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Study of Structural and Magnetic Response in Metallic (M= Ni,Co)/CoO Core-Shell Nanowires

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ABSTRACT

Magnetic nanostructures including nanowires (NWs) and nanotubes (NTs) have attracted considerable scientific interest during the last decade because of their potential applications in sensors, microwave absorption, biological separation and high density recording media. A comprehensive study of magnetization properties for M-CoO (M=Ni, Fe) core-shell nanowires has been carried out. Ferromagnetic nanowires arrays layered with Cobalt oxide shell are fabricated by sol gel route followed by DC electrodeposition into AAO templates. Scanning electron microscope was used to analyse the morphology of fabricated nanowires. Structural analyses reveal the formation of highly ordered, dense and uniformly distributed core-shell nanowires. Magnetic hysteresis loops indicated that for core-shell nanowires easy axis of magnetization lie parallel to the wire long axis.

Key words: *Dc Electrodeposition; core-shell nanowires; easy axis*

1.1 Introduction

Coaxial nanostructures, which may exhibit additional effects and have potential applications as multi-functional materials, have attracted considerable attention both for fundamental and technological interest [1–4]. Compared with the single-phase nanomaterials, such hybrid nanostructures with a combination of two or more components may show enhanced properties or offer multifunctional properties. To date, various methods have been developed to synthesize these coaxial nanostructures. Among them, the template-assisted technique can be easily integrated with other methods such as electrochemical deposition [5,6], sol–gel [7], atomic layer deposition (ALD) [8], supercritical uids (SCF) [9], and chemical vapor deposition (CVD) [10] for the preparation of numerous functional nanomaterials. Moreover, easily controllable morphologies of the nanostructures makes the low-cost template-assisted technique one of the most commonly used methods for the fabrication of one-dimensional (1D) coaxial nanostructures.

The magnetic behaviour of virtually all magnetic materials is mainly controlled by domains separated by domain walls. In the case of Fe, Ni, Co, and other transition metal based magnetic materials where magneto-crystalline anisotropy is not very high, shape anisotropy plays a dominant role in governing the magnetic properties such as

coercivity and remanence of the nanowires. Magnetic behaviour of the nanowire arrays is determined by the magnetic nature of individual nanowires controlled by the orientation of crystal axes, texture, and geometrical characteristics, as well as by the interactions among the nanowires. After a nanowire has been magnetized, its magnetization remains along the wire's long axis, with only two possible orientations. In an array of magnetic nanowires in a template, the dipolar interactions are negligible for wires with low densities but substantial for wires with high densities [a]. For free magnetic nanowires removed from the template and suspended in a solution, dipolar forces between nearby wires help determine the type of ordered, multi-wire structures that can be assembled.
In this paper the efforts has been made to investigate the structure and magnetic ordering of metallic (Ni, Fe) nanowire arrays layered with CoO shell.

1.2 Experimental Detail

The chemical solutions for Ni(CoO) and Fe(CoO) core/shell nanowires were prepared by dissolving nickel sulfate [$NiSO_4.6H_2O$] and iron nitrate [$Fe(NO_3)_3.9H_2O$] in ethylene glycol [$C_3H_8O_2$] to form the final products. All chemicals were used without any further purification. For templates with a diameter of 200 nm were bought from Whatman International Ltd. CoO nanotubes were fabricated by sol-gel method. The sol was stirred for 1 hour at room temperature. AAO templates with pore size 200 nm were then dipped into the sol for 20 min. Templates containing the precursors were annealed at 650 °C, resulting in the formation of nanotubes in the pores of the AAO templates. The next step was deposition of nanowires into shell, this process was followed by electrodeposition method. First, a Cu layer with a thickness of about 200 nm was sputtered on one side of the anodic aluminium oxide (AAO) template serving as the conductive contact. Then the electrodeposition of metallic nanowires was performed in a conventional three electrode configuration at room temperature. Applied potentials were measured with respect to a saturated calomel electrode (SCE) as the reference electrode and we used platinum (Pt) foil as the counter electrode. The AAO templates coated with a Cu layer served as the working electrode. The morphologies of the nanostructures were characterized by scanning electron microscope (SEM; Hitachi S-4800). SEM analysis was performed after dissolving the AAO template in 1 M NaOH solution. Magnetic hysteresis curves (M-H) of the core-shell nanostructures were measured by VSM (Microsense EV-9).

1.3 Results and Discussion

Figure 1 (a, b) shows the top and cross-sectional SEM image of AAO template, which represents the inter-pore distance in the alumina template. The high pore density in the case of alumina results in high interwire interactions which induce a dipolar field due to the adjacent wire interactions.

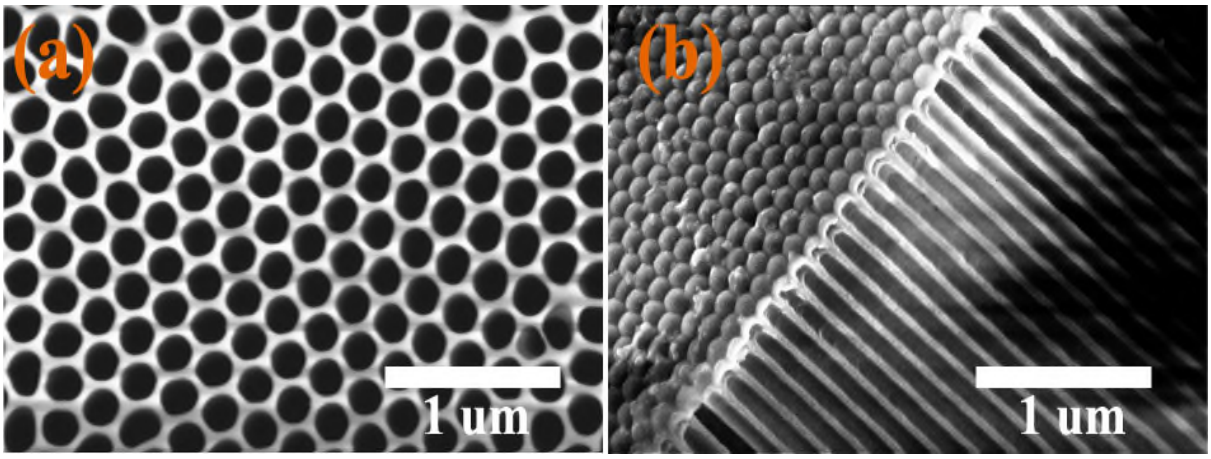

Figure 1: (a) Top view of AAO template (b) Cross-sectional view of AAO template taken from SEM.

Figure 2 (a, b) shows morphology of one of the representative sample of core shell nanowires taken at different resolution. These images are captured after removal of template from Ni-CoO core-shell nanowires. The length and diameters for all core-shell structures are consistent with the diameter of AAO template. Fig 2 (a) depicts fabrication of uniform and highly ordered core shell nanowires. The darker colour represents core nanowire, while the lighter one if for shell. Figure 2(b) shows the free standing core-shell nanowires and it is seen that most of the NWs have formed bunches and groups with no individual NW present in the images. This may arise due to the fact that Ni is ferromagnetic and magnetostatic interactions are present among these NWs, which keep them together to form bunches.

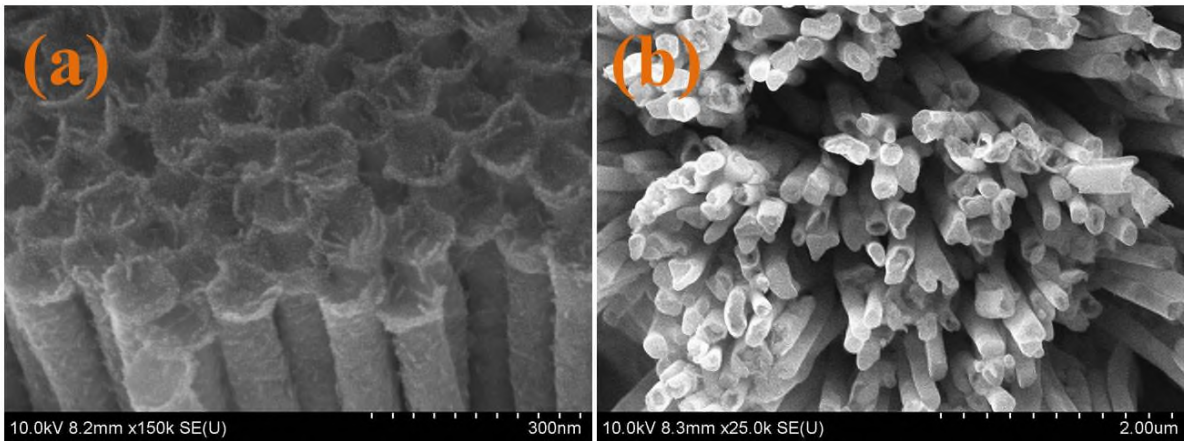

Figure 2: (a, b) SEM micrographs of Ni-CoO core-shell nanowires.

Figures 3 (a, b) shows the magnetic hysteresis loops obtained from the Ni-CoO and Fe-CoO core-shell nanowire arrays, respectively, with the applied field parallel and perpendicular to the wire axes. It is clear that coercivity is greater when the field is applied parallel to the magnetic core shell nanowires as compared to perpendicular. This suggests that the field required to reach the saturation magnetization is larger in parallel case and may be attributed to the anisotropy of the core-shell nanowires.

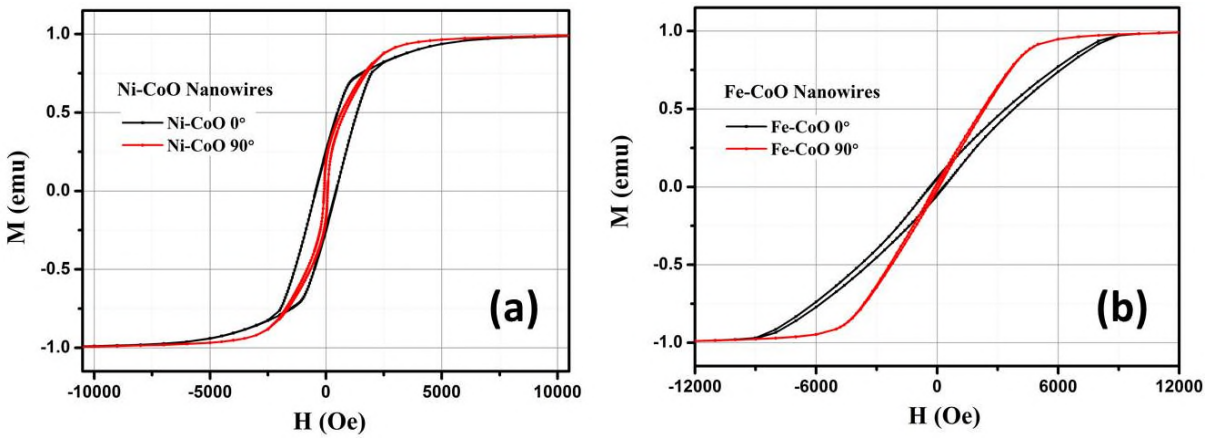

Figure 3: Hysteresis loops for (a)Ni-CoO core-shell nanowires (b) Fe-CoO core-shell nanowires, measured with the applied field parallel and perpendicular to the template surface.

Magnetic parameters calculated from MH loops are listed in Table I. It can be also seen from the difference of the loop squareness, that the easy axis is parallel to the nanowire axis. As known, the easy axis is dominant by the effective anisotropy field (H_k). The effective anisotropy field is determined by three contributions: (i) the shape anisotropy field ($2\pi Ms$), which will induce the easy axis parallel to the nanowires, (ii) the magnetostatic interaction field, which will induce the easy axis perpendicular to the nanowires, and (iii) the magnetocrystalline anisotropy (Hma). The total effective anisotropy field (H_k) is given by the following formula:

$$H_k = 2\pi Ms - 6.3\pi Msr^2L/D^3 + H_{ma}$$

where Ms is the saturation magnetization, r is the radius of the wire, L is the length, and D is the interwire distance. The first term represents the shape anisotropy field and the second term represents the total magnetostatic interaction field. $H_k > 0$ means that the easy axis is parallel to the nanowires, and $H_k < 0$ represents that the easy axis is perpendicular to the nanowires.

Table I: Magnetic parameters estimated from MH loops for Core-shell nanowires

Sample	Ms (emu)	Hc (Oe)	Mr (emu)	Mr/Ms
Ni-CoO (90˚)	0.991	73.90	0.178	0.179
Ni-CoO (0˚)	0.988	439.05	0.247	0.25
Fe-CoO (90˚)	0.991	88.03	0.0199	0.0197
Fe-CoO (0˚)	0.991	336.25	0.053	0.0534

1.4 Conclusions

Core-shell nanowires have been fabricated by sol gel and electrodeposition method. Their structural and magnetic properties have been studied through SEM and VSM techniques. Investigations of magnetic properties of core-shell nanowires indicated that magnetic parameters yield higher values when the field is applied parallel to the wire axis. Results show that easy axis of magnetization for Ni-CoO and Fe-CoO core-shell nanowires lie along the parallel to wire long axis.

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