Preparation of Fe3O4/PVP magnetic nanofibers via in situ method with electrospinning

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Abstract. Ferroferric oxide (Fe3O4) magnetic nanoparticles are easily agglomerated due to their large specific surface area, and cannot be uniformly dispersed in polymer fiber matrix fabricated from electrospinning solution. In order to obtain uniform dispersion of Fe3O4 in composite nanofibers, a new method is used by mixing organic precursor of ferroferric oxide iron acetylacetonate (Fe(acac)3) and organic polymer polyvinylpyrrolidone (PVP), then subjected nanofibers through electrospinning and formed ferric oxide/polyvinylpyrrolidone (Fe3O4/PVP) fibers via in-situ calcination at low temperature. The morphology of the fibers and the dispersion of Fe3O4 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. 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.

1. Introduction
There are many types of iron oxides in the nature, the most common are magnetite (Fe3O4), maghemite (γ-Fe2O3) and hematite (α-Fe2O3). Fe3O4 has strong magnetic properties, especially nanometer-sized Fe3O4 has superparamagnetism. Superparamagnetic Fe3O4 nanoparticles are widely used in the field of biomedicine, magnetic health care, magnetic recording materials, especially in the field of biomedicine due to their good biocompatibility and special magnetic effects. Especially in biomedicine field, magnetic nanomaterials are used as carriers of various anticancer drugs [1], forming a magnetic targeted drug delivery system.

Polyvinylpyrrolidone (PVP) is a commonly used water-soluble polymer [2, 3], which is easily soluble in ethanol and isopropanol, and widely used in food, OTC medicine, wound dressing, cosmetics and other fields. It is also a polymer matrix commonly used in the preparation of nanofibers by electrospinning. Compared with conventional drug delivery systems, electrospinning fibers have the characteristics of high specific surface area, high drug loading, low manufacturing cost, and low residual organic solvents in drug release field. At present, PVP fiber membranes have been widely used in drug loading.
Magnetic fiber is a fibrous magnetic material, which has both textile fiber characteristics and magnetic functions. Traditional magnetic nanofibers can be prepared by adding and dispersing ferric iron oxide nanoparticles in a polymer solution. After uniformly mixing, magnetic nanofibers were prepared by electrostatic spinning. However, the method require long preparation process, and poor stable of the ferric oxide synthesized at earlier time result in uneven fiber diameter distribution and agglomeration of Fe$_3$O$_4$ in the fibers.

Problems to be solved in this paper is to overcome the drawbacks of the recent technology, and to provide a method of in-situ preparation for ferric oxide magnetic nanofibers. Magnetite / polyvinylpyrrolidone (Fe$_3$O$_4$ / PVP) fiber can be prepared as following process: preparing spin solution with organic polymer polyvinylpyrrolidone (PVP) and an organic precursor iron acetylacetonate (Fe(acac)$_3$), which has pyrolysis characteristics [4, 5], electrospinning and then calcined in situ [6] at low temperature to form magnetic fibers. This method can avoid problems such as uneven particle size distribution of ferric oxide prepared by co-precipitation method [7], poor spinning solution stability [8], and complicated preparation process. It can provide key technologies and solutions for preparing nano-magnetic fibers with different ferric oxide content and magnetic properties.

2. Experimental

2.1. Materials and equipments

| Table 1. Materials |
|---------------------|
| Names | Specifications | Manufacturers |
| Polyvinylpyrrolidone | Mw:1,300,000 | Alfa Aesar |
| Iron Acetylacetonate | Mw:353.17 | Alfa Aesar |
| Absolute ethanol | Analytical pure | Beijing Chemical Plant |
| Distilled water | Analytical pure | self made |

| Table 2. Equipments |
|---------------------|
| Names | Models | Manufacturer |
| Electronic balance | CP214 | Ohaus Instrument (Shanghai) Co., Ltd. |
| CNC ultrasonic cleaner | KQ 5200DB | Kunshan Ultrasound Instrument 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-voltage DC power supply | DW-P403-1ACCC | Tianjin Dongwen High Voltage Power Plant |
| High-temperature electric heating blast drying box | | Shanghai Fuma Experimental Equipment Co., Ltd. |
| Precision booster electric mixer | JJ-1 | Changzhou Guohua Electric Co., Ltd. |
| Muffle furnace | | |

2.2. Preparation of Fe$_3$O$_4$ / PVP magnetic fibers

0.5g Fe(acac)$_3$ and 1.2g PVP (mass ratio 5:12) were dissolved in 20mL ethanol solvent, and stirred magnetically for more than 18h. The spinning solution mixed uniformly was put into the electrospinning equipment [9] which used a syringe pump to control the flow rate and set the flow rate to 0.5 mL/h. The high voltage DC generator which was set 15kV was connected to the spinneret. The
distance of the receiver was 15cm. 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. The obtained dried fibers were calcined in situ in a muffle furnace, the temperature was controlled at 245 °C, and the calcination time was 1 h.

In order to research whether the calcined product of organic precursor Fe (acac)₃ at a certain temperature has strong magnetic properties, and the thermal stability of Fe (acac)₃ and organic polymer PVP at a certain temperature, the crystallinity of the calcined products of Fe (acac)₃ at different temperatures, the thermogravimetric analysis of Fe (acac)₃ and PVP were studied to determine the calcination temperature and conditions of Fe₃O₄ / PVP magnetic fibers prepared by in-situ spinning, which provide theoretical basis for subsequent experimental research in this direction.

2.3. Test and characterization

(1) X-ray diffraction (XRD) analysis

The calcined product of Fe (acac)₃ and Fe₃O₄ / 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 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

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

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, Fe₃O₄ nanoparticles were observed under TEM Distribution and binding of PVP nanofibers inside and on the surface. The interplanar spacing and crystallization of the nanoparticles were observed by HR-TEM.

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

A total reflection Fourier transform infrared spectrometer was used to analyze the changes of chemical groups in materials.

(6) Thermal weight loss (TGA) analysis

A TGA spectrum analysis was performed on the material using a thermal weight loss instrument to determine its weightless behavior under high temperature conditions.

3. Results and discussion

3.1. Performance analysis of experimental materials

3.1.1. Fe (acac)₃ (Iron acetylacetonate). The XRD of the products obtained by Fe (acac)₃ treated at different temperatures in the air were shown in Fig. 1. It can be seen that Fe₃O₄ was obtained at 230 ~ 280 °C as the heating temperature increases, and the higher the intensity of the diffraction peak was shown. When the temperature rose to 365 °C, diffraction peaks of γ-Fe₂O₃ appear in the product crystals, which were quickly transformed to non-magnetic α-Fe₂O₃. At 500 ° C, the products were completely transformed to α-Fe₂O₃.
Figure 1. XRD patterns of Fe(acac)$_3$ calcined at different temperatures for 1.5h

The above research results were consistent with the research by B. Pal et al. [4] who used the thermal decomposition of the metal-organic precursor Fe(acac)$_3$ to prepare iron oxide films. From the schematic diagram of the decomposition process of Fe(acac)$_3$ (Fig. 2), it can be seen that when the temperature was reached 361.49 °C, Fe(acac)$_3$ decomposed to γ-Fe$_2$O$_3$, and when the temperature was increased to more than 500 °C, non-magnetic α-Fe$_2$O$_3$ was produced, which was consistent to the results of easy conversion to α-Fe$_2$O$_3$ above 400 °C.

Figure 2. Fe(acac)$_3$ decomposition reaction in air

In addition, it can be seen from the TGA thermal weight loss curve of Fe(acac)$_3$ (Fig. 4) that Fe(acac)$_3$ began to decompose at 200 °C, and the DTG peak was around 230 °C, which proved the rate of organic iron source conversion to Fe$_3$O$_4$ is the fastest at that time.

Figure 3. TGA curve of Fe(acac)$_3$
3.1.2. PVP (Polyvinylpyrrolidone). From the TGA curve of PVP (Fig. 4), it can be seen that PVP began to decompose at around 400 °C and completely decomposes to 490 °C. Therefore, compared with the XRD spectrum of the calcined product of Fe (acac)₃ at different temperatures, the technical route of Fe₃O₄ / PVP magnetic composite fiber calcined by low temperature (230-280 °C) was feasible.

![Figure 4. TGA curve of PVP](image)

Therefore, combined with the TGA and XRD test results of Fe (acac)₃ decomposition products and PVP, Fe₃O₄ / PVP fibers can be prepared by electrospinning of spinning solution, calcining in situ at low temperature (between 230 °C and 280 °C), which was lower than the initial decomposition temperature of PVP, and the longer the calcination time, which lead to larger the particle size and the more complete the crystal.

3.2. Characterization of Fe₃O₄ / PVP magnetic nanofibers

3.2.1. SEM analysis

![Figure 5. SEM photos of primary fibers (a) (b) and fibers (c) (d) after calcination at 230 °C for 4 h](image)
As shown in Fig. 5, scanning electron microscope photographs of electrospun primary fibers and low-temperature calcined at 10,000 and 50,000 times magnifications, the obtained Fe$_3$O$_4$ / PVP magnetic nanofibers were three-dimensional network structures composed of continuous fibers, which were intertwined and criss-crossed. 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 was slightly reduced while the primary fiber was 150nm comparing with 120nm after calcination, and the surface of fiber is smooth after calcination.

3.2.2. TEM analysis

![Figure 6](image)

**Figure 6.** TEM (a) (b) and HR-TEM (c) photos of Fe$_3$O$_4$ / PVP fiber calcined in situ

Transmission electron micrograph of the prepared Fe$_3$O$_4$ / PVP magnetic nanofibers was shown in Fig.6. It can be seen that Fe$_3$O$_4$ nanoparticles were evenly distributed in the fiber without agglomeration, and the particles were evenly arranged in the axial direction. It can be seen that the particle size of Fe$_3$O$_4$ was about 5-10 nm, and the obvious Fe$_3$O$_4$ particles on the surface of the fibers can also be observed in the b picture from the transmission electron microscope photograph.

3.2.3. XRD analysis

![Figure 7](image)

**Figure 7.** XRD pattern of Fe$_3$O$_4$ / PVP fibers calcined at 230 °C for 4h

As shown in Fig.7, the characteristic peaks of (220), (311), (222), (400), (422), (511), (440), (533) of Fe$_3$O$_4$ appear at 30.1, 35.4, 37.1, 43.1, 53.4, 56.9, 62.5, 73.9°, while the polymer Morphological arch can be seen in the XRD spectrum of the prepared ferric oxide magnetic nanofibers.
3.2.4. **FT-IR analysis**

![FT-IR spectrum](image)

**Figure 8.** FTIR spectra of Fe$_3$O$_4$/PVP fibers calcined in situ at low temperature

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 FTIR spectrum of Fe$_3$O$_4$/PVP fiber (Fig. 8), the strong characteristic peak at 1652 cm$^{-1}$ represented the carbonyl C = O in PVP, but the C = O peak obviously moves from 1661 cm$^{-1}$ to 1652 cm$^{-1}$, which showed that there was a weak chemical bond between C = O and Fe$_3$O$_4$ 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$_3$O$_4$ nanoparticles in the fibers.

3.2.5. **VSM analysis**

![VSM curve](image)

**Figure 9.** VSM curve of low-temperature calcined in-situ Fe$_3$O$_4$/PVP fibers

As shown in Fig. 9, 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

The preparation of Fe$_3$O$_4$ / PVP magnetic fibers by in-situ electrospinning can obtain superparamagnetic composite nanofibers, in where Fe$_3$O$_4$ was evenly distributed on the surface and inside of the fiber, and no obvious particle agglomeration, no beadings or uneven thickness of fiber occurred. Problems like uneven particle size distribution of ferric oxide prepared by the traditional co-precipitation method, poor spinning solution stability, and complicated preparation process were avoided in the method.

Based on the method of preparing Fe$_3$O$_4$ / PVP fiber by in-situ low-temperature calcination, nanomagnetic fibers with different iron oxide content and magnetic properties by adjusting the electrospinning parameters, calcination temperature, and amount of precursor can be prepared by this study. Within the calcination temperature range specified in the experimental scheme, the higher the calcination temperature, the better the crystallization performance of Fe$_3$O$_4$ nanoparticles and the larger the particle size. Properly increasing the amount of precursor Fe (acac)$_3$ within a certain range can increase the content of Fe$_3$O$_4$ inside the fiber and the saturation magnetization of the magnetic fibers.

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