

## Preparation of II-VI group semiconductor nanowire arrays by dc electrochemical deposition in porous aluminum oxide templates\*

Dongsheng Xu, Dapeng Chen<sup>1</sup>, Yajie Xu, Xuesong Shi, Guolin Guo<sup>†</sup>, Linlin Gui, and Youqi Tang

*Institute of Physical Chemistry, Peking University, Beijing 100871, P. R. China*

*Abstract:* II-VI group compound semiconductors such as CdS, CdSe, and CdTe nanowire arrays have been prepared by direct current electrodeposition in porous anodic aluminum oxide template from nonaqueous electrolyte. SEM and TEM results show that these nanowires have a highly anisotropic structure of aligned nanowires with diameters of 15–200 nm, which are consistent with the diameters of the templates used. Electron diffraction and HREM investigations demonstrate that the crystalline structures of these nanowires are uniform hexagonal single crystal. This approach can be used to fabricate single crystal nanowire arrays of a wide range of semiconductors and other materials.

### INTRODUCTION

In the past few years, one-dimensional nanostructural materials, such as nanotubes and nanowires, have attracted much attention both because of their fundamental importance and the wide-ranging potential of their application in nanodevices [1–5]. Many experimental approaches to fabricate nanowires have been reported, utilizing a variety of nanofabrication techniques [6–10] and crystal growth methods, including arc discharge [1], laser ablation [4, 5], catalytic CVD growth [11,12], and template synthesis [13], etc. In this field, it is still a challenge to synthesize aligned and well-distributed nanowire arrays as well as highly crystallized structures.

It is well known that template synthesis is a simple and versatile method for preparing nanostructural materials, which entails synthesizing the desired material within the pores of a microporous template membrane. On the other hand, due to cylindrical pore geometry and monodisperse diameters, corresponding cylindrical and well-distributed nanostructural materials are obtained. The electrochemical synthesis in templates has been taken as one of the most efficient methods in controlling the growth of nanowires because the growth is controllable almost exclusively in the direction normal to the substrate surface [13]. To date, a variety of metal and conductive polymer nanowire arrays have been produced by electrodeposition in template [13–18]. However, the study on preparation of semiconductor nanowires by electrodeposition in template is still scarce, and only CdS nanowires have been produced by ac electrodeposition in porous aluminum anodic oxidization (AAO) template [19–21].

---

\**Pure Appl. Chem.* **72**, 1–331 (2000). An issue of reviews and research papers based on lectures presented at the 1<sup>st</sup> IUPAC Workshop on Advanced Materials (WAM1), Hong Kong, July 1999, on the theme of nanostructured systems.

<sup>†</sup>Corresponding author: E-mail: guogl@csb0.ipc.pku.edu.cn; Fax: 86-10-62751725

<sup>1</sup>Permanent address: Department of Material Science & Engineering, Yunnan Polytechnic University, Kunming 650051, P. R. China

In this paper, we will report our work of fabricating II-VI group compound semiconductor single crystal nanowire arrays based on dc electrolysis into the pores of AAO templates. The nanostructure and morphology as well as the atomic composition characterization of the nanowires are carried out.

## EXPERIMENTAL SECTION

The AAO templates with pore sizes of about 20, 50, and 100 nm were grown by potentiostatically anodizing aluminum plates (0.15 mm thick, 99.9+%) in an aqueous solution of 14% H<sub>2</sub>SO<sub>4</sub>, 4% and 2% oxalic acid respectively. After the anodization, the remaining aluminum was etched by a 20% HCl-0.1 mol·L<sup>-1</sup> CuCl<sub>2</sub> mixed solution. Then, the barrier layer was dissolved using 20% H<sub>2</sub>SO<sub>4</sub>. Finally, a silver film was deposited by vacuum evaporation onto a surface of the template membrane to provide a conductive contact.

A II-VI group semiconductor such as CdS, CdSe, or CdTe was cathodically deposited in a glass cell fitted with platinum counter electrode as the anode, and the AAO template with Ag substrate as the cathode. After the deposition, the AAO templates with the nanowires were immediately removed from the electrolyte and rinsed firstly with hot dimethylsulfoxide (DMSO) or glycol, followed by acetone and washed with double distilled water, finally dried in air at room temperature, and subjected to further analysis.

The electrodeposited semiconductor nanowires were examined by electron microscopy by first liberating them from their AAO matrix by dissolving the AAO template in 1M NaOH at 25 °C. After 1 h of dissolution, the nanowires were freed from the template completely and subjected to further analysis. SEM was carried out on AMARY 1910FE. A TEM, JEM-200CX operated at 160 keV, was employed for the study of the morphology of CdS nanowires. The X-ray energy diffraction analysis was carried out on EDAX 9100/6 (Philips). For the high-resolution electron microscope (HREM) observation, a JEOL-2010 electron microscope was employed at 300 kV at room temperature. X-ray powder diffraction (XRD) had been carried out on a BD-86, PKU diffractometer using filtered Cu K $\alpha$  radiation.

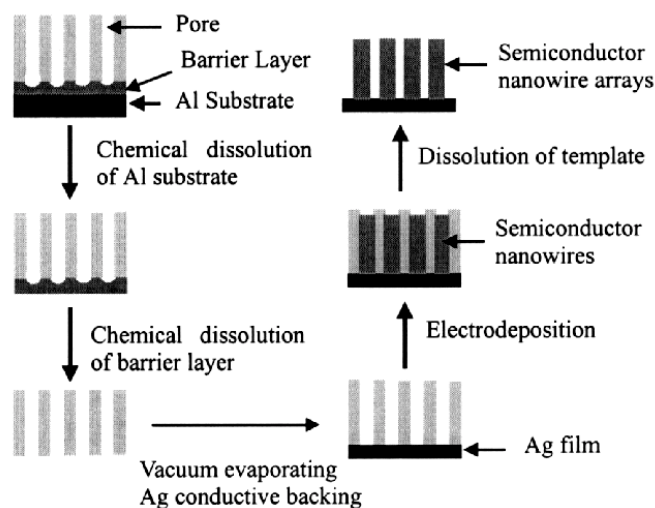
## RESULTS AND DISCUSSION

### CdS nanowires

The compact barrier layer between the porous AAO and Al substrate is insulating, which obstructs the passage of direct current. Thus, it is difficult that materials are directly deposited on the AAO/Al substrate by dc electrodeposition.

Usually, this problem may be resolved by retaining the barrier layer and using ac electrolysis. Routkevitch *et al.* [19] have fabricated CdS nanowire arrays by a single-step ac electrodeposition in an electrolyte containing Cd<sup>2+</sup> and S in DMSO. They reported that on average the thicker wires (with diameters larger than 12 nm) consisted of a large number of crystallites in the axial direction and rather few in the radial direction, but the thinner wires (with diameters less than 12 nm) were single crystal structure. However, HREM structural studies revealed that even for the thinner wires, large numbers of stacking faults and twinned segments are present in this nanowire and the structure of CdS nanowire by ac electrodeposition appears to be mainly the hexagonal form, interleaved with domains of cubic structure [21].

On the other hand, we believed that a dc electrodeposition approach would enable us to obtain aligned and well-distributed nanowire arrays, as well as uniform single crystal structure (Fig. 1). First, the Al substrate and the barrier layer of the AAO template were chemically dissolved in 20% HCl. Then, a silver film was deposited by vacuum evaporation onto the back of the template membrane. Finally,



**Fig. 1** Schematic diagram illustrating the dc electrochemical synthesis of semiconductor nanowires in AAO template.

CdS was cathodically deposited at the constant direct current density of  $2.5 \text{ mA}\cdot\text{cm}^{-2}$  for 2–10 min at  $110^\circ\text{C}$  by immersing the cell in an oil bath. The electrolyte solution consisted of  $0.055 \text{ mol}\cdot\text{L}^{-1}$   $\text{CdCl}_2$  and  $0.19 \text{ mol}\cdot\text{L}^{-1}$  S in dimethylsulfoxide (DMSO).

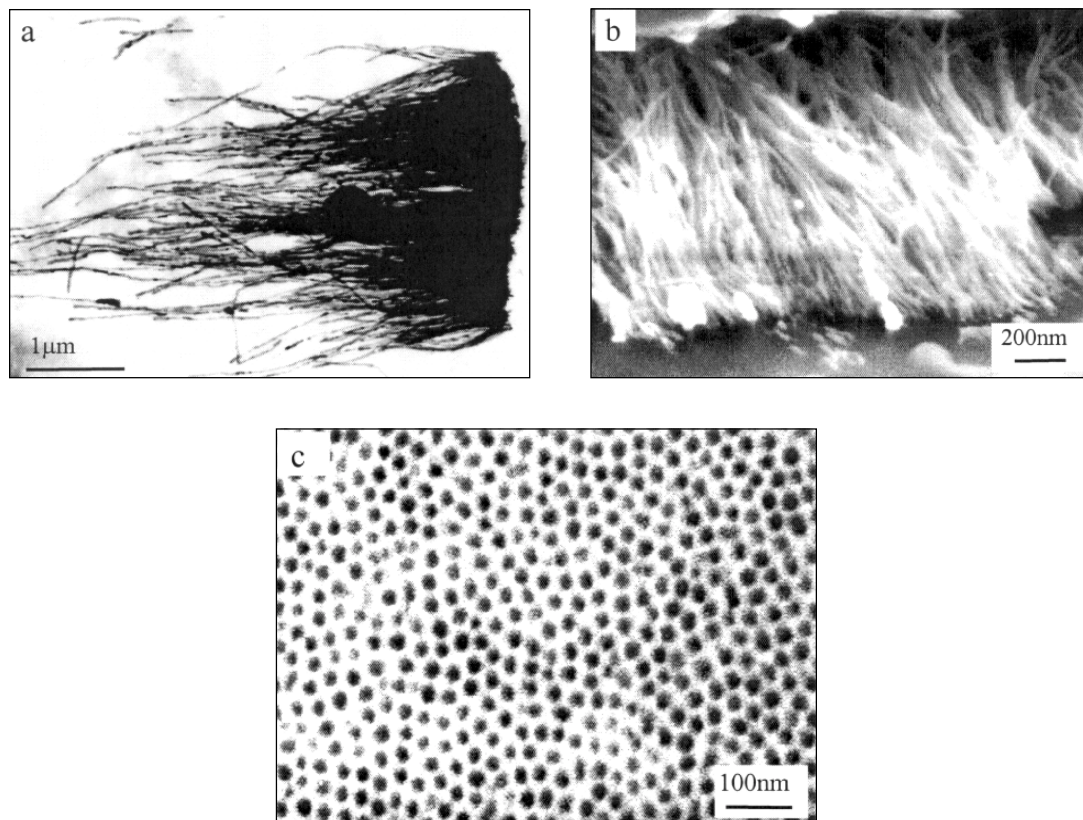
Figure 2a shows a typical TEM image of the CdS nanowires prepared by dc electrodeposition in porous AAO template with a diameter of 20 nm. These nanowires have a diameter around 20 nm, which corresponds to the diameters of the pores of the template used (Fig. 2c). Their length may vary from 1 to tens micrometers controlled by the deposition time, speed, etc. Figure 2b shows the SEM image of the nanowires without the AAO templates. The nanowires with uniform length, diameter, and direction of growth are observed in this figure. Also, it is clearly shown that the growth of CdS nanowires begins at the bottom of the pores and the wires are continuous.

The quantitative analysis of the EDAX spectrum of CdS nanowires (Fig. 3) shows that the atomic composition of S and Cd is close to a 1:1 stoichiometry. The electron diffraction pattern of the CdS nanowires (Fig. 4) obviously exhibits the hexagonal single crystalline structure of CdS.

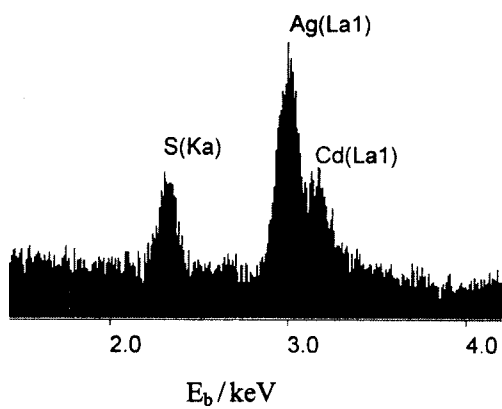
Figure 5 shows an HREM image of a single CdS nanowire with a diameter of about 20 nm. The interplanar spacing is about 0.32 nm, which corresponds to the {101} plane of hexagonal system of CdS. The {101} lattice fringes are approximately vertical to the wire axis of a single CdS nanowire. This image furthermore reveals that the nanowires have a uniform hexagonal single crystalline structure of CdS.

In addition, the CdS nanowire can not be obtained in aqueous electrolyte directly by ac electrodeposition on the AAO/Al substrate because the electrodeposition becomes dominated by the processes much more accessible to the cracks and defects, which will result in pitting corrosion without any CdS deposition [19]. However, this problem also can be avoided by using dc electrolysis.

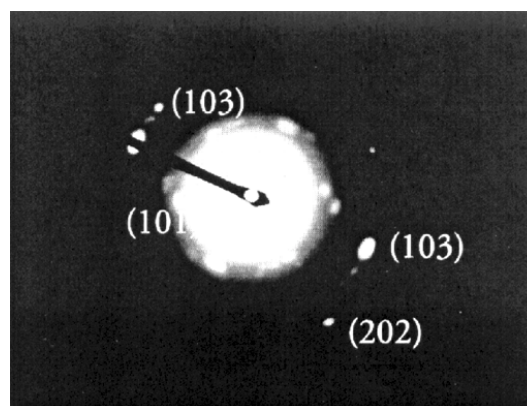
Figure 6 shows the SEM images of CdS nanowires prepared by dc electrolysis in aqueous solution consisted of 0.5 M CdS, 0.1 M EDTA and  $0.5 \text{ M S}_2\text{O}_3^{2-}$  in a pH range of 5–6 at a constant current density of  $1 \text{ mA}/\text{cm}^2$  for 60 min. It is visible that the length of the nanowire array is up to  $30 \mu\text{m}$  and the diameters of the nanowires are about 90 nm, which correspond to the pore sizes of the template used. The EDAX spectrum quantitative analysis of the nanowires shows that the atomic composition of S and



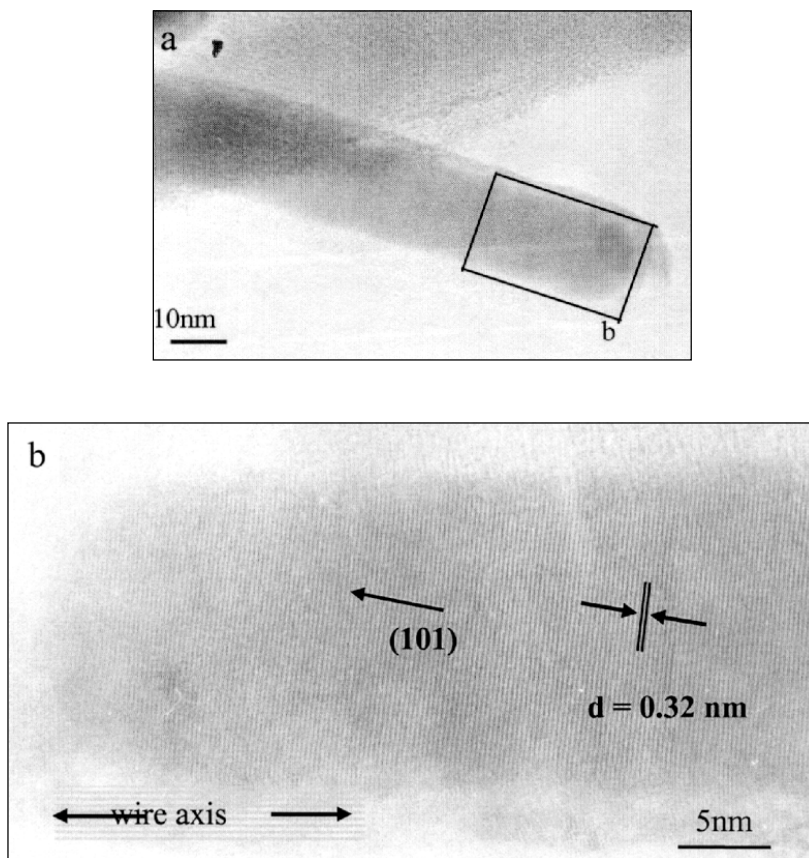
**Fig. 2** The electron microscope images of the CdS nanowires by dc electrodeposition in the porous AAO template with pore diameters of 20 nm: (a) TEM, (b) SEM image of the CdS nanowires and (c) SEM image of the template.



**Fig. 3** The X-ray energy diffraction analysis spectrum of the CdS nanowires produced by dc electrodeposition in AAO template.



**Fig. 4** The electron diffraction pattern of the CdS nanowires.



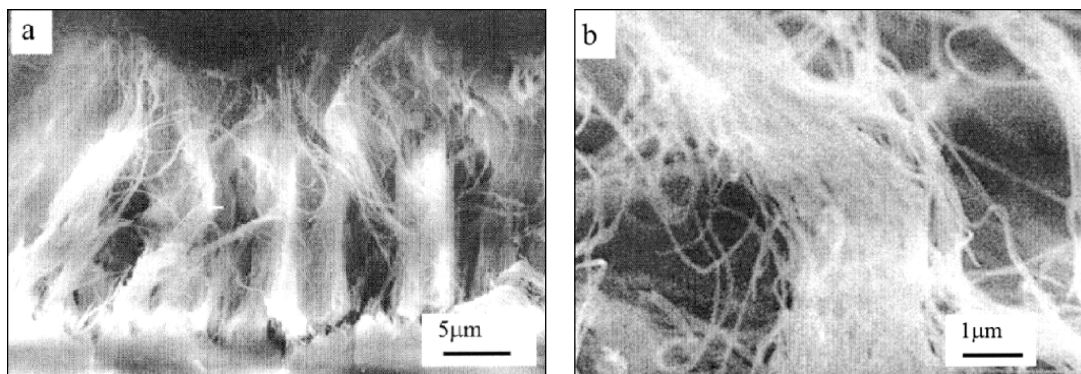
**Fig. 5** A typical HREM image of a single CdS nanowire with a diameter of 20 nm.

Cd is close to a 1:1 stoichiometry. However, electron diffraction and HREM results demonstrate that there was no evidence for crystalline structure of CdS in these nanowires. Furthermore, we propose that the ordering of crystalline structure of the nanowires may be improved by annealing. This study is in progress and will be discussed elsewhere.

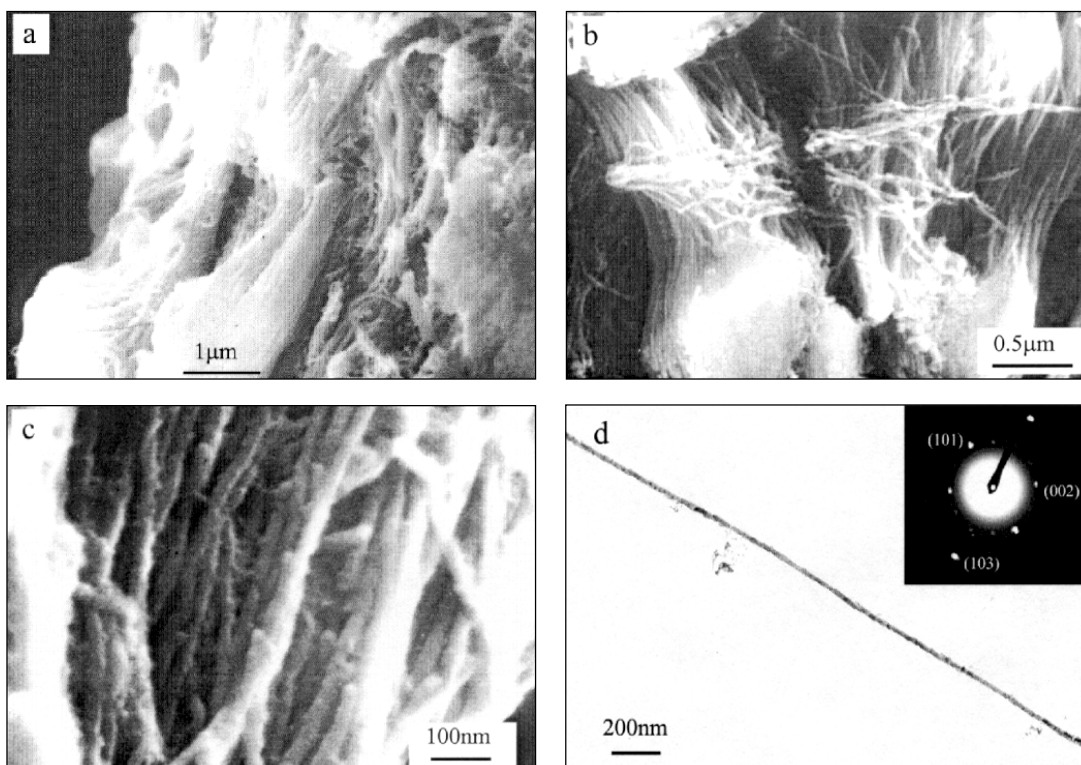
### CdSe nanowires

Figures 7a–c show the SEM images of CdSe nanowire arrays exposed from the AAO template. CdSe was cathodically deposited at the constant current density of  $0.85 \text{ mA}\cdot\text{cm}^{-2}$  for 30–60 min at  $185^\circ\text{C}$  by immersing the cell in an oil bath. The electrolyte solution consisted of  $0.05 \text{ mol}\cdot\text{L}^{-1}$   $\text{CdCl}_2$  and saturated elemental selenium in di-methylsulfoxide (DMSO). It is visible that all of CdSe nanowires are not randomly oriented and the length, diameter, and direction of growth of CdSe nanowires are quite uniform. Figure 7d shows a typical TEM image of single CdSe nanowire. The CdSe nanowire has a relatively straight morphology and a uniform width of 20 nm. The electron diffraction pattern taken from the CdSe nanowires is shown in the inset on the upper right of the micrograph, which are respectively corresponded to (002), (101) and (103) diffraction plane of the hexagonal CdSe single crystal.

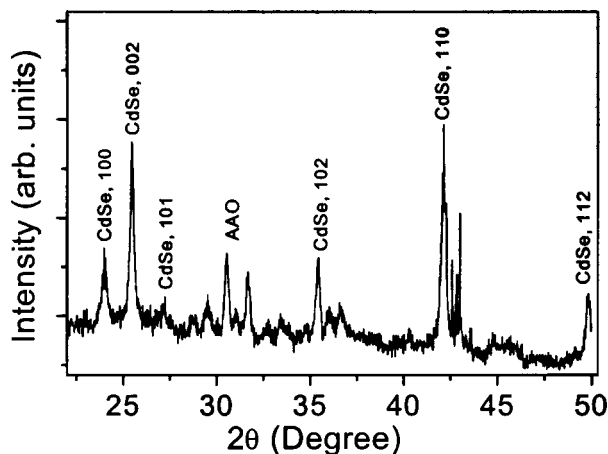
The X-ray diffractogram of the CdSe nanowire arrays by dc electrodeposition in AAO template with a diameter of 20 nm is shown in Fig. 8, in which the diffraction peaks could be assigned to CdSe,



**Fig. 6** SEM images of the CdS nanowires electrodeposited in the AAO template with a pore diameter about 100 nm from aqueous solution: (a) low-magnification and (b) higher magnification.



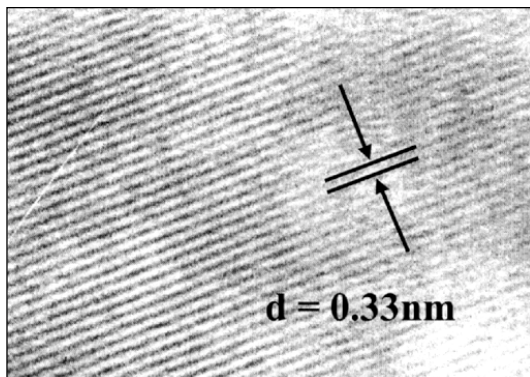
**Fig. 7** The electron microscopy images of CdSe nanowire arrays exposed by dissolving the AAO template: (a) low-magnification SEM, (b) higher magnification SEM at the bottom and (c) in the middle of the arrays, (d) TEM image of single nanowire with a diameter of 20 nm. The inset plot in Fig. 8d is the electron diffraction pattern of the single CdSe nanowire.



**Fig. 8** The X-ray diffractogram of the CdSe nanowire arrays produced by dc electrodeposition in AAO template.

Ag, and AAO without elemental Se and Cd. These XRD data indicate that the nanowires have diffraction patterns corresponding to the hexagonal phase of CdSe (ASTM standard 8-459). The interplanar diffraction spacing ( $d_{hkl}$ ) of CdSe nanowires with diameters of 20 nm differ slightly from those reported for polycrystalline CdSe. The relative intensity of the 002 diffraction peak, which corresponds to interplane distances  $d = 3.49\text{--}3.51$  (Å), is greater than that of the polycrystalline CdSe powder. This fact indicates that the *c*-axis of hexagonal crystals is preferentially aligned along the direction normal to the substrate rather than oriented randomly.

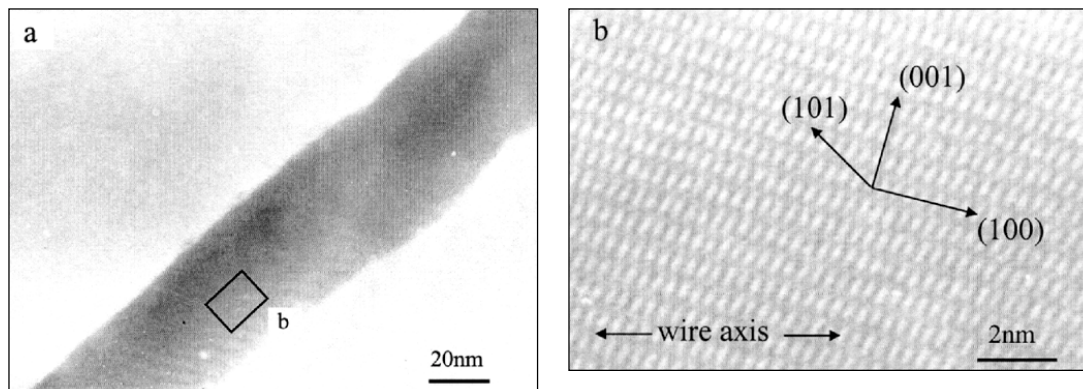
Figure 9 shows a typical HREM image of single CdSe nanowire with a diameter of 20 nm. The interplanar spacing is about 0.33 nm, which corresponds to the {101} plane of hexagonal system of CdSe. This image furthermore reveals that the structure of CdSe nanowire is a uniform hexagonal CdSe crystalline.



**Fig. 9** HREM image of CdSe nanowire produced by dc electrodeposition in AAO template.

### CdTe nanowires

CdTe was cathodically deposited in AAO template at the constant current density of  $1.5\text{ mA}\cdot\text{cm}^{-2}$  for 30–45 min at  $160^\circ\text{C}$ . The electrolyte solution consisted of  $1.00\text{ mol}\cdot\text{L}^{-1}$   $\text{CdCl}_2$ ,  $0.01\text{ mol}\cdot\text{L}^{-1}$   $\text{TeCl}_4$  and  $0.3\text{ mol}\cdot\text{L}^{-1}$  KI in glycol [22]. SEM and TEM results demonstrate that the oriented CdTe nanowire arrays have also been fabricated in this case. Figures 10a and 10b show the TEM and HREM images of single CdTe nanowire with a diameter of about 40 nm. In Fig. 10b, the interplanar spacings are about 0.74, 0.39, and 0.31 nm, which corresponds to the {001}, {100}, and {101} planes of hexagonal system



**Fig. 10** (a) TEM image of single CdTe nanowire produced by dc electrodeposition in AAO template. (b) HREM image of the CdTe nanowire.

of CdTe, respectively. The two-dimensional lattice image reveals that the single CdTe nanowire is a hexagonal single crystalline and the growth direction is along the [111] axis of the single nanowire.

## CONCLUSION

In summary, dc electrodeposition directly in the AAO template is a simple and efficient method to produce single crystal II-VI group compound semiconductor nanowire arrays. The diameters of the nanowires can be controlled by the pore diameters of the template. Furthermore, this approach can be used to fabricate other semiconductor (ZnS(Se, Te), Hg(S, Se, Te), GaAs, InP, etc.) nanowires both in aqueous solution and in nonaqueous solution system.

## REFERENCES

1. S. Iijima. *Nature (London)* **354**, 56 (1991).
2. A. P. Alivisatos. *Science* **271**, 933 (1996).
3. A. M. Morales and C. M. Lieber. *Science* **279**, 208 (1998).
4. D. P. Yu, C. S. Lee, I. Bello, X. S. Sun, Y. H. Tang, G. W. Zhou, Z. G. Bai, S. Q. Feng. *Solid State Commun.* **105**, 403 (1998).
5. G. T. Hu, T. W. Odom, C. M. Lieber. *Acc. Chem. Res.* **32**, 435 (1999).
6. H. I. Liu, N. I. Maluf, R. F. Pease. *J. Vac. Sci. & Tech. B* **10**, 2846 (1992).
7. T. Ono, H. Saitoh, M. Esashi. *Appl. Phys. Lett.* **70**, 1852 (1997).
8. S. Hu, A. Hamidi, S. Altmeyer, T. Koster, B. Spangenberg, H. Kurz. *J. Vac. Sci. & Tech. B*, **16**, 2822 (1999).
9. M. Andersson, A. Iline, F. Stietz, F. Trager. *Appl. Phys. A, Mater. Sci. & Proc.* **68**, 609 (1999).
10. G. Palasantzas, B. Ilge, J. De Nijs, L. J. Geerligs. *J. Appl. Phys.* **85**, 1907 (1999).
11. K. Hiruma, M. Yazawa, T. Katsuyama, K. Okawa, K. Haraguchi, M. Koguchchi, H. Kakibayashi. *J. Appl. Phys.* **77**, 477 (1995).
12. W. Q. Han, S. S. Fan, Q. Q. Li, Y. D. Hu. *Science* **277**, 1278 (1997).
13. C. R. Martin. *Science* **266**, 1961 (1994).
14. C. A. Foss, Jr. Gabor, L. Hornyak, J. A. Stockert, C. R. Martin. *J. Phys. Chem.* **98**, 2963 (1994).



15. S. Dubois, A. Michel, J. P. Eymery, J. V. Duvail, L. Piraux. *J. Mater. Res.* **14**, 665 (1999).
16. C. Jerome and R. Jerome. *Angew. Chem.* **37**, 2488 (1998).
17. S. A. Sapp, D. T. Mitchell, C. R. Martin. *Chem. Mater.* **11**, 1183 (1999).
18. L. Sun, P. C. Searson, C. L. Chien. *Appl. Phys. Lett.* **74**, 2803 (1999).
19. D. Routkevitch, T. Bigioni, M. Moskovits, J. M. Xu. *J. Phys. Chem.* **100**, 14037 (1996).
20. J. S. Suh and J. S. Lee. *Chem. Phys. Lett.* **281**, 384 (1997).
21. J. L. Hutchison, D. Routkevitch, M. Moskovits, R. R. Nayak. *Inst. Phys. Conf. Ser.* **157**, 389 (1997).
22. R. B. Gore, R. K. Pandey, S. K. Kulkarni. *J. Appl. Phys.* **65**, 2693 (1988).