# Electrochemical Fabrication of CdS/Co Nanowire Arrays in Porous Aluminum Oxide Templates

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A procedure for preparing semiconductor/metal nanowire arrays is described, based on a template method which entails electrochemical deposition into nanometer-wide parallel pores of anodic aluminum oxide films on aluminum. Aligned CdS/Co heterostructured nanowires have been prepared by ac electrodeposition in the anodic aluminum oxide templates. By varying the preparation conditions, a variety of CdS/Co nanowire arrays were fabricated, whose dimensional properties could be adjusted.

**Key Words :** Cadmium sulfide, Cobalt, Nanowire, Template, Anodic aluminum oxide

## Introduction

The scientific and technological aspects of nanostructured materials, which are of much current interest for extensive potential applications in electronic, optical and mechanical devices or in mesoscopic physics, are currently drawing considerable attention.[1] Nanostructures may adopt various shapes such as spheroids, platelets, fibrils or tubules, which are critical factors in determining the basic properties of materials. Recently, one dimensional structures on the nanoscale, such as nanorods, nanowires and nanotubes have become the focus of much interest in view of possible future applications in areas such as photocatalysis, electrochemistry, battery research and enzyme immobilization. They are of paramount importance in understanding the dependence of the basic properties, for example, the electronic, optical and mechanical properties, on dimensionality and size.

Several procedures have been proposed and applied to the synthesis of nanostructures, such as molecular beam epitaxy, microlithography, vapor-liquid-solid growth, solution-liquid-solid growth and template-mediated methods.[2] A method which entails synthesizing the desired material within the pores of a nanoporous material is called template synthesis. There are different concepts of using the pores in nanoporous films as templates for preparing nanomaterials. This general template synthesis is an elegant chemical or electrochemical approach for the fabrication of nanostructures, particularly in view of its flexibility to produce nanowires with different compositions. The prepared fibrils or tubules can be composed of metals, semiconductors, carbon, conductive polymers or other materials.

Many research groups have reported the anisotropic magnetic behavior of the ferromagnetic metal (Fe, Co and Ni) nanowires electrodeposited in the pores of anodic alumina and suggested a possibility of using them as high-density perpendicular recording media similar to Co-Cr films.[3] Semiconductor nanowires are of considerable interest as they are capable of being used in optical devices and microelectronic technology.[4] Cadmium sulfide is a typical wide band gap II-VI semiconductor having a band gap of 2.42 eV at room temperature. It has many commercial or potential applications in light-emitting diodes, solar cells or other optoelectronic devices. The synthesis and study of cadmium sulfide nanowires should stimulate much research and technological applications. Moreover, electrodeposition of CdS/Co heterostructured nanowires is an expanding subject in materials science.

To the best of our knowledge, the anodic aluminum oxide (AAO) films have not been used as a template to prepare CdS/Co nanowires. We report here the template synthesis of CdS/Co nanowires utilizing the technique which entails using the nanopores in an AAO film as a template for growth through ac electrodeposition. Anodically grown porous aluminum oxide, which is known to have a very regular structure, has been chosen as template material, whose structure can be adjusted by variation of the experimental anodization conditions.[5] However, the electrochemical deposition of these materials on an insulating and rather thick barrier layer at the pore tips is not straightforward. High potentials are required for the tunneling of the electrons through the barrier layer. Electrodeposition on the barrier layer by direct current is very unstable and uniform filling of the pores cannot be achieved. This is due to a cathodic side reaction, which leads to a partial removal of the barrier oxide, formation of holes in the barrier layer, and local deposition in these pores. We have developed the chemistry for fabricating CdS/Co nanowires within templates of this type; arrays of CdS/Co nanowires were obtained. The morphological and surface properties of the resulting free standing nanowire arrays were investigated by XPS, SEM, and their electrochemical response.

## Experimental Section

**Anodization**. An electrochemical cell for electropolishing

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and anodizing aluminum, and electrodepositing cobalt consists of a 500-mL single-compartment glass vessel with a double jacketed wall, an aluminum working electrode, two graphite counter electrodes and a reference electrode placed in the electrolyte vessel. The distance between the aluminum electrode and each graphite electrode was kept at 5 cm. The reference electrode was saturated Ag/AgCl set at 1 cm next to the working electrode for reproducibility purposes. These electrochemical processes were performed at a constant temperature to within ±1°C by circulation of thermostated water through the jacketed vessel using an FTS Systems Model FC55-P1 refrigerated chiller with immersion probe controlled by a Eurotherm Model 2404 temperature controller and an ITT Industries Model Duplex II all-plastic double-diaphragm pump. The electrolyte vessel was stirred with a magnetic stirrer during the electrochemical processes. An electrical circuit includes an Agilent Technologies Model E3612A DC power supply, the aluminum working electrode, the graphite counter electrodes and the reference electrode placed. The current and voltage were recorded throughout all the electrochemical processes using a computer interfaced to an Agilent Technologies Model 34970A data aquisition/switch unit.

AAO films were grown on 0.50 mm thick 99.999% aluminum foil (Aldrich). Aluminum samples were electropolished to a mirror finish under potentiostatic conditions in a 5:1 v/v solution of 95 wt % ethanol / 70 wt % perchloric acid at 15 V dc and 2°C for 3 min. Then AAO films were formed by anodizing the electropolished aluminum at a constant potential in a solution of 0.3 M oxalic acid or 0.5 M sulfuric acid. We also postfabricated the anodic porous alumina by etching it in phosphoric acid for variable lengths of time so as to widen the pores to a desired target value before metal deposition was carried out. After anodization, each sample was washed thoroughly with distilled water and dried with an air jet.

**Nanowire growth**. Cobalt was deposited in the pores of AAO films at 8-17 V ac (60 Hz) in an electrolyte consisting of 240 g/L $CoSO_4 \cdot 7H_2O$, 1 g/L ascorbic acid and 40 g/L $H_3BO_3$ in the electrolyte vessel at 25°C for 0.3-15 min.

Cadmium sulfide electrodeposition was carried out in a 1000-mL glass cell fitted with adaptors for an aluminum working electrode, two graphite counter electrodes, a thermocouple temperature sensor and a coiled condenser. The temperature of the electrolyte was maintained to within ±1 °C with a heater controlled by a Eurotherm Model 2404 temperature controller and a Eurotherm Model TE10A single phase compact thyristor. Deposition of cadmium sulfide in the pores of AAO films was carried out in a solution containing 0.055 M $CdCl_2$ and 0.19 M elemental sulfur dissolved in dimethyl sulfoxide at 120°C and 41 V ac (60 Hz) applied between the aluminum electrode and each graphite electrode for 2-15 min. After electrodeposition, each sample was washed with warm dimethyl sulfoxide, methanol and distilled water.

**Characterization**. Scanning electron microscopy (SEM) was used to obtain morphological information as well as the size of metal and semiconductor wires. SEM was carried out on a JOEL Model JSM-840A instrument operated in the secondary electron image mode at 5 to 30 kV. Before SEM investigations, a thin gold film of a few nanometers thickness was sputtered onto the filled structure to enhance the surface conductivity for SEM observations and mounted to an aluminum stub with conductive silver paint. Nanowire diameter and length were determined by SEM, assuming that nanowires were faithful replica of their matrix.

Atomic force microscopy (AFM) topography examinations were carried out with a PSIA Model AP-2000 AutoProbe CP Research using ultralever Si conical tips with a typical radius of curvature of 10 nm and an aspect ratio of about 3:1.

X-ray diffraction (XRD) was carried out on a Siemens Model D5005 diffractometer using filtered Cu $K_\alpha$ radiation in the $\theta/2\theta$ configuration. For routine measurements the counting time per step and the step size were 1.5 s and 0.02°, respectively.

## Results and Discussion

**Formation of anodic aluminum oxide films on aluminum**. The hexagonally ordered porous alumina templates have been prepared *via* a two-step anodization process, which is described in detail elsewhere.[6] Figure 1 shows representatively the AFM images of a pore morphology produced by anodizing aluminum. The interpore separation and pore diameter for this sample are about 110 nm and 45 nm, respectively. Here the aluminum substrate was prestructured by anodizing in a solution of 0.3 M $H_2C_2O_4$ at 16°C and 40 V dc for 24 h and removing the AAO film by chemically dissolving in a solution of 6 wt % $H_3PO_4$ and 1.8 wt % $CrO_3$ at 60°C for 12 h. A highly ordered aluminum oxide pore structure was obtained in a second anodization step by reanodizing for 10 min. When the anodization was complete, the anodizing voltage was decreased from 40 V to 24 V stepwise with 4 V intervals over a period of 5 min in order to reduce the thickness of the barrier layer. These resulted in an AAO film about 1.0 $\mu$m thick with pores running almost the full width of film and separated from underlying aluminum by only 25 nm-thick aluminum oxide barrier layer.

Our previous studies[7] demonstrated that the pores in AAO films are quite uniform, parallel, and open only at oxide electrolyte interface and that different anodization conditions such as anodizing voltage, current density, anodization time and electrolyte temperature are related directly to the dimensions of the AAO films. These regimented nanoporous AAO templates were used for electrochemical fabrication of the CdS/Co nanowires.

**Electrodeposition of cobalt into pores of anodic aluminum oxide films**. The electrodeposition was carried out at constant ac potential so that the deposition process could be monitored from the current response. Metal is deposited during the cathodic half of the ac cycle. The anodic oxide is rectifying so that the current is suppressed during the anodic half cycle. The effect of varying the

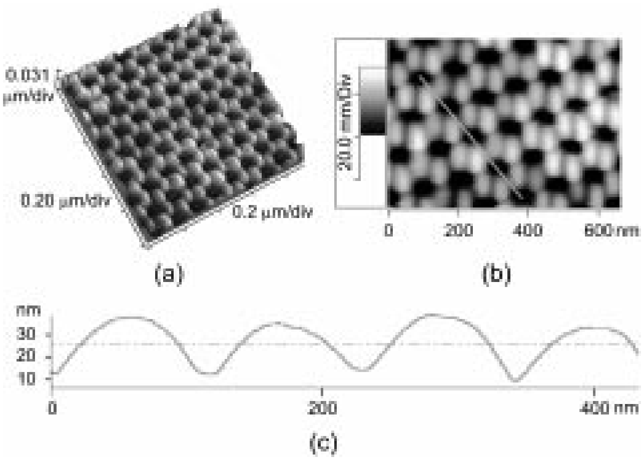


**Figure 1**. AFM images of 3-dimensional view (a), plan view (b) and height profile (c) of a pore morphology produced by anodizing aluminum.

deposition time was investigated in order to determine the connection between the deposition time and the quantity of cobalt deposited. At any given potentials, the electrodeposition current was directly proportional to the area of the electrodeposit. Hence the current-time curves recorded during the electrodeposition process revealed various stages of the electrodeposition. For example, the current-time curve for electrodeposition of cobalt into an AAO film is shown in Figure 2. Here the aluminum substrate was prestructured by anodizing in a solution of 0.5 M $H_2SO_4$ at 2°C and 25 V dc for 12 h and removing the AAO film by chemically dissolving in a solution of 6 wt % $H_3PO_4$ and 1.8 wt % $CrO_3$ at 60°C for 12 h. A highly ordered aluminum oxide pore structure was obtained in a second anodization step by reanodizing for 15 min. Finally cobalt was deposited in the pores of the AAO film at 15 V ac (60 Hz) in an electrolyte consisting of 240 g/L $CoSO_4 \cdot 7H_2O$, 1 g/L ascorbic acid and 40 g/L $H_3BO_3$ in the electrolyte vessel at 15°C. The interpore separation, pore diameter and pore length for this sample were about 65 nm, 30 nm and 1.9 $\mu$m, respectively. As electrodeposition continues, cobalt fills the pores from the bottom upward. After an initial transient, the current-time curve exhibits two distinct regions. Region I corresponds to the electrodeposition of cobalt into the pores in the AAO film. Region II results from the rapid increase in the deposition area that occurs when the pores are completely filled with the deposited metal and the electrodeposit begins to form hemispherical caps over the end of each nanowire. The formation of this structure causes an increase in the deposition current that will continues until the caps coalesce into a planar and contiguous metallic top layer. Thus, by stopping the electrodeposition process at the transition point between region I and II, an array of nanowires can be formed.

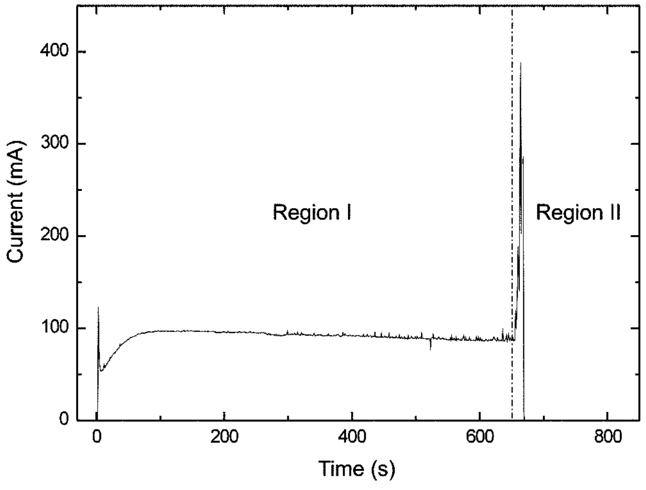


**Figure 2**. Current-time curve for electrodeposition of cobalt into an AAO film.

Figure 3 shows the prospective view SEM images of cobalt-filled AAO films. The AAO film in Figure 3a was prepared in similar to that in Figure 2 and 0.67 C was consumed. The AAO film in Figure 3b was prepared in similar anodization conditions to that in Figure 1 and total electric charge of 14 C was consumed during cobalt deposition. Although SEM is less sensitive to density variations than transmission electron microscopy (TEM), it can be seen that cobalt was underdeposited at the bottom of pores in Figure 3a and that cobalt was overdeposited on the outer surface of the oxide film in Figure 3b. The deposited cobalt

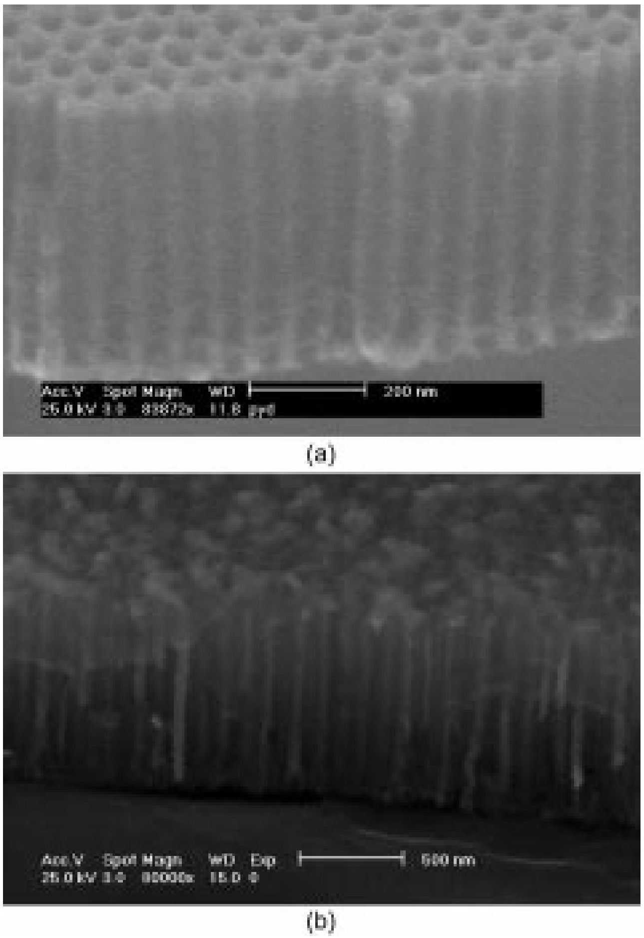


**Figure 3**. Prospective view SEM images of cobalt-filled AAO films underdeposited (a) and overdeposited (b).

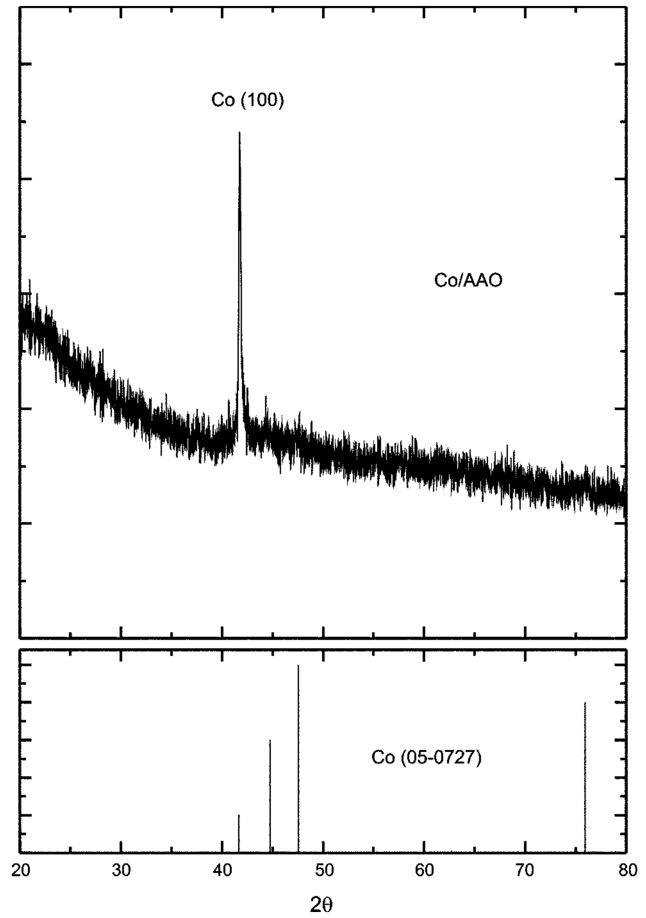
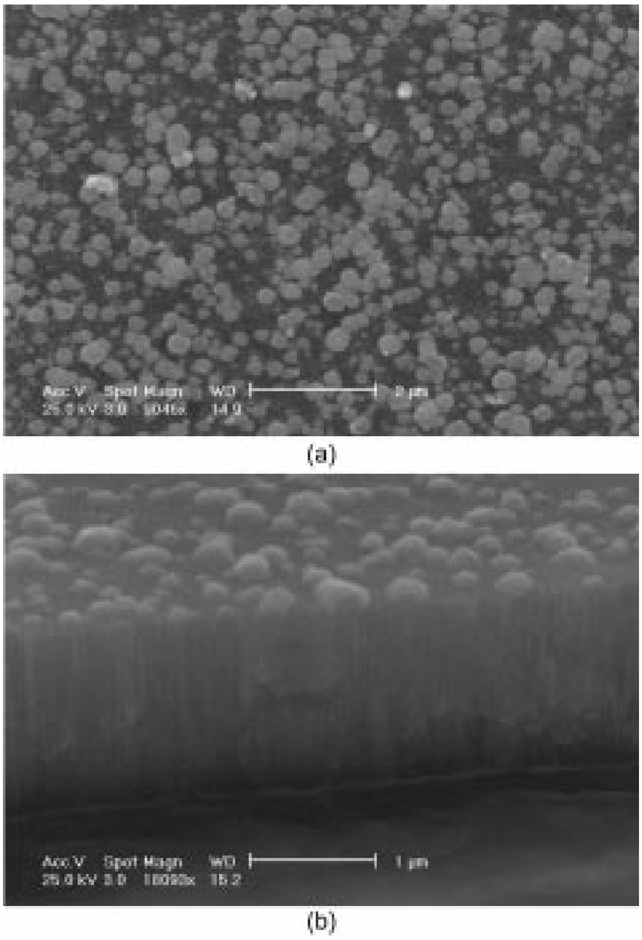


**Figure 4**. X-ray diffractogram of an as-deposited cobalt nanowire array in Figure 3b. The vertical lines at the bottom of the figure indicate the standard position and relative intensities of hexagonal cobalt (ASTM 05-0727).



(a)

(b)

**Figure 5**. SEM images of a plan view (a) and a prospective view (b) of an CdS/Co nanowire array deposited in an AAO template.

fills the pores uniformly and only a small fluctuation in growth rate of cobalt nanowires is observed.

X-ray diffractogram of an as-deposited cobalt nanowire array in Figure 3b is shown in Figure 4. The X-ray sample was prepared by dissolving aluminum in a saturated solution with mercuric chloride to avoid spectral interference from big signals of the substrate aluminum. The diffraction peak corresponds to the (100) diffraction plane of a hexagonal cobalt crystal. The 1-dimensional nanowire array is X-ray crystalline even as deposited and highly textured. The diffraction pattern with a distinct line implies that the crystals in the nanowires should have a similar orientation, *i.e.*, the nanowires should have a similar growth direction.

**Electrodeposition of cadmium sulfide on cobalt into pores of anodic aluminum oxide films**. Figure 5 shows the SEM images of a CdS/Co nanowire array deposited in an AAO template. The CdS/Co nanowires were prepared by ac electrodeposition in the AAO template partially filled with cobalt as in Figure 3a. It is observed that an aligned nanowire array was formed. If it is assumed that cadmium sulfide is initially deposited on cobalt nanowires in the oxide film pores, then the onset of noise as in Figure 2 may reflect the fact that cadmium sulfide deposition in the pore is now complete and subsequent cadmium sulfide deposition is occurring on the outer surface of the oxide film. The possible development of a high surface area, fragile dendritic cadmium sulfide deposit at this stage could make the rate of further cadmium sulfide deposition dependent on mass transport in solution, *i.e.*, either by diffusion or convection, hence leading to noisy current response.

The X-ray diffractogram of an as-deposited CdS/Co nanowire array in Figure 5 is shown in Figure 6. The diffraction peaks correspond to the (200) and (111) diffraction planes of a hexagonal cadmium sulfide crystal. This is consistent with columnar deposits whose long axes are perpendicular to the surface. Routkevitch *et al.*[8] prepared cadmium sulfide nanowires into the pores of AAO films by ac electrochemical deposition, where more polycrystalline phases were observed. Any diffraction peaks for the cobalt layer were not observed in the X-ray diffractogram of the CdS/Co nanowire array. This might indicate that only a small amount of cobalt was deposited at the bottom of the pores, compared with that of cadmium sulfide since the as-deposited cobalt nanowires were X-ray crystalline (Figure 4). Unlike the elegant precipitation techniques developed to fabricate semiconductors within glass, polymer, micelle or zeolite matrices, the present technique employs electrodeposition, which has been

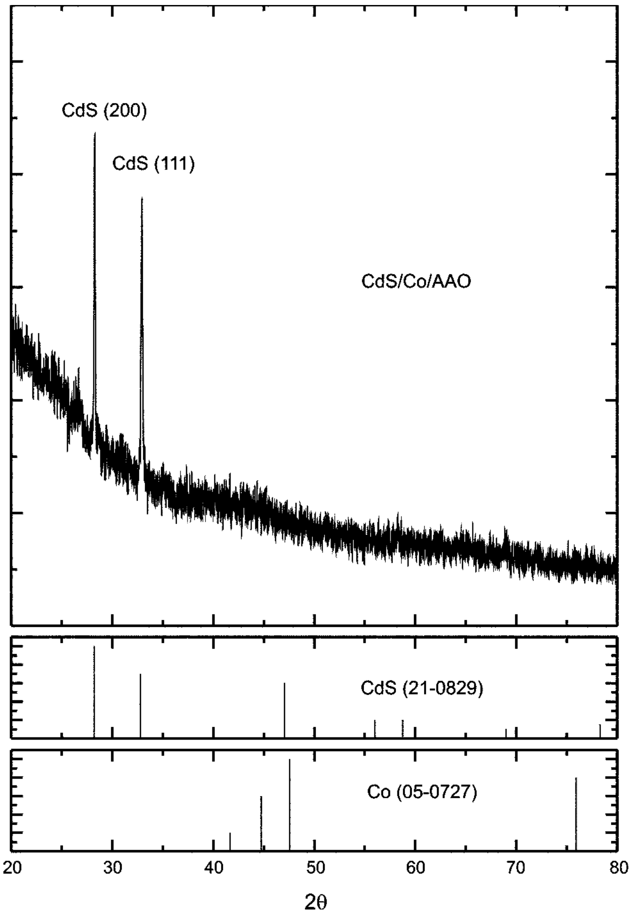


**Figure 6**. X-ray diffractogram of an as-deposited CdS/Co nanowire array in Figure 5. The vertical lines at the bottom of the figure indicate the standard position and relative intensities of hexagonal cadmium sulfide (ASTM 21-0829) and hexagonal cobalt (ASTM 05-0727), respectively.

shown to provide very precise control of both the dimension and composition of the metal and semiconductor materials. The results represent the first synthesis of large CdS/Co heterostructure arrays. In addition, the restricted dimensions of the AAO templates are found to eliminate the fractal-like cauliflower morphology often observed in the electrodeposited II-VI materials. In this way, we can electrochemically prepare CdS/Co nanowires with uniform diameters of about 10~250 nm and lengths of about 0.1~100 $\mu$m, copying exactly naturally occurring structures. These results may be important for the fabrication of high-resolution optical detectors, solar cells or high-definition displays.

## Conclusions

We have synthesized highly crystalline CdS/Co nanowire arrays by ac electrodeposition in the AAO templates. The approach to the fabrication of a highly ordered metal and semiconductor nanowire array is inexpensive and very flexible with respect to the size and thickness of the pore structure. In addition, the thickness of the barrier layer and the pore diameter could in principle be varied independently of each other. Our experimental results strongly demonstrate that the ac electrodeposition process can produce less perfect but more highly oriented crystalline CdS/Co nanowires than the dc technique. It is expected that this fabrication process can also be applied to the deposition of other metals and semiconductors for the synthesis of nanowire systems. Optical transparency of the AAO matrix suggests the possibility of producing optoelectronic devices based on these relatively monodispersed semiconductor/metal heterostructures. The controlled variability of the particle diameter and compositions might also be used to tune in desired optical properties.

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