Research Article
Simple Synthesis and Luminescence Characteristics of PVP-Capped GeO₂ Nanoparticles

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Polyvinylpyrrolidone (PVP)-capped rutile GeO₂ nanoparticles were synthesized through a facile hydrothermal process. The obtained nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA), and photoluminescence spectroscopy (PL). The capped GeO₂ nanoparticles showed significantly enhanced luminescence properties compared with those of the uncapped ones. We attributed this result to the effect of reducing surface defects and enhancing the possibility of electron-hole recombination of the GeO₂ nanoparticles by the PVP molecules. PVP-capped GeO₂ nanoparticles have potential application in optical and electronic fields.

1. Introduction

Germanium oxide (GeO₂) is an important semiconductor material that has attracted much interest owing to its unique optical property and silica analogue [1, 2]. Moreover, nanostructured GeO₂ possesses the superior physical and chemical properties compared with its bulk counterparts. Nowadays, it is being widely used in optoelectronic devices, vacuum technology, and catalysis. For example, GeO₂ nanowires were used in one-dimensional luminescence nanodevices by Sahnoun et al. [3]. And GeO₂ nanotubes and nanorods as an important optical fibre material have been used in thermal vacuum test successfully by Jiang et al. [4].

It is well known that GeO₂ forms in two stable crystalline structures at ambient temperature, the α-quartz trigonal structure and the rutile tetragonal structure [5]. Over the past decades several properties of α-quartz-type GeO₂ have been investigated, for instance blue luminescence and dielectric properties. Compared with α-quartz-type GeO₂, rutile GeO₂ has some unique properties, such as excellent transmissivity and green luminescence [6–8]. For these properties, rutile GeO₂ has been considered as a potential material for luminescent device [9]. However, rutile GeO₂ nanoparticles, like other semiconductor nanoparticles, have high surface energy, and they agglomerate or coalesce extremely quickly [10]. For this reason, many methods have been used to improve the stability of nanoparticles, such as changing of annealing temperature and doping of semiconductor and surfaces capped by various organic or inorganic layers, [11–13]. Among these methods, polymer capping as a newly chemical method has been developed to synthesize nanoparticles with high surface stability and also has significant influence on the morphology and optical properties of nanoparticles [14]. Moreover, compared with the aforementioned methods, it also has several other advantages, such as facile process and gentle reaction conditions. However, the rutile GeO₂ modified by PVP had never been synthesized successfully before. So this is a problem that should be solved quickly.

In this present work, we report, for the first time, the synthesis of PVP-capped rutile GeO₂ nanocrystals through a simple hydrothermal process. PVP, which is a water soluble polymer, was used as capping polymer molecule to stabilize the GeO₂ nanoparticles. Through the surface modification by PVP, highly monodisperse GeO₂ nanoparticles were prepared, which exhibited highly chemical stability and
2. Experimental Section

2.1. Material and Methods. We synthesize the samples through hydrothermal synthesis method. In a typical preparation process, 0.1 g GeO\textsubscript{2} was added in 15 mL HCl aqueous solution (PH = 1) in a Teflon-lined autoclave of 20 mL capacity. The autoclave was maintained at 180°C for 12 hours and then naturally cooled to room temperature. The obtained solution was discarded. The powder samples were then redispersed in distilled water in an ultrasonic bath. The centrifugation was repeated twice so as to remove the HCl residue. After that, the powder samples were dried in an oven at 60°C for 24 hours in air. Then the powder samples were added in a Teflon-lined autoclave of 20 mL capacity again with 15 mL distilled water and 0.2 g PVP. The autoclave was maintained at 140°C for 6 hours and then naturally cooled to room temperature. The centrifugation was repeated twice so as to remove the aqueous solution PVP again. The powder samples were dried in an oven at 60°C for 24 hours in air. Then PVP-capped GeO\textsubscript{2} was obtained. These powder samples were collected for further characterization. All the chemical reactants were analytical grade.

2.2. Characterizations Used. The as-prepared products were characterized using X-ray powder diffractometer (XRD, Rigaku, D/max-RA), transmission electron microscopy (TEM, HITACHI H-8100), Fourier transform infrared spectrometer (FTIR, NA-360), thermogravimetric analyzer (TGA, Perkin-Elmer), and Raman spectrometer (Renishaw 1000) using excitation wavelengths of 325 nm (He-Cd laser). Besides, the particle size and distribution were determined by measuring the maximum diameter of more than 100 particles on the TEM images.

3. Results and Discussion

3.1. XRD. Figure 1 shows a typical powder XRD pattern of uncapped (a) and PVP-capped (b) GeO\textsubscript{2} nanocrystals prepared by the hydrothermal experiments. All the diffraction peaks could be indexed to rutile structure GeO\textsubscript{2} with cell constants a\textsubscript{o} = 4.831 Å and c\textsubscript{o} = 5.568 Å. These XRD peaks are in good agreement with those of the JCPDS card (no. 88-0285). It indicates that the obtained products are all of pure rutile phase GeO\textsubscript{2}. No obvious differences can be observed in the XRD patterns of the uncapped (Figure 1(a)) and PVP-capped (Figure 1(b)) GeO\textsubscript{2} nanoparticles. This shows that PVP modification does not influence the structure of GeO\textsubscript{2}.

3.2. TEM. Figure 2 shows typical TEM images of the non-capped (Figure 2(a)) and PVP-capped (Figure 2(b)) GeO\textsubscript{2} nanoparticles. We also provide the particle size and distribution histograms of the non-capped (Figure 3(a)) and PVP-capped (Figure 3(a)) GeO\textsubscript{2} nanoparticles. Average sizes of the uncapped GeO\textsubscript{2} are in the range of 700–800 nm estimated from TEM images (Figure 2(a)). The obvious aggregation of the uncapped GeO\textsubscript{2} nanocrystals may be due to the high surface energy of the nanocrystals. From Figure 2(b), the PVP-capped GeO\textsubscript{2} nanoparticles had the same size (about 500 nm) compared with those without PVP modification. Moreover, we found that there were some smaller particles appeared in the TEM images. We thought that these small particles are also done when the GeO\textsubscript{2} samples were uncapped with PVP. Because of the aggregation are much bigger than single particle, especially for the small size particle. When the small size is particle adsorbed on the aggregation, it is difficult to find it in the TEM images. Above all, from the TEM images, we could find that PVP plays an important role in monodispersion property of the GeO\textsubscript{2} nanoparticles. In this process PVP lowered the surface energy of the nanocrystals, so capped GeO\textsubscript{2} nanoparticles with monodispersion property were obtained as observed [15].

3.3. FTIR. The polymer capping of germanium oxide is confirmed through FTIR spectroscopy. Figure 4 shows typical FTIR spectra of GeO\textsubscript{2} nanoparticles (Figure 4(a)) and the GeO\textsubscript{2} nanoparticles modified with PVP (Figure 4(b)). The absorption bands around 3400 cm\textsuperscript{-1} observed in both spectra are attributed to O-H stretching mode of water and hydroxyl. The band (Figure 4(a)) at ~550 cm\textsuperscript{-1} corresponds to Ge-OH stretching motion, and the band at ~899 cm\textsuperscript{-1} corresponds to Ge-O-Ge stretching motion. The two stretching vibration bands located at ~550 and ~889 cm\textsuperscript{-1} are the characteristic peaks of GeO\textsubscript{2} crystal [16]. The FTIR spectrum of PVP-capped GeO\textsubscript{2} shows some remarkable spectral changes. The most prominent and informative bands in the spectrum of compounds occur in the high frequency range between 400 and 1900 cm\textsuperscript{-1}. For example the band at 750 cm\textsuperscript{-1} replaces the dominant peak of GeO\textsubscript{2}, which corresponds to the Ge-O-C bending [17]. The most convincing evidence from FTIR spectra of the PVP-modified GeO\textsubscript{2} is the absorption peaks at 1265 and 1628 cm\textsuperscript{-1} which
Figure 2: TEM images of the noncapped (a) and PVP-capped (b) GeO₂ nanoparticles.

Figure 3: Particle size distribution histograms of the noncapped (a) and PVP-capped (b) GeO₂ nanoparticles.

Figure 4: FTIR spectra of noncapped (a) and PVP-capped (b) GeO₂ nanoparticles.

correspond to C-N stretching motion and C=O stretching motion of monomer for PVP, respectively [18–20]. The band at ~680 cm⁻¹ of Ge-O-C indicates that stable bonding exists between the GeO₂ and some organic. Moreover the absorption peaks at 1265 and 1628 cm⁻¹ occurred in Figure 4(b), this is due to the presence of PVP [21]. These previous discussions of the FTIR spectroscopy confirm that the surface of obtained GeO₂ particles is modified with PVP successfully.

3.4. TGA. The TGA of PVP-capped GeO₂ samples was carried out in an inert nitrogen atmosphere in the temperature range of 50–900°C. The heating rate employed was 20°C/min. The obtained TGA curve is shown in Figure 5. A continuous weight loss in TGA from 500 to 700°C indicates PVP decomposition. This suggests that the PVP decomposition in GeO₂ modified by PVP starts at a temperature much higher than its synthesized temperature (~150°C). These results indicate that the GeO₂ nanoparticles were also successfully modified with PVP.

3.5. PL Spectra. The PL spectra were recorded with the excitation wavelength of 325 nm. The PL spectra of the noncapped (Figure 6(a)) and PVP-capped (Figure 6(b)) GeO₂ nanoparticles were shown in Figure 6. Both samples exhibited an emission band from 570 to 690 nm, but the relative intensity varied. Contrasting the PL spectra of PVP-capped and uncapped GeO₂ nanoparticles, it is obvious that
the emission band of the uncapped particle is quite broad, and the PL intensity of capped nanoparticles is enhanced about one order of magnitude stronger than that of the noncapped ones. This result clearly justifies that the PVP as the capping agent can significantly enhance the PL intensity for GeO₂ nanoparticles.

As it is known, the emission band was assigned to the surface trap-induced fluorescence, which involved the recombination of electrons trapped inside a germanium vacancy with a hole in the valence band of the GeO₂ nanoparticles [22]. In our case, the enhanced luminescence properties of the capped GeO₂ nanoparticles may be due to the PVP surface modification which may have the effect of minimizing surface defects and enhance the possibility of electron-hole recombination [23]. Besides PVP, other polymers, such as poly(ethylene glycol) (PEG), cetyltrimethylammonium bromide (CTAB), and oleic acid were also used. However, PVP was the effective polymer that could improve the luminescence properties of GeO₂ nanoparticles obviously.

4. Conclusion

In summary, we have successfully synthesized monodisperse PVP-capped rutile GeO₂ nanoparticles, via a facile hydrothermal process. This result indicates that PVP could control the morphology of rutile GeO₂ effectively. In addition, the PL intensity of capped nanoparticles is enhanced about one order of magnitude stronger than that of the noncapped ones. We suggested that this performance improvement is due to the PVP surface modification which has the effect of minimizing surface defects and enhance the possibility of electron-hole recombination.

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