JOURNAL OF Materials CHEMISTRY

An array of iron nanowires encapsulated in polyaniline nanotubules and its magnetic behavior

Huaqiang Cao,[a,c] Zheng Xu,*[a,c] Dong Sheng,[d] Jianming Hong,[d] Hai Sang[b,c] and Youwei Du[b,c]

[a]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China. E-mail: profzxu@jlonline.com; Fax: 86-25-3314502*
[b]*National Laboratory of Solid State Microstructure, Nanjing University, Nanjing 210093, P. R. China*
[c]*Center of Nanometer Science and Technology, Nanjing University, Nanjing 210093, P. R. China*
[d]*Center for Materials Analysis, Nanjing University, Nanjing 210093, P. R. China*

Received 8th August 2000, Accepted 13th December 2000
First published as an Advance Article on the web 6th February 2001

An array of iron nanowires within polyaniline nanotubules was obtained using a two-step template synthesis. First, an array of polyaniline nanotubules was synthesized in an alumina template, and then it was used as a "second-order template" for electrodeposition of iron within the polyaniline nanotubules. The polyaniline envelope may protect the iron nanowires against the corrosive atmosphere. The composite nanostructure was characterized by EDX, XRD and SEM and its magnetic properties were measured by VSM. Coercive forces of the array of iron nanowires encapsulated within polyaniline range from about 119 to 210 Oe with an increase from 0 to 90° for θ, the angle between the applied field and the surface of the alumina template. The array has the axis of easy magnetization in the membrane plane and may be a promising candidate for horizontal magnetic recording materials.

Recently, great efforts have been devoted to the development of perpendicular recording materials.[1–4] The template synthesis method provides a versatile approach and has had considerable success in the preparation of arrays of Fe, Co, Ni and alloy nanowires which have the easy axis perpendicular to the film plane.[5–8] However, magnetic metal nanowires are quite active and can be corroded under a corrosive atmosphere In particular, iron nanowires can be easily corroded in humid air and this limits their application. Recently we have been interested in the development of the preparation of metal-nanowire arrays encapsulated within a polymer, and we have had some success. Here we report on the synthesis of an array of iron nanowires by electrodeposition inside the polyaniline nanotubules (abbreviated to APF). The latter was synthesized in the pores of the commercial available alumina filter (anodic®) made by Whatman Inc. with a thickness of 60 μm. The magnetic properties of the APF are also described.

Experimental

The synthesis is composed of two steps. Synthesis of the polyaniline nanotubules in the pores of the alumina template membrane is carried out by simply immersing the alumina template membrane in 10 ml of a solution of 0.3 M aniline (chemically pure (CP)) and 1 M HCl, and to this mixture 10 ml of 0.5 M toluene-*p*-sulfonic acid sodium salt (CP), 0.12 M ammonium metavanadate (CP) and 1 M HCl solution were added.[9] The solution was bubbled with nitrogen gas prior to the polymerization reaction and throughout the polymerization. The reaction lasted 1.5–2.5 h at room temperature, then, the membrane was removed from the solution, and the polyaniline on the surfaces of the alumina membrane was removed by polishing with alumina powder. An array of polyaniline nanotubules formed within the pores of the alumina template was obtained (Fig. 1). A silver paste which covered one side of the "second-order template" membrane as a working electrode was applied by the spread coating method. The electrochemical deposition solution with $FeSO_4 \cdot 7H_2O$ 140 g l^{-1}, H_3BO_3 50 g l^{-1}, and ascorbic acid 1 g l^{-1}, was confined to the bare side of the "second-order template" membrane, so that deposition was initiated onto the Ag film from within the polyaniline nanotubules. The iron was deposited in a bottom-up fashion in the "second-order template" membrane so as to fill up the pores. The extra iron that overflowed from the pores was removed by chemical etch using $FeCl_3$ solution. Powder X-ray diffraction of the above sample was recorded on a Rigaku X-ray diffractometer (Cu-Kα radiation, $\lambda = 0.15418$ nm). The APF composite membrane was immersed in 6 M NaOH solution to dissolve the alumina template and the silver film was removed as far as possible by chemical and mechanical methods. The template was then sputtered with a thin film of gold on the silver film side as the testing sample for scanning electron micrograph (SEM) and energy dispersive X-ray analysis (EDX) measurements. SEM and EDX were carried out on a Hitachi, X650 electron microscope and EDAX PV9100. Magnetization loops were measured at room temperature, using a LakeShore, EM 7037 vibrating sample magnetometer (VSM).

Results and discussion

SEM images of the polyaniline nanotubules and APF nanowires after dissolving a part of the alumina membrane are shown in Fig. 1a, 1b, respectively. The tubular structure of the polyaniline is observed clearly in Fig. 1a, and the outer diameter of the tubules is *ca.* 200 nm, corresponding to the pore diameter of alumina. From Fig. 1b, we can see that APF stands on the substrate surface like the bristles of a brush. The nanowires are 60 μm long, corresponding to the thickness of

 DOI: 10.1039/b006474m

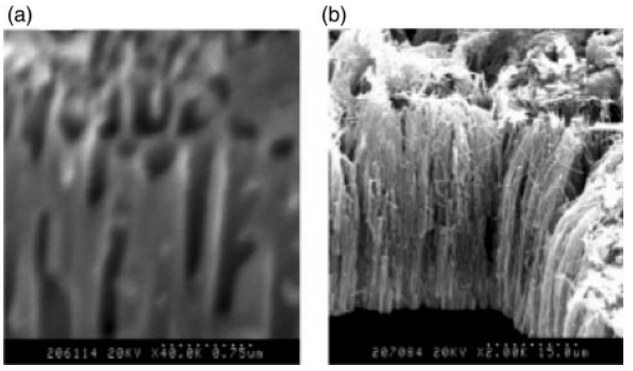

Fig. 1 Scanning electron microscopic images of (a) polyaniline nanotubules obtained after dissolution of the top layer of alumina membrane, (b) iron nanowires filled within polyaniline nanotubules obtained after dissolution of the top layer of alumina template, showing nanowires of monodisperse length corresponding to the membrane thickness (60 μm).

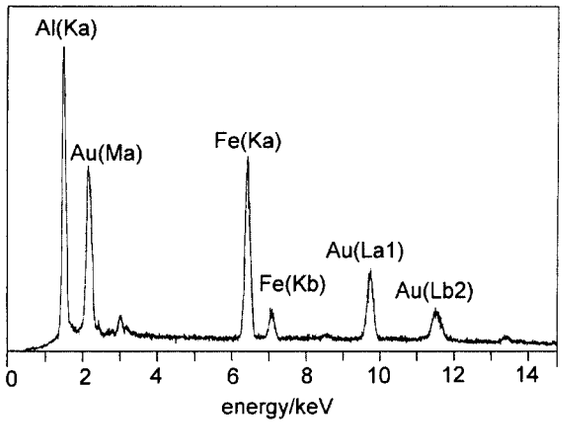

Fig. 2 EDX profile of APF.

the template membrane, and are continuous and mechanically stable.

The presence of iron in the polyaniline nanotubules is demonstrated by EDX (Fig. 2). There are three elements: iron, aluminium and gold in the EDX spectrum. Aluminium comes from the alumina template, and gold comes from the thin film of gold sputtered before SEM and EDX measurements. In order to identify the structure of the iron in the nanowires, XRD measurements on the APF were carried out (Fig. 3). We have proved the presence of iron by EDX and VSM measurements, even though Ag (ASPDF 4-0784) and Fe (ASPDF 6-0696) have some similar XRD diffraction peaks in the range of $38^\circ < 2\theta < 82^\circ$. We can index the iron as (110),

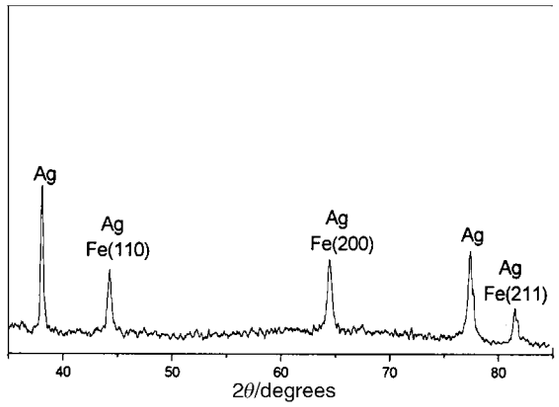

Fig. 3 X-Ray powder diffraction spectrum of APF.

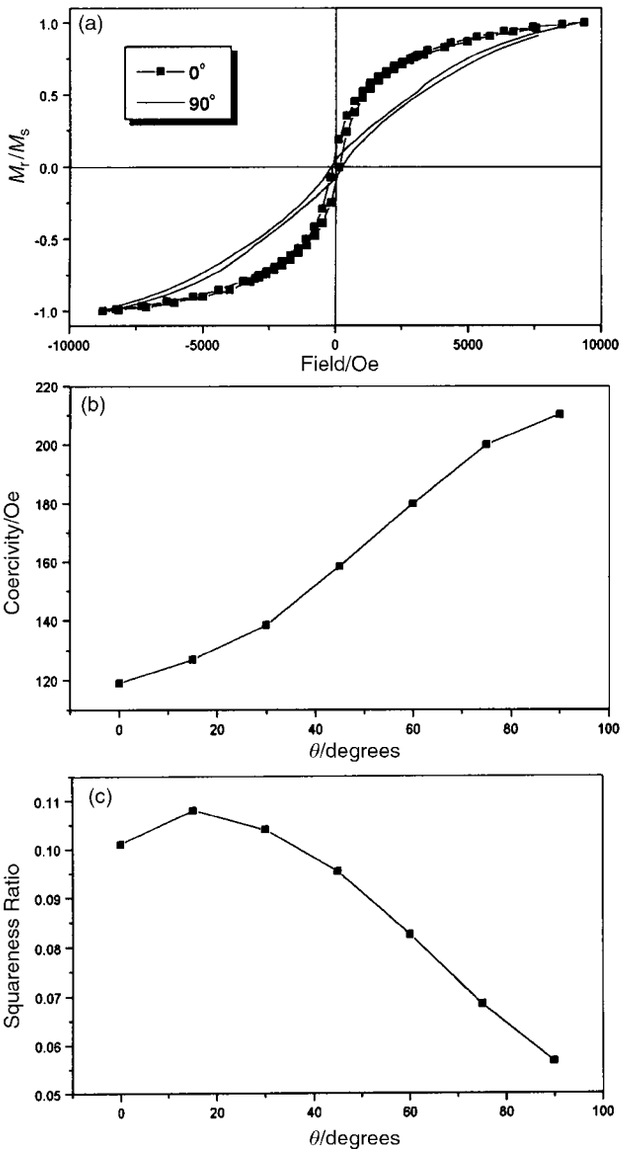

Fig. 4 VSM. (a) Magnetization curves with the field applied parallel and perpendicular to the APF membrane recorded at room temperature. (b) The variation of coercive force. (c) The variation of squareness with the angle (θ) between the magnetic field applied and the APF membrane.

(200) and (211) cubic iron metal from XRD, and this suggests that the nanowire is composed of pure iron metal rather than an iron compound.

The M–H hysteresis curves of the APF are shown in Fig. 4a, and shows that the easy axis lies in the membrane plane. The coercivity forces increase from 119 to 210 Oe as θ increases from 0 to 90°, where θ is the angle between the surface of membrane plane (Fig. 4b) and the applied field. The squareness ratio (Mr/Ms) of the array decreases from 0.108 to 0.056, with the maximum at $\theta = 15^\circ$ (Fig. 4c). The remanence of the array is 11% less than the saturation magnetization, because of the magnetic interaction among the adjacent nanowires. The results show that the array of iron nanowires encapsulated within polyaniline may be a candidate material for horizontal magnetic recording.

Conclusions

A two-step template synthesis provides a versatile approach in the preparation of an array of polymer nanotubules filled with

metal nanowires. An array of iron nanowires encapsulated within polyaniline has been prepared. The magnetic behaviors were determined. The easy axis of the array lies in the membrane plane. The polyaniline envelope might protect the iron nanowires against the corrosion under humid air. The array we prepared may be a promising candidate material for horizontal magnetic recording.

Acknowledgements

This research was supported by the grant from National Natural Science Foundation of China for the key project No. 29823001, and from Natural Science Foundation of Jiangsu Province for the key project No. BK99207 and analysis and measurement of Nanjing University.

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