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Research Note

Synthesis of brush-like CdS nanorod arrays through a novel hydrothermal reaction of simultaneous solvent-oxidation-hydrolysis

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Brush-like CdS arrays composed of well-arranged nanorods have been successfully synthesized for the first time through a novel chemical reaction under the low-temperature hydrothermal condition. The reaction can be described as the solvent-oxidation-hydrolysis reaction among Cd, H_2O and thiourea. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence (PL). TEM results showed that these nanorods were about 20 nm wide with lengths varying from 1.25 μm to 3.5 μm. XRD pattern indicated that as-obtained CdS was hexagonal phase with good crystallinity. PL spectrum showed the products had novel optical property from the bulk counterpart. The formation mechanism was also explored.

Keywords: CdS; Nanorod array; Hydrothermal; Solvent-oxidation-hydrolysis reaction

1. Introduction

Over the past few years, shape control of nanomaterials has raised significant concerns in the preparation of one-dimensional (1D) nanomaterials such as nanorods, nanowires, nanotubes and nanobelts because they are expected to play an important role in fabricating nanodevices with novel electrical, magnetic and optical properties [1–4] etc. Much research has been done on CdS 1D nanomaterials because of its good catalytic performances and excellent nonlinear optical properties [5–6]. Many methods have been developed to synthesize 1D CdS nanostructured materials such as solvothermal route, DC electrode position, precipitation in micelles solution, thermal decomposition, sonochemical synthesis [7–12], etc. In these methods, reactions used include the direct redox reaction of Cd metal with S powders under high temperature, the direct or indirect precipitation of metal ions with Na_2S or some other

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sources of S^{2-} ions, and the thermal decomposition of molecular precursors containing M-S bonds, etc. Though there have been some reports of nanoarrays [13–14], the preparation of 1D nanorods arrays has never been reported.

Herein, we develop a novel kind of reaction based on a redox reaction of Cd metal with H_2O in the presence of thiourea to produce brush-like arrays of CdS nanorods.

2. Experimental

2.1. *Reagents and equipments*

Cadmium powder and thiourea (NH_2CSNH_2) used in this work were A.R. reagents purchased from Shanghai Chemical Reagent Factory, China. And these reagents were used without any pretreatment.

The transmission electron microscope (TEM) images and selected area electron diffraction (SAED) were acquired on a Hitachi H-800 transmission electron microscope (TEM) operated at 200 kV. X-ray powder diffraction (XRD) pattern was measured on Philips PW1700 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Room temperature photoluminescence (PL) spectrum was obtained on Perkin-Elmer LS-55 luminescence spectrophotometer.

2.2. *Synthesis of CdS nanorod arrays*

1.1240 g (0.01 mol) Cd powder and 1.5224 g (0.02 mol) thiourea (NH_2CSNH_2) were put into a PTFE-lined autoclave of 40 ml capacity. Then the autoclave was filled with 25 ml of deionized water, N_2 was passed to eliminate oxygen inside the solution. The autoclave was sealed and heated at 180 °C for 60 h, and was let to cool to room temperature naturally. The products were collected by filtration, washed with deionized water and absolute ethanol. An orange-yellow powder was obtained and was preserved in absolute ethanol for about two weeks for further characterization.

3. Results and discussions

3.1. *Morphology and structure*

TEM and ED pictures are shown in figure 1. Figure 1a shows that the sample is array composed of well-arranged nanorods. These rods have width of about 20 nm and lengths varying from 1.25 μm to 3.5 μm. Figure 1b is the magnified image of a certain part in figure 1a as shown in the picture. There are homogeneous nanorods with thin-ends. The electron diffraction (ED) pattern indicates that the products are single crystals. And it can be deduced from the ED pattern that the crystal is primitive hexagonal. The brighter spots have reciprocal poles which indicate that the products have orientational growth. Usually, nanoarray materials were synthesized through physical method or in the inducement of hard templates such as Al_2O_3, Si templates. The work in this paper successfully synthesized nanoarrays without any hard templates

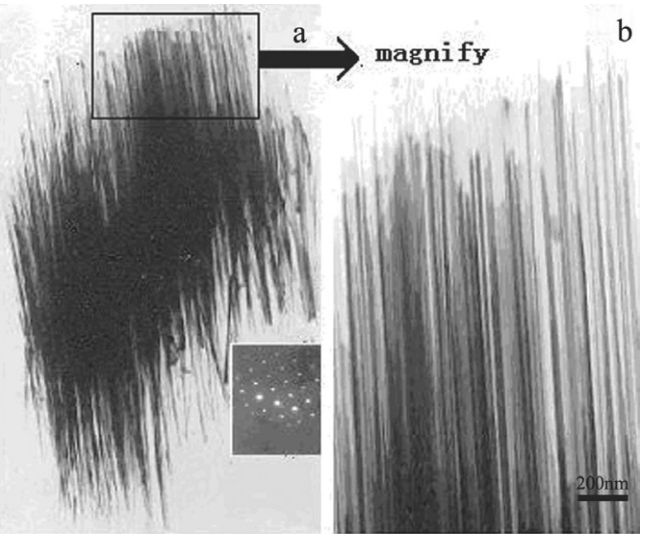

Figure 1. TEM image of thin-ends CdS nanorods array.

through facile chemical method. And the products can be used in preparing semiconductor nanodevices.

XRD pattern of as-prepared CdS array is given in figure 2. The pattern shows that the products are well-crystallized pure hexagonal greenockite phase with a calculated lattice parameter of $a = 4.138$ Å, $c = 6.725$ Å, very close to the reported data (JCPDS 6-0314). The unusually high peak of [100] shows that the sample has a preferential orientation in crystal face. And this is consistent with what shows in TEM picture.

3.2. *Optical properties*

Photoluminescence emission spectrum is shown in figure 3. The spectrum shows two widen peaks with the emission maximum at 545 nm and another at $\lambda_{em} = 485$ nm when excitation wavelength is 365 nm. It indicates that the as-obtained nanorod arrays have different optical properties from the bulk counterpart. Furthermore, these two emission peaks are both in visible area, thus the products can be used in fabricating green light emitting nanodevices.

3.3. *Mechanism of formation*

In this reaction, H_2O oxidize Cd and coordinate with it. And S atoms in $CS(NH_2)_2$ moleculars then attack the complex of $Cd(H_2O)_x$. Because there are amidogens in thiourea molecules, so H bonds make the molecules organize into the pattern shown in figure 4a. It is believed that $Cd(H_2O)S$ clusters in metastable state are formed in the reaction process. Then these clusters decompose to CdS crystal nuclei. And the NH_2 groups are absorbed on nuclei's surface, which restrain the crystal faces growth and make the nuclei grow into nanoparticles orientationally (figure 4b). These nanoparticles

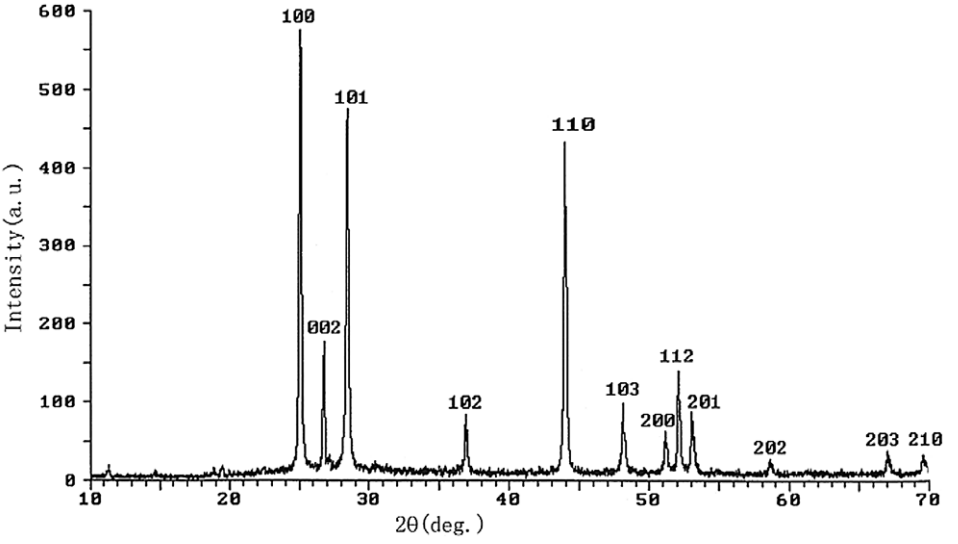

Figure 2. XRD pattern of as-synthesized CdS array.

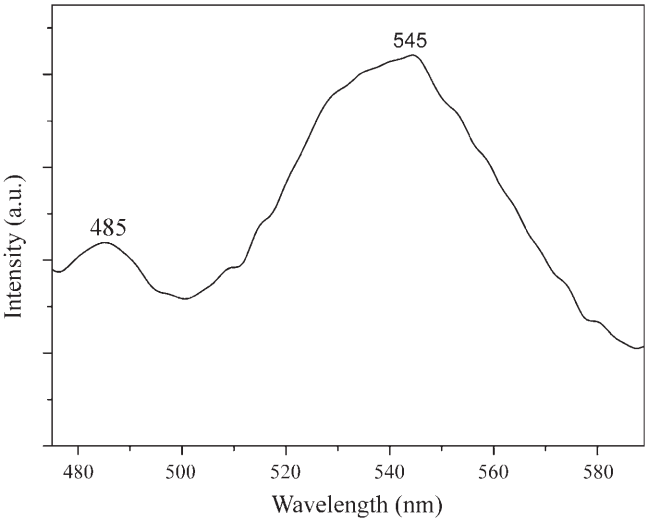

Figure 3. PL emission spectrum of CdS nanorods array (excited at 365 nm).

assemble into nanorods subsequently. These nanorods organize into array in the weak force such as H bond between NH_2 groups (figure 4c).

4. Conclusions

In conclusion, a new hydrothermal reaction of solvent-oxidation-hydrolysis to fabricate CdS was successfully established for the first time. Through this reaction, brush-like

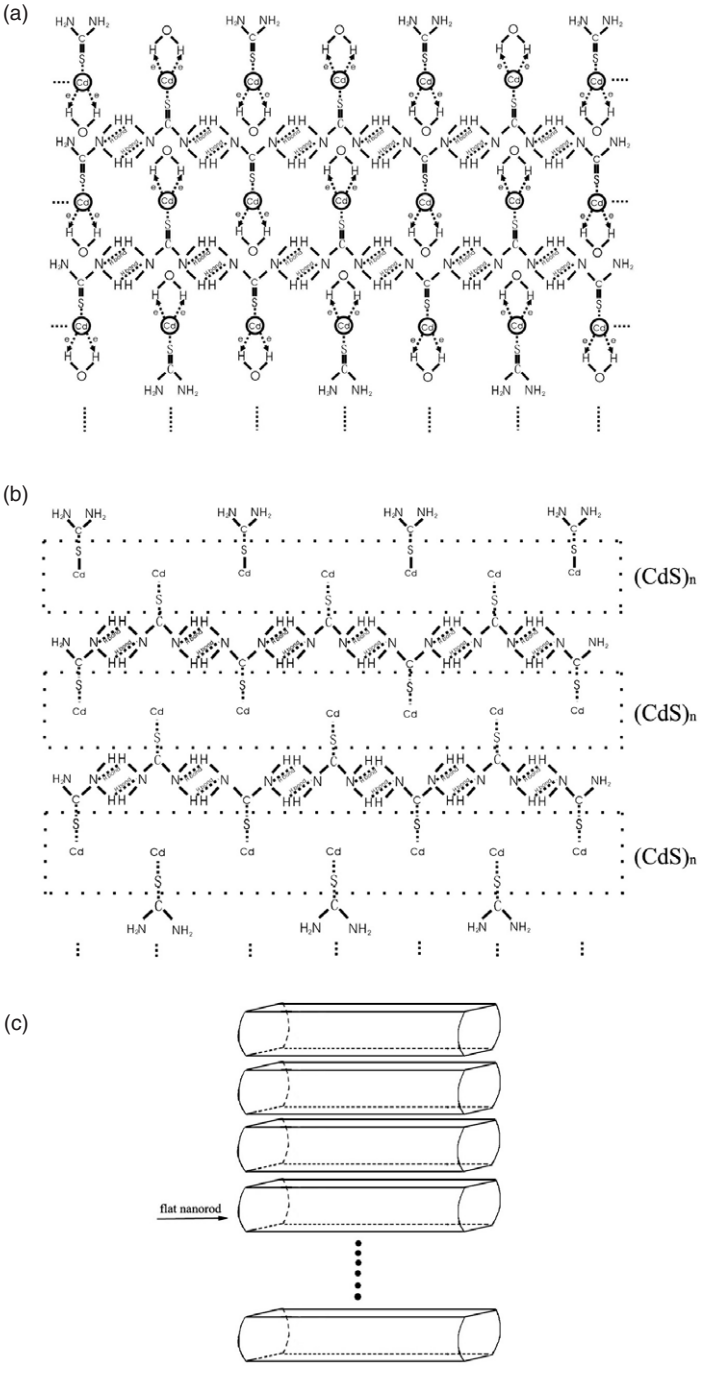

Figure 4. (a–c) The mechanism of the formation of brush-like CdS nanorods array.

array of nanorods was obtained. The work in this paper successfully synthesized nanoarrays without any hard templates through facile chemical method, which breaks through the tradition that nanoarray materials were synthesized through physical method or in the inducement of hard templates such as Al_2O_3, Si templates. This novel method can surely be used to synthesize other metallic sulfides with good morphologies, and it may be easily applied to large-scale manufacture for its merits, such as high yield and low reaction temperature. CdS nanorod arrays can also be used to fabricate semiconductor biosensors, light emitting nanodevices, etc.

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References

[1] Z.W. Pan, Z.R. Dai, Z.L. Wang. Nanobelts of semiconducting oxides. *Science*, **291**, 1947 (2001).
[2] D.J. Hornbaker, S.J. Kahng, S. Misra, B.W. Smith, A.T. Johnson, E.J. Mele, D.E. Luzzi, A. Yazdami. Mapping the one-dimensional electronic states of nanotube peapod structures. *Science*, **295**, 828 (2002).
[3] A.K. Wanekaya, W. Chen, N.V. Myung, A. Mulchandani. Nanowire-based electrochemical biosensors. *Electroanal*., **18**, 533 (2006).
[4] R. Agarwal, C.M. Lieber. Semiconductor nanowires: optics and optoelectronics. *Appl. Phys. A*, **85**, 209 (2006).
[5] Z.L. Zhang, Q.S. Wu, Y.P. Ding. Inducing synthesis of CdS nanotubes by PTFE template. *Inorg. Chem. Commun*., **6**, 1393 (2003).
[6] I.D. Parker. Carrier tunneling and device characteristics in polymer light-emitting diodes. *J. Appl. Phys*., **75**, 1656 (1994).
[7] Y.D. Li, H.W. Liao, Y. Ding, Y.T. Qian, L. Yang. Nonaqueous synthesis of CdS nanorod semiconductor. *Chem. Mater*., **10**, 2301 (1998).
[8] H. Zhang, G. Yang, W. Wang, D. Li, Y. Xie, N. Xia, Y.T. Qian. Polymer-controlled growth of CdS nanowires. *Adv. Mater*., **12**, 1348 (2000).
[9] D.S. Xu, Y.J. Xu, D.P. Chen, G.L. Guo. Preparation and characterization of CdS nanowire arrays by dc electrodeposit in porous anodic aluminum oxide templates. *Chem. Phys. Lett*., **325**, 340 (2000).
[10] C.C. Chen, C.Y. Chao, Z.H. Lang. Simple solution-phase synthesis of soluble CdS and CdSe Nanorods. *Chem. Mater*., **12**, 1516 (2000).
[11] Y.W. Jun, S.M. Lee, N.J. Kang, J. Cheon. Controlled synthesis of multi-armed CdS nanorod architectures using monosurfactant system. *J. Am. Chem. Soc*., **123**, 5150 (2001).
[12] S.M. Zhou, Y.S. Feng, L.D. Zhang. Sonochemical synthesis of large-scale single crystal CdS nanorods. *Mater. Lett*., **57**, 2936 (2003).
[13] V. Lionel, R. Lew, M. Arumugam. Aqueous chemical route to ferromagnetic 3-D arrays of iron nanorods. *Nano. Lett*., **2**, 1393 (2002).
[14] Z.R.R. Tian, J.A. Voigt, J. Liu, B. Mckenzie, M.J. Mcdermott. Biomimetic arrays of oriented helical ZnO nanorods and columns. *J. Am. Chem. Soc*., **124**, 12954 (2002).