Asian Journal of Chemistry; Vol. 27, No. 5 (2015), 1742-1744

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17600

Preparation of Monodisperse Fe_3O_4 Microspheres/Polyaniline Composites

L. SHI, W. LIU* and Z.F. WANG*

Department of Chemistry, Honghe University, Mengzi 661199, P.R. China

*Corresponding authors: E-mail: wangzefeng841006@163.com; liuwei4728@126.com

Received: 14 March 2014; *Accepted*: 19 May 2014; *Published online*: 20 February 2015; AJC-16883

The synthesis of monodisperse magnetic ferrite nanomaterials plays an important role in several scientific and technological areas. In this work, Fe_3O_4/polyaniline (Fe_3O_4/PANI) microspheres have been successfully prepared through a novel liquid-liquid interface polymerization method. In this technique, Fe^{3+} was used as a milder polymerization oxidant which makes the aniline grow on the surface of Fe_3O_4 uniformly. The scanning electron microscope images demonstrate that obtained composites present a uniform particle size and good dispersibility. Meantime, the UV/visible spectra prove that the Fe_3O_4/PANI microspheres have been prepared successfully. The present method can be extendable to fabricate other magnetic/conductive composites and these unique core/shell spherical materials could find applications in catalyst supports or biomedical areas.

Keywords: Fe_3O_4, Polyaniline, Magnetic properties, Monodispersity.

INTRODUCTION

Nanostructured materials possessing functional properties have been extensively studied because they have potential uses in diverse applications such as catalysis, nanodevice and biosensor. Among these nanomaterials, magnetic nanoparticles have been extensively studied and applied in numerous fields, such as sensors, spintronics, cell recognition, drug delivery, targeted therapeutics and catalysis[1-4]. As one of the most important and basic magnetic materials, Fe_3O_4 nanoparticles have been extensively studied both for its scientific interests and technological applications. One of the main advantages of Fe_3O_4 is also environmentally friendly, low cost, easy to prepare and possesses excellent water solubility. It exhibits unique electrical and magnetic properties due to the transfer between[5] Fe^{2+} and Fe^{3+}. However, functional materials are often used as a protective coating shell to ensure the stability of the inner magnetic core and as the intrinsic functions of the core/shell particles being electronconductive, biocompatible, inert, hydrophilic, or hydrophobic, *etc*[6,7].

On the other hand, conducting-polymer nanostructures have recently received special attention in the areas of nanoscience and nanotechnology because of their highly π-conjugated polymeric chains, reversible doping/de-doping process, unusual conducting mechanism and controllable chemical and electrochemical properties. These unique properties not only suggest promising applications of conducting polymers in technology but also hold an important position in materials science research[8]. Among the known conducting polymers, polyaniline (PANI) is one of the widely studied conducting polymers owing to its good environmental stability, tunable conductivity switching between insulating and semiconducting materials, facile synthesis and potential application in many areas[9,10]. Polyaniline composite materials possess the potential for a multitude of applications, such as in sensors and supercapacitors[11,12]. Therefore, conductive organic/inorganic nanocomposites have recently been studied intensively. Concerning the above-stated fields of research, superparamagnetic and conducting polymer hybrid materials in which inorganic magnetic cores are augmented with insoluble outer layers of conductive polyaniline belong to an important class of materials. Recently, Fe_3O_4/PANI nanocomposite has attracted intensive attention for applications of nanomaterials due to their novel magnetic and conductive properties. Several methods have been developed to synthesize Fe_3O_4/PANI nanocomposite. Leung's group[13] reported the preparation of Fe_3O_4@PANI nanocomposite with well-defined core/shell nanostructure via an ultrasound-assisted in situ surface polymerization method. Xu *et al.*[14] synthesised the functionalized Fe_3O_4 microspheres/PANI composites by two-step oxidative polymerization. However, such methods result in fluctuations in the size for which the as-synthesized composites had nonuniform magnetite fraction in each nanosphere composite due to nanoscale clustering of magnetic particles. Furthermore, many of these materials show relatively a small amount of magnetic contents, which usually resulted in the reduction of

their response to magnetic fields. It is therefore of interest to achieve high loads of superparamagnetic materials in each Fe_3O_4/PANI particle, keeping in mind that each particle should have a well-defined structure.

In this paper, we use a general approach for the fabrication of monodisperse, hydrophilic ferrite microspheres by a solvothermal reduction method. And then, the Fe_3O_4/PANI microspheres composites prepared *via* a novel liquid-liquid interface polymerization method. In this technique, Fe^{3+} was used as a milder polymerization oxidant which makes the aniline grow on the surface of Fe_3O_4 uniformly and high-content superparamagnetic Fe_3O_4 containing Fe_3O_4/PANI microparticles were obtained. Although we have demonstrated this procedure only with a Fe_3O_4 core and polyaniline shell as examples, it is believed that this method should be extendable to other magnetic core materials (Fe, γ-Fe_2O_3, Co, Ni and ferrite) and to a range of other conductive shell materials (such as polypyrrole, polythiophene, *etc*).

EXPERIMENTAL

Ferric chloride hexahydrate, ethylene glycol, sodium acetate, polyethylene glycol, ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used without further purification. Aniline was also obtained from Sinopharm Chemical Reagent Co., Ltd. and was freshly distilled prior to use. Doubly deionized water was used throughout the synthetic processes.

Synthesis of Fe_3O_4 microspheres: Synthesis of Fe_3O_4 microsphere followed the process reported in the literature[15]: $FeCl_3 \cdot 6\,H_2O$ (1.35 g, 5 mmol) was dissolved in ethylene glycol (40 mL) to form a clear solution, followed by the addition of sodium acetate (3.6 g) and polyethylene glycol (1 g). The mixture was stirred vigorously for 0.5 h and then sealed in a teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated to and maintained at 180 ºC for 6 h and allowed to cool to room temperature. The black products were separated with the help of a magnet and then washed with ethanol.

Synthesis of Fe_3O_4/PANI nanocomposite: Fe_3O_4/PANI nanocomposite were synthesized using a novel liquid-liquid interface polymerization method[16]. Typically, the interfacial reaction was performed in a beaker (800 mL). Aniline (200 mg) was dissolved in CH_2Cl_2 (200 mL) to form the lower organic layer. Fe_3O_4 microspheres (6 mg) and $FeCl_3 \cdot 6H_2O$ (200 mg) were dispersed in aqueous HCl (200 mL, 1 M) by sonicating for 1 h and formed the upper layer. After the interfacial system was established, the resulting two-phase system was left undisturbed at ambient temperature for 48 h. At the end of the polymerization reaction, the aqueous layer was carefully collected. The Fe_3O_4/PANI suspension was washed with deionized water several times and finally redissolved in double distilled water.

Scanning electron microscopy (SEM) measurements were carried out by using a FEI QUANTA 200F microscope. The SEM samples were prepared by placing a drop of a dilute dispersion of the composites in double-distilled water on conducting glass (ITO). UV/visible absorbance spectra were recorded on a PERSEE TU-1901 spectrophotometer.

RESULTS AND DISCUSSION

The well-dispersed Fe_3O_4 microspheres were prepared by a solvothermal reduction method[15]. Fe_3O_4 spheres retain superparamagnetic behavior at room temperature while possessing higher saturation magnetization. Therefore, these Fe_3O_4 microspheres are the most suitable template to fabricate super paramagnetic microspheres. Many strategies have also been developed to construct inorganic-organic core/shell structures by coating these cores with polymers[14,17]. In this work, we prepared inorganic-organic bifunctional Fe_3O_4/PANI core/shell structures by a novel liquid-liquid interface polymerization method. In this technology, the polyaniline form a thin films onto the surface of Fe_3O_4 microspheres due to the Fe^{3+} was used as a milder polymerization oxidant. The UV-visible was used to character the prepared nanocomposites. No obvious absorption peak was observed for the Fe_3O_4 (Fig. 1a), in agreement with the literature[18]. While the Fe_3O_4/PANI nanocomposite show two absorption bands peaking at 360 and 690 nm (Fig. 1b). The first one can be attributed partly to the π-π* transition of the benzenoid ring and partly to polaron band transistion due to its broad feature, while the second one can be assigned to polaron band transition, suggesting that conducting polyaniline was formed[19,20].

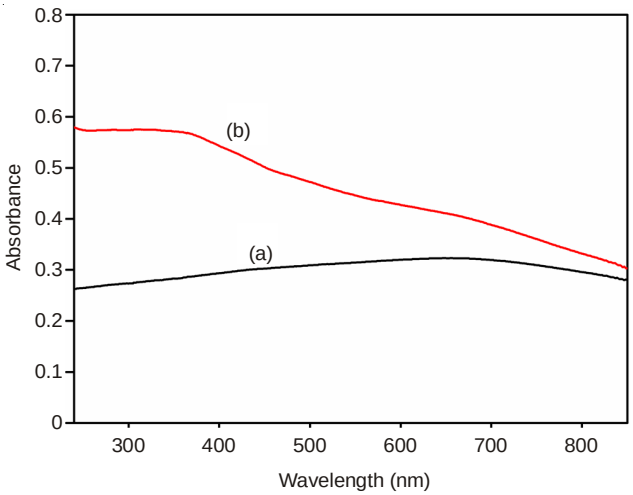

Fig. 1. UV/visible spectra of (a) Fe_3O_4, (b) Fe_3O_4/PANI nanocomposites

The size and shape of the products were examined by SEM images. Fig. 2a shows SEM images of Fe_3O_4 microspheres, which are spherical and have very narrow diameter distributions ranges from 140 to 200 nm. Fig. 2b shows SEM images of Fe_3O_4/PANI nanocomposites, no obvious changes in size or shape of the Fe_3O_4 cores are observed, but the Fe_3O_4 microspheres is well wrapped by the coating layer. It implies that the coating of an extremely thin polyaniline film on the surface of Fe_3O_4 microspheres.

Conclusion

In summary, we have demonstrated a simple, reproducible and facile method of preparing Fe_3O_4/PANI nanocomposites. On the basis of the functional group on Fe_3O_4 microspheres, polyaniline shell with thin films can be directly coated on the cores to form the mondisperse Fe_3O_4/PANI nanocomposites. On the other hand, Fe^{3+} was used as a milder polymerization

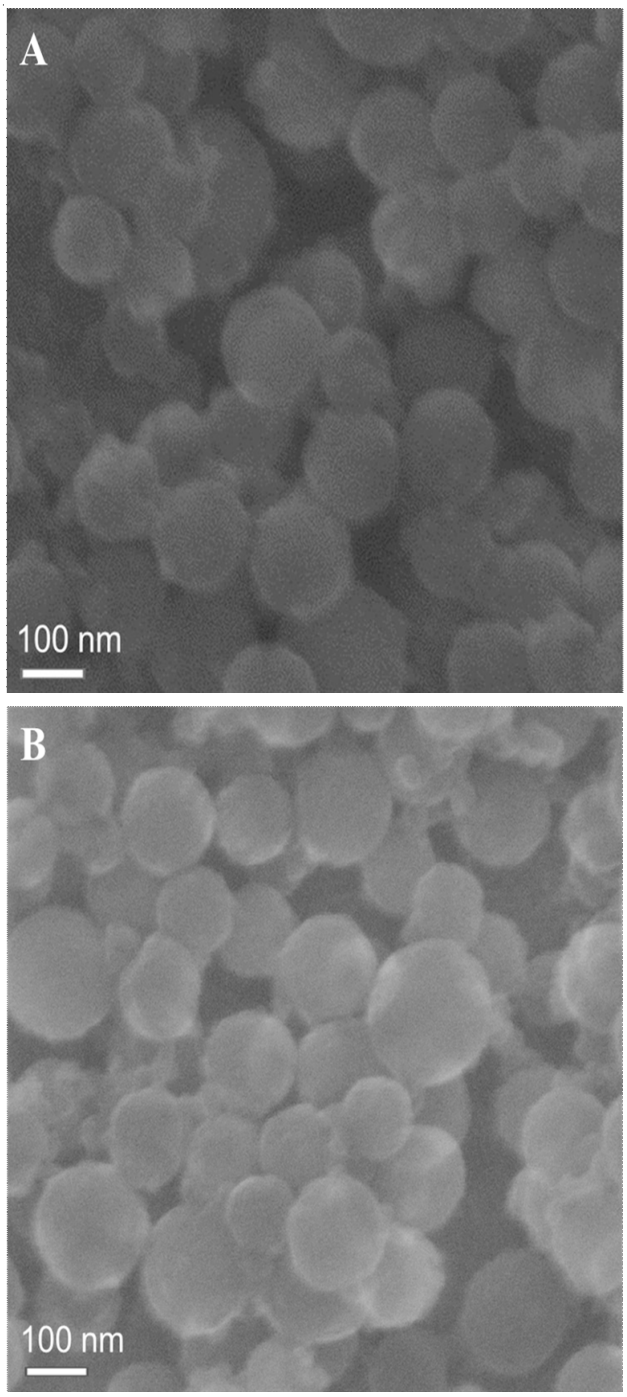

Fig. 2. SEM images of (a) Fe_3O_4, (b) Fe_3O_4/PANI nanocomposites

oxidant which makes the aniline grow on the surface of Fe_3O_4 uniformly. Furthermore, the present method can be extendable to fabricate other magnetic/conductive composites and these unique core/shell spherical materials could find applications in catalyst supports or biomedical areas.

ACKNOWLEDGEMENTS

This work was supported by the Key Project of Open Fund for Master Construction Disciplines of Yunnan Province (No. HXZ1304), the Youth project of Yunnan Province (No. 2014FD054), the National Natural Science Foundation of China (No. 61361002) and The scientific research fund project of Honghe University (XJ14Z02).

REFERENCES

1. D.K. Yi, S.S. Lee and J.Y. Ying, *Chem. Mater*., **18**, 2459 (2006).
2. C.M. Yu, L.L. Gou, X.H. Zhou, N. Bao and H.Y. Gu, *Electrochim. Acta*, **56**, 9056 (2011).
3. H.Y. Chen, D. Sulejmanovic, T.L. Moore, D.C. Colvin, B. Qi, O.T. Mefford, J.C. Gore, F. Alexis, S.J. Hwu and J.N. Anker, *Chem. Mater*., **26**, 2105 (2014).
4. C.R. Sun, J.S.H. Lee and M.Q. Zhang, *Adv. Drug Deliv. Rev*., **60**, 1252 (2008).
5. R.F. Chen, G.Q. Song and Y. Wei, *J. Phys. Chem. C*, **114**, 13409 (2010).
6. A. Pich, S. Bhattacharya, Y. Lu, V. Boyko and H.J.P. Adler, *Langmuir*, **20**, 10706 (2004).
7. H. Xu, L. Cui, N. Tong and H. Gu, *J. Am. Chem. Soc*., **128**, 15582 (2006).
8. M. Wan, *Adv. Mater*., **20**, 2926 (2008).
9. A.G. MacDiarmid, *Angew. Chem. Int. Ed*., **40**, 2581 (2001).
10. M. Zhao, X.M. Wu and C.X. Cai, *J. Phys. Chem. C*, **113**, 4987 (2009).
11. L. Nikzad, S. Alibeigi, M.R. Vaezi, B. Yazdani and M.R. Rahimipour, *Chem. Eng. Technol*., **32**, 861 (2009).
12. Q. Wu, Y. Xu, Z. Yao, A. Liu and G. Shi, *ACS Nano*, **4**, 1963 (2010).
13. S.H. Xuan, Y.X.J. Wang, J.C. Yu and K.C.F. Leung, *Langmuir*, **25**, 11835 (2009).
14. C.K. Cui, Y.C. Du, T.H. Li, X.Y. Zheng, X.H. Wang, X.J. Han and P. Xu, *J. Phys. Chem. B*, **116**, 9523 (2012).
15. H. Deng, X.L. Li, Q. Peng, X. Wang, J.P. Chen and Y.D. Li, *Angew. Chem. Int. Ed*., **117**, 2842 (2005).
16. J.D. Qiu, L. Shi, R.P. Liang, G.C. Wang and X.H. Xia, *Chem. Eur. J*., **18**, 7950 (2012).
17. S. Xuan, Y.X.J. Wang, K.C.F. Leung and K. Shu, *J. Phys. Chem. C*, **112**, 18804 (2008).
18. D.Q. Tang, R. Yuan and Y.Q. Chai, *J. Phys. Chem. B*, **110**, 11640 (2006).
19. W. Liu, J. Kumar, S. Tripathy, K.J. Senecal and L. Samuelson, *J. Am. Chem. Soc*., **121**, 71 (1999).
20. P. Xu, X. Han, C. Wang, B. Zhang, X. Wang and H.L. Wang, *Macromol. Rapid Commun*., **29**, 1392 (2008).