM micrograph showed the particles with rodlike shape are rutile while the spherical shapes are anatase in nature. It was also found the pH of the solution affect the agglomeration of the particles. Results of photocatalytic studies exhibits that titania powder prepared at pH 9 has an excellent photocatalytic activity with degradation 74.7% within 60 minutes.

Keywords: TiO₂ nanoparticles, sol gel, photocatalytic

I. INTRODUCTION

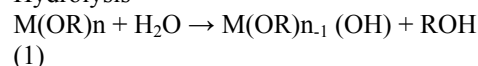
TITANIA (TiO₂) nanoparticles is a promising materials and widely used in many applications due to its high photocatalytic activity [1,2], excellent gas-sensitive properties [3] and dielectric properties [4]. Crystalline titania has three modification phases which are rutile (tetragonal, *P4₂/mnm*), anatase (tetragonal, *I4₁/amd*) and brookite (orthorhombic, *Pcab*). Anatase-type TiO₂ has excellent photocatalytic activity and widely used as catalysts for decomposition of a wide variety of organic and inorganic pollutants. Many methods have been established for titania synthesis such as sol-gel technique [5-8], hydrothermal method [5,9], chemical vapor deposition [10], direct oxidation and others. Among

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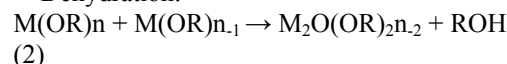
them, the sol-gel technique is one of the most used methods due to its possibility of deriving unique metastable structure at low reaction temperatures and excellent chemical homogeneity. In sol gel processes, TiO₂ is usually prepared by the reactions of hydrolysis and polycondensation of titanium alkoxide, (TiOR)_n to form oxopolymers, which are transformed into an oxide network. These reactions can be schematically represented as follows:

Hydrolysis

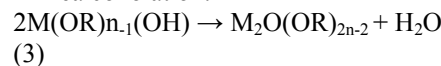


Condensation

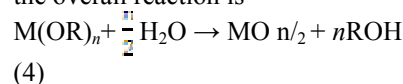
Dehydration:



Dealcoholation:



the overall reaction is



where M= Si, Ti, Zr, etc and R = alkyl group. The relative rates of hydrolysis and polycondensation strongly affected the structure and properties of metal oxides. Factors that crucial in the formation of metal oxides includes reactivity of metal alkoxides, water to alkoxides ratio, pH of reaction medium, nature of solvent and additives and reaction temperature. By varying these process parameters, materials with different surface chemistry and microstructure can be obtained.

Typically, in sol gel method, the sol-gel derived precipitates are amorphous in nature. Therefore, it is require for further heat treatment to induce crystallization. To induce transition from amorphous to anatase phase, generally an annealing temperature higher than 300 °C is required, and this will result in the dramatic growth of the particle sizes. However, titania for photocatalytic activity is dependent on both particle size and degree of crystallinity

In this work, nanocrystalline anatase and rutile TiO₂ particles with crystallite size ranging from 7 to 14 nm have been derived via sol gel precipitation of alkoxides

followed by calcination. The effect of pH towards the development of titania nanocrystal structure and their performance as photocatalyst is investigated.

II. EXPERIMENTAL SECTION

Synthesis. TiO₂ nanocrystal were prepared by sol gel hydrolysis precipitation of titanium (IV) isopropoxide (Ti(OC₃H₇)₄) (Sigma Aldrich, 97%), followed by calcination treatment. A specific amount of titanium isopropoxide was dissolved in isopropyl alcohol (Merck, 95%) solution and the solution was dropped slowly into distilled water, pH was adjusted by HNO₃ for acidic condition and NaOH for basic condition. Molar ratio of water to alkoxide was 110. Upon dropping, white precipitates of hydrous oxide were produced instantly, and the mixture was stirred vigorously for 4 hours at room temperature. The precipitates were centrifuged and were redispersed in ethanol to minimize agglomeration. This process was repeated five times. The resulting materials were then dried and annealed at 400°C.

Characterization. The titania samples were characterized by powder X-ray diffraction (XRD) with Bruker D8 powder diffractometer (40 kV, 30mA) using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). XRD patterns were obtained in the range of 20–70° by step scanning mode with the step size of 0.1°. The crystallite size and peak broadening was determined based on anatase (101) and rutile (110) diffraction using Scherrers equation. Specific surface area of the samples was calculated using formula as :

$$S = 6 \times 10^3 / \rho L \quad (5)$$

Where, S is the specific surface area (m²g⁻¹), L is the average crystallite size, and ρ is the density of titania (3.9 gcm⁻³) The morphologies and particle size of titania particles were examined using a field emission scanning electron microscope (FESEM SUPRA 35VP ZEISS).

Photocatalytic degradation studies were performed by mixing 0.1 g TiO₂ powder into 30 ppm methyl orange (MO) in quartz tube and sealed with stopper. The quartz tubes were then irradiated by UV light (Germicidal 36 watt) for 5 hours and samples were collected for every 1 hour. The concentration of the degraded methyl orange was determined using UV-Vis spectrometer (PerkinElmer Lambda 35).

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of the powder samples prepared in initial solution with different pH. As seen in figure 1, distinct peaks were noted in the XRD patterns at 25.4°. It is also noticed that pH affects particles size and degree of crystallinity. A trace of rutile was found in sample prepared at pH 1 at

27.3 ° corresponding to anatase phase (110). In this case, it is found that high acidity in medium solution will favor the formation of rutile phase while lower acidity will favor anatase formation [11, 12]. The results show high acidity favor formation of rutile.

This mechanism may be explained using the concept of partial charge model [13]. According to this model, hydrolysis of titanium cation is occurred at strong acidity condition. In this condition, a stable species of [Ti(OH)(OH₂)₅]³⁺ will form, but due to the positive charge of hydroxo group, these species are not able to condense. When acidity is not sufficiently low to stabilize these precursor, deprotonation will take place forming new species of [Ti(OH)₂(OH₂)₅]²⁺. However, these species also do not condense probably because of spontaneous intramolecular oxolation to [TiO(OH₂)₅]²⁺[14]. Condensation to both anatase and rutile starts when the solution activity is sufficient enough to allow further deprotonation to [TiO(OH)(OH₂)₄]⁺, which can undergo intramolecular of deoxolation [TiO(OH)₃(OH₂)₃]⁺ depending in exact pH. In lower pH region, deoxolation does not happen and oxolation leads to linear growth along the equatorial plane of cations. This reaction leads to rutile formation due to oxolation between resulting linear chains. Meanwhile, in higher pH values, when deoxolation occurs, condensation can proceed along apical direction and leads to the skewed chain of anatase structure. Therefore, based on this study, it is believe that the determination of resulting crystal structure is affected by pH values [13,15]. The higher acidity promotes rutile formation and lower acidity will lead to anatase formation.

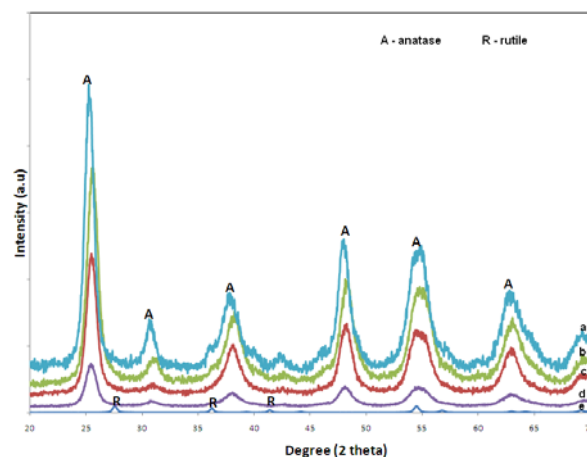


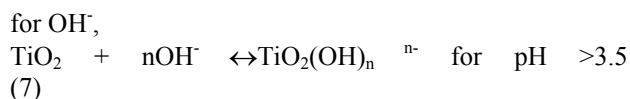
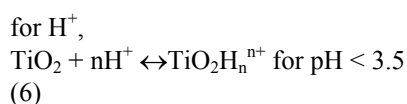
Figure 1. XRD patterns of nanocrystalline titania samples prepared by sol gel method with various pH condition as (a) pH 9, (b) pH 7, (c) pH 5, (d) pH 3 and (e) pH 1.

The crystallite size was determined by Scherrer equation and summarized in Table 1. It was found the crystallite size vary from 7 to 14 nm and specific surface area ca. ranging from 112 to 194 m²g⁻¹.

Table 1. Crystallite size and specific surface area of sample prepared via sol gel method annealed at temperature 400°C

pH	Sample Code	Crystallite size (nm)	Specific Surface area (m ² g ⁻¹)
1	C400-1	13.6	112.8
3	C400-3	8.2	187.4
5	C400-5	7.9	193.8
7	C400-7	9.0	171.7
9	C400-9	8.4	184.2

Figure 2 shows the surface morphology of TiO₂ powders C400-1, C 400-3 and C400-5, respectively. The picture showed that TiO₂ powders of C400-1 prepared at pH 1 consist rodlike shaped particles while C400-3 and C400-5, prepared at pH 3 and 5 respectively are spherical in shape. The size of the particles at higher pH values is smaller and agglomerate. According to several studies, the variety of TiO₂ surface charge is pH dependent. TiO₂ in sols possess electrical charge due to the absorption of H⁺ or OH⁻ in aqueous suspension. According to Bahnemann et al [16], the surface charges of TiO₂ can be determined by chemisorptions of :



In acidic and alkaline media, the strong repulsive charge among particles reduces the probability to coalesce and more stable sol can be formed. Studies by Su et al have indicated that isoelectric of TiO₂ powder varies between the pH ranges 5-6.8 [17]. Based on this work, since sample C400-1 prepared at pH 1 is away from the range of isoelectric point, less aggregates and bigger TiO₂ particles is formed.

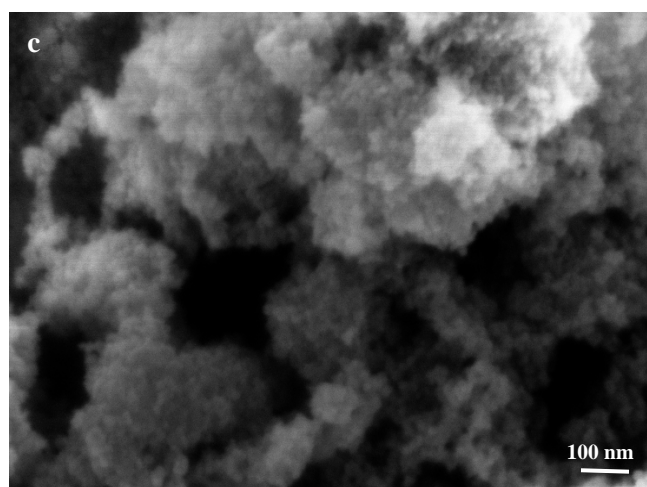
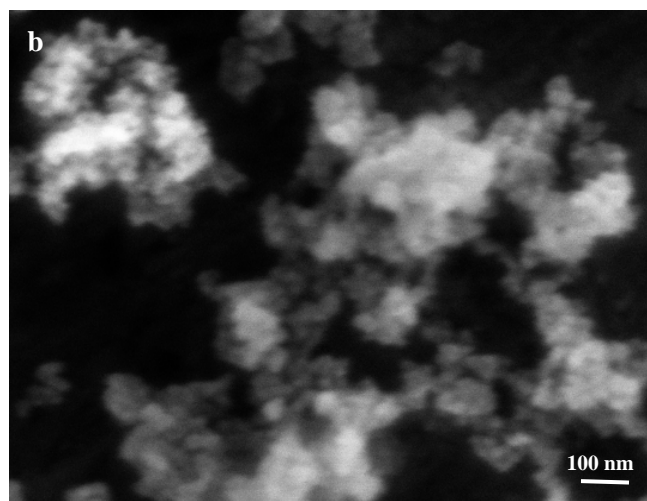
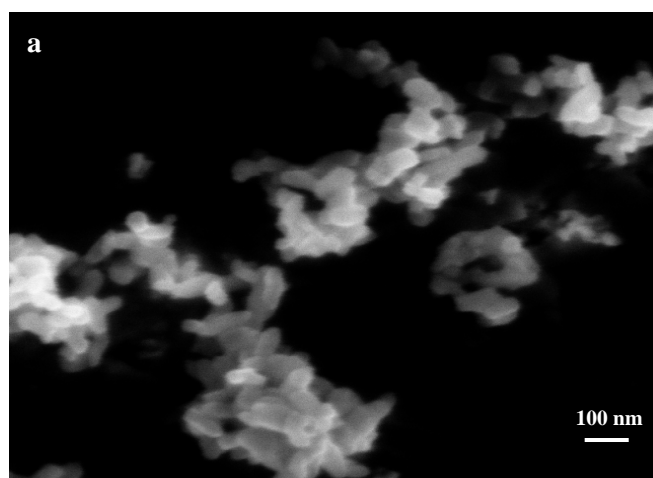


Figure 2. Effect of pH on the titania nanoparticles: (a) C400-1 prepared at pH 1(b) C400-3 prepared at pH 3(c) C400-5 prepared at pH 5.

Figure 3 presents the plots of methyl orange degradation by TiO₂ powder prepared at different pH under UV light irradiation. Most samples showed fast degradation within first 2 hours as more than 90% of MO degraded by sample C400-5, C400-7 and C400-9 while sample C400-3 and C400-1 show 79% reduction and 62% respectively. Based on these results, it is believed to be associated to good crystalline of anatase rather than the particle size. Thus, higher crystallinity of C400-9 could compensate its larger particles to perform faster photocatalytic process since it will lead to form more charge carriers at photocatalyst surface [18]. However, the low efficiency of photocatalytic activity of powder C400-1 is due to the facts that the presence of rutile in its XRD analysis. Maeda et al [19] also reported that anatase shows greater photocatalytic activity compared to rutile.

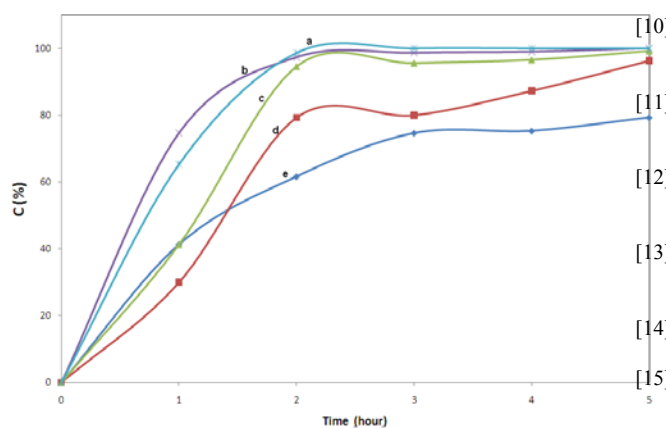


Figure 3. Comparison of the photocatalytic degradation of MO (%) in presence of titania powder of (a) C400-9, (b) C400-7, (c) C400-5, (d) C400-3 and (e) C400-1

IV. CONCLUSION

Crystalline titania has been prepared by sol gel using titanium (IV) isopropoxide and subsequently annealed at 400°C. It was observed that pH plays an important role towards the formation of TiO₂ structure. Lower acidity promotes anatase structure while higher acidity results in rutile phase. Degree of crystallinity of anatase is pH dependent and lower acidity enhanced the crystallinity also promotes formation of big crystallite size. Results of methyl orange degradation show the most efficient photocatalyst is the TiO₂ made at pH 9 with following characteristic as anatase and crystallite size of 8.4 nm.

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