

Controllable synthesis of $Zn_{0.95}Co_{0.05}O$ nanowires and nanotubes by electrophoretic deposition method

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Abstract: $Zn_{0.95}Co_{0.05}O$ nanotubes, as well as nanowires, were controllably synthesized by electrophoretic deposition method using anodic aluminum oxide (AAO) as template, and the mechanism of electrophoretic deposition was discussed. Careful characterization indicates that the prepared nanotubes and nanowires are of poly-crystal wurtzite structure and composed with 8–15 nm nano-crystals. The doped Co^{2+} occupied the Zn^{2+} sites in the ZnO lattice. Magnetic investigation indicates that the obtained nanotubes and nanowires are of room-temperature ferromagnetic. The magnetism of the nanotubes is much higher than that of the nanowires for the surface-preferential Co distribution.

Key words: $Zn_{1-x}Co_xO$; nanowires; nanotubes; electrophoretic deposition; AAO template; room-temperature ferromagnetism

1 Introduction

Diluted magnetic semiconductors (DMSs) have attracted great interests for their potential applications in semiconductor spintronics devices. Transition-metal doped ZnO has been predicted to be one of the most promising candidate DMSs for achieving room-temperature Curie temperature and thus, it has been receiving great attentions in recent years [1]. Current studies mainly focus on $Zn_{1-x}Co_xO$ nanoparticles, thin films, and bulk materials [2–7]. In contrast, the studies on one-dimensional (1D) $Zn_{1-x}Co_xO$ DMSs are still at a nascent stage despite very limited previous efforts, mostly focusing on $Zn_{1-x}Co_xO$ nanowires [8,9]. However, the integration of DMS materials into modern electronics requires very low dimensions in order to make real use of the advantage offered by spins, where dimensionality and size are known to play a significant role in determining various properties of the systems. Therefore, synthesis and study of 1D $Zn_{1-x}Co_xO$ DMSs nanomaterials are of great importance. Since the tubular form is generally available in layered materials such as carbon nanotubes, it seems more difficult to obtain the

tubular nano-structure for the unlayered ZnO materials [10]. In this work, uniform morphology, highly ordered $Zn_{0.95}Co_{0.05}O$ nanotube and nanowire arrays were fabricated via electrophoretic deposition method with the aids of AAO template. Their structure and magnetic property were carefully investigated and the mechanism of electrophoretic deposition was discussed.

2 Experimental

2.1 Reagent and apparatus

The AAO template used in this work was purchased from Whatman Co., England, with pore diameter of 200 nm. All the reagents used in this experiment were of analytical grade, purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd.

2.2 Experiment and characterizations

The $Zn_{0.95}Co_{0.05}O$ nanotubes were synthesized by an electrophoretic deposition method. Certain molar ratio of $Zn(OAc)_2 \cdot 2H_2O$ and $Co(OAc)_2 \cdot 4H_2O$ were dissolved in 200 mL of dimethyl sulfoxide. Then 50 mL of 0.5 mol/L $NH_4(CH_3)_4OH \cdot 4H_2O$ dissolved in ethanol were added dropwise to the previous solution. The colloid was stirred

under 333 K for 2 h. Electrophoretic deposition was performed in a bi-electrodes system under constant voltage mode. An AAO template membrane, with a surface sputter-coated with gold, acted as working electrode (negative electrode) and a reeled Pt thread acted as counter electrode. The electrodes were set parallel to each other and 3.6 cm apart. For $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanowire electrophoretic deposition, a direct potential of 4.5 V was applied on the electrodes and sustained for 45 min. While for the nanotube electrophoretic deposition, the deposition potential and time were 5.5 V and 2 h, respectively. At the end of electrophoretic deposition, excess sol was blotted off the membrane with filter paper. Then the prepared samples were annealed at 550 °C for 6 h in air atmosphere. Careful wet chemical etching with 1 mol/L NaOH was required to remove the alumina membrane before structural and magnetic characterization.

The scanning electron microscopy (SEM) image and back-scattered electron image (BEI) were obtained by a JSM-5600LV SEM equipped with energy dispersive spectrometer (EDS). The transmission electronic microscopy (TEM) and high resolution transmission electronic microscopy (HRTEM) images were obtained by a JEM-2100F TEM operated at 200 kV.

The structure of the nanowires were characterized by a Rigaku D/Max-2200 X-ray diffraction (XRD) with $\text{Cu K}\alpha$ (15.4 nm) line. The Raman spectra were obtained with JY-T64000 micro-Raman spectrometer in the backscattering geometry excited by Ar^+ laser 532 nm line. The UV-vis absorption spectra (UV-vis) were measured on a Cintra-10e spectrophotometer in diffuse reflectance mode and the magnetic properties were characterized by a vibrating sample magnetometer (VSM, LakerShore 7410) at 300 K.

3 Results and discussion

The prepared nanotubes and nanowires have unique morphology and orderly distribution, as shown in the SEM images (Fig. 1(a) and (b)). They are tens of microns in length, corresponding to the thickness of the AAO template. The EDS spectrum (Fig. 1(c)) suggests that the nanotubes are only composed of Zn, Co, and O elements. The presence of the Au peak is due to the sputt-coated Au layer on the sample for SEM observation. The EDS surface scan results (not shown) indicate the homogenous distribution of Zn and Co element in the nanotubes. The atomic ratio of Zn to Co is measured as 92:5, very close to the nominal Co doping

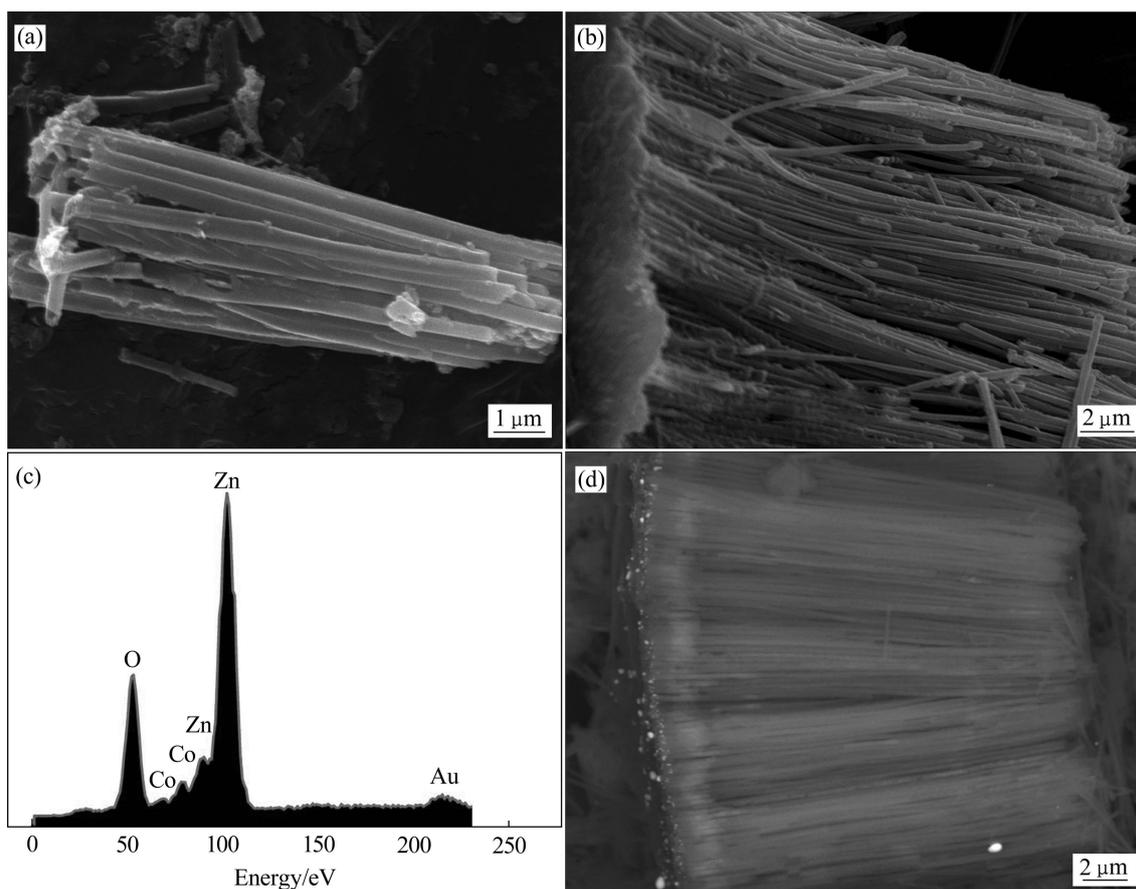


Fig. 1 SEM images ((a), (b)) of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanotubes and nanowires and EDS spectrum (c) and BEI image (d) of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanotubes arrays

ratio. From the BEI image (Fig. 1(d)), the morphology and inner structure of the nanotubes in the array can be clearly observed. The brightest point on the bottom area of the array is the gold layer, which act as working electrode for the electrophoretic deposition. The filled part of the nanotubes near the bottom is brighter than the hollow part. This implies the electrophoretic deposition is a bottom up process.

Figure 2(a) shows the TEM image of the $Zn_{0.95}Co_{0.05}O$ nanotubes. It is seen that the diameter of $Zn_{0.95}Co_{0.05}O$ nanotubes is around 190 nm, a little thinner than those of the AAO template pores, which is owing to the densification of the gel during annealing process [10, 11]. It is interesting that some of the nanotubes are half filled. Considering the BEI results, the bottom up process of the electrophoretic deposition can be concluded. HRTEM investigation (Fig. 2(b)) indicates that the nanotubes are composed of 8–15 nm width nano-crystallines. The labeled diffraction fringe distances is 0.248 nm, well corresponding to the interplanar distance of (101) planes of wurtzite ZnO. Some amorphous structure is observed between $Zn_{0.95}Co_{0.05}O$ nano-crystallines. The corresponding fast Fourier transform image (the inset in Fig. 2(b)) suggests that the $Zn_{0.95}Co_{0.05}O$ nanotubes are of polycrystal, no second-phase structure can be found in the view scope.

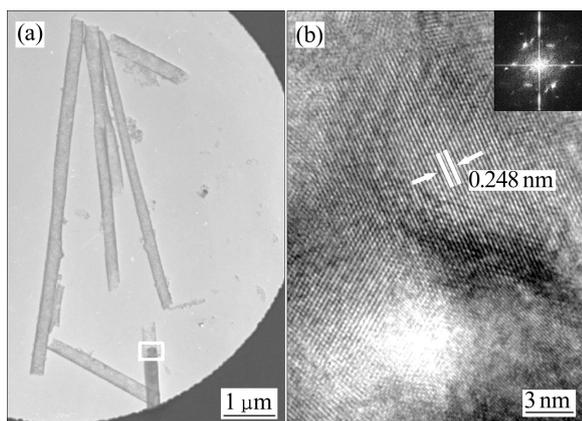


Fig. 2 TEM (a) and HRTEM (b) images of $Zn_{0.95}Co_{0.05}O$ nanotubes (The insert in Fig. 2(b) shows the fast Fourier transform of HRTEM picture)

Figure 3 shows the XRD spectra of the $Zn_{0.95}Co_{0.05}O$ nanowires and nanotubes. Both of them are found of hexagonal structure wurtzite ZnO (JCPDS number: #65-3411), no second phase could be found in both the spectra. This suggests the obtained nanotubes keep the wurtzite structure of hexagonal ZnO and the doped Co^{2+} replace the Zn^{2+} in ZnO lattice. This is supported by the UV-vis absorption and Raman results (not shown). As shown in Fig. 4, typical d-d transitions peaks of the tetrahedral coordinated Co^{2+} are found in the

UV-vis absorption spectra. The absorption peaks at 566, 611, and 655 nm are attributed to ${}^4A_2(F) \rightarrow {}^2E(G)$, ${}^4A_2(F) \rightarrow {}^4T_1(P)$, and ${}^4A_2(F) \rightarrow {}^2A_1(G)$ transitions in high spin state $Co^{2+}(d^7)$, respectively [12]. It suggests that the doped Co^{2+} are in high spin state, and they mainly occupy the Zn^{2+} sites of wurtzite ZnO. The band-gap energies of the samples were measured from the plots of $(ah\nu)^2$ versus photon energy ($h\nu$), and the value estimated from the intercept of the tangents to the plots was 3.36, 2.94, and 2.92 eV for pure ZnO, $Zn_{0.95}Co_{0.05}O$ nanotubes, and $Zn_{0.95}Co_{0.05}O$ nanowires, respectively. The redshift of the E_g edge with inserting Co in ZnO matrix has been already observed in film and powder samples [13] and explained as mainly due to sp-d exchange interactions between the band electrons and the localized d electrons of the Co^{2+} [14]. The sp-d exchange was thought to be one of the necessary conditions for achieving ferromagnetism in DMSs materials [15].

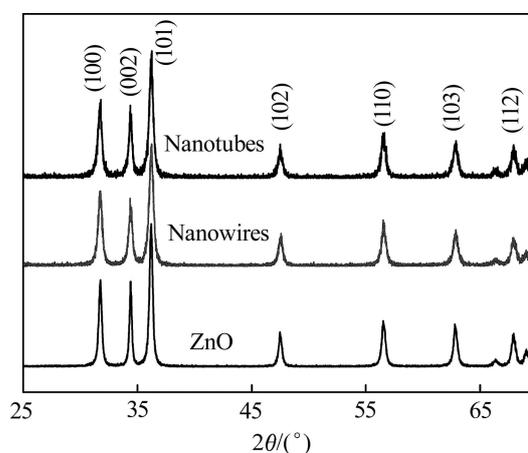


Fig. 3 XRD spectra of $Zn_{0.95}Co_{0.05}O$ nanotubes, nanowires, and pure ZnO powders

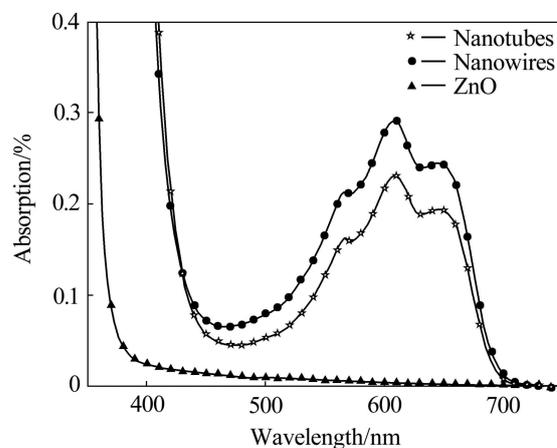


Fig. 4 UV-vis diffuse reflectance absorption spectra of $Zn_{0.95}Co_{0.05}O$ nanotubes, nanowires, and pure ZnO powders

Figure 5 shows the hysteresis loops of the $Zn_{0.95}Co_{0.05}O$ nanotubes and nanowires measured by VSM at 300 K. Both the nanowires and nanotubes

exhibit room-temperature ferromagnetism with clear hysteresis. The ferromagnetism of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanotubes is 0.047 emu/g, much higher than that of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanowires, 0.022 emu/g. This may be derived from the surface-preferential of the doped Co ions and the specific surface area difference between nanowires and nanotubes. Obviously, nanotubes have a larger specific surface area. Since the formation of ZnO:Co colloid is a self-purification process [15], the Co concentration at the surface area is higher than that in the inner part [2,16]. Higher Co concentration and related defects structures are beneficial to the ferromagnetic coupling between Co ions [17,18], leading to the higher ferromagnetism of nanotubes.

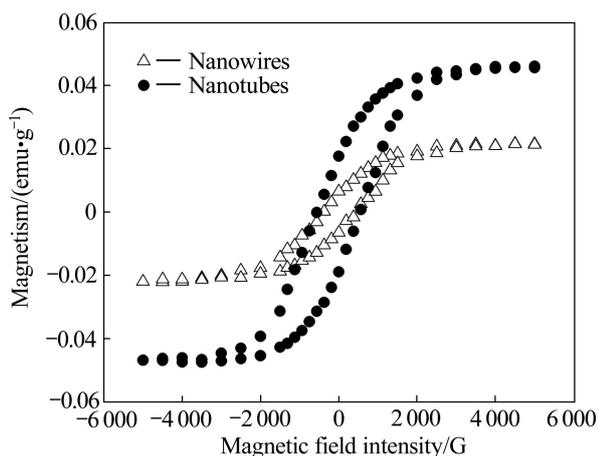


Fig. 5 Magnetism–Magnetic field intensity curves of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanotubes and nanowires investigated at 300 K

The mechanism of the electrophoretic deposition can be explained as follows. The preparation of $\text{Zn}^{2+}:\text{Co}^{2+}$ colloid is a complex chemical process, in which the coordination of Co^{2+} converts from octahedral to tetrahedral [12]. The colloidal particles had typical double-layer structure and positively charged (inside of the slip plane). As illustrated in Fig. 6, colloidal particles with a little adsorbed liquid moved to cathode when the external electric field was applied on the electrodes. At the beginning of the deposition, a colloidal tube formed on the tube surface due to the adsorption effect of the AAO template inner wall. Then the tubes were filled from the bottom to the top. The filled length of the pore is determined by the electrophoretic deposition potential, deposition time, and the δ potential of the colloidal particles. Along with the electrophoretic deposition, the colloidal particles gelled in the AAO template pore for a condensation process, to form $\text{Zn}^{2+}:\text{Co}^{2+}$ gel, the precursor of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$. After enough deposition time, the AAO template pores were filled up and solid composite nanotubes were obtained. If the deposition potential, time, and the pH value were properly tuned, tubular structural $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ could be obtained.

During the annealing process, the $\text{Zn}^{2+}:\text{Co}^{2+}$ gel were dehydrated and crystallized, leading to the formation of crystalline $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanotubes. Since the size of $\text{Zn}^{2+}:\text{Co}^{2+}$ gel is of nano-scale, the obtained nanotubes and nanowires are certainly to be polycrystal and composed of tiny nano-crystals.

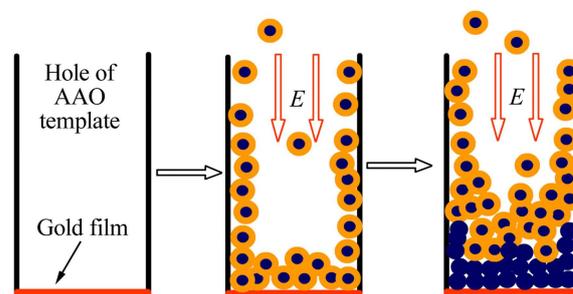


Fig. 6 Schematic diagram of electrophoretic deposition process of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanotubes

4 Conclusions

1) Poly-crystal $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanotubes, nanowires, and half-filled nanotubes, are synthesized by electrophoretic deposition method using AAO as template. The filled length of the half-filled nanotubes is determined by the electrophoretic deposition potential, deposition time, and the δ potential of the colloidal particles.

2) Magnetic investigation indicates that both the $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanotubes and nanowires are of room-temperature ferromagnetism, but the magnetism of the nanotubes is higher than that of the nanowires for larger surface area.

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Zn_{0.95}Co_{0.05}O 纳米线和纳米管的电泳沉积法可控合成

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摘 要: 以阳极氧化铝为模板通过电泳沉积法制备 Zn_{0.95}Co_{0.05}O 纳米线和纳米管, 并对电泳沉积法制备纳米线(管)的机理进行研究。系统的结构表征表明所得的纳米管和纳米线是由 8~15 nm 的纤锌矿纳米晶构成的多晶结构, Co^{2+} 离子以代位掺杂形式掺入晶格, 取代了晶格中的 Zn^{2+} 离子。磁性表征显示制备的纳米线和纳米管具有室温铁磁性。由于 Co 在纳米线(管)中表面择优分布, 纳米管的磁性明显高于纳米线。

关键词: Zn_{1-x}Co_xO; 纳米线; 纳米管; 电泳沉积; 阳极氧化铝模板; 室温铁磁性

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