Brief communication

Photoluminescence from TiO$_2$/PMMA nanocomposite prepared by $\gamma$ radiation

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Received 16 April 2005; accepted in revised form 17 May 2005

Key words: $\gamma$ radiation, nanocrystal, photoluminescence, surface modification, TiO$_2$/PMMA nanocomposite

Abstract

The surface of anatase TiO$_2$ nanocrystals with an average size of ~20 nm was modified by PMMA through $\gamma$ radiation. The modified nanocrystals were investigated with photoluminescence (PL) and Fourier transform infrared (FTIR) spectra. A stable blue luminescence peak (~420 nm) can be observed for the modified anatase TiO$_2$ nanocrystal.

Introduction

Luminescence is one of the most important properties of the nanoparticles. However, it is difficult to obtain a uniform dispersion system of nanoparticles owing to their strong tendency of agglomeration for the high surface energy. In recent years, the nanoparticles/polymer composites have attracted attention (Guo et al., 2000a, 2000; Levine et al., 2004). The polymer not only improve the dispersion of the nanoparticles, but also bring some new optical properties of the nanocomposite. Zou et al. (Zou et al., 1991) found that TiO$_2$ ultrafine particles coated with a layer of stearic acid can have 540 nm fluorescence. The ZnO can generate stable luminescence peaks down to the 465 nm (blue region) after coated with poly (ethylene glycol) (Abdullah et al., 2003). In this paper, we report the surface modification of TiO$_2$ nanocrystals by polymethyl methacrylate (PMMA) through $\gamma$ radiation. The modified TiO$_2$ nanocrystals emit blue luminescence. The modified TiO$_2$ nanocrystals have potential for the development of a class of luminescent polymer/nanoparticles composite with the modified TiO$_2$ as the luminescent centers.

Experimental details

The investigation had been carried out on commercial TiO$_2$ nanocrystals (about 20 nm) which were purchased from Zhejiang Zhoushan Mingri Nano Materials Co Ltd. Before the radiation the TiO$_2$ nanocrystals had been heated at 120°C for 20 h in order to eliminate the possible adsorbed water on the surface of the particles.

Methyl methacrylate (MMA), which was purchased from Chinese Shanghai First Chemical Work of Reagent, was distilled at reduce pressure and preserved at 4°C before the $\gamma$ irradiation. All other reagents were analytical pure and were used without further purification.

The treated TiO$_2$ nanocrystals were fully mixed with prepared MMA solution (20% in volume) and were put into the ampoule, and then sealed. The solvent of MMA solution was the mixture of n-heptane/chloroform (2:3 in volume). The
samples were irradiated to a dose of 10, 20, 30, 50, 70 and 90 kGy by $\gamma$ radiation from a $^{60}$Co source at a dose rate 10 kGy/h. After the irradiation the synthesized polymer/nanopowder composite were wrapped with filter paper, and extracted 72 h in a Soxhlet extractor with boiling xylene (the homopolymer is thought to be completely removed by this way), the extracted composite were dried in air at 70°C until a constant weight was reached.

Fourier transform infrared (FTIR) spectra of the sample in KBr pellets were recorded on a Nicolet 560 FTIR spectrometer. The Spectra were collected from 4000 to 400 cm$^{-1}$, with a 4 cm$^{-1}$ resolution over 20 scans. Steady state photoluminescence studies were carried out on the dispersion of nanopowder in purified water. For the optical measurements, nanopowders were first suspended in purified water. The solutions were dispersed with 50 W KQ-50B ultrasonic irradiation cleaner. Photoluminescence was recorded on a Shimadzu RF-5301PC fluorometer employing a 150 W Xe lamp as the light source.

**Results and discussion**

Figure 1 shows the photoluminescence of the modified TiO$_2$ nanocrystals at room temperature after radiated to different dose. It is obvious that a broad photoluminescence spectra occur at around 420 nm after the radiation. The mechanism of the photoluminescence is still unclear, but it should be induced by the surface modification of the radiation induced polymerization.

The comparison between the nanocomposite obtained after 72 h extraction and pure nanoparticles is shown in Figure 2. Compared with the curves of pure samples, it can be seen that the new peaks attributed to carbonyl stretching vibration appear at about 1730 cm$^{-1}$ after the $\gamma$ irradiation, which is the characteristic peak at 1730 cm$^{-1}$ of PMMA. The peak at $\sim$1399 cm$^{-1}$ is attributed to the bend vibration of $-\text{CH}_3$ group of polymer. The new peak is an indication the existence of unextractable PMMA. The characteristic absorption peak of anatase (1630 cm$^{-1}$) shift to higher wavenumber (about 1635 cm$^{-1}$) after radiation induced polymerization. These results show that the composites are not the simple mixtures of polymer and TiO$_2$ nanocrystals. There should be strong interactions between the PMMA and nanoparticles, maybe new chemical bonds are formed on the interface between PMMA and TiO$_2$.

The unextractable polymer indicates the presence of chemical bonds between the polymer and