Single Flexible Nanofiber to Simultaneously Realize Electricity-Magnetism Bifunctionality

Xiangting Dong**, Guixia Liu*

*Key Laboratory of Applied Chemistry and Nanotechnology at Universities of Jilin Province,
Changchun University of Science and Technology, Changchun, 130022, China

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In order to develop new-typed multifunctional composite nanofibers, PANI/Fe₃O₄/PVP flexible bifunctional composite nanofibers with simultaneous electrical conduction and magnetism have been successfully fabricated via a facile electrospinning technology. Polyvinyl pyrrolidone (PVP) is used as a matrix to construct composite nanofibers containing different amounts of polyaniline (PANI) and Fe₃O₄ nanoparticles (NPs). The bifunctional composite nanofibers simultaneously possess excellent electrical conductivity and magnetic properties. The electrical conductivity reaches up to the order of 10⁴ S·cm⁻¹. The electrical conductivity and saturation magnetization of the composite nanofibers can be respectively tuned by adding various amounts of PANI and Fe₃O₄ NPs. The obtained electricity-magnetism bifunctional composite nanofibers are expected to possess many potential applications in areas such as electromagnetic interference shielding, special coating, microwave absorption, molecular electronics and future nanomechanics. More importantly, the design concept and construct technique are of universal significance to fabricate other bifunctional one-dimensional nanostructures.

Keywords: Electrical conductivity, Magnetism, Polyaniline, Electrospinning, Nanofibers

1 Introduction

Electrospinning is an outstanding technique to process viscous solutions or melts into continuous fibers with diameters ranging from micrometer to nanometer. This technique attracts extensive academic investigations,¹³ and is also applied in many areas such as filtration,⁴ optical and chemical sensors,⁵ biological scaffolds⁶ and electrode materials.⁷

PANI is one of the most important conducting polymers because of its high electrical conductivity, good redox reversibility, processibility, and environmental stability⁸,⁹ as well as its a variety of potential applications.⁹,¹⁰ In recent years, one-dimensional (1D) structures of PANI including nanowires, rods and tubes have been studied with the expectation that such materials will combine the advantages of both low-dimensional systems and organic conductors.¹¹ Sub-micron fibers of pure PANI doped with sulfuric acid or hydrochloric acid were prepared by electrospinning PANI with suitable molecular weight dissolved in hot sulfuric acid,¹² but it remains a great challenge to apply electrospinning to PANI as limited by its molecular weight and solubility. To overcome this problem, most of the researchers electrospin PANI through blending it with other spinnable polymers.¹³,¹⁴

Magnetic Fe₃O₄ nanocrystals have been extensively studied owing to their unique and tunable magnetic properties. Their magnetic features have found widespread uses in applications as diverse as environmental remediation, magnetic recording, biomacromolecule separation, catalyst separation, drug/gene delivery and release, and magnetic resonance imaging.¹⁵-¹⁸

In the past few years, multifunctional composite materials have attracted inevitable attention of scientists.¹⁹-²¹ Some preparations of Fe₃O₄@RE complex (RE=rare earth) core-shell structure NPs have been reported.²²-²⁴ Recently, Ma, et al. have prepared Fe₃O₄/RE complex magnetic-fluorescent bifunctional composite nanofibers and nanobelts via electrospinning process.²⁵-²⁹ Wang et al., have prepared PANI particles/rare earth complex/PVP luminescent-electrical bifunctional composite nanofibers via electrospinning process.³⁰ It is found from the above discussion that multifunctional composite materials have attracted extensive academic researches and become one of the popular subjects of study in materials science. To the best of our knowledge, there have been rare reports on the preparation and performance of electricity-magnetism bifunctional nanofibers in the literature.

In the present study, we successfully assembled electricity-magnetism bifunction into single PANI/Fe₃O₄/PVP flexible nanofiber via a facile electrospinning technique using PANI as a conductive polymer and Fe₃O₄ NPs as a magnetic material. The structure, morphology and performances of the bifunctional flexible nanofibers were systematically studied, and some new results were obtained.
2 Experimental

2.1 Chemicals

Polyvinyl pyrrolidone (PVP, Mw≈90,000) and dimethylformamide (DMF) were bought from Tianjin Tiantai Fine Chemical Co., Ltd. Anhydrous ethanol, aniline (ANI), FeCl₃·6H₂O, FeSO₄·7H₂O, NH₄NO₃, polyethylene glycol (PEG, Mw=20,000), ammonia and (IS)-(+)-Camphor-10 sulfonic acid (CSA) were bought from Sinopharm Chemical Reagent Co., Ltd. Ammonium persulfate (APS) was purchased from Guangdong Xilong Chemical Co., Ltd. All the reagents were of analytical grade and directly used as received without further purification. Deionized water was homemade.

2.2 Preparation of Fe₃O₄ NPs

Fe₃O₄ NPs were obtained via a facile coprecipitation synthetic method, and PEG was used as a protective agent to prevent the particles from aggregation. One typical synthetic procedure was as follows: 5.4060 g of FeCl₃·6H₂O, 2.7800 g of FeSO₄·7H₂O, 4.04 g of NH₄NO₃ and 1.9 g of PEG were added into 100 mL of deionized water to form uniform solution under vigorous mechanical stirring (400 r·min⁻¹) at 50 °C. To prevent the oxidation of Fe³⁺, the reactive mixture was kept under argon atmosphere. After the mixture had been bubbled with argon for 30 min, 0.1 mol·L⁻¹ of NH₃·H₂O was dropwise added into the mixture to adjust the pH value above 11. Then the system was continuously bubbled with argon for 20 min at 50 °C, and black precipitates were formed. The precipitates were collected from the solution by magnetic separation, washed with deionized water for three times, and then dried in an electric vacuum oven at 60 °C for 12 h with the vacuum degree of 0.08 MPa.

2.3 Fabrication of electricity-magnetism bifunctional composite nanofibers via electrospinning

In the preparation of spinning solution, the masses of ANI and Fe₃O₄ NPs were respectively proportional to the mass of PVP, and the molar ratio among ANI, CSA and APS were 2:1:2. ANI was dissolved in 3.100 g of DMF with magnetic stirring at room temperature, and then 0.9 g of PVP and CSA were slowly added into the above solution. The mixture was then cooled down to 0 °C in an ice-bath. The mixture was denoted as solution I. A mixed solution of ammonium persulfate (APS) and 2.000 g of FeSO₄·7H₂O, 4.04 g of NH₄NO₃ and 1.9 g of PEG were added into 100 mL of deionized water to form uniform solution under vigorous mechanical stirring (400 r·min⁻¹) at 50 °C. To prevent the oxidation of Fe³⁺, the reactive mixture was kept under argon atmosphere. After the mixture had been bubbled with argon for 30 min, 0.1 mol·L⁻¹ of NH₃·H₂O was dropwise added into the mixture to adjust the pH value above 11. Then the system was continuously bubbled with argon for 20 min at 50 °C, and black precipitates were formed. The precipitates were collected from the solution by magnetic separation, washed with deionized water for three times, and then dried in an electric vacuum oven at 60 °C for 12 h with the vacuum degree of 0.08 MPa.

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During the electrospinning process, a traditional electrospinning apparatus was used to prepare the PANI/Fe₃O₄/PVP composite nanofibers. Spinning solution was loaded into a plastic syringe with a plastic spinneret, and the inner diameter of the spinneret was 1 mm. Carbon rod used as anode was inserted into spinning solution. A flat iron net was used as cathode and collector and put about 11 cm away from the tip of the spinneret. A positive direct current (DC) voltage of 13 kV was applied between the spinneret and the collector to generate stable, continuous PVP-based composite nanofibers under the ambient temperature of 20 °C-25 °C, and the relative humidity was 45%-50%.

2.4 Characterization Methods

The as-prepared Fe₃O₄ NPs and PANI/Fe₃O₄/PVP composite nanofibers were identified by an X-ray powder diffractometer (XRD, Bruker, D8 FOCUS) with Cu Ka radiation. The morphology and internal structure of PANI/Fe₃O₄/PVP composite nanofibers were observed by a field emission scanning electron microscope (FESEM, XL-30) and a transmission electron microscope (TEM, JEM-2010), respectively. The elementary compositions of the PANI/Fe₃O₄/PVP nanofibers were determined by an energy dispersive X-ray spectrometer (EDX, GENESIE 2000). The electrical conductivity was detected by a Hall effect measurement system (ECOPIA HMS-3000). Then, the magnetic performances of Fe₃O₄ NPs and PANI/Fe₃O₄/PVP composite nanofibers were measured by a vibrating sample magnetometer (VSM, MPMS SQUID XL). All measurements were performed at room temperature in air atmosphere, and the relative humidity was 40%-45%.

3 Results and discussion

3.1 Characterizations of the Structure and Morphology

XRD patterns of Fe₃O₄ NPs and composite nanofibers (S3) are shown in Fig. 1. The XRD patterns in Fig. 1a reveal that the as-prepared Fe₃O₄ NPs are conformed to the cubic structure of Fe₃O₄ (PDF 74-0748). No characteristic diffraction peaks of any other impurities are detected. XRD analysis result of the PANI/Fe₃O₄/PVP composite nanofibers demonstrates that the composite nanofibers contain Fe₃O₄ NPs, as indicated in Fig. 1b.

The morphology of the as-prepared Fe₃O₄ NPs is observed by means of TEM, as presented in Fig. 2a. The size distribution of the spherical Fe₃O₄ NPs is almost uniform, and the diameter of the Fe₃O₄ NPs is 9-13 nm. In order to characterize the size and morphology of the
presented PANI/Fe$_3$O$_4$/PVP composite nanofibers, FESEM observation is conducted. Fig. 2b shows FESEM image of PANI/Fe$_3$O$_4$/PVP composite nanofibers, indicating that the as-prepared nanofibers are relatively smooth. The Image-Pro Plus 6.0 software is used to measure the diameters of the nanofibers, and the results are analyzed with statistics. The diameter for composite nanofibers is 400±20 nm under the confidence level of 95%, as indicated in Fig. 3. The TEM image of PANI/Fe$_3$O$_4$/PVP composite nanofibers is presented in Fig. 2c. It is obviously seen from the TEM image that Fe$_3$O$_4$ NPs are well dispersed in the composite nanofibers. A slightly agglomeration phenomenon which can be observed via FESEM and TEM is caused by the large surface energy of the nano-sized Fe$_3$O$_4$ particles. The TEM image of PANI/Fe$_3$O$_4$/PVP composite nanofibers is presented in Fig. 2c. It is obviously seen from the TEM image that Fe$_3$O$_4$ NPs are well dispersed in the composite nanofibers. A slightly agglomeration phenomenon which can be observed via FESEM and TEM is caused by the large surface energy of the nano-sized Fe$_3$O$_4$ particles. The EDX analysis, as shown in Fig. 2d, reveals that the composite nanofibers consist of C, N, O, S, Fe and Au elements. The Au peak in the spectrum comes from gold conductive film plated on the surface of the sample for SEM observation. No other elements are found in the sample, implying that the PANI/Fe$_3$O$_4$/PVP composite nanofibers are highly pure.

3.2 Magnetic Property

The magnetic properties of Fe$_3$O$_4$ NPs and PANI/Fe$_3$O$_4$/PVP composite nanofibers are examined by a vibrating sample magnetometer. No remanence is detected for the as-prepared Fe$_3$O$_4$ NPs. The zero coercivity and the reversible hysteresis Fig. 1 XRD patterns of Fe$_3$O$_4$ NPs (a) and PANI/Fe$_3$O$_4$/PVP composite nanofibers (b) with PDF standard card of Fe$_3$O$_4$
behavior indicate the superparamagnetic nature of the Fe₃O₄ NPs, as revealed in Fig. 4. The composite nanofibers also demonstrate superparamagnetic performance owing to Fe₃O₄ NPs introduced into the composite nanofibers. The variation of saturation magnetization value results from the different amounts of Fe₃O₄ introduced in composite nanofibers. With the increase of Fe₃O₄ content in composite nanofibers, saturation magnetization of composite nanofibers increases, as demonstrated in Fig. 4 and Table 2, implying that the magnetic properties of the composite nanofibers can be tuned via addition of various amounts of Fe₃O₄ NPs.

3.3 Electrical Conductivity Analysis

The average electrical conductivity values of the samples are summarized in Table 3. The electrical conductivity is greatly increased from 1.357×10⁻⁶ to 7.175×10⁻³ S·cm⁻¹ at the beginning when the PANI is incorporated into composite nanofibers, meaning that the electrical conductivity of the composite nanofibers can be tunable by adjusting amount of PANI. With further increase in PANI content, the electrical conductivity of composite nanofibers is only slightly increased. The increase in electrical conductivity of PANI/Fe₃O₄/PVP composite nanofibers with increasing in PANI content is due to forming a better continuous net structure for PANI polymer. Furthermore, it is found from Table 3 that the electrical conductivity of the composite nanofibers is slightly increased with increasing in the mass ratios of Fe₃O₄ to PVP when fixing the other parameters, as shown in samples S3, S6, S7 and S8.

3.4 Formation Mechanism for PANI/Fe₃O₄/PVP Composite Nanofibers

We propose the formation mechanism for PANI/Fe₃O₄/PVP composite nanofibers, as shown in Fig. 5. Firstly, ANI and PVP are dissolved in DMF to form solution with certain viscosity. Secondly, ammonium persulfate (APS) is added into above solution and allowed to react at 0 °C for 24 h. Finally, the prepared Fe₃O₄ NPs are added into the mixture under magnetic stirring at room temperature, thus the spinning solution is prepared. The spinning solution is loaded into a plastic syringe, and then PANI/Fe₃O₄/PVP composite nanofibers are fabricated by electrospinning. Fe₃O₄ NPs are well dispersed in the composite nanofibers. PANI also forms a continuous network in the nanofibers, leading to high electrical conductivity of the electricity-magnetism bifunction composite nanofibers.

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Table 2 Saturation magnetization of Fe₃O₄ NPs and PANI/Fe₃O₄/PVP composite nanofibers

<table>
<thead>
<tr>
<th>Samples</th>
<th>Saturation magnetization (Ms)/emu·g⁻¹</th>
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<tbody>
<tr>
<td>Fe₃O₄ NPs</td>
<td>51.40</td>
</tr>
<tr>
<td>Fe₃O₄ : PVP=1:1 (S7)</td>
<td>10.90</td>
</tr>
<tr>
<td>Fe₃O₄ : PVP=1:2 (S6)</td>
<td>6.62</td>
</tr>
<tr>
<td>Fe₃O₄ : PVP=1:3 (S3)</td>
<td>4.19</td>
</tr>
<tr>
<td>Fe₃O₄ : PVP=1:4 (S8)</td>
<td>3.35</td>
</tr>
</tbody>
</table>

Table 3 Electrical conductivity of the samples doped with various amount of PANI and Fe₃O₄ NPs

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electrical conductivity/ S·cm⁻¹</th>
</tr>
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<tbody>
<tr>
<td>PANI:PVP=10% (S1)</td>
<td>1.357×10⁻⁶</td>
</tr>
<tr>
<td>PANI:PVP=20% (S2)</td>
<td>1.745×10⁻⁶</td>
</tr>
<tr>
<td>Fe₃O₄:PVP=1:3 (S3)</td>
<td>7.175×10⁻³</td>
</tr>
<tr>
<td>PANI:PVP=30% (S4)</td>
<td>8.666×10⁻³</td>
</tr>
<tr>
<td>PANI:PVP=70% (S5)</td>
<td>9.176×10⁻³</td>
</tr>
<tr>
<td>Fe₃O₄:PVP=1:2 (S6)</td>
<td>7.616×10⁻⁴</td>
</tr>
<tr>
<td>PANI:PVP=30% Fe₃O₄:PVP=1:1 (S7)</td>
<td>8.167×10⁻⁴</td>
</tr>
<tr>
<td>Fe₃O₄:PVP=1:4 (S8)</td>
<td>6.864×10⁻³</td>
</tr>
</tbody>
</table>

Fig. 3 Histogram of diameter distribution of PANI/Fe₃O₄/PVP composite nanofibers

Fig. 4 Hysteresis loops of Fe₃O₄ NPs (a) and PANI/Fe₃O₄/PVP composite nanofibers with various ratios of Fe₃O₄ to PVP (b, c, d and e)
4 Conclusions

In summary, the electricity-magnetism bifunctional composite nanofibers are successfully prepared by electrospinning. Electrical conductivity and saturation magnetization of composite nanofibers can be tuned by adding different amount of PANI and Fe$_3$O$_4$ NPs into them, respectively. The composite nanofibers exhibit superparamagnetic performance and their saturation magnetizations are increased with the increase of Fe$_3$O$_4$ NPs. The best electrical conductivity of composite nanofibers reaches the order of $10^{-3}$ S·cm$^{-1}$. Besides, the design conception and preparation method of the composite nanofibers are of universal significance for the fabrication of other electricity-magnetism one-dimensional nanostructures. The new electricity-magnetism bifunctional PANI/Fe$_3$O$_4$/PVP composite nanofibers have potential applications in many fields such as electromagnetic interference shielding, special coating, microwave absorption, molecular electronics and future nanodevices.

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