Synthesis of MnFe$_2$O$_4$/cellulose aerogel nanocomposite with strong magnetic responsiveness

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Abstract  Cellulose aerogel, with abundant three-dimensional architecture, has been considered as a class of ideal eco-friendly matrix materials to encapsulate various nanoparticles for synthesis of miscellaneous functional materials. In the present paper, hexagonal single-crystal-line MnFe$_2$O$_4$ was fabricated and inserted into the cellulose aerogel using an in situ chemical precipitation method. The as-prepared MnFe$_2$O$_4$ nanoparticles were well dispersed and immobilized in the micro/nanoscale pore structure of the aerogel, and exhibited superparamagnetic behavior. In addition, the nanocomposite was easily actuated under the effect of an external magnetic field, revealing its strong magnetic responsiveness. Combined with the advantages of environmental benefits, facile synthesis method, strong magnetic responsiveness, and unique structural feature, this class of MnFe$_2$O$_4$/cellulose aerogel nanocomposite has possible uses for applications such as magnetically actuated adsorbents.

Keywords  cellulose aerogel, MnFe$_2$O$_4$, magnetic responsiveness, nanocomposite

1 Introduction

Aerogel based on cellulose, the most abundant and renewable natural polymer, is considered as one of the most promising cellulose products. Cellulose aerogel consists of a cross-linked three-dimensional (3D) network. The unique structural characteristic endows itself with low density, high porosity and large specific surface area[1-3]. As a result, cellulose aerogel finds applications in multidinous fields such as adsorbing materials[4], catalyst supports[5], and super-thermal and sound insulators[6]. In recent years, cellulose aerogel has gained increasing attention for magnetic devices. Magnetic cellulose aerogel is a kind of cellulose aerogel which shows magnetic responsiveness under the action of an additional magnetic field. In general, magnetic nanoparticles (e.g., α-FeOOH, CoFe$_2$O$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$ and MnFe$_2$O$_4$) are loaded in the aerogel in order to endow magnetic properties, and the resultant magnetic aerogel has diamagnetic, paramagnetic, ferromagnetic, ferrimagnetic or antiferromagnetic characteristics[7,8], mainly dependent on the inserted magnetic nanoparticles. Chin et al. prepared magnetic cellulose aerogel by in situ incorporation of magnetic Fe$_3$O$_4$ nanoparticles into the cellulose aerogel[9]. The hybrid aerogel can be easily recovered from water by applying an external magnetic field. Liu et al. obtained magnetic CoFe$_2$O$_4$/cellulose hybrid aerogel by using cellulose aerogel as a template, and the formed magnetic composite aerogel was lightweight, flexible, and highly porous[10]. Wan and Li prepared superparamagnetic γ-Fe$_2$O$_3$ nanoparticles encapsulated in 3D architecture of cellulose aerogel for the application of removing Cr$^{6+}$ ions from contaminated water[11]. Based on these reports, it was found that the magnetic composite aerogel not only had strong magnetic responsiveness, but also the unique physicochemical properties of cellulose aerogel. These multifarious functions contribute to expanding the scope of its potential application.

MnFe$_2$O$_4$ is a typical soft ferrite with a small magnetic anisotropy constant of about 10$^5$ J·m$^{-3}$[12]. MnFe$_2$O$_4$ nanoparticles have attracted considerable attention because of their potential as contrast enhancement agents in magnetic resonance imaging technology[13,14]. It is well-known that nanoparticles readily agglomerate due to high surface energy, which leads to performance deterioration. Therefore, integration of magnetic nanoparticles, such as MnFe$_2$O$_4$, within a porous substrate, such as cellulose aerogel, might not only provide magnetically actuated aerogel, but also effectively reduce the particle agglomeration.

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In the present study, hexagonal single-crystalline MnFe₂O₄ was fabricated and inserted into the cellulose aerogel using an in situ chemical precipitation method. The morphology, crystal structure, chemical components and thermodynamic stability of the as-prepared MnFe₂O₄/cellulose aerogel (coded as MnFe₂O₄/CA) nanocomposite were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction (XRD), thermogravimetric (TG) analysis and X-ray photoelectron spectroscopy (XPS). The magnetic properties of the nanocomposite was also tested by superconducting quantum interference device.

2 Materials and methods

2.1 Materials

Chemical reagents including FeSO₄·7H₂O, KNO₃, MnCl₂·4H₂O, and NaOH were of analytical grade and purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China) and used without further purification.

2.2 Preparation of MnFe₂O₄/CA

The preparation process of cellulose hydrogel (the precursor of cellulose aerogel) was described in previous reports\(^\text{[15,16]}\). The prepared cellulose hydrogel was immersed in a freshly prepared aqueous solution of FeSO₄·7H₂O and MnCl₂·4H₂O (40 mL) with the stoichiometric ratio of Mn:Fe of 1:2. After 1 h of immersion, the mixture was heated to 90°C and held at this temperature for 2 h. KNO₃ and NaOH were dissolved in 40 mL of distilled water. This solution was heated to 90°C, and quickly added to the suspension of metal ions/cellulose aerogel (coded as MnFe₂O₄/CA) nanocomposite system was kept for an additional 6 h at 90°C. All reactions were performed in air. The resulting product was washed repeatedly with distilled water and tert-butyl alcohol to remove residual chemicals, and then underwent a tert-butyl alcohol freeze-drying treatment of the cellulose aerogel and MnFe₂O₄/CA, corresponding to (110), (110) and (200) planes, respectively. Also, the peaks of MnFe₂O₄/CA at 29.7°, 34.9°, 42.5°, 52.7°, 56.2° and 61.6° are related to (220), (311), (400), (422), (511) and (440), respectively, according to the Joint Committee on Powder Diffraction Standards file of MnFe₂O₄ (No. 10-0319). This analysis indicates the formation of MnFe₂O₄ with a spinel ferrite crystalline structure. In addition, there is no

3 Results and discussion

The SEM image demonstrates that MnFe₂O₄/CA maintained a 3D interconnected network after the incorporation of MnFe₂O₄ (Fig. 1a). However, it is difficult to distinguish the MnFe₂O₄ nanoparticles from the complicated network structure. Even the higher-magnification SEM image still cannot identify the nanoparticles (Fig. 1b), possibly due to their extremely small particle size. The following TEM observation confirmed this. Compared with the pure cellulose aerogel, apart from the common C and O, the EDX spectrum of MnFe₂O₄/CA exhibited new peaks assigned to S, K, Fe and Mn (Fig. 1c). The Fe and Mn originated from the synthetic MnFe₂O₄, while the S and K are attributed to the residual chemicals. Further insight into the microstructure of the MnFe₂O₄ in the cellulose aerogel was gained by using TEM and HRTEM. It can be seen in Fig. 1d that the nanoparticles (the dark spots of hexagon) with the sizes ranging from 70 to 140 nm were homogeneously dispersed and immobilized in the cellulose aerogel matrix, which indicates that the cellulose aerogel with 3D architecture is a suitable template for the synthesis of nanoparticles. The SAED pattern was obtained on an individual MnFe₂O₄ nanoparticle, as shown in Fig. 1e. It clearly demonstrates that the hexagonal MnFe₂O₄ was essentially a single crystalline structure. Figure 1f presents the HRTEM image of the hexagonal MnFe₂O₄. The lattice spacing between two adjacent fringes was 0.26 nm, corresponding to the (311) plane of MnFe₂O₄.

For clarifying the crystal structure and phase purity of the synthesized particles, XRD analysis was conducted. As shown in Fig. 2, the characteristic peaks of cellulose can be observed at 12.3°, 20.2° and 22.0° for both the cellulose aerogel and MnFe₂O₄/CA, corresponding to (110), (110) and (200) planes, respectively. Also, the peaks of MnFe₂O₄/CA at 29.7°, 34.9°, 42.5°, 52.7°, 56.2° and 61.6° are related to (220), (311), (400), (422), (511) and (440), respectively, according to the Joint Committee on Powder Diffraction Standards file of MnFe₂O₄ (No. 10-0319). This analysis indicates the formation of MnFe₂O₄ with a spinel ferrite crystalline structure.
indication of any other phases in the XRD pattern of MnFe$_2$O$_4$/CA.

The chemical states of elements in MnFe$_2$O$_4$/CA were investigated by XPS. The nanocomposite is composed of C, O, Mn and Fe, consistent with the results of EDX analysis. The photoelectron lines at around 284, 531, 642 and 711 eV (Fig. 3a) are attributed to C 1s, O 1s, Mn 2p and Fe 2p, respectively. Three different C 1s signals are observed at 284.8, 286.4 and 287.8 eV (Fig. 3b). The main peak at 284.6 eV is ascribed to the carbon atoms in C–C, C=O, and C–H bonds\textsuperscript{[18]}. The other peaks at 286.4 eV, is assigned to the C–O, and the peak at 287.8 eV is attributed to the C=O bond\textsuperscript{[19]}. The signals at 710.9 and 724.7 eV are related to the Fe 2P$_{3/2}$ and Fe 2P$_{1/2}$ (Fig. 3c), respectively, confirming the presence of Fe$^{3+}$\textsuperscript{[20]}. The Mn 2P$_{3/2}$ (Fig. 3d) signal appears at 641.6 eV, and the peak at 653.1 eV is ascribed to the Mn 2P$_{1/2}$ signal, providing clear evidence for Mn$^{2+}$ chemical state on the nanocomposite surface\textsuperscript{[21]}. The loading content of MnFe$_2$O$_4$ in MnFe$_2$O$_4$/CA was measured by TG technique. As shown in Fig. 4a, the residual char yields above 800°C were 21.7% for the cellulose aerogel and 32.2% for MnFe$_2$O$_4$/CA, respectively. Thus, the content of MnFe$_2$O$_4$ can be roughly calculated as 10.5% in MnFe$_2$O$_4$/CA. In addition, it is seen in Fig. 4b that the room-temperature hysteresis curve of the nanocomposite shows the absence of hysteresis and coercivity, which is characteristic of superparamagnetic behavior\textsuperscript{[22]}. The curve increases rapidly with increasing applied magnetic field, and exhibits saturation magnetization values of 7.7 emu·g$^{-1}$.

The synthetic hybrid aerogel (i.e., MnFe$_2$O$_4$/CA) was verified to be a magnetically responsive material and actuator, as shown in Fig. 5. It can be tightly adhered to the surface of a magnet and maintain well-defined shape. Therefore, this class of aerogel with favorable shape stability and strong magnetic responsiveness may be used as a recyclable eco-friendly magnetically driven adsorbent for water purification, or a biodegradable electromagnetic device.

### 4 Conclusions

We demonstrate that the 3D architecture of cellulose aerogel can be used as a suitable eco-friendly template to encapsulate the superparamagnetic MnFe$_2$O$_4$ nanoparticles via a facile in situ chemical precipitation approach. The hexagonal MnFe$_2$O$_4$ nanoparticles have the sizes of 70 to 140 nm and were homogeneously immobilized in the cellulose aerogel. Moreover, the composite aerogel tightly
Fig. 3  Survey scan (a), O 1s (b), Fe 2p (c), and Mn 2p (d) XPS spectra of MnFe₂O₄/CA, respectively.

Fig. 4  (a) TG curves of the cellulose aerogel and MnFe₂O₄/CA; (b) hysteresis curve of MnFe₂O₄/CA.

Fig. 5  Magnetic responsiveness of MnFe₂O₄/CA.
adhered to the magnet surface, indicative of superior magnetic responsiveness. Therefore, this class of MnFe₂O₄/CA nanocomposite is expected to be useful as a kind of environmentally-friendly magnetically actuated adsorbent for the treatment of contaminated water.

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Compliance with ethics guidelines Jian Li, Yue Jiao, and Caichao Wan declare that they have no conflict of interest or financial conflicts to disclose. This article does not contain any studies with human or animal subjects performed by any of the authors.

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