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Synthesis of TiO_2 nanoparticles by hydrolysis and peptization of titanium isopropoxide solution

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Abstract

Titanium dioxide nanoparticles have been prepared by hydrolysis of titanium isopropoxide. Aqueous solution with various pH and peptizing the resultant suspension has been applied for preparation of the TiO_2 nanopowder with narrow size distribution. The influence of pH on the particle size and morphology of prepared powder has been evaluated. Synthesized powder is characterized by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Experimental results have shown that the as-prepared powders have entirely consisted with anatase crystalline phase. Only powder acquired from an acidic solution has fine particle size with spherical morphology. The anatase to rutile transformation occurred at temperatures lower than 600 °C.

Keywords: Hydrolysis; Peptization; Titanium isopropoxide; Crystallinity; TiO_2

1. Introduction

One of the most important nanomaterials which have attracted a great attention due to its unique properties is titanium dioxide. Titania (TiO_2) powders possess interesting optical, dielectric, and catalytic properties, which leads to industrial applications such as pigments, fillers, catalyst supports, and photo-catalysts [1–5].

It has been demonstrated that the final properties of this material depend to size, morphology and crystalline phase of the prepared TiO_2 nanopowder. In order to prepare of 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 [6–9], solvothermal [10,11], hydrothermal [5,12,13]), solid state processing routes (mechanical alloying/milling [14,15], mechanochemical [16,17]), RF thermal plasma [18] and other routes such as laser ablation [19]. From the above methods, the sol–gel method is normally used for preparation nanometer TiO_2 powder. Experimental results have shown that the prepared powders by uncontrolled sol–gel method generally lack the properties of uniform size, shape, and unagglomerated state and providing the titanium oxide with favour properties need to control process conditions. There are several parameters for controlling sol–gel process to prepare TiO_2 nanopowder with significant properties. It has been demonstrated that the precursor's concentration of titanium alkoxide greatly affects the crystallization behavior and characteristics of the final powder [20]. In addition, the size, stability, and morphology of the produced sol from alkoxides is strongly affected by the water titanium molar ratio ($r = [H_2O]/[Ti]$) [21,22]. The formation of colloidal TiO_2 at high r ratio is of great interest, because the small size of particles is formed under this condition. Also, the peptization process in which the reaction can be carried out at 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 [23–25]. Finally, the pH of prepared solution has a great influence on the final size of TiO_2 nanoparticles [26,27]. Therefore, the controlled size and narrow size distribution of prepared powder can be obtained with optimization the preparation conditions. In this research work, we have tried to optimize preparation condition for providing narrow size distribution of the nanometer TiO_2 powders by controlling the pH of the solution.

2. Experimental

In this work, the precursor solution was a mixture of 5 ml titanium isopropoxide, TTIP (97%, and supplied by Aldrich Chemical) and 15 ml isopropanol

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(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 HNO_3 or NH_4OH. The gel preparation process started when both solutions were mixed together under vigorous stirring. Hydrolysis of TTIP offered a turbid solution which heated up to 60–70 °C for almost 18–20 h (peptization). After peptization process, the volume of the solution decreases to 50 cm^3 and a suspension was produced. Depending on the preparation conditions, the resultant suspension was white-blue or opaque with high viscosity. The prepared precipitates were washed with ethanol and dried for several hours at 100 °C. After being washed with ethanol and dried at 100 °C in a vacuum system for 3 h, a yellow-white powder is obtained. Finally, the prepared powder was annealed at temperature ranging from 200 to 800 °C for 2 h.

Several techniques were employed for characterization of the powders. Powder X-ray diffraction (Philips PW 1800) was used to identify the crystal phase and to estimate the average crystallite size as well. The particle size and morphology of the powder were observed by Philips XL 30 scanning electron microscope (SEM) and Philips 200 transmission electron microscope (TEM).

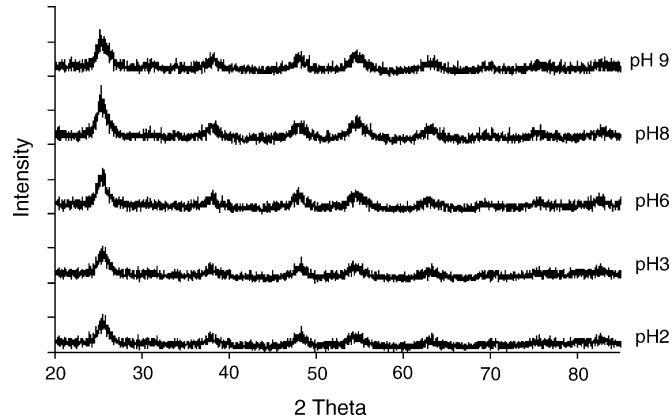

Fig. 1. XRD patterns for TiO_2 particles obtained from different pH solutions and dried at 100 °C for 3 h.

3. 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:

$$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH \quad \text{(hydrolysis)} \tag{I}$$

$$Ti(OH)_4 \rightarrow TiO_2 xH_2O + (2-x)H_2O \quad \text{(condensation)} \tag{II}$$

where R is ethyl, *i*-propyl, *n*-butyl, etc. [28]. It is well known that the tetravalent cations are too much acidic so that the nucleation of stable hydroxide $Ti(OH)_4$ cannot occur.

Water molecules formed according to reaction (II) always bear a positive partial charge [29]. Therefore, oxolation and olation can proceed simultaneously during nucleation and growth leading to amorphous hydrous oxide ($TiO_2{\cdot}nH_2O$) where the number n of water molecules depends on experimental conditions. Depending on the experimental procedure, the precipitation of TiO_2 lead to rutile or anatase phases [30,31]. The formation of such structures from aqueous molecular precursors can be described as follows. When deoxolation (O=Ti–OH_2 → HO–Ti–Ti–OH) dose not occur during nucleation olation lead to a linear growth along one of the two equivalent directions in the equatorial plan of $[Ti_2O_2(OH)_4(OH_2)_4]^0$ dimers. Then, oxolation between the resulting $TiO(OH)_2(OH)_2$ linear chains after an internal proton transfer leads to corner-sharing octahedral chains (Ti_3O bridges) characteristics of the rutile structure. The formation of rutile may then be associated to the metastability of apical Ti=O bonds within monomers or dimers. Now, if deoxolation occur prior to olation, condensation can proceed along apical direction leading to skewed chains typical of the anatase structure. Controlling the stage of deoxolation prior to olation can be obtained by adjusting the pH and initial water concentration. This control leads to precipitation of anatase nanopowder TiO_2 in the experimental procedure. Fig. 1 shows the XRD pattern of the prepared powder in the different pH. When the pH level of the solution is higher than 2, a white suspension of rough precipitant is formed immediately after hydrolysis reaction. Otherwise, when the pH level of the solution is 2, a homogenous suspension of fine particles is formed. The crystallite size of the particles has been estimated from the Debye–Scherrer's equation using the XRD line broadening as follows [32]:

$$B = \frac{k\lambda}{s\cos\theta} \tag{1}$$

where s is the crystallite size, λ the wavelength of the X-ray radiation (Cu Kα = 0.15406 nm), k a constant taken as 0.94, θ the diffraction angle and B is the line width at half maximum height. The (1 0 1) plane diffraction peak is used for anatase and (1 1 0) peak for rutile. Fig. 2 shows the crystalline size of as-prepared TiO_2 nanoparticles in the different pH. As it can be found from Fig. 2 the smallest crystallites have been obtained from the hydrolysis of TTIP in the acidic solution (pH 2) and the dried powder at 100 °C. Fig. 3, shows the XRD pattern of the prepared powder from acidic solution (pH 2) and calcined at various temperatures in atmospheric condition for 2 h. It can be found that all samples are crystalline and the dried powder at 100 °C has anatase phase. It shows that the control of deoxolation process by initial water concentration and peptization could accelerate the anatase crystallization and shift it to temperatures lower than even 100 °C. The temperature observed in our result is much lower than that achieved by others [33]. The effect of calcination temperatures on the crystalline size of TiO_2 was shown in Figs. 4 and 5. When the temperature has been

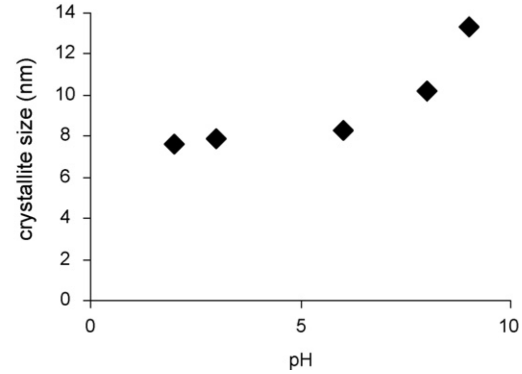

Fig. 2. Crystalline size variation of prepared powders at different pH.

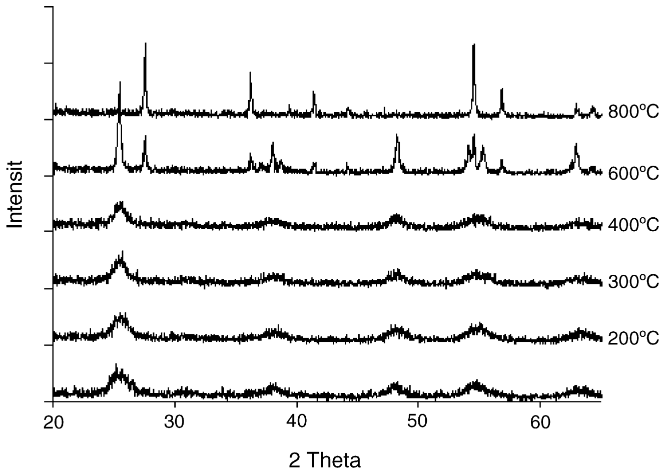

Fig. 3. XRD patterns of prepared powders at different calcination temperatures.

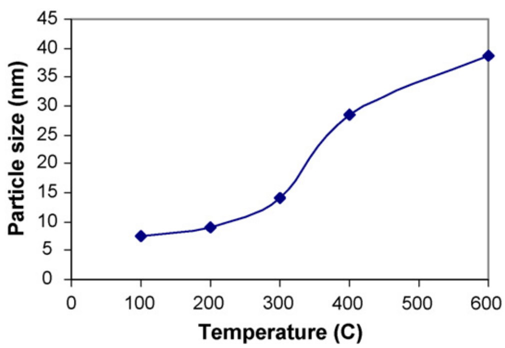

Fig. 4. Particle size variation via calcination temperatures.

raised to 200 and then 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 7.6 to 38.7 nm when calcination temperature has been elevated to 600 °C. At 600 °C, apart from anatase, sharp rutile peaks was also observed in the XRD result. The formed rutile showed quite different behavior having larger size than the remained anatase particles. This, in fact, reveals that nucleation and growth of rutile phase would have been initiated at temperature somewhere from 400 to 600 °C [34]. Anatase to rutile transformation temperature is shifted to the very low temperature level for nanosize crystallites because of the high surface energy of the particles.

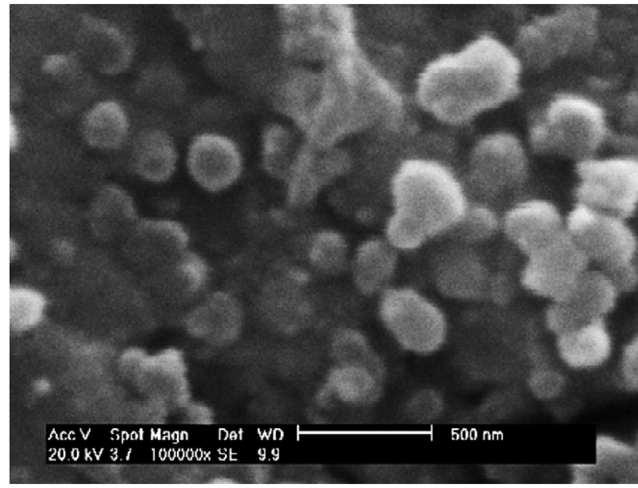

Fig. 6. SEM micrographs of powders prepared at 400 °C.

This temperature has been mostly reported from 600 to 900 °C for the initiation and finishing temperature respectively [32]. It is then possible to assume that the growth of rutile particle starts right after its nucleation. Furthermore, the rutile crystallite size is 47.5 nm at 600 °C, while it increases slightly to 53.4 nm when the temperature goes to 800 °C. At this temperature, anatase phase has been eliminated and there were only large rutile particles in the sample. Fig. 6 shows the SEM micrographs of TiO_2 particles prepared at different pH and calcined at 100 °C temperatures. As shown in Fig. 6, the as-prepared powder in acidic solution (pH 2) consist of spherical particles with poor agglomeration and aggregation 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 nonspherical particles with high agglomeration.

It is observed that, in the higher calcination temperatures, the larger particle size with spherical morphology is obtained. For the sample calcined at 400 °C (Fig. 7), the particle size is almost 100 nm. Shape and morphology is clearly observed in the SEM micrographs of the samples calcined at that temperature. From the SEM photographs of samples prepared under different pH values, it has been revealed that the spherical morphology was a specification of the prepared powder under acidic solution of pH 2 and it was not seen in other samples. The TEM image and the select-area electron diffraction (SAED) pattern

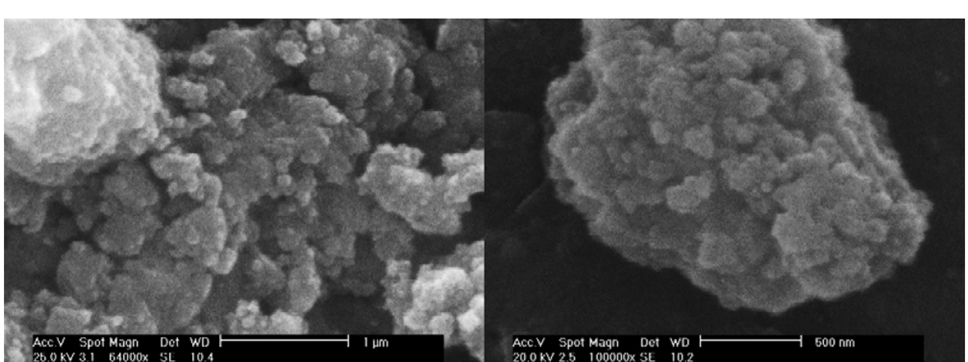

Fig. 5. SEM micrographs of dried powders at 100 °C: (a) pH 2; (b) pH 9.

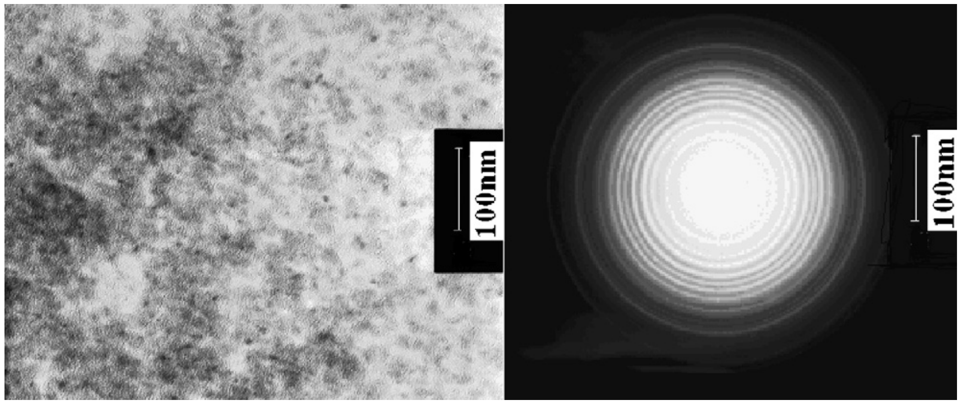

Fig. 7. (a) TEM and (b) SAED photograph of as- prepared sample dried at 100 °C for 3 h.

of the as-prepared sample are shown in Fig. 7(a and b), respectively. It is obviously shown that the as-prepared powder is completely crystalline and entirely consists of anatase phase. From the micrograph their diameter is estimated to be below 10 nm which is in good agreement with XRD results. In Fig. 7(b) the SARD pattern of as-prepared TiO_2 particles which is dried at 100 °C is shown. The first four rings are assigned to the (1 0 1), (0 0 4), (2 0 0), (0 0 5) reflections of the anatase phase. The SAED studies are in good agreement with XRD measurements.

4. Conclusion

Nanocrystalline TiO_2 powder can be prepared by the hydrolysis of titanium isopropoxide alcoholic solution and then peptization of the resultant suspension up to 60–70 °C for 18–20 h. According to the particle size obtained from Debye–Scherrer equation, the powder obtained from a solution at pH 2 consist of very fine anatase crystallites even at temperature lower than 100 °C. When the powder is treated thermally at 400 °C, the diameter of nanoparticles is approximately 28 nm and still consists of pure anatase phase. As the calcinations temperature is increased, the particle size increases. Rutile phase is formed at calcinations temperatures below 600 °C and grows slightly when heated up to 800 °C. Powder morphology in these criteria is almost spherical which is due to acidic condition that prevents agglomeration.

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