Металлофиз. новейшие технол. / Metallofiz. Noveishie Tekhnol.
2013, т. 35, № 5, сс. 623–632
Оттиски доступны непосредственно от издателя
Фотокопирование разрешено только
в соответствии с лицензией

СТРОЕНИЕ И СВОЙСТВА НАНОРАЗМЕРНЫХ И МЕЗОСКОПИЧЕСКИХ МАТЕРИАЛОВ

PACS numbers: 61.46.Hk, 78.30.Jw, 78.40.Me, 78.67.Bf, 81.07.Pr, 81.40.Tv, 82.35.Np

Microstructure and Optical Properties of PMMA Matrix Composites Containing LaB_6 Nanoparticles

Lijie Hu, Lin Zhang, Yifei Yuan, and Guanghui Min

School of Materials Science and Engineering, Shandong University,
73 Jingshi Road,
250061 Jinan, China

The lanthanum hexaboride (LaB_6) nanoparticles are synthesized via a solid state reaction in vacuum. Silane coupling agent is used for modifying the surface of the nanoparticles. This process is carried out in different solutions so as to ascertain the best modification technology. Modified LaB_6 nanoparticles are added to polymethyl methacrylate (PMMA) matrix by *in-situ* polymerization. Synthesized nanoparticles are characterized by XRD and TEM, the results show that the obtained particles have high degree of crystallinity and elliptical or cubic shape, the size ranged from 20 nm to 100 nm. In addition, FESEM and Medium infra-red spectrometers are used to prove the effect of surface modification of nanoparticles, alcohol solution can provide the best modification atmosphere for the modifying process, as LaB_6 nanoparticles modified in alcohol solution appear in uniformly elliptic shape and smallest size. Furthermore, the microstructure of PMMA/LaB_6 composites are characterized, and optical properties of the composites are tested by UV-vis-NIR spectrophotometry. Experimental results show that modified LaB_6 nanoparticles dispersed well in the PMMA matrix, the relationship between added LaB_6 nanoparticles and optical properties of PMMA matrix is demonstrated as well. PMMA matrix contained 0.02% wt. LaB_6 nanoparticles can block NIR effectively with slight influence on the high transparency of PMMA matrix.

Наночастинки гексабориду лантану LaB_6 синтезовано шляхом твердотільної реакції у вакуумі. Для модифікування поверхні частинок використовувалась сполучна речовина силан. Цей процес виконувався в різних розчинах для визначення найкращої технології модифікування. Модифіковані наночастинки LaB_6 додавалися до матриці поліметилметакрилату (ПММК) під час полімеризації. Синтезовані наночастинки досліджувались методом рентгеноструктурного аналізу та просвічуючої електронної мікроскопії, результати показують, що одержані наночастинки мають

високий ступінь кристалічності, еліптичну або кубічну форму і розміри від 20 до 100 нм. Крім того, для підтвердження впливу модифікації поверхні наночастинок використовувались автоемісійний сканувальний електронний мікроскоп та спектрометр середнього інфрачервоного діапазону. Спиртовий розчин може забезпечити найкраще навколишнє середовище для процесу модифікації, тому що наночастинки LaB_6, модифіковані в спиртовому розчині, мають однакову еліптичну форму та мінімальний розмір. Більше того, охарактеризовано мікроструктуру композитів ПММК/LaB_6, а їх оптичні властивості досліджено методами спектрофотометрії в ультрафіолетовому, видимому і ближньому інфрачервоному діапазонах. Результати експерименту показують, що модифіковані наночастинки LaB_6 добре розподілені в матриці ПММК. Продемонстровано також зв'язок між додаванням наночастинок LaB_6 та оптичними властивостями матриці ПММК. Матриця ПММК з 0,02% мас. LaB_6 може ефективно блокувати випромінення ближнього інфрачервоного діапазону при слабкому впливі на високу прозорість матриці ПММК.

Наночастицы гексаборида лантана LaB_6 синтезированы путем твердотельной реакции в вакууме. Для модифицирования поверхности наночастиц использовалось связующее вещество силан. Этот процесс выполнялся в различных растворах для определения наилучшей технологии модифицирования. Модифицированные наночастицы LaB_6 добавлялись к матрице полиметилметакрилата (ПММК) во время полимеризации. Синтезированные наночастицы исследовались методами рентгеноструктурного анализа и просвечивающей электронной микроскопии, результаты показали, что полученные наночастицы имеют высокую степень кристалличности, эллиптическую или кубическую форму и размеры от 20 до 100 нм. Кроме того, для подтверждения влияния модификации поверхности наночастиц использовались автоэмиссионный сканирующий электронный микроскоп и спектрометр среднего инфракрасного диапазона. Спиртовой раствор может обеспечить наилучшую окружающую среду для процесса модификации, так как наночастицы LaB_6, модифицированные в спиртовом растворе, имеют одинаковую эллиптическую форму и минимальный размер. Более того, охарактеризована микроструктура композитов ПММК/LaB_6, а их оптические свойства исследованы методами спектрофотометрии в ультрафиолетовом, видимом и ближнем инфракрасном диапазонах. Результаты эксперимента показывают, что модифицированные наночастицы LaB_6 хорошо распределены в матрице ПММК. Продемонстрирована также взаимосвязь между добавлением наночастиц LaB_6 и оптическими свойствами матрицы ПММК. Матрица ПММК с 0,02% масс. LaB_6 могла эффективно блокировать излучение ближнего инфракрасного диапазона при слабом влиянии на высокую прозрачность матрицы ПММК.

Key words: LaB_6 nanoparticles, PMMA, microstructure, optical properties, surface modification.

(Received September 27, 2012)

1. INTRODUCTION

Lanthanum hexaboride (LaB_6) was widely used in cathode as an excellent thermionic electron emitter material, the relatively low work function yield high current at low cathode temperature, resulting in greater brightness and longer life [1, 2]. Recently, LaB_6 had drawn much attention due to other excellent characteristics such as great absorbance in near-infrared light, bringing itself wide applications in solar heat control [3].

It was advantageous to add nanomaterials into polymer to prepare a nanocomposite since this kind of material often showed excellent properties that neither of the two components would have [4–7]. Polymers containing LaB_6 are studied extensively because of their outstanding performance in daily sunlight regulation. PMMA was the primary choice for the preparation of polymeric nanocomposites because of its superior properties such as high strength, compatibility with ceramics, dimensional stability, and especially high optical clarity [8–10]. LaB_6-doped polyvinylbutyral (PVB) laminates [11] and PMMA [12] prepared through melt extrusion exhibited effective absorption of near infrared (NIR) and good transmittance of visible radiation (VIS). However, it is difficult to get a good distribution of inorganic nanoparticles in the polymer matrix, because the problem of nanoparticle agglomeration often existed, moreover the interfacial adhesion between inorganic nanoparticles and the matrix is poor. Modifying agents could be used to improve the wettability between nanoparticles and matrix [13–16], however modification technology of LaB_6 nanoparticles had not been dealt in depth, it is of vital importance as it could allow LaB_6 nanoparticles to be incorporated into a polymer matrix to give a well combined composite material.

In this report, the best atmosphere for modifying the surface of LaB_6 is ascertained among several solutions using silane coupling agent first. Then modified LaB_6 nanoparticles were added to PMMA matrix by *in-situ* polymerization and microstructure and optical properties of the composites are also characterized.

2. EXPERIMENTAL PROCEDURE

2.1. Surface Modification of LaB_6 Nanoparticles

LaB_6 nanoparticles were synthesized via solid state reaction at 1200°C for 2 hours in the vacuum with $LaCl_3$ and $NaBH_4$. Obtained particles were dissolved in deionized water (DW), dilute hydrochloric acid (8% HCl) and alcohol solution (AL, 50%), separately. And then 0.4 ml silane coupling agent (KH550) is added into 20 ml above-mentioned solutions to finish the surface modification of LaB_6 particles. The process is accompanied by supersonic vibration at 40°C. As the reference sam-

ple, LaB_6 nanoparticles were also added into DW without silane coupling agent existing and underwent supersonic vibration at 40°C as well.

2.2. Composites Preparation

The PMMA matrix composites containing LaB_6 nanoparticles were prepared as shown in Fig. 1. The silane coupling agent treated LaB_6 was well dispersed in methyl methacrylate (MMA) under supersonic vibration. A certain amount of benzoyl peroxide (BPO) working as initiating agent was added to above mentioned solution and the pre-polymerization of MMA was carried out at about 90°C accompanied by mechanical mixing. After pre-polymerization, the mixture was poured into a mold and then kept at 45°C in vacuum for 20 hours.

2.3. Testing Methods

X-ray diffraction (XRD) measurement is performed on Japan Rigaku D/max-RB X-ray diffractometer ($\lambda = 1.5406$ Å). The transmission electron microscopy (TEM) image is obtained on a Hitachi H-800 transmission electron microscopy with 200 keV accelerated voltage. Medium infra-red spectrum (MIS) is recorded on a VERTEX-70 infrared spectrometer. Field emission scanning electron microscopy (FESEM) images are taken on a JSM-6700F scanning electron microscope at 3.0 kV acceleration voltages. Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra of the products are recorded on UV-vis-NIR spectrophotometry (U-4100).

3. RESULTS AND DISCUSSION

3.1. Formation of LaB_6 Nanoparticles

The formation of LaB_6 nanoparticles is confirmed through XRD analysis, FESEM and TEM characterization, as shown in Fig. 2 and Fig. 3. XRD result shown in Fig. 2 indicated the products were pure LaB_6 and had good crystallinity. Fig. 3 demonstrated that most particles were elliptical or

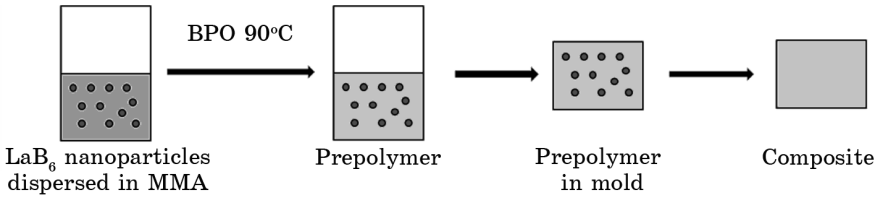

Fig. 1. Procedure of preparation of PMMA matrix composites containing LaB_6 nanoparticles.

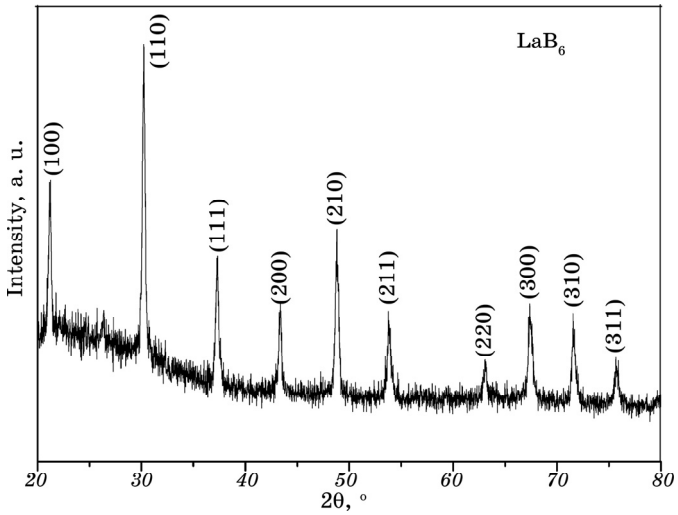

Fig. 2. XRD image of LaB_6 nanoparticles.

cubic shaped with sizes ranging from 20 nm to 100 nm. The inserted image in Fig. 3, *b* depicted the crystalline structure, it clearly showed an interplanar distance of 4.16 Å, corresponding to the theoretical value 4.15 Å of LaB_6 (100) planes.

3.2. Modification of LaB_6 Particles

Figure 4 showed the MIS result of LaB_6 nanoparticles treated in different solutions. The peaks observed at 3440 cm^{-1} and 1630 cm^{-1} in Curves *1*, *2*, and *3* were that of B_6 structure according to the literature [17].

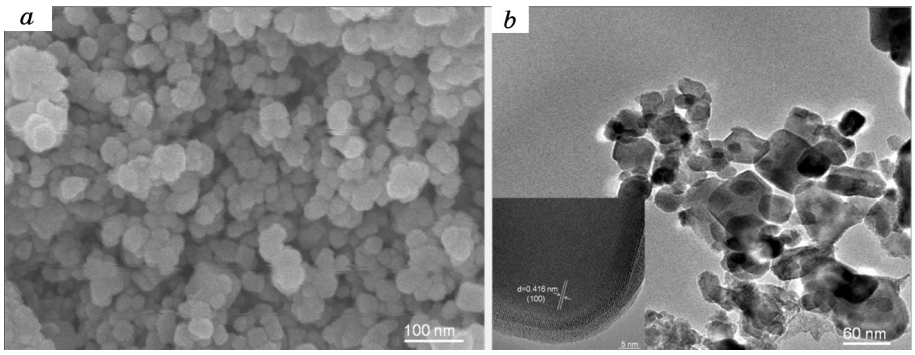

Fig. 3. Morphology and structure images of LaB_6 nanoparticles: FESEM image of the products (*a*), TEM image of LaB_6 nanoparticles (*b*). The inserted image: lattice structure.

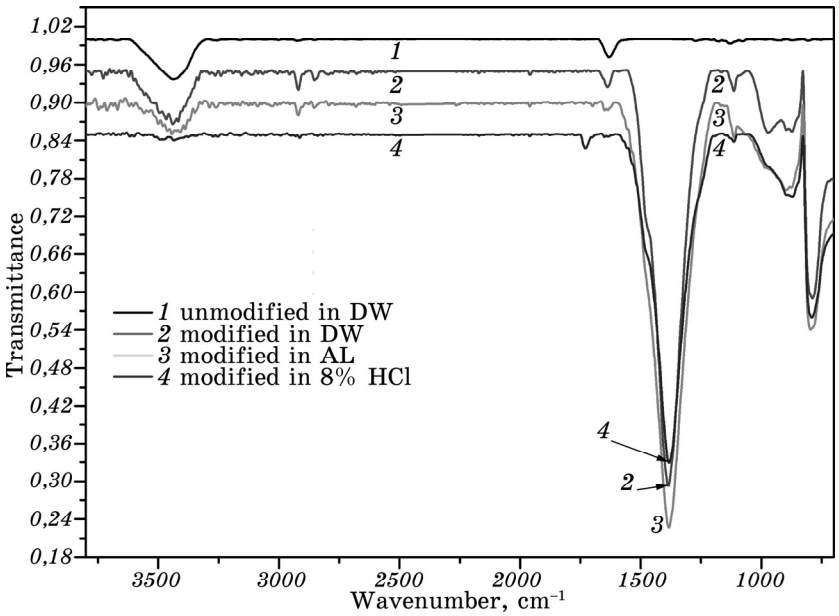

Fig. 4. Medium infra-red spectrum of LaB_6 treated in different solutions.

Two faint peaks disappeared in Curve *4*, this might be caused by destructive effect of strong acid atmosphere to B_6 structure. Compared with Curve *1*, new characteristic peaks around 1380 cm^{-1}, 1113 cm^{-1}, 900 cm^{-1} and 785 cm^{-1} appearing in Curves *2*, *3* and *4* are attributed to the symmetric bending vibration of C–CH_3, stretching vibration of C–N, rocking vibration of –CH_3 and stretching vibration of Si–C (usually two or more peaks in the range of 690–890 cm^{-1}) in SCA, respectively [18]. So it could be concluded that silane coupling agent exists in LaB_6 nanoparticles by certain kind of connecting mode.

Figure 5 showed the morphology of LaB_6 nanoparticles modified in different solutions. It could be seen from Fig. 5, *a* that the unmodified sample is mostly composed of cubic nanoparticles appearing in agglomeration to some extent. Particles modified in DW show different morphology with an elliptic shape, indicating that their surface had been, though not uniformly, covered by silane coupling agent. Sample modified in 8% HCl exhibits serious grain agglomeration in spite of similar morphology, as shown in Fig. 5, *a*, so acid atmosphere could not guarantee satisfactory surface modification of LaB_6 particles using silane coupling agent. Particles in Fig. 5, *d* appear in uniformly elliptic shape and the degree of grain agglomeration is reduced to the smallest.

Based on the results above, we come to the conclusion that the solution adopted during surface modification process has strong effect on the modification result of LaB_6 nanoparticles, and AL is the best solu-

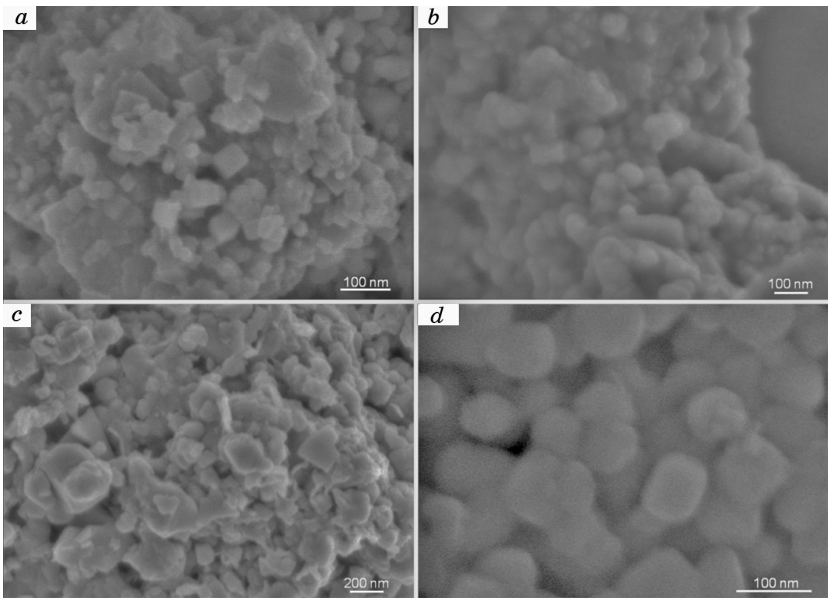

Fig. 5. FESEM results of LaB_6 nanoparticles modified in different solutions: (*a*) unmodified in DW, (*b*)–(*d*) modified in DW, HCl and AL, respectively.

tion among all these mentioned above for this process.

3.3. Microstructure of PMMA Matrix Composites Containing LaB_6 Nanoparticles

Figure 6 shows the distribution of LaB_6 particles with different weight ratios from zero to 0.03% in PMMA matrix. Most nanoparticles dispersed well in matrix and the shape is intact. The nanoparticles show uniform morphology, although LaB_6 content in the composites increases. Because of the silane modification of LaB_6 nanoparticles, inorganic nanoparticles used to agglomerate spontaneously are not shown here. First, the addition of silane coupling agent reduced surface activity of nanoparticles and prevents LaB_6 nanoparticles from aggregation together successfully. Meanwhile it works as the bridge between inorganic nanoparticles and polymer matrix, and then improves compatibility between organic and inorganic particles, producing more evenly distributed inorganic nanoparticles within organic matrix.

3.4. Optical Properties of PMMA Matrix Composites Containing LaB_6 Nanoparticles

Figure 7 showed the result of UV-vis-NIR absorption spectra of the

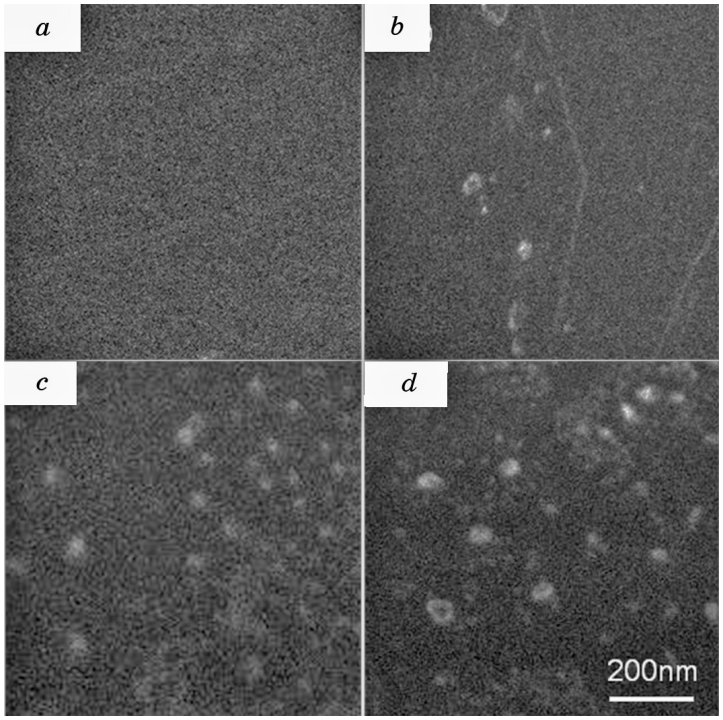

Fig. 6. FESEM images of LaB_6 particles with different weight percents in PMMA: 0% (*a*), 0.01% (*b*), 0.02% (*c*), 0.03% (*d*).

composites. Spectral absorption of the composites had an increasing tendency as LaB_6 mass fraction increased, especially at the wavelength 300–1600 nm. There is linear relationship between the absorption and LaB_6 weight ratios, as the absorption value substantially increases 0.5 with the addition of the LaB_6 increased by 0.01% wt. This linear formulation could be given as follows

$$y = A_{\mathrm{PMMA}} + 50x \quad (x = 0.01, 0.02, 0.03), \tag{1}$$

where y and A_{PMMA} are the absorption of PMMA contained LaB_6 composites and pure PMMA, respectively, x equals to the LaB_6 mass fractions in the composites. However, LaB_6 content had a slight effect on the absorption value from 1700 nm. One can note that Curve *2* is substantially parallel to Curve *1* from 300 to 600 nm. The absorption of Curve *3* decreases sharply around 600 nm, while curve *4* displayed similar but weaker tendency. That is to say, Curve *3* had comparatively lower absorption at VIS-light, and comparatively higher transmittance meanwhile. So, PMMA matrix containing 0.02% wt. LaB_6 nanoparticles could prevent NIR effectively with slight influence on the high

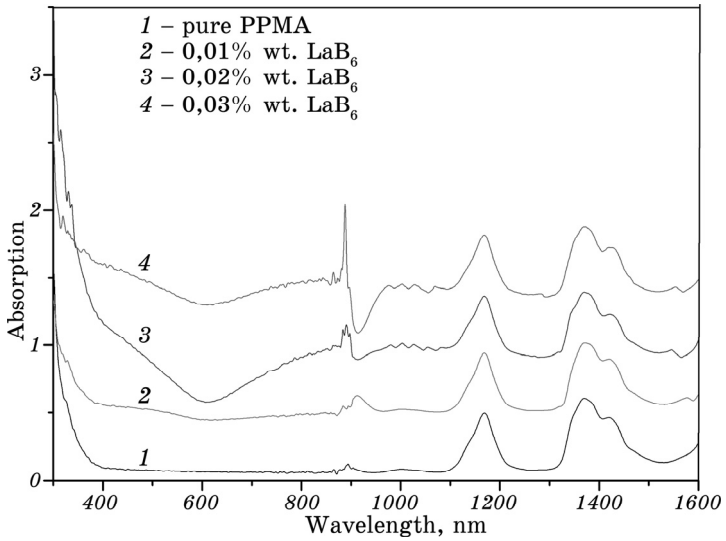

Fig. 7. Absorption spectra of PMMA matrix composites contained LaB_6 nanoparticles.

transparency of PMMA matrix.

4. CONCLUSION

The surface of LaB_6 nanoparticles is treated by silane coupling agent among several solutions, and the modified atmosphere is found to have a strong influence on the morphology of the nanoparticles. LaB_6 sample modified in AL is composed of uniformly elliptic particles without agglomeration. So, silane coupling agent could perform as an excellent modifier for surface treatment of LaB_6 materials in AL solution. Furthermore, modified LaB_6 nanoparticles are dispersed well in PMMA matrix, and one can conclude that modification of nanoparticles plays a significant role in preventing inorganic nanoparticle agglomeration and in improving interfacial adhesion between inorganic nanoparticles and polymer matrix. PMMA matrix containing 0.02% wt. LaB_6 nanoparticles has a significant effect on blocking NIR among mentioned groups of composites.

This research was supported by Key Project of Natural Science Foundation of Shandong Province China (No. Z2007F09) and National Science Foundation of China (No. 51102154).

REFERENCES

1. A. Hirakimoto, S. Ohnishi, H. Maeda, T. Kishi, T. Shiota, T. Tamura, M. Ukita,

S. Fujita, and M. Kamegawa, *J. Spectrochim. Acta B. Atomic Spectroscopy*, **59**: 1101 (2004).
2. H. Zhang, J. Tang, J. S. Yuan, J. Ma, N. Shinya, K. Nakajima, H. Murakami, T. Ohkubo, and L. C. Qin, *Nano Lett.*, **10**: 3539 (2010).
3. S. Schelm and G. B. Smith, *Appl. Phys. Lett.*, **82**: 4346 (2003).
4. K. M. Yun, A. B. Suryamas, C. Hirakawa, F. Iskandar, and K. Okuyama, *Langmuir*, **25**: 11038 (2009).
5. M. Inkyo, Y. Tokunaga, T. Tahara, T. Iwaki, F. Iskandar, C. J. Hogan, and K. Okuyama, *Ind. Eng. Chem. Res.*, **47**: 2597 (2008).
6. M. J. Yang and Y. Dan, *J. Appl. Polym. Sci.*, **101**: 4056 (2006).
7. F. M. Pavel and R. A. Mackay, *Langmuir*, **16**: 8569 (2000).
8. S. H. Li, J. Qin, A. Fornara, M. Toprak, M. Muhammed, and D. K. Kim, *Nanotechnology*, **20**: 185607 (2009).
9. H. C. Kuan, S. L. Chiu, C. H. Chen, C. F. Kuan, and C. L. Chiang, *J. Appl. Polym. Sci.*, **113**: 1959 (2009).
10. G. B. Smith, C. A. Deller, P. D. Swift, A. Gentle, P. D. Garrett, and W. K. Fisher, *J. Nanopart. Res.*, **4**: 157 (2002).
11. S. Stefan and G. B. Smith, *J. Appl. Phys.*, **97**: 124314 (2005).
12. L. J. Hu, G. H. Min, and X. Yang, *Adv. Mater. Res.*, **150–151**: 703 (2011).
13. H. Y. Chen and E. Ruckenstein, *J. Chem. Phys.*, **131**: 244904 (2009).
14. Y. Xiong, G. S. Chen, and S. Y. Guo, *J. Polym. Sci., Part B Polym. Phys.*, **46**: 938 (2008).
15. R. Y. Hong, J. H. Li, L. L. Chen, D. Q. Liu, H. Z. Li, Y. Zheng, and J. Ding, *Powder Technol.*, **189**: 426 (2009).
16. W. Pan, H. Q. Zhang, and Y. Chen, *J. Mater. Sci. Technol.*, **25**: 247 (2009).
17. P. Teredesai, D. V. S. Muthu, N. Chandrabhas, S. Meenakshi, V. Vijayakumar, P. Modak, R. S. Rao, B. K. Godwal, S. K. Sikka, and A. K. Sood, *Solid State Commun.*, **129**: 791 (2004).
18. S. F. Weng, *Fourier Transform Infrared Spectrometer* (Beijing: Chemical Industry Press: 2010) (in Chinese).