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One-step synthesis of $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ ferrite nanowire arrays using a template method

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A B S T R A C T

$Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays were fabricated by a simple ethanol–nitrate method using anodic aluminum oxide (AAO) templates. XRD result indicated that the nanowires are of cubic spinel structure. SEM and VSM were used to characterize morphology and magnetic anisotropy properties of the nanowire arrays, respectively. It is believed that this method should be applicable to other multi-component oxide nanowires.

1. Introduction

During the last years, synthesis and functionalization of one-dimensional (1D) nanostructures, such as nanotubes and nanowires, have attracted much interest, due to their unique properties and potential applications as electronics, photonics and magnetic materials [1–5]. NiCuZn ferrite is a soft magnetic material with a completely inverse spinel structure and has been widely used in commercial area. Although considerable studies have been reported on preparation and characterization of NiCuZn ferrite nanoparticles [6,7], less information is available on fabrication and magnetic properties of NiCuZn ferrite nanowires in the open literature.

Various approaches have been developed to fabricate 1D nanostructured materials. Template method, especially those based on porous anodic aluminum oxide (AAO) templates, is a simple and effective way to synthesize 1D nanostructures. Various nanowires and nanotubes have been fabricated by chemical vapor deposition (CVD) [8–10], sol–gel technique [11,12], electrodeposition [13,14] and electroless deposition [15–17], assisted with AAO templates. However, CVD requires expensive equipment, sol–gel process has difficulty to fill a high concentration sol into the pores of templates, electrodeposition consumes electricity, whereas electroless deposition needs a complex sensitization–preactivation process to modify the pore walls of templates [15–17]. In this communication, we report on a simple wetting chemical deposition technique to fabricate NiCuZn ferrite nanowire arrays using AAO templates. Their structure, morphology and magnetic properties will be characterized and discussed. This one-step technique is cost-effective, easy to control and can be conducted at low temperature and ambient atmospheric pressure. It is believed that this simple method will also be applicable to fabrication of other oxide nanowires.

2. Experimental details

2.1. Preparation of AAO templates

Anodic aluminum oxide (AAO) templates with hexagonally ordered arrays of nanopores were prepared by a new oxalic-acid-based anodization process (hard anodization) [18]. A high purity (99.99%) aluminum foil supplied by Alfa Aesar (USA) was used as substrate material. The foil was annealed at 500 °C in air for 5 h and then was cleaned using acetone. The as-treated foil was direct current (DC) anodized in 0.3 mol/L $H_2C_2O_4$ at 40 V for 5–10 min to form a protective layer with about 0.5 μm thickness on the aluminum surface. This layer has two main functions, namely: (i) suppressing breakdown effects due to high temperature and (ii) enabling uniform oxide film growth at high voltages [19]. Subsequently, the voltage was slowly increased to the anodization voltage (110 V) at a rate of $0.6\,V\,s^{-1}$ for hard anodization. The anodization voltage was maintained until the desired pore depth was reached (around 90 min in our experiment). After hard anodization process, the foil was immersed into 6 wt% phosphoric acid for approximately 40 min to widen pore sizes. The residual aluminum was removed from the formed AAO template using a 0.1 mol/L $CuCl_2$ solution to obtain the AAO template with exposed barrier film. Finally, the template was repeatedly rinsed with distilled water.

2.2. Preparation of $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowires

The method of fabricating the aligned polycrystalline nanowires is shown schematically in Fig. 1. Powders of $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were respectively dissolved in ethanol at a molar ratio of about 0.23:0.66:0.11:2 to form a nitrate–ethanol solution using a magnetic stir. Molar concentration of the metallic ions in the ethanol solution was about 0.06 mol/L. It should be noted that if the concentration is too high, deposition of the metallic nitrates proceeds too fast, and the pores may be blocked at the template surface

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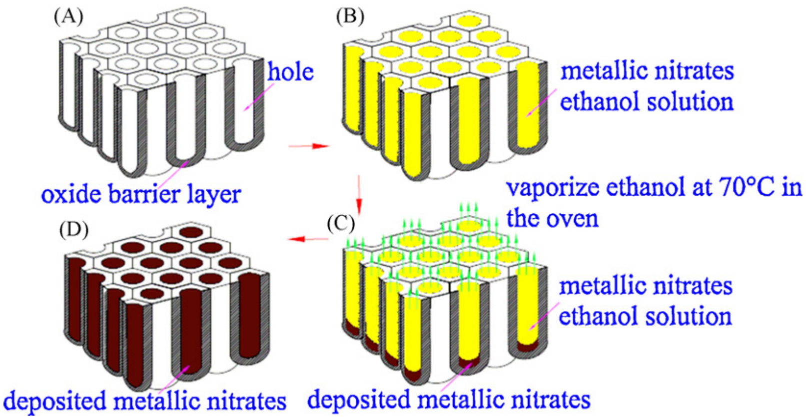

Fig. 1. Fabrication process of the ferrite nanowire arrays using AAO template.

before nanowire growth can be completed. The AAO templates were put into an evaporating dish containing an appropriate amount of the above-mentioned metallic nitrates ethanol solution (Fig. 1B). The evaporating dishes were located in an oven at 70 °C until the solution was dried (Fig. 1C and D). During evaporation of ethanol, the metallic nitrate ethanol solution was moved into the pores of the AAO template by a capillary action and the metallic nitrates were deposited within the holes after the ethanol was completely evaporated. Subsequently, the AAO templates were taken out and cooled down to room temperature, excessive products on the AAO surfaces were carefully wiped off with laboratory tissue. The as-treated AAO templates were calcined from room temperature up to 600 °C in air with a heating rate of 1 °C/min and held at 600 °C for 4 h to obtain $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ ferrite nanowires.

2.3. Characterization of $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowires

Surface profile of the AAO templates and morphology of the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowires were examined by Field Emission Scanning Electron Microscope (SEM, JEOL, JSM-6500). The specimens for SEM analysis were prepared as follows. A piece of AAO template embedded with an array of NiCuZn ferrite nanowires was fixed to a SEM holder. About 0.5 mL of 1 M NaOH solution was dropped onto the template to partially dissolve the alumina film on the surface and uncover nanowires from the nanochannels of the template. After carefully rinsing with distilled water and drying in air, the samples were coated with a Pt thin layer by sputtering under vacuum conditions to form conducting film. Crystalline structures of the nanowires were identified using an X-ray diffractometer (XRD, Philips X'Pert, Holland) with Cu Kα radiation of $\lambda = 1.54056$ Å. Magnetic properties of the samples at room temperature were measured by a vibrating sample magnetometer (VSM, ADE magnetics EV-7, USA).

3. Results and discussion

3.1. Morphology and structure

Fig. 2 shows a representative surface morphology of the AAO template after pore widening. Thickness of the template is about 65 µm and average diameter of the pores is about 100 nm.

High temperature calcination treatment might result in a crystallization of the amorphous AAO templates. Previous study showed that AAO remained amorphous below 800 °C, but crystallized to γ-Al_2O_3 at temperatures of 800–850 °C. Once AAO crystallizes, it is difficult to dissolve it in NaOH solution. Thus, in the present study, the AAO template with the metallic nitrates inside was calcined at 600 °C, in order to retain the AAO templates to be amorphous. During calcination, the metallic nitrates were decomposed into metal oxides, O_2 and NO_2 [20]. The metal oxides reacted and grew within the AAO pores to form $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowires. Related decomposition and oxidation reactions can be expressed as follows:

$$Ni(NO_3)_2 \Rightarrow NiO + NO_2\nearrow + O_2\nearrow$$

$$Zn(NO_3)_2 \Rightarrow ZnO + NO_2\nearrow + O_2\nearrow$$

$$Cu(NO_3)_2 \Rightarrow CuO + NO_2\nearrow + O_2\nearrow$$

$$Fe(NO_3)_3 \Rightarrow Fe_2O_3 + NO_2\nearrow + O_2\nearrow$$

$$NiO + ZnO + CuO + Fe_2O_3 \Rightarrow Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$$

SEM images of the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ ferrite nanowires are shown in Fig. 3. Fig. 3a is a top-view of the nanowires within the AAO template, with the template being dissolved partly by NaOH. Heads of the nanowires can be observed. Fig. 3b shows many islands consisting of bundles of $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ ferrite nanowires.

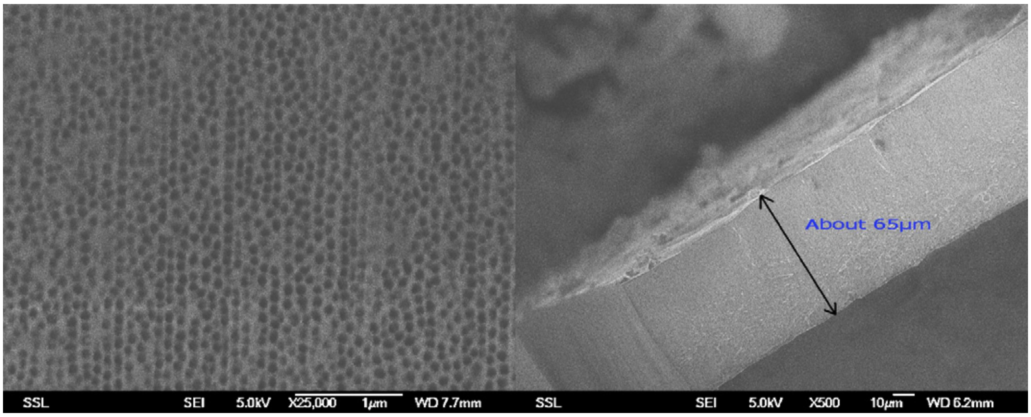

Fig. 2. SEM images of a blank AAO template.

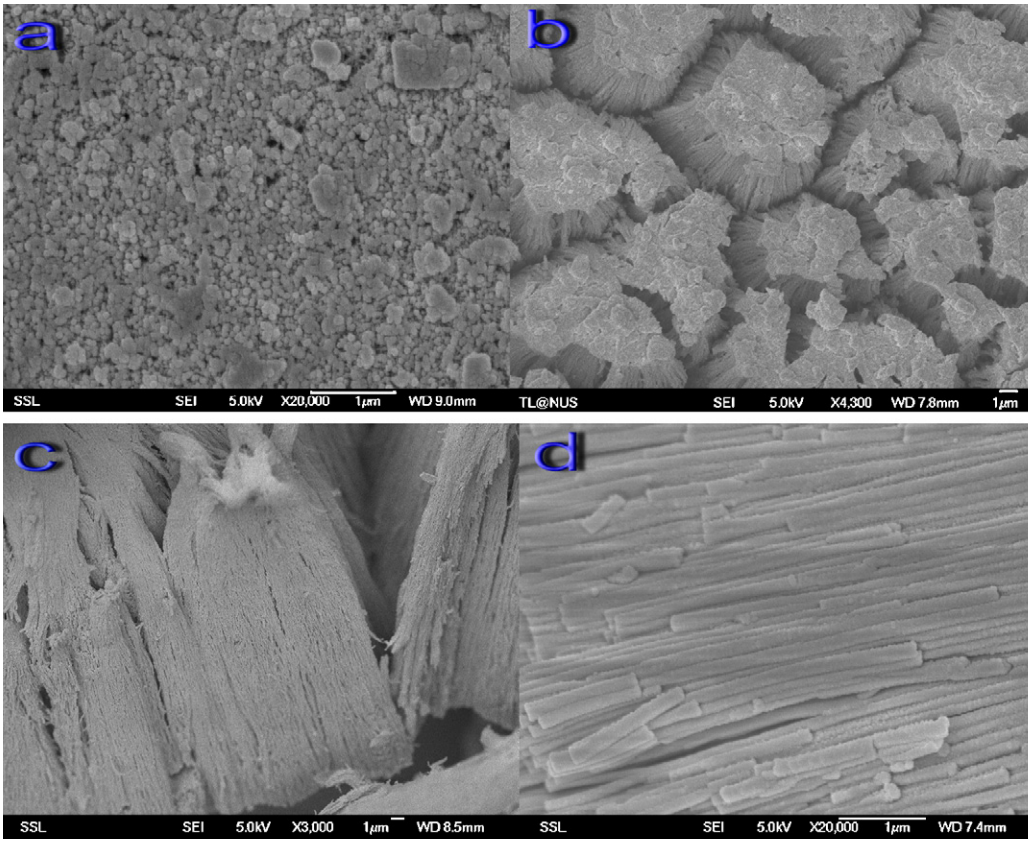

Fig. 3. SEM imagines of the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays.

As shown in the micrograph, the nanowires are orderly upstanding, but their tops are inclined to agglutinate together. Fig. 3c reveals a cross-section image of the sample where the AAO template matrix has almost been dissolved away. It is found that the nanowires are roughly parallel to one another and are distributed orderly and uniformly. Diameter of the nanowires is almost the same, about 100 nm, which is in a good agreement with the pore size of the AAO template, as shown in Fig. 3d.

Fig. 4 shows XRD patterns of the as-prepared $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire array embedded in the AAO template, along with a powder sample that was prepared using the same nitrate mixtures and the same calcining condition. All diffraction lines can be indexed to cubic spinel structure. It should be noted that the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowires have much broader diffraction width than the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanopowders, indicating that the nanowires have much smaller crystal size than the nanopowders. The averaged crystal size of $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowires was estimated to be about 11 nm using the Scherrer equation, $D = 0.89\lambda/\beta\cos\theta$. The phase formation of the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays at such a low temperature of 600 °C is attributed to the molecular or atomic level mixing of the components in the nitrate–ethanol solution, which reduces diffusion path and energy and favors the evolution of a solid-state structure at low temperature [21].

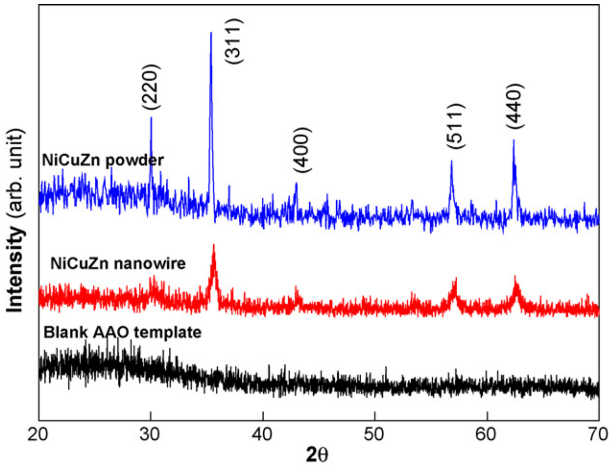

Fig. 4. XRD patterns of an AAO template (bottom), the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire array (middle) and nanopowder (top).

3.2. Magnetic properties

Fig. 5 shows hysteresis loops with external applied field parallel or perpendicular to the nanowires. The loops were measured between 20 and −20 kOe at room temperature together with the AAO template. The two loops are obviously different. As the applied field is parallel to the nanowire axis, the sample can be easily magnetized. Its coercivity is small, as compared to the case of the applied field perpendicular to the nanowire axis. Therefore, the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays have obvious magnetic anisotropy due to the different demagnetizing factors, which are approximately equal to 0 and 2π, respectively, for the applied fields along and perpendicular to the nanowire axis. In addition, the coercivities of the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire array measured in parallel and perpendicular fields are 3.1 and 3.8 Oe, which are larger than the coercivity, 2.5 Oe, of the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanopowder.

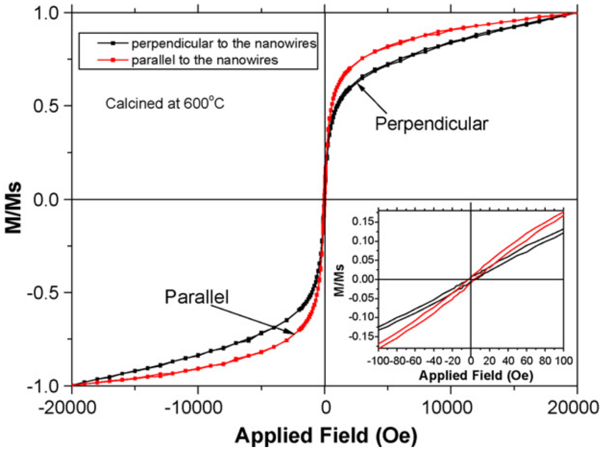

Fig. 5. Magnetic hysteresis loops at room temperature of the $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays.

4. Conclusions

High quality $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays were prepared by a one-step ethanol–nitrate solution method using anodic aluminum oxide (AAO) templates. The $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays were uniformly distributed and well aligned. They have cubic spinel structure. The $Ni_{0.23}Cu_{0.11}Zn_{0.66}Fe_2O_4$ nanowire arrays exhibit obvious magnetic anisotropy; with easy axis parallel to the nanowire length direction. It is expected that the method developed in the present study is also applicable to the preparation of other ferrite and oxide nanowires.

References

[1] G.B. Ji, S.L. Tang, B.L. Xu, B.X. Gu, Y.W. Du, Chem. Phys. Lett. 379 (2003) 484–489.
[2] F.F. Liu, X.Y. Li, Q. Zhao, Y. Hou, et al., Acta Mater. 57 (2009) 2684–2690.
[3] Z.X. Luo, Y. Yang, X.F. Zhou, J.N. Yao, Mater. Chem. Phys. 107 (2008) 91–95.
[4] H.Y. Wu, Y. Zhao, Q.Z. Jiao, J. Alloys Compd. 487 (2009) 591–594.
[5] L.H. Lin, H.T. Li, S.H. Fan, J.J. Gu, et al., J. Magn. Magn. Mater. 321 (2009) 3511–3514.
[6] T. Nakamura, J. Magn. Magn. Mater. 168 (1997) 285–291.
[7] M.A. Gabal, Y.M. Al Angari, S.S. Al-Juaid, J. Alloys Compd. 492 (2010) 411–415.
[8] L.S. Yu, N. Liu, X.B. Wang, Z. Hu, J. Alloys Compd. 478 (2009) 121–124.
[9] W. Jung, S. Jung, P. Kung, M. Razeghi, Nanotechnology 17 (2006) 54–59.
[10] T. Yanagishita, M. Sasaki, K. Nishio, H. Masuda, Adv. Mater. 16 (2004) 429–432.
[11] X.F. Qu, J.H. Dai, J.T. Tian, X. Huang, et al., J. Alloys Compd. 469 (2009) 332–335.
[12] Z. Hua, S. Yang, H. Huang, L. Lv, M. Lu, B. Gu, Nanotechnology 17 (2006) 5106–5110.
[13] S.K. Sharma, A. Rammohan, A. Sharma, J. Colloid Interf. Sci. 344 (2010) 1–9.
[14] G. Ali, M. Ahmad, J.I. Akhter, K. Maaz, S. Karim, M. Maqbool, S.G. Yang, IEEE Trans. Nanotechnol. 9 (2010) 223–228.
[15] V.P. Menon, C.R. Martin, Anal. Chem. 67 (1995) 1920–1928.
[16] M.D. Leo, F.C. Pereira, L.M. Moretto, P. Scopece, S. Plizzi, P. Ugo, Chem. Mater. 19 (2007) 5955–5964.
[17] C.M. Yang, H.S. Sheu, K.J. Chao, Adv. Funct. Mater. 12 (2002) 143–148.
[18] W. Lee, R. Ji, U. Gosele, K. Nielsch, Nat. Mater. 5 (2006) 741–747.
[19] A. Santos, L. Vojkuvka, J. Pallares, J. Ferre-Borrull, L.F. Marsal, J. Electroanal. Chem. 632 (2009) 139–142.
[20] R.N. Moshaie, A. Ataie, S.A.S. Ebrahimi, J. Alloys Compd. 429 (2007) 324–328.
[21] H.N. Joong, J.P. Sang, K.K. Won, IEEE Trans. Magn. 39 (2003) 3139–3141.