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快 报

# 原位氧化水解法制备网状结构 $\text{Fe}_3\text{O}_4$ 薄膜\*

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**摘 要:** 在壳聚糖膜上通过原位氧化水解反应制备了网状结构的  $\text{Fe}_3\text{O}_4$  薄膜. 采用 X 射线衍射、扫描电子显微镜和热重-差热分析对产物进行了分析和表征, 结果表明, 所制备的  $\text{Fe}_3\text{O}_4$  膜为纯相反尖晶石结构; 网孔直径大约 50 ~ 300 nm, 网壁厚度大约 30 nm;  $\text{Fe}_3\text{O}_4$  转化为  $\gamma\text{Fe}_2\text{O}_3$  的温度约为 458 °C.

**关键词:** 网状结构;  $\text{Fe}_3\text{O}_4$  薄膜; 原位氧化水解反应; 壳聚糖

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## Preparation of Network $\text{Fe}_3\text{O}_4$ Film by In-situ Oxidative Hydrolysis\*

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**Key words** Network structure,  $\text{Fe}_3\text{O}_4$  film, In-situ oxidative hydrolysis, Chitosan

$\text{Fe}_3\text{O}_4$  is currently received a lot of attention due to a potential application in giant magnetoresitive (GMR) devices such as magnetic field sensors, magnetoresistive random access memories (MRAM), read heads, and galvanic isolators<sup>[1]</sup>. Moreover, the Curie temperature of  $\text{Fe}_3\text{O}_4$  is 858 K, and a high Curie temperature is important for the above applications. Various methods have been reported for preparing  $\text{Fe}_3\text{O}_4$  thin films, such as molecular beam epitaxy<sup>[2]</sup>, sputtering<sup>[3]</sup>, pulsed laser deposition<sup>[4]</sup>, metalorganic chemical vapor deposition<sup>[5]</sup> and solid reaction<sup>[6]</sup>. However, these methods need high temperature and vacuum conditions, and the requisite apparatus are quite expensive.

Chitosan is one of the promising film materials and has been widely studied<sup>[7]</sup>. Because the molecules are rich in amino groups, chitosan demonstrates the unique adsorption characteristic for some transition metal and

rare metal ions, such as  $\text{Ag}^+$ ,  $\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cd}^{2+}$  and so on<sup>[8,9]</sup>. Based on this characteristic, various inorganic-organic chitosan composite films have been investigated by some researchers<sup>[10,11]</sup>.

In this paper, a novel network  $\text{Fe}_3\text{O}_4$  film with nanopores was prepared by in-situ oxidative hydrolysis on chitosan film at the temperature of 30 °C. The detail structures and characteristics of the prepared  $\text{Fe}_3\text{O}_4$  films were investigated by XRD, SEM and TG-DTA.

Chitosan solution was prepared by dissolving about 4 g of chitosan in 100 mL of 2% aqueous acetic acid solution. The solution was filtered in order to remove undissolved chitosan and debris, and then was filmed onto a clean slide. The transparent film was obtained after drying at room temperature for 24 h in dustproof conditions. The film was immersed in a NaOH liquor (0.5 mol/L) for 30 min to ensure complete removal of any residual acid from the film. The film was

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adequately washed with distilled water and immersed in  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  liquor (0.05 mol/L) in order to adsorb  $\text{Fe}^{2+}$  on its surface. During this process the film turned green. The film adsorbing  $\text{Fe}^{2+}$  was immersed in 0.5 mol/L NaOH liquor at 30 °C for 30 min, into which bubbling nitrogen (Industrial Grade) was introduced (50 mL/min). The miniscule amount of oxygen in nitrogen (about 6%) acted as the oxidant. The color of the film became deep brown during the formation of  $\text{Fe}_3\text{O}_4$  by in-situ oxidative hydrolysis. The samples could be magnetized with permanent magnet.

Figure 1 a and b show XRD patterns of the chitosan film and the  $\text{Fe}_3\text{O}_4$ -chitosan composite film. The  $\text{Fe}_3\text{O}_4$ -composite film was prepared with adsorbing  $\text{Fe}^{2+}$  for 1 min. It was found that the spectrum of composite film is a close match with the standard spectrum of  $\text{Fe}_3\text{O}_4$  with a cubic inverse spinel structure. So, it can be predicated that the product over the chitosan film is pure  $\text{Fe}_3\text{O}_4$ . The crystalline diameter estimated from XRD patterns using Debye-Scherrer formula is 5.5 nm. It was also found that  $\text{Fe}^{2+}$  would be over-oxidized by the dissolved oxygen in solution and the main product was FeOOH if there was no nitrogen protection during the reaction process. Figure 1c is the XRD pattern of the  $\text{Fe}_3\text{O}_4$ -chitosan film prepared without bubbling nitrogen. It is a close match with the spectrum of FeOOH (JCPDS card No. 70-0714). The reflection peaks appeared at  $2\theta = 14^\circ$ ,  $27^\circ$ ,  $36^\circ$  correspond to the (0 2 0), (0 2 1), (1 3 0) planes of FeOOH, respectively.

The SEM photographs of the  $\text{Fe}_3\text{O}_4$ -chitosan composite films are showed in Fig. 2. It is obvious that the  $\text{Fe}_3\text{O}_4$  films are well ordered network structures. The pore size varied from 50 – 300 nm, and the thickness of the net-wall is about 30 nm. The net-wall of the sample prepared with more  $\text{Fe}^{2+}$  adsorption (10 min) is partly higher than that with fewer  $\text{Fe}^{2+}$  adsorption (1 min), but the appearance of sub-layer of the former is same as that of the latter. It is well known that chitosan can cross-link to a macromolecule network structure<sup>[12,13]</sup>, so it can be deduced that the formation of  $\text{Fe}_3\text{O}_4$  film is based on the network structure of chitosan film. During the adsorption

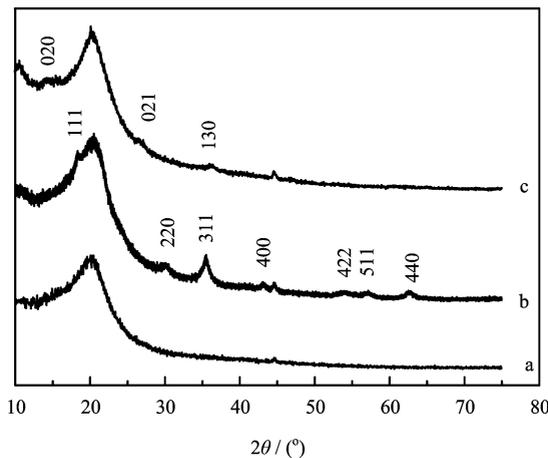


Fig. 1 XRD patterns (a) chitosan film, (b)  $\text{Fe}_3\text{O}_4$ -chitosan composite film, and (c) FeOOH-chitosan composite film

process in this study,  $\text{Fe}^{2+}$  is mainly adsorbed on the surface of network structure, rarely in the pores<sup>[14]</sup>. As  $\text{Fe}^{2+}$  is oxidized and hydrolyzed, the created  $\text{Fe}_3\text{O}_4$  crystal cores mainly exist on the network of chitosan film. Along with the growth of the  $\text{Fe}_3\text{O}_4$  crystals and the conglomeration of adjacent crystals, the  $\text{Fe}_3\text{O}_4$  film will be gained with network structures. Apparently, the up-layer  $\text{Fe}_3\text{O}_4$  in Fig. 2b was created from the redundant  $\text{Fe}^{2+}$  based on the sub-layer  $\text{Fe}_3\text{O}_4$  film. Additionally, the pore sizes of the  $\text{Fe}_3\text{O}_4$  film can be controlled by the preparation technology of chitosan film. Further work on this is in progress.

In order to determine the thermostability of the  $\text{Fe}_3\text{O}_4$ -chitosan film, thermoanalysis was carried out and a thermogravimetric-differential thermal analysis (TG-DTA) curve was obtained. A typical TG-DTA curve is shown in Fig. 3. The TG curve exhibits two weight loss steps, which correspond to an endothermic peak and an exothermic peak on the DTA curve, respectively. The first weight loss step in the temperature range of 30 – 120 °C is accompanied by an endothermic peak around 75 °C on the DTA curve, due to the evaporation of water absorbed in the film. The second weight loss step in the temperature range of 270 – 340 °C corresponds to the degradation of chitosan, which is accompanied by an exothermic peak around 305 °C. It is clear that there is another exothermic peak around 458 °C on the DTA curve. This peak is attributes to the phase transfer from  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$ .

The phase transformation temperature is higher than that in reference<sup>[15]</sup>(431 °C), which is possibly due to

the network structure.

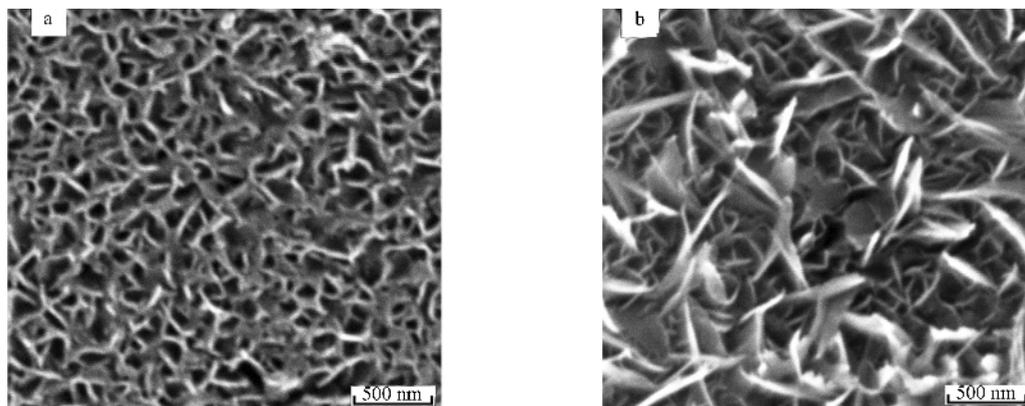


Fig. 2 SEM of surface of the  $\text{Fe}_3\text{O}_4$ -chitosan films

a. Adsorb  $\text{Fe}^{2+}$  for 1 min, b. Adsorb  $\text{Fe}^{2+}$  for 10 min.

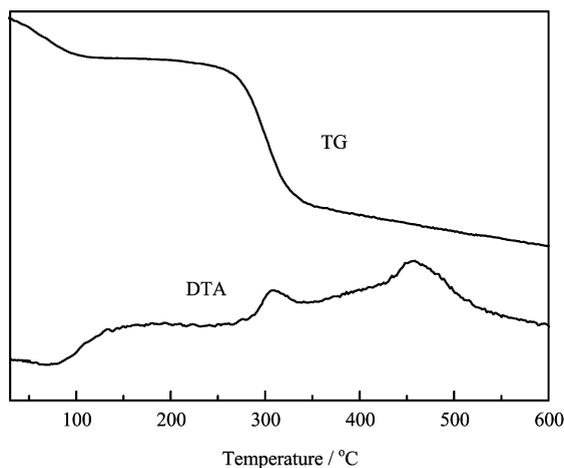


Fig. 3 The TG-DTA curves for the  $\text{Fe}_3\text{O}_4$ -chitosan film

A network  $\text{Fe}_3\text{O}_4$  film, which has pore sizes from 50 – 300 nm and a net-wall thickness of 30 nm, was prepared and investigated by XRD, SEM and TG-DTA. It was found that the prepared sample was pure  $\text{Fe}_3\text{O}_4$  with cubic inverse spinel structure. The temperature of phase transfer from  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$  was about 458 °C. Additionally, the formation mechanism of the  $\text{Fe}_3\text{O}_4$  film was presented. This method is easy to implement and the reaction condition is easily controlled. Such a novel  $\text{Fe}_3\text{O}_4$  film should have potential applications in GMR devices.

## References

[ 1 ] Sorenson T A, Morton S A, Waddill G D, Switzer J A. *J. Am. Chem. Soc.*, 2002, **124**: 7604

- [ 2 ] Horng L, Chern G, Chen M C, Kang P C, Lee D S. *J. Magn. Magn. Mater.*, 2004, **270**: 389
- [ 3 ] Watts S M, Nakajima K, Dijken S V, Coey J M D. *J. Appl. Phys.*, 2004, **95**: 7465
- [ 4 ] Bollero A, Ziese M, Höhne R, Semmelhack H C, Köhler U, Setzer A, Esquinazi P. *J. Magn. Magn. Mater.*, 2005, **285**: 279
- [ 5 ] Shalini K, Subbanna G N, Chandrasekaran S, Shivashankar S A. *Thin Solid Films*, 2003, **424**: 56
- [ 6 ] Chiba M, Morio K, Koizumi Y. *J. Magn. Magn. Mater.*, 2002, **239**: 457
- [ 7 ] Ge J J, Cui Y F, Yan Y, Jiang W Y. *J. Mem. Sci.*, 2000, **165**: 75
- [ 8 ] Liu X D, Tokura S, Haruki M, Nishi N, Sakairi N. *Carb. Polym.*, 2002, **49**: 103
- [ 9 ] WanNgah W S, Ghani S A, Kamari A. *Biore. Tech.*, 2005, **96**: 443
- [ 10 ] Wang S, Fang Y, Zhang Y, Wang M Z, Hu D D, Liao Y K. *Acta Phys. Chim. Sin.*, 2003, **19**: 514
- [ 11 ] Luo X L, Xu J J, Zhang Q, Yang G J, Chen H Y. *Biosens. Bioelectron.*, 2005, **21**: 190
- [ 12 ] Chen R H, Tsaih M L. *J. Appl. Polym. Sci.*, 1997, **66**: 161
- [ 13 ] Berger J, Reist M, Mayer J M, Felt O, Peppas N A, Gurny R. *Eur. J. Pharm. Biopharm.*, 2004, **57**: 19
- [ 14 ] Zhang X J, Lang H Y, Wei Y F, Zhang W P. *J. Appl. Chem.*, 2003, **20**: 749
- [ 15 ] Suri K, Annapoorni S, Tandon R P, Mehra N C. *Syn. Met.*, 2002, **126**: 137