An Array of Concentric Composite Nanostructure of Metal Nanowires Encapsulated in Zirconia Nanotubes: Preparation, Characterization, and Magnetic Properties

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An array of highly ordered ZrO_2 nanotubes has been prepared by a simple sol−gel method using the alumina membrane as a template. Furthermore, with use of this nanotube array with an alumina membrane support as a "second-order template", the novel composite nanostructures of metal nickel- or copper-filled ZrO_2 nanotubes have been synthesized by electrodeposition. TEM images show that these encapsulated metals present as continuous and uniform nanowires in each and all ZrO_2 nanotubes. It is more important that the wall thickness of the ZrO_2 tubules, and the different morphologies of the encapsulated metals (metal nanowires or nanoparticles) can be controlled by the template used and synthesis conditions. Magnetic measurements on the ordered array of a concentric composite of ZrO_2 nanotubes/Ni nanowires reveal that the coercivities are $Hc_{\parallel} \sim 237$ Oe and $Hc_{\perp} \sim 138$ Oe, respectively, which exhibits enhanced coercivities by comparison with that of the bulk Ni.

Introduction

The large range of potential new materials applications made possible by the fabrication of monodispersed aligned nanostructures has generated a large amount of interest recently.[1−4] Of the various methods for preparing such a type of nanostructures with different compositions and morphologies, the template method that entails synthesis of a desired material within the pores of a membrane has proved to be a versatile approach and an inexpensive technique.[4−9] The size, shape, and structural properties of the synthesized materials are controlled by the template used and a number of experiment parameters. Martin and others have successfully prepared tubules and fibrils composed of metals, alloys, semiconductors, diamond, and conductive polymers using alumina membranes or track-etched membranes as templates.[7−9] Also, they, combined with CVD, electroless deposition, and electropolymerization, have synthesized some novel concentric composite nanostructures,[10−12] such as TiS_2/Au,[10,11] ZnO/Au,[11] TiO_2/Au,[11] and TiO_2/PPy.[12] These materials often have useful optical,[8] electronic,[7] magnetic,[5,7,13,14] and catalytic properties.[15]

ZrO_2 is an important functional material. The ZrO_2 film deposited on the metal surface has been extensively used in the field of corrosion protection,[16] catalytic films,[17] sensor films,[18] and transparent conducting films.[19] Recently, much research has focused on the synthesis of ordered porous zirconia by using a surfactant, such as cetyltrimethylammonium bromide, as the structure-directing template agent.[20,21] To date, however, there are only a few examples of zirconia nanotubes that exist in the literature.[22] Such nanotubular

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structures might have some potential applications in the fields of heterogeneous catalysis, adsorption, separation, chemical sensors and so forth. Furthermore, ZrO_2 nanotubes may serve as ideal nanoreactors for preparing composite nanostructures with novel properties such as optic, electronic, magnetic, and catalytic properties. For example, such a semiconductor nanotube filled with metal is an important nanostructure in which metal nanowire may act as a collecting electrode for conducting an electronic current. It shows promise in solar energy cells and sensors. Many of these proposed applications will require membranes that consist of monodispersed aligned nanotubes. Although a number of one-dimensional nanostructures have been synthesized using an alumina membrane as a template, few examples of the ZrO_2 nanotube-based composite nanostructures have been reported. In this work, we report the preparation of an array of ordered ZrO_2 nanotubes using an alumina membrane as a template and of an ordered array of a concentric composite nanostructure of ZrO_2 nanotubes/nickel or copper nanowires using this ZrO_2 nanotube array as a "second-order template". The metal nanowire in each ZrO_2 nanotube is continuous and uniform. Interestingly, when just the experimental condition was changed, a different concentric composite nanostructure composed of ZrO_2 nanotube and the closely packed nickel nanoparticles was obtained. The results of magnetic measurements on the ordered array of a concentric composite of ZrO_2 nanotubes/Ni nanowires are presented. The ZrO_2 envelope protects the metal manowires from oxidation and corrosion, therefore making them stable in air.[23] This type of composite nanostructure is more suitable for microelectronic devices such as nanosize conducting materials, chemical sensors, and ultra-high-density magnetic recording.[5,24,25]

Experimental Section

The porous alumina membrane was obtained from Whatman Corporation (quoted pore diameter, 100 nm, and thickness, about 50 μm).[26] ZrO_2 nanotubes were prepared using a modified sol−gel method as follows: $ZrOCl_2{\cdot}8H_2O$ (1.0 g, 3.1 mmol) was dissolved in 20 mL of a mixture solvent of ethanol and water (volume ratio of ethanol:H_2O is 5:3). This solution was aged at 70 °C for 1 h to obtain ZrO_2 sol.

The alumina template membrane was immersed into the ZrO_2 sol for 30 min and 1 h, respectively, and then the membrane was removed from the sol and dried in air at room temperature. After that, the membrane was annealed with the temperature being ramped up (100 °C h^{-1}) to 500 °C, maintained at 500 °C for 6 h, and then ramped back down (30 °C h^{-1}) to room temperature.

The composite nanostructure of Ni nanowires encapsulated in the ZrO_2 nanotubes was prepared by electrodeposition as follows. The array of ZrO_2 nanotubes with Al_2O_3 membrane support was used as the second-order template. Before electrochemical deposition, silver paste was spread on one side of the second-order-template membrane used as a working electrode. Electrodeposition was completed in a three-electrode electrochemical cell with the bare side of the second-order-template membrane facing upward, and the deposition solution containing 15 g/L $NiSO_4{\cdot}6H_2O$ and 50 g/L H_3BO_3 was confined to the bare side of the second-order-template membrane. There is no separate compartment for the counter electrode, which is a nickel plate. A saturated calomel electrode (SCE) was used as reference for the applied potential. The Ni was deposited in a bottom-up fashion within the pore of the second-order-template membrane. During the electrodeposition, complete filling of the pores was monitored by measuring the supplied current.[5] The array of Cu nanowires encapsulated in the ZrO_2 nanotubes was prepared by a similar method, except the electrolyte containing 20 g/L $CuSO_4{\cdot}5H_2O$ and 50 g/L H_3BO_3 and the copper plate as a counter electrode. The temperature was maintained at 15 °C in the process of electrodeposition.

Structural characterization was performed by means of X-ray diffraction using a D/Max-RA diffractometer with Cu Kα radiation. Samples for transmission electron microscopy (TEM) were prepared by immersing an ≈2-mm^2 section of the template containing the products in 3 M aqueous NaOH for 10 min to remove the alumina membrane. The solution was slowly removed via syringe and the sample was carefully washed with distilled water more than two times, collected on a carbon-coated copper grid, and dried in air before measurements. TEM images were obtained on a JEM-200CX TEM, working at an accelerating voltage of 100 kV. Specimens for scanning electron microscopy (SEM) were fixed to a piece of copper tape and soaked in 2 M NaOH for 0.5 h to remove the alumina template. After being carefully rinsed with deionized water in three static rinse baths, the tape was attached to the SEM stub and an ≈5-nm layer of gold was sputtered onto it. SEM images were obtained using an Hitachi X650/EDAX, PV9100 SEM, operating at an accelerating voltage of 20 kV and a JEOL 5610 LV SEM. The chemical compositions of the nanotubes and composite nanostructures were characterized by energy dispersive spectroscopy (EDS), which was performed in the scanning electron microscope with a WD-8 analyzer. Room-temperature magnetic characterization of the arrays of a concentric composite nanostructure was performed by using a Lake Shore 7303-9309 vibrating sample magnetometer (VSM).

Results and Discussion

Synthesis and Characterization of ZrO_2 Nanotubes. Of several preparation methods of ZrO_2, the sol−gel technique has attracted a lot of attention because of low cost and processing simplicity.[27,28] We use zirconyl chloride octahydrate solution, which is cheaper than alkoxide (a common precursor in sol−gel processing), as a precursor in sol−gel processing and an alumina membrane as a template for preparing the ZrO_2 nanotubes. A modified method for preparation of the ZrO_2 sol has been developed, which is more facile than previous work.[28] According to our modified method, with just dissolution of $ZrOCl_2$ in a mixture solvent of ethanol and water and heating for 1 h at 70 °C, ZrO_2 sol was obtained without the addition of any other chemical agents. Such sol is a suitable precursor for fabricating nanostructure without any interference elements, which is very important for the performance of the nanodevices. Figures l and 2 show the TEM images of ZrO_2 nanotubes prepared by immersing alumina membrane into the sol of ZrO_2 for 30 min and 1 h at room temperature, respectively. From the TEM images, we can see that the pore diameter of the nanotubes is ≈170 nm. The wall thickness of ZrO_2 nanotubes is controllable

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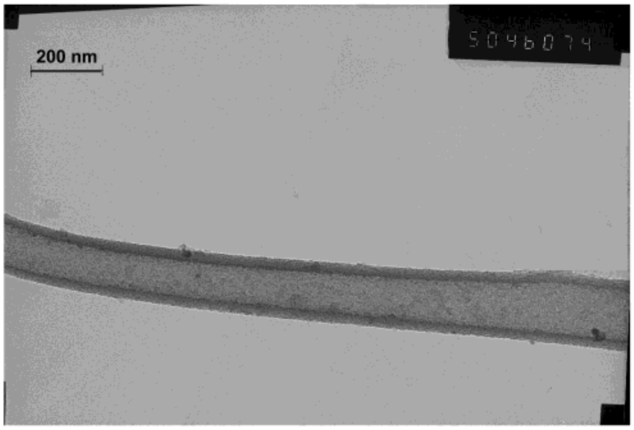

Figure 1. TEM image of a ZrO_2 nanotube after removal of the alumina membrane (the immersion time: 30 min).

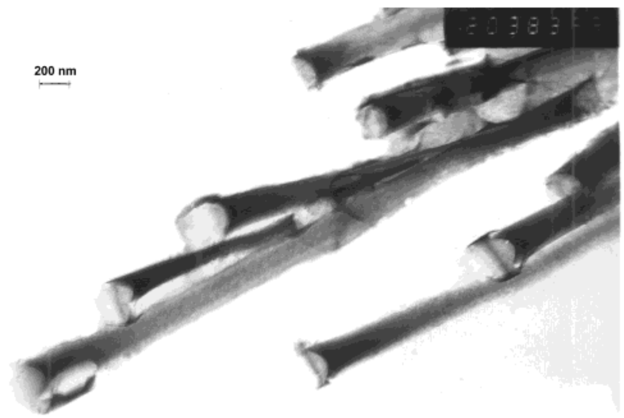

Figure 2. TEM image of ZrO_2 nanotubes after removal of the alumina membrane (the immersion time: 1 h).

by adjusting the immersion time of alumina membrane in the ZrO_2 sol. The longer the immersion time, the thicker the wall. The nanotubes in Figure 2 look darker than the one in Figure 1, indicating that the tubule wall is thicker and the electron beam is difficult to penetrate. These results suggest that sol particles of ZrO_2 are preferentially adsorbed and grown on the pore wall of alumina membrane. An electron diffraction pattern (not shown here) of the nanotubes in Figures 1 and 2 indicates that the ZrO_2 nanotubes are composed of amorphous ZrO_2 particles. Figure 3 shows the SEM image of ZrO_2 nanotubes after removal of the alumina membrane in 6 N NaOH. From the SEM image we can see that the ZrO_2 nanotubes are a highly ordered and perfect array. In all cases, the length of the nanotubes corresponds to the thickness of the alumina membrane.

Characterization of the Composite Nanostructure of Metal Nanowires Encapsulated in Zirconia Nanotubes. An important characteristic of the ZrO_2 nanotubes is the open end (see Figure 3), which makes it possible to serve as a catalyst and chemical sensor, to fill other materials, or to carry out chemical reactions in it. Using the array of ZrO_2 nanotubes with the alumina membrane support as the second-order template and combining it with the electrodeposition technique, we have successfully prepared the composite nanostructures of Ni or Cu nanowires encapsulated in the ZrO_2 nanotubes. Figure 4 shows the TEM image of Ni nanowire encapsulated in a ZrO_2 nanotube after

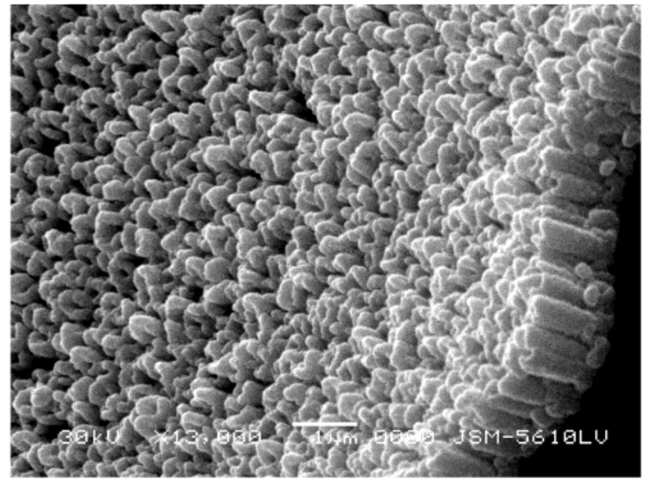

Figure 3. SEM image of the array ZrO_2 nanotubes after removal of the alumina membrane.

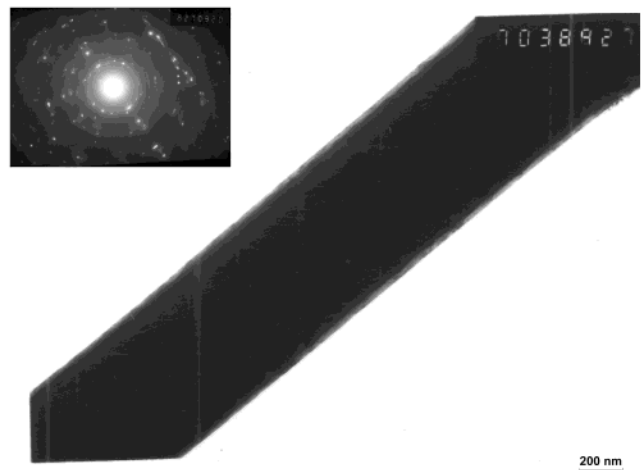

Figure 4. TEM image of the composite nanostructure of Ni nanowire encapsulated in a ZrO_2 nanotube after removal of the alumina membrane. Inset shows the SAD pattern of the corresponding composite nanostructure.

removal of the alumina membrane with 6 N NaOH. From Figure 4, we can see that the nanotube is completely filled with nickel. The wall thickness of the ZrO_2 nanotube is $\approx$18 nm and the diameter of the Ni nanowire is about 230 nm. The corresponding SAD pattern of the Ni/ZrO_2 composite nanostructure shown in the inset of Figure 4 as diffraction rings indicates the Ni nanowire is polycrystal. Interestingly, when the temperature drops down to 5 °C from 15 °C in the electrodeposition process, the nickel nanowires in the ZrO_2 tubules are composed of the closely packed Ni nanoparticles, which has not been found in previous work,[29] and means that we can control the shape of Ni nanoparticles easily via changing the temperature. The TEM image of this composite nanostructure and the corresponding SAD pattern are shown in Figures 5 and 6. The clear spots in Figure 6 indicate that the Ni nanoparticles are single crystals and can be indexed to {111}, $\{11\bar{1}\}$, and {220} reflections from face-centered cubic (fcc) nickel, and the zone axis projection is along [110]. Whether they are single-crystalline or polycrystalline nanostructures of nickel, their X-ray diffraction

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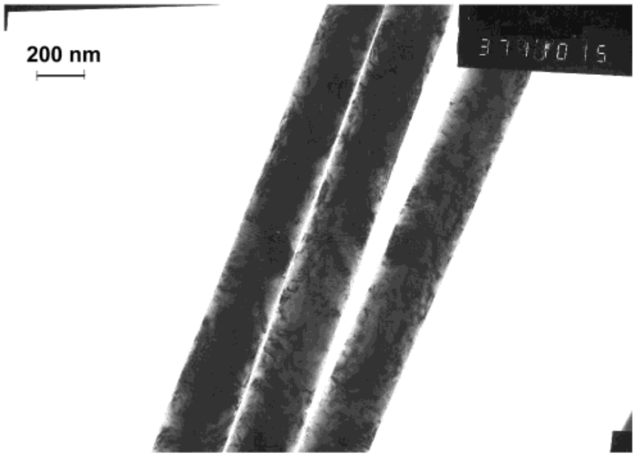

Figure 5. TEM image of the composite nanostructure of Ni nanoparticles encapsulated in ZrO_2 nanotubes after removal of the alumina membrane.

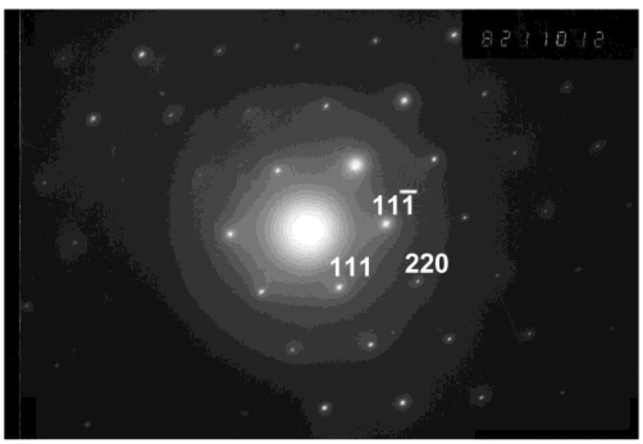

Figure 6. Electron diffraction pattern taken from the sample in Figure 5.

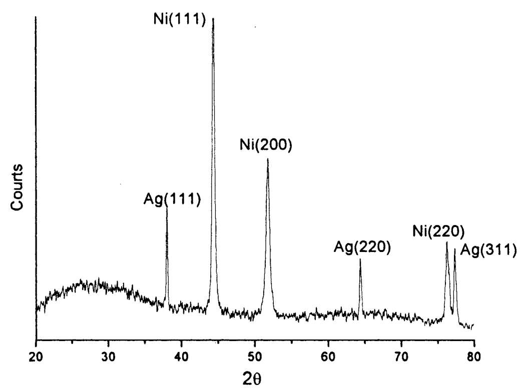

Figure 7. X-ray diffraction pattern of the supported membrane of the composite nanostructure of Ni encapsulated in ZrO_2 nanotubes.

patterns are similar (Figure 7). The diffraction peaks in the $20° < 2\theta < 80°$ can be indexed as Ni (111), (200), and (220), which belongs to the fcc structure in good concordance with ASTM standard 4-850. Figure 8 shows the SEM image of Ni nanowires encapsulated in ZrO_2 nanotubes after removal of the template membrane with 6 N NaOH. An energy-dispersive spectrometry analysis has been performed for this sample. The result further indicates unambiguously that the nanostructure is composed of Ni and Zr. Compared to the end of the tubules in Figure 3, we can know from Figure 8 that

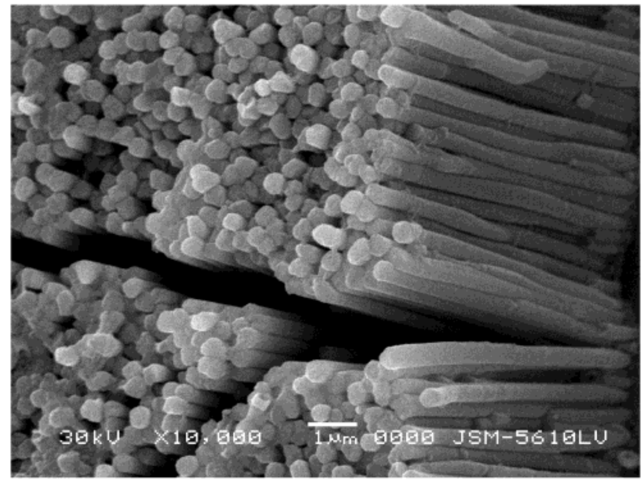

Figure 8. SEM image of the composite nanostructure of Ni nanowires encapsulated in ZrO_2 nanotubes after removal of the alumina membrane.

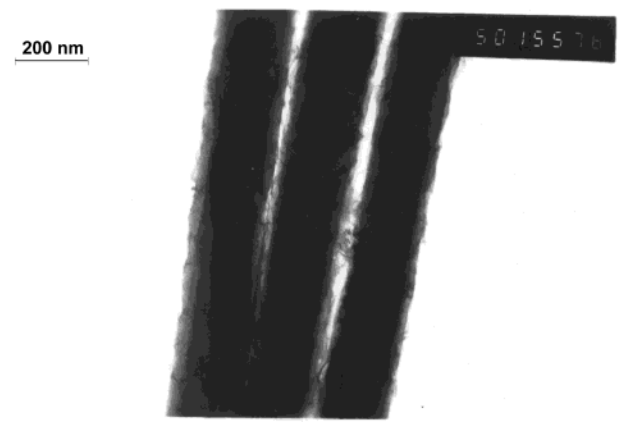

Figure 9. TEM image of the composite nanostructure of Cu nanowires encapsulated in ZrO_2 nanotubes after removal of the alumina membrane.

almost every ZrO_2 nanotube is filled with Ni and the composite nanostructure is an ordered and intact array.

The composite nanostructure of copper nanowires encapsulated in ZrO_2 nanotubes was obtained using a similar method for the preparation of Ni/ZrO_2 composite nanostructure. Figure 9 shows the TEM image of Cu nanowires encapsulated in ZrO_2 nanotubes after removal of the alumina membrane with 6 N NaOH. From Figure 9, we can see that the nanotubes are completely filled with Cu. The wall thickness of the ZrO_2 nanotube is $\approx$20 nm and the diameter of the Cu nanowire is about 170 nm. The corresponding SAD pattern (Figure 10) of the Cu/ZrO_2 composite nanostructure indicates the Cu nanowires are highly crystalline. The X-ray diffraction pattern of the Cu/ZrO_2 composite nanostructure is shown in Figure 11. The diffraction peaks in the $20° < 2\theta < 80°$ range can be indexed as Cu (111), (200), and (220), which belongs to the cubic structure in good concordance with ASTM standard 4-836. Figure 12 shows the SEM image of Cu nanowires encapsulated in ZrO_2 nanotubes after removal of the alumina membrane with 6 N NaOH. From Figure 12 we can see that the composite nanostructure is still a highly ordered and intact array. Such a nanostructure of ZrO_2 nanotubes/Cu nanowires in which the Cu nanowires may act as a good collecting electrode for conducting electronic current is an important one and has potential applications in cells and sensors.

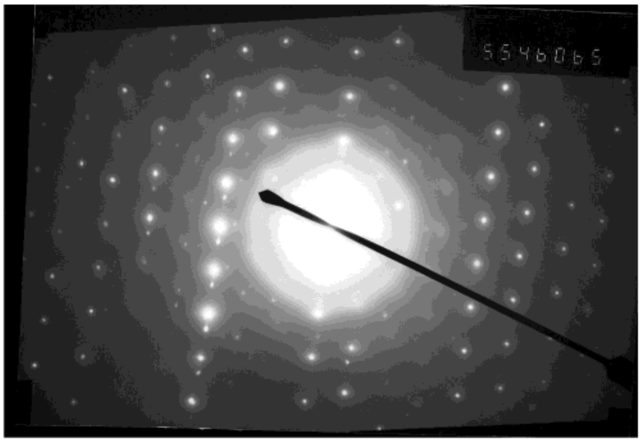

Figure 10. Electron diffraction pattern taken from the sample in Figure 9.

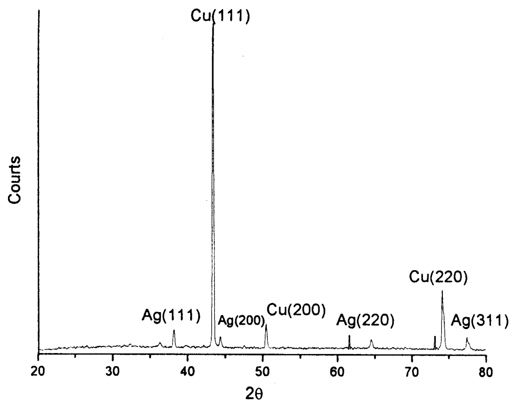

Figure 11. X-ray diffraction pattern of the supported membrane of the composite nanostructure of Cu nanowires encapsulated in ZrO_2 nanotubes.

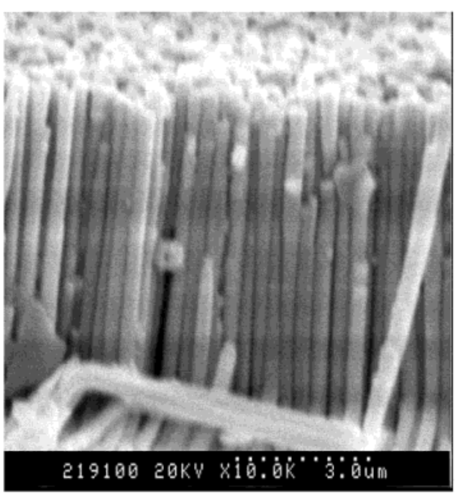

Figure 12. SEM image of the composite nanostructure of Cu nanowires encapsulated in ZrO_2 nanotubes after removal of the alumina membrane.

Magnetic Properties of the Composite Nanostructure of Ni Nanowires Encapsulated in ZrO_2 Nanotubes. The magnetic properties of the array of Ni nanowires encapsulated in ZrO_2 nanotubes were measured and the hysteresis loops of this composite nanostructure with the membrane support were shown in Figure 13. Typical coercivities are $Hc_{\|} \sim 237$ Oe and $Hc_{\perp} \sim 138$ Oe, respectively, which exhibits enhanced coercivities by comparison with that of the bulk Ni (around 0.7 Oe for Ni).[30] These hysteresis loops show that the array exhibits uniaxial magnetic anisotropy with the easy axis parallel to the nanowires. Also, both curves are highly sheared, indicating strong interwires interaction. Further evidence about this is that the array of nickel nanowires appears to have very low remanent magnetization, which is <19% of M_{sat}. Such strong interwires interaction is expected since the Ni nanowires in the array are very close to each other.

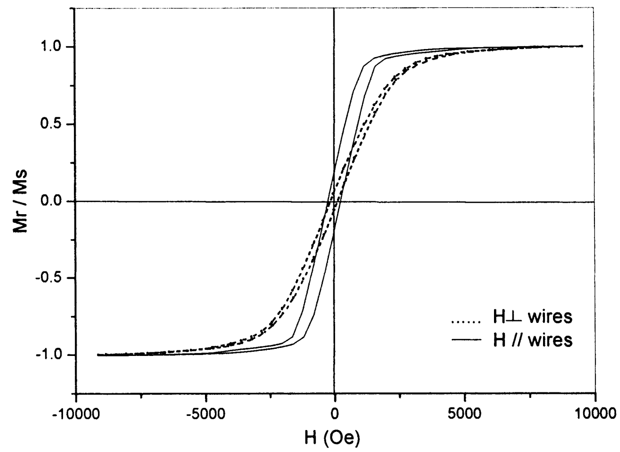

Figure 13. Hysteresis loops of the supported array of the composite nanostructure of Ni nanowires encapsulated in ZrO_2 nanotubes. Dotted line: with the applied field perpendicular to the nanowires. Solid line: with the applied field parallel to the nanowires.

Conclusions

The present study demonstrates that the novel composite nanostructures of metals encapsulated in ZrO_2 nanotubes can be readily prepared with high metal filling ratio in the nanotubes by the two-step-template method: (i) preparing an ordered array of ZrO_2 nanotubes in a porous alumina membrane by the sol−gel method; (ii) filling metal in the ZrO_2 nanotubes by electrodeposition. The size, structures, and morphologies of the composite nanostructures are easily controlled by the template used and synthesis conditions, which might be useful in adjusting the catalytic activity of the ZrO_2 nanotubes and metal filled, the length of the collecting electrode formed, and the magnetic properties of the encapsulated metal. ZrO_2 is quite inert in ambient conditions, and the envelope of ZrO_2 protects the metal from oxidation and corrosion. From the technological point of view, this novel zirconia-based composite nanostructure is more suitable for application in microelectronic devices such as nanosize conducting materials, chemical sensors, nanoelectrode assembly for batteries and electrochemistry, and ultra-high-density magnetic recording.

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