

One-Step Process To Fabricate Fe Core/Fe–Dimethylsulfoxide Shell Coaxial Nanocables

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The coaxial nanocables of Fe/Fe–dimethylsulfoxide (DMSO) were electrodeposited at 40 °C in the solution of DMSO with 17 g/L FeCl₃. It is the first report about the preparation of nanocables by electrodeposition in a simple one-step process. The Fe–DMSO sheaths are predicted as coordination compounds of [Fe(DMSO)₄Cl₂] and [Fe(DMSO)₃Cl₃] that are amorphous in structure and paramagnetic at room temperature. The Fe cores are bcc structure with a preferred orientation of (110). The morphology of resulting nanostructures can be precisely controlled by varying the concentration of FeCl₃ in DMSO solution and the electrodeposition temperature. The walls of Fe–DMSO sheaths are very thin; therefore, the outer diameters of nanocables are nearly the same as the central Fe cores about 40 nm, with an aspect ratio of 100. The arrays exhibit an obvious anisotropy with the easy magnetizing axis along the length of nanocables, which are useful magnetic storage materials.

Introduction

The coaxial nanocables as a new type of one-dimensional nanostructure have attracted considerable attention in recent years because of their unique structure and many novel properties.^{1–4} The core/shell structure properties of nanocables provide a great possibility to take advantage of different functions and properties of different materials within a single nanoscale component, which are expected to be widely used in chemistry, physics, medicine, materials science, and many other fields.^{5–7} Recently, semiconductor/semiconductor,^{8–10} metal/semiconductor,^{11,12} metal/metal oxide,^{13,14} and metal/polymer¹⁵ coaxial nanocables have been successfully synthesized and investigated. Usually, the method used to

fabricate these ordered wire–sheath-structured nanocables is template-processing. Using different templates, such as small organic molecules,¹⁶ surfactants,^{17,18} nanometer-sized granulars of silica,¹⁹ porous anodic aluminum oxide (AAO),^{20–22} carbon nanotube,²³ etc., ordered nanostructures with different diameters can be synthesized. Among these templates, the AAO membrane with its ordered honeycomb structure has attracted considerable interest because its pore diameter, distance between pores, and membrane thickness can be controlled by adjusting the anodizing parameters. In this method, the surface of nanowires could be coated with conformal sheaths made of different materials by electrochemical deposition,²⁴ high-temperature chemical vapor deposition,²⁵ layer-by-layer deposition,²⁶ sol–gel,²⁷ hydrothermal,²⁸ and other means.

Currently, coaxial nanostructures, containing metal or inorganic electrical, optical, and magnetic nanorods or nano-

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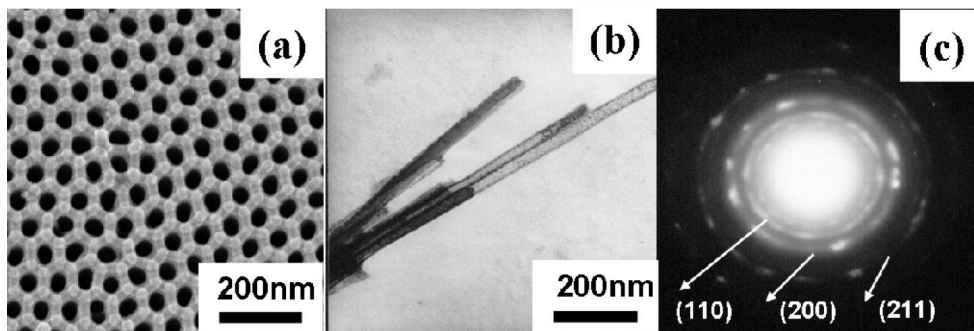


Figure 1. (a) SEM image of AAO templates. (b) Typical TEM image of nanocables. (c) SAED pattern of corresponding nanocable.

wires coated with conducting polymers are of particular interest for various electronic device applications. Furthermore, the polymers can protect metal nanowires from oxidation and corrosion, keeping good performance for a long time, which are useful for us to study the magnetic, optical, electronic, and mechanical properties of individual nanowire. Xu et al., for example, reported the template synthesis and magnetic behavior of arrays of cobalt nanowires encapsulated in polyaniline nanotubes.²⁹ Shi et al. have reported the electrochemical fabrication of polythiophene-film-coated metallic nanowire arrays.^{30,31} Kim et al. also synthesized Au/polypyrrole core-shell nanorods with Au nanorods as the template.³² The main route of preparing core-shell nanostructures mentioned above is two-step processes: nanotubes were fabricated as templates, and then materials were confined to form core-shell nanowires. Niu prepared the Au/polyaniline by a self-assembly process in one step.³³ Li et al. reported the Ag/polypyrrole coaxial nanocables through a one-step process of redox reaction between silver nitrite and pyrrole.³⁴ In comparison to two-step processes, the one-step process can simplify the procedure to prepare nanocables: the core-sheath structure of nanocables can be formed at the same time. However, the degree of order of those nanocable arrays is deficient for the previous report of the one-step process. In this paper, we first present a simple one-step process to fabricate ordered Fe/Fe–DMSO coaxial nanocables in AAO templates by electrodeposition.

Experimental Section

The coaxial nanocables of Fe/Fe–DMSO were prepared at 40 °C in the solution of DMSO with 17 g/L FeCl₃ by AC electrodeposition in AAO templates. The highly ordered AAO templates were fabricated in 0.3 M oxalic acid solution at 40 V_{DC} by a two-step anodizing process. The DMSO was dehydrated with 4 Å molecular sieves and distilled to remove impurities at reduced pressure. FeCl₃·6H₂O (AR) was dehydrated in vacuum at 453 K. The electrodeposition of the nanocables was performed using a standard double electrode bath and conducted at 200 Hz and 15 V, at different electrodeposited temperature from 40 to 130 °C for the

duration of 10 min. The method of electrodeposition is nearly the same as previous reports of Fe nanowires; the difference is the solution and electrodeposited temperature.³⁵

The morphologies of the AAO templates and the nanocables were obtained by a scanning electron microscope (SEM, HitachiS-4800) and transmission electron microscope (TEM, JEOL 2000), where the nanocables were separated from the AAO templates by dissolving the AAO templates in the mixed solution of 0.2 M H₂CrO₄ and 0.4 M H₃PO₄ about 2 days at 30 °C. If the dissolving time is too long or the temperature is too high, the nanocables may be oxidized or the sheaths can be separated from nanowire core, but the velocity of oxidation is much slower than that of the simple Fe nanowires. The selected area electron diffraction (SAED), X-ray diffraction (X'Pert PRO PHILIPS with Cu K α radiation), and Mössbauer spectrometer in a constant acceleration spectrometer with a source of ⁵⁷Co in rhodium were employed to study the structure of the nanocable arrays. The Mössbauer spectrum was computer-fitted with a Lorentzian peak using a least-squares method. The isomer shift determined is relative to α -Fe at room temperature (RT). RT magnetic properties of nanocable arrays were characterized using a vibrating sample magnetometer (Lakeshore 7304).

Results and Discussion

The coaxial nanocables of Fe/Fe–DMSO were electrodeposited at 40 °C in the solution of DMSO with 17 g/L FeCl₃. A SEM image of AAO template is shown in Figure 1a. It is found that the nanopores of the template are uniform and highly ordered, with an average diameter of 40 nm. To observe the morphology of nanocables clearly, a representative TEM image of nanocables that nanowire cores fill in sheaths is partly shown in Figure 1b, from which it can be seen that the Fe/Fe–DMSO composites are coaxial nanocable structures composed of Fe–DMSO sheaths and Fe nanowire cores. Moreover, Figure 1b clearly demonstrates a sharp contrast between the light sheaths of Fe–DMSO and the inner, dark Fe cores. The wall of sheaths is very thin; therefore, the outer diameter of nanocables is nearly the same as the central Fe cores about 40 nm, with an aspect ratio of 100. The corresponding SAED pattern of the Fe core encapsulated within the Fe–DMSO sheath (Figure 1c), indicates that the Fe cores are polycrystalline and can be indexed to the {110}, {200}, and {211} reflections from bcc Fe metal, and there is also a halo besides Fe diffraction dots or circles indicating that Fe–DMSO sheaths are amorphous.

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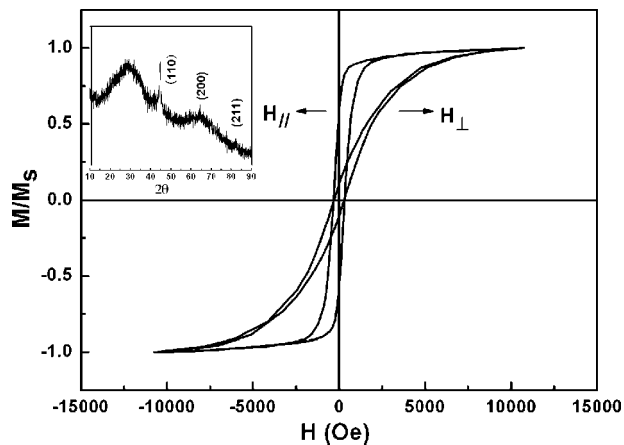


Figure 2. Magnetic hysteresis loops of nanocables with AAO templates and the inset with the corresponding X-ray diffraction pattern.

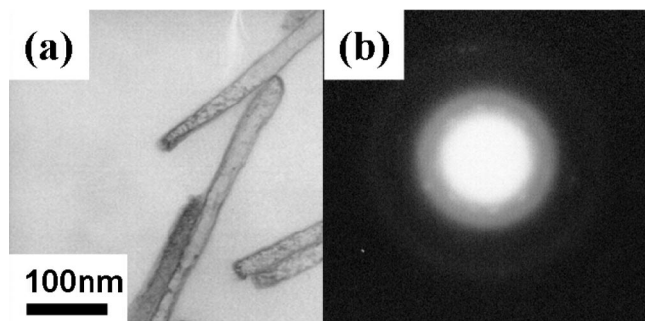


Figure 3. (a) TEM image of Fe-DMSO sheaths. (b) Corresponding SAED of the Fe-DMSO sheath.

The magnetic properties of AAO templates that filled the nanocable arrays were measured at RT, and the magnetic hysteresis loops of this composite nanostructure are shown in Figure 2, where the signs of $H_{||}$ and H_{\perp} represent that the applied field H is parallel and perpendicular to the nanocable axis, respectively. The different shapes of magnetic hysteresis loops in parallel and perpendicular directions indicate that the arrays exhibit an obvious anisotropy with the easy magnetizing axis along the length of nanocables. The inset shows the X-ray diffraction pattern of the nanocables with AAO templates measured at RT. The diffraction peaks in the $10^{\circ} < 2\theta < 90^{\circ}$ region can be indexed as Fe (110), (200), and (211), indicating a bcc structure with a preferred orientation of (110), which are in good concordance with the result of SAED. The broad peak in the XRD at 25° is the glass diffraction peak. The glass was used to put the nanocables with the template in the measurement of XRD.

To elucidate the forming mechanism of the Fe/Fe-DMSO nanocables, the influence of the synthesis conditions (such as the concentration of reactants and the electrodeposited temperature) on the morphology of resulting nanostructures was investigated. In this method, it was found that the concentration of FeCl_3 in DMSO has a significant effect on the formation of Fe/Fe-DMSO nanocables at the same electrodeposited temperature of 40°C . Figure 3 shows a typical example of the effect of the concentration on the morphology, measured using TEM. When the content of FeCl_3 is 3 g/L in DMSO at the electrodeposited temperature of 40°C , the hollow sheath structure of Fe-DMSO can be

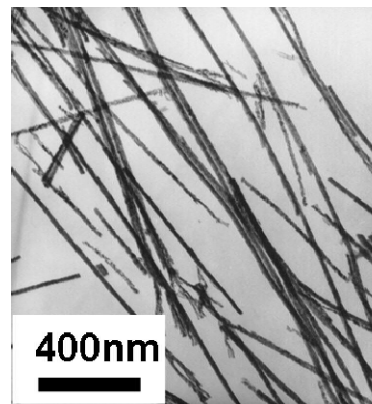


Figure 4. TEM image of nanocables electrodeposited at 130°C with 17 g/L FeCl_3 dissolved in DMSO.

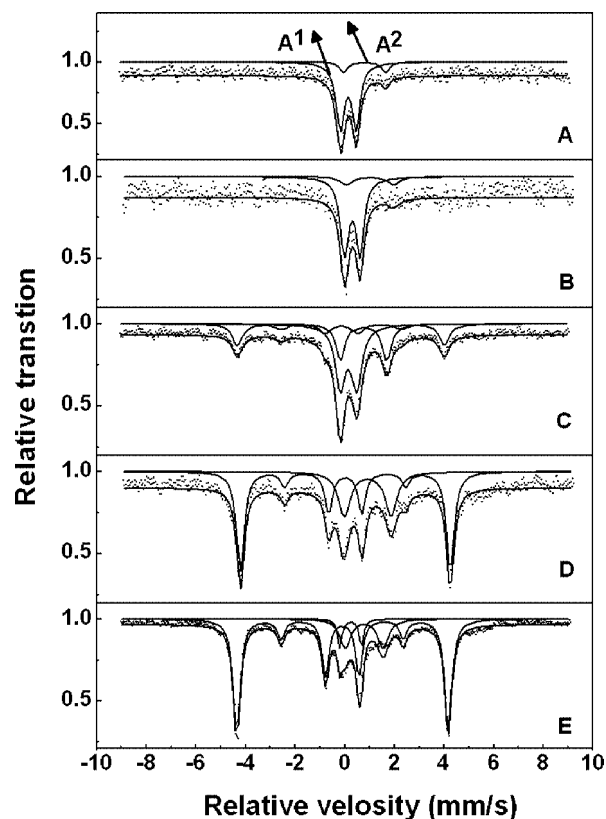


Figure 5. RT transmission Mössbauer spectra of A-E.

observed clearly in the TEM image shown in Figure 3a. The diameter of the outshells and the central hollow cores of the Fe-DMSO sheaths are consistent with the above-mentioned nanocable values (as shown in Figure 1b). The corresponding SAED pattern in Figure 3b does not display Fe diffraction dots or circles, confirming that the sheaths are only amorphous Fe-DMSO. The coordination compound of Fe-DMSO can be adsorbed easily by the AAO template; therefore, the sheath can easily form in electrodeposition. The mechanism is the same as the preparing of the Co nanotube, where AAO templates were silanized before electrodeposition.³⁶

The influence of electrodeposited temperature on the morphology of resulting nanostructures was also studied. The

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Table 1. Fitted Parameters of RT Transmission Mössbauer Spectra of A–E

	electrodeposition products	relative intensity (%)	isomer shift (mm/s)	quadruple splitting (mm/s)	hyperfine field (T)
	A	0	X	X	X
	B	0	X	X	X
sextet	C	26.7	0.00 ± 0.02	−0.01 ± 0.02	32.9 ± 0.1
	D	63.0	0.01 ± 0.02	0.00 ± 0.02	33.0 ± 0.1
	E	76.1	0.00 ± 0.02	0.01 ± 0.02	33.1 ± 0.1
	A	86.5	0.35 ± 0.02	0.79 ± 0.02	0
doublet A ¹	B	84.7	0.34 ± 0.02	0.71 ± 0.02	0
	C	48.4	0.37 ± 0.02	0.81 ± 0.02	0
	D	9.1	0.40 ± 0.02	0.99 ± 0.02	0
	E	7.0	0.45 ± 0.02	0.94 ± 0.02	0
	A	13.5	1.17 ± 0.02	2.11 ± 0.02	0
doublet A ²	B	15.3	1.22 ± 0.02	2.28 ± 0.02	0
	C	24.9	1.13 ± 0.02	2.32 ± 0.02	0
	D	27.9	1.12 ± 0.02	2.33 ± 0.02	0
	E	16.9	1.04 ± 0.02	2.11 ± 0.02	0

TEM image of the nanocables, which were electrodeposited at 130 °C with 17 g/L FeCl₃ in DMSO, is shown in Figure 4. The morphology of these nanocables is nanowire cores almost. The length of the nanowire cores are about 4 μm, and the aspect ratio is about 100, which is consistent with that of above-mentioned nanocables.

Further evidence for elucidating the forming mechanism comes from the RT transmission Mössbauer spectra that can be used to study the microstructure and micromagnetic properties. The nanocables electrodeposited at 40 °C in DMSO with different contents of FeCl₃ of 3, 5, 10, and 17 g/L are marked as A, B, C, and D, respectively. The nanocables of E were electrodeposited at 130 °C in DMSO with 17 g/L FeCl₃. RT transmission Mössbauer spectra of A–E are shown in Figure 5. The Mössbauer spectra of A and B were fitted by two doublets of A¹ and A², while C–E were fitted by a sextet besides the two doublets mentioned above. The fitted result and TEM result show that the materials corresponding to A¹ and A² are sheath and that the materials corresponding to sextet are core. The fitted parameters are shown in Table 1, indicating that the sextet corresponds to α-Fe and the two doublets of A¹ and A² can be considered as coordination compounds of [Fe(DMSO)₄Cl₂] and [Fe(DMSO)₃Cl₃],³⁷ respectively. The two doublets of A¹ and A² indicate that the coordination compounds of [Fe(DMSO)₄Cl₂] and [Fe(DMSO)₃Cl₃] are paramagnetic at RT. The relative intensity of fitted parameters can be used to indicate the content of α-Fe and coordination compounds. With the increase of FeCl₃ content from 3 to 17 g/L in DMSO at the electrodeposited temperature of 40 °C, the relative intensity of sextet and the doublet A² increase, indicating that the electrodeposited products of Fe and [Fe(DMSO)₃Cl₃] increase. The reason is that the reduction process of [Fe(DMSO)₃Cl₃] to [Fe(DMSO)₄Cl₂]³⁸ is harder than that of Fe³⁺ to Fe.

With the increase of electrodeposited temperature, the relative intensity of sextet increases and that of the two doublets A¹ and A² decreases, indicating that the content of Fe increases, while the coordination compounds of [Fe(DMSO)₄Cl₂] and [Fe(DMSO)₃Cl₃] decrease. The chemical bonds of [Fe(DMSO)₄Cl₂] and [Fe(DMSO)₃Cl₃] are unstable in solution at higher temperature, which results in the sheaths of nanocables becoming thinner and even disappearing in some nanocables. It is consistent with the result of the morphology of nanocable E that is Fe cores nearly.

Conclusions

We have successfully developed an electrodeposition method for synthesizing arrays of orderly Fe/Fe–DMSO coaxial nanocables with an average diameter of 40 nm and the aspect ratio of 100 in AAO templates through only a one-step process. The synthetic strategy is simple and effective, which could be extended to the preparation of a variety of metal/metal–DMSO nanocables under appropriate conditions. The core/shell nanostructure has been confirmed by TEM images and RT transmission Mössbauer spectra. The morphology of resulting nanostructures can be precisely controlled by varying the concentration of FeCl₃ in DMSO solution. The Fe–DMSO sheaths are amorphous in structure and paramagnetic at room temperature, which can form first when a small quantity of FeCl₃ is dissolved in DMSO. The Fe cores are bcc structure with a preferred direction of (110). To the best of our knowledge, this is the first example of metal nanowire cores encapsulated within metal–DMSO sheaths by electrodeposition in a one-step process.

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