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Synthesis of nanosized TiO_2 powder by Sol-Gel method in acidic conditions

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Abstract

The preparation of nano-sized TiO_2 by titanium tetraisopropoxide ($Ti(O\textit{i}Pr)_4$) via sol-gel method using acid as a catalyst is investigated and the optimized conditions concerning the proportional amount of acid, water, alcohol is established by XRD and SEM. The effect of calcination temperature on phase transformation of TiO_2 (rutile, anatase and brookite) was determined by XRD. The smallest grain size of TiO_2 powder we have obtained is 25 nm for anatase at 400 ºC by controlling the acidity and the mole ratio of starting materials.

Keywords: Titania; Sol-Gel; Rutile; Anatase; X-ray diffraction (XRD)

1. Introduction

It is well known that titanium dioxide has three crystalline forms of brookite, anatase and rutile. Among these crystalline forms, rutile phase is the most thermodynamically stable, whereas brookite and anatase are metastable and transformed to rutile on heating [1]. Various synthesis methods such as sol-gel [2, 3], microemulsion or reverse micelles [4], and hydrothermal synthesis [5] have been used to prepare nanoparticles of titanium dioxide. Compared to other methods, sol-gel route is regarded as a good method to synthesis ultra-fine metallic oxide [6] and has been widely employed for preparing titanium dioxide particles [7]. In sol-gel synthesis, two simultaneous reactions (hydrolysis and condensation) take place when organometallic precursors react with water. These two reactions are sensitive to many experimental parameters such as raw material concentration, pH, hydrolysis temperature and mixing conditions [8].

The formation of the anatase and rutile phases is predominating determined by the pH and Ti concentration of the solutions [9]. Morals et al., investigated the effect of hydrolysis catalyst on crystallite size of titanium dioxide prepared by the sol-gel method. When no hydrolysis catalyst or HCl catalyst was used, the fresh samples prepared at 70°C were composed of anatase having crystalline size of 5 nm. After calcinations of titanium dioxide powders at 300°C, anatase partially transferred into rutile, but brookite did not change. When the sample was calcined at 600°C, most of anatase and brookite particles transferred into rutile [10].

In this paper, titanium dioxide nano-powders were prepared by the hydrolysis of titanium tetraisopropoxide by sol-gel method in acidic condition.

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2. Experimental

TiO_2 nano-powders were prepared via sol–gel method using titanium tetraisopropoxide (TTIP, Merck), distilled water, ethyl alcohol (EtOH, Merck) and hydrochloric acid (HCl, Merck) as the starting materials. Concentrations (the volume ratio of TTIP: EtOH: H_2O: HCl) were chosen as 1:15:60:0.2 (1), 1:15:90:0.2 (2), 1:15:120:0.2 (3) and 1:15:60:0.4 (4). Titanium tetraisopropoxide was dropped slowly into the solution of water, alcohol and acid while magnetic agitating continuously to get white slurry solution. The obtained solutions were kept under slow-speed constant stirring on a magnetic stirrer for 48 h at room temperature. Then the precipitated TiO_2 was filtered and dried at 50ºC for 2 h until it was turned into white block crystal. After ball milling the dried powders obtained were calcinated at 400 and 900 ºC for 3 h to observe the phase changes accompanying the heat treatments.

Powder X-ray diffraction (XRD) was used for identification of crystalline phases and estimation of the crystallite size. The X-ray diffraction (XRD) patterns were performed on a Seimens/D5000 X-ray diffractometer. From the line broadening of corresponding X-ray diffraction peaks and using the Scherrer formula the crystallite size, L has been estimated [11].

$$L = K\lambda / (\beta \cos \theta)$$

where λ is the wavelength of the X-ray radiation (Cu Kα = 0.15406 nm), K is a constant taken as 0.89, β is the line width at half maximum height, and θ is the diffracting angle. The surface morphology of the calcinated powders at 400ºC was observed on a Philips XL30 scanning electron microscopy (SEM).

3. Results and discussion

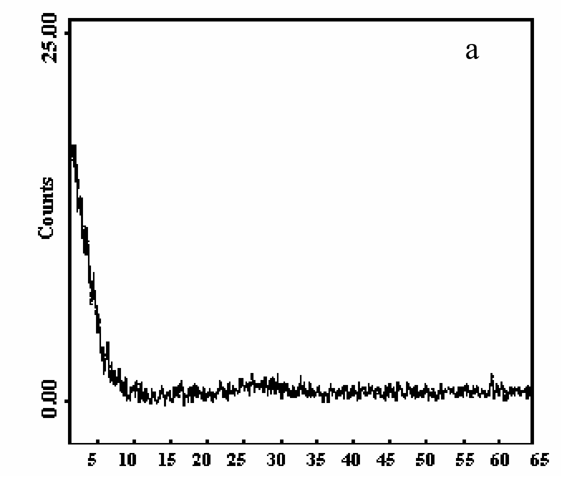
3.1. Calcination temperature

XRD patterns of dried samples of 1, 2 and 3 at 50 ºC were largly amorphous (Fig. 1-a), while the dried sample of 4 at 50 ºC was mainly brookite (Fig. 1-b). XRD patterns of TiO_2 powders calcinated at 400ºC and 900ºC are shown in Figs. 2 and 3. Calcination is a common treatment used to improve the crystallinity of TiO_2 powders. It can be obviously seen from Fig. 2a, in the case of samples 1, 2 and 3, the phase transformation from amorphous to anatase occurred at about 400ºC, while in the case of sample 4 anatase, brookite and traces of rutile were distinguished at Fig. 2b. The phase transformation from anatase to rutile completed at 900ºC as is evident from the Fig. 3.

The crystalline size was estimated by the Scherrer formula, which is generally the accepted method to estimate the mean crystallite size. The crystallite sizes were found to be in nanometer regime (Table 1).

Table 1
Average particle size of obtained nano-TiO_2 powders.

Sample No.	400 °C	900 °C
1	25 nm	65 nm
2	40 nm	107 nm
3	35 nm	103 nm
4	50 nm	90 nm



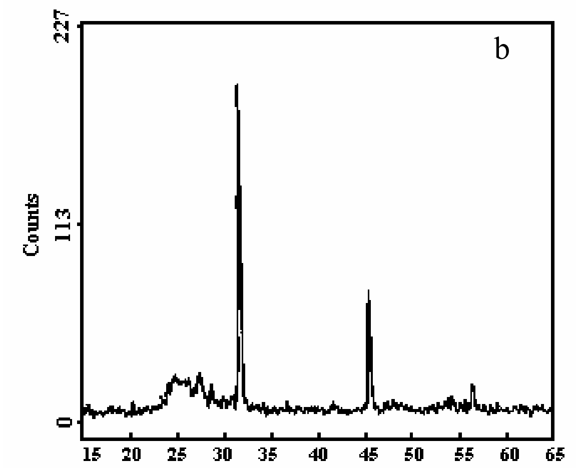
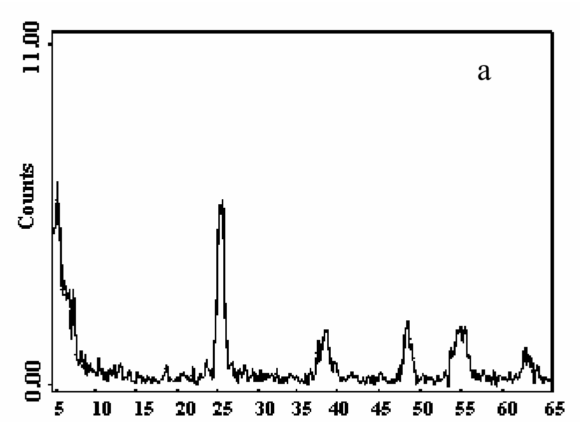


Fig. 1. XRD patterns of titania particles dried at 50°C (a) samples 1,2,3 (b) sample 4.



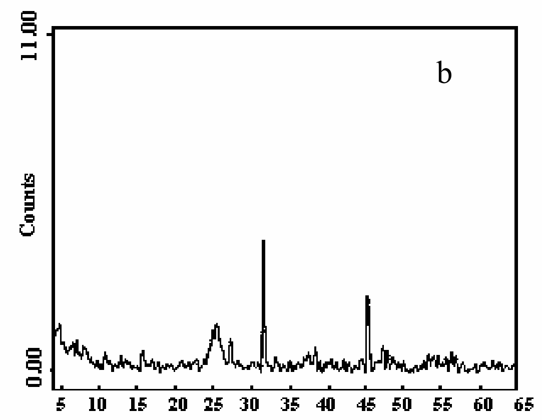


Fig. 2. XRD patterns of titania particles calcined at 400°C (a) samples 1,2,3 (b) sample 4.

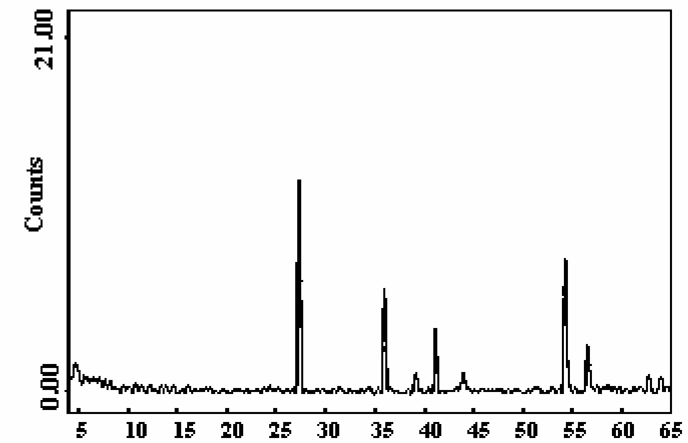


Fig. 3. XRD pattern of titania particles calcined at 900°C samples 1,2,3,4.

3.2. The effect of starting material mole ratio

The morphology of calcinated titania powders at 400 ºC observed by SEM is shown in Fig. 4. Significant differences are observed when comparing the microphotographs (Fig. 4a–d). As shown in Figure 4a, at mole ratio of TTIP(1): EtOH(15): H_2O(60): HCl(0.2), the size of titania particles was about 25 nm and non hard-grained aggregates that are constituted of sharp faceted nanoscaled crystals were formed.

However, when the mole ratio was changed to TTIP(1): EtOH(15): H_2O(90): HCl(0.2) and TTIP(1): EtOH(15): H_2O(120): HCl(0.2), the size increased to about 35- 40 nm (Fig. 4b and 4c).It seems that the increased mole ratio of H_2O affects on the size of particles. Also, the morphology was changed to non hard-grained aggregates that are constituted of nearly spherical nanoscaled particles. SEM micrograph of titania prepared at the mole ratio of TTIP(1): EtOH(15): H_2O(60): HCl(0.4) is shown in Fig. 4d. The sizes of particles were larger to about 50 nm and the morphology is changed to hard-grained aggregates and nearly spherical nanoparticles.

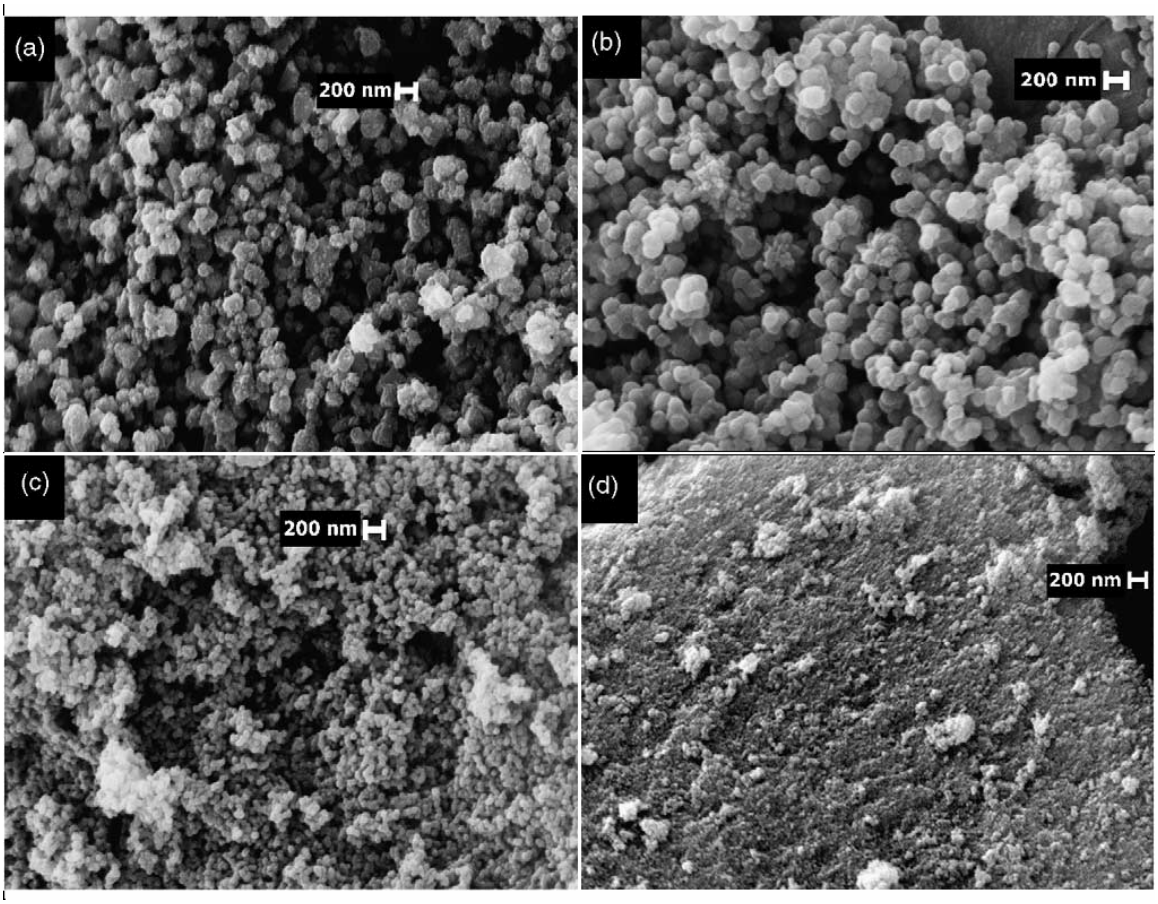


Fig. 4. SEM images of surface morphology of calcinated titania powder at 400 ºC at different mole ratio of starting materials (TTIP:EtOH:H_2O:HCl): (a) 1:15:60:0.2, (b) 1:15:90: 0.2, (c) 1:15:120:0.2 and (d) 1:15:60:0.4.

4. Conclusion

Nano-TiO_2 powders have been prepared by sol-gel method in acidic solution successfully. By controlling the conditions properly, nano-TiO_2 powders of anatase form with the grain size of 25 nm could be obtained. Among the factors which may have effect upon the grain size of nano-TiO_2 powders, the mole ratio of starting materials and calcination temperatures were highly predominant. The grain size increase with increasing the calcination temperatures and the phase transformation of nano-TiO_2 from anatase to rutile completely occurred at 900 ºC. The mole ratio of starting materials chosen for sample 1 gave out very fine and uniform nano- TiO_2 particles. By controlling the acidity and the mole ratio of starting materials, a nanosize particles of 25 nm can be obtained for anatase at 400 ºC.

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