

Decoration of Electrospun Nanofibers with Magnetic Nanoparticles via Electrospinning and Sol-gel Process

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Abstract Polyacrylonitrile(PAN)/Fe₃O₄ composite nanofibers were successfully obtained through electrospinning and sol-gel technology. The resulting magnetic Fe₃O₄ nanoparticles were homogeneously distributed on the surface of PAN nanofibers and the diameters of polyacrylonitrile nanofibers and nanoparticles were easily controlled, respectively. The distribution of Fe₃O₄ nanoparticles inside the nanofibrous composite was investigated by field emission scanning electron microscopy and transmission electron microscopy. X-ray diffraction reveals the presence of Fe₃O₄ nanoparticles in the composite nanofiber. The resulting sample shows a super paramagnetic behavior.

Keywords Electrospinning; Magnetic; Fe₃O₄; Nanoparticle; Sol-gel

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1 Introduction

Recently, nanoscale magnetic particles have attracted a great interest in fundamental and application researches with special emphasis on their size dependent properties^[1]. Among magnetic nanoparticles, Fe₃O₄ has become the focus due to its magnetic, catalytic, conductive and biological properties which could be applied in many fields including magnetic storage devices^[2], ferrofluids^[3], magnetic carriers for drug targeting^[4], the separation of biochemical products^[5] and catalysis^[6]. For these purposes, well-dispersed chemically stable nanoparticles with uniform size and shape are desired. In this respect, the synthesis of composite nanomaterials where the magnetic nanoparticles are integrated into organic or inorganic matrix is particularly promising since it allows not only the control over the particle growth but also the spatial arrangement in some cases. Polymers^[7], glass^[8] or ceramic materials^[9] have been extensively used as matrix in the preparation of nanocomposites containing Fe₃O₄ nanoparticles. These composites would be a perfect candidate for heterogeneous catalysis with excellent thermal and chemical stability and good magnetic performance.

Electrospinning technique^[10—14] has been established as a unique and cost effective approach for fa-

bricating fibers with large surface area for various application. Electrospun nanofibers are good matrices to support nanoparticles. A lot of work has been done about the synthesis of nanoparticles/electrospun nanofiber composites. Li *et al.*^[15] provided a simple method for fabricating size controllable single-crystal Ag nanoparticles on the surface of polyacrylonitrile(PAN) nanofibers *via* electrospinning followed by UV irradiation. Dong *et al.*^[16] have illustrated the synthesis of gold and silver nanoparticles on the surface of electrospun Poly(4-vinylpyridine)(P4VP) fibers and P4VP/poly(methyl methacrylate)(PMMA) composite fibers by absorption of metal ions from a colloidal gold solution and subsequent reduction. Li *et al.*^[17] demonstrated that nanostructures can be selectively deposited on electrospun anatase nanofibers *via* the photocatalytic feature of titania. Di *et al.*^[18] manufactured magnetic PAN/Fe₃O₄ nanocomposite fibers by electrospinning PAN/DMF solution with suspended Fe₃O₄ nanoparticles, they also examined the influence of the operating parameters and the rheological behavior of the solution. However, they did not show how the particles were dispersed inside the nanofibers and using this method is hard to fabricate well dispersed magnetic nanoparticles/nanofibers composites with their surface homogeneously covered by

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mono-dispersed metal nanoparticles with controllable size because the major difficulty to manufacture magnetic nanoparticles is their undesirable agglomeration to form larger particles.

In this study, we demonstrated the synthesis of ultrafine PAN fibers containing mono-dispersed Fe_3O_4 nanoparticles *via* electrospinning followed by a sol-gel process, the morphological characteristics and magnetic properties of the resulting nanofibrous composites were characterized by scanning electron microscopy, X-ray diffraction, transmission electron microscopy and vibrating sample magnetometry.

2 Experimental

PAN with a relative molecular mass of 150000 was purchased from Aldrich Co. *N,N*-dimethylformamide(DMF), ferrous chloride($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), hydrochloric acid(HCl), sodium hydroxide(NaOH) were purchased from Tianjin Tiantai Fine Chemicals Co., all the reagents were analytical grade and used as received without further purification.

Fibers of PAN/ FeCl_3 were obtained by electrospinning *via* an apparatus and process described previously^[15]. PAN/DMF solution was prepared by dissolving 10% PAN and 2%(mass fraction) FeCl_3 (the molar ratio of Fe^{3+} : AN = 1:30) in DMF for 6 h under 90 °C. During electrospinning, the applied voltage was held constant at 15 kV, and the distance between the syringe and the aluminum foil collector was kept at 25 cm. After 0.2 mL of 12.1 mol/L HCl and 25 mL of purified, deoxygenated water (by nitrogen gas bubbling for 30 min) were mixed, 1.44 g (0.0053 mol) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.55 g (0.00267 mol) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in the solution with stirring. A piece of 0.075 g electrospun PAN/ FeCl_3 mat was cut into several tiny pieces and immersed in the solution for 3 h. The resulting solution with fiber mats suspended in was added dropwise to 250 mL of 1.5 mol/L NaOH/deoxygenated water solution under vigorous stirring, an instant black precipitate was generated in the solution during this step. The paramagnetism was checked *in situ* by placing a magnet near the black precipitate of Fe_3O_4 . When the reaction was completed, the mats were rinsed by plenty of distilled water, followed by a 30 min ultrasonic process.

The PAN/ FeCl_3 nanofibers were analyzed by scanning electron microscopy(SEM)(SSX-550, Shi-

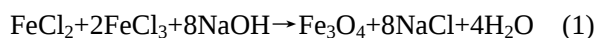
madzu). A drop of Fe_3O_4 nanoparticle sol was carefully placed on the copper grid surface and dried for transmission electron microscopy(TEM, Hitachi-600) study. X-ray diffraction(XRD) patterns of the product were recorded on a Rigaku D/max 2500/PC diffractometer with Cu $K\alpha$ radiation at a tube voltage and current of 40 kV and 200 mA, respectively. The room-temperature magnetization in an applied magnetic field was performed on a model JDM-13 vibrating sample magnetometer.

3 Results and Discussion

Fig.1 shows SEM and TEM images of PAN/ FeCl_3 electrospun nanofibers under magnifications. Fig.1(A) is a low-magnification view of the nanofibers [the molar ratio of Fe^{3+} :AN(Cyano) is 1:30], showing the electrospun nanofibers have smooth morphology with an average diameter of about 150 nm, and the nanofibers diameter could be well controlled by adjusting electrospinning parameters such as polymer concentration and the operational conditions such as the strength of applied electric field. During the process of Fe_3O_4 formation in solution, the color of PAN/ FeCl_3 nanocomposite fibers gradually changed from yellow to black, indicating that Fe^{3+} on the surfaces of PAN nanofibers reacted with Fe^{2+} in the solution and to form small aggregated Fe_3O_4 nanoparticles. Fig.1(B) is a typical TEM image of as-prepared product, showing that the surfaces of the PAN nanofibers are homogeneously covered by uniform Fe_3O_4 nanoparticles with an average diameter of 8 nm, the inset shows the electron diffraction pattern(ED) image of Fe_3O_4 nanoparticles, which confirms that the oxide is crystal and has an inverse cubic spinel structure. Because of the salts distributed simultaneously within the polymer and in the solution, the nanoparticles are easily dispersed homogeneously in the circumstance and the sizes could be precisely controlled by the sol-gel process which had been intensely investigated^[19].

The size distribution of the formed particles in the solution and on the surface of polymer fibers are quite the same, indicating a homogeneous atmosphere between polymer-inside and polymer-outside [see Fig.1(D)], so we assumed that each Fe^{3+} on the surface of polymer nanofiber reacted with another Fe^{3+} and a Fe^{2+} in the solution according to reaction(1), just as the other Fe^{3+} in the solution, forming Fe_3O_4

nanoparticles immobilized firmly and imbedded on the fibers' surface which hardly come off within 30 min ultrasonication.



To verify this mechanism, a piece of pure electrospun PAN mat was used instead of PAN/FeCl₃ electrospun nanofibers to repeat the reaction as in the experiment. The TEM result[Fig.1(C)] shows that the formed Fe₃O₄ nanoparticles did not grow on the po-

lymer surface, the formed Fe₃O₄ nanoparticles have not any reaction with PAN fibers, indicating the PAN surface-polymer-chains(or the cyanos) extended to the solution phase can not adsorb the Fe₃O₄ nanoparticles onto the polymer surface, which demonstrates that Fe₃O₄ nanoparticles immobilized on the fibers were formed from the Fe³⁺ which were doped in the PAN fibers.

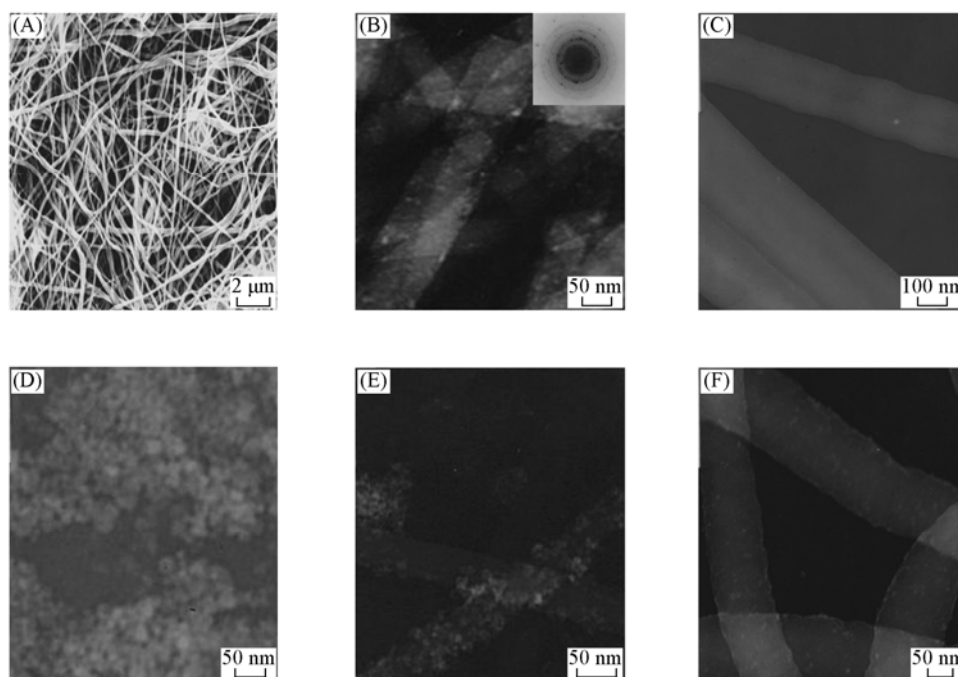


Fig.1 SEM images of PAN/FeCl₃ nanofibers(A) and TEM images of PAN nanofibers and Fe₃O₄ nanoparticles[(B)—(F)]

(A) The molar ratio of Fe³⁺:AN is 1:30; (B) PAN nanofibers with uniform, mono-dispersed Fe₃O₄ nanoparticles[electrospun nanofibers with the molar ratio of Fe³⁺:AN=1:30]; (C) PAN nanofibers without Fe₃O₄ nanoparticles growing on their surfaces; (D) Fe₃O₄ nanoparticles forming in solution; (E) PAN nanofibers with Fe₃O₄ nanoparticles on their surfaces. Electrospun nanofibers with the molar ratio of Fe³⁺:AN=1:5; (F) electrospun nanofibers with the molar ratio of Fe³⁺:AN=1:100.

In our experiment, the sizes and distribution density of the Fe₃O₄ nanoparticles can be adjusted by varying the molar ratio of Fe³⁺ to AN in the electrospinning process. If the molar ratio of Fe³⁺:AN was 1:5, the sizes of the Fe₃O₄ nanoparticles would be enlarged to 15 nm and aggregated as shown in Fig.1(E), and the distribution density would be much thicker than that of the sample with a molar ratio of 1:30 of Fe³⁺:AN. When the molar ratio of Fe³⁺:AN⁻ was lowered to 1:100, scattered mono-dispersed Fe₃O₄ nanoparticles with an average diameter of 4 nm could be obtained on the surface of PAN nanofibers[Fig.1(F)].

The XRD patterns of Fe₃O₄ nanoparticles and Fe₃O₄/PAN composites are shown in Fig.2. The diffraction peaks of the Fe₃O₄ nanoparticles(Fig.2 pattern a) were measured to be 2θ=30.38°, 35.62°, 43.18°, 53.45°, 57.08, and 62.84°, which can be assigned to

(220), (311), (400), (422), (511) and (440), respectively. These data are in good agreement with those of Fe₃O₄(JCPDS No.). The XRD patterns of Fe₃O₄/PAN composites(Fig.2b) show a broad non-crystalline peak(2θ=20°—30°) and a crystalline peak(2θ=18°)

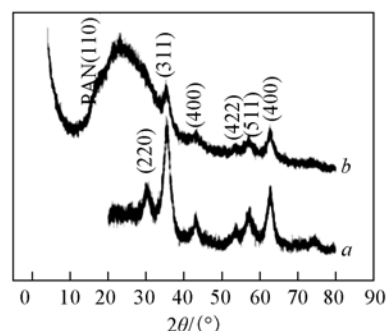


Fig.2 XRD patterns of pure Fe₃O₄ nanoparticles(a), and Fe₃O₄/PAN composites(b)

corresponding to the orthorhombic PAN (110) reflection^[20], and besides the diffraction peaks of the PAN phase, another six peaks appeared corresponding to the above peaks, indicating that the Fe₃O₄ nanoparticles on the PAN nanofibers have the same crystal diffraction as pure Fe₃O₄. On the other hand, the broadening of these peaks suggests the presence of Fe₃O₄ nanoparticles.

Fig.3 shows the dependence of the magnetization on the applied magnetic fields for Fe₃O₄ nanoparticles and Fe₃O₄/PAN composite at room temperature. The observation of hysteresis loop indicating this superparamagnetic behavior is similar to that of Fe₃O₄ nanoparticles. Because the magnetic properties are contributing to the Fe₃O₄ nanoparticles in the composites, it is reasonable to believe that the superparamagnetic behavior of the composites can be enhanced by increasing the doping concentration of Fe₃O₄ nanoparticles.

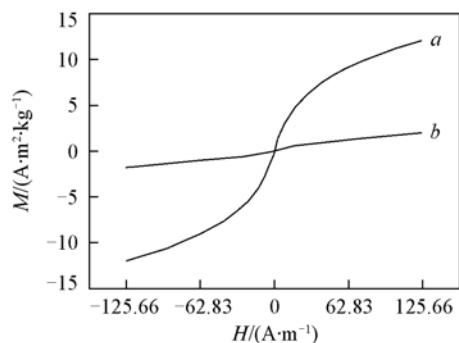


Fig.3 Magnetization versus applied magnetic field at room temperature for Fe₃O₄ nanoparticles(a), Fe₃O₄/PAN composites(b)

4 Conclusions

We have demonstrated the synthesis of ultrafine PAN fibers containing monodisperse Fe₃O₄ nanoparticles *via* electrospinning followed by a sol-gel process. Magnetic Fe₃O₄ nanoparticles on the PAN nanofibers are almost uniform and most of Fe₃O₄ nanoparticles are approximately spherical with a diameter of about 8 nm. The magnetic Fe₃O₄ nanoparticles

with controllable sizes are homogeneously distributed on the surface of the PAN nanofibers. The diameters of the PAN nanofibers and Fe₃O₄ nanoparticles could be controlled by varying the electrospinning and sol-gel process parameters, respectively. The nanocomposite fibers have a large ratio of surface area to volume and the PAN nanofibers have superior mechanical properties and also have super paramagnetic behavior which would find a lot of application.

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