Simplified Synthesis of Cobalt Ferrite Nanotubes Using Sol–Gel Method

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Cobalt ferrite nanotubes with diameter of 50 nm were prepared using a simple sol–gel process within the pores of anodic aluminum oxide (AAO) template. SEM, TEM, XRD, VSM were used to characterize the morphology, crystalloid structure, and magnetic properties of the samples. The results indicate that the cobalt ferrites thus prepared were polycrystalline phase with the smooth and uniform tube-like structure. The method is also expected to be applicable to the preparation of other multicomponent oxide nanotubes.

As an important way to prepare one-dimensional nanomaterials, template synthesizing is an elegant approach. This method entails synthesizing the desired metallic or organic material with the pores of a nanoporous host material. Though there now exists a huge range of hosts, porous anodic aluminum oxide (AAO) template is considered as particularly attractive template for fabricating nanowires or nanotubes in view of their uniform and nearly parallel porous structures and good chemical inertia and physical stability.[1] Sol–gel method has recently evolved as a powerful approach for preparation of inorganic materials motivated by its advantages over other conventional synthetic procedures. For example, high-purity materials can be synthesized at a low temperature. In addition, homogeneous multicomponent system can be obtained by mixing precursor solutions. Sol–gel deposition has been widely used to fabricate nanowire arrays in the nanochanles of template.[2,3]

Among the family of ferrite materials, cobalt ferrite has received attention for its large magnetic anisotropy and moderate saturation magnetization as well as a remarkable chemical stability and a mechanical hardness chosen as a good candidate for recording media.[4,5] Cobalt ferrite films and nanowires have attracted the interests on the exploration of recording media.[6–8] Although there are many studies of preparation and properties of cobalt ferrite materials, still there is no report on the synthesis of cobalt ferrite nanotubes so far. Here we have combined the concept of sol–gel synthesis and template preparation to fabricate cobalt ferrite nanotubes.

Hexagonally ordered porous alumina template was formed by a two-step anodization process as described previously.[9] The pores are arranged in a regular hexagonal array and pore densities as high as 10^{11} pores cm^{-2} can be achieved. An in-house prepared membrane with 50-nm-diameter pores was used in these studies. $FeCl_3$ and $Co(OAc)_2$ were used as the precursor salts for the sol–gel preparation of the cobalt ferrite nanotubes. All reagents are of analytical grade and used without further purification. $FeCl_3$ and $Co(OAc)_2$ with a molar ratio of 2:1 were dissolved in a volume of mixture solution (40 mL) containing citric acid and ethylene glycol (1:4, molar ratio). Stirring to form a homogeneously mixed solution, and then the solution was heated at 140 °C to induce esterification. A transparent sol was formed upon evaporation of the excess ethylene glycol. The viscosity of the sol is dependent on the extent of ethylene glycol evaporation. The alumina template was then dipped into this sol under vigorous stirring at 100 °C for the desired time, removed, and allowed to dry under vacuum at 80 °C for 2 h. The sol-containing membranes were then heated in open air at 500 °C for 10 h. This procedure yielded cobalt ferrite nanotubes within the pores of the template.

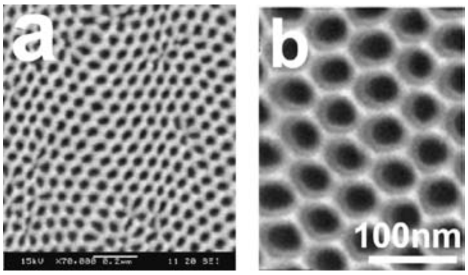

Figure 1. SEM images of AAO template with 50-nm-diameter pores (a); cobalt ferrite nanotube arrays (b).

Figure 1a shows a SEM image of AAO template. One can see that the AAO has almost perfectly arranged nanochannel array with the channel diameter of about 50 nm. A typical SEM image of cobalt ferrite nanotube arrays is shown in Figure 1b. The nanotubes grown by AAO template fill the nanochannels uniformly and the measured diameter of the nanotubes is about 50 nm. The morphology of the samples was observed by TEM after completely dissolving AAO template in an aqueous solution of 1 M NaOH and washing several times with double-distilled water and dispersing by the ultrasonic stirring for 10 min. Figure 2a presents a typical TEM image of a single cobalt ferrite nanotube. The sample has primarily a smooth and uniform tube-like structure with length up to 1 µm. The outer and inner diameters of these tubes are 50 and 40 nm, respectively. The TEM diffraction pattern shown in the inset of Figure 2a indicates that the samples are polycrystalline phase. Figure 2b shows a representative HRTEM image, demonstrating that the nanotubes are smooth and dense, with the wall thickness of $\approx$5 nm. The crystal size along the tube axis is about 5–15 nm and the cross section of a nanotube consists of one grain for a number of crystal. However, in the local region, crystal size can be extremely small, about 2–3 nm, and the cross section of a tube consists of 4–5 grains, and the corresponding diffraction ring is very broad. Additionally, a number of defects and disorder seen in the wall fringes and surfaces are most likely caused by the radical and rapid reaction during which the gel burns liberating vapors such as H_2O, CO_2 in a short time.

Figure 3 shows the XRD spectrum recorded for the as-

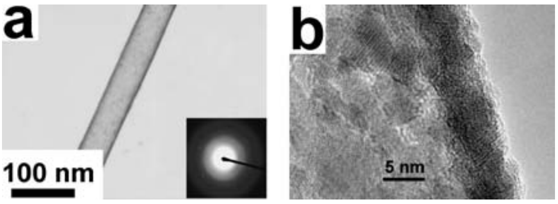

Figure 2. (a) Typical TEM image of a multiwall cobalt ferrite nanotube, demonstrating that the nanotube wall is quite smooth and uniform; (b) High-resolution TEM image of the as-prepared cobalt ferrite nanotube.

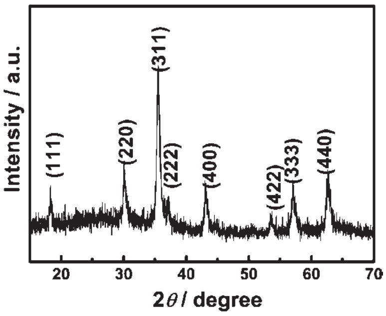

Figure 3. XRD patterns of the as-prepared cobalt ferrite nanotubes.

formed cobalt ferrite nanotubes within AAO template. No clear diffraction peaks of the crystalline phase of the metal precursor are observed in the XRD pattern. The peaks are found to be very close to (311), (220), (400), (440), (111), (333), (222), and (422) for bulk cobalt ferrite, indicating that the pure cobalt ferrite nanotubes are obtained. The crystallite size of the nanotubes can be estimated to be 15 nm from the full-width at half-maximum (FWHM) of the strongest reflection using the Scherrer equation.

On the basis of the observations reported above, we propose a possible growth mechanism for the formation of cobalt ferrite nanotubes within AAO template. In the early stages, sol particles held together by a network of –Fe–O–Co bonds are obtained. These particles ultimately coalesce to form a three-dimensional infinite network, the gel. When the AAO template was dipped into this sol, the cobalt ferrite sol is adsorbed to fill the pores owing to the capillary action, and the interaction of the sol particles with the alumina pore wall accelerates the rate of the gelation process. Along with the evaporation of solution, condensation of the metal ions dispersed in the ethylene glycol solution will occur, which leads to formation of a hydroxo bridge M–OH–M or an oxo bridge M–O–M.[10] These condensation can be followed by successive associations, leading to polymerization and consequently viscous sol, which facilitating the conservation of the precursor of cobalt ferrite when the AAO template is taken out of the sol. The sol change into gel and further spontaneously combust and give off vapors such as H_2O, CO_2 during the heating treatment.[10] These tubules are initially obtained when the samples are heated at 500 °C in the AAO template. However, if the samples were slowly beated from room temperature to 500 °C, only nanowires can be obtained.[11]

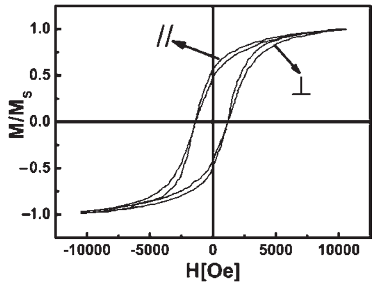

Figure 4. Typical magnetic hysteresis loops for the cobalt ferrite nanotubes grown in an AAO membrane measured at room temperature with the applied field parallel or perpendicular to the long axis of the nanotubes.

Figure 4 shows the typical hysteresis loops for the cobalt ferrite nanotubes with the diameter of about 50 nm. The external field was applied parallel or perpendicular to the long axes of the nanotubes. Similarly to our previous work,[12] the samples do not show a preferential magnetic orientation. For cobalt ferrite nanotubes, the magneto-crystalline anisotropy ($K_1 = 270 \times 10^3\ \mathrm{J/m^3}$) makes the main contribution to the total anisotropy and the samples obtained in our experiments are inhomogeneous polycrystalline with the magnetic domain irregularly distributed, resulting in the absence of perpendicular anisotropy.

In summary, a simple synthesis approach has been successfully developed to prepare the cobalt ferrite nanotubes with an average diameter of 50 nm. TEM revealed that the nanotubes have a smooth and uniform mutiwall tube-like structure. HRTEM illustrated that a number of defects and disorder are in the wall fringes and surfaces. XRD and TEM diffraction pattern indicated that the nanotubes were polycrystalline phase. This method is expected to be feasible for synthesizing other multicomponent oxides nanotubes.

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