



Synthesis and Characterization of Titanium Dioxide Nanoparticles under Different pH Conditions

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Abstract— Titanium dioxide solution was prepared by mixing of ethanol as a solvent, titanium isopropoxide as a precursor and hydrochloric acid and ammonium hydroxide as a stabilizer in synthesis aqueous solution. Both aqueous solutions with various pH and the resultant reaction morphology of the prepared of titanium dioxide nanoparticles were investigated. The influence of pH on the reaction morphology of using a titanium tetraisopropoxide was evaluated depending on the amounts of the catalysts. The X-ray diffraction exhibits rutile structures are more favorable to grow on titanium dioxide synthesis with an acidic solution even at very low temperature. Otherwise, basesolution of titanium dioxide tends to synthesize anatase phase at low and average temperatures. The scanning electron microscopy was used to observe the crystalline form and to re-confirm the crystallite size growth. The relation between roughness and thickness are correlated with the pH level were confirmed by atomic force microscopy.

Keywords: TiO₂ nanoparticle, hydrolysis, TTIP, pH

I. INTRODUCTION

Nanocrystalline metal oxides have gained a lot of attention because of their unique properties. One of the most important nanomaterials which have attracted a great attention due to its unique properties is titanium dioxide. Titania (TiO₂) powders possess interesting optical, dielectric, and catalytic properties, which leads to industrial applications such as pigments, fillers, catalyst supports, and photo-catalysts [1-5]. Titanium dioxide has various crystalline structures which are used in solar cells, air purifier catalysts, photovoltaic materials, gas and humidity sensors and antireflection coatings [6-8]. Titanium dioxide has 6 polymorphs of anatase, rutile, brookite, TiO2-B, TiO2-H and TiO2-II [9]. Among these polymorphs, rutile with tetragonal structure (space group p42/mmm), anatase with tetragonal structure (space group I41/amd) and brookite with orthorhombic structure (space group Pcab) are more important because of their higher stability and useful properties. Rutile, the only thermodynamically stable phase at normal pressure and room temperature, have a lower band gap energy (3 eV) in comparison with brookite and anatase phases (3.2 eV) which are metastable and can be transformed into rutile phase by calcination processing at 600-800°C [10,11].

It has been demonstrated that the final properties of this material depend on size, morphology and crystalline phase of the prepared TiO_2 nanopowder. In order to prepare for TiO_2 nanostructured material with significant properties several processes have been developed over the last decade and can be classified as liquid process (sol-gel) [12,13], solvothermal [14], hydrothermal [5,15], solid-state processing routes (mechanical alloying/milling)[16], mechano-chemical [17], thermal plasma [18] and other routes such as laser ablation [19]. From the above methods, the sol-gel method is normally used for the preparation of nanometer TiO₂ powder. There are several parameters for controlling sol-gel process to prepare TiO₂ nanopowder with significant properties. The peptization is a process in which the reaction can be carried out at the molecular level by heating the solution or using peptization agent has the same effect on the characteristics of the final powder which has been prepared by sol-gel method [20]. Also, the pH of the prepared solution has a great influence on the final size of TiO₂ nanoparticles [21]. Therefore, the controlled size and narrow size distribution of prepared powder can be obtained with the optimization of the preparation conditions. In this research work, we have tried to optimize preparation condition for providing a narrow size distribution of the nanometer TiO_2 powders by controlling the pH of the solution.

II.EXPERIMENTAL AND METHODS

II.1. Materials

All reagents used were of analytical grade purity. They were used as received, with no further purification, tetraisopropoxide (purity, 97 %), Ti $[OC_3H_7]_4$ was used as a starting material and supplied by Sigma-Aldrich company. Ammonium hydroxide $[NH_4OH]$ and hydrochloric acid [HCI]were supplied by High Media and ethanol was supplied by Merck. De-ionized water was used to prepare all standard solutions.

II.2. PREPARATION OF TiO₂NANOPARTICLES

In this work, the precursor solution was a mixture of 5 ml titanium isopropoxide, TTIP (97%, supplied by Aldrich Chemical) and 15 ml ethanol (99%, supplied by Merck). A 250 ml solution of distilled water with various pH was used as





the hydrolysis catalyst. The desired pH value of the solution was adjusted by adding HCl and NH₄OH. The gel preparation process started when both solutions were mixed together under vigorous stirring. Hydrolysis of TTIP offered a turbid solution which was heated up to 60-70 °C for almost 16 h (peptization). After peptization process, the volume of the solution decreases to 50 cm³ and a suspension was produced. The prepared precipitates were washed thrice with de-ionized water and then thrice with ethanol. The product was dried for 12 hours at 100°C in a drying box. Finally, the prepared powder was annealed at a temperature ranging from 200 to 700°C for 3 hours.

II.3. CHARACTERIZATION OF TiO2 NANOPARTICLES

The crystal phase composition and the crystallite size of the TiO_2 nanoparticles were recorded using X-ray diffraction (XRD) with a Rigaku D/max-RB diffractometer in reflection mode using Cu Ka radiation with a voltage of 40 kV. The morphology and structure of the particles were investigated using field emission scanning electron microscopy (SUPRA 55VP). The specific surface area (BET) was determined using Micromeritics ASAP 2020 Accelerated Surface Area & Porosimetry System.

III. RESULTS AND DISCUSSION

The preparation of the TiO_2 colloids in the nanometer range can be effectively conducted through the hydrolysis and condensation of titanium alkoxides in aqueous media. In the presence of water, alkoxides are hydrolyzed and subsequently polymerized to form a three-dimensional oxide network. These reactions can be schematically represented as follows:

Hydrolysis:

$$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH$$
(1)

Condensation:

$$\operatorname{Fi}(OH)_4 \to \operatorname{Ti}O_2 \cdot xH_2O + (2-x)H_2O \tag{2}$$

Where; R is ethyl, i-propyl, n-butyl, etc. It is well known that the tetravalent cations are too acidic so that the nucleation of the stable hydroxide $Ti(OH)_4$ cannot occur. Water molecules formed according to reaction (2) always bear a positive partial charge. Therefore, oxolation and olation can proceed simultaneously during nucleation and growth leading to an amorphous oxide $TiO_2 \cdot nH_2O$ where the number n of water molecules depends on the experimental conditions. Depending on the experimental procedure, the precipitation of TiO_2 leads to rutile or anatase phases. The stage of deoxilation prior to olation can be controlled by adjusting the pH and initial water concentration. This control leads to precipitation of anatase nanoparticles of TiO_2 in the experimental procedure.

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 particle size and degree of crystallinity. A trace of rutile was found in the

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. The results show high acidity favor formation of rutile. This mechanism may be explained using the concept of partial charge model [22].

According to this model, hydrolysis of titanium cation occurred at strong acidity condition. In this condition, a stable species of $[Ti(OH)(OH_2)_5]^{3+}$ 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 precursors, deprotonation will take place forming new species of $[Ti(OH)_2(OH_2)_5]^{2+}$. However, these species also do not condense probably because of spontaneous intramolecular oxolation to $[TiO(OH_2)_5]^{2+}$,[23]. Condensation to both anatase and rutile starts when the solution activity is sufficient enough to allow further deprotonation to $[TiO(OH)(OH_2)_4]^+$, which can undergo intramolecular of deoxolation [TiO(OH)₃(OH₂)₃]⁺ depending on 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 an apical direction and leads to the skewed chain of anatase structure. Therefore, based on this study, it is believed that the determination of resulting crystal structure is affected by pH values [22, 24]. The higher acidity promotes rutile formation and lower acidity will lead to anatase.

Figure 2 presents the XRD patterns of calcined TiO₂ powder at different temperatures 400, 500, 600 and 700°C respectively. The peaks of samples at 400 and 500°C were identified by comparison with JCPDS-84-1286 according to 20 which confirmed that an anatase structure at 20=25.4. It is noteworthy that the diffractograms of the samples do not present any peak assigned to rutile phase (20=27.36).

The average crystallite size of TiO_2 was estimated according to the Scherrer's equation:

$$D = K\lambda/\beta \cos\theta \tag{3}$$

K is the Scherer constant, λ , the X-ray wavelength, β , the peak width of half maximum, and θ is the Bragg diffraction angle. The content of anatase and rutile of all TiO₂ samples was calculated as:

$$X = 1/(1 + 0.8 \text{ IA/IR})$$
(4)

where,

X; weight fraction of rutile in the powders

IA; X-ray integrated intensity of the strongest peaks of anatase $(2\theta = 25.3^{\circ}, (101) \text{ plane})$

IR; X-ray integrated intensity of the strongest peaks of rutile $(2\theta = 27.5^{\circ}, (110) \text{ plane}).$





The anatase to rutile transformation is shown as a function of the temperature and pH level in Figure 3. It is noted that the temperature of the rutile ratio is shifted to a low temperature of 400-500 $^{\circ}$ C in strong acid. This is attributed to the high surface energy of the particles in strong acid. Therefore, the rutile ratio increases rapidly depending on the lower pH level as well as at higher temperatures, while increases slowly at the higher pH level. It is assumed that the anatase phase has been eliminated following large rutile particles with poor agglomeration, and aggregation takes place during the particle growth process at higher temperatures.



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 4, (d) pH 3 and (e) pH 1



Figure 2 XRD pattern of the TiO₂ powder at various calcining temperatures



Figure 3 Calculated rutile weight fractions of the TiO_2 powders as a function of pH.

Table 1 shows the formation of various phases for the TiO_2 powders as a function of pH and the calcination temperature (Am: amorphous, A: anatase, R: rutile). When the temperature was raised, the anatase phase was transformed to the rutile phase, which could be attributed to the thermally promoted crystallite growth. In particular, the phase transformation of amorphous $Ti(OH)_4$ to anatase TiO_2 and anatase to rutile were significantly activated by the HCl catalyst. On the other hand, the phase transformation and the crystallization of the particles were not activated by the NH₄OH catalyst. This reveals that nucleation and growth of the rutile phase have been initiated at temperatures somewhere from 400-700°C. It may be assumed that the growth of rutile crystallization was affected by the pH value of acid.

Figure 4 shows the crystalline size of as-prepared TiO_2 nanoparticles in the different pH. As it can be found from Fig. 3, the smallest crystallites have been obtained from the hydrolysis of TTIP in the acidic solution (pH 1) and the dried powder at 100 °C.

Table 1. Formation of various phases for the TiO_2 powders as a function of pH and calcination temperature.

nН	Dried (100)	Calcination Temperature, °C			
pn		400	500	600	700
9	Am*	А	A+R	A+R	A+R
7	Am	А	A+R	A+R	A+R
4	Am	А	А	A+R	A+R
3	Am	А	A	A+R	A+R



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	2	А	A+R	A+R	A+R	A+R
	1	А	A+R	A+R	A+R	A+R
*Am Amorphous A Anatase R Rutile						



Figure 4. Crystalline size variation of prepared powders at different pH.

The effect of calcination temperatures on the crystalline size of TiO₂ was shown in Figure 5. When the temperature has been raised to 200°C and then to 400°C, the size of formed crystallites has increased, which could be attributed to the thermally promoted crystallite growth. The size of anatase crystallites increases from 7.8 to 38.2 nm when calcination temperature has been elevated to 700°C. At 700°C, apart from anatase, sharp rutile peaks were also observed in the XRD result. The formed rutile showed quite different behavior having a larger size than the remained anatase particles. This, in fact, reveals that nucleation and growth of rutile phase would have been initiated at a temperature somewhere from 400 to 700°C [25].

Figures 6 and 7 show the SEM micrographs of TiO_2 particles prepared at different pH and calcined at 100°C temperatures. As shown in this figure the as-prepared powder in acidic solution (pH 1) consist of spherical particles with poor agglomeration and aggregation that takes place during the particle growth process at higher temperatures. On the other hand, the as-prepared powder in basic solution (pH 9) consists of non-spherical particles with high agglomeration.



Figure 4. Crystalline size variation of prepared powders at different temperatures.



Figure 6 SEM micrographs of dried powders at 100 °C:(pH=1)



Figure 7 SEM micrographs of dried powders at 100 °C: (pH=9)

The formation of the grain size and morphology were controlled by the nucleation and growth procedures of TiO_2 nanoparticles which is strongly related to the pH in TiO_2 synthesized solution. At pH 9, the crystallites are found to be sphere-shaped and relatively rough while a granular and elongated morphology starts to appear on the deposited TiO_2 with pH range (1 to 4). As shown in Figure 8(a) and (b), it was demonstrated that as the pH of the TiO_2 solutions decreases, it





improves the crystallinity of the films and decrease the crystallite size as obtained from XRD and SEM analysis.







Figure 8 The AFM images of TiO_2 with (a) pH=11, (b) pH=4 (c) pH=9

IV. CONCLUSIONS

The nanocrystalline TiO₂ powder can be prepared by the hydrolysis of the titanium isopropoxide alcoholic solution and then peptization of the resultant suspension up to 60-70 °C for 16 h. 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. The degree of crystallinity of anatase is pH dependent and

lower acidity enhanced the crystallinity also promotes the formation of big crystallite size.

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