

One-pot synthesis of polyaniline/Fe₃O₄ nanocomposite in ionic liquid: electrical conductivity and magnetic studies

Xiaoyang Li, Genwang Zhang, Binwei Wang, Tan Lin, Wang Guo, and Feng Huixia*

School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050

Abstract. One-pot synthesis of polyaniline/Fe₃O₄ nanocomposite in 1-methyl-3-alkylcarboxylic acid imidazolium chloride ([CMMIm]Cl) ionic liquid (IL) was introduced for the first time in this work. Transmission electron microscopy (TEM), X-ray diffraction (XRD), four probes method and vibrating sample magnetometer (VSM) were used to explore the influence of IL on the structure, conductivity and magnetic properties of polyaniline/Fe₃O₄ composite. Compared with Fe₃O₄ particles prepared in water, the results show that Fe₃O₄ particles prepared in imidazolium-based ionic liquid were more regular in shape and dispersed uniformly. So the Fe₃O₄ nanoparticles prepared in IL can easier serve as cores to form the polyaniline/Fe₃O₄ nanocomposite via in situ chemical oxidative polymerization of aniline molecule. The saturation magnetization of polyaniline/Fe₃O₄ nanocomposite prepared in ionic liquid shows about 2 times higher than polyaniline/Fe₃O₄ composite prepared in water. And the conductivities of PANI/Fe₃O₄ composite prepared in IL decreased and the saturated magnetization increased with the increasing amount of Fe₃O₄.

1 Introduction

Owing to the unique electronic and magnetic properties of electromagnetic functionalized conducting polymers, they have recently received more and more attention for kinds of applications, such as microwave absorption [1], electromagnetic interference [2], catalytic materials[3],and sensor[4].Among the known conducting polymers, polyaniline (PANI) has been extensively studied due to its unique proton doping ability, low cost, thermal and chemical stability [5, 6]. Combining magnetic nanoparticles (Fe₃O₄), which contain ferromagnetic and supermagnetic properties, the polyaniline/Fe₃O₄ (PANI/Fe₃O₄) nanocomposite has been studied in various fields [7, 8].

Usually, the traditional methods of synthesizing electromagnetic composite contain two steps. First, magnetic nanoparticles are prepared in aqueous solution and dried for further use. Second, electromagnetic nanocomposite is prepared via in situ polymerization of aniline with magnetic nanoparticles [9, 10]. Recently, ionic liquid (IL) has introduced to prepare electromagnetic materials due to its excellent thermal stability, good electrical conductivity [11, 12]. However, the magnetic nanoparticles, which dried at first step are hard to disperse in IL again and easy to agglomerate [13].

In this work, we introduced one-pot reaction method to synthesize PANI/Fe₃O₄ nanocomposite directly. Firstly, Fe₃O₄ nanoparticles were synthesized in IL, and then, after adding aniline in IL, the polymerization carried out without any other treatment process. This method prevents the agglomeration of Fe₃O₄

nanoparticles effectively and enhances the saturation magnetization of PANI/Fe₃O₄ nanocomposite. The influence of IL on the structure, electrical conductivity and magnetic properties were discussed in detail. This novel method was found to be a straightforward, fast way to obtain conducting PANI coated magnetic Fe₃O₄ electromagnetic composite.

2 Experimental

Aniline monomer was purified by distilled under reduced pressure prior to use. The other chemicals and reagents were used as received from commercial sources without further purification.

2.1. Preparation of ionic liquid

1-methyl-3-alkylcarboxylic acid imidazolium chloride ([CMMIm]Cl) ionic liquid was prepared according to the previous report [14]. 0.17 mol chloroacetic acid solid was added to 0.15 mol N-Methylimidazole liquid with stirring until the mixed solution became uniformly. Then the solution was heated at 70 °C for 3-5 h. Finally, the sample was dried in the oven at 40°C for 12 h to yield the white solid of [CMMIm]Cl.

2.2 Preparation of PANI/Fe₃O₄

The PANI/Fe₃O₄ nanocomposite was synthesized by one-pot reaction. Firstly, Fe₃O₄ nanoparticles were prepared by co-precipitation method with IL as synthetic

* Corresponding author: fenghx@lut.cn

environment. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and the according amounts of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Table 1) were dissolved in distilled water with vigorous stirring under nitrogen protection. 5.0 g of IL was added to the mixture above. The molar ratio of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was 3:2. Then the solution was heated to 90°C and the pH value of the reaction mixture was kept in the range of 10-11 with addition of NaOH. As soon as the reaction started, black precipitate appeared immediately. The solution was kept under stirring for 1 h. Then the reaction mixtures were cooled to room temperature under ultrasonic treatment. Secondly, The PANI/ Fe_3O_4 nanocomposites were prepared by in situ chemical oxidative polymerization of

aniline with Fe_3O_4 . After adding 10 mmol of aniline, 10 mmol sulfamic acid (SA) and 30 ml HCl (1 M) to the above mixture under vigorous stirring, 10 ml 7.5 mmol ammonium persulphate (APS), which dissolved in 1M HCl solution, was added dropwise over 30 min (Table 1). Then, the reaction mixture was stirred for 2 h. The produced blackish green precipitate was filtered, washed with distilled water till colorless filtrate was obtained and then dried at 50°C for 24 h under vacuum.

The PANI/ Fe_3O_4 composite with ionic liquid was denoted as PF-I. For comparison, we also prepared PANI/ Fe_3O_4 sample using the same condition like sample 3 just without IL (PF) (Table 1)

Table .1 Preparation conditions for the PF-I and PF composite.

| Samples | Preparation conditions | | | | | | | Theoretical mass of Fe_3O_4 (g) |
|-------------------------------|--|--|--------|-----------|------------|-----------|----------------------------------|---|
| | $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (mmol) | $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (mmol) | IL (g) | An (mmol) | APS (mmol) | SA (mmol) | $n(\text{Fe}^{3+})/n(\text{An})$ | |
| PANI/ Fe_3O_4 | | | | | | | | |
| sample 1 | 0.862 | 0.575 | 5.0 | 10 | 7.5 | 10 | 0.0862 | 0.1 |
| sample 2 | 1.72 | 1.15 | 5.0 | 10 | 7.5 | 10 | 0.172 | 0.2 |
| sample 3 | 2.59 | 1.72 | 5.0 | 10 | 7.5 | 10 | 0.259 | 0.3 |
| sample 4 | 3.45 | 2.30 | 5.0 | 10 | 7.5 | 10 | 0.345 | 0.4 |
| sample 5 | 4.31 | 2.87 | 5.0 | 10 | 7.5 | 10 | 0.431 | 0.5 |
| PF | 2.59 | 1.72 | 0 | 1.0 | 7.5 | 10 | 0.259 | 0.3 |

2.3 Sample characterization

The powder XRD patterns were recorded on an X-ray diffractometer (Panalytical X'Pert PRO) equipped with $\text{CuK}\alpha$ as radiation source. Transmission electron microscope (TEM) analysis was carried out on a Tecnai G2 F30 microscope, working at 100 KV. A vibrating sample magnetometer (VSM, model Lake Shore, new 7304 series) was used to investigate the magnetic properties of the samples at room temperature. Four probes method was used to measure the conductivity of the obtained sample by a four-probe resistivity/square resistance tester (Kund Technology Co. Ltd., Guangzhou, China), the test samples were prepared in pellet form (diameter: 13mm, thickness: 0.6mm).

3 Results and Discussion

The morphology of Fe_3O_4 and PANI/ Fe_3O_4 composite which prepared in water and IL were investigated (Fig. 1). It is obviously to see that, the size distribution of Fe_3O_4 prepared in water (Fig. 1a) is about 4-17 nm with aggregation. On the other hand, for PF (Fig 1b), Fe_3O_4 prepared in water is hard to be dispersed in polymeric matrix evenly. However, by introducing IL in the synthesis process, large-scale Fe_3O_4 nanoparticles with a relatively uniform size of 5-11 nm were obtained (Fig. 1c). And the Fe_3O_4 nanoparticles are nearly spherical. Compared with PF, the Fe_3O_4 nanoparticles prepared in IL (Fig. 1d) are dispersed in polymeric matrix evenly.

And PANI is well coated or grown on the surface of Fe_3O_4 nanoparticles to form core-shell structured electromagnetic functioned composite. So one-pot synthesis of PANI/ Fe_3O_4 composite in IL could prevent agglomeration of Fe_3O_4 effectively.

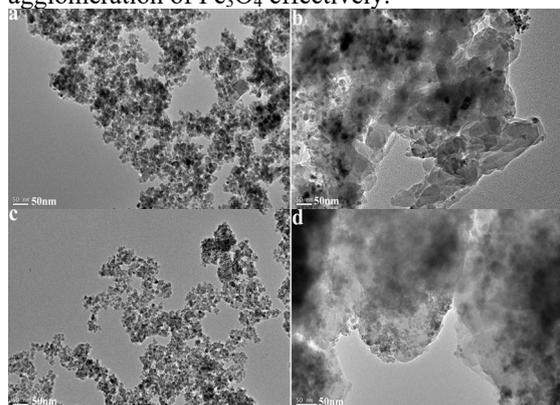


Fig. 1. TEM images of Fe_3O_4 prepared in water (a), PF (b), Fe_3O_4 prepared in IL (c) and PF-I (d)

Fig. 2 shows the XRD patterns of Fe_3O_4 and PF-I prepared in IL. The X-ray diffraction data of Fe_3O_4 nanoparticles reveals the crystalline peak at $2\theta=30.00^\circ$, 35.40° , 43.02° , 53.56° , 57.06° and 62.68° , corresponding to the (220), (311), (400), (422), (511) and (440) reflections. The crystallite size for the most intense peak (311) at $2\theta=35.40^\circ$ was calculated from the XRD data using the Scherrer formula and found to be 11 nm. The crystallite size is consistent with the result

obtained from TEM. The broad peak at $2\theta=20-30^\circ$ is ascribed to the polymer chains of PANI, suggesting that PANI is almost amorphous [15]. It is obviously to see that Fe_3O_4 retained its cubic structure on dispersion in PANI matrix during in situ polymerization reaction. On the other hand, it also conformed the formation of PANI/ Fe_3O_4 composite.

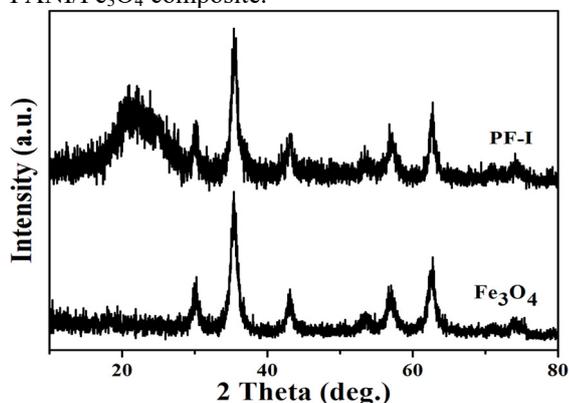


Fig. 2. XRD patterns of PF-I and Fe_3O_4 prepared in IL.

Fig. 3a shows the room temperature conductivity of PF-I series. The conductivity of pure PANI prepared in IL is 3.3 S/cm. As we know, with the adding of Fe_3O_4 particles, the conductivity of PANI/ Fe_3O_4 composite decreases dramatically[9].The decreased electrical conductivity is mainly due to the presence of semiconducting Fe_3O_4 nanoparticles that lowers conductivity of PANI/ Fe_3O_4 composite and partially baffle the formation of conductivity path .To figure out the influence of IL on materials electromagnetic property, we also prepared PF sample using the same condition like sample 3 just without IL (Table 1). Compared with PF-I, the conductivity of PF changed randomly from 2.0S/cm to 0.1S/cm at different points. It' s perhaps due to two reasons. First, the existence of IL reduced the intercontact resistance which caused by PANI conducting nanofibers entwinding around the Fe_3O_4 magnet.Second, Fe_3O_4 nanoparticles which were synthesized in IL directly are much easier to be incorporated into PANI matrix during one-pot in situ chemical oxidative polymerization of aniline than traditional methods. The new methods results the uniform dispersal of Fe_3O_4 nanoparticles in PANI, which is consistent with the result obtained from TEM.

Fig. 3b shows the magnetic properties of PF-I, PF and Fe_3O_4 prepared in IL. It can be seen that the saturation magnetization (M_s) of PF-I are less than that of pure Fe_3O_4 (54.08 emu/g). The M_s values of PF-I decreased with the decreasing of Fe_3O_4 nanoparticles. It due to the fact that conducting PANI is not magnetic, and the magnetic properties of nanocomposite are strongly dependent on the contents of Fe_3O_4 nanoparticles. However, the M_s values of PF-I (sample 3, 18.11 emu/g) is much higher than that of PF (8.04 emu/g, Fig. 3b, inset) which prepared at the same condition just without IL. This can be attributed to the fact that Fe_3O_4 nanoparticles were easier aggregation without IL.

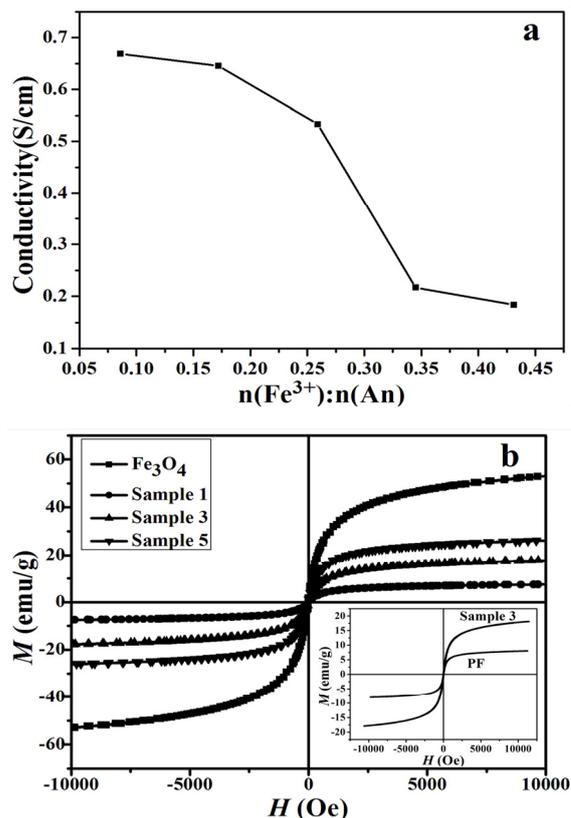


Fig. 3. Room temperature conductivity of PF-I series (a), magnetic hysteresis loops of PF-I, PF (the inset), and pure Fe_3O_4 prepared in IL (b).

In conclusion, electromagnetic Fe_3O_4 /PANI nanocomposite was successfully synthesized via the in situ polymerization using IL as synthetic environment by one-pot method. For PF-I, structure analysis showed that the ferrite nanoparticles were incorporated in the polyaniline matrix evenly to form a core-shell structure. The introduction of IL in the composite synthesis process not only helped to form uniform structure but also helped to enhance electromagnetic property of composite. It perhaps provide a new strategy to fabricate functionalized nanocomposite easily

Acknowledgement

We are grateful for financial support from the National Natural Science Foundation of China (NSFC. 21664009, 51063003), the Ministry of Science and Technology project (No. 2009GJG10041), the Fundamental Research Funds for the Universities of Gansu (No. 1105ZTC136), the Natural Science Foundation of Gansu Province (No. 17JR5RA135)

References

1. P.B. Liu, Y. Huang, X. Zhang, Mater. Lett. 129, 35 (2014)
2. K.Y. Chen, C. Xiang, L.C. Li, H.S. Qian, Q.S. Xiao, F. Xu, J Mater Chem. 22, 6449 (2012)

3. Yan W, Wu X, Zhang W, et al. *Materials Chemistry & Physics*, 209(2018)
4. T.T. Wen, W.Y. Zhu, C. Xue, J.H. Wu, Q. Han, X. Wang, X.M. Zhou, H.J. Jiang, *Biosens Bioelectron.* 56, 180 (2014)
5. L. Wang, X.P. Lu, S.B. Lei, Y.H. Song, *J Mater Chem A* 2, 4491 (2014)
6. Zhao Y, Chen H, Li J. *J Colloid Interface Sci*, 450:189-195 (2015)
7. L.H. Han, Y. Wei, *Mater. Lett.* 70, 1 (2012)
8. B.J. Jaramillo-Tabares, F.J. Isaza, *Mater. Chem. Phys.* 132, 529 (2012)
9. Hou J, Long Z, Hu Q. *Journal of Materials Science Materials in Electronics*,28,13 (2017)
10. G.D. Prasanna, H.S. Jayanna, A.R. Lamani, S. Dash, *Synth. Met.* 161, 2306 (2011)
11. A. Baykal, M. Günay, M.S. Toprak, H. Sozeri, *Mater. Res. Bull.* 48, 378 (2013)
12. C.J. Leng, J.H. Wei, Z.Y. Liu, J. Shi, *J. Alloy. Compd.* 509, 3052 (2011)
13. H. Kavas, M. Günay, A. Baykal, M.S. Toprak, H. Sozeri, B. Aktas, *J. Inorg. Organomet. Polym. Mater.* 23, 306 (2013)
14. Guo Y, Zhang L, Hou J. *Chemical Journal of Chinese Universities*, 25,545(2016)
15. Y.P. Sun, F. Xiao, X.G. Liu, C. Feng, C.G Jin. *RSC Adv.* 3, 22554 (2013)