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# Template Synthesis and UV-Vis Absorption Spectra of the Nanowire Arrays of Cadmium Chalcogenides

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The porous alumina membrane formed in the anodic oxidation of highly pure aluminum foil has attracted a great deal of attention in recent years[1]. It can be served as a desired template to prepare nanometer scale materials[2] due to its unique structure of discrete and cylindrical nanopores, paralleled one another, with the homogeneous size and distribution[3]. Chalcogenide semiconductors have promising prospect in the applications of photovoltaic[4] and photoconducting devices[5] and have been extensively exploited for many years. Olbright and his co-workers studied experimentally and theoretically the optical nonlinearties of $CdS_xSe_{1-x}$-doped glass[6]; Britt and Ferekides reported that the conversion efficiency in a solar cell of thin-film CdS/CdTe could be as high as 15.8 %[7]. Here we report the fabrication and UV-Vis absorption spectra of CdS、CdSe and $Cd_xZn_{1-x}S$ nanowire arrays deposited into the template matrix of porous alumina. The diameters of these nanowires were varied from 10 nm to 50 nm in our experiments.

Prior to anodization, a piece of highly pure (99.99 %) aluminum foil was degreased in acetone for two days and then electrochemically polished in a mixture of perchloric acid (70～72 wt %) and anhydrous ethanol in the volume ratio of 1∶5 under the DC voltage of 8V at temperature 30 ℃for 3 min to obtain a mirror surface. Aluminum anodization was conducted in 15 wt % sulfuric acid and 0.3 mol/L or 0.03 mol/L oxalic acid under DC voltages of 10 to 50 V at different temperatures for 30 min to produce varied diameters in the range from 7 nm to 50 nm.

Dsposition of CdS was carried out in a solution containing 0.055 mol/L $CdCl_2$ and 0.19 mol/L element S in dimethysulphoxide (DMSO) under AC voltage 30 V at 160 ℃for 5 min[8,9].

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We found that the deposition of CdSe could also be formed in a similar way. The co-deposition of $Cd_xZn_{1-x}S$ was done in a solution containing 0.055 mol/L $CdCl_2$ + $ZnCl_2$ with various Zn/Cd ratios and 0.19 mol/L element S in DMSO under AC voltage 50 V at 160 ℃ for 5 min[10]. After the deposition, the sample was rinsed with successive acetone, ethanol and double distilled water thoroughly. The anodic oxide membrane deposited with the semiconductor nanowire arrays was detached from the Al substrate by a treatment of saturated $HgCl_2$ solution. The thickness of the membrane was ca. 10 μm for the anodization in 15 wt % $H_2SO_4$ under DC 10 V at 25 ℃ for 30 min and ca. 20 μm in 0.3 mol/L $H_2C_2O_4$ under DC 25 V at 0～5 ℃ for 30 min.

Fig. 1 is a TEM (Transmission Electron Microscopy) image of a cross section of $Cd_{0.67}Zn_{0.33}S$ nanowire array in the template matrix of alumina. To characterize the structure and morphology of the chalcogenide nanowires, the deposited membrane was dissolved in 10 wt % NaOH solution and the nanowires were freed from the alumina matrix. After the complete removal of salts produced in the previous procedures, the solution with the suspension of nanowires was dropped onto a carbon coated Cu grid for TEM examination. Fig. 2 and Fig. 3 are the TEM and SAED (Selected Area Electron Diffraction) images of CdS and CdSe nanowires freed from the alumina matrix, respectively. The SAED analysis as shown in Tab. 1 revealed their wurtzite (hexagonal) structure.


Fig. 1 The cross section of $Cd_{0.67}Zn_{0.33}S$ nanowire arrays deposited in the matrix of anodic aluminum oxide(AAO)

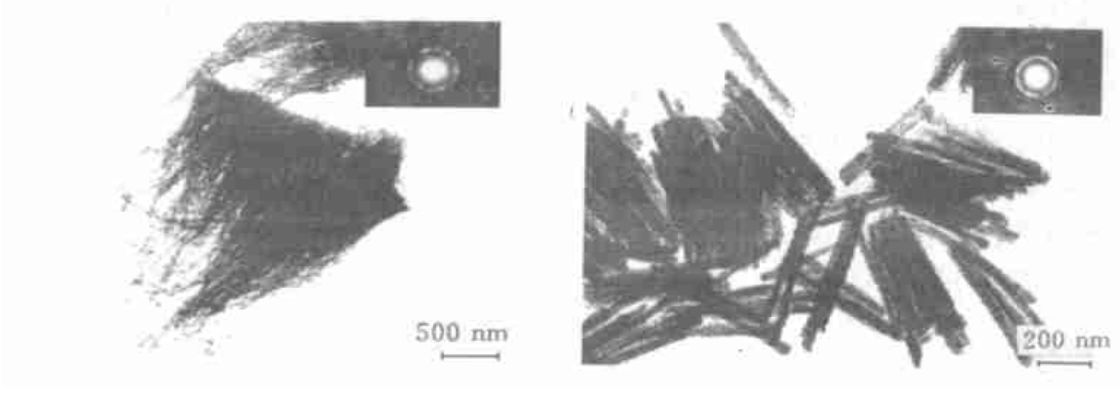


Fig. 2 The TEM and SAED images of CdS nanowires with the diameter of 10 nm

Fig. 3 The TEM and SAED images of CdSe nanowires with the diameter of 40 nm

Tab. 1　The d values in literature * and from the SAED images in our experiments

| | hk1 | d | |
|---|---|---|---|
| | | Literature data | Calculated results |
| CdS (Hexagonal) | 101 | 3.16 | 3.16 |
| | 002 | 3.36 | 3.36 |
| | 100 | 3.59 | 3.59 |
| CdSe (Hexagonal) | 100 | 3.72 | 3.73 |
| | 002 | 3.51 | 3.50 |
| | 110 | 2.15 | 2.15 |

* Power diffraction standards file, inorganic and organic. International centre for diffraction data. 1601 Parlane, Swarthmore, Pennsylvania. 1991, CdS, set: 41-1409; CdSe, set: 8-459

The UV-Vis absorption spectra of the semiconductor nanowire arrays electrochemically deposited in the porous alumina were recorded on the Hitachi U-3400 Spectrophotometer. Fig. 4 and Fig. 5 are the absorption spectra of CdS and CdSe nanowire arrays with different diameters respectively. It shows that the absorption edges of the nanowire arrays shift towards higher energies when the diameters are less than 25 nm, with respect to their bulk band gap (2.4 eV for CdS[11], 1.7 eV for CdSe[12], respectively. The data shown in Fig. 4 are in good agreement with the results obtained from the resonance Raman spectroscopy measured by Haslett and his co-workers[13]. Fig. 6 shows the absorption spectra of the $Cd_{0.67}Zn_{0.33}S$ nanowire arrays with different diameters but the same composition. The content of elements Cd and Zn was determined by an ICP (induced coupled plasma) measurement. In this figure, the absorption edge of the spectrum for the array with the diameter of 10 nm is about 50 nm less than the array with the diamter of 40 nm in their wavelength. To clarify whether the blue shift occurred in the above experiments had some connections with the template matrix of alumina, the absorption spectra, one with a reference of blank quartz plate and another with a reference of the quartz plate plus a membrane of blank alumina, were compared as shown in Fig. 7. The two curves in the figure coincided very well, showing that the free alumina matrix had no contribution to the blue shift in our experiments. It is worthy to notice that the absorption edges in UV-Visible spectra of clusters of cadmium Chalcogenide semiconductors show blue shift due to the quantum confinement effects[14,15] only when the size is less than or at least around the respective Bohr radius[16] (2.16 nm for CdS and 3.23 nm for CdSe), but the blue shift occurred for the nanowire arrays of Chalcogenide semiconductors in our experiments even when the diameters of nanowires were as great as 25 nm. It is under way in our group to ascertain the reasons for the phenomena.

In conclusion, porous alumina can be used as a template to fabricate the Cadmium chalcogenide arrays of nanowires with the discrete and parallel arrangement and the homogeneous size of diameter. The arrays possess many characteristics, such as showing blue shifts of edges in their

absorption spectra even when diameters are as high as 25 nm. The reasons for the results are waiting to be revealed.

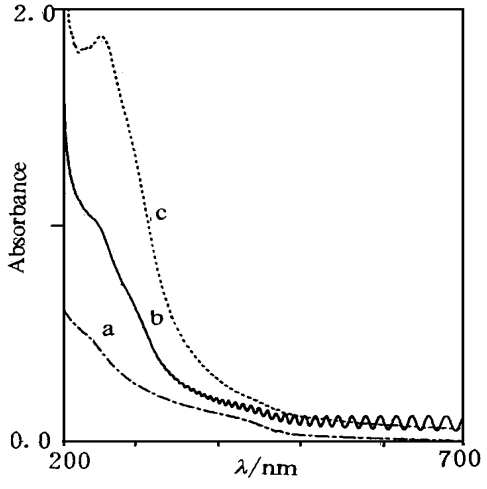


Fig. 4 The UV-Vis absorption spectra of CdS nanowire arrays with the diameters of (a) 7 nm, (b) 25 nm, and (c) 40 nm, respectively

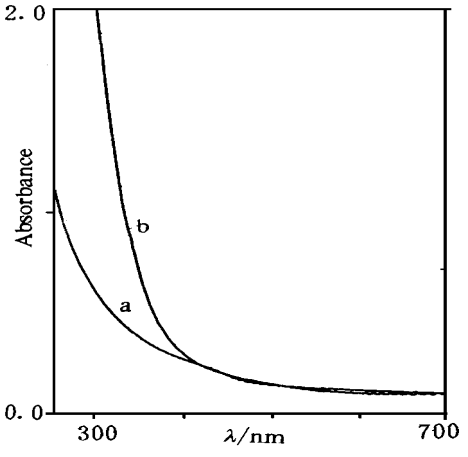


Fig. 5 The UV-Vis absorption spectra of CdSe nanowire arrays with the diameters of (a) 10 nm, (b) 25 nm, and (c) 50 nm, respectively

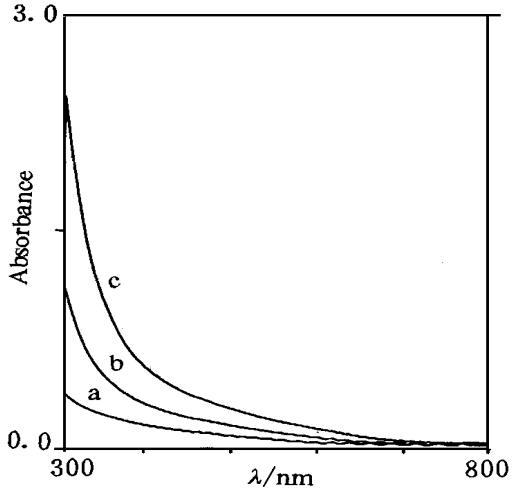


Fig. 6 The UV-Vis absorption spectra of $Cd_{0.67}Zn_{0.33}S$ nanowire arrays with different diameters of (a) 10 nm, (b) 40 nm

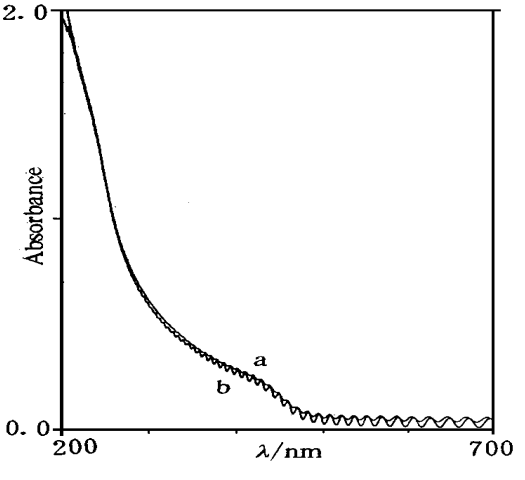


Fig. 7 The UV-Vis spectra of the same sample of a CdS nanowire array with different references, one being blank quartz plate (a) and another being the quartz plate plus a membrane of blank alumina(b)

Key words: Template synthesis, Porous alumina, Semiconductor, Cadmium chalcogenide, Nanowires

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# 镉的硫族化合物半导体纳米线阵列的模板法合成及其紫外可见吸收光谱研究

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**摘要**: 以多孔氧化铝为模板,用交流电分别通过含有相应的 $CdCl_2$、$ZnCl_2$、单质 S、Se 等的二甲亚砜(DMSO)溶液,沉积 CdS、CdSe 以及 $Cd_xZn_{1-x}S$ 半导体纳米线阵列并研究其紫外可见吸收光谱. 实验结果表明,当半导体纳米线的直径小于 25 nm 时,其吸收边相对于体相的吸收边产生蓝移,而且蓝移的幅度随着半导体纳米线直径的减小而增加,显示了明显的量子限域效应.

**关键词**: 模板法合成,多孔氧化铝,半导体,硫族化镉,纳米线
**中国分类号**: O 646, O 649.4 **文献标识码**: A