Research Article

Preparation of Magnetic Hybrid Microspheres with Well-Defined Yolk-Shell Structure

Yuan Zhao,^{1,2} Tao Chen,^{1,2} Shaofa Sun,^{1,2} and Long Zhao¹

¹Hubei Collaboration Innovative Center for Nonpower Nuclear Technology, Hubei University of Science and Technology, Xianning 437100, China

²School of Nuclear Technology and Chemistry and Biology, Hubei University of Science and Technology, Xianning 437100, China

Correspondence should be addressed to Tao Chen; taochen518@163.com

Received 15 June 2016; Revised 6 September 2016; Accepted 8 September 2016

Academic Editor: Peter Majewski

Copyright © 2016 Yuan Zhao 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.

A facile and efficient route was reported to prepare a kind of yolk-shell magnetic hybrid microspheres by suspension polymerization and calcinations method. The morphology, structure, and composition of the magnetic microspheres were characterized by FTIR, XRD, TEM, SEM, and TGA analysis. The vibrating-sample magnetometry (VSM) results clearly showed that the magnetic particles were superparamagnetic with saturation magnetization of 32.82 emu/g which makes the microcomposites easily controlled by an external magnetic field. The results revealed that the magnetic hybrid microspheres might have important applications in magnetic bioseparation and drug delivery.

1. Introduction

In recent years, magnetic particles have been paid considerable attention due to their superparamagnetic properties and potential applications, for example, magnetic bioseparation [1, 2], drug delivery [3, 4], magnetorheological fluid [5], magnetic resonance imaging contrast enhancement [6, 7], targeted drug [8], gene separation from biochemical products and cells [9], microwave absorption [10], high saturation magnetization, high magnetic susceptibility, biocompatibility, and low toxicity. Therefore, more and more researchers have focused on the fascinating feature of targeting [11–13]. However, because bare magnetic particles are liable to aggregation and rapid biodegradation when they are exposed to a biological system, coupled with a limited carrying capacity, it is quite necessary to combine magnetic particles with other carriers to achieve targeted delivery efficiently [14–16].

Various inorganic and polymeric materials have been reported as carriers of magnetic materials [17–20]. Recently, polymers which could stabilize magnetic particles are receiving more and more attention. Polymers can increase repulsive forces more than surfactants. In addition, a polymer coating on the surface used for the designed purpose of a well-defined composite of materials and their dispersions offers a high

potential of application in several fields [21–24]. There are mainly two methods to prepare Fe_3O_4 @polymer composite particles: first polymer coating Fe_3O_4 or modified Fe_3O_4 is used directly [25–27]; second Fe_3O_4 is first prepared by the coprecipitation of ferrous and ferric ions at the ratio of 1 : 2 in an alkaline medium and at the same time Fe_3O_4 @polymer is prepared, because Fe_3O_4 contains ferrous and ferric iron at this ratio [28, 29].

In this contribution, we report a simple and efficient route to prepare yolk-shell monodisperse superparamagnetic polymer@ Fe_3O_4 composite microspheres, using ferric ions as the only source of iron. Unlike traditional synthesis methods, we first prepare $\text{Fe}(\text{OH})_3$ @PMMA. Then, the magnetic hybrid microspheres were obtained by calcination. The well control of the calcination temperature contributes to getting well-defined yolk-shell magnetic hybrid microspheres. The unique advantage of the yolk-shell morphology lies in the presence of internal void space to accommodate the targeted drug.

2. Experimental Details

2.1. Materials. Methyl methacrylate (MMA, 99 wt.%, Shanghai Chemical Reagent Company, China) was distilled under

FIGURE 1: Schematic illustration of the synthesis process of magnetic microspheres.

reduced pressure before polymerization. Absolute ethanol was of reagent grade. Benzoyl peroxide (BPO) (97 wt.%, Aldrich) was used as received. Poly(vinyl pyrrolidone) (PVP, K30) was purchased from Shanghai Chemical Reagent Company, China. Ferric nitrate ($\text{Fe}(\text{NO}_3)_3$), sodium hydroxide (NaOH), and sodium dodecylbenzene sulfonate (SDBS) were purchased from Tianjin Guangfu Chemical Reagents Company, China. Water used throughout all experiments was distilled followed by deionization.

2.2. Preparation. The overall synthesis procedure and possible mechanisms for formation of the monodisperse magnetic hybrid microspheres were illustrated in Figure 1, and the detailed procedures are described as follows.

(1) Preparation of $\text{Fe}(\text{OH})_3$ @PMMA Composite Microspheres. In a typical preparation procedure, 0.5 g SDBS and 80 mL deionized water were added into a 250 mL four-necked flask fitted with a condenser, coupled with a mechanical overhead stirrer, and at the same time inlet for nitrogen gas. 3 mL 1 M NaOH and 1 mL 1 M $\text{Fe}(\text{NO}_3)_3$ were added in turns as the water was heated to 60°C. Then, 5 mL methyl methacrylate was injected into the mixture above under continuous vigorous stirring. The initiator BPO (0.15 g) that dissolved in 20 mL deionized water was then added into the flask, and the flask was heated to 70°C gradually in an oil bath with stirring. The polymerization was maintained for 2 h. The particles, which appear yellow in color, were centrifuged at 7000 rpm for 5 min, the supernatant was removed, and the pellet was resuspended in water. This wash process was performed three times. After the last wash, the supernatant was removed, and the pellet was dried under ambient conditions.

(2) Preparation of Magnetic Particles. The obtained $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres were heated to 350°C at a ramp rate of 100°C h⁻¹ under N₂ atmosphere in a pipe furnace and kept at this temperature for 2 h to remove CO₃²⁻

and water. Then, a kind of black powder was obtained from the crucible after calcinations [30]. A possible mechanism was that by calcination of PMMA@ $\text{Fe}(\text{OH})_3$ at 350°C for 3 h under N₂ atmosphere, Fe₂O₃ nanoparticles were formed, and part of PMMA coating was carbonized. Then, the inner Fe₂O₃ NPs were reduced to Fe₃O₄ by the resulting outer carbon layers during the calcination process [31, 32].

2.3. Characterizations. A Hitachi S3400 SEM was used to determine the morphology and composition of the products with samples previously coated with gold via vapour deposition. TEM measurements were made on a Philips CM12 TEM/STEM with an accelerating voltage of 120 kV. XRD analysis was carried out on a D/Max 2500V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation. FTIR spectroscopy was done in solid state on a Perkin Elmer Spectrum 100. TGA were performed on a TGA Q50 from TA Instrument using a temperature ramp from 30 to 600°C at 10°C/min under nitrogen atmosphere. Specific surface area N₂ adsorption measurements were performed on a Micromeritics ASAP 2010 V4 analyzer (Nor-mass, GA) and the data were subjected to the Brunauer-Emmett-Teller (BET) treatment. The magnetic properties were investigated with a BHV-55 vibrating-sample magnetometer (VSM) at room temperature.

3. Results and Discussion

3.1. FTIR Analysis. Figure 2 shows the infrared spectra of $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres (a) and magnetic microspheres (b). The prominent bands in the FTIR spectrum (Figure 2(a)) were associated with the polymerization of the acrylic (C=O at 1728 cm⁻¹, -CH between 2840 and 2955 cm⁻¹, -CH₂ at 1457 cm⁻¹, and C-O between 1082 and 1270 cm⁻¹) [28, 33]. As seen from Figure 2(b), the typical adsorption peaks of PMMA were weakened, which further demonstrated that PMMA template was mostly removed

FIGURE 2: IR spectrum of (a) $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres and (b) magnetic microspheres.

from the composite microspheres by means of calcination. And the adsorption centered at 580 cm^{-1} corresponding to the Fe-O vibration related to the magnetite phase [34, 35]. The IR analysis provides some insights into the composition of the core and the composite.

3.2. Nanostructure and Component. The surface morphology and components of the prepared sample $\text{Fe}(\text{OH})_3$ @PMMA were examined by SEM and EDS, respectively, as shown in Figures 3(a) and 3(b). The SEM image showed that the products were composed of some well monodispersed spheres with a coarse surface. As illustrated in Figure 3(b), EDS analysis indicated that, besides weak Al peaks, only C, Fe, and O were detected, which provides evidence for the presence of $\text{Fe}(\text{OH})_3$ @PMMA particles. Based on the above results, it has been confirmed that PMMA was hybridized with $\text{Fe}(\text{OH})_3$ [28].

TEM measurements could provide further insights into the morphology and structure of composite particles, and TEM images of resultant microspheres were shown in Figure 3(c). It shows that magnetic microspheres were of spherical shape with a particle size in the range of 150–300 nm, and they have two phases [31, 36]. The bright phase maybe is partly carbonized polymer and the dark phase is magnetic Fe_3O_4 . Most interestingly, these composite particles have a novel yolk-shell morphology. Moreover, it is observed that very thin layer was facily coated on the surface of Fe_3O_4 NPs which maybe is partly carbonized PMMA [37]. It could be noted that the calcination temperature was controlled pretty well. Figure 3(d) shows the corresponding SAED pattern taken from the single sphere. The diffraction rings suggest that the magnetite spheres were polycrystalline, confirming that the sphere was composed of many small particles. From inside to outside, the rings can be indexed to (220), (311), (400), (422), and (440) planes of spinel Fe_3O_4 , respectively. The magnetic hybrid microspheres are composed of the porous hollow spheres reported by Cheng et al. [36].

3.3. XRD Analysis. XRD measurement was an effective way to further investigate the presence of intercalation in composites. Figure 4 shows the X-ray diffraction pattern of $\text{Fe}(\text{OH})_3$ @PMMA (a) and magnetic microspheres (b). Because of the high concentration of PMMA, there were no sharp diffraction peaks in the diffractogram of $\text{Fe}(\text{OH})_3$ @PMMA microspheres, which could confirm their noncrystalline nature (Figure 4(a)). Based on Figure 4(b), characteristic diffraction peaks at 2θ of 30.2° , 35.7° , 43.3° , 57.2° , and 62.6° were assigned to [220], [311], [400], [333], and [440] lattice planes of Fe_3O_4 . On the basis of the analysis above, it was confirmed that magnetic microspheres were successfully prepared. XRD patterns of the magnetic hybrid microspheres indicate that all the characteristic peaks match well with the standard crystal phase of magnetite (JCPDS numbers 894319, 19-0629) [38, 39]. So the spinel structures of magnetite in the samples were retained. Moreover, the intensity of diffraction peaks for the magnetic composite microspheres became lower as the Fe_3O_4 content decreased [4]. XRD patterns revealed that Fe_3O_4 content significantly affected the characteristic peak intensities of the Fe_3O_4 /PMMA composite microspheres. PMMA had little influence because of its transparency over the Fe_3O_4 peak range.

3.4. Nitrogen Sorption Isotherm. The nitrogen adsorption-desorption isotherms of $\text{Fe}(\text{OH})_3$ @PMMA (a) and magnetic microspheres (b) were presented in Figure 5. It could be observed from Figure 5(a) that the sorption isotherm was of type III, which demonstrated that $\text{Fe}(\text{OH})_3$ @PMMA nearly have no porous. After being calculated, the BET surface area increased from $3.19\text{ m}^2/\text{g}$ to $32.98\text{ m}^2/\text{g}$ and the sorption isotherm was of type IV (Figure 5(b)) and displayed an obvious hysteresis loop, which demonstrated that magnetic microspheres were typical porous materials. This may be explained by the fact that after calculating part of PMMA was carbonized and the BET surface area was increased [40]. Furthermore, the relatively large pore volume was $1.33\text{ cm}^3/\text{g}$ by using the BET method, which could endow magnetic microspheres with large drug loading capacity.

3.5. TGA Analysis. The materials were quantified by TGA under nitrogen atmosphere. Figure 6 shows the TGA curves of $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres and magnetic microspheres. After being calcined at 600°C , the $\text{Fe}(\text{OH})_3$ @PMMA composite nanosphere sample lost 80.5% of its weight in two steps (Figure 6(a)). The weight loss before 270°C can be assigned to the dehydration of $\text{Fe}(\text{OH})_3$. It was noted that the decomposition temperature of PMMA ranged from 270°C to 500°C , and it was completely decomposed at 500°C [28]. Figure 5(a) exhibited the residual weight of about 19.5%, which suggested that the content of PMMA was about 80.5% in the $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres. Figure 6(b) shows that magnetic microspheres begin to lose weight at 270°C and ended at 500°C and exhibited a residual weight of about 70.5%. The result shows that most of the PMMA in the composite microspheres decomposed after being carbonized at 350°C for 2 h, but there still have a small amount of residue PMMA [41].

FIGURE 3: SEM image (a) and EDS spectrum (b) of $\text{Fe}(\text{OH})_3\text{@PMMA}$ microspheres; TEM image (c) and single sphere SAED pattern (d) of magnetic microspheres.

FIGURE 4: XRD patterns of (a) $\text{Fe}(\text{OH})_3\text{@PMMA}$ composite microspheres and (b) magnetic microspheres.

FIGURE 5: Nitrogen sorption isotherm of (a) $\text{Fe}(\text{OH})_3\text{@PMMA}$ composite microspheres and (b) magnetic microspheres.

FIGURE 6: TGA curves of (a) $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres and (b) magnetic microspheres.

FIGURE 7: The optical images of the (vial A) $\text{Fe}(\text{OH})_3$ @PMMA microspheres and (vial B) magnetic microspheres dispersed in water: (a) before being attracted by a magnet and (b) being attracted by a magnet.

3.6. Magnetic Property Testing. The $\text{Fe}(\text{OH})_3$ @PMMA composite and the magnetic microspheres were dispersed in water by vigorous shaking, respectively; the $\text{Fe}(\text{OH})_3$ @PMMA composite results in a brown-colored suspension and it cannot be aggregated in the presence of an external magnetic field [42]. However, the magnetic microspheres result in a black-colored suspension and they could be separated from solution in a short period under an external magnetic field. Once the external magnetic field was evacuated, the magnetic hybrid microspheres can be redispersed into the solution with slight shaking (Figure 7). These results show that magnetic microspheres have been successfully produced; they possess excellent magnetic responsivity and redispersibility, which is of great importance in practical manipulation [30, 43].

3.7. VSM Analysis. The magnetization of samples was evaluated by VSM. Figure 8 shows the magnetization curve

of $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres and magnetic microspheres, respectively. It can be seen that the $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres (Figure 8(a)) almost have no magnetism, but after calcining, they possessed a characteristic of paramagnetic with the saturation magnetization value of about 32.82 emu/g. They also exhibited superparamagnetism at room temperature because of no hysteresis and remanence (Figure 8(b)) [44].

4. Conclusions

In conclusion, we have successfully prepared the magnetic microspheres with diameters in the range of 150–300 nm. TEM results demonstrated that the obtained magnetic microspheres have a novel yolk-shell structure and were well mono-dispersed. The magnetic microspheres exhibited the feature of polycrystalline, increased BET surface area, and the high

FIGURE 8: Room temperature hysteresis curves of magnetite with (a) $\text{Fe}(\text{OH})_3$ @PMMA composite microspheres and (b) magnetic microspheres.

magnetic saturation. Taking into account the suitable size, special structure, and good hydrophilic and biocompatible properties, the magnetic microspheres will have wide applications in biomedical fields such as targeted drug delivery, biomolecular separations, cancer treatment, and magnetic resonance imaging.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (11475112) and Programs Foundation of Ministry of Education of China (20130073120051).

References

- [1] F. Lan, Y. Wu, H. Hu, L. Xie, and Z. Gu, "Superparamagnetic Fe_3O_4 /PMMA composite nanospheres as a nanopatform for multimodal protein separation," *RSC Advances*, vol. 3, no. 5, pp. 1557–1563, 2013.
- [2] C. Velez, I. Torres-Díaz, L. Maldonado-Camargo, C. Rinaldi, and D. P. Arnold, "Magnetic assembly and cross-linking of nanoparticles for releasable magnetic microstructures," *ACS Nano*, vol. 9, no. 10, pp. 10165–10172, 2015.
- [3] A. Yakar, G. Tansık, T. Keskin, and U. Gündüz, "Tailoring the magnetic behavior of polymeric particles for bioapplications," *Journal of Polymer Engineering*, vol. 33, no. 3, pp. 265–274, 2013.
- [4] A. Cervadoro, M. Cho, J. Key et al., "Synthesis of multifunctional magnetic nanoflakes for magnetic resonance imaging, hyperthermia, and targeting," *ACS Applied Materials & Interfaces*, vol. 6, no. 15, pp. 12939–12946, 2014.
- [5] B. J. Park, F. F. Fang, and H. J. Choi, "Magnetorheology: materials and application," *Soft Matter*, vol. 6, no. 21, pp. 5246–5253, 2010.
- [6] K. R. Hurley, H. L. Ring, H. Kang, N. D. Klein, and C. L. Haynes, "Characterization of magnetic nanoparticles in biological matrices," *Analytical Chemistry*, vol. 87, no. 23, pp. 11611–11619, 2015.
- [7] C. Wan and J. Li, "Facile synthesis of well-dispersed superparamagnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles encapsulated in three-dimensional architectures of cellulose aerogels and their applications for Cr(VI) removal from contaminated water," *ACS Sustainable Chemistry & Engineering*, vol. 3, no. 9, pp. 2142–2152, 2015.
- [8] S. K. Suh, K. Yuet, D. K. Hwang, K. W. Bong, P. S. Doyle, and T. A. Hatton, "Synthesis of nonspherical superparamagnetic particles: in situ coprecipitation of magnetic nanoparticles in microgels prepared by stop-flow lithography," *Journal of the American Chemical Society*, vol. 134, no. 17, pp. 7337–7343, 2012.
- [9] L.-K. Shen, K.-H. Fan, T.-L. Wu et al., "Fabrication and magnetic testing of a poly-L-lactide biocomposite incorporating magnetite nanoparticles," *Journal of Polymer Engineering*, vol. 34, no. 3, pp. 231–235, 2014.
- [10] J. Liu, R. Che, H. Chen et al., "Microwave absorption enhancement of multifunctional composite microspheres with spinel Fe_3O_4 cores and anatase TiO_2 shells," *Small*, vol. 8, no. 8, pp. 1214–1221, 2012.
- [11] S. Chuayjuljit, N. Sukasem, and A. Boonmahitthisud, "Effects of silica, poly(methyl methacrylate) and poly(methyl methacrylate)-grafted-silica nanoparticles on the physical properties of plasticized-poly(vinyl chloride)," *Polymer-Plastics Technology and Engineering*, vol. 53, no. 2, pp. 116–122, 2014.
- [12] A. R. Mahdavian, Y. Sehri, and H. Salehi-Mobarakeh, "Nanocomposite particles with core-shell morphology II. An investigation into the affecting parameters on preparation of Fe_3O_4 -poly (butyl acrylate-styrene) particles via miniemulsion polymerization," *European Polymer Journal*, vol. 44, no. 8, pp. 2482–2488, 2008.
- [13] A. Kumari, S. K. Yadav, and S. C. Yadav, "Biodegradable polymeric nanoparticles based drug delivery systems," *Colloids and Surfaces B: Biointerfaces*, vol. 75, no. 1, pp. 1–18, 2010.
- [14] H. Ahmad, K. Kumar, M. A. Rahman et al., "Preparation and characterization of conducting polyaniline layered magnetic nano composite polymer particles," *Polymers for Advanced Technologies*, vol. 24, no. 8, pp. 740–746, 2013.
- [15] Z. Shi, Z. Zhang, R. Fan et al., "Synthesis and characterization of iron particles hosted in Porous Alumina," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 21, no. 4, pp. 836–840, 2011.
- [16] N.-N. Song, H.-T. Yang, H.-L. Liu et al., "Exceeding natural resonance frequency limit of monodisperse Fe_3O_4 nanoparticles via superparamagnetic relaxation," *Scientific Reports*, vol. 3, article 3161, 2013.
- [17] M. Gunay, H. Kavas, and A. Baykal, "Simple polyol route to synthesize heptanoic acid coated magnetite (Fe_3O_4) nanoparticles," *Materials Research Bulletin*, vol. 48, no. 3, pp. 1296–1303, 2013.
- [18] K. Zhang, W. Wu, K. Guo, J.-F. Chen, and P.-Y. Zhang, "Magnetic polymer enhanced hybrid capsules prepared from a novel Pickering emulsion polymerization and their application in controlled drug release," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 349, no. 1–3, pp. 110–116, 2009.
- [19] H. Alamri, N. Ballot, J. Long et al., "Integrative synthesis of coordination polymers, metal oxides, and alloys magnetic nanoparticles in MSU mesoporous silica," *Chemistry of Materials*, vol. 26, no. 2, pp. 875–885, 2014.

- [20] M. Eid and A. Mansour, "Preparation and magnetic investigation of magnetic nanoparticles entrapped hydrogels and its possible use as radiation shield," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 23, no. 6, pp. 1255–1265, 2013.
- [21] M. Faraji, Y. Yamini, and M. Rezaee, "Magnetic nanoparticles: synthesis, stabilization, functionalization, characterization, and applications," *Journal of the Iranian Chemical Society*, vol. 7, no. 1, pp. 1–37, 2010.
- [22] T. Seckin, S. Vural, and S. Köytepe, "Preparation and structural properties of Fe_3O_4 -polyimide hybrid nanocomposites," *Polymer Bulletin*, vol. 64, no. 2, pp. 115–126, 2010.
- [23] A. B. Rajput, S. J. Rahaman, G. Sarkhel, M. K. Patra, S. R. Vadera, and N. N. Ghosh, "Preparation, characterization and properties of flexible magnetic nanocomposites of NiFe_2O_4 -polybenzoxazine-LLDPE," *Polymer-Plastics Technology and Engineering*, vol. 52, no. 11, pp. 1097–1105, 2013.
- [24] J. Hu, M. Chen, and L. Wu, "Organic-inorganic nanocomposites synthesized via miniemulsion polymerization," *Polymer Chemistry*, vol. 2, no. 4, pp. 760–772, 2011.
- [25] M. Ashjari, A. R. Mahdavian, N. G. Ebrahimi, and Y. Mosleh, "Efficient dispersion of magnetite nanoparticles in the polyurethane matrix through solution mixing and investigation of the nanocomposite properties," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 20, no. 2, pp. 213–219, 2010.
- [26] S. Xuan, F. Wang, J. M. Y. Lai et al., "Synthesis of biocompatible, mesoporous Fe_3O_4 nano/microspheres with large surface area for magnetic resonance imaging and therapeutic applications," *ACS Applied Materials & Interfaces*, vol. 3, no. 2, pp. 237–244, 2011.
- [27] Q. Yang, Y. Wu, F. Lan et al., "Hollow superparamagnetic PLGA/ Fe_3O_4 composite microspheres for lysozyme adsorption," *Nanotechnology*, vol. 25, no. 8, Article ID 085702, 2014.
- [28] R. Y. Hong, B. Feng, X. Cai et al., "Double-mini-emulsion preparation of Fe_3O_4 /poly(methyl methacrylate) magnetic latex," *Journal of Applied Polymer Science*, vol. 112, no. 1, pp. 89–98, 2009.
- [29] P. Xiao, J. J. Zhang, Z. Q. Wang, and H. Lin, "Photon conversion and radiation synergism in Eu/Tb complexes incorporated poly methyl methacrylate," *Advances in Materials Science and Engineering*, vol. 2016, Article ID 2618253, 11 pages, 2016.
- [30] J. A. Medford, J. W. Hubbard, F. Orange, M. J.-F. Guinel, B. O. Calcagno, and C. Rinaldi, "Magnetothermal repair of a PMMA/iron oxide magnetic nanocomposite," *Colloid and Polymer Science*, vol. 292, no. 6, pp. 1429–1437, 2014.
- [31] L. Li, T. Wang, L. Zhang, Z. Su, C. Wang, and R. Wang, "Selected-control synthesis of monodisperse Fe_3O_4 @C core-shell spheres, chains, and rings as high-performance anode materials for lithium-ion batteries," *Chemistry—A European Journal*, vol. 18, no. 36, pp. 11417–11422, 2012.
- [32] Y. Du, W. Liu, R. Qiang et al., "Shell thickness-dependent microwave absorption of core-shell Fe_3O_4 @C composites," *ACS Applied Materials and Interfaces*, vol. 6, no. 15, pp. 12997–13006, 2014.
- [33] L. Li, Y. Feng, Y. Li, W. Zhao, and J. Shi, " Fe_3O_4 core/layered double hydroxide shell nanocomposite: versatile magnetic matrix for anionic functional materials," *Angewandte Chemie—International Edition*, vol. 48, no. 32, pp. 5888–5892, 2009.
- [34] C. C. Zhang, X. Li, Y. Yang, and C. Wang, "Polymethylmethacrylate/ Fe_3O_4 composite nanofiber membranes with ultra-low dielectric permittivity," *Applied Physics A: Materials Science & Processing*, vol. 97, no. 2, pp. 281–285, 2009.
- [35] J. Shen, K. Chen, L. Li, W. Wang, and Y. Jin, "Fabrication and microwave absorbing properties of (Z-type barium ferrite/silica)/polypyrrole composites," *Journal of Alloys and Compounds*, vol. 615, pp. 488–495, 2014.
- [36] W. Cheng, K. Tang, Y. Qi, J. Sheng, and Z. Liu, "One-step synthesis of superparamagnetic monodisperse porous Fe_3O_4 hollow and core-shell spheres," *Journal of Materials Chemistry*, vol. 20, no. 9, pp. 1799–1805, 2010.
- [37] B. J. Park, M. K. Hong, and H. J. Choi, "Atom transfer radical polymerized PMMA/magnetite nanocomposites and their magnetorheology," *Colloid and Polymer Science*, vol. 287, no. 4, pp. 501–504, 2009.
- [38] H. Kavas, M. Günay, A. Baykal, M. S. Toprak, H. Sozeri, and B. Aktaş, "Negative permittivity of polyaniline- Fe_3O_4 nanocomposite," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 23, no. 2, pp. 306–314, 2013.
- [39] L. Chen, Q. Zhou, Q. Xiong, W. Li, J. Liu, and X. Yang, "Shape-evolution and growth mechanism of Fe_3O_4 polyhedrons," *Advances in Materials Science and Engineering*, vol. 2015, Article ID 763124, 7 pages, 2015.
- [40] M. Shao, F. Ning, J. Zhao, M. Wei, D. G. Evans, and X. Duan, "Preparation of Fe_3O_4 @ SiO_2 @ layered double hydroxide core-shell microspheres for magnetic separation of proteins," *Journal of the American Chemical Society*, vol. 134, no. 2, pp. 1071–1077, 2012.
- [41] K. Zhang, J. Y. Lim, and H. J. Choi, "Amino functionalization and characteristics of multi-walled carbon nanotube/poly(methyl methacrylate) nanocomposite," *Diamond and Related Materials*, vol. 18, no. 2-3, pp. 316–318, 2009.
- [42] Y. Tan, Z. Zhuang, Q. Peng, and Y. Li, "Room-temperature soft magnetic iron oxide nanocrystals: synthesis, characterization, and size-dependent magnetic properties," *Chemistry of Materials*, vol. 20, no. 15, pp. 5029–5034, 2008.
- [43] F. F. Fang, J. H. Kim, and H. J. Choi, "Synthesis of core-shell structured PS/ Fe_3O_4 microbeads and their magnetorheology," *Polymer*, vol. 50, no. 10, pp. 2290–2293, 2009.
- [44] S. Kanagesan, M. Hashim, S. Tamilselvan et al., "Synthesis, characterization, and cytotoxicity of iron oxide nanoparticles," *Advances in Materials Science and Engineering*, vol. 2013, Article ID 710432, 7 pages, 2013.