RAPID PAPER

Synthesis of Nano-particles of TiO_2 by Simple Aqueous Route

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Edited by K. Takagi, Nagoya Univ., and accepted February 16, 2006 (received for review January 18, 2006)

Abstract: Nanoparticles of Titanium dioxide (TiO_2) was successfully synthesized from simple aqueous peroxo route using TiOSO_4 and H_2O_2 as the precursors. Amorphous titanium-peroxo complex powder was obtained at room temperature, which was then converted into anatase by heat-treating at 300°C . This new method is simple, inexpensive, environmentally benign and promising to be used for the preparation of large quantity of TiO_2 nanoparticles.

Key words: sintering, microstructure, crystal growth, nanomaterial

1 Introduction

Semiconductor nanoparticles have attracted a great deal of attention due to their potential applications in solar energy conversion (1), dielectrics (2) and heterogeneous photocatalysis (3). Although, several semiconductor nanoparticles such as ZnO , SnO_2 , WO_3 and Fe_2O_3 have been used for the above-mentioned applications, TiO_2 is believed to be the most promising currently known material, due to its excellent optical properties of a high refractive index leading to a high hiding power and whiteness, high chemical durability, strong oxidizing power, nontoxicity, low cost and availability (4-8). However, it has been found that the process and processing conditions under which the TiO_2 nanoparticles are synthesized lead to significant variations in their structure, stoichiometry, particle size, optical and electronic properties, and hence, photoactivity (9).

TiO_2 nanoparticles can be synthesized by precipitation from solutions of either titanium salts or titanium alkoxides. TiOSO_4 is particularly attractive as a raw material of TiO_2 owing to the low cost. A large amount of commercial TiO_2 particles is currently produced by

neutralization of TiOSO_4 aqueous solutions followed by the heat treatment of the precipitates. Amorphous titanium hydrous oxide with micrometer-sized particles has also been synthesized using TiOSO_4 and urea (10). However, the particles synthesized in these ways are unsuitable for many applications because of small surface area. In order to prepare the nanometer-sized TiO_2 particles, in this study a new attempt was made using low cost TiOSO_4 precursor material in combination with H_2O_2 and indeed succeeded in such an attempt. In this letter, a novel and simple aqueous peroxo route for the preparation of nanometer sized TiO_2 particles is reported.

2 Experimental

$\text{TiOSO}_4 \cdot 5\text{H}_2\text{O}$ (Nacalai tesque Co.Ltd) was dissolved in water at room temperature and then 30% H_2O_2 was added in to this solution. A yellow colored solution was immediately obtained, indicating the formation of peroxo complex of Titanium solution (11). This yellow colored peroxo-titanium solution yields water insoluble yellow gel, titanium oxy-hydroxide

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after keeping at room temperature for few hours. Then the gel was separated by centrifugation at a rotation speed of 10,000 rpm, washed with double distilled water and then dried over night in the oven. Finally, the dried titanium-peroxo complex was annealed in air at different temperatures ranging from 200 to 550°C for 1 hr to obtain TiO₂. The FT-IR spectra of the as-prepared and heat-treated samples were measured by the KBr pellet method (Jasco FT/IR 610). The powder was analyzed by an X-ray diffractometer (RIGAKU RAD-2R) with Cu K α radiation. The average sizes of anatase crystallites were calculated from the full width at half maximum (FWHM) of diffraction peaks from the (101) plane of anatase, using scherrer's equation. The particle shape was observed by using field emission-SEM (FE-SEM HITACHI S-4300SE/N).

3 Results and Discussion

Figure 1 shows the FT-IR spectra of the as-prepared and sintered titanium dioxide powders. The absorption from 3000 to 3600 cm⁻¹ in **Fig. 1a** can be assigned to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water and the titanium hydroxide. The absorption peak at around 1620 cm⁻¹ may be due to the bending vibration of coordinated H₂O as well as from the Ti-OH. The absorption peak at around 900 cm⁻¹ in **Fig. 1a** can be assigned to characteristic stretching vibration of peroxo groups; hence the shoulder observed at around 690 cm⁻¹ may have been due to the vibration of the Ti-O-O bond in the titanium peroxo gel (13,14). It is believed that Ti⁴⁺ ions and H₂O₂ interact strongly and thereby it forms a Ti-peroxy compound

Fig. 1 FT-IR Spectra of the (a) As-prepared Powder and Those after Annealed at Different Temperatures (b) 200 (c) 300 (d) 450 and (e) 550°C for 1 hr in Air.

(15, 16). The above results indicate the presence of Ti-O bonds, peroxo groups and OH groups in the as-prepared powder. The sample, which is annealed at 200°C, shows that the shoulder assigned to peroxo groups became weak and it reveals the decomposition of peroxo group by thermal annealing. The peaks attributed to the adsorbed water almost disappeared but the vibration of hydroxyl groups still can be seen at about 3400 cm⁻¹, which was not detected after annealing at 300°C. The powder samples annealed at more than 300°C do not show the peaks, which corresponds to the peroxo group and adsorbed water. Therefore it is concluded that the peroxo group was completely decomposed due to the heat-treatment.

The X-ray diffraction (XRD) of the TiO₂ powder obtained by annealing the Ti-oxy-hydroxide at various temperatures is shown in **Fig. 2**. Pattern (a), (b), (c) and (d) in **Fig. 2** shows the characteristic peaks of the heat-treated samples at 200, 300, 450 and 550°C, respectively for 1 hr. The powder annealed at 200°C was amorphous, while the powder annealed at 300°C and above was crystalline. The broad peaks in pattern (b) indicate the possibility of either the low degree of crystallinity of TiO₂ or the ultrafine particle size of the powder. Patterns (c) and (d) are almost the same except the more sharpness of the peaks in pattern (d), which indicates the increase of particle size due to the effect of sintering.

Further, in order to investigate the effect of sintering temperature on the crystallite growth, the crystallite size was calculated using the Scherrer's equation. Indeed, it has been found that there was an increase in crystallite size with increase of sintering temperature. A crystallite

Fig. 2 X-ray Diffractograms of TiO₂ Powder Annealed at (a) 200 (b) 300 (c) 450 and (d) 550°C for 1 hr in Air.

size of 28, 39 and 50 nm were determined from the FWHM of the (101) peak of the anatase for the heat-treated at 300, 450 and 550°C respectively. The XRD analysis reveals that the heat-treatment at 200 and 300°C lead to the formation of amorphous and nanocrystalline TiO_2 respectively. It is interesting to note that the onset temperature of crystallization in the present study is much lower as compared to the sol-gel method (12). Organic compounds in sol prepared by the sol-gel method decompose during the heat-treatment and hinder aligned grain growth and densification. The low temperature (below 200°C) decomposition of peroxo group (**Fig. 1**) and the absence of organic compound could be the reasons for the low temperature crystallization of TiO_2 synthesized by this new method. On the other hand, it can be assumed that the low onset temperature of crystallization be due to the synergistic effect between the decomposition of peroxo group and crystallization.

Figure 3 presents the typical photomicrographs of the as-prepared and sintered titanium dioxide powders. SEM Pictures (a), (b), (c) and (d) in **Fig. 3** shows the surface morphology of the as-prepared and heat-treated samples at 300, 450 and 550°C, respectively for 1 hr in air. It reveals the morphological homogeneity with the

grain size falling mostly in submicron range. Careful examination of SEM pictures clearly evinces that each grain is made up with an aggregation of (nanometer size) very small crystallites. There is a significant differences can be seen when comparing the microphotographs (**Fig. 3a-d**). The as-prepared and low temperature sintered samples (**Fig. 3a** and **b**) consist of non-porous aggregates, which are made of small crystallites. However, when the annealing temperature increases to higher temperature (i.e from 300 to 450°C or higher), the crystallite size and the porosity are increased (**Fig. 3c** and **d**). The increase of crystallite size may be due to the effect of heat-treatment. The estimated crystallite sizes of the sintered samples also support the crystallite growth of the samples by thermal annealing.

In order to investigate the composition of the prepared TiO_2 powder, EDX analysis was carried out for the powder samples heated at 200, 300, 450 and 550°C respectively. The EDX analysis shows that all the samples contain only titanium and oxygen elements and there is no impurity in the samples.

TiO_2 nanoparticles prepared by this new method have considerable high surface area, indicates the possibility of using them for solar cell, catalysis, and electronic devices. Further investigations have to be carried out to

Fig. 3 SEM Photographs of the (a) As-prepared Powder and Those after Annealed at Different Temperatures (b) 300 (d) 450 and (d) 550°C for 1 hr in Air.

understand in more detail the formation mechanism, thermal stability, catalytic property of the present TiO₂ nanostructure, and the interesting interconnectivity among the nanocrystallites.

4 Conclusions

A simple and inexpensive technique has been established to prepare amorphous and nanocrystalline TiO₂ powder from aqueous solution in room temperature. The particle size of the TiO₂ nanoparticles increased from 28 to 50 nm with an increase in the sintering temperature from 300 to 550°C. It is expected that the present method can be easily extended to the similar nanostructures of other oxide materials, which is under-way.

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