Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2008, Article ID 245981, 4 pages
doi:10.1155/2008/245981

Research Article

Synthesis of High-Thermal Stable Titanium Dioxide Nanoparticles

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Received 7 April 2008; Accepted 11 August 2008

Recommended by J. Yu

Nanosized crystals of anatase phase TiO_2 with high-thermal stability was synthesized in the range of 15–17 nm via sol-gel method using titanium n-butoxide precursor. Synthesize was done at two different temperatures, that is, 200 and 300°C and the final products were calcined at 400°C. The final products were characterized by N_2 adsorption, X-ray diffraction, FT-IR, and TEM and tested in a photoreactor using fluorescien as model molecule. For thermal stability investigation, the sample prepared at 300°C was heated up to 800, 850, and 900°C, the XRD results showed that the synthesized anatase phase was stable up to 850°C. Photocatalytic activity of the prepared samples showed that the fluorescien degradation followed a pseudo-first-order kinetic.

1. INTRODUCTION

TiO_2 crystals exist in three different crystalline forms: anatase, brookite, and rutile. Anatase is metastable and rutile is considered to be the stable form of titania. Among these polymorphs, anatse has attracted more attention for its use as photocatalyst and catalyst support in industrial processes [1–5]. Generally, large surface areas are required for catalyst supports to disperse a catalyst-active material effectively to increase the number of active sites. Since the catalyst is usually used at high temperature, high-thermal stability, as well as large surface area is also important. Meanwhile, the synthesis of TiO_2-photocatalyst with high-thermal stable anatase phase is one of the key challenges in smart coating for building materials application [6–8]. Photocatalytic activity and also catalytic properties of titania varies depending on its crystallinity, particle size, crystal phase, and surface area [2, 5, 9, 10]. Nanosized TiO_2 powders are prepared by several methods such as hydrothermal, sol-gel, microemulsion, and thermal decomposition of alkoxides [11–15]. Hydrothermal synthesis is a promising method to obtain nanocrystalline titania particles. The hydrothermal process in which the chemical reaction take place under autogenerated pressure upon heating is sufficient to achieve the crystalline phase at relatively low temperature [16]. In this work, titania photocatalyst with high performance and high-thermal stability was prepared via sol-gel method followed by hydrothermal process. The photocatalytic activity, thermal stability, and degradation kinetics on a model dye, Fluorescein, of synthesized samples as well as commercial sample were investigated.

2. EXPERIMENTAL

All reagents used in this study were analytical grade. Degussa P25 sample, TiO_2 (S_{BET}: 54 m^2/gr, particle size: 29 nm) was used as reference. 21 mmol of titanium n-butoxide (TNB) was dissolved in specified amount of toluene in a glass tube, which was placed in a stainless Teflon-lined autoclave. Eight mL of deionized water was added outside the glass tube in the autoclave. The autoclave was then heated up the reaction temperature (i.e., 200 and 300°C) and held at that temperature for 8 hours. During the heating, water was vaporized and TNB was hydrolyzed. After the autoclave was cooled to ambient temperature, the supernatant was decanted and the resulting precipitates were washed with acetone and dried at room temperature. Finally, the dried samples calcined at 400°C for 3 hours. A part of samples were further heated at 800, 850, and 900°C and held at these temperatures for 3 hours.

2.1. Characterization

The surface area of the samples was determined by nitrogen adsorption using a quantasorb analyzer. Infrared spectra of samples were recorded on a Bruker spectrometer IFS-88. The concentration of Fluorescein in all aqueous solutions was analyzed using a UV-Vis. DU-500 spectrophotometer. Morphology and the size of TiO_2 nanocrystallites were studied and analyzed by TEM with a CM200, FEG-Philips. X-ray diffractometer type Philips PW 1840 ($\lambda = 1.54060$ Å at 40 kv and 20 mA) was used to identify the crystalline phase and also crystal size, using the Scherrer method (4).

Scherrer equation is as follows:

$$D = \frac{K\lambda}{B\cos\theta} \quad (1)$$

where K was taken as 0.9 and B is the full width of the diffraction line at half of the maximum intensity.

2.2. Photocatalytic activity

The photocatalytic activity of the samples was estimated by decomposition of 90 ppm Fluorescein solution by using a 50–100 ppm of photocatalyst. The photoreactor consisted of cylindrical glass reactor that a light source from a 6 W Hg Philips lamp located axially at the center of the vessel. A special glass atomizer as air diffuser was fixed at the bottom of the reactor to uniformly disperse air into the above reaction mixture. A magnetic stirrer was used to produce homogeneous reaction mixture. Degradation was monitored by taking aliquots at different time intervals. These aliquots were filtered and UV-vis absorption spectra of the samples were recorded at $\lambda_{max} = 490$ nm.

3. RESULTS AND DISCUSSION

The FT-IR spectra of the titania samples hydrothermally synthesized at various temperatures showed strong bands at 3403 and 1631 cm^{-1} which are related to the stretching mode of the OH group and the bending mode of molecular water, respectively (Figures 1(a) and 1(b)).

The absorption of these bonds decreased with an increase in the synthesize temperature, which indicates that surface hydroxyl groups enable the condensation under hydrothermal condition. The broadband over the range of 400–700 cm^{-1}, related to bending and stretching mode of Ti–O–Ti and characteristic of well-ordered TiO_6 octahedrons [17]. There is no peak at 2900 cm^{-1} regarding to C–H stretching band, which means all organic compounds removed from the samples after calcination at 400°C. The XRD patterns of prepared samples and P25 obtained by calcination at different temperature are shown in Figures 2–4. It can be seen from Figure 2(a) that all diffraction peaks can be assigned to pure anatase phase. Comparison of two XRD patterns in Figures 2(a) and 2(b) shows that the diffraction peaks sharpened with increasing hydrothermal sharpened with increasing hydrothermal temperature, indicating increasing crystallite size. The average crystal sizes of the samples calculated using the Scherrer equation, where

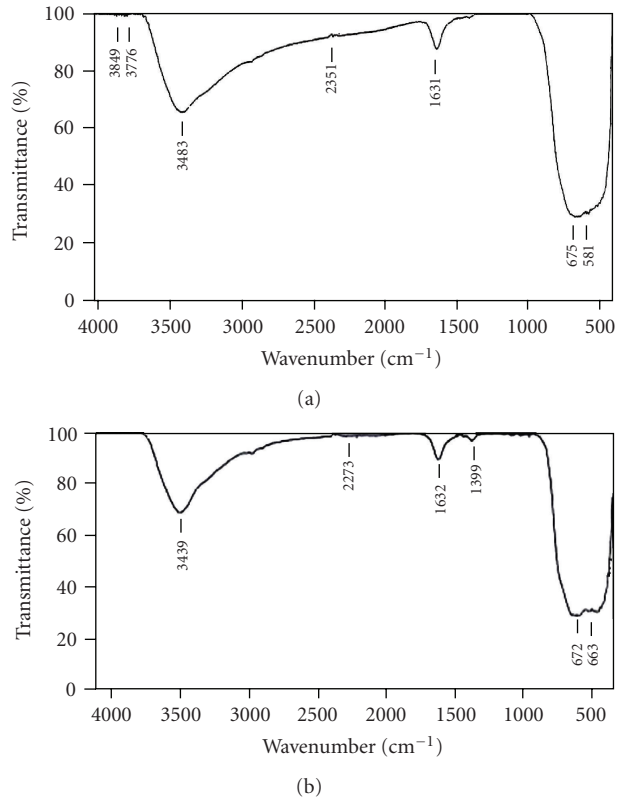


Figure 1: FT-IR spectra of titania powders prepared at (a) 200°C and (b) 300°C.

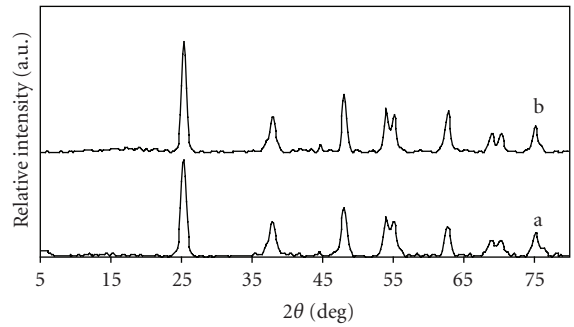
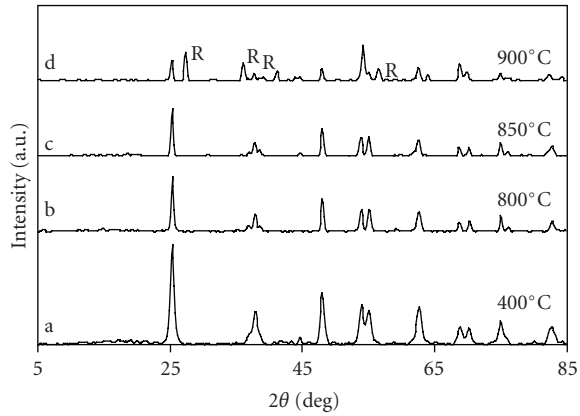


Figure 2: XRD patterns of the samples prepared at (a) 200°C and (b) 300°C.

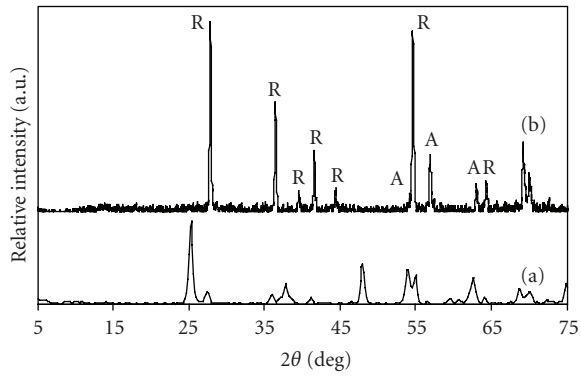
15 nm, 17 nm, and 19 nm for sample prepared at 200°C, 300°C, and P25, respectively, whereas the result showed that the crystal size increased with increasing the synthesize temperature. For thermal stability investigation, the sample synthesized at 300°C was calcined at 800, 850, and 900°C. Their XRD patterns show that anatase phase was stable until 850°C and only after this temperature, transformation to rutile had occurred (Figures 3 and 4).

P25 sample received from Degussa had transformed to rutile at 800°C. It is reported that the transformation from anatase to other crystalline phase, that is, rutile occurred at 600–700°C [18, 19].



R: Rutile

Figure 3: XRD patterns of TiO_2 prepared at 300°C and calcined at different temperature.



A: Anatase
R: Rutile

Figure 4: XRD patterns of (a) P-25 Degussa and (b) P-25 Degussa calcined at 800°C.

TEM image of the titania sample hydrothermally synthesized at 300°C is presented in Figure 5. The average particle size of nanocrystallites was 15 nm, which agrees with that obtained by the XRD analysis. BET surface area of samples prepared at 200 and 300°C were 114 and 78 m^2/gr, respectively. The BET equivalent particle diameter was calculated as $d_{BET} = 6/(\rho_{TiO_2} \times S_{BET})$, where ρ_{TiO_2} is the weighted density of the particles ($\rho_{TiO_2} = 3.84\,g/cm^3$). It was 14 and 20 nm for samples prepared at 200 and 300°C, respectively.

3.1. Photocatalytic studies

The photocatalytic activity of hydrothermally synthesized nano-TiO_2 at 300°C as well as commercial sample was examined by degradation of Fluorescein dye. Concentrations change during degradation at different irradiation time with different amounts of photocatalyst is shown in Figure 6. The photoactivity was increased by increasing the TiO_2 amount in slurry. The conversion of Fluorescein after 8

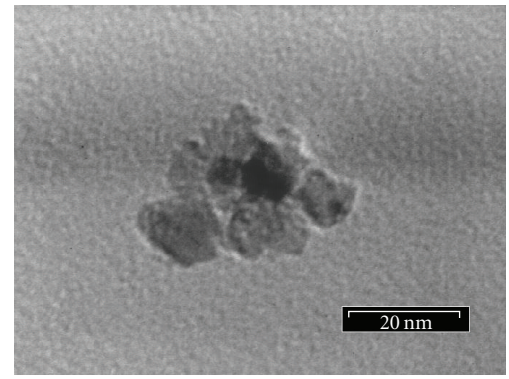


Figure 5: TEM image of nanoparticles prepared at 300°C.

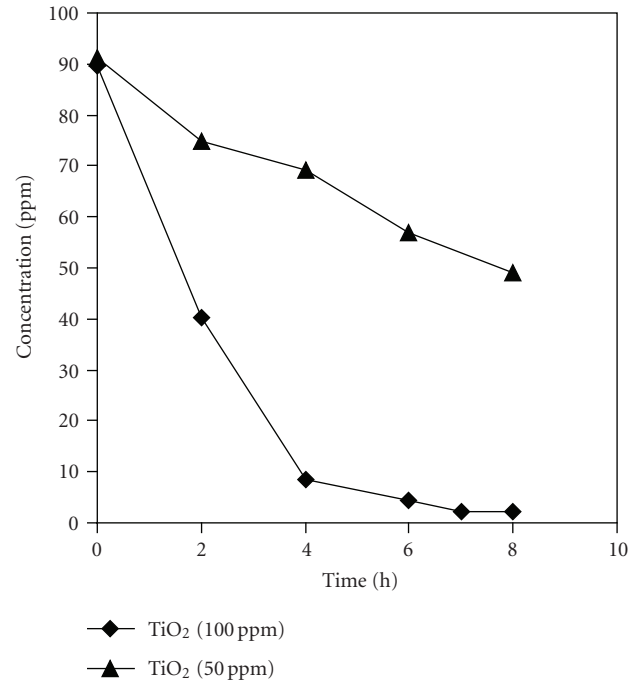


Figure 6: Change in the concentration of Fluorescein at different irradiation time with different amount of nano-TiO_2 (prepared at 300°C).

hours was 97% for sample prepared at 300°C (calcined at 400°C) and 70.91% for same sample calcined at 800°C. The degradation process, involving hydroxyl radical formation and subsequent degradation of the dye by the hydroxyl radical, obeys Pseudo-first-order kinetics.

The rate of degradation was assumed to obey pseudo-first-order kinetics and hence the rate constant for degradation, K, was obtained from the first-order plot according to the following equation:

$$\mathrm{Ln}\left(\frac{C_0}{C}\right) = Kt, \tag{2}$$

where C_0 is the initial concentration, C is the concentration at instant time (t), and K is the first-order rate constant.

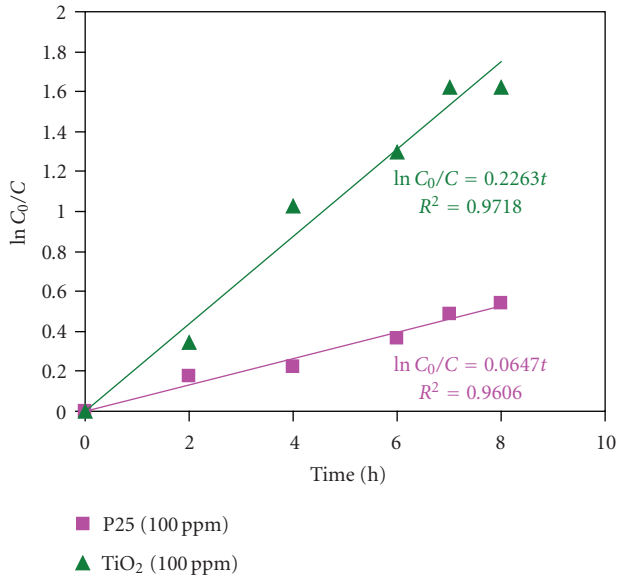


FIGURE 7: First-order photodegradation kinetics of Fluorescein for P25 and TiO_2 sample (prepared at 300°C).

First-order degradation rate constants, obtained by plotting the natural logarithm of the concentration against irradiation time, were 0.2263 h^{-1} for synthesized TiO_2 and 0.0647 h^{-1} for P25 (Figure 7). The prepared sample exhibits better activity than the commercial type (P25).

4. CONCLUSION

A method for making a high-temperature stable anatase phase without using any dopants was successfully achieved by hydrothermal method. In prepared sample, the anatase phase was stable up to 850°C. The crystallinity of anatase phase increased with the hydrothermal temperature. This method is, therefore, suitable to synthesize samples for the high-temperature photocatalytic application in building materials. A high-thermal stable anatase phase and simplicity of preparation technique are the main advantages of this work.

The photodegradation reaction of Fluorescein followed pseudo-first-order reaction kinetics. The kinetic data showed that the prepared sample is somehow more active than the commercial one.

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