Research Article

Fabrication of Polystyrene/Detonation Nanographite Composite Microspheres with the Core/Shell Structure via Pickering Emulsion Polymerization

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Polystyrene microspheres coated with detonation nanographite particles have been prepared by Pickering emulsion polymerization using azobisisobutylonitrile (AIBN) as initiator in aqueous solutions. In the present techniques, the pristine detonation nanographite particles were employed as stabilizer of Pickering emulsion and then were armored on the as-prepared polystyrene cores by the thermal polymerization. The composite microspheres of polystyrene/detonation nano-graphite (PS/DNG) were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), thermogravimetric and differential thermal analysis (TGA-DTA), and Fourier transformation infrared spectrum (FT-IR). FE-SEM indicates that the resulting samples retain spherical shape, with the uniform size ranging from 100 to 150 μm and good dispersity. FT-IR presents the possible formation mechanisms of PS/DNG composites. The functional groups on the surface of polystyrene and modified detonation nano-graphite particles have played an important role for the formation of PS/DNG composites. Moreover, the wettability of different nano-graphite was also tested.

1. Introduction

In the past years, constructions of inorganic-organic composites have open up a novel route to get new materials with predefined structure and performance [1, 2]. In such hybrid inorganic-organic materials, the armored nanoparticles can endow the composites with some special properties [3], such as excellent photovoltage properties [4], photocatalytic performance [5, 6], special optical property [7], and magnetic property [8]. In such hybrid inorganic-organic materials, the inorganic particles contribute to increasing the complexity and functionality of the composites through incorporation as one component in a multilevel-structured material where there is a synergistic interaction between the organic and inorganic components [9, 10].

Graphite, which is naturally abundant, has been widely used as electronically conducting filler for preparing and conducting polymer composites in the last decades [11–13].

To achieve a high performance graphite-based inorganic-organic composite, disperses of the expanded graphite nanosheets, layered graphite oxide, or nature flake graphite in the various polymer matrixes have attracted active research interest. Typically, graphite/PMMA [14], graphite/PS [15], graphite/PVC [16], graphite/nylon 6 [17], and other hybrid composites have been obtained in the presence of graphite particles. Meanwhile, the introduction of inorganic expanded graphite particles into polymer matrix has lead to a remarkable improvement in thermal, mechanical, and electrical properties in comparison with the pure polymer materials and hence can offer a wide range of potential applications, such as electromagnetic interference (EMI) shielding of computers and electronic equipments, electrode materials, conductive adhesive for electronics packaging, flip-chips, cold solders, static charge dissipating materials, cathode ray tubes and fuel cells, corrosion resistant and radar absorbent coating, and switching devices [18–21]. Up to now,

a variety of methods have been established to fabricate the above-mentioned graphite-based inorganic-organic composites including the mechanical mixing [22], melt mixing [23], and in situ controlled radical polymerization [24]. Among those techniques, the emulsion polymerization has been paid much attention because of its versatile and robust traits to prepare well-defined hybrid composites. The graphite-based inorganic-organic composites were facilely attained by the free radical emulsion polymerization of styrene in the presence of the graphite particles. However, in comparison with the great achievement in the expended graphite/polymer composites, few studies have been reported on the fabrication of composites of polystyrene/detonation nanographite with the core/shell structure.

Detonation nanographite materials synthesized by detonation of oxygen-deficient explosives, with their advantages of good thermal and electrical conductivity, microwave absorption, and lubricating ability, have been widely used in industry, for example, as coating materials for electrical conductors, as graphite emulsions for kinescopes, as electromagnetic shields, as gaskets, and as absorbents for removing spilled oil from water system [25–27]. In order to further develop and widen the applications of detonation nanographite (DNG), we attempt to fabricate the polystyrene/detonation nanographite (PS/DNG) composites via Pickering emulsion of styrene in the presence of the detonation nanographite particles. In this route, nanographite solid particles are absorbed irreversibly on the monomer-water interface and act as effective stabilizers to construct the Pickering emulsion firstly. Then, the particles are captured on the surface of polymer microspheres during the processes of thermal polymerization. Compared with conventional preparation techniques, the polystyrene/detonation nanographite (PS/DNG) composites could be obtained in a one-pot synthesis with the absence of common stabilizers via Pickering emulsion [28–30]. Moreover, the structures of resultant PS/DNG composites have been characterized by FESEM, XRD, TGA-DTA, and FT-IR, respectively. A possible formation mechanism was proposed to explain the structure of products accordingly.

2. Experimental Section

2.1. Materials.
Detonation nanographite particle samples (primary particle size, 16 nm; specific surface area $583.6 \, m^2 \cdot g^{-1}$ by BET, density $1.58 \, g \cdot cm^{-3}$) used for this investigation were provided by Shaanxi Yilin Company, a professional detonation diamond producer. Ethyl alcohol, sulphuric acid, and oleic acid were purchased from Xi'an Reagent Company (analytical grade). Styrene of analytical grade (Tianjin Reagents Company) was distilled under reduced pressure before use. Azobisisobutylonitrile (AIBN, Tianjin Reagents Company) was of chemical grade and was utilized without further purification. Deionized water was used throughout the experimental work.

2.2. Synthesis of PS/DNG Composites.
Acid treatment of primitive detonation nanographite was used to improve their wettability behaviors in water by the soak methods with the sulphuric acid and oleic acid, respectively. In a typical procedure, 0.5 g DNG was mixed with 40 mL concentrated sulphuric acid (98%). The mixture was then heated to 60°C for 20 min and cooled naturally to room temperature (25°C). Afterwards, the suspensions were centrifuged. The obtained solid particles were named as sulphuric acid-modified nano-graphite. Similarly, mixture of 0.5 g DNG and 40 mL oleic acid was used to prepare the oleic-modified nano-graphite.

Polystyrene/detonation nanographite (PS/DNG) composites were synthesized through Pickering emulsion polymerization. A typical preparation procedure is detailed as follows: a quantity of 0.0020 g of detonation nanographites was dispersed in 30 mL of deionized water to form the detonation nanographite/water dispersions. A quantity of 0.3000 g of azobisisobutyronitrile was dissolved in 2 mL of styrene and subsequently was mixed with the aqueous detonation nanographite dispersions. The stable styrene-in-water Pickering emulsion stabilized by detonation nanographite was generated via ultrasonic processor for 20 min. The system was degassed by purging with nitrogen gas for 10 min and was subsequently polymerized at 75°C for 8 h. After reaction, the mixture systems were centrifuged. The obtained polystyrene/detonation nanographite (PS/DNG) composites were washed with water and ethyl alcohol, respectively, and followed by being dried in vacuum at 40°C for 4 h.

2.3. Characterizations of PS/DNG Composites.
The type of Pickering emulsion was inferred by observing what happened when a drop of emulsion was added into water or styrene. Oil-in-water emulsions were dispersed in water and remained as drops in oil, while water-in-oil emulsions were dispersed in oil and remained as drops in water [31, 32]. X-ray diffraction (XRD) patterns were obtained by a Rigaku D/MAX-3C X-ray diffraction meter, using Cu Kα radiation ($\lambda = 1.54178 \, Å$) in the 2θ range from 20° to 70° with 0.02°/min. FT-IR traces of products were collected by a Nicolet 360 Fourier transmitting infrared spectrometer. The differential thermal analysis (DTA) and thermogravimetry analysis (TGA) were performed using a TA-50H thermal analyzer (Shimadzu) at a heating rate of 20°C/min under the stream of nitrogen.

3. Results and Discussion

The scheme, as illustrated in Figure 1, was the formation processes of polystyrene (PS) microspheres encapsulated with the detonation nanographite by Pickering emulsion method. In this route, the detonation nanographite was employed as Pickering stabilizer and encapsulated in the Pickering droplet by sonication emulsification. After thermal polymerization, polystyrene (PS) microspheres armored with detonation nanographite were formed.

3.1. Character of Pickering Emulsion.
According to the fundamentals of Pickering emulsions, the wettability behaviors of inorganic nanosized particles in oil-water (styrene-water) system should play critical roles for the fabrication of stable Pickering emulsions [33, 34]. Hereby, it is essential to
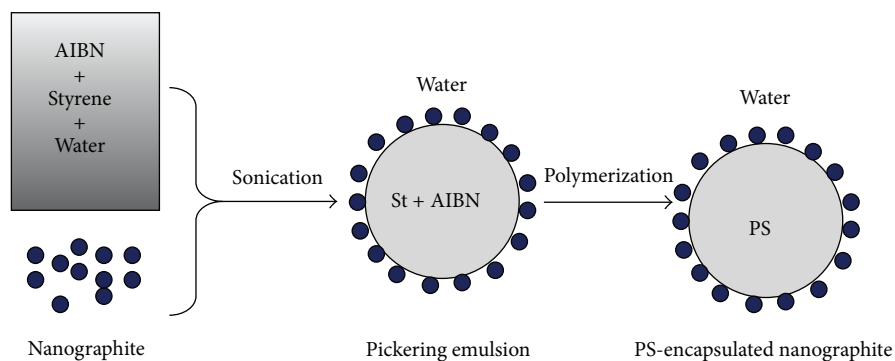
FIGURE 1: Formation of PS microspheres with encapsulated nanographite by Pickering emulsion.
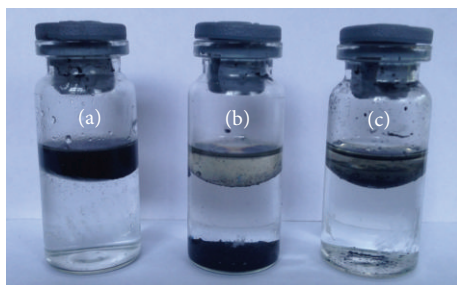

FIGURE 2: Distribution of pristine detonation nano-graphite, sulphuric acid-modified nanographite, and oleic-modified nanographite in styrene-water system.

check the location of detonation nanographite particles in oil-water system during the formation processes of stable nanographite-styrene (AIBN)-water Pickering emulsion. In the experiment of hydrophilicity or hydrophobicity testing of detonation nanographite particles, a droplet of nanographite suspension was diluted into a styrene-water mixture, followed by violent shaking and undisturbed settling. The optical micrograph of distribution of pristine detonation nano-graphite, sulphuric acid modified-nanographite, and oleic-modified nanographite in styrene-water system are shown in Figure 2, respectively. From Figure 2(a), it can be seen that the oleic-modified nanographite particles disperse preferentially in the upper layer of styrene due to their hydrophobicity, while sulphuric acid-modified nanographite particles disperse mainly in the under layer of water due to their hydrophilicity in Figure 2(b). Only pristine detonation nanographite particles can assemble spontaneously at water-styrene interface and congregate into an elastic particle-formed film at interface as shown in Figure 2(c). Therefore, the pristine detonation nanographite particles should be the optimal nanosized inorganic particles to form a stable nanographite-styrene (AIBN)-water Pickering emulsion in comparison with the oleic-modified or sulphuric acid-modified nanographite particles.

Based on the above-mentioned test, the nanographite-styrene (AIBN)-water Pickering emulsion can be formed via adding pristine detonation nanographite particles into styrene (AIBN)-water system by succeeding sonication emulsification technique. In our experiments, the optical images were taken firstly to analyze the status of nano-graphite-styrene (AIBN)-water Pickering emulsion. Figure 3 shows the typical optical micrographs of Pickering emulsion for the fabrication of polystyrene/detonation nanographite (PS/DNG) microspheres. It can be seen that the emulsions are oil-in-water type, as referred from the fact that the emulsions were dispersed rapidly in water and remained as drops of styrene. The droplets were polydispersive in size due to employing sonication emulsification technique, in which the droplets size is governed by the sonication time and ultrasonic intensity on the emulsion droplets [35]. Compared to the pure styrene droplets, the decline in transparency is ascribed to the cases that large amount of nanographite particles were densely anchored onto the surface of styrene droplets as seen in Figure 3(b), while a few nanographite particles were encapsulated within the droplets. Moreover, it has been ascertained that the Pickering emulsion stabilized by the detonation nanographite particles depended largely on the nanographite concentrations [36]. When nanographite concentration was low, the droplets were sparsely covered by particles and were more liable to coalesce into big droplets.

3.2. Morphology of PS/DNG Composite Microspheres. The formation of polystyrene/detonation nanographite (PS/DNG) composite microspheres can be classified as polymerization initiated by AIBN. During the emulsification process of styrene and nanographite dispersion, styrene is a hydrophobic monomer, and the droplets of styrene dispersing in the aqueous phase can be well-protected by nanographite particles to form a stable suspension in water. That is to say, the detonation nanographite particles as surfactants have anchored at the interface of styrene monomer and water. The styrene monomer and AIBN initiator were well-protected by detonation nanographite particles. From above-mentioned mechanisms, it can be inferred that polymerization reaction should occur mainly in styrene droplets since AIBN is also a hydrophobic initiator. As a result, the core-shell structure polystyrene/detonation nanographite microspheres should be fabricated by subsequently thermal polymerization in the Pickering emulsion system of nanographite-styrene (AIBN)-water.
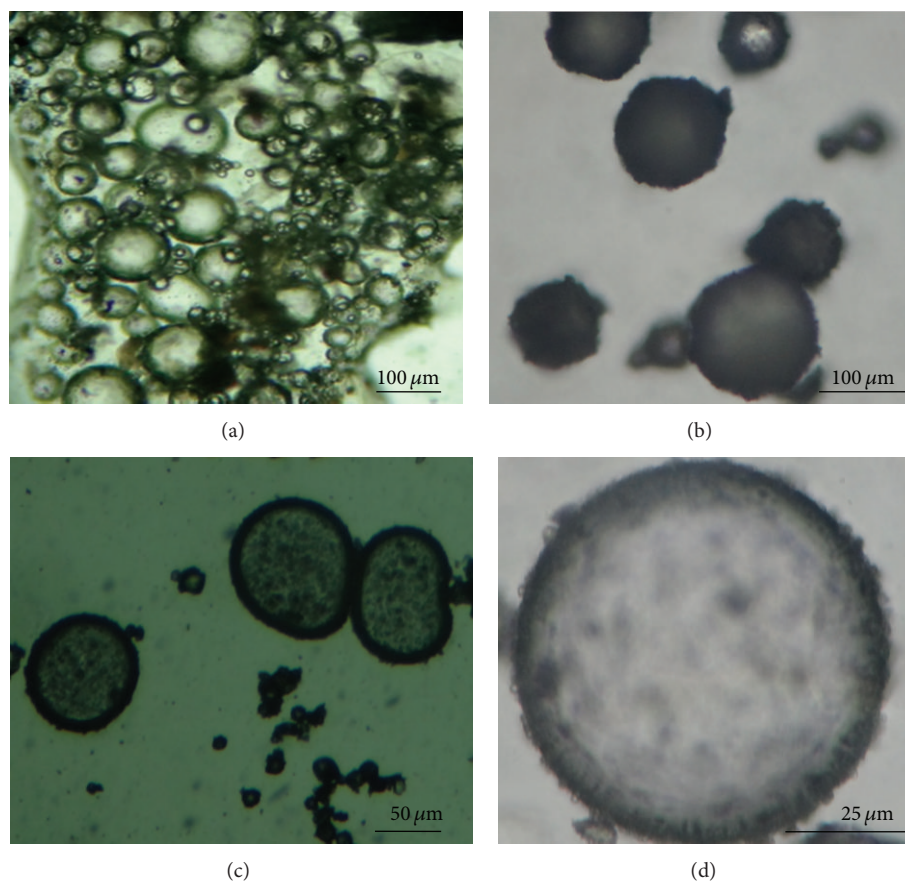
(a)

(b)

(c)

(d)

FIGURE 3: Optical picture of a droplet of the styrene-in-water Pickering emulsion stabilized by detonation nanographite particles.

SEM micrographs of PS/DNG samples are shown in Figure 4. Figure 4(a) displays general images of PS/DNG composite microspheres; it can be clearly seen that the polystyrene/detonation nanographite (PS/DNG) composite microspheres have ordered spherical shape and possess a good dispersion. SEM image in Figure 4(b) reveals the morphology of PS/DNG microspheres under high magnifications observation. In Figure 4(c), the spherical structure of polystyrene/detonation nanographite microspheres can be further verified, and the diameter of PS/DNG microspheres ranges from 100 μm to 150 μm. Careful observation of a typical PS/DNG microsphere in Figure 4(d) shows that the surfaces of the PS cores are attached by many detonation nanographite particles, and the shells have roughly textural properties, exhibiting a distinct core-shell morphology. Moreover, the diameter of nanographite attached onto the PS cores is about 10–20 nm estimated from Figure 4(d).

3.3. FT-IR of PS/DNG Composite Microspheres. The formation textures of polystyrene (PS) microspheres encapsulated with the detonation nano-graphites by Pickering emulsion method can be demonstrated by the changes of Fourier transformation infrared spectrum. The transformations of surface functional groups of pristine detonation nano-graphite, sulphuric acid-modified nano-graphite,

oleic-modified nanographite particle, pure polystyrene, and polystyrene/detonation composite samples are observed in Figure 5, respectively. In Figures 5(a) and 5(b), the typical adsorption bands of polystyrene at 3030–2800 cm^{-1}, 1400–1300 cm^{-1}, and 756–698 cm^{-1} are clearly seen [37, 38], confirming that PS indeed has been synthesized in the emulsion polymerization using azobisisobutylonitrile (AIBN) as initiator in aqueous solutions. For the spectrum of pristine and surface modified detonation nanographite samples, the broadband from 3500 to 3300 cm^{-1} is the absorption peak corresponding to the stretching of –OH. The band at 1329 cm^{-1} is attributed to the stretching vibration of –OH. The characteristic absorption peaks of graphite at 1212 and 1096 cm^{-1} are due to the stretching of the –C–O bonds. The absorptions at 1475, 812, and 505 cm^{-1} are overlapped and related to the C–H outer bending vibrations [39–41]. In the FT-IR spectrum of sulphuric acid-modified nanographite (Figure 5(e)), the bands at 2750~3000 cm^{-1} are the C–H out-of-plane bending vibrations. The peaks at 1700 cm^{-1} and 1200 cm^{-1} are corresponded to the –C=O and –C=C stretching vibration [42]. In the FT-IR spectrum of oleic-modified nanographite particle (Figure 5(d)), one strengthening –OH vibration absorption bands at 3500 to 3300 cm^{-1} appears when the nanographite is treated by oleic acid [43]. In comparison, the characteristic peaks in
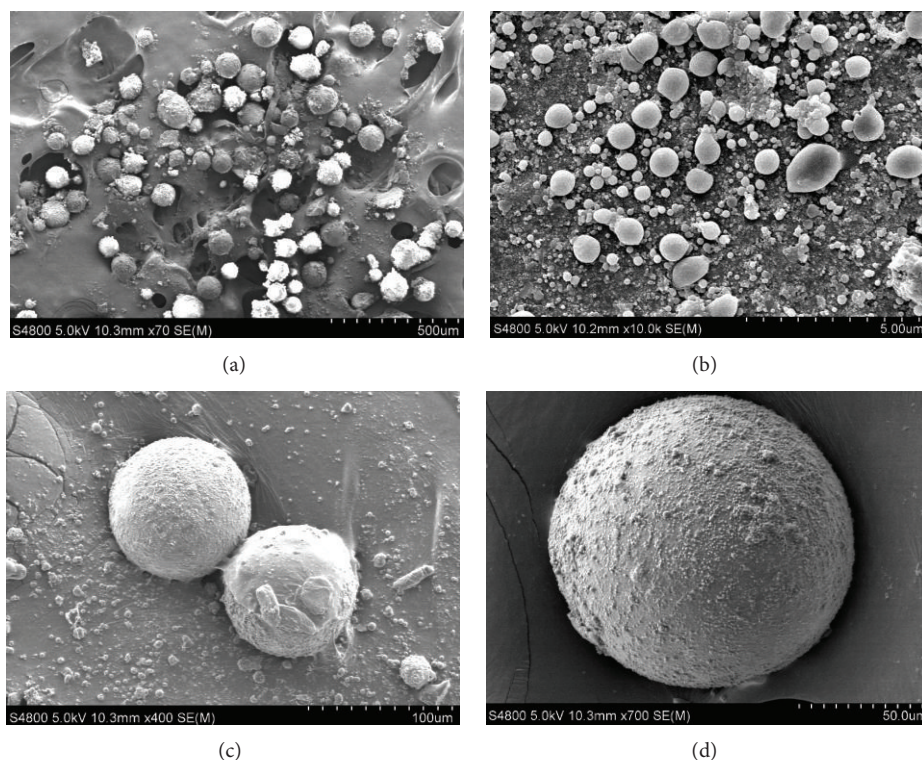
(a)

(b)

(c)

(d)

FIGURE 4: SEM micrographs of polystyrene/detonation nanographite (PS/DNG) composite microspheres.
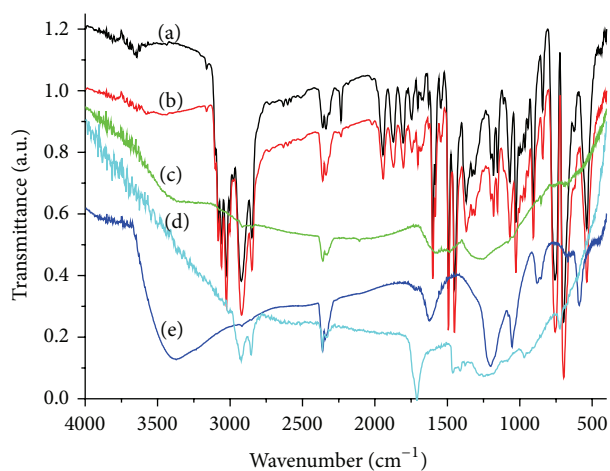

FIGURE 5: FT-IR of samples of (a) pure polystyrene, (b) polystyrene/detonation nanographite (PS/DNG), (c) pristine detonation nanographite, (d) oleic-modified nanographite particle, and (e) sulphuric acid-modified nanographite samples.

the polystyrene/detonation nanographite (PS/DNG) composite microspheres expected at $3425 \, cm^{-1}$, $1700 \, cm^{-1}$ and $1200 \, cm^{-1}$ have shifted, respectively, to 3432, 1708, and $1206 \, cm^{-1}$. All of these shifts imply that the –OH, –C=O, –C=C functional groups of PS have interacted with the nanographite particles [44, 45]. Hence, it is further illustrated that PS cores were not simply encapsulated by detonation nanographite particles, but a molecular interaction may

exist at the interface of PS copolymer and nanographite particles.

3.4. XRD of PS/DNG Composite Microspheres. XRD patterns of nanographite particles, polystyrene/detonation nanographite (PS/DNG) composites, and pure polystyrene are shown in Figure 6, respectively. In Figure 6(a), detonation nanographite particles are belonged to graphite-2 h structure (JCPDS file no. 41-1487) [46]. The three main peaks at $2\theta =$ 26.6°, 44.6°, and 76.4° can be attributed to (002), (101), and (110) planes [46]. Thereinto, the (002) peak represents the perpendicular direction (*c*-axis) of graphite hexagonal planes [47]. The spectrum in Figure 6(a) is a broadened band, which shows that the nanographite grains are very small. The crystallite size can be estimated from broadening peaks by Scherrer equation [48]:

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos\theta}, \qquad (1)$$

where D is the crystallite size, λ is the wavelength of X-ray radiation (Cu Kα radiation λ = 1.5418 Å), k is a constant and usually taken as 0.89, β is the full width at half maximum (FWHM), after subtraction of equipment broadening, and θ is the Bragg angle of peak. From XRD results, the average sizes of the building blocks are estimated to be for about 15.0 nm. XRD patterns of pure polystyrene are shown in Figure 6(b). The largest specific diffraction peak at 2θ between 15°–22° indicates that the polystyrene is amorphous. In comparison with the pristine detonation nanographite samples and

(a) Nanographite samples
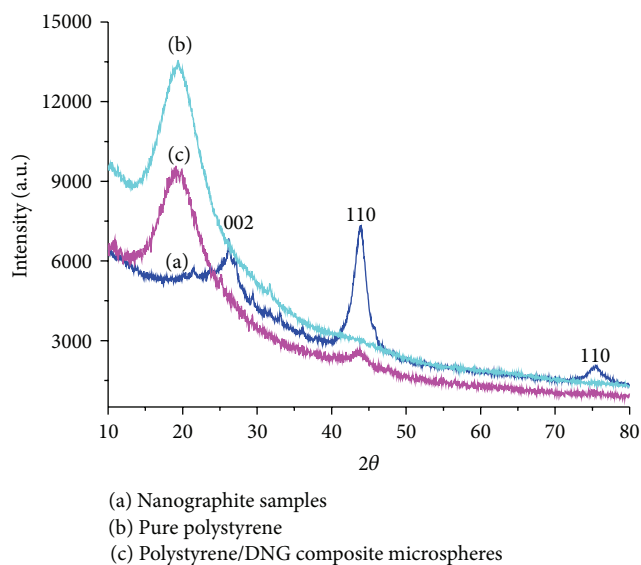(b) Pure polystyrene
(c) Polystyrene/DNG composite microspheres

FIGURE 6: XRD patterns of detonation nanographite particles, polystyrene/detonation nanographite (PS/DNG) composites, and pure polystyrene samples.

— Pure PS samples
— PS-DNG composite samples

FIGURE 7: TGA-DTA curves of polystyrene/detonation nanographite (PS/DNG) composites and pure polystyrene samples.

pure polystyrene, XRD patterns of polystyrene/detonation nanographite (PS/DNG) composite microspheres are almost the same as that of pure polystyrene. Nevertheless, the main peaks corresponding to (110) planes of nanographite particles can be distinguished. From the XRD patterns, it can be further ascertained that the crystal structures of detonation nanographite particles are not altered by the polystyrene. In the polymerization process of nano-graphite-styrene (AIBN)-water Pickering emulsion, detonation nanographite particles play an important role as surfactants, which are adsorbed on the surfaces of styrene (AIBN) droplets to form stable latex. The final composite products have distinct core-shell morphology (detonation nanographite particles acting as shell particles and polystyrene as cores). As a result, XRD pattern of polystyrene/detonation nanographite (PS/DNG) composite microspheres combines the characteristics of both detonation nanographite particles and polystyrene.

3.5. TGA-DTA of PS/DNG Composite Microspheres. In order to provide more details information about the covalent nature of the grafting, thermogravimetric measurements and differential thermal analysis (TGA-DTA) were carried out. TGA-DTA curves of polystyrene/detonation nanographite (PS/DNG) composites and polystyrene are shown in Figure 7. The gradual and slight weight loss is the release of water molecular and residual organic solute in pure PS samples between 50°C and 200°C. Correspondingly, a small exothermic peak appeared. Then, an abrupt decrease in weight of composite samples is observed in a narrow temperature range of 350–450°C, accompanied with single shoulder peaks at about 410°C. Pure PS polymer matrix has completed decomposition at approximately 450°C, and it is pyrolyzed directly to gaseous species without forming any molten states during the thermal decomposition [49, 50]. Compared
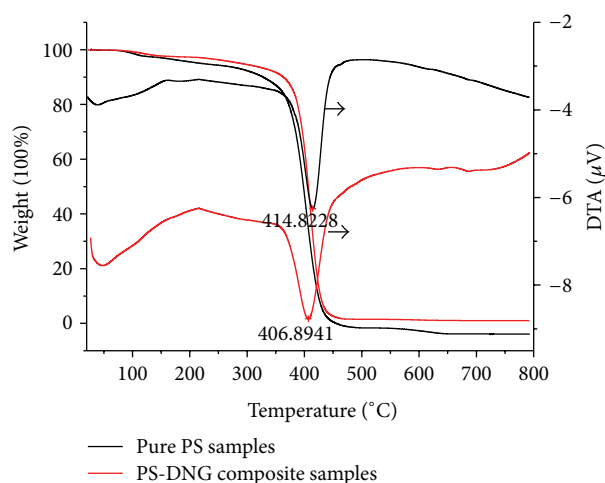
to the thermogram of pure PS polymer, decomposition of polystyrene/detonation nanographite (PS/DNG) composites begins at about 370°C, which is 5°C lower than that of pure polystyrene. Correspondingly, the glass transition temperature of the composites is also lower than that of pure polystyrene in DTA curves. The excellent thermal conductivity functions of the detonation nanographite particles should contribute to the heat transferring from the shell of the nanographite particles to the core of polystyrene. After 450°C, the PS/DNG composite samples are no longer loss of weight with the increasing of temperature. The total weight loss of composite samples attains to approximately 100% at 450°C. Specifically, the shell of inorganic nanosized detonation graphite particles and the core of organic polystyrene are burned to gaseous CO_2 and H_2O entirely.

4. Conclusion

In summary, the polystyrene/detonation nanographite (PS/DNG) with core-shell structure was successfully obtained via Pickering emulsion polymerization using detonation nanographite particles as emulsifier for the stabilization of styrene (AIBN)-water Pickering emulsions. The as-prepared products have a well-defined spherical morphology and uniform diameters of 100~150 μm. The possible formation mechanisms of PS/DNG composites based on the interaction between the functional groups of the PS and detonation nano-raphite particles have been proposed. Using styrene as monomer, azobisisobutylonitrile (AIBN) as initiator, and detonation nanographite particles as stabilizer, the method has combined the advantages of suspension polymerization and Pickering emulsion polymerization. Moreover, the present strategy also can be extended for the simple and robust synthesis of other hybrid microspheres with similar structure.

Acknowledgment

References

[1] P. J. Hagrman, D. Hagrman, and J. Zubieta, "Organic-inorganic hybrid materials: from simple coordination polymers to organodiamine-templated molybdenum oxides," *Angewandte Chemie*, vol. 38, no. 18, pp. 2638–2684, 1999.

[2] M. F. Ashby and Y. J. M. Bréchet, "Designing hybrid materials," *Acta Materialia*, vol. 51, no. 19, pp. 5801–5821, 2003.

[3] H. P. Cong and S. H. Yu, "Self-assembly of functionalized inorganic-organic hybrids," *Current Opinion in Colloid and Interface Science*, vol. 14, no. 2, pp. 71–80, 2009.

[4] M. Zhang, G. Gao, D. C. Zhao et al., "Crystallization and surface photovoltage properties of polystyrene coated by TiO_2 nanoparticles," *Chemical Journal of Chinese Universities*, vol. 25, no. 11, p. 2122, 2004.

[5] Y. H. Chen, Y. Y. Liu, R. H. Lin, and F. S. Yen, "Photocatalytic degradation of p-phenylenediamine with TiO_2-coated magnetic PMMA microspheres in an aqueous solution," *Journal of Hazardous Materials*, vol. 163, no. 2-3, pp. 973–981, 2009.

[6] M. E. Fabiyi and R. L. Skelton, "Photocatalytic mineralisation of methylene blue using buoyant TiO_2-coated polystyrene beads," *Journal of Photochemistry and Photobiology A*, vol. 132, no. 1-2, pp. 121–128, 2000.

[7] K. J. Huang, P. Rajendran, and C. M. Liddell, "Chemical bath deposition synthesis of sub-micron ZnS-coated polystyrene," *Journal of Colloid and Interface Science*, vol. 308, no. 1, pp. 112–120, 2007.

[8] D. Z. Yin, X. Du, H. Liu, Q. Y. Zhang, and L. Ma, "Facile one-step fabrication of polymer microspheres with high magnetism and armored inorganic particles by Pickering emulsion polymerization," *Colloids and Surfaces A*, vol. 414, pp. 289–295, 2012.

[9] J. Pyun and K. Matyjaszewski, "Synthesis of nanocomposite organic/inorganic hybrid materials using controlled/"living" radical polymerization," *Chemistry of Materials*, vol. 13, no. 10, pp. 3436–3448, 2001.

[10] P. D. Cozzoli, T. Pellegrino, and L. Manna, "Synthesis, properties and perspectives of hybrid nanocrystal structures," *Chemical Society Reviews*, vol. 35, no. 11, pp. 1195–1208, 2006.

[11] G. Chen, C. Wu, W. Weng, D. Wu, and W. Yan, "Preparation of polystyrene/graphite nanosheet composite," *Polymer*, vol. 44, no. 6, pp. 1781–1784, 2003.

[12] D. S. Saunders, S. C. Galea, and G. K. Deirmendjian, "The development of fatigue damage around fastener holes in thick graphite/epoxy composite laminates," *Composites*, vol. 24, no. 4, pp. 309–321, 1993.

[13] T. A. Ezquerra, M. Kulescza, and F. J. Baltá-Calleja, "Electrical transport in polyethylene-graphite composite materials," *Synthetic Metals*, vol. 41, no. 3, pp. 915–920, 1991.

[14] G. H. Chen, D. J. Wu, W. G. Weng, and W. L. Yan, "Preparation of polymer/graphite conducting nanocomposite by intercalation polymerization," *Journal of Applied Polymer Science*, vol. 82, no. 10, pp. 2506–2513, 2001.

[15] J. Roussel and B. Boutevin, "Preparation of polystyrene-graphite conducting nanocompositesvia intercalation polymerization," *Polymer International*, vol. 50, no. 9, pp. 980–985, 2001.

[16] G. H. Chen, D. J. Wu, W. G. Weng, and W. L. Yan, "Dispersion of graphite nanosheets in a polymer matrix and the conducting property of the nanocomposites," *Polymer Engineering and Science*, vol. 41, no. 12, pp. 2148–2154, 2001.

[17] Y. X. Pan, Z. Z. Yu, Y. C. Ou, and G. H. Hu, "A new process of fabricating electrically conducting nylon 6/graphite nanocomposites via intercalation polymerization," *Journal of Polymer Science B*, vol. 38, no. 12, pp. 1626–1633, 2000.

[18] W. Zheng, X. Lu, and S. C. Wong, "Electrical and mechanical properties of expanded graphite-reinforced high-density polyethylene," *Journal of Applied Polymer Science*, vol. 91, no. 5, pp. 2781–2788, 2004.

[19] G. Chen, C. Wu, W. Weng, D. Wu, and W. Yan, "Preparation of polystyrene/graphite nanosheet composite," *Polymer*, vol. 44, no. 6, pp. 1781–1784, 2003.

[20] R. K. Goyal, P. A. Jagadale, and U. P. Mulik, "Thermal, mechanical, and dielectric properties of polystyrene/expanded graphite nanocomposites," *Journal of Applied Polymer Science*, vol. 111, no. 4, pp. 2071–2077, 2009.

[21] A. Yasmin and I. M. Daniel, "Mechanical and thermal properties of graphite platelet/epoxy composites," *Polymer*, vol. 45, no. 24, pp. 8211–8219, 2004.

[22] H. Wu, W. Zhao, H. Hu, and G. Chen, "One-step in situ ball milling synthesis of polymer-functionalized graphene nanocomposites," *Journal of Materials Chemistry*, vol. 21, no. 24, pp. 8626–8632, 2011.

[23] F. M. Uhl and C. A. Wilkie, "Preparation of nanocomposites from styrene and modified graphite oxides," *Polymer Degradation and Stability*, vol. 84, no. 2, pp. 215–226, 2004.

[24] R. Ding, Y. Hu, Z. Gui, R. Zong, Z. Chen, and W. Fan, "Preparation and characterization of polystyrene/graphite oxide nanocomposite by emulsion polymerization," *Polymer Degradation and Stability*, vol. 81, no. 3, pp. 473–476, 2003.

[25] X. Li, Y. Qu, H. Yan, and X. Wang, "Research progress on nanosized materials synthesized by detonation method," *Rare Metal Materials and Engineering*, vol. 36, no. 12, pp. 2069–2074, 2007.

[26] C. Wen, Z. Jin, J. Guan, X. Li, G. Zhou, and G. Zhou, "Nanographite synthesized by explosive detonation," *Rare Metal Materials and Engineering*, vol. 33, no. 6, pp. 628–631, 2004.

[27] Q. Chen and S. R. Yun, "Exploration of the mechanism of synthesis ultradispersed diamond by detonation," *Explosion and Shock Waves*, vol. 16, no. 4, pp. 326–332, 1996.

[28] J. H. Chen, C. Y. Cheng, W. Y. Chiu, C. F. Lee, and N. Y. Liang, "Synthesis of ZnO/polystyrene composites particles by Pickering emulsion polymerization," *European Polymer Journal*, vol. 44, no. 10, pp. 3271–3279, 2008.

[29] Z. Cao, A. Schrade, K. Landfester, and U. Ziener, "Synthesis of raspberry-like organic-inorganic hybrid nanocapsules via pickering miniemulsion polymerization: colloidal stability and morphology," *Journal of Polymer Science A*, vol. 49, no. 11, pp. 2382–2394, 2011.

[30] X. Li, Y. Qu, H. Yan, and X. Wang, "Research progress on nanosized materials synthesized by detonation method," *Rare Metal Materials and Engineering*, vol. 36, no. 12, pp. 2069–2074, 2007.

[31] D. Yin, Q. Zhang, H. Zhang, and C. Yin, "Fabrication of covalently-bonded polystyrene/SiO_2 composites by Pickering emulsion polymerization," *Journal of Polymer Research*, vol. 17, no. 5, pp. 689–696, 2010.

[32] K. Zhang, W. Wu, H. Meng, K. Guo, and J. F. Chen, "Pickering emulsion polymerization: preparation of polystyrene/nano-SiO$_2$ composite microspheres with core-shell structure," *Powder Technology*, vol. 190, no. 3, pp. 393–400, 2009.

[33] S. Sacanna, W. K. Kegel, and A. P. Philipse, "Thermodynamically stable pickering emulsions," *Physical Review Letters*, vol. 98, no. 15, Article ID 158301, 2007.

[34] B. P. Binks and J. H. Clint, "Solid wettability from surface energy components: relevance to pickering emulsions," *Langmuir*, vol. 18, no. 4, pp. 1270–1273, 2002.

[35] G. Chen, C. Wu, W. Weng, D. Wu, and W. Yan, "Preparation of polystyrene/graphite nanosheet composite," *Polymer*, vol. 44, no. 6, pp. 1781–1784, 2003.

[36] H. O. Zhou, T. J. Shi, and X. Zhou, "Preparation of polystyrene/SiO$_2$ microsphere via Pickering emulsion polymerization: synergistic effect of SiO$_2$ concentrations and initiator sorts," *Applied Surface Science*, vol. 266, pp. 33–38, 2013.

[37] N. Liu, S. Qi, S. Li, X. Wu, and L. Wu, "Preparation and characterization of phenol formaldehyde/Ag/graphite nanosheet composites," *Polymer Testing*, vol. 30, no. 4, pp. 390–396, 2011.

[38] G. M. Chen, S. H. Liu, S. J. Chen, and Z. N. Qi, "FTIR spectra, thermal properties, and dispersibility of a polystyrene/montmorillonite nanocomposite," *Macromolecular Chemistry and Physics*, vol. 202, no. 7, pp. 1189–1193, 2001.

[39] Y. Rong, H. Z. Chen, G. Wu, and M. Wang, "Preparation and characterization of titanium dioxide nanoparticle/ polystyrene composites via radical polymerization," *Materials Chemistry and Physics*, vol. 91, no. 2-3, pp. 370–374, 2005.

[40] A. Imhof, "Preparation and characterization of titania-coated polystyrene spheres and hollow titania shells," *Langmuir*, vol. 17, no. 12, pp. 3579–3585, 2002.

[41] W. Lin, X. Xi, and C. Yu, "Research of silver plating nano-graphite filled conductive adhesive," *Synthetic Metals*, vol. 159, no. 7-8, pp. 619–624, 2009.

[42] D. Ni, L. Wang, Y. Sun, Z. Guan, S. Yang, and K. Zhou, "Amphiphilic hollow carbonaceous microspheres with permeable shells," *Angewandte Chemie*, vol. 49, no. 25, pp. 4223–4227, 2010.

[43] R. Gnanasambandam and A. Proctor, "Determination of pectin degree of esterification by diffuse reflectance Fourier transform infrared spectroscopy," *Food Chemistry*, vol. 68, no. 3, pp. 327–332, 2000.

[44] C. Wen, Z. H. Jin, J. Q. Guan et al., "Infrared spectroscopy studies of nano-graphite synthesized by explosive detonation," *Chemical Research in Chinese Universities*, vol. 25, no. 6, pp. 1043–1045, 2004.

[45] N. Liu, S. Qi, S. Li, X. Wu, and L. Wu, "Preparation and characterization of phenol formaldehyde/Ag/graphite nanosheet composites," *Polymer Testing*, vol. 30, no. 4, pp. 390–396, 2011.

[46] P. S. Gaal, *Thermal Conductivity 24: and Thermal Expansion 12*, CRC Press, Pennsylvania, Pa, USA, 1999.

[47] G. Sun, X. Li, Y. Qu, X. Wang, H. Yan, and Y. Zhang, "Preparation and characterization of graphite nanosheets from detonation technique," *Materials Letters*, vol. 62, no. 4-5, pp. 703–706, 2008.

[48] A. Hagfeldt and M. Gratzel, "Light-induced redox reactions in nanocrystalline systems," *Chemical Reviews*, vol. 95, no. 1, pp. 49–68, 1995.

[49] B. N. Jang and C. A. Wilkie, "The thermal degradation of polystyrene nanocomposite," *Polymer*, vol. 46, no. 9, pp. 2933–2942, 2005.

[50] F. Vilaplana, A. Ribes-Greus, and S. Karlsson, "Degradation of recycled high-impact polystyrene. Simulation by reprocessing and thermo-oxidation," *Polymer Degradation and Stability*, vol. 91, no. 9, pp. 2163–2170, 2006.