OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 11, No. 1-2, January-February 2017, p. 68 - 71

Photoluminescence performance of SiC nanoparticles synthesized from corn

DONG-HUA WANG*, XIN FU
College of Chemistry and Materials, Weinan Normal University, Weinan 714000, PR China

β-SiC nanoparticles and core-shell nanoparticles were synthesized by sol-gel and carbothermal reduction methods, in which corn and tetraethoxysilane (TEOS) were respectively employed as carbon and silica precursors, cobalt nitrate as additive. These particles were characterized by X-ray diffraction, scanning electron microscope, transmission electron microscope and photoluminescence. The results show that the β-SiC nanoparticles and core-shell nanoparticles with a diameter of 20-80 nm. A possible growth mechanism was proposed for the nanoparticles according to the characterization results. The synthesized nanoparticles exhibit different photoluminescence properties due to their core-shell structure, quantum size-confinement, core–shell interface defects and internal structure defects.

(Received December 2, 2015; accepted February 10, 2017)

Keywords: Carbide, Nanoparticle, Corn, Core-shell structure, Luminescence

1. Introduction

Silicon carbide (SiC) nanoparticles possess more promising mechanical, electronic, and optical properties because of their low dimensionality, quantum confinement, and shape effect [1-3]. So they have attracted great interest due to their wide application potential in high-temperature electronic devices, sensors, and electromechanical systems [4, 5]. Recently, the photoluminescence properties of the different morphology SiC were reported [6-9].

Consequently, economical and efficient routes for synthesizing SiC nanoparticles become more important than ever. For example, Meng et al. successfully prepared SiC nanoparticles by plastic waste [10]. Yu et al. produced β-SiC particles by plasma [11]. Wu et al. achieved SiC nanoparticles by implantation method and direct etching of bulk SiC [12]. Herlin et al synthesized small SiC particles with diameter about 10nm from C_2H_2 and SiH_4 mixture by laser pyrolysis [13]. Little work has been done on how to synthesize the core-shell SiC nanoparticles and whether it can enhance the luminescence efficiency.

In this paper, we synthesized SiC nanoparticles and core-shell nanoparticles by corn and TEOS via the carbothermal reduction method. The experimental results indicated that the SiC nanoparticles and core-shell nanoparticles have especial photoluminescence properties under the different excitation wavelength.

2. Experimental

2.1. SiC preparation

The corn were washed with water to remove the impurity, they were dried at 150 °C for 1h. Then they were cooled down to room temperature and comminuted.

The solution preparation is briefly described as follows. Firstly, 1.5 g of cobalt nitrate was dissolved in 100 ml of ethyl alcohol (anhydrous, AR) and then mixed with 50 ml of tetraethoxysilane (TEOS, AR) under stirring. Then, 10 ml of oxalic acid (3.4 wt%) was added into the mixture under stirring to enhance the hydrolysis of TEOS. After 24 h, 16 g of corn was added into the above mixture. After 48 h, 10 ml of hexamethylenetetramine aqueous (35.8 wt%) solution was dropped into the above mixture for rapid gelation. Finally, the gel was dried at 110 ◦C for 3 h to obtain the sample.

The sample were put into the a horizontally tubular reactor and heated to 1000 °C at a rate of 5 °C/min in Ar flow, then to 1300 °C at a rate of 2 °C /min and maintained at this temperature for 7h. The raw product was collected after the furnace was cooled down to room temperature and then purified by air calcination and acid treatment (HF + HCl) to eliminate the impurities.

2.2. Characterization

The crystalline structures of the samples were characterized by using a Rigaku D/max rA X-Ray diffractometer (XRD) with CuKα radiation. The microstructure of the samples was examined by Hitach S-4800 scanning electron microscope (SEM). The structural features of the samples were observed by a Hitach H-7650 transmission electron microscope (TEM). The photoluminescence (PL) spectrum measurement was performed in an F-7000 FL Spectrophotometer with a Xe lamp as an excitation source at room temperature.

3. Results and discussion

The sample was greenish powders. The XRD pattern of the as-obtained products is shown in Fig. 1. From the patterns, all of the strong diffraction peaks can be indexed to β-SiC (JCPDS, No. 29-1129 a=4.359 Å), no other crystalline phases such as silica, carbon or other impurities were detected. The low-intensity peak marked with SF is due to stacking faults [14]. Strong and sharp diffraction peaks indicate that the sample consists of pure β-SiC with good crystalline structure.

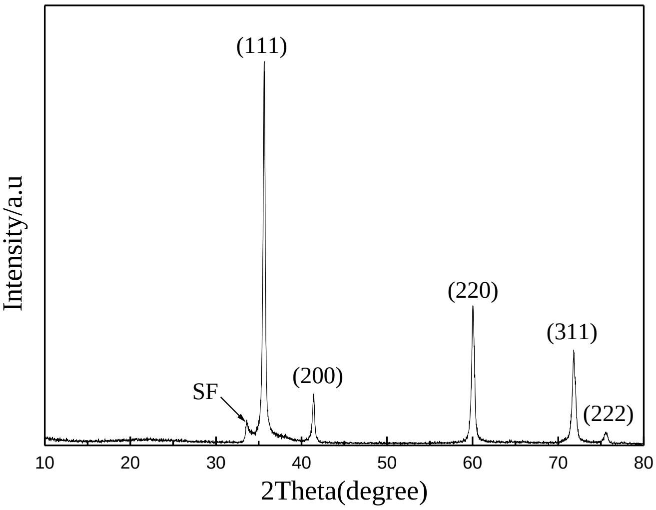

Fig. 1. XRD pattern of SiC nanoparticles

The low-magnification SEM surface image (Fig. 2(a)) shows that the as-obtained products are composed of nanoparticles. From high-magnification SEM images (Fig. 2(b)), the nanoparticles with the diameters lie between 10 nm and 100 nm can be clearly observed. Some particles look like a cluster agglomerated by small nanoparticles.

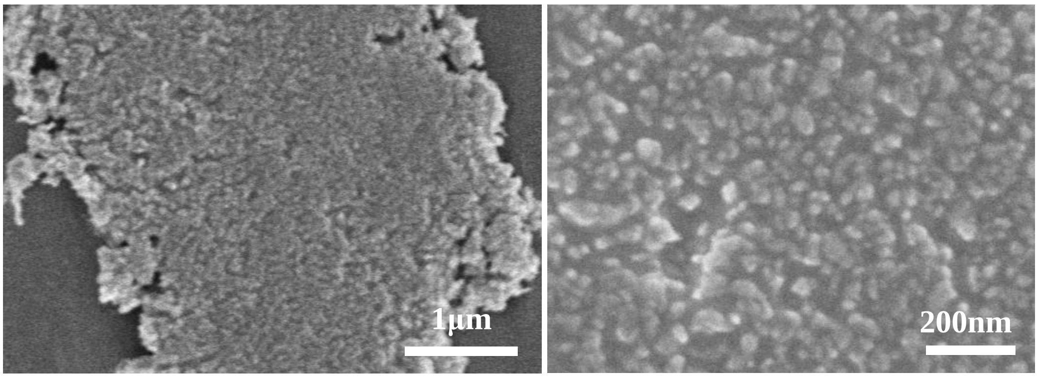

Fig. 2. SEM images of the synthesized β-SiC nanoparticles: (a) low-magnification; and (b) high-magnification

In order to investigate the microstructure of the SiC nanoparticles, the TEM is employed. A large amount of small SiC nanoparticles had a uniform size about 20-50 nm, as shown in Fig. 3(a). Fig. 3(b) is a typical TEM image of an individual nanoparticle, from which it can be seen that the small SiC nanoparticles are typical solid particle with diameter about 50 nm. With the further observation, some SiC nanoparticles had core-shell structure with the diameters lie between 40 nm and 80 nm, as shown in Fig. 3(c). From Fig. 3(d), a individual core-shell SiC nanoparticle can be clearly observed. The diameter of nanoparticle about 60 nm, the outer shell has a thickness about 5 nm, the inner cores have diameter about 50 nm. Fig. 3(e) displays a cracked core-shell nanoparticle. The obvious shell has a thickness about 5 nm. The obvious bumps formed nuclei. The intact outer shell and the imperfect core structure of nanoparticle are significant because it verifies the formation mechanism of the core-shell SiC nanoparticle.

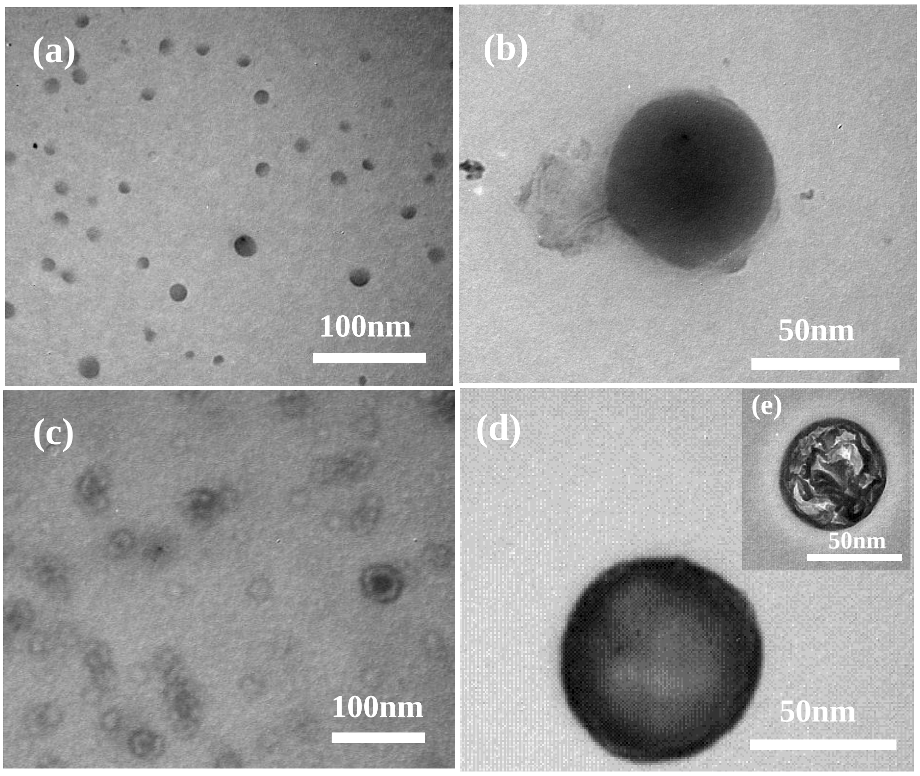

Fig. 3. (a) TEM image of the SiC nanoparticles; (b) TEM image of the individual SiC nanoparticles; (c) TEM image of the core-shell SiC nanoparticles; (d) TEM image of the individual core-shell SiC nanoparticle; (e) TEM image of the individual cracked SiC-1 nanoparticle

The results from XRD, SEM and TEM analyses altogether implied that the growth mechanism of SiC nanoparticles and core-shell nanoparticles should be illustrated as follows. In the sol-gel process, the corn powder was surrounded by silica and cobalt ions when the corn powder was added in the system. First, corn was decomposed into C particles, and metallic cobalt particles were formed from decomposition of cobalt nitrate during the carbothermal reduction. Subsequently, melted cobalt particles react with silica and produce various cobalt silicide active phases. The active phases exist between the C-SiO_2 interface and absorb carbon and silica to produce SiC. The reaction may occur between the C and silica therefore the outer shell will be formation. Unde the reaction conditions, silica layers outside the C particles will be changed into SiC, which forms the SiC outer shell. With the reaction proceeding, Si atoms enter into the inner of C particles, some small C particles completely chang into SiC. With Si atoms was gradually consumed, the SiC ceases to grow, so some big C particles chang into core-shell SiC.

To investigate PL properties of the synthesized SiC nanoparticles, the corresponding measurement was carried out at room temperature and a PL spectrum was obtained (Fig. 4). The SiC nanoparticles show especial photoluminescence properties under the different excitation wavelength. When the excitation wavelength moves from 290 to 330 nm, the peak intensity increases and the emission peak shifts from 378 to 372 nm (a blueshifted). When the excitation wavelength continues to increase, the emission peak disappears. The blueshifted is rarely observed before in SiC nanoparticles. Some studies have reported that the abnormal blueshifted when the excitation wavelength is smaller than 350 nm, which is likely caused by surface structures [5,8,15]. It is thus reasonable to conjecture that there are numerous core-shell nanoparticle with the special core–shell interface which can affect photoluminescence properties. When the excitation wavelength moves from 290 to 410 nm, two strong broad emission peaks centered at 452 nm and 469 nm. The emergence of peak at 452 nm and 469 nm may be caused by the defects in the special rough core–shell interface, the quantum size-confinement and internal structure defects. In addition, a strong broad ultra-violet emission at 414 nm under the excitation wavelength of 410 nm which exist weakly in other excitation wavelength, compared with the previous reported SiC/SiO_2 core-shell structure nanoparticles [3]. The emission at 414 nm is due to the core-shell structure effects. Thus, the luminescence characteristic of the synthesized SiC nanoparticles and core-shell nanoparticles depends strongly on their core–shell structure, quantum size-confinement, internal structure defects and core–shell interface defects.

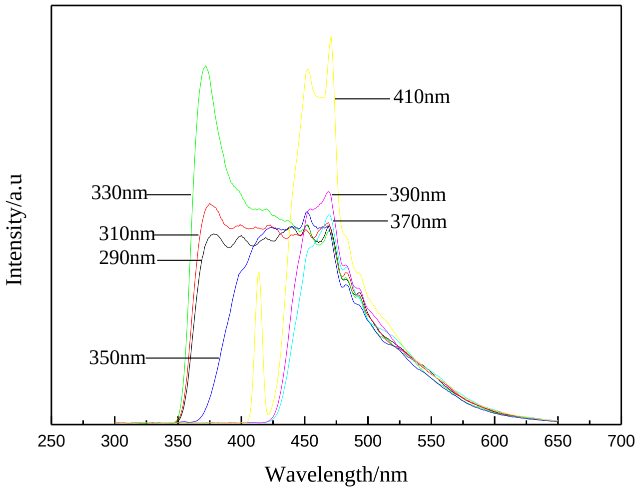

Fig. 4. PL spectrum of the synthesized SiC nanoparticles and core-shell nanoparticles

4. Conclusions

In summary, we have synthesized β-SiC nanoparticles and core-shell nanoparticles successfully by corn and TEOS via the carbothermal reduction method. A possible growth mechanism was proposed for the nanoparticles according to the characterization results. The synthesized nanoparticles and core-shell nanoparticles exhibit different photoluminescence properties and are expected to find a wide range of important applications in optoelectronic devices.

Acknowledgments

This work has been supported by Scientific Research Program Funded by Shaanxi Province Education Department (No. 16JK1270), The Scientific Research Projects of Weinan Normal University (No. 15YKS002).

References

[1] S. Yamada, B. Song, T. Asano, S. Noda, Appl. Phys. Lett. **99**, 201102 (2011).
[2] C. Dong, G. Zou, E. Liu, B. Xi, T. Huang, Y. Qian, J. Am. Ceram. Soc. **90**, 653 (2007).
[3] J. Wei, K. Z. Li, H. J. Li, H. B. Ouyang, Z. J. Li, C. Wang, Physica E **41**, 1616 (2009).
[4] E. J. Henderson, J. G. C. Veinot, J. Am. Chem. Soc. **131**, 809 (2009).
[5] J. Wang, S. J. Xiong, X. L. Wu, T. H. Li, P. K. Chu, Nano. Lett. **10**, 1466 (2010).
[6] L. Z. Cao, H. Jiang, H. Song, Z. M. Li, G. Q. Miao, J. Alloy. Compd. **489**, 562 (2010).
[7] H. J. Li, Z. B. He, Y. H. Chu, L. H. Qi, Q. G. Fu, Mater. Lett. **109**, 275 (2013).
[8] S. K. Yang, B. Kiraly, W. Y. Wang, S. L. Shang, B. Q. Cao, H. B. Zeng, Y. H. Zhao, W. Z. Li, Z. K. Liu, W. P. Cai, T. J. Huang, Adv. Mater. **24**, 5598 (2012).
[9] A. P. Magyar, I. Aharonovich, M. Baram, E. L. Hu, Nano. Lett. **13**, 1210 (2013).
[10] S. Meng, D. H. Wang, G. Q. Jin, Y. Y. Wang, X. Y. Guo, Mater. Lett. **64**, 2731 (2010).
[11] I. K. Yu, J. H. Rhee, S. Cho, H. K. Yoon, J. Nucl. Mater. **386-388**, 631 (2009).
[12] X. L. Wu, J. Y. Fan, T. Qiu, X. Yang, G. G. Siu, P. K. Chu, Phys. Rev. Lett. **94**, 026102 (2005).
[13] N. Herlin-Boime, J. Vicens, C. Dufour, F. Tenegal, C. Reynaud, R. Rizk, J. Nanopar. Res. **6**, 63 (2004).
[14] G. C. Xi, Y. Y. Peng, S. M. Wan, T. W. Li, W. C. Yu, Y. T. Qian, J. Phys. Chem. B. **108**, 20102 (2004).
[15] X. L. Wu, S. J. Xiong, J. Zhu, J. Wang, J. C. Shen, Paul K. Chu, Nano. Lett. **9**, 4053 (2009).

---

[*] Corresponding author: wangdongh1978@163.com