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Preparation of Cadmium Sulfide Nanowire Arrays in Anodic Aluminum Oxide Templates

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The ordered structures of nanomaterials have been attracting more and more attention recently due to their unusual physical properties.[1−4] There are mainly two routes to fabricate such structures. One method is preparing nanomaterials and then organizing them.[5] The two- and three-dimensional ordered structures of CdSe,[6] Ag_2S,[7] Au,[8] Ag,[4,9] Pd,[10] and Co[11] have been fabricated through this method. The other method is the direct preparation of ordered structures from molecular or atomic precursors either physically or chemically. The solid-state methods for the fabrication of nanomaterials, such as physical and chemical vapor deposition (PVD[12] and CVD[1,13]), molecular beam epitaxy (MBE),[14] and manipulation through scanning tunnel microscopy (STM),[15] often need harsh conditions, expensive equipment, and state-of-the-art techniques.[16] However, the solution chemistry methods can avoid the above limitations.[16] And if some ordered systems are adopted as templates in the synthesis process, the ordered structure of nanomaterials can be obtained. Braun et al.[17] reported the synthesis of semiconductor−organic superlattices based on cadmium sulfide and cadmium selenide templated by hexagonal liquid crystals. We have prepared the parallel nanowires of CdS[18] and ZnS[19] with the diameter as small as 3 nm templated, also by hexagonal liquid crystals. These kinds of template are known as “soft” ones. The “hard” templates of porous polymer membranes and anodic aluminum oxides (AAO) are widely applied in the synthesis of nanowires and nanoparticles.[20,21] The AAO template takes a great advantage of arranging cylindrical pores, of uniform diameter, in a hexagonal array.[20] This greatly benefits the fabrication of ordered nanowire arrays. The Martin group has reported the synthesis of nanoparticles, nanowires, and nanotubules of metals, semiconductors, and polymers by electrodeposition,[22] sol−gel deposition,[23] and polymerization[24] in AAO membranes. Routkevitch fabricated CdS nanowire arrays by electrochemical deposition into an AAO template.[25] In this paper, we study the synthesis of CdS nanowire arrays with a solution reaction method by injecting the reactants into the pores of the AAO membrane.

Although Martin et al.[23] prepared several kinds of metal oxide nanofibrils and nanotubes through immersion of the AAO membranes into the corresponding sols and then calcination, there are few other reports about the synthesis of one-dimensional nanostructures in AAO membranes in aqueous solutions with methods other than electrodeposition. The reason usually is that the in situ formed nanoparticles hinder the dispersion of reactants into the inner part of the pores. We tried to prepare CdS nanowires in AAO with aqueous solutions of Cd^{2+} and H_2S or Na_2S as the reactants, but only low aspect ratio nanoparticles were obtained. We adopted thioacetamide (TAA) as the precursor of H_2S in this research. It can gradually liberate H_2S in aqueous solution, and react with Cd^{2+} slowly. It effectively eliminates the problem of the transfer of reactants into the inner part of the pores. The reactions are as follows:

$$CH_3CSNH_2 + 2H_2O = CH_3COONH_4 + H_2S$$

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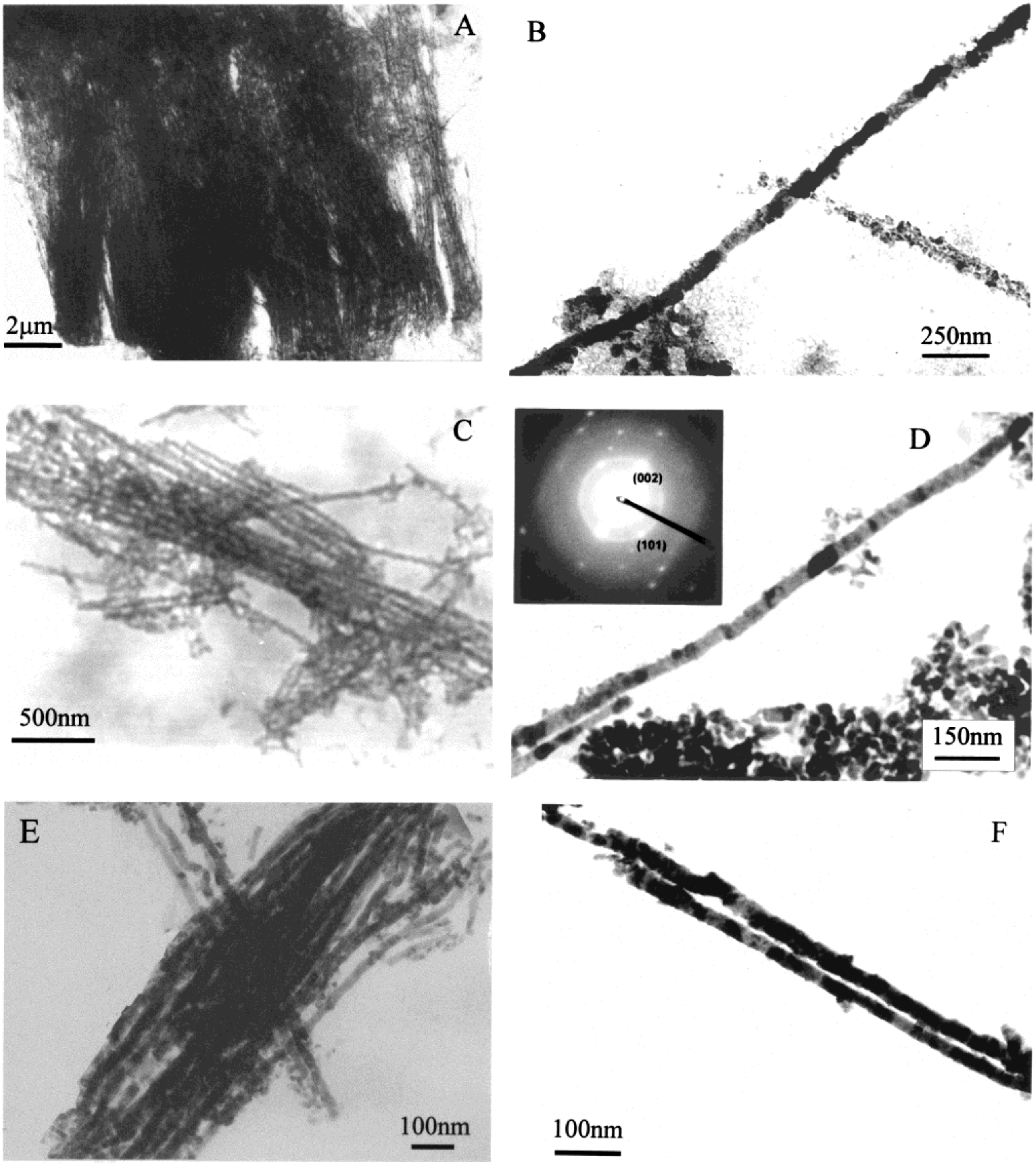

Figure 1. The TEM images of CdS nanowires formed in AAO membranes with different pore sizes: (A and B) 48 nm; (C and D) 32 nm; (E and F) 20 nm.

$$\mathrm{Cd(Ac)_2 + H_2S = CdS + 2HAc}$$

The AAO membranes were fabricated as reported in ref 26. The pore sizes were determined by SEM images to be 48 ± 10, 32 ± 6, and 20 ± 4 nm, respectively. The membranes were immersed into the aqueous solution of 1.0 mol dm^{-3} cadmium acetate ($Cd(Ac)_2$) under reduced pressure in a flask. The flask was then exposed to the atmosphere, and the $Cd(Ac)_2$ solution was poured into the pores of the membranes due to the pressure differentiation. After the membranes were dried and washed, the aqueous solution of TAA with the same concentration was poured into the membrane similarly. But this time the membrane was dried very slowly to ensure the CdS nanocrystals could grow well. The above procedure was repeated twice. The membranes were then annealed at 500 °C under N_2 for 1 h. The XRD measurement of the membranes containing CdS was performed with a Rigaku D/MAX2000 X-ray diffractometer. Finally, the membranes were dissolved in 1 mol dm^{-3} of aqueous NaOH, then dispersed in water under

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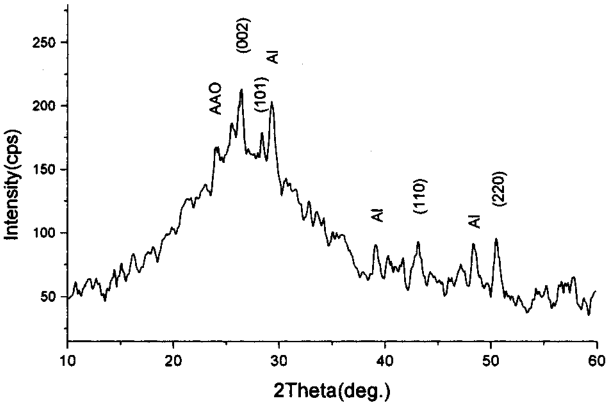

Figure 2. The XRD patern of AAO membrane containing CdS with the pore size of 48 nm (smoothing mode: Savitzkey-Glolay's, 10 points)

sonication, and dropped on the grids to investigate under a JEM-200CX TEM. The X-ray energy diffraction analysis was performed with a Philips 9100/6 EDAX.

Figure 1 shows the TEM images of CdS nanowires formed in AAO membranes with pore sizes of 48, 32, and 20 nm. Nanowire bunches were found and are shown in parts A, C, and E of Figure 1. Parts C and E of Figure 1 also present the parallel arrangements of nanowires. Parts B, D, and F of Figure 1 clearly show the separated nanowires. It can be found that the diameters of the wires are almost the same as the pore sizes. This indicates that the AAO membrane can act as a good template for CdS nanowires, and the wires should arrange into arrays. The EDAX result of the 48 nm sample shows that the abundance ratio of Cd and S is 51.35:48.65. This proves that the nanowires are composed of CdS. The electron diffraction pattern of the nanowire in Figure 1D indicates the nanowire is single crystal of hexagonal structure.

Figure 2 shows the XRD pattern of the 48 nm sample. It also indicates that the CdS crystals belong to hexagonal system. The diffraction peaks of (002), (101), (110), and (220) were all presented although they are all very weak. The amorphous halo may stem from the AAO membrane.

It can be concluded that the CdS nanowire arrays can be prepared by injecting the reactants into the pores of the AAO membranes in our study. Thioacetamide plays an important role as the precursor of H_2S to eliminate the resistance from the in situ formed CdS nanoparticles to the reactant transfer, and greatly benefits the crystallization of CdS nanowires in AAO. The fabricated CdS nanowire arrays are expected to present special electronic and optical properties.

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