OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 5, No. 4, April 2011, p. 407 - 409

Synthesis of TiO_2 nanoparticles in silica microspheres via precipitation in situ and reverse-emulsion approach

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This study described the synthesis of TiO_2 nanoparticles in silica microspheres (nano-$TiO_2 \cong SiO_2$ microspheres) via precipitation in situ and reverse-emulsion approach. FT-IR spectra indicated the presence of Ti—O—Si chemical bonds in these nanocomposite microspheres. TEM images of the nanocomposites revealed that TiO_2 nanoparticles having particle sizes laying in the range of 10-50 nm were encapsulated in the network of silica (mosaic structure). XRD confirmed heat treatment at 650 °C, the formation of anatase phases in the nanocomposites. UV-vis revealed that ultraviolet (260-350 nm) can be absorbed by the nanocomposites with potential applications in photocatalysis sciences.

(Received April 11, 2010; accepted April 11, 2011)

Keywords: Silica, TiO_2, Reverse-emulsion, Precipitation, Nanoparticles

1. Introduction

Anatase crystalline form of Titanium dioxide (TiO_2) is a potent photocatalyst that can break down almost any organic compound when exposed to ultraviolet (UV) light, and TiO_2's photocatalytic characteristics are greatly enhanced due to the advent of nanotechnology. At nano-scale, not only the surface area of titanium dioxide particle increases dramatically but also it exhibits other effects on optical properties and size quantization. An increased rate in photocatalytic reaction is observed as the redox potential increases and the size decreases. For this reason, TiO_2 nanoparticles is one of the most promising applications of photocatalysts for treatment of polluted water and air [1]. However, the main drawback for its practical utilization is that the involved liquid–solid separation is expensive at the end of the photocatalytic treatment. So far, two approachs have emerged especially for the purpose of solving the separation issues. One approach involves the use of the highly dispersed nanoparticles in porous material, and the other is concerned with TiO_2 thin films [2].

Therefore, there is an increasing interest in incorporating photoactive functionalities into various matrix materials such as tiles, silica, glass, paints and plastics in order to be convenient for separation. But photocatalytic efficiency of TiO_2 nanoparticles incorporated the lighttight matrix materials such as tiles and paints are not sufficient because of the small surface area per reactor volume. So a number of researchers are seeking to focus on TiO_2 nanoparticles incorporated the transparent matrix silica. TiO_2 nanoparticles were coated on nonporous transparent silica by sol-gel route or prepared by impregnated method in porous silica granulate, that improve the mechanical properties, high temperature stability and photocatalytic activities of anatase TiO_2 nanoparticles [3-8]. However, few studies have attempted to incorporate the TiO_2 nanoparticles into porous silica microspheres.

In the present work, the synthesis of TiO_2 nanoparticles in silica microspheres was proposed via the following progress. $TiCl_4$, water glass and HCl solution were first mixed and added in the oil, and then heated to form network silica micro-spheres, still heated up to crystallize TiO_2 nanoparticles, and lastly the nano-TiO_2 $\cong SiO_2$ microspheres were formed. Schematic of the synthesis is given in Fig. 1.

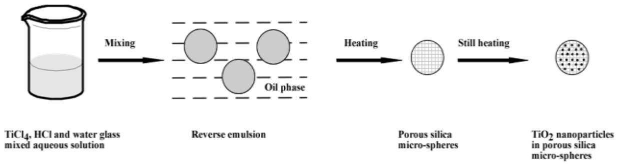

Fig. 1. Schematic of the synthesis of TiO_2 nanoparticles in silica microspheres.

The morphologies, phase structure, interfacial interaction and the optical properties of the $SiO_2 \cong$ nano-TiO_2 microspheres were characterized.

2. Experimental details

2.1. Synthesis

The reagents were titantium (χ) chloride (TiCl4, A.R. grade), hydrochloric acid (HCl, A.R. grade), commercial water glass ($Na_2O \cdot nSiO_2$, n=2.6-3.0) and refined vegetable oil. In the procedure of synthesis, the distilled water was used. Typically, the TiO_2 nanoparticles in porous silica micro-spheres were prepared in the following route: 0.10 ml $TiCl_4$ was added into 1.00 ml, 20 vol. % HCl aqueous solution at ambient temperature. Then 15.00 ml, 25 vol. %

water glass was slowly dropped into the above solution with stirring as a precursor. Then the precursor was injected into refined vegetable oil, heated up to 70 °C, and then incubated for 1h. Subsequently, the micro-spheres were isolated, washed with distilled water and treated at 80 °C for 4h. Finally, the products were dried at 80 °C for 8h and calcined at 650 °C for 4h.

1.2. Characterization

Digital images of samples were obtained by an AIGO T1028 digital camera. Electron microscopy images were acquired on a HITACHI H-8100 transmission electron microscopy (TEM) with an accelerating voltage of 100kv. The nano-$TiO_2 \cong SiO_2$ microspheres were ground, dispersed in ethanol and then directly deposited in copper grid. Fourier transform infrared (FT-IR) spectra were determined with SHIMADZU AIM-8800 FT-IR spectrometer. X-ray diffraction (XRD) patterns were taken on an SHIMADZU XRD-6000 X-ray diffractometer, with CuKα (λ=1.54056Å) radiation being used at 40 kv and 30 mA. UV-visible spectroscopy (UV-vis) spectra were measured in a SHIMADZU UV-2550 UV-vis spectrometer. A certain amount of micro-spheres were dispersed in 7wt. % polyvinyl alcohol aqueous solution, painted film, and dried at ambient temperature.

3. Results and discussion

3.1 Morphology of the $SiO_2 \cong$ nano-TiO_2 microspheres

The images of the nano-$TiO_2 \cong SiO_2$ microspheres are shown in Fig. 2. It is clearly seen that the nano-$TiO_2 \cong SiO_2$ microspheres are almost spherical with the diameter in the range of 1-3 mm. The pure TiO_2 powders are white, but the TiO_2 nanoparticles in porous silica microspheres become transparent, dispersed and incorporated into the transparent silica.

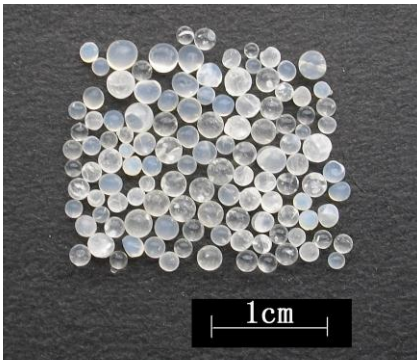

Fig. 2. Images of the nano-$TiO_2 \cong SiO_2$ microspheres.

The TEM image in Fig. 3 evidences rare nonagglomerated TiO_2 nanoparticles domains of size in the range mostly between 10 and 50 nm. These TiO_2 nanoparticles are surrounded by amorphous silica matrix visualized by low-contrast gray slabs and spots (Fig. 3B). Therefore, the structure of nano-$TiO_2 \cong SiO_2$ microspheres belongs to the typical mosaic type.

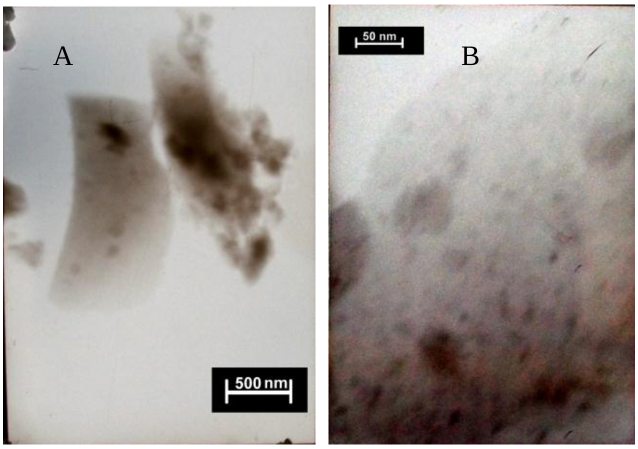

Fig. 3. TEM images of (A) fragments from the nano-$TiO_2 \cong SiO_2$ microspheres and (B) magnified part of a fragment.

3.2 FT-IR analysis

The FT-IR spectra of the pure silica microspheres and nano-$TiO_2 \cong SiO_2$ microspheres with different Ti/Si based on the weight radio of $TiCl_4$ and water glass are shown in Fig. 4. According to the research of Refs [9], it can be found that the band in the range of 2800–3800 cm^{-1} can be attributed to the stretching vibrations of O–H bond from the adsorbed water and structural hydroxyl groups, a relatively broad band centered at 1100 cm^{-1} corresponds to the Si–O–Si stretching vibration and the peaks at about 800 cm^{-1} are assigned to the symmetric stretching of Si–O–Si bond. After the nano-$TiO_2 \cong SiO_2$ microspheres forming, the peak at wave number near 936 cm^{-1} due to the Si–O–Ti stretching vibration was marked, which clearly indicates the presence of nano-TiO_2. By comparing the spectra of the different weight ratios of Ti/Si, it is showed that the peak of Si–O–Ti stretching vibration gets sharper, with increasing the Ti/Si.

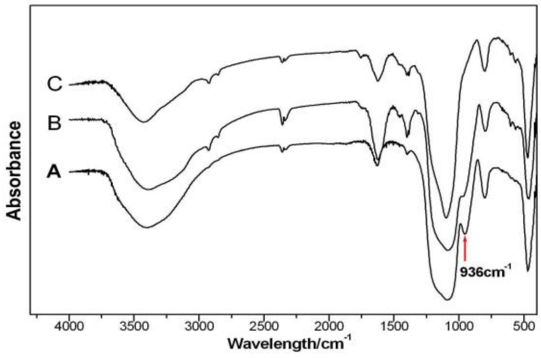

Fig .4. FT-IR spectra of the nano-$TiO_2 \cong SiO_2$ microspheres with different Ti/Si: (A) 1:7, (B) 1:10, and (C) 0.

3.3 XRD analysis

Corresponding to our previous work [10], it is confirmed that the silica microspheres prepared via above method are amorphous and porous. The XRD patterns of the nano-$TiO_2 \cong SiO_2$ microspheres with different Ti/Si are shown in Fig. 5. In the patterns, it is conformed only anatase phase is obtained, and the peak intensity of anatase TiO_2 is very weak but increases with increasing Ti/Si. In addition, while the weight ratio of Ti/Si arrives at 1:7, the strong and sharp peaks indicate the well crystallized anatase form are acquired.

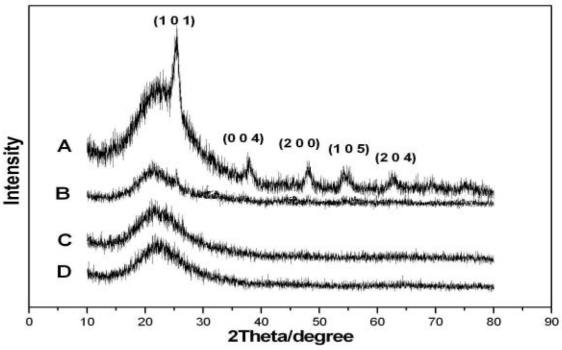

Fig. 5. XRD patterns of the nano-$TiO_2 \cong SiO_2$ microspheres with different Ti/Si :(A) 1:7, (B) 1:10, (B) 1:15, and (D) 0.

3.4 Optical properties of the nano-$TiO_2 \cong SiO_2$ microspheres

The UV–vis adsorption spectra of the nano-$TiO_2 \cong SiO_2$ microspheres and the SiO_2 microspheres are shown in Fig. 6. Compared to the SiO_2 microspheres, the nano-$TiO_2 \cong SiO_2$ microspheres exhibit the absorption band at around 260–350 nm, indicating the presence of potential applications in photocatalysis sciences. The absorption and corresponding bandgap energy of bulk TiO_2 is 385 nm (Eg = 3.2 eV) for anatase, while TiO_2 nanoparticles in porous silica microspheres is shifted toward shorter wavelength (blue shift), Because of the TiO_2 nanoparticles in confined state within silica Network [11, 12].

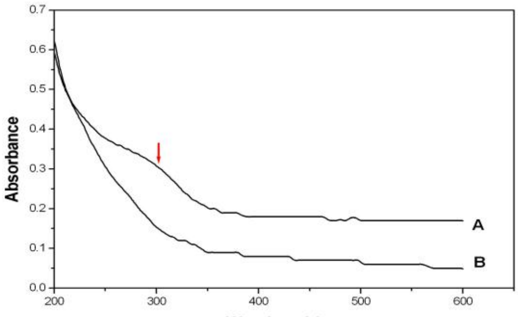

Fig. 6. UV-vis spectra of (A) the nano-$TiO_2 \cong SiO_2$ microspheres and (B) the SiO_2 microspheres (without Ti).

4. Conclusions

The nano-$TiO_2 \cong SiO_2$ microspheres were prepared by using reverse-emulsion approach and precipitation in situ. This method provided a facile approach to synthesize TiO_2 nanoparticles in silica microspheres. In the composites, anatase TiO_2 nanoparticles dispersed and incorporated into the porous silica with Ti—O—Si chemical bonds. Moreover, it was found that the composites were transparent, absorbed ultraviolet (260-350 nm) and could be potentially used as a photocatalyst.

Acknowledgements

This work was financially supported by the foundation of Chongqing University of Arts and Sciences.

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