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Synthesis of Well-Dispersed TiO_2 Nanoparticles by a Sol-Hydrothermal Method†

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Phase pure anatase TiO_2 nanoparticles have been synthesized using a simple sol-hydrothermal method. The products were characterized by X-ray diffraction, Raman spectroscopy, transmission electron microscopy and ultraviolet-visible spectroscopy. The results showed that the TiO_2 particles were well-dispersed and the average size was limited in the range of 10 nm. The optical measurement displayed the obvious quantum-size effect of the products.

Key Words: TiO_2 nanoparticles, Sol-hydrothermal method, Quantum-size effect.

INTRODUCTION

Nowadays, nanostructured materials have attracted considerable attention due to their unusual electronic, optical, mechanical properties and potential applications. Among a large amount of nanomaterials, the nanostructured titania particles are of great interest for possible application to semiconductor photo-catalyst[1], catalyst support[2] and photoelectric conversion[3] because of their broadened absorption spectra, much larger efficient areas, quantum size effects and more efficient separation of photogenerated charges. The properties will be more superior if the titania has high surface area, fine particle size, high homogeneity and definite phase composition.

To date, some soft chemical methods have been developed to synthesize TiO_2 nanoparticles, such as sol-gel[4], precipitation/coprecipitation[5], cryochemical[6], hydrothermal[7], *etc*. In these methods, sol-gel technique is a conventional preparation method which could realize evenly mixed gelatin, while hydrothermal technique, in which reactions could take place under elevated pressure and temperature, is considered as a prospective method for the preparation of different classes of inorganic materials in a nanocrystalline state[8]. Some authors have reported the hydrothermal treatment of $TiO_2{\cdot}nH_2O$ amorphous gels[9-11], gel powders need to be gotten first and then treated during the process.

In this paper, a simple and direct sol-hydrothermal approach was used to synthesize phase pure anatase TiO_2 nanoparticles with homogeneous size and high disperse at low temperature. In comparison with the sol-gel-hydrothermal method, the need for getting gel powders first and the subsequent milling process are eliminated. Moreover, the appealing feature of this work lies that the structure of particles surface is determined during the synthesize process so that they are more difficult to agglomerate. The improved disperse is beneficial to the further application of TiO_2 nanoparticles. Some parameters (time, temperature and pH value) of the hydrothermal conditions were studied in detail.

EXPERIMENTAL

All chemicals were analytic grade and were used without further purification. Fig. 1 illustrates a typical flowchart of our sol-hydrothermal route for synthesizing TiO_2 powders.

General procedure: Titanium(IV) *n*-butoxide $[Ti(OBu)_4]$ and acetyl acetone (ACA) (molar ratio is 1:1), cetyl trimethylammonium bromide (CTAB) and H_2O (molar ratio is 1:25) were blended separately and were stirred for 15 min at room temperature, thereinto, $[H_2O]/[Ti] = 140$. Then, mingling the two kinds of mixture (the pH value was respectively kept at 2, 4, 6, 8 and 10 by H_2SO_4 or $NH_3{\cdot}H_2O$) and stirring at 40 ºC for 2 h, consequently, a sol was obtained.

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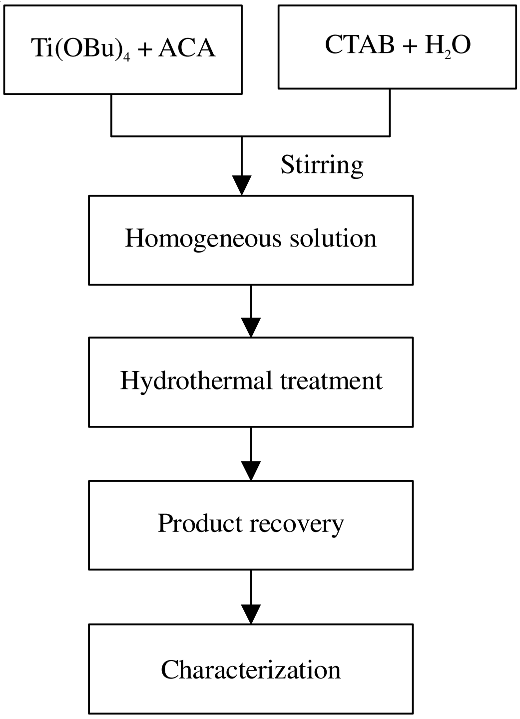

Fig. 1. Flowchart for the synthesis of TiO$_2$ nanoparticles by sol-hydrothermal method

The sol was then transferred to a 50 mL Teflon-lined autoclave. The autoclave was sealed and heated under auto-generated pressure at different temperature, pH value and reaction time. The as-formed solid precipitate was centrifuged, washed with ethanol and distilled water and then dried at 100 ºC for 2 h to give the product.

Detection method: The structure of the products was examined by X-ray diffractometry (XRD, Japan Rigaku D/Max-3C) using CuK$_\alpha$ radiation (λ = 1.5405 Å). The morphology and the particle size of the samples were investigated by transmission electron microscopy (TEM, Model Hitachi H-700H, 200 KV). Raman spectra were collected in backscattering geometry at room temperature using a Spex 1403 double-grating monochrometer with a C31034 photomultiplier tube. The source for excitation was argon laser lines with 488.0 nm and instrument resolution was 2 cm^{-1}. Optical absorption studies were carried out using a UV-Vis-NIR spectrophotometer (Shimadzu UV-3101PC).

RESULTS AND DISCUSSION

Fig. 2 displays the XRD patterns of TiO$_2$ particles synthesized at different temperature. In this experiment, the sol precursor is treated at 140, 160 and 180 ºC when the reaction time is fixed on 2 h and pH = 6. These XRD patterns reflect the crystallinity and size variation during the process. When the reaction temperature is 140 ºC, the intensity of peaks is weak and the full width of half maximum intensity (FWHM) is wide, indicating that the size is small. With an increase in temperature, the intensity of peaks becomes stronger and the FWHM decreases, which indicates that the crystallinity becomes higher and the size becomes larger accordingly. According to the Scherrer formula, the particles size is 4.13, 4.81 and 4.82 nm for the sample synthesized at 140, 160 and 180 ºC, respectively. There is no obvious difference between the consequences of 160 and 180 ºC, though a clear improvement can be seen relative to the consequence of 140 ºC. There is no question that a higher temperature is helpful to the growth of particles, but the process is not only a thermodynamic one. From the opinion of economics or energy sources, 160 ºC is considered as the optimal temperature.

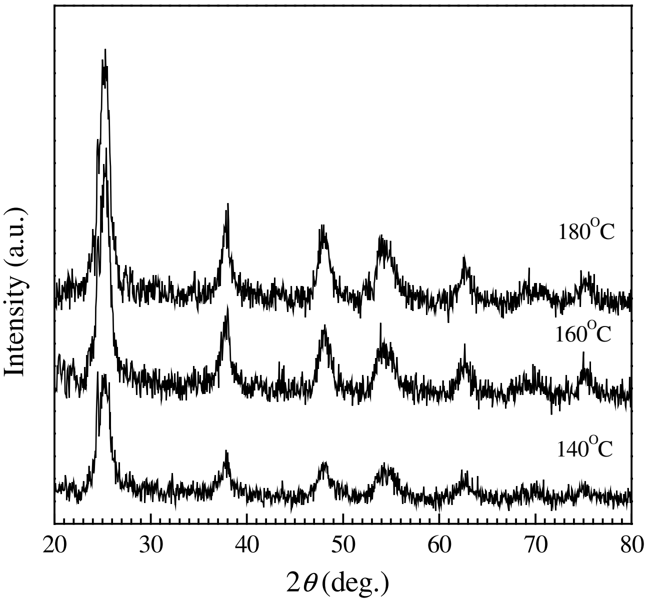

Fig. 2. XRD patterns of samples synthesized at pH = 6 for 2 h at different temperature

Fig. 3 displays the XRD patterns of TiO$_2$ particles synthesized at different reaction time. In this experiment, the sol precursor was treated at pH = 6 and 160 ºC for 2-24 h. According to the Scherrer formula, when 2, 6, 12 and 24 h are chosen as the reaction time, the size of as-synthesized particles is 4.81, 5.71, 6.38 and 6.39 nm, respectively. The above results indicate that when the reaction temperature is fixed at 160 ºC, the reaction time plays an important role in determining the size of products. When the time was prolonged from 2 to 12 h, the size increased accordingly but the increasing speed became

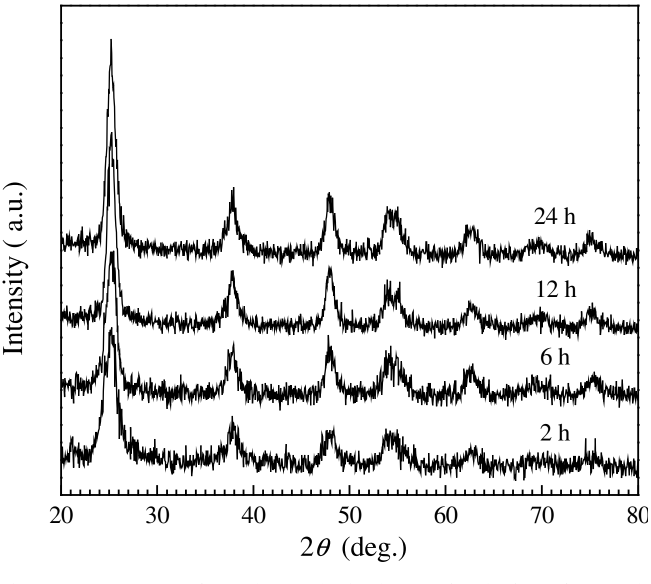

Fig. 3. XRD patterns of samples synthesized at pH 6 and 160 ºC for 2-24 h

slower gradually. When the time was further prolonged from 12 h to 24 h, there was nearly no change in size, so it is nearly impossible to get a much larger size by prolonging the reaction time infinitely. We have also investigated the effect of the reaction time on the size of the resulting products at the temperatures of 140 and 180 ºC and obtained the similar results. It is suggested that, in this study, the formation of TiO_2 can be attributed to a process that is controlled by kinetics.

Fig. 4 shows the XRD patterns of TiO_2 particles synthesized at different pH value. In this experiment, the reaction time was fixed on 2 h and temperature was fixed on 160 ºC. According to the Scherrer formula, for pH = 2, 4, 6, 8, 10, the particles size is 4.14, 4.45, 4.81, 5.71 and 7.16 nm, respectively. It is obvious that the particle size became larger accordingly with the increasing of the pH value and the increasing speed became faster in alkaline atmosphere. It is known that the size of the particles depend on the nucleation rate and the growth rate. If the nucleation rate is faster than the growth rate, the size is small and if the nucleation rate is slower than the growth rate, the size is large. With the increasing of pH value, the absorption of hydroxide ion the embryos of TiO_2 led to the reduction of the concentration of a precursor complex, $Ti(OH)_3^+$, which resulted in a significant reduction of the nucleation rate, thus forming some large-size particles[12].

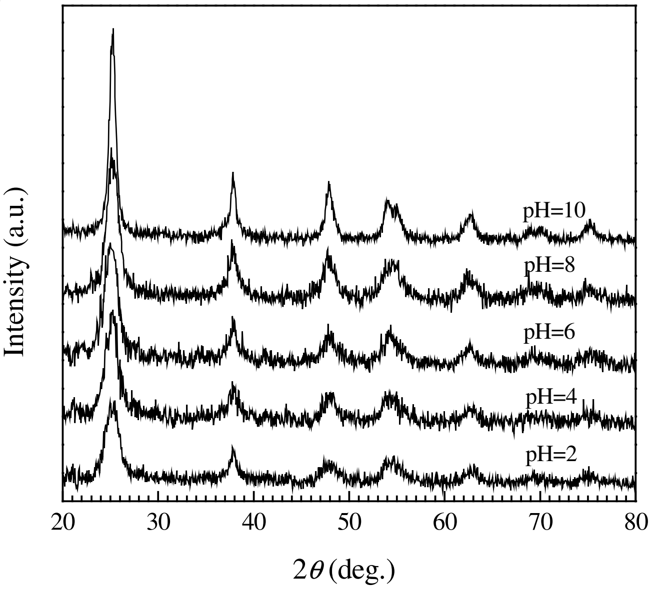

Fig. 4. XRD patterns of samples synthesized at160 ºC for 2 h at different pH value

It can been seen from the above results, the particles size is always limited to the range of 10 nm in this study no matter how to change the reaction parameters, it may be due to the existence of CTAB. Particle formation is a very complex process. It involves nucleation, growth, coagulation and flocculation, all of which may be influenced significantly by the surfactant assemblies[13]. The addition of surfactant CTAB can effect the nucleation, particle growth, coagulation and flocculation of the particles. It is considered that the existence of CTAB may afford a confined environment for the growth of nanoparticles. The surfactant adhered to the surface of nanoparticles served as a protective layer to prevent from collision and amalgamation of the particles. Therefore, CTAB plays an important role in modulating and confining the particle size of TiO_2. Further work will devote to investigate the effect of CTAB on the size of TiO_2 in detail.

All the data about the size of particles from the results of XRD patterns are consistent with the results deduced from the TEM images. Fig. 5 gives the TEM image of the product synthesized at 160 ºC and pH = 6 for 2 h. In this situation, the size of products is calculated as 4.81 nm according to the Scherrer formula. It is clear from the figure, the product has simple particle-shape and is well dispersed. The high disperse is beneficial to the further application of TiO_2 nanoparticles.

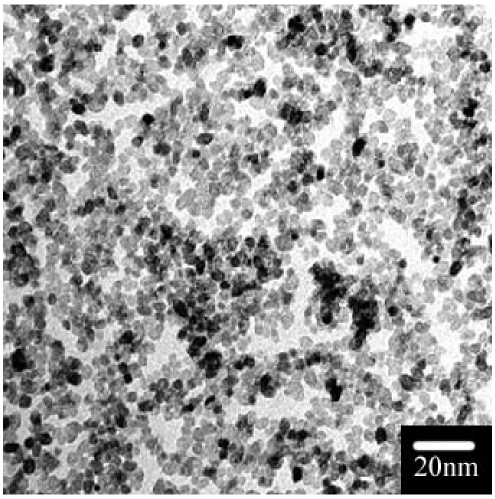

Fig. 5. Typical TEM image of sample synthesized at 160 ºC, pH = 6 for 2 h

Fig. 6 shows Raman spectra of the powders synthesized at different pH value and a fixed temperature of 160 ºC for 2 h. The Raman spectrum for anatase has been investigated[14] to show the six characteristic bands at 144, 197, 399, 513, 519 and 639 cm^{-1}. In the figure, five bands which are characteristic of anatase-type of TiO_2 appeared and no other bands are found.

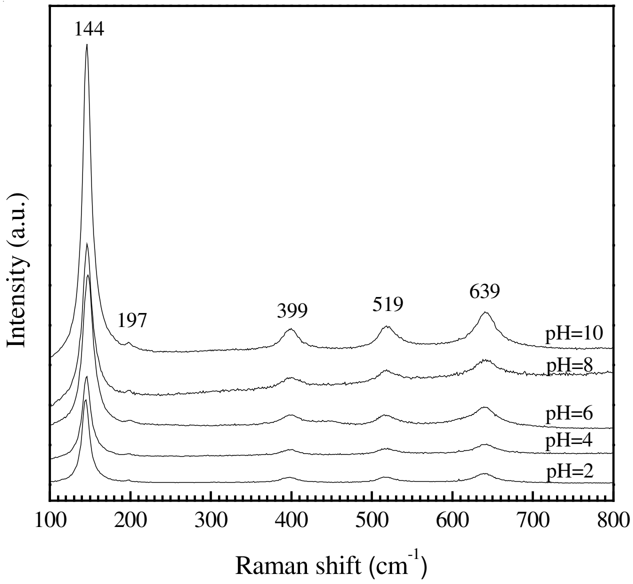

Fig. 6. Raman spectra of samples synthesized at 160 ºC for 2 h at different pH value

All of the acid atmospheres are adjusted by controlling the quantity of sulfuric acid. It is known that the coordinated complex consist of SO_4^{2-} and Ti^{4+} may replace partially the $Ti(OH)_4$ ligand, thus forming some kind of lower symmetry coordination ion which is proportionate to the forming of anatase-type TiO_2. Some work have reported that the brookite-type TiO_2 was synthesized in a weak alkaline atmosphere[15], in this work (XRD shown in Fig. 4 and Raman shown in Fig. 5), the brookite-type TiO_2 did not appear in alkaline atmosphere.

UV-Vis spectroscopy has been utilized to characterize the optical quality of the as-synthesized TiO_2. Fig. 7 gives the UV-Vis spectra of the samples, curve A shows the absorbance of the largest particle (7.16 nm) in present samples and curve B shows the smallest (4.13 nm). The position of the absorption edge for anatase-type TiO_2 bulk corresponds to its known bandgap energy of 3.2 eV (393 nm). It is also observed in the spectra that the absorption edge of as-synthesized TiO_2 nanoparticles are blue-shifted obviously, sample A by about 16 nm in comparison with bulk TiO_2 and sample B by 25 nm. According to their absorption edge 377 and 368 nm, their bandgap energy can be calculated as 3.29 and 3.37 eV. It is clear that with the decreasing of particles size, the bandgap of anatase-type TiO_2 becomes wider and the blue shifting becomes more obvious. It is the typical appearance of the quantum-size effect of nano-semiconductor.

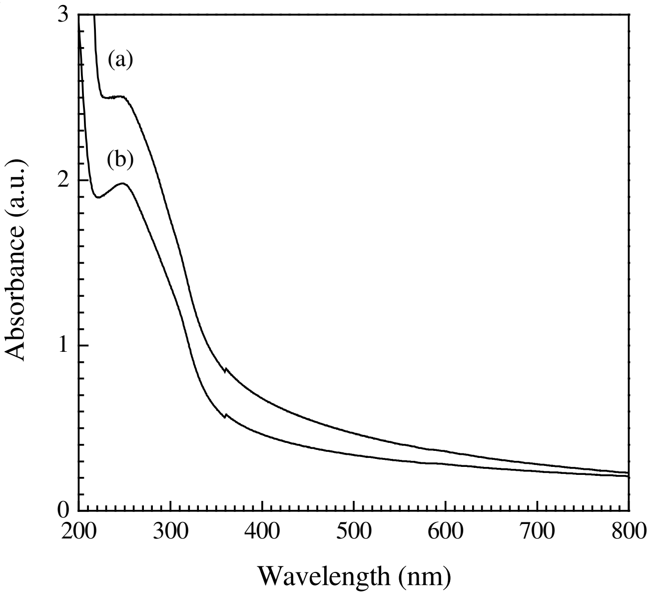

Fig. 7. Uv-vis spectra of sample (A) with the size of 7.16 nm and (B) 4.13 nm

Conclusion

In this study, we have fabricated phase pure anatase TiO_2 nanoparticles with homogeneous size and high disperse through a simple sol-hydrothermal approach at low temperature. Some reaction parameters, such as temperature, time and pH value are discussed. With the increasing of temperature, time or pH value, the size of particles becomes larger, but they are all limited in the range of 10 nm. In UV-Vis spectra, an obvious blue-shifting can be observed.

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