Preparation of Fe$_3$O$_4$ @ CaP magnetic fiber scaffold with electrospinning

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Abstract. Fe$_3$O$_4$@CaP magnetic fiber scaffold is prepared with electrospinning by compounding ferroferric oxide nanoparticles into the calcium phosphate ceramic. The composite scaffold combines the superparamagnetism of ferroferric oxide nanoparticles and the good biocompatibility and bone tissue guidance of calcium phosphate, and has a high specific surface area and provides a suitable regeneration space for bone tissue, which is expected to be used for biomedical field.

Keywords: Electrospinning, Fe$_3$O$_4$, magnetic, scaffold, bone

1. Introduction

Fe$_3$O$_4$ has a wide range of applications in the field of magnetic sealing, biomedicine, magnetic health care, magnetic recording materials, etc. Especially in the field of biomedicine, magnetic nanomaterials are widely used as carriers of various anti-cancer drugs, forming a magnetic targeted drug delivery System; Magnetic microspheres made of magnetic nanomaterials can also be used in the separation of magnetic immune cells, and MRI imaging. Magnetic nanomaterials which can generate heat [1,2,3] under the action of an alternating electromagnetic field can kill tumor cells and achieve the purpose of treating tumors [4].

Calcium phosphate has good biocompatibility and biodegradability. After the calcium phosphate three-dimensional fiber scaffold material prepared by electrospinning method is implanted in the body, a bone bond with the body tissue is formed in a short time due to the fibers’ large specific surface area, and then the bone tissue is guided to grow into the scaffold material through the pores. Therefore, it is necessary to combine Fe$_3$O$_4$ and calcium phosphate to prepare a three-dimensional calcium phosphate composite fiber scaffold loaded with Fe$_3$O$_4$ nanoparticles, which is expected to be used for bone tissue regeneration [5,6], drug loading, tumor treatment, bone repair and treatment under the action of a magnetic field.
2. Experimental

2.1. Materials and equipments

| Table 1. materials |
|-------------------|
| Names | Specifications | Manufacturers |
| FeCl₃ | Analytical pure | Sinopharm Chemical Reagent Co., Ltd. |
| FeCl₂·4H₂O | Analytical pure | Tianjin Fuchen Chemical Reagent Factory |
| NaOH | Analytical pure | Beijing Chemical Plant |
| Absolute ethanol | Analytical pure | Beijing Chemical Plant |
| Distilled water | Chemically pure | Self-made |
| C₆H₅Na₃O | Analytical pure | AMRESCO |
| Triethyl phosphate | 98%+ | Alfa Aesar |
| Polyvinylpyrrolidone | Mw:1,300,000 | Alfa Aesar |

| Table 2. Equipments |
|---------------------|
| Names | Models | Manufacturer |
| Electronic balance | CP214 | Ohaus Instrument (Shanghai) Co., Ltd. |
| CNC ultrasonic cleaner | KQ 5200DB | Kunshan Ultrasonic 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 |
| Electric heating vacuum drying oven | DZF-6050 | Shanghai Jinghong Experimental Equipment Co., Ltd. |
| Horizontal tube furnace | GSL-1600X | Hefei Kejing Materials Co., Ltd. |

2.2. Preparation of Fe₃O₄ @CaP magnetic fiber scaffold

FeCl₂·4H₂O and FeCl₃ were dissolved in the mixture of ethanol solvent and distilled water according to the ratio of iron ions mole number 1:1.7, and stirred and heated in water bath to 80°C. Fe₃O₄ magnetic nanoparticles are synthesized by slowly adding NaOH with a concentration of 3 mol/L to the solution to pH=10, and reacting for 30 minutes. The obtained Fe₃O₄ magnetic nanoparticles are washed and put into deionized water at a mass ratio of 1:10 with sodium citrate, and ultrasonically stirred for 12 hours, then removed by centrifugation, and 30ml of deionized water was poured into a stable magnetic fluid.

A calcium nitrate solution with a calcium-phosphorus molar ratio of 1.2 was added dropwise to fully hydrolyzed triethyl phosphate, ethanol, and an aqueous solution (molar ratio 1:3:3), and then aged at -20°C for 7 days to obtain a precursor solution.

The solution was diluted into water at a weight ratio of 5:1, and added 5wt.% polyvinylpyrrolidone (PVP). After mixing uniformly, Fe₃O₄ magnetic fluid (volume ratio is 1:20) is added to the precursor solution, mechanically stirred evenly and then ultrasonically dispersed in the spinning solution.

The spinning solution was put into the electrospinning equipment [7] which used a syringe pump to control the flow rate and set the flow rate to 1.0 mL/h. The high voltage DC generator which was set 14kV was connected to the spinneret. The distance of the receiver was 15cm. The electrospinning equipment is controlled at the temperature of 35±2°C and the humidity of below 30%. The prepared fiber material is wound into a cylindrical shape and dried in a vacuum oven to prevent the fiber from
being dissolved due to water absorption during storage, then placed in a horizontal tube furnace for pressureless sintering to obtain Fe$_3$O$_4$ @ CaP magnetic fiber scaffold.

2.3. Test and characterization
The calcined product of Fe$_3$O$_4$ @ CaP magnetic fiber scaffold were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), vibration sample magnetometer (VSM) magnetic analysis and Energy Disperse Spectroscopy (EDS).

3. Results and discussion

3.1. XRD analysis
As shown in Fig.1, the diffraction characteristic peaks of Fe$_3$O$_4$ appear at 18.0°, 35.4°, 37.1°, 43.1°, 53.4°, 56.9°, 62.5°, while the characteristic peaks of hydroxyapatite (HA) appear at 28.9°, 31.8°, 32.2°, 32.9°, 46.7°, 49.5°, 50.5°, and strong characteristic peaks of β-tricalcium phosphate (β-TCP) appear at 31.03° and 34.37°.

![Fig. 1 XRD pattern of Fe$_3$O$_4$ @ CaP magnetic fiber scaffold](image)

3.2. SEM analysis
As shown in Fig. 2, the surface of primary fibers containing Fe$_3$O$_4$ are not completely smooth and not fused, with diameter of about 0.8~1.9μm.

The SEM image of the sintered calcium ferric oxide calcium phosphate magnetic fibers show the interconnected fibers form a three-dimensional fiber network structure, with the diameter of the fiber scaffold is 1.17 μm on average. The fiber surface is rough, porous and has a large specific surface area.

![Fig. 2 SEM photos of primary fibers containing Fe$_3$O$_4$](image)
3.3. EDS analysis
From the EDS energy spectrum of the sintered magnetic fibers (Fig. 4), it shows that the fiber scaffold contains a certain amount of calcium, phosphorus, and iron.

3.4. VSM analysis
As shown in Fig. 5, the hysteresis loop of the obtained ferroferric oxide magnetic nanofibers has a saturation magnetization of about 0.35 emu/g, which shows good magnetic properties and superparamagnetism.

![Fig. 3 SEM photos of Fe₃O₄@CaP magnetic fiber scaffold](image)

![Fig. 4 EDS of Fe₃O₄ @ CaP magnetic fiber scaffold](image)
4. Conclusion

Fe$_3$O$_4$ @ CaP magnetic fiber scaffold obtained through preparing ferroferric oxide magnetic nanoparticles and the calcium phosphate sol precursor, electrospinning, and then sintered at high temperature. The composite fiber scaffold shows its high porous, large specific surface characteristic and superparamagnetism. In the future’s work, the fiber scaffold with higher magnetic properties can be obtained by adjusting the ratio of Fe$_3$O$_4$ in the preparation process based on the preparation method.

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