Catalytic Growth of Large-Scale Single-Crystal CdS Nanowires by Physical Evaporation and Their Photoluminescence

Yewu Wang,* Guowen Meng, Lide Zhang, Changhao Liang, and Jun Zhang

Institute of Solid State Physics, Chinese Academy of Sciences,
Hefei 230031, People's Republic of China

Received November 2, 2001. Revised Manuscript Received January 22, 2002

Large-scale CdS nanowires were achieved by a new, simple, and low cost process based on thermal evaporation of CdS powders under controlled conditions with the presence of Au catalyst. The synthesized CdS nanowires have lengths up to several tens of micrometers and diameters about 60−80 nm. The growth of CdS nanowires is controlled by the conventional vapor−liquid−solid (VLS) mechanism. A strong red emission with a maximum around 750 nm was observed from the synthesized CdS nanowires at room temperature, which was attributed to their surface states. The technique we used is, in principle, generalizable as a means of fabricating other group II−VI semiconductor nanowires.

1. Introduction

Quasi one-dimensional nanostructured materials, such as nanowires and/or nanotubes, have been successfully synthesized and have received much attention because of their peculiar physical properties and potential applications in nanodevices.[1] Considerable effort has been made on the synthesis of nanowires with different compositions and/or nanotubes using laser ablation,[2−4] template,[5,6] solution,[7] and other methods.[8−11]

As CdS is one of the most important group II−VI semiconductors, having vital optoelectronic applications for laser light-emitting diodes and optical devices based on nonlinear properties, the synthesis of CdS nanowires has been rapidly developed. For instance, Routkevitch et al. and Xu et al. have fabricated CdS nanowires in porous anodic aluminum membranes (AAMs) by electrochemical deposition.[12−15] Meanwhile, Qian's group has established some new chemical techniques to synthesize CdS nanowires via a solvothemal route and polymer-controlled growth.[16,17] However, it is difficult to separate CdS nanowires from the products synthesized by the above-mentioned methods, and moreover, their yield is very low. Recently, laser-assisted catalytic growth has been developed for the synthesis of CdS and other semiconductor nanowires.[18] But the equipment for the laser-assisted catalytic method is very expensive and complicated.

Herein we report a new, simple, and inexpensive process to prepare large quantities of single crystalline CdS nanowires based on thermal evaporation of CdS powders under controlled conditions with the presence of Au catalyst. The nanowire growth is mediated by a vapor−liquid−solid (VLS) mechanism. A key feature of the VLS growth process and our method is that the equilibrium phase diagrams can be used to predict catalysts and growth conditions, thereby enabling rational synthesis of new nanowire materials. In addition, the compositions of raw materials are the same as those of the synthesized products. Therefore, this method can be used to continuously synthesize and produce large quantities of single-crystalline CdS nanowires at relatively high purity and low cost. Photoluminescence (PL) measurements show that the synthesized CdS nanowires exhibit a strong, broad, and stable red emission at room temperature, which could be attributed to their surface states.

2. Experimental Section

2.1. Sample Preparation. A silicon wafer (0.5 cm × 1 cm) was used as a substrate for the growth of CdS nanowires. The Si substrate was cleaned using a standard treatment in piranha solution (30% H_2O_2/20% H_2SO_4), rinsed with deionized

---

* To whom correspondence should be addressed. Fax: +86-551-5591434. E-mail: ywwangcn@china.com.

(1) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435.
(2) Duan, X. F.; Lieber, C. M. *Adv. Mater.* **2000**, *279*, 208.
(3) Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.
(4) Zhang, Y.; Suenaga, K.; Colliex, C.; Iijima, S. *Science* **1998**, *281*, 973.
(5) Huang, M. H.; Choudry, A.; Yang, P. *Chem. Commun.* **2000**, *12*, 1603.
(6) Zhu, J.; Fan, S. *J. Mater. Res.* **1999**, *14*, 1175.
(7) Holmes, J. D.; Johnston, K. P.; Doty, R. C.; Korgel, B. A. *Science* **2000**, *287*, 1471.
(8) Wu, Y. Y.; Yang, P. D. *Chem. Mater.* **2000**, *12*, 605.
(9) Bai, Z. G.; Yu, D. P.; Zhang, H. Z.; Ding, Y.; Wang, Y. P.; Gai, X. Z.; Hang, Q. L.; Xiong, G. C.; Feng, S. Q. *Chem. Phys. Lett.* **1999**, *303*, 311.
(10) Yu, D. P.; Bai, Z. G.; Ding, Y.; Hang, Q. L.; Zhang, H. Z.; Zou, y. H.; Wang, J. J.; Qian, W.; Zhou, H. T.; Xing, G. E.; Feng, S. A. *Appl. Phys. Lett.* **1998**, *72*, 3458.
(11) Tenne, R.; Margulis, L.; Genut, M.; Hodes, G. *Nature* **1992**, *360*, 444.
(12) Xu, D. S.; Xu, Y. J.; Chem, D. P.; Guo, G. L.; Gui, L. L.; Tang, Y. Q. *Adv. Mater.* **2000**, *12*, 520.
(13) Routkevitch, D.; Bigioni, T.; Moskovits, M.; Xu, J. M. *J. Phys. Chem.* **1996**, *100*, 14037.
(14) Suh, J. S.; Lee, J. S. *Chem. Phys. Lett.* **1997**, *281*, 384.
(15) Hatchison, J. L.; Routkevich, D.; Morkovits, M.; Nayak, R. R. *Inst. Phys. Conf. Ser.* **1997**, *157*, 389.
(16) Yang, J.; Zeng, J. H.; Yu, S. H.; Yang, L.; Zhou, G. E.; Qian, Y. T. *Chem. Mater.* **2000**, *12*, 3259.
(17) Li, Y. D.; Liao, H. W.; Ding, Y.; Qian, Y. T.; Yang, L.; Zhou, G. E. *Chem. Mater.* **1998**, *10*, 2301.
(18) Duan, X. F.; Lieber, C. M. *Adv. Mater.* **2000**, *12*, 298.

10.1021/cm0115564 CCC: $22.00

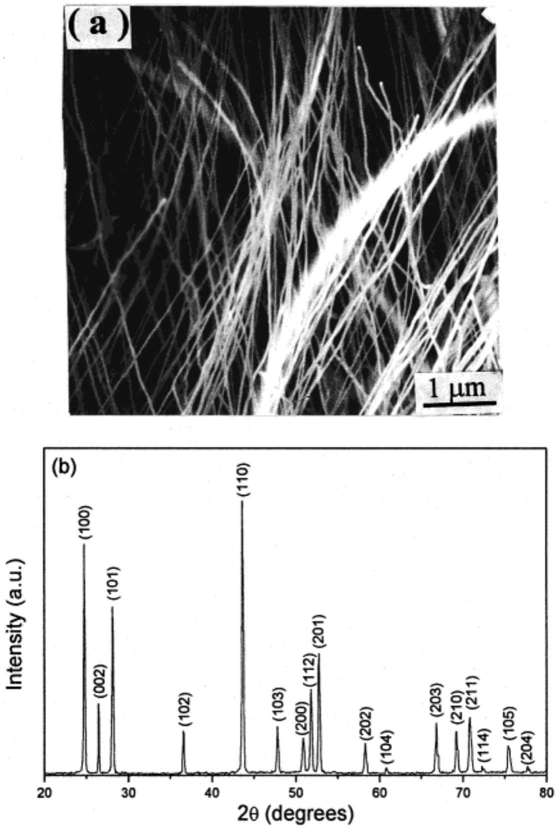

Figure 1. (a) Typical SEM image of bulk CdS nanowires. Large quantities of the nanowires were distributed homogeneously on the Si substrate. (b) XRD pattern taken on bulk CdS nanowires. The numbers above the peaks correspond to the (*hkl*) values of the wurtzite CdS structure.

water, and then deposited with an Au layer (about 40 nm) using a vacuum thermal evaporator. CdS (99.99%) powders were used as source materials, and Au film coated on the Si substrate was used as catalyst to synthesize CdS nanowires. The CdS powders were put into half of an alumina boat, and the Si substrate with Au layer was placed next to the CdS powders and along the downstream side of the flowing argon. The alumina boat, covered with a quartz plate to maintain a higher CdS vapor pressure, was placed in the middle of the quartz tube that was inserted in a horizontal tube furnace. Prior to heating, the system was flushed with high-purity Ar for 1 h to eliminate O_2. And then under a constant flow of Ar (100 sccm), the furnace was rapidly heated to 800 °C (about 4 min), held at this temperature for 120 min, and subsequently cooled to room temperature. It was observed that yellow spongelike products had appeared on the surface of the Si substrate.

2.2. Characterization and PL Measurement. The synthesized products were characterized using scanning electron microscopy [(SEM) JEOL JSM-6300], X-ray diffraction [(XRD) MXP18AHF], Raman scattering spectroscopy with a 514.5 nm incident wavelength, high-resolution transmission electron microscopy [HRTEM, (JEOL-2010)], and energy-dispersed X-ray spectrometry (EDS). For HRTEM observation, the synthesized products were ultrasonically dispersed in ethanol and a drop of the solution was then placed on a Cu grid coated with a holey carbon film. Photoluminescence (PL) measurements were carried out on a HITACHI 850-type visible−ultraviolet spectrophotometer with a Xe lamp as the excitation light source at room temperature.

3. Results and Discussion

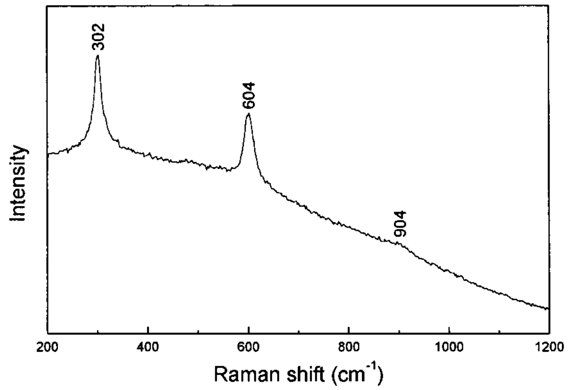

Figure 2. Raman spectrum of bulk CdS nanowires.

SEM observation (Figure 1a) reveals that the products are composed of large quantities of wirelike nanostructures with typical lengths in the range of several micrometers to several tens of micrometers; moreover, several hundred-micrometer nanowires can also be observed in the SEM image. Meanwhile, it can be observed that there exist a few nanoparticles at the tips of these nanowires, as indicated by the arrowhead (Figure 1a). XRD measurement (Figure 1b) shows that the products are wurtzite (hexagonal) structured CdS with lattice constants of $a = 0.4132$ nm and $c = 0\ 0.6710$ nm, consistent with the standard values for bulk CdS.[19] No diffraction peaks from CdO, Cd, S, or other impurities have been found in the synthesized products. The Raman spectrum of the bulk CdS nanowires (Figure 2) shows characteristic Raman shifts analogous to those of pure crystalline CdS.[14] The Raman peaks located at around 302, 604, and 904 cm^{-1} correspond to the first-, second-, and third-order transverse optical (TO) phonon modes of CdS, respectively. The morphology, structure, and composition of the CdS nanowires were characterized in detail using HRTEM, selected area electron diffraction (SAED), and EDS. Low-magnification TEM observation demonstrates that the nanowires are straight with uniform diameters and are typically terminated with a nanoparticle at one end. Figure 3a reveals a typical TEM image of one such single crystalline CdS nanowire with a diameter of 80 nm. The nanowire has a high aspect ratio, and its length is about several micrometers. The nanoparticle at the tip of the nanowire (Figure 3b) generally appears darker and has high contract compared with the nanowire stem. EDS measurements made on the nanoparticle and the nanowire stem indicate that the nanoparticle is composed of Au, Cd, and S (shown in Figure 4a) and that the nanowire stem is only composed of Cd and S (shown in Figure 4b). It is obvious that the Cu peaks in EDS spectra come from the copper grid. EDS analysis of the nanowire demonstrates that a 1:1 Cd/S composition within experimental error is consistent with stoichiometric CdS. The SAED pattern and HRTEM image (Figure 3c) reveal that the CdS nanowires are structurally uniform and single crystalline. The SAED pattern (Figure 3c, inset) recorded perpendicular to the nanowire long axis can be indexed for the [613] zone axis of single crystalline CdS, indicating that the nanowire growth occurs along the $\langle 131 \rangle$ direction. In addition, the lattice-resolved image of a CdS nanowire with diameter about

---

(19) Powder Diffraction File, Inorganic Vol. No PD1S-SiRB, 6-314 file. Published by the Joint Committee on Powder Diffraction Stardards USA, 1601 Park Lane, Swarthmere, PA 19081.

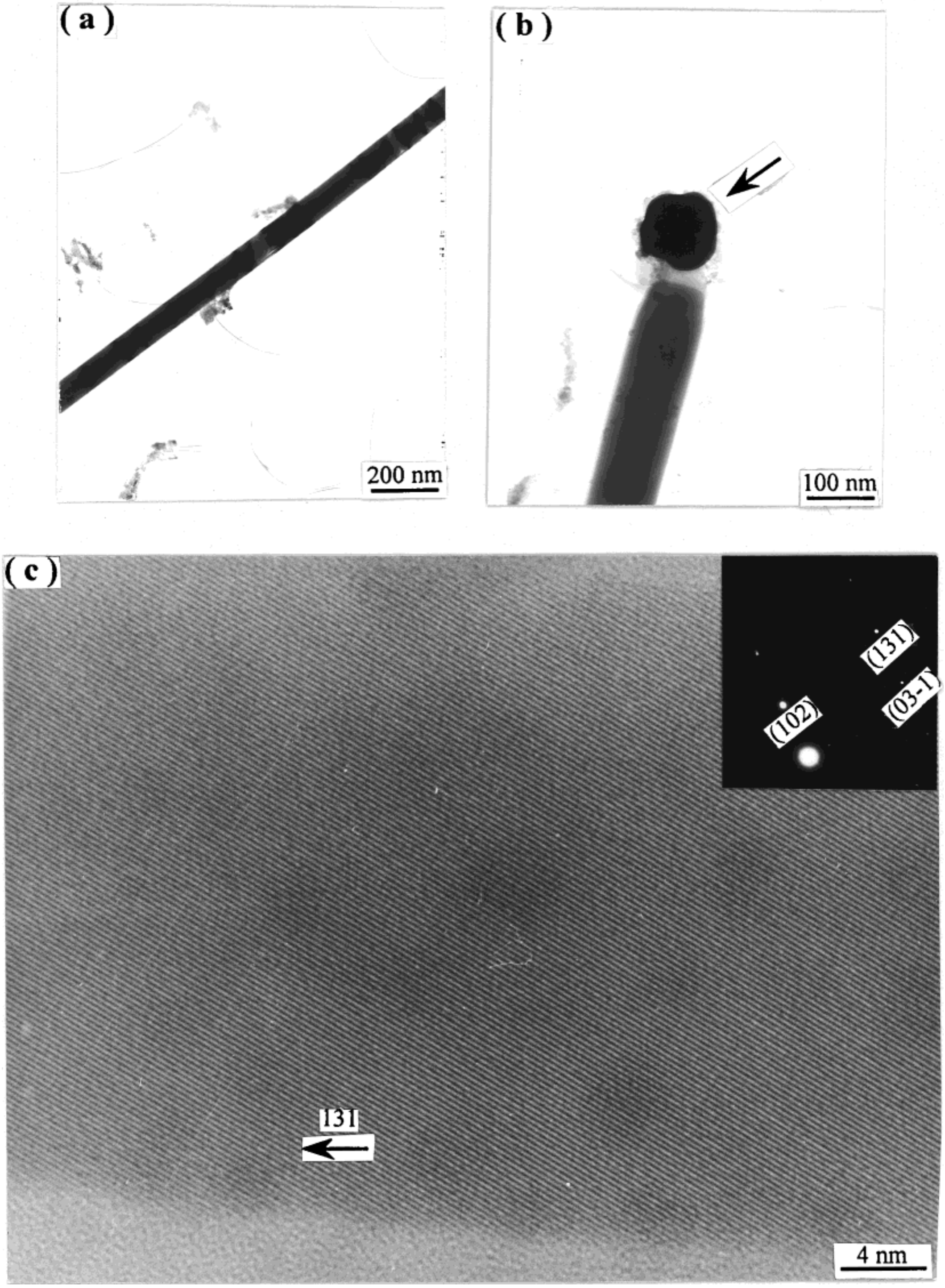

Figure 3. TEM and HRTEM images of the CdS nanowires: (a) image of a single CdS nanowire; (b) Au/CdS alloy cluster at the tip of a nanowire; (c) HRTEM image of CdS nanowire showing that the nanowire is single crystalline and free from dislocation and defects; (inset) corresponding electron diffraction pattern recorded with the electron beam perpendicular to the long axis of a nanowire, showing the growth direction to be $\langle 131\rangle$.

80 nm clearly reveals the (102) atomic planes with separation of 0.2486 nm. The growth plane (102) here is different from those of the CdS nanowires produced by ac and dc electrodeposition in DMSO solution containing $CdCl_2$ and S, in which the closely packed planes are the {111}[15] and {100}[12] planes, respectively.

There are two possible models for the growth of conventional crystal whiskers or nanowires, the screw dislocation and vapor–liquid–solid (VLS). It is well-known that the presence of a liquid drop is essential for the effective operation of the VLS mechanism. The solidified spherical droplets at the tips of the nanowires are commonly considered to be evidence for the operation of the VLS mechanism, which is in agreement with our experimental conditions and the observed results (Figure 2b). On the basis of the SEM, XRD, EDS, and HRTEM investigations, we believe that these nanowires are grown through the well-known VLS process with Au film as the catalyst.[20–22] This is apparent from the

---

[20] Tang, C. C.; Fan, S. S.; Dang, H. Y.; Li, P.; Liu, Y. M. *Appl. Phys. Lett.* **2000**, *77*, 1951.

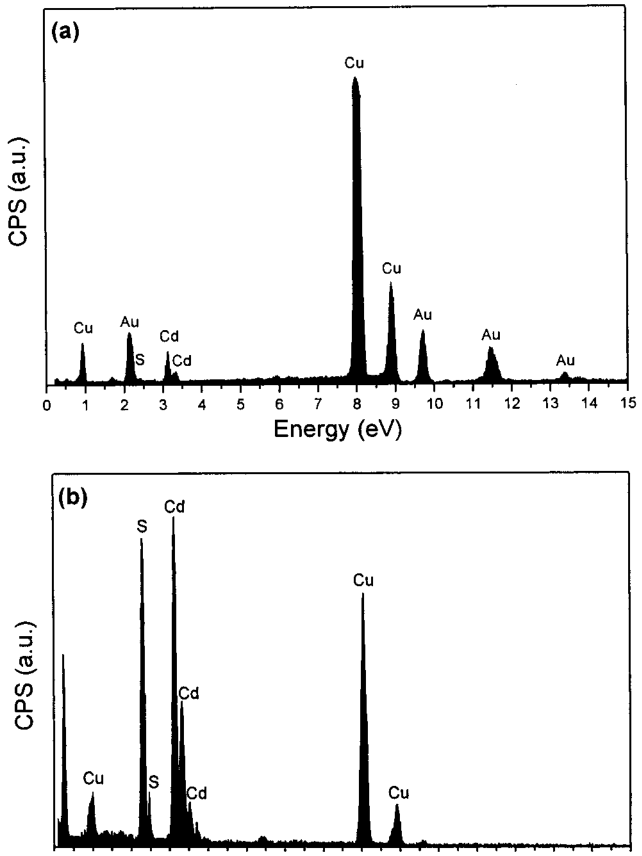

Figure 4. EDS spectra taken from the nanoparticle (a) and nanowire stem (b), respectively, in Figure 3c.

observation of Au–CdS alloy at the tip of nanowires. Although the detailed mechanism on ternary phase diagrams of Au–CdS is still not fully understood, we think that very small miscible droplets of Au–CdS may be generated rapidly during the heating process of the reaction and hence act as nucleation sites in the VLS growth of CdS nanowires.[23] In our experiment process, CdS vapor is rapidly generated at relatively high temperature for the fast heating speed by vaporizing the CdS powders. And then the CdS vapor is transported to and reacted with Au on the Si substrate to form Au–CdS alloy droplets. Subsequently, continuous dissolution of Cd and S atoms in alloy droplets leads to formation and growth of CdS nanowires through a VLS process.

The room-temperature photoluminescence (PL) measurement results of the CdS nanowires are shown in Figure 5. The excited wavelength was 510 nm, and no filter was used. Only a strong red emission band with a maximum around 750 nm has been observed in the PL spectrum patterns of CdS nanowires. Although some short wavelengths had been used as excitation light in PL measurements, only one emission band with a maximum at about 750 nm could be observed and its intensity was relatively weak. In the past several decades, the luminescence mechanisms of CdS have been studied. Usually, two emissions are observed from semiconductor nanoparticles—excitonic and trapped luminescence.[24,25] The excitonic emission is sharp and located near the absorption edge of the particles, while the trapped emission is broad and stokes-shifted. Butty et al.[26] have reported that two emission bands were observed in the PL spectrum of CdS nanoparticles. One is at 475 nm while the other is at about 690 nm. The band at 475 nm around the band edge has an intrinsic character while the other at 690 nm is due to trap or surface states. Zhan et al.[27] have reported that the PL spectrum of CdS nanowires consisted of one strong narrow emission at 380 nm (3.26 eV). The absence of emission from trap states suggests the stoichiometric nature of CdS nanowires, without a surface excess of Cd^{2+} or S^{2-} vacancies. The luminescence at 380 nm is attributed to higher-level transition CdS crystallites. It has been reported that this kind of band-edge luminescence arose from the recombination of excitons and/or shallowly trapped electron–hole pairs. The excitonic emission around 400 nm was observed in the CdS clusters encapsulated in zeolite-Y, which is considered to be the recombination of the bound excitons.[28] The photoluminescence spectra recorded at 298 and 77 K show a peak highly shifted toward long wavelengths with a maximum at 725 nm.[29] This can be attributed to trap emission. No direct recombination of the excitons is observed. It is thought that the trap emission is mainly due to the excess of sulfur at the interface, which is well-known to quench radiative band gap recombination, and not to the low crystallinity of the particles. In addition, the diameters of our synthesized CdS nanowires are significantly larger than the exciton Bohr diameter in CdS (6 nm). Therefore, the luminescence at 750 nm observed from the synthesized CdS nanowires (shown in Figure 5) is trapped emission. We believe that nanowires with high ratios (length/diameter) should have more surface and subsurface defects. It is therefore reasonable to believe that the red light emission from

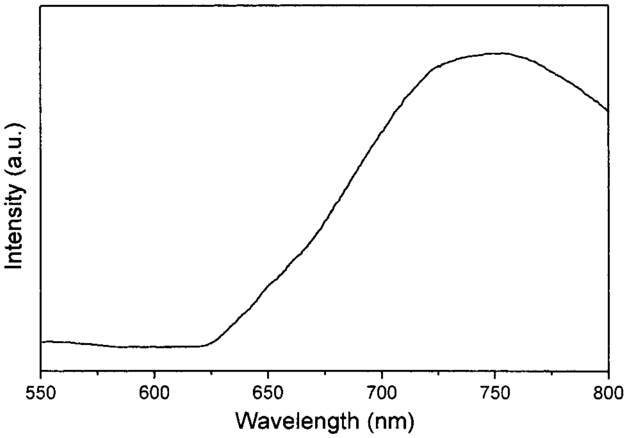

Figure 5. PL spectrum of bulk CdS nanowires.

---

(21) Peng, H. Y.; Pan, Z. W.; Xu, L.; Fan, X. H.; Wang, N.; Lee, C. S.; Lee, S. T. *Adv. Mater.* **2001**, *13*, 317.

(22) Zhang, H. Z.; Kong, Y. C.; Wang, Y. Z.; Du, X.; Bai, Z. G.; Wang, T. T.; Yu, D. P.; Ping, Y.; Hang, Q. L.; Feng, S. Q. *Solid State Commun.* **1999**, *109*, 677.

(23) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.

(24) Nell, M.; Marohn, J.; Mclendon, G. *J. Phys. Chem.* **1990**, *94*, 4359.

(25) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.

(26) Butty, J.; Peyghambarian, N. *Appl. Phys. Lett.* **1996**, *69*, 3224.

(27) Zhang, J. H.; Yang, X. G.; Wang, D. W.; Li, S. D.; Xie, Y.; Xia, Y. N.; Qian, Y. T. *Adv. Mater.* **2000**, *12*, 1348.

(28) Chen, W.; Wang, Z. G.; Lin, Z. J.; Lin, L. Y. *Solid State Commun.* **1997**, *101*, 371.

(29) Pinna, N.; Weiss, K.; Urban, J.; Pileni, M.-P. *Adv. Mater.* **2001**, *13*, 261.

the CdS nanowires in our work can be attributed to the above-mentioned surface states.

4. Conclusion

In conclusion, vapor transport has been employed to synthesize large-scale single crystalline CdS nanowires using the Au film as catalyst. SEM, EDS, and HRTEM results show that the CdS nanowires have diameters of about 60−80 nm and lengths up to several tens of micrometers. Photoluminescence (PL) measurements at room temperature show that the synthesized CdS nanowires emit a strong and stable visible light and that their luminescent peak is at about 750 nm. It is likely that our method may be extended to synthesize other semiconductor nanowires such as ZnS, $ZnCd_xS$, and (Cd, Zn)Se. The successful synthesis of these single crystalline semiconductor nanowires may open up new possibilities for using these materials as building blocks to create functional two-dimensional or three-dimensional nanostructured materials.

Acknowledgment. This work was supported by the Ministry of Sciences and Technology of China (Grant No. G1999064501) and the Natural Science Foundation of China (Grant No. 19974055).

CM0115564