

In situ hybridization to chitosan/magnetite nanocomposite induced by the magnetic field

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Abstract

Chitosan/magnetite nanocomposite was synthesized induced by magnetic field via in situ hybridization in ambient condition. Results of XRD patterns and TEM micrographs indicated that magnetite particles with 10–20 nm were dispersed in chitosan homogeneously. An interesting result is that magnetite nanoparticles were assembled to form chain-like structures under the influence of the external magnetic field, which mimics the magnetite chains inside of magnetotactic bacteria. The saturated magnetization (Ms) of nano-magnetite in chitosan was 50.54 emu/g, which is as high as 54% of bulk magnetite. The remanence (Mr) and coercivity (Hc) were 4 emu/g and 14.8 Oe, respectively, which indicated that magnetite nanoparticles were superparamagnetic. The key of route is that a pre-precipitated chitosan hydrogel membrane, used as chemical reactor, which controlled the precipitation of chitosan precipitation and in situ transformation of magnetite from the precursor simultaneously in the magnetic field environment.

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1. Introduction

The research on hybrid materials composed of polymer and magnetic particles are of great interest due to their potential application in biomedicine. Iron oxide particles, including magnetite and maghemite, were incorporated into polymer, especially water soluble polymer such as poly(vinyl alcohol) [1], Poly(ethylene glycol) [2], poly(acrylic acid) [3], DNA [4], protein [5], and polysaccharide [6] matrix to improve the biocompatibility or bioactivity for biomedical application, such as magnetic cell separation, target drug delivery system and magnetic resonance imaging of clinical diagnosis [7].

Iron oxides with ordered structure have been found in the living organisms such as bacteria [8], teeth of chiton [9].

The magnetic response of magnetite in magnetic field provides a chance to manipulate or assemble the magnetite particles via in situ method or in a controlled manner. Magnetite particles inside of magnetotactic bacteria were controlled to form chain or ring-like structure with microelectromagnets after the cellular membrane of bacteria was destroyed by the cell lysis [10]. Dipolar chains structure of magnetite nanoparticles in the ferrofluid were directly observed by the cryogenic TEM in zero field [11]. Magnetite nanoparticles coated polymer formed chains or orientated structure in external magnetic field [12,13]. However magnetite particles were found to redistribute randomly when magnetic field was withdrew.

Different approaches had been used to generate magnetic chitosan materials such as blending [14,15], polymer microgel template [16] and coprecipitation methods [17]. Most of traditional routes to prepare magnetite/chitosan composite are coprecipitation stoichiometric ferrous and ferric ions in presence of polymer with aqueous NaOH or

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$\text{NH}_3 \cdot \text{H}_2\text{O}$ directly, rapidly and without considering effects of magnetic field. The homogeneous dispersion of magnetite nanoparticles with orientation structure in polymer matrix have been key problem for high-performance hybrid materials. Here we report a novel and simple method to prepare magnetite/chitosan nanocomposite via in situ hybridization in the magnetic field. Furthermore, magnetite nanoparticles dispersed in chitosan matrix uniformly were assembled into chain-like structure simultaneously when applied external magnetic field, and ordered structure was fixed by the chitosan hydrogel process.

2. Experimental section

2.1. Materials

Biomedical grade chitosan (viscosity-average molecular weight 3.4×10^5) was supplied by Qingdao Haihui Bioengineering Co., Ltd with 91% degree of the deacetylation. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were purchased from the Chinese Pharmacy Group Shanghai Reagent Company. Acetic acid and sodium hydroxide was obtained from Hangzhou Xiaoshan Chemical reagent Corporation. Permanent magnets (N-35, 12000G, Ningbo Sanhe Qiangci Co. Ltd) were used as external magnetic field.

2.2. Preparation of magnetite/chitosan nanocomposite

The 10 g of chitosan powder were added into 150 ml acetic acid aqueous solution with concentration of 2% (v/v) under vigorous agitation for 1 h, then 50 ml of magnetite precursor containing FeCl_3 and FeCl_2 in 2% (v/v) acetic acid solution with the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+} = 2$ was added into the chitosan solution. The mixture was stirred until chitosan were entirely dissolved at room temperature to obtain a homogeneous dark red resulting solution. The solution was held for 6 h to remove air bubbles trapped in viscous liquid.

Chitosan solution (approximate 5 ml) was cast on the internal surface of mold and the redundant chitosan solution was poured out, and then the mold was soaked in 5% (wt/v) NaOH aqueous solution for 2 h to precipitate a chitosan hydrogel membrane. The mold filled with the resulting solution of the magnetite precursor/chitosan was allowed to soak in 5% (wt/v) NaOH aqueous solution in external magnetic field and was taken off immediately. Yellowish-orange color magnetite/chitosan gel formed after 8 h in the external magnetite field. The hydrogel was washed with distilled water until the pH of washed water is about 7 and removed the pre-precipitated chitosan hydrogel membrane, then air-dried in oven at 60°C for 24 h. Black magnetite/chitosan (5.5/94.5, wt/wt) composite was obtained.

2.3. Characterization of magnetite/chitosan composite

The crystal structure of iron oxide distributed in chitosan matrix was determined with X-ray diffraction (XRD, Rigaku D/Max-2550 PC) using Cu K_α radiation at 40 KV and 50 mA. The sample was scanned from 5° to 90° in 2θ .

Transmission Electron microscopy (TEM, JEM-1200 EX) was used to evaluate the dispersion and particle size of magnetite in chitosan after samples were treated by ultra thin cutting. The histogram of magnetite nanoparticles distribution was obtained by DigitalMicrograph, and then the data were fit by the Fit wizard of Origin tools.

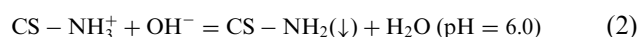
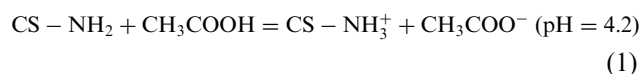
The magnetic properties of magnetite/chitosan composite were carried out using physical properties measurement system (PPMS)-9, Quantum Design, SQUID magnetometer at room temperature (300 K).

3. Results and discussions

3.1. Mechanism of synthesis of magnetite/chitosan via in situ hybridization

In our previous study, a similar method to prepare hydroxyapatite/chitosan nanocomposite was reported [18]. The prerequisites of the in situ hybridization to magnetite/chitosan were summarized as follows:

- (1) Both chitosan and magnetite precursor such as ferric and ferrous ions can coexist in the ionic state when solved in 2% acetic acid aqueous solution.
- (2) Both chitosan and magnetite precursor can react with ions such as OH^- diffused from the outside of chitosan membrane due to the variation of pH.
- (3) A pre-precipitated chitosan hydrogel membrane was used as chemical reactor which controls precipitation of chitosan and in situ transformation of magnetite from the precursor simultaneously with or without influence of external field environment, such as magnetic field or electric field.



The presence of amino group enables chitosan to exist in a soluble or solid state depending on the pH value of environments. The free amino group of chitosan (CS-NH_2) was protonated to CS-NH_3^+ at $\text{pH} = 4.2$ (Eq. (1)) when chitosan was dissolved in an acetic acid aqueous solution. The precipitation pH of chitosan is generally close to 6.0 or 6.5 in presence of metal ions (Eq. (2)). Chitosan is a very active chelating agent, which can absorb ferric and ferrous ions through the amino group and avoid the oxidation reaction of ferrous during removing air bubbles in the resulting solution. The amount of adsorbed ferric [19] and

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