

A Hydrothermal Reduction Route to Single-Crystalline Hexagonal Cobalt Nanowires

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Hexagonal close-packed (hcp) cobalt nanowires with diameters of 150–300 nm and lengths of up to several hundreds of micrometers have been synthesized by a hydrothermal reduction method. These cobalt nanowires were generated by the reduction of cobalt(II) citrate complexes by hypophosphite (H_2PO_2^-) in basic solution at 160 °C. High-resolution TEM and SAED reveal that the as-prepared Co nanowires

have a single-crystalline structure with a [001] growth direction. The room-temperature hysteresis loop of these nanowires shows a ferromagnetic behavior with enhanced coercivity. A formation mechanism for these Co nanowires is proposed.

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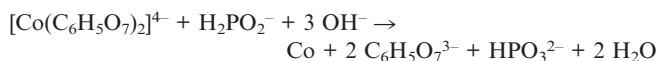
Introduction

Magnetic nanomaterials have attracted considerable interest due to their novel properties and many applications in magnetic recording media, sensors and other devices.^[1–4] In particular, nanocrystalline Co has sparked intensive studies not only due to its multiple crystal structures (hcp, fcc, and ϵ), but also because of its structure-dependent magnetic and electronic properties.^[5] It has been reported that the anisotropic high magnetic coercivity of hcp-Co is the preferred structure for permanent magnet applications, as compared with the more symmetric low coercivity fcc phase used for soft magnetic applications.^[6] A series of possible techniques have been applied for the structure-controlled synthesis of Co nanocrystals. For example, ϵ -Co nanoparticles (2–17 nm) have been synthesized in a mixture of an organic solvent and surfactant by the pyrolysis of carbonyl compounds^[6,7] or a solution-phase metal salt reduction.^[8,9] Thermodynamically stable hcp-Co nanorods have been obtained by the decomposition of $[\text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\eta^4\text{-C}_8\text{H}_{12})]$ in the presence of oleic acid and a long amine ligand.^[10]

Anisotropic magnetic nanoparticles are expected to exhibit interesting properties because of their shape anisotropy,^[11,12] and an hcp-Co nanowire array has been fabricated by an electrochemical deposition technique using polycarbonate membranes,^[13] porous AAO,^[14] and mesoporous silica films^[15] as templates. However, most Co

nanowires obtained by electrodeposition techniques are either very wide in diameter (380–420 nm) or polycrystalline.

Wet chemical methods have proved to be very effective for the production of single-crystalline, low-dimensional hexagonal cobalt nanocrystals. For example, hcp-Co nanodisks and their assembly of ribbons have been prepared by rapid decomposition of carbonylcobalt in the presence of trioctylphosphane (TOP) and oleic acid (OA),^[16] and a superlattice of monodisperse hcp-Co nanorods and nanowires has been selectively synthesized by the decomposition of organometallic precursors in the presence of a mixture of long-chain amines and acid molecules.^[17] A surfactant-assisted hydrothermal reduction route has been used to synthesize hexagonal cobalt nanobelts (diameter: 200–500 nm) in a mixed solvent of water and ethanol.^[18] Up to now, the preparation of shape-anisotropic magnetic nanomaterials by wet chemical methods has mainly been achieved in a hot organic solvent containing a surfactant. However, recent studies have shown that low-dimensional magnetic nanostructures (such as Ni nanobelts^[19] and nanoflowers^[20] and Fe_2O_3 nanorod arrays^[21]) can be formed in aqueous solution under properly controlled conditions even without the presence of surfactants. Herein, we report a facile hydrothermal method to synthesize single-crystalline hcp-Co nanowires, in which citrate salts have been introduced as a complexing reagent and shape modifier to control the growth process. The chemical reduction can be formulated as follows:



Results and Discussion

The crystalline nature of the phase and its purity were determined by X-ray diffraction (XRD). A representative

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XRD pattern of the as-prepared product is shown in Figure 1a. All the diffraction peaks can be well indexed to hexagonal-phase cobalt, with lattice constants of $a = 2.506$ and $c = 4.072$ Å, which is consistent with the standard values reported in JCPDS 05-0727 (space group $P6_3/mmc$). No characteristic peaks due to the impurities of cobalt oxides or hydroxides were detected, which indicates that the nanostructures obtained by the present synthetic route consist of a pure hcp phase. In addition, the relative intensity of the peaks corresponding to the (002)/(100) and (002)/(101) planes is significantly higher than the standard values, which indicates a different growth tropism of the products. X-ray energy dispersive (EDS) microanalysis (shown in Figure 1b) of the Co nanowires indicated that the sample is essentially pure Co. Only a very small amount of oxygen (element ratio: 0.54%) was detected, which was possibly from slight oxidation of the surface. Considering that the experiment was carried out in air, it is not difficult to explain this.

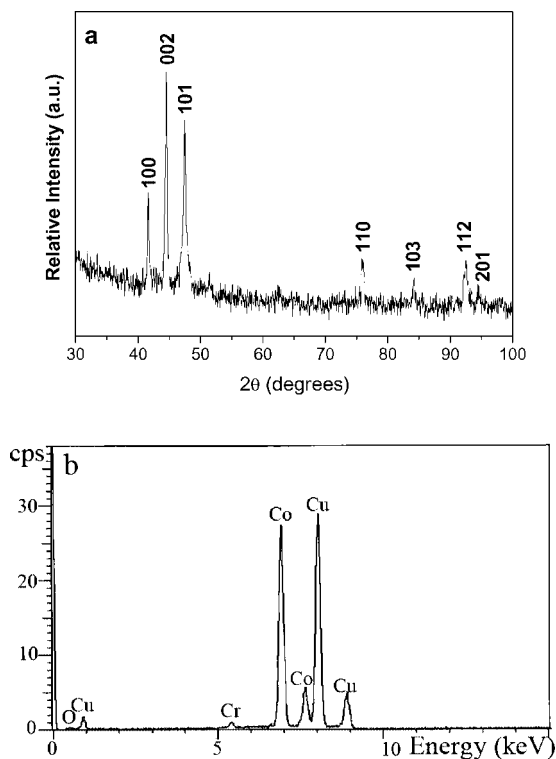


Figure 1. (a) XRD pattern of the final product obtained at 160 °C after 20 h. (b) EDS pattern of the final product (Cr and Cu signals can be attributed to the copper microgrid supporting the sample).

The morphologies and structures of the as-prepared products were examined by SEM and TEM. SEM observation (in Figure 2a) shows that the products consist of a large quantity of wire-like nanostructures. The nanowires range from several tens to several hundreds of micrometers in length. Figures 2b and c are TEM images that show the morphology of the nanowires. Each nanowire has a uniform width over its entire length, and the typical diameter of the wires is in the range 150–300 nm. Figure 2c displays the twist feature of a nanowire with an “M” shape, thus indicating the flexibility of the nanowire.

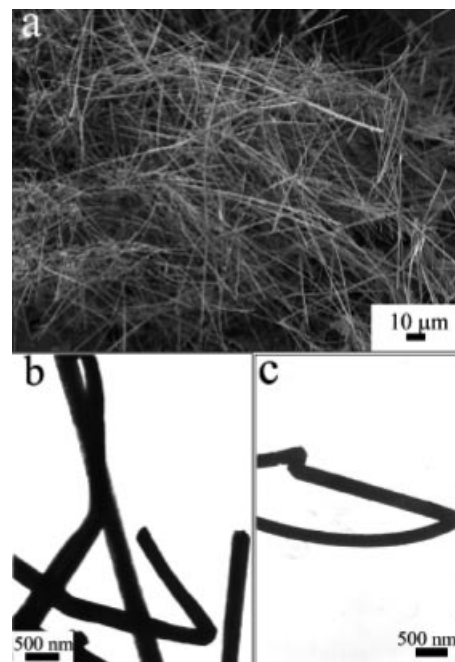


Figure 2. SEM and TEM images of the sample: (a) typical SEM image of the as-prepared Co nanowires; (b) and (c) TEM images of the Co nanowires, displaying the twist feature of the nanowire (c).

A more detailed study of the nanowires was performed by high-resolution TEM (HRTEM). Figure 3a shows a TEM image of an individual Co nanowire with a diameter of 200 nm. Figure 3b is a typical selected-area electron diffraction (SAED) pattern that was recorded from this nanowire. These pattern spots demonstrate the single-crystalline nature of this Co nanowire. Figure 3c is an HRTEM image recorded near the edge of this Co nanowire. The fringe spacing of 2.04 Å corresponding to the separation of the {002} planes of hcp-Co can be seen from Figure 3c; this also shows that the nanowire is single-crystalline. Further studies of both the HRTEM image and SAED patterns confirm that the single-crystalline nanowire grows along the [001] direction. The preferential crystal growth direction along the c axis is the magnetic easy axis of hexagonal cobalt crystals.^[22]

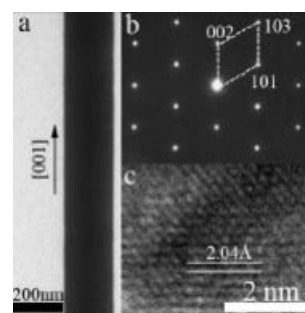


Figure 3. (a) Typical nanowire with a diameter of 200 nm. (b) SAED pattern recorded from this nanowire. (c) HRTEM image taken from the edge of this nanowire.

To investigate the nucleation and growth process of these nanowires, the evolution of the Co nanostructures was studied at various growth stages of the hydrothermal reaction by XRD and SEM techniques. Figure 4 shows the XRD patterns of samples that were taken after hydrothermal treatment for 6, 12, and 18 h. After heating for 6 h, the blue color of the mixture had disappeared and a large amount of grey solid product had formed. The XRD pattern (shown in Figure 4a) of the sample obtained at this stage indicates that hexagonal-phase cobalt had been produced. The SEM image (Figure 5a) shows that the sample is composed of cobalt particles and that they aggregate, driven by their natural magnetism. When the hydrothermal reaction time was extended to 12 h, the diffraction peaks of cobalt strengthened (Figure 4b). The SEM image (Figure 5b) reveals that radial nanowires were generated on the particles, and the surfaces of nanowires were covered with large numbers of nanoparticles. The inset of Figure 5b shows a magnified view of this radial structure. This image distinctly demonstrates that the Co nanowires grow from the particles. After 18 h, the diffraction peak of (002) planes has clearly strengthened, as shown in Figure 4c, which indicates that the sample has preferential tropism. The SEM image shown in Figure 5c shows that most of the products evolve into nanowires with smooth surfaces. After 20 h, the yield of cobalt nanowires was above 90%.

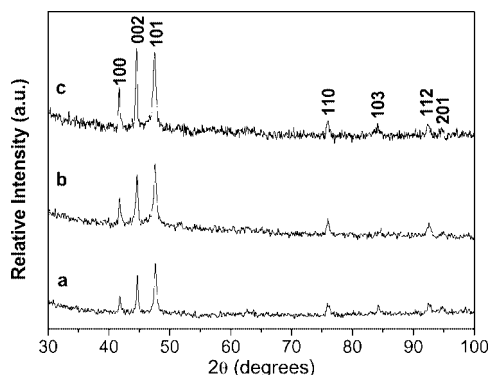


Figure 4. XRD patterns of the as-prepared samples at various growth stages of the hydrothermal process: (a) 6 h, (b) 12 h, and (c) 18 h.

On the basis of previous investigations on the evolution of cobalt nanowires, we found that this growth mode is very similar to the recent reports for the growth of one-dimensional metals in solution.^[19,23] Under the present condi-

tions, the formation of Co nanowires can also be attributed to nucleation and continuous growth by Ostwald ripening. In this mechanism, the small particles are generated by reduction of the cobalt(II) citrate complex by H_2PO_2^- in basic solution in the initial stage of the hydrothermal process. In a subsequent step, the larger particles will grow at the expense of the smaller nanoparticles through the Ostwald ripening process. In the presence of citrate, most particles grow into nanowires. Finally, the nanoparticles are gradually consumed, resulting in the formation of long nanowires (shown in Figure 2a).

The presence of citrate ions is crucial for the formation of Co nanowires. Control experiments have shown that without citrate ions, only Co particles (diameter ca. 500 nm) are obtained (Figure 6a), and at a low concentration of citrate ions (0.04 M), the product (shown in Figure 6b) is a flower-like aggregation of plates (width 200 nm). In addition, we also found that by keeping all other reaction conditions the same, wire-like structures can be obtained in the presence of either citric acid or potassium citrate, but cannot be obtained in the presence of other complexing reagents such as tartrate and ethylenediamine tetraacetate. This indicates that citrate anions play a crucial role in the formation of Co nanowires. Furthermore, the different stability and structures of the Co complex precursors may affect the reaction conditions for the formation of wire-like structures, as reported for the ligand-mediated synthesis of shape-controlled materials.^[20,24]

Citrate is an important biological ligand for metal ions and at high concentrations (ca. 0.2 mM) forms strong complexes with metal ions such as Ag^+ , Ca^{2+} , Mg^{2+} , Ni^{2+} , and Zn^{2+} .^[25] Citrate has been used as a shape modifier for the synthesis of ZnO complex structures^[26] and Ag nanowires.^[27] Citrate plays two major roles in our system. First, citrate ions can coordinate with cobalt ions to form $[\text{Co}(\text{C}_6\text{H}_5\text{O}_7)_2]^{4-}$ complexes in the excess citrate solution,^[28,29] which decreases the free Co^{2+} concentration in solution and results in the slow generation of Co nanoparticles. The relatively slow reaction rate may be favorable for the subsequent growth of Co nanostructures along the easy magnetic axis of the hexagonal cobalt, namely the [001] direction. In addition, citrate may bind to certain crystal faces of the cobalt particles through its COO^- and OH functions. An FT-IR spectrum of the sample, hydrothermally treated in 0.2 M citrate solution for 12 h and unwashed before measurement, is shown in Figure 6c. It exhibits the characteristic absorption for the carbonyl groups of the citrate carbox-

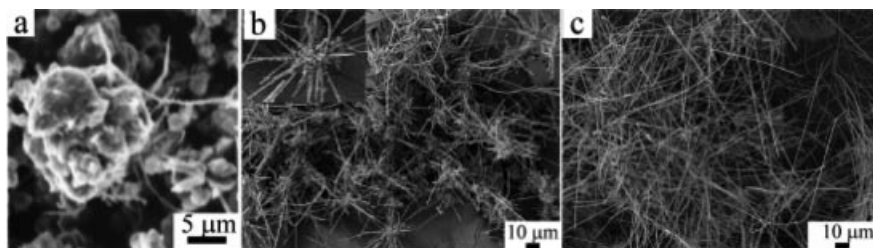


Figure 5. SEM images of the samples obtained at 160 °C after a hydrothermal treatment of (a) 6 h, (b) 12 h, and (c) 18 h.

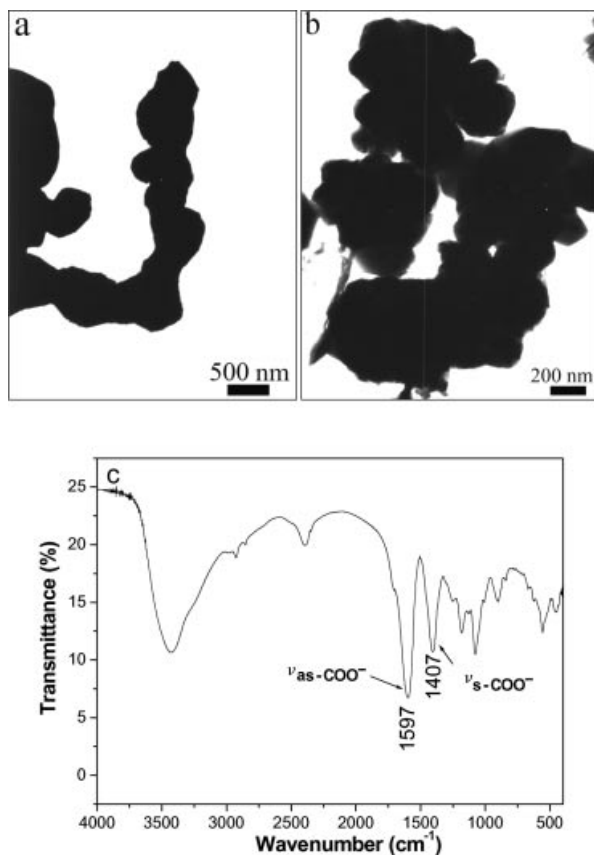


Figure 6. TEM images of products from syntheses with no sodium citrate (a) and 0.04 M sodium citrate solution (b). (c) FT-IR spectrum of the sample hydrothermally treated in 0.2 M citrate solution for 12 h and unwashed before measurement.

ylate ligands in the asymmetric and symmetric vibration regions. The asymmetric stretching vibrations $\nu_{\text{as-COO}^-}$ appear at 1597 cm^{-1} and the symmetric stretching vibration $\nu_{\text{s-COO}^-}$ at 1407 cm^{-1} . The bands are shifted to lower frequencies compared to those of free citric acid, which suggests some interaction between metal and citrate ligand. These interactions could force the nanoparticles to grow along only one axis. In this case, citrate plays a similar role to that in the formation of Ag nanowires.^[27]

Other reaction conditions, such as the concentration of NaOH in the reaction system and the reaction temperature, are also important factors in determining the shape of the final product. We found that a low concentration of NaOH solution (1 M) led to the formation of bamboo-like nanostructures with an average diameter of 300 nm (shown in Figure 7a). The reaction at a higher concentration of NaOH solution (4 M) produced Co dendrites (Figure 7b). Furthermore, if the other reaction conditions were maintained and the reaction temperature was reduced to less than $140\text{ }^{\circ}\text{C}$, the product was only aggregated particles. A higher temperature (such as $180\text{ }^{\circ}\text{C}$) resulted in wider wire-like structures and even some dendritic Co crystals. A temperature between 140 and $160\text{ }^{\circ}\text{C}$ is therefore optimal for the growth of Co nanowires.

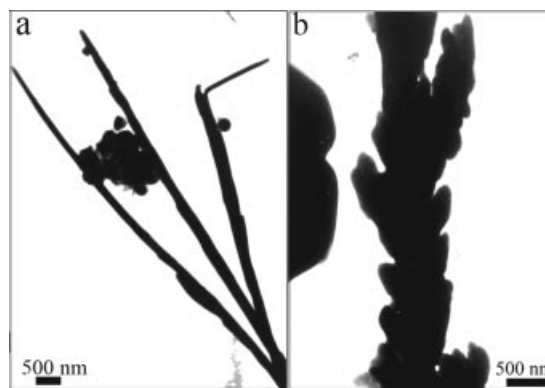


Figure 7. TEM images of the samples prepared at different NaOH concentrations: (a) 1 M NaOH solution, (b) 4 M NaOH solution.

The M/H hysteresis loop (Figure 8) of the powdered Co nanowires measured at room temperature (300 K) shows a ferromagnetic behavior. The coercivity (H_c) and saturation magnetization (M_s) values are 166.8 Oe and 133.1 emu g^{-1} , respectively. The saturation magnetization is reduced relative to the bulk value (168 emu g^{-1}).^[30] Surface oxidation at grain boundaries has been shown to cause a decrease in saturation magnetization.^[30,31] Under the present experimental conditions, such a surface oxidation could be the reason for the decrease of M_s . In addition, although the

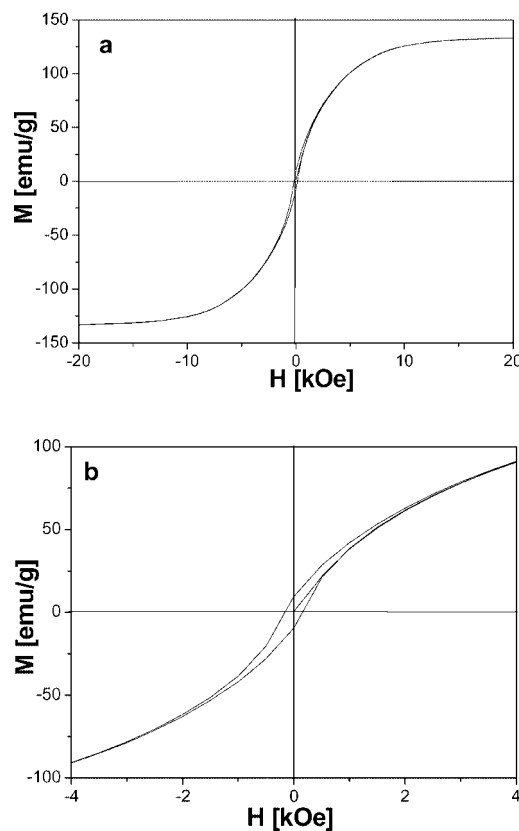


Figure 8. (a) Magnetic hysteresis loop of as-prepared cobalt nanowires measured at room temperature (300 K). (b) Enlargement of (a) at low field.

sample was washed before the measurement, a very small quantity of citrate molecules adsorbed on the Co nanowires could quench the magnetic moment through electron exchange between the ligand and surface atoms, which would partly result in the reduction of saturation magnetization.^[32] Compared to the value for bulk material (a few tens of oersteds),^[33] Co nanowires exhibit enhanced coercivity, which may be attributed to the small size and anisotropic shape of the nanowires. However, the coercivity value is much lower than that of the 2D and 3D superlattice of nanorods (740, 3200, and 7200 Oe)^[17] or nanobelts (410.6 Oe)^[18] with smaller sizes. Because a higher coercivity is an important factor for high-density information storage, further experiments are in progress to improve the coercivity of these nanowires.

Conclusions

In summary, we have reported a simple hydrothermal reduction route for the synthesis of hexagonal Co nanowires in high yield. Citrate salts are introduced as a reagent and shape modifier to control the growth of Co nanostructures. The effects of the reaction temperature and the concentration of sodium citrate and NaOH have also been discussed. The as-prepared Co nanowires show ferromagnetism with a greater coercivity (H_c) than the bulk materials. Such a simple and environmentally friendly synthetic route may be extended to the fabrication of one-dimensional structures of other transition metals or their alloys.

Experimental Section

All the reagents used were of analytical grade (purchased from Shanghai Chemical Industrial Co.) In a typical procedure for the preparation of cobalt nanowires, 10 mmol of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 2 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and 10 mmol of NaH_2PO_2 were dissolved in 40 mL of distilled water, and then NaOH (10 M, 10 mL) aqueous solution was added with constant magnetic stirring. The final concentration of the raw materials in solution was 40 mM Co^{II} , 0.2 M citrate, 0.2 M NaH_2PO_2 , and 2 M NaOH. The mixture was stirred for 10 min and then transferred into a 55-mL Teflon-lined autoclave. The autoclave was sealed and maintained in a furnace at 160 °C for 20 h, and then cooled to room temperature naturally. The grey powders were collected and washed with alcohol and distilled water several times and then dried in a vacuum oven at 60 °C for 5 h.

The X-ray diffraction (XRD) pattern was recorded with a Rigaku (Japan) D/max-rA X-ray diffractometer equipped with graphite-monochromated Cu-K_α radiation ($\lambda = 0.154187$ nm). The SEM images were obtained with a field emission scanning electron microscope (FESEM, JEOL-6300F) or a Hitachi X-650 SEM. The TEM images were captured with a Hitachi Model H-800 instrument at an acceleration voltage of 200 kV. The high-resolution transmission electron microscopy (HRTEM) images and the corresponding selected area electron diffraction (SAED) pattern were taken with a JEOL 2010 high-resolution transmission electron microscope with X-ray energy-dispersive spectroscopy (EDS) performed at 200 kV. The FT-IR spectrum was recorded with a Bruker Vector-22 FT-IR spectrometer from 4000 to 400 cm^{-1} at room tem-

perature on KBr mulls. The magnetic measurement of the sample was carried out with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL-7) with 6.4 mg of sample sealed in a small cylindrical vessel.

Acknowledgments

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