Fabrication and Magnetic Properties of Ni/Cu Shell/Core Nanocable Arrays

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Ordered Ni/Cu shell/core structured nanocable arrays were successfully fabricated by a two-step electrodeposition process. First, nickel (Ni) nanotubes were obtained by chemical electrodeposition in nanoporous anodic aluminum oxide (AAO) template. Then the AAO/Ni nanotube composite membrane was used as a secondary template to deposit copper (Cu) nanowires into Ni nanotubes. The morphology and microstructure of the nanocables has been characterized using scanning electron microscopy and transmission electron microscopy. The chemical composition of the nanocables has been confirmed by X-ray diffraction. Magnetization measurements revealed that Ni/Cu nanocable arrays have a high remanence ratio.

1. Introduction

Since the discovery of carbon nanotubes by Iijima,[1] a great deal of attention has been paid to the preparation of nanotubes. Various nanotubes such as polymer, metal, and other material nanotubes have been reported,[2−4] especially metal nanostructures because of the unique quantum physical and chemical properties.[5] Among various preparation processes, template synthesis has been proven to be a versatile approach and an inexpensive technique for the fabrication of diverse nanostructured materials.[6] Martin and co-workers first used nanoporous membranes.[7,8] Chemical, electrochemical, and vacuum deposition techniques have all been used to deposit the metals in the nanoporous templates,[9,10] as well as single and multiwalled nanotubes, nanowires, and nanorods of noble metals.[11,12] In recent years, one-dimensional (1D) nanostructured metal materials, especially ferromagnetic nanostructures have attracted great attention due to their magnetic, electrical, and novel optical properties.[13−16] Ferromagnetic nanostructured materials such as Fe,[17] Co,[18] and Ni,[19] as well as ferromagnetic alloys,[20,21] have been prepared using electrochemical template synthesis. Magnetic composite materials may be more favorable than single-component magnetic materials, for example, Ni/Cu, and Ni/Pt multilayered nanowire arrays can enhance coercivity and remanence ratio,[8,9,22] and Ni/γ-Fe_2O_3 shell/core nanocables are more interesting due to its potential application in electromagnetism.[23] Up to now, only a few examples[24] about the fabrication of Ni/Cu shell/core nanocables have been reported. It is still a critical challenge to produce Ni/Cu nanocables.

In this work, we report fabrication of Ni/Cu nanocable arrays using a two-step deposition process. Ni nanotubes were produced first by depositing nickel atoms into the pores of AAO template, and then AAO/Ni nanotube composite membrane was used as a "secondary template" to deposit copper atoms into the Ni nanotubes. Ni/Cu nanocable arrays are more likely to be used in devices or memorizers because of their electrical and magnetic properties.

2. Experimental Section

The anodic aluminum oxide (AAO) templates with a specified pore diameter of 200 nm are commercial templates (from Whatman Corp.). The actual diameters of the pores range from 150 to 300 nm, and the depth of the templates is 50−60 μm. In the experiment, Ni nanotube arrays are direct-current (dc) electrodeposited in pores of AAO templates using a potentiostat with a standard three-electrode system. A platinum film was used as the counter electrode and a Ag/AgCl electrode in saturated KCl solution as the reference electrode. A thin layer of Au was evaporated onto one side of the AAO template to serve as the working electrode. Ni nanotube arrays were produced in the template pores from a solution of 0.8 M $NiSO_4 \cdot 6H_2O$, 0.5 M H_3BO_3, and 0.3 M KCl for 10 min. All the potential was shown as −0.8 V/SCE. On the condition of this electrodeposition parameters, Ni nanotubes can be obtained. Details can be found in our previous paper.[25] Then AAO/Ni nanotube composite membrane was used as a "secondary template", and Cu nanowires were deposited into the Ni nanotubes from a solution of 0.5 M $CuSO_4$ and 0.1 M H_2SO_4. The potential was shown as −0.2 V/SCE.

Scanning electron microscopy (SEM; JEOL JSM-6390LV), transmission electron microscopy (TEM; CM200-FEG equipped with a GIF) were used to characterize the nanotubes, nanowires, and nanocables. The chemical composition of the nanocables were confirmed by X-ray diffraction (XRD; Bruker D8 Advance with a Cu−Kα radiation, $\lambda = 1.5418$ Å). Selected-area electron diffraction (SAED) pattern was used to determine the structure of the nanotubes, nanowires. The magnetization measurements of the Ni/Cu nanocable arrays were carried out at room temperature on a vibrating sample magnetometer (VSM, Lakeshore 7307).

3. Results and Discussion

Figure 1a,b presents SEM images of the front and back of AAO templates, respectively. From the two images, it can be

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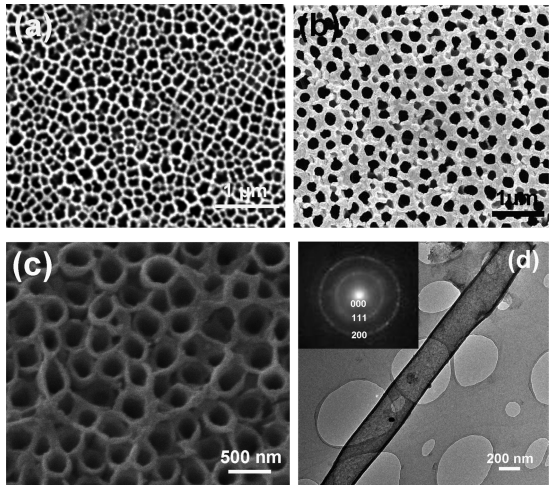

Figure 1. (a,b) SEM images of the front and the back of AAO template respectively; (c) SEM image of Ni nanotube arrays; (d) TEM image of a single Ni nanotube. The inset is the SAED pattern.

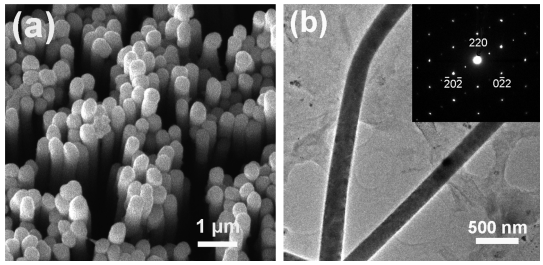

Figure 2. (a) Typical SEM image of Cu nanowire arrays; (b) typical TEM image of Cu nanowires and the inset is the corresponding SAED pattern.

seen clearly that the diameter of the pores in the front of AAO template is larger than that in the back, and yet the wall of the pores is thinner in the front of AAO template compared with that in the back. So the outside diameter of the nanostructures obtained in the bottom is thinner than that in the top. Figure 1c shows a typical SEM image of Ni nanotube arrays after partially removing the AAO template with 3.0 mol/L NaOH solution. The ordered arrays of Ni nanotubes clearly have open ends. It shows that each pore of AAO template is filled with Ni nanotubes. The diameters of the Ni nanotubes range from 150 to 300 nm, in good agreement with those of AAO template. Figure 1d shows a typical TEM image of a single Ni nanotube after completely removing the AAO template with a 3.0 mol/L NaOH solution. The diameter is about 250 nm, and the length is about 3 μm. The inset selected-area electron diffraction (SAED) pattern of the wall of Ni nanotube presents concentric ring-like patterns, which is characteristic of polycrystalline.

Figure 2a shows a typical SEM image of Cu nanowire arrays after completely removing the AAO template with 3.0 mol/L NaOH solution. The deposition process was carried at -0.2 V, and the deposition time was 10 min. The Cu nanowires filled all the pores of AAO template. There is a distribution in the length of nanowires. This is due to the difference in the thickness of the barrier layer at each pore and due also to the hydrogen evolution caused by water splitting reaction.[26] Consequently, the rate of deposition becomes different at each pore. As can be seen from Figure 2b, the Cu nanowire is continuous and uniform. The length is about 8 μm. The inset SAED pattern presents that the Cu nanowires are single crystalline.

Figure 3a shows a typical SEM image of Ni/Cu nanocable arrays after partially removing the AAO template. The top of

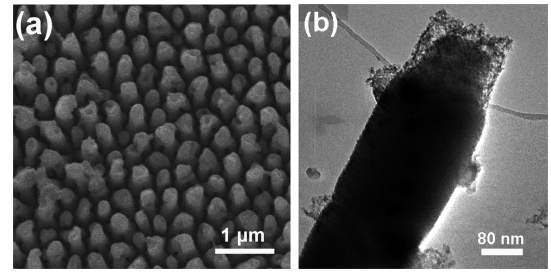

Figure 3. (a) SEM image of Ni/Cu nanocable arrays; (b) a typical TEM image of Ni/Cu nanocable.

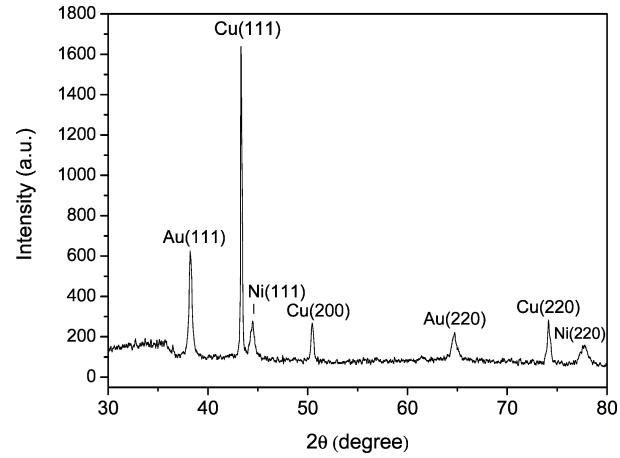

Figure 4. Typical XRD pattern of Ni/Cu nanocable arrays.

the AAO template was removed, and the nanocable bottom is embeded in the pore. The deposition for the sample was carried at -0.8 V for Ni nanotube and the deposition time is 10 min, and then -0.2 V for Cu nanowire, 5 min. The length of wires were increased with the deposition time. The details of the relationship of the length of Cu nanowires and deposition time have been indicated in our previous paper.[27] It can be clearly seen that some ends are open while the others are closed. The reason may be due to the fact that the morphology of each Ni channel is different, and the growth rate is different in the Ni channels when the Cu nanowire was deposited into the channels. In Figure 3b, the microstructure of outer shell (Ni nanotube) and inner core (Cu nanowire) can be seen clearly from the upper end, and the top end is open. The nanocable diameter is about 200 nm.

To confirm the chemical composition of the Ni/Cu nanocables, the composition of the Ni/Cu nanocables has been confirmed by XRD. Figure 4 displays the XRD pattern of Ni/Cu nanocable arrays. The diffraction peaks are indexed to the (111) and (220) planes of Ni, and (111), (200), and (220) planes of Cu, respectively. In addition, the origin of the Au(111) reflection is due to Au film sputtered on the bottom of the AAO membrane. All peaks of Ni and Cu exhibit face-centered cubic (fcc) structure. All the nanocables show Ni−Cu phase-separated nanostructures.

The magnetization behavior of both Ni/Cu nanocables and Ni nanotubes was investigated. Figure 5 shows the magnetization hysteresis (M-H) loops of Ni nanotube arrays and Ni/Cu nanocable arrays. In Figure 5, the squareness in the perpendicular-to-nanocable/nanotube direction (nanocable/nanotuble direction means the axis of nanostructures) is higher than in the parallel direction, that is, $S_{\perp} = 0.25$, $S_{||} = 0.058$ for Ni/Cu nanocables, and $S_{\perp} = 0.15$, $S_{||} = 0.064$ for Ni nanotubes, respectively. It can be seen clearly that the squareness in the perpendicular

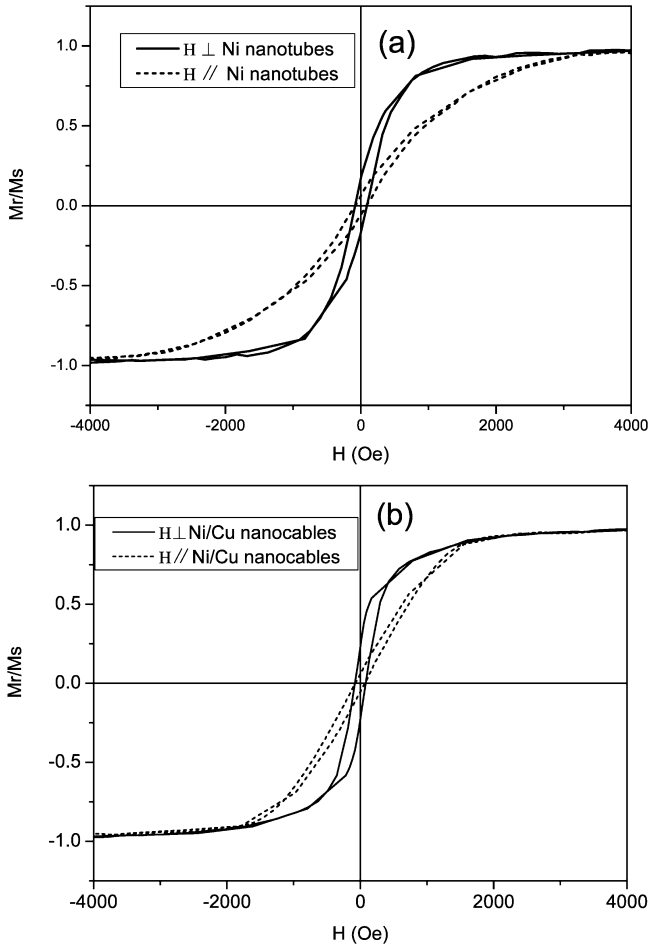

Figure 5. (a) M-H loops of Ni nanotube arrays; (b) M-H loops of Ni/Cu nanocable arrays.

direction is higher in Figure 5b than that in Figure 5a. It means that the remanence is higher in Ni/Cu nanocables than that in Ni nanotubes. Meanwhile, the saturation fields in the perpendicular-to-nanocable direction (*H*s) are smaller than those in parallel-to-nanocable direction ($Hs^{||}$), which indicates that Ni/Cu nanocable arrays are easier to be radially magnetized.

The remanence of Ni/Cu nanocables was greatly improved due to the introduction of Cu nanowires. Ni/Cu nanocable arrays will be made of membrane and used in chemical sensors, nanodevices, and magnetic memories.

4. Conclusions

In summary, ordered arrays of Ni/Cu nanocables have been successfully fabricated by electrodeposition in the pores of AAO template via a two-step deposition process. The characterization of morphology and chemical composition confirmed the obtained Ni/Cu nanocable arrays. Magnetic measurements show that the Ni/Cu nanocable arrays have higher remanence ratio than Ni nanotube arrays, and Ni/Cu nanocables are easier to be radially magnetized. Ni nanotubes can be filled into other materials such as metals, and semiconductors to form new composites that will be used in the nanodevices due to their magnetic, electrical, and optical properties.

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