Research Article

Simple Synthesis and Luminescence Characteristics of PVP-Capped GeO₂ Nanoparticles

Wei Wu, Xu Zou, Qianjun Li, Bingbing Liu, Bo Liu, Ran Liu, Dedi Liu, Zepeng Li, Wen Cui, Zhaodong Liu, Dongmei Li, Tian Cui, and Guangtian Zou

State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

Correspondence should be addressed to Bingbing Liu, liubb@jlu.edu.cn

Received 30 April 2010; Accepted 28 July 2010

Academic Editor: Quanqin Dai

Copyright © 2011 Wei Wu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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

FIGURE 1: XRD pattern of the uncapped (a) and PVP-capped (b) GeO_2 nanoparticles.

significantly enhanced luminescence. Our study provides a new hybrid material which has potential application in the field of nanoscale device.

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_2 was added in 15 mL HCl aqueous solution ($\text{PH} = 1$) 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 cooled to room temperature naturally. 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_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_2 nanocrystals prepared by the hydrothermal experiments. All the diffraction peaks could be indexed to rutile structure GeO_2 with cell constants $a_0 = 4.831 \text{ \AA}$ and $c_0 = 5.568 \text{ \AA}$. 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_2 . No obvious differences can be observed in the XRD patterns of the uncapped (Figure 1(a)) and PVP-capped (Figure 1(b)) GeO_2 nanoparticles. This shows that PVP modification does not influence the structure of GeO_2 .

3.2. TEM. Figure 2 shows typical TEM images of the non-capped (Figure 2(a)) and PVP-capped (Figure 2(b)) GeO_2 nanoparticles. We also provide the particle size and distribution histograms of the noncapped (Figure 3(a)) and PVP-capped (Figure 3(a)) GeO_2 nanoparticles. Average sizes of the uncapped GeO_2 are in the range of 700–800 nm estimated from TEM images (Figure 2(a)). The obvious aggregation of the uncapped GeO_2 nanocrystals may be due to the high surface energy of the nanocrystals. From Figure 2(b), the PVP-capped GeO_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_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_2 nanoparticles. In this process PVP lowered the surface energy of the nanocrystals, so capped GeO_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_2 nanoparticles (Figure 4(a)) and the GeO_2 nanoparticles modified with PVP (Figure 4(b)). The absorption bands around 3400 cm^{-1} observed in both spectra are attributed to O-H stretching mode of water and hydroxyl. The band (Figure 4(a)) at $\sim 550 \text{ cm}^{-1}$ corresponds to Ge-OH stretching motion, and the band at $\sim 899 \text{ cm}^{-1}$ corresponds to Ge-O-Ge stretching motion. The two stretching vibration bands located at ~ 550 and $\sim 889 \text{ cm}^{-1}$ are the characteristic peaks of GeO_2 crystal [16]. The FTIR spectrum of PVP-capped GeO_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^{-1} . For example the band at 750 cm^{-1} replaces the dominant peak of GeO_2 , which corresponds to the Ge-O-C bending [17]. The most convincing evidence from FTIR spectra of the PVP-modified GeO_2 is the absorption peaks at 1265 and 1628 cm^{-1} which

FIGURE 2: TEM images of the noncapped (a) and PVP-capped (b) GeO_2 nanoparticles.

FIGURE 3: Particle size distribution histograms of the noncapped (a) and PVP-capped (b) GeO_2 nanoparticles.

FIGURE 4: FTIR spectra of noncapped (a) and PVP-capped (b) GeO_2 nanoparticles.

correspond to C-N stretching motion and C=O stretching motion of monomer for PVP, respectively [18–20]. The band at $\sim 680 \text{ cm}^{-1}$ of Ge-O-C indicates that stable bonding exists between the GeO_2 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 GeO_2 particles is modified with PVP successfully.

3.4. TGA. The TGA of PVP-capped GeO_2 samples was carried out in an inert nitrogen atmosphere in the temperature range of $50\sim 900^\circ\text{C}$. The heating rate employed was $20^\circ\text{C}/\text{min}$. 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 GeO_2 modified by PVP starts at a temperature much higher than its synthesized temperature ($\sim 150^\circ\text{C}$). These results indicate that the GeO_2 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)) GeO_2 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 GeO_2 nanoparticles, it is obvious that

FIGURE 5: TGA curve for PVP-capped GeO_2 taken in nitrogen atmosphere.

FIGURE 6: PL spectra of the noncapped (a) and PVP-capped (b) GeO_2 nanoparticles.

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 GeO_2 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 GeO_2 nanoparticles [22]. In our case, the enhanced luminescence properties of the capped GeO_2 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 GeO_2 nanoparticles obviously.

4. Conclusion

In summary, we have successfully synthesized monodisperse PVP-capped rutile GeO_2 nanoparticles, via a facile hydrothermal process. This result indicates that PVP could control the morphology of rutile GeO_2 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.

Acknowledgments

This paper was supported financially by the NSFC (10979001 and 20773043), the National Basic Research Program of China (2005CB724400), the Program for the Changjiang Scholar and Innovative Research Team in University (IRT0625), the Cheung Kong Scholars Programme of China, and the National Fund for Fostering Talents of Basic Science (J0730311).

References

- [1] S. Grandi, P. Mustarelli, S. Agnello, M. Cannas, and A. Cannizzo, "Sol-gel GeO_2 -doped SiO_2 glasses for optical applications," *Journal of Sol-Gel Science and Technology*, vol. 26, no. 1–3, pp. 915–918, 2003.
- [2] T. M. Davis, M. A. Snyder, and M. Tsapatsis, "Germania nanoparticles and nanocrystals at room temperature in water and aqueous lysine sols," *Langmuir*, vol. 23, no. 25, pp. 12469–12472, 2007.
- [3] M. Sahnoun, C. Daul, R. Khenata, and H. Baltache, "Optical properties of germanium dioxide in the rutile structure," *European Physical Journal B*, vol. 45, no. 4, pp. 455–458, 2005.
- [4] Z. Jiang, T. Xie, G. Z. Wang et al., " GeO_2 nanotubes and nanorods synthesized by vapor phase reactions," *Materials Letters*, vol. 59, no. 4, pp. 416–419, 2005.
- [5] L. Pajasová, "Optical properties of GeO_2 in the ultraviolet region," *Czechoslovak Journal of Physics*, vol. 19, no. 10, pp. 1265–1270, 1969.
- [6] A. Trukhin, M. Kink, Y. Maksimov, J. Jansons, and R. Kink, "Luminescence of GeO_2 glass, rutile-like and α -quartz-like crystals," *Journal of Non-Crystalline Solids*, vol. 352, no. 2, pp. 160–166, 2006.
- [7] E. Ghobadi and J. A. Capobianco, "Crystal properties of α -quartz type GeO_2 ," *Physical Chemistry Chemical Physics*, vol. 2, no. 24, pp. 5761–5763, 2000.
- [8] M. Micoulaut, L. Cormier, and G. S. Henderson, "The structure of amorphous, crystalline and liquid GeO_2 ," *Journal of Physics Condensed Matter*, vol. 18, no. 45, pp. R753–R784, 2006.
- [9] M. R. Khanlary, P. D. Townsend, and N. Gustavsson, "Luminescence of rutile-like GeO_2 crystals," *Radiation Effects and Defects in Solids*, vol. 127, no. 1, pp. 61–74, 1993.
- [10] H. P. Wu, J. F. Liu, M. Y. Ge et al., "Preparation of monodisperse GeO_2 nanocubes in a reverse micelle system," *Chemistry of Materials*, vol. 18, no. 7, pp. 1817–1820, 2006.
- [11] M. Zheng, M. Gu, Y. Jin, and G. Jin, "Preparation, structure and properties of TiO_2 -PVP hybrid films," *Materials Science and Engineering B*, vol. 77, no. 1, pp. 55–59, 2000.

- [12] A. A. Bol and A. Meijerink, "Doped semiconductor nanoparticles—a new class of luminescent materials?" *Journal of Luminescence*, vol. 87, pp. 315–318, 2000.
- [13] S. J. Xu, X. C. Wang, S. J. Chua et al., "Effects of rapid thermal annealing on structure and luminescence of self-assembled InAs/GaAs quantum dots," *Applied Physics Letters*, vol. 72, no. 25, pp. 3335–3337, 1998.
- [14] S. V. Manorama, K. Madhusudan Reddy, C. V. Gopal Reddy, S. Narayanan, P. Rajesh Raja, and P. R. Chatterji, "Photostabilization of dye on anatase titania nanoparticles by polymer capping," *Journal of Physics and Chemistry of Solids*, vol. 63, no. 1, pp. 135–143, 2002.
- [15] N. Varghese, K. Biswas, and C. N. R. Rao, "Investigations of the growth kinetics of capped CdSe and CdS nanocrystals by a combined use of small angle X-ray scattering and other techniques," *Chemistry*, vol. 3, no. 8-9, pp. 1435–1442, 2008.
- [16] Y.-W. Chiu and M. H. Huang, "Formation of Hexabranched GeO₂ Nanoparticles via a Reverse Micelle System," *Journal of Physical Chemistry C*, vol. 113, no. 15, pp. 6056–6060, 2009.
- [17] R. Fajgar, M. Jakoubková, Z. Bastl, and J. Pola, "Germanium-containing coatings by IR laser-induced decomposition of ethoxy(trimethyl) germane and tetramethylgermane," *Applied Surface Science*, vol. 86, no. 1–4, pp. 530–532, 1995.
- [18] X. Feng, Y. Liu, C. Lu, W. Hou, and J.-J. Zhu, "One-step synthesis of AgCl/polyaniline core-shell composites with enhanced electroactivity," *Nanotechnology*, vol. 17, no. 14, pp. 3578–3583, 2006.
- [19] X. Lu, L. Li, W. Zhang, and C. Wang, "Preparation and characterization of Ag₂S nanoparticles embedded in polymer fibre matrices by electrospinning," *Nanotechnology*, vol. 16, no. 10, pp. 2233–2237, 2005.
- [20] E. Hao and T. Lian, "Buildup of polymer/Au nanoparticle multilayer thin films based on hydrogen bonding," *Chemistry of Materials*, vol. 12, no. 11, pp. 3392–3396, 2000.
- [21] M. Zawadzki and J. Okal, "Synthesis and structure characterization of Ru nanoparticles stabilized by PVP or γ -Al₂O₃," *Materials Research Bulletin*, vol. 43, no. 11, pp. 3111–3121, 2008.
- [22] M. Sahnoun, C. Daul, R. Khenata, and H. Baltache, "Optical properties of germanium dioxide in the rutile structure," *European Physical Journal B*, vol. 45, no. 4, pp. 455–458, 2005.
- [23] S. H. Liu, X. F. Qian, J. Yin, X. D. Ma, J. Y. Yuan, and Z. K. Zhu, "Preparation and characterization of polymer-capped CdS nanocrystals," *Journal of Physics and Chemistry of Solids*, vol. 64, no. 3, pp. 455–458, 2003.