Fabrication and characterization of Fe3O4/PVP magnetic nanofibers via gas-solid reaction method

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Abstract. In order to obtain uniform dispersion of Fe_3O_4 in composite nanofibers, a new method is used by mixing compound of Fe^{3+} and Fe^{2+} with organic polymer polyvinylpyrrolidone (PVP), then subjected nanofibers through electrospinning and formed ferric oxide/polyvinylpyrrolidone (Fe_3O_4/PVP) fibers via in-situ by gas-solid reaction under the condition of NH_3. The morphology of the fibers and the dispersion of Fe_3O_4 particles in the fibers were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The crystallization of the magnetic fibers was characterized by X-ray diffraction (XRD). The vibrating sample magnetometer (VSM) was used to observe the superparamagnetic behavior. The morphology charaterization show Fe_3O_4 particles in the nanofibers were evenly distributed with no obvious particle agglomeration. The magnetic measurement of the fiber shows that the magnetic nanofibers have better superparamagnetism, which are expected to be used as a drug-loaded magnetic cloth in the field of biomedicine.

Keywords: electrospinning, Fe_3O_4, gas-solid, magnetism, dispersion.

1. Introduction

Electrospinning is an important method for preparing ultra-fine fibers from polymer-containing spinning solutions by high voltage. Compared with conventional drug delivery systems, electrospinning has the advantages of high specific surface area, high drug loading, low cost and low residual organic solvents.

Due to its superparamagnetic properties, iron oxide nanoparticles have a wide range of applications, including magnetic fluids, medical magnetic resonance imaging, and magnetic induction heating for cancer treatment. Magnetic fibers have many applications such as magnetic paper, health-care cloth, magnetic filters and sensors, information storage, magnetic imaging, etc. Polymer-based Fe_3O_4/PVA, Fe_3O_4/PAN, Fe_3O_4/PMA, Fe_3O_4/PEO, etc. have been reported[1]. Mostly, the magnetic fibers were produced by using the method of co-precipitation： First, Fe_3O_4 magnetic nanoparticles were prepared by co-precipitation method; then mixed into the solution containing polymer and solvent for spinning solution; finally, nanofibers were prepared by electrospinning. However, this method can not avoid the problems of uneven diameter distribution and severe agglomeration. S. Wang et al [2] prepared Fe_3O_4 nanoparticles directly in polymer solution by co-precipitation, and then prepared the spinning solution through a series of post-treatment and prepare the composite nanofibers containing Fe_3O_4 by electrospinning. Wang et al [3] used thermal decomposition [4] method for formation of C/Fe_3O_4 composite nanofibers in situ for application in lithium-ion battery anode materials. Inspired by the above methods, Fe_3O_4/PVP fibers were prepared in situ by gas-solid reaction in this paper.

Polyvinylpyrrolidone (PVP) fiber membranes have been widely used in the field of drug-loading. Besides, PVP is also a common carrier for electrospinning fibers, which has the characteristics of uniform diameter, strong spinnability and good stability[5][6]. Using the polymer as the fiber matrix, the advantages of PVP and Fe_3O_4 can be fully developed, and the nanofibers with different composition and structure can be controlled by electrospinning. The products can be used as magnetic drug-carrying cloth, targeted drug therapy and tissue regeneration scaffold in the field of bio-medicine.

2. Experimental

2.1. Materials and equipments

Table 1 materials

Names	Specifications	Manufacturers
Polyvinylpyrrolidone	Mw:1,300,000	Alfa Aesar
Ferrous chloride tetrahydrate	Mw:198.83	Fuchen Chemical Reagent Work
Ferric trichloride	Mw: 162.20	Fuchen Chemical Reagent Work
Absolute ethanol	Analytical pure	Beijing Chemical Plant
NH_3	Analytical pure	self made
Distilled water	Analytical pure	self made

Table 2 Equipments

Names	Models	Manufacturer
Electronic balance	CP214	Ohaus Instrument (Shanghai) Co., Ltd.
Digital display constant temperature magnetic stirrer	HJ-3	Changzhou Guohua Electric Co., Ltd.
Injection pump	TOP-5300	Senjunakai-cho, Adachi-ka, Japan
Dual channel syringe pump	JZB-1800D	Changsha Jianyuan Medical Technology Co., Ltd.
High-temperature electric heating blast drying box		Shanghai Fuma Experimental Equipment Co., Ltd.
High-voltage DC power supply	DW-P403-1ACCC	Tianjin Dongwen High Voltage Power Plant
Precision booster electric mixer	JJ-1	Changzhou Guohua Electric Co., Ltd.

2.2. Electrospun Fe3O4 /PVP magnetic nanofibers

$FeCl_2 \cdot 4H_2O$ and $FeCl_3$ (ferric ion mole ratio 1:1.7) were mixed in distilled water and ethanol solvent containing PVP while magnetically stirring for30 minutes at room temperature. This spinning solution mixed uniformly was put into the electrospinning equipment from a 10 ml syringe with an inner needle diameter of 0.37 mm which used a syringe pump to control the flow rate and set the flow rate to 1 mL/h. A high voltage DC generator which was set 15kV was applied to the tip of the needle attached to the syringe when a fluid jet was ejected. A flat aluminum plate was used as the collector. The distance between the needle and the receiver was 20cm. Under these conditions, electrospinning time was 15h. The prepared nanofiber membrane material was dried in a high-temperature electric blast drying box for 48 hours in order to remove the organic solvents remaining on the nanofibers. Fe_3O_4 /PVP magnetic composite fibers were prepared by gas-solid reaction under the condition of NH_3. The fibrication process was shown in Fig.1.

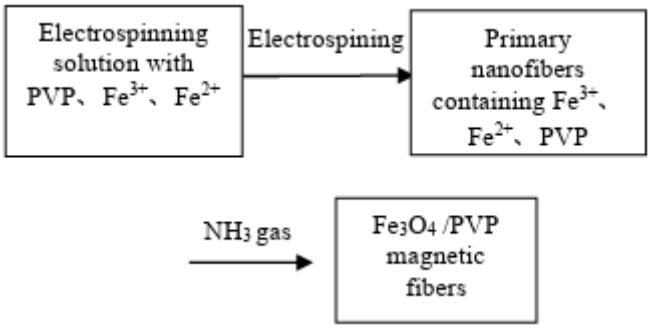


Fig.1 process of Fe_3O_4/PVP magnetic nanofibers via gas-solid reaction

2.3. Test and characterization

(1) X-ray diffraction (XRD) analysis

The crystal structure of Fe_3O_4 nanoparticles obtained was analyzed by X-ray diffraction (XRD). The product of Fe_3O_4 / PVP fibers were fixed in a sample tank, and the types and crystal forms of the obtained samples were analyzed on a 2500VB2 + / PC Rigaku D / max type X-ray diffraction apparatus. The Cu target scan speed is 10°/min, the acceleration voltage is 40kV, the tube current is 200mA, and the angle is 5-90 °.

(2) Scanning electron microscope (SEM) observation

The microstructures of the Fe_3O_4/PVP composite nanofibers were evaluated using scanning electron microscopy (Hitachi S-3400 scanning electron microscopy).The prepared fibers were sprayed with platinum to improve the conductivity of the surface of the material, and then the dispersion and local micro-morphology of the material were observed under SEM. Local micro-morphology of the material under high magnification and the uniformity of the whole material under low magnification were observed.

(3) Vibration sample magnetometer (VSM) magnetic analysis

The magnetic property of the Fe_3O_4/PVP composite nanofibers was measured using a vibrating sample magnetometer (VSM, LakeShore 7307).Take some sample to weigh and record the weight, and fill it into the vibrating rod sample chamber. The PPMS-9T vibration sample magnetometer measures the saturation magnetization of the sample with a 40Hz sample vibration frequency and 0.5-10mm sample vibration amplitude.

(4) Transmission electron microscope (TEM) observation

The dispersion of Fe_3O_4 nanoparticles in composite nanofibers was determined using transmission electron microscopy (TEM, Hitachi H-600-II, Japan). In the process of preparing magnetic composite nanofibers by electrostatic spinning, the nanofibers were directly collected on a 200-mesh copper mesh for 1 to 2 minutes. After a large number of nanofibers were observed on the copper mesh under an optical microscope, Fe_3O_4 nanoparticles were observed under TEM distribution and binding of PVP nanofibers inside and on the surface.

(5) Fourier transform infrared (FT-IR) analysis

FTIR was performed on a Nicolet Nexus 670 FTIR spectrometer using potassium bromide as a nonabsorbent medium. A total reflection Fourier transform infrared spectrometer was used to analyze the changes of chemical groups in materials.

3. Results and discussion

3.1. The principle of the fabrication

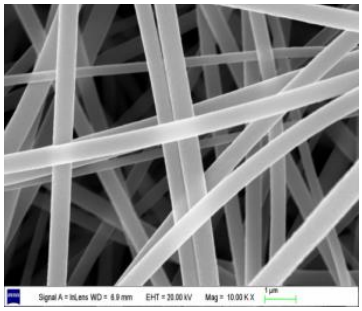
The most common synthetic method of Fe_3O_4 is coprecipitation. Based on the following chemical reaction equation, Fe_3O_4 nanoparticles are formed by Fe^{3+} and Fe^{2+} in a 2:1 stoichiometry under oxygen-free alkaline conditions. The pH of the solution in which Fe_3O_4 is synthesized is adjusted between 8 and 14.

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

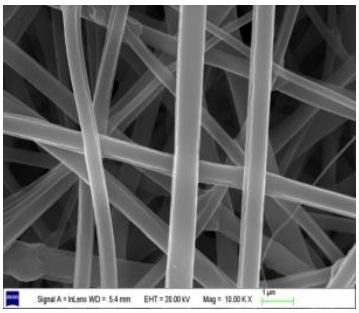
NaOH and ammonia are usually used. In order to avoid the aggregation and uneven distribution of Fe_3O_4 in PVP matrix prepared by traditional coprecipitation, ammonia gas used as alkali was coprecipitate with Fe^{3+} and Fe^{2+} in the process of preparing nanofibers in situ. Fe_3O_4 was obtained directly in the nanofibers. The problem of oxidation and loss of magnetism caused by high temperature thermal decomposition preparing Fe_3O_4 was avoided by using this method.

3.2. SEM anylsis

As shown in Fig. 2, scanning electron microscope photographs of electrospun PVP/iron ion fibers and PVP/Fe_3O_4 reacting with NH_3 were observed. Obviously, Both kinds of fibers were three-dimensional network structures composed of continuous fibers, which were intertwined and criss-crossed.Uniform and straight composite nanofibers were obtained. The fibers reacting with NH_3 have not changed much from the original. At the same time, the diameter of the fibers was relatively uniform, and there was no discontinuous particle protrusion on the surface of the fibers. The average diameter of PVP/iron ion fibers and PVP/Fe_3O_4 was 150nm, and the surface of fiber is smooth before and after reaction.



a



b

Fig. 2 SEM image of PVP/iron ion fibers(a) and PVP/Fe_3O_4 (b)

3.3. TEM analysis

Transmission electron micrograph of the prepared Fe_3O_4/PVP magnetic nanofibers was shown in Fig.3. It can be seen that Fe_3O_4 nanoparticles were evenly distributed in the fibers without agglomeration, and the particles were evenly arranged in the axial direction.The particle size of $Fe_3O_4$was about 5-10 nm, and obviously there are little Fe_3O_4 particles on the surface of the fibers from the transmission electron microscope photograph.

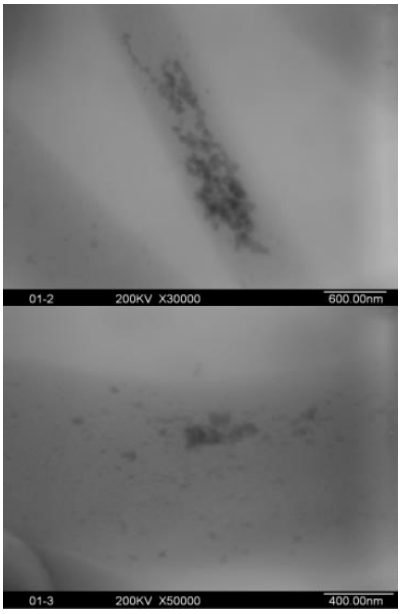


Fig.3 TEM images of PVP/Fe_3O_4 fiber after reaction with NH_3 gas with different magnification

3.4. XRD analysis

XRD analysis of the nanofibers was performed to determine the chemical state of iron oxide incorporated within the PVP. Typical diffraction pattern for the uncured Fe_3O_4/PVP nanofibers is shown in Fig.4. The characteristic peaks of (220), (311), (222), (400), (422), (511), (440), (533) of Fe_3O_4 appear at 30.1°, 35.4°, 37.1°, 43.1°, 53.4°, 56.9°, 62.5°, 73.9°, while identify that Fe_3O_4 nanoparticles have a cubic spinel structure. The crystallite size of Fe_3O_4 nanoparticles in PVP is 10 nm, which is consistent with the result determined by statistical analysis of the TEM images, indicating that each individual particle is a single crystal. Morphological arch of the polymer (PVP) can be seen in the XRD spectrum of the prepared ferric oxide magnetic nanofibers.

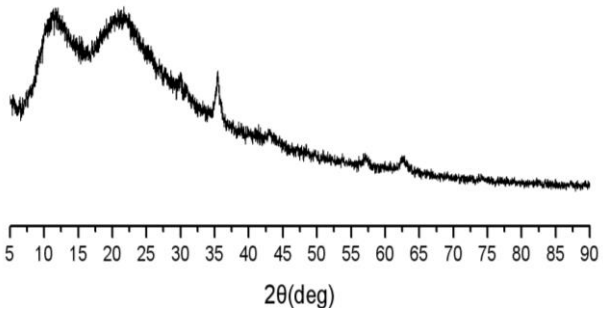


Fig.4 XRD pattern of Fe_3O_4 / PVP fibers

3.5. FT-IR analysis

FT-IR spectra were collected in order to determine whether PVP were incorporated onto the Fe_3O_4 nanoparticles respectively. The infrared characteristic peaks of PVP are at 2956, 1661, 1466, and 1285 cm^{-1}, which correspond to C-H, C = O, C = C, and C-N, respectively. According to the analysis of the FT-IR spectrum of Fe_3O_4 / PVP fiber (Fig. 5), the strong characteristic peak at 1652cm^{-1} represented the carbonyl C = O in PVP, but the C = O peak obviously moves from 1661cm^{-1} to 1652cm^{-1}, which showed that there was a weak chemical bond between C = O and Fe_3O_4 nanoparticles in PVP. This kind of interaction with the carbonyl group caused by the inorganic nanoparticle receiving the carbonyl oxygen electron pair caused the IR band to move. The peak at 595 cm^{-1} was the characteristic peak of Fe-O, which confirmed the existence of Fe_3O_4 nanoparticles in the fibers.

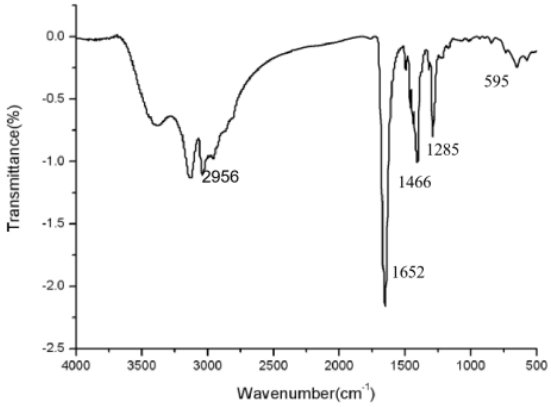


Fig.5 FTIR spectra of Fe_3O_4 / PVP fibers

3.6. VSM analysis

The superparamagnetic behavior of Fe_3O_4/PVP nanofibers is evident from the magnetic hysteresis loops represented in Fig. 6. Remanence is the sample magnetization when the applied magnetic field is zero. Ideally, the coercitivity and remanence of superparamagnetic material should be equal to zero. The coercitivity and remanence of the nanofibers tended to zero.

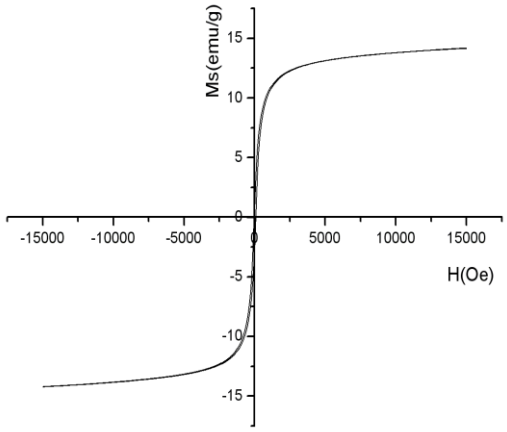


Fig.6 VSM curve of in-situ Fe_3O_4 / PVP fibers

The hysteresis loop of the obtained ferroferric oxide magnetic nanofibers has a saturation magnetization of about 14 emu/g, which showed good magnetic properties and superparamagnetism.

4. Conclusions

In summary, the preparation of Fe_3O_4 / PVP magnetic fibers by in-situ electrospinning can obtain superparamagnetic composite nanofibers, in where Fe_3O_4 was evenly distributed inside of the fiber, and no obvious particle agglomeration, no beadings or uneven thickness of fiber occurred. The experimental results also show that Fe_3O_4 particles in PVP fibers have good crystallization properties. Problems like uneven particle size distribution of ferric oxide prepared by the traditional co-precipitation method[7][8], poor spinning solution stability, and complicated preparation process were avoided in this method.

Based on the method of preparing Fe_3O_4 / PVP fiber by in-situ reaction with NH_3,the nanofibers with different Fe_3O_4 content and magnetic properties can be prepared by adjusting the mass ratio of raw materials and electrospinning parameters.

Acknowledgments

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