Polymer Bulletin 61, 435–441 (2008)
DOI 10.1007/s00289-008-0970-2

Polymer Bulletin

Polymer-assisted solvothermal growth of CdS nanowires

Hongde Gai[1], Youshi Wu[2] (✉), Zhigang Wang[3], Lili Wu[2], Yuanchang Shi[2], Min Jing[3], Ke Zou[2]

[1]Shandong Special Equipment Inspection and Research Academy, Jinan 250061, China
[2]College of Materials Science and Engineering, Shandong University, Jinan 250061, China
[3]College of Materials Science and Engineering, Shandong Jianzhu University, Jinan, 250101, China
E-mail: gired@163.com

Received: 19 November 2007 / Revised version: 15 February 2008 / Accepted: 6 July 2008

Summary

Large quantities of CdS nanowires were successfully synthesized through a one-step poly (ethylene glycol)-assisted solvothermal route. The nanowires obtained were characterized by XRD, SEM, TEM, HRTEM, UV-vis and PL. The single crystalline nanowire is uniform in morphology with a [001] growth direction. Optical properties measurement reveals the quantum confinement effect of the CdS nanowires. Based on the comparative experimental results, a possible growth mechanism of CdS nanowires was proposed that the formation of CdS nanowires was controlled by the number of CdS nucleus at the initial reaction stage. The applicability of the growth mechanism for CdS nanowires was further verified by substituting poly (vinyl alcohol) for poly (ethylene glycol).

Introduction

During the past decades, one-dimensional (1D) semiconductor nanostructures, such as nanorods, nanowires and nanobelts, have been extensively investigated owing to their special properties and the potential applications in many fields [1-3]. Among these semiconductors, CdS, one of the most vital direct band-gap II-VI group semiconductors, has stimulated intense interest due to their wide application in photoelectric conversion for solar cell [4], light-emitting diodes for flat panel display [5] and photocatalyst for chemical reaction [6]. Over the past few years, various new routes have been developed to synthesize 1D CdS nanostructures including template-assisted synthesis [7], laser ablation [8], vapor-liquid-solid [9], colloidal micelle [10] and solvothermal methods [11], etc. For example, a nanocluster-catalyzed VLS route using $Cd(S_2CNEt_2)$ as precursor was explored by Lieber et al [9]. Xie and his group obtained CdS nanotubes through a micelle template interface reaction route [10]. Qian and coworkers found that CdS nanowires could be obtained in a mixed solvent of ethylenediamine and dodecanethiol [11]. However, further studies on controlling the length, aspect ratio and crystallization of the nanowires are still necessary for widespread application.

In this paper, a facile poly (ethylene glycol) (PEG)-assisted solvothermal route was reported to synthesize CdS nanowires in a large scale by using cadmium chloride and thioglycolic acid (TGA) as starting materials. Comparative experiments were carried out to investigate the influence of PEG on the growth of CdS nanowires. Based on the experimental results, a possible growth mechanism was proposed, according to which CdS nanowires could also be synthesized by substituting poly (vinyl alcohol) (PVA) for PEG.

Experimental section

Synthesis

Typical experiment (using 2g PEG to preparing CdS nanowires): 1mmol $CdCl_2 \cdot 2.5H_2O$, 2mmol thioglycolic acid (TGA) and 2g PEG10000 were put into a 50ml Teflon-lined autoclave, and then 40ml ethylenediamine was added into the autoclave as solvent. The autoclave was sealed and maintained at 150°C for 12 days and then cooled to room temperature naturally. The yellow precipitate was rinsed several times with distilled water and absolute alcohol. The product was dried at 50°C for 10h. The sample obtained was called T.

Comparative experiment 1 (using distilled water as solvent): 1mmol $CdCl_2 \cdot 2.5H_2O$, 2mmol TGA, 40ml distilled water and 2gPEG10000 were added into a Teflon-lined autoclave with 50 ml capacity. The autoclave was sealed and maintained at 150°C for 12 days. After rinsed and dried, the sample was named C1.

Comparative experiment 2 (without PEG): 1mmol $CdCl_2 \cdot 2.5H_2O$, 2mmol TGA and 40ml ethylenediamine were added into a Teflon-lined autoclave with 50 ml capacity. The autoclave was sealed and maintained at 150°C for 12 days. After rinsed and dried, the sample was named C2.

Comparative experiment 3 (without PEG at the initial stage): The starting reactants were the same as comparative experiment 2. After one day's reaction at 150°C, 2g PEG10000 was added into the solution, and then the solution was kept at 150°C for another 11 days. After rinsed and dried, the sample was named C3.

Comparative experiment 4 (using 0.5g PEG): The experimental process is similar to the typical experiment expect that the amount of PEG10000 was 0.5g. The sample obtained was named C4.

Comparative experiment 5 (using PVA instead of PEG): PEG was substituted by PVA of equal weight while the other conditions were the same as the typical experiment. The sample obtained was named C5.

Characterization

X-ray power diffraction (XRD) analysis was performed on a Riganku D/max-rc X-ray diffractometer equipped with Ni-filtered Cu Kα radiation (λ=1.5418Å). The morphology and selected-area electron diffraction (SAED) patterns were examined with a JEOL JEM-100CX II transmission electron microscope (TEM). Field-emission scanning electron microscope (FESEM) images were obtained on a JEOL JSM-6700F scanning electron microanalyzer. High-resolution transmission electron images were recorded using a JEOL JEM-2100 electron microscope. UV-vis absorption spectrum was measured on a 760CRT double beam UV-vis spectrophotometer. Photoluminescence (PL) spectrum was recorded on an Edinburgh FLS920 luminescence spectrophotometer.

Results and Discussion

Figure 1 shows a typical XRD pattern of the sample T obtained from typical experiment. All the strong and sharp diffraction peaks are consistent with wurtzite CdS phase. The lattice constants of a=4.136Å and c=6.711Å calculated from the XRD pattern are in agreement with the values in JCPDS Cards 060314. No other impurities could be detected, indicating the high purity of the sample.

Figure 2 shows the SEM and TEM images of the sample T. A large number of nanowires with high aspect ratio can be observed. The length of single CdS nanowire is up to ten micrometers. The microstructure of CdS nanowires was examined by SAED and HRTEM, as shown in Figure 3. In Figure 3a, the nanowire is uniform with diameter about 40 nm. The corresponding SAED pattern (the inset in Figure 3a) demonstrates that the well crystalline CdS nanowire has a [001] growth direction, which can be further verified by HRTEM image. The lattice fringes can be clearly seen in Figure 3b and the lattice spacing of 3.36 Å between adjacent lattice planes corresponds to the distance of (002) planes of wurtzite CdS, confirming that [001] is the preferred growth direction for the CdS nanowires.

In order to understand the growth mechanism of CdS nanowires, comparative experiments were carried out. Figure 4 shows the TEM images of the samples C1-C5. As shown in Figure 4a, Sample C1, which is prepared by using distilled water

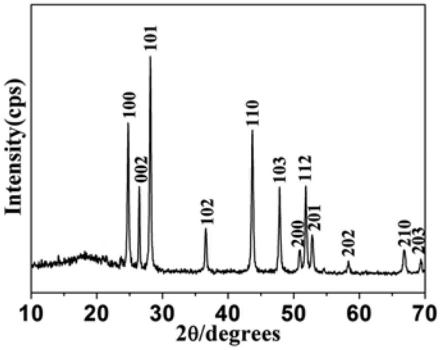

Figure 1. Typical XRD pattern of sample T obtained from typical experiment

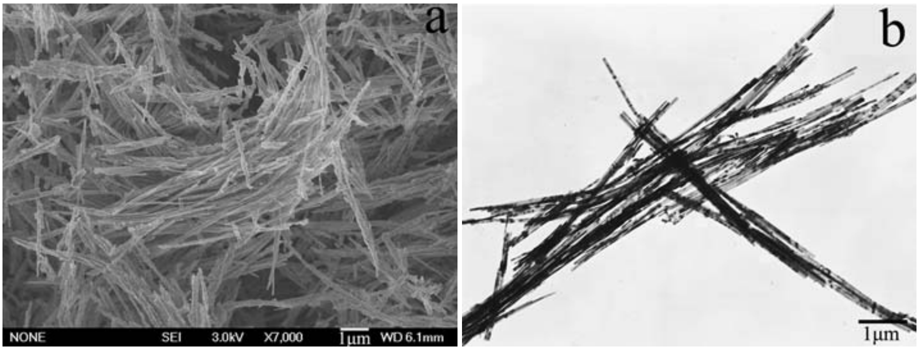

Figure 2. SEM (**a**) and TEM images (**b**) of CdS sample T synthesized via PEG-assisted solvothermal process

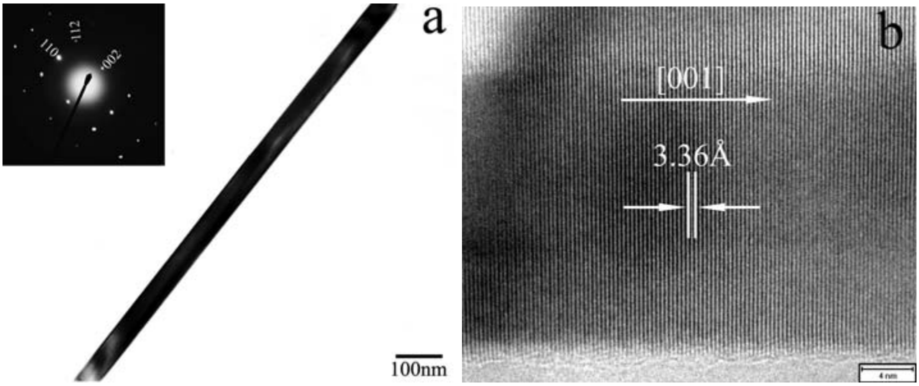

Figure 3. (**a**) Typical TEM image of a single CdS nanowire, the inset shows the corresponding SAED pattern. (**b**) HRTEM image of a single CdS nanowire with clear lattice fringes

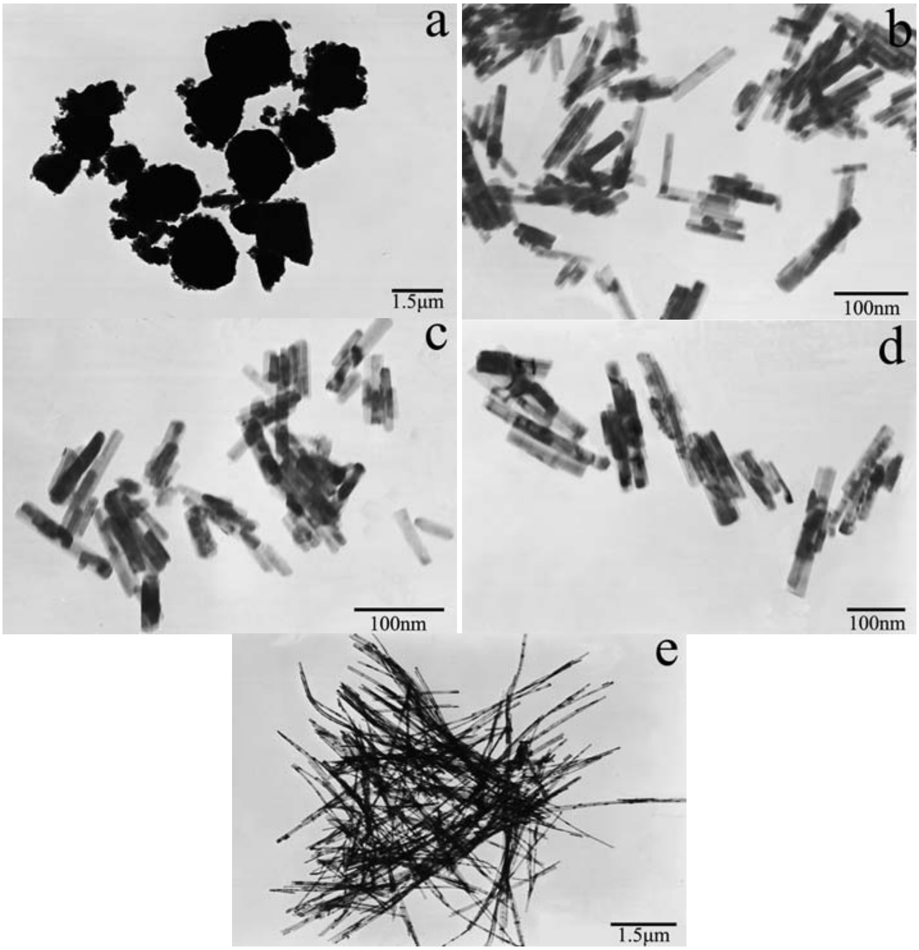

Figure 4. TEM images of CdS samples: (**a**) C1 (**b**) C2 (**c**) C3 (**d**) C4 (**e**) C5

replaced ethylenediamine as solvent, is composed of irregular particles, demonstrating the crucial role of ethylenediamine for the 1D growth of CdS product. Sample C2, which is prepared by using ethylenediamine as solvent but without PEG, is composed of short nanorods with aspect ratio around 4, as shown in Figure 4b, similar to that obtained by Qian [12]. Sample C2 is short nanorod but not irregular micrometer particles that can be attributed to the selective absorption of ethylenediamine on different crystal planes of CdS. However, the aspect ratios of these CdS short nanorods are far less than sample T, owing to the absence of PEG. Therefore, it can be found that the formation of CdS nanowires with high aspect ratio is highly dependent on the PEG added into the solution. Another two comparative experiments were carried out to prepare sample C3 and C4 in order to explore the effect of adding time and amount of PEG on morphology of CdS product. Sample C3 was prepared by adding PEG after 24h reaction and it is also constitutive of CdS nanorods as shown in Figure 4c, like sample C2, indicating that PEG plays a crucial role at the initial reaction stage during the formation of CdS nanowires. In comparative experiment 4, the amount of added PEG is 0.5g which is a quarter of that used in typical experiment, and sample C4 obtained is comprised of unhomogeneous nanorods, as shown in Figure 4d. The length of these nanorods are shorter than sample T but longer than sample C2, which demonstrats that the length of CdS nanowires can be controlled by altering the amount of PEG added into the solution.

As stated above, a possible mechanism can be proposed to explain the growth of CdS nanowires under the assistance of PEG. At the initial reaction stage, owing to the break of C-SH bond in thioglycolic acid at 150°C, S^{2-} is released slowly and then combines with Cd^{2+} to form CdS nuclei. However, the addition of PEG increases the viscosity of solution, resulting in the reduction of mobility of Cd^{2+} and S^{2-}, and ultimately resulting in the decrease of the nucleation rate. Therefore, the number of CdS nuclei in the presence of PEG is greatly less than that in the absence of PEG. With the progress of the reaction, owing to the 1D structure-directing template effect of ethylenediamine, the newly generated CdS adopts appropriate position in these nuclear, and CdS nanorods gradually grow into nanowires with the assistance of PEG.

The above mechanism can explain why sample C3 and C4 are nanorod-like. In comparative experiment 3, the addition of PEG is after 24-hour's reaction when much CdS nuclei has been formed and aggregated together. The newly added PEG does not reduce the number of CdS nuclei, so there are only CdS nanorods formed like sample C2. In comparative experiment 4, only 0.5g PEG is added and the solution viscosity is less than that of typical experiment but more than that of comparative experiment 2(without PEG). Thus, the nanorods of sample C4 is longer than sample C2 but shorter than sample T.

The applicability of the mechanism for CdS nanowires growth is verified by substituting PEG with other polymer. In comparative experiment 5, sample C5 obtained by using PVA as assistant reagent is also composed of CdS nanowires with high aspect ratio, as shown in Figure 4e, like the typical procduct of Figure 2. This experimental result indicates that PVA has the same contribution as PEG for the growth of CdS nanowires. Therefore CdS nanowires can be prepared by using appropriate assistant reagent which can increase the solution viscosity and sequentially control the nucleation number at the initial reaction stage.

The optical properties of CdS nanowires(sample T) are characterized by UV-vis and PL. Figure 5a is the UV-vis absorption spectrum. The obvious absorption peak around 486nm can be assigned to the first excitation of CdS. Comparing to the absorption

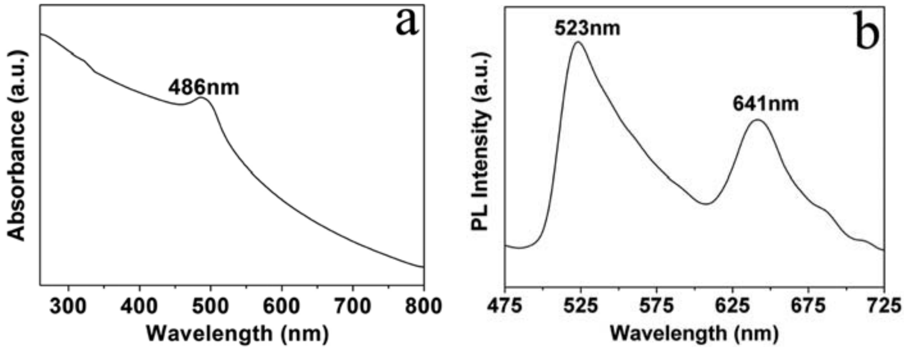

Figure 5. UV-vis absorption spectrum (**a**) and photoluminescence emission (λ_{ex}=400 nm) spectrum (**b**) of CdS nanowires obtained from typical experiment

peak of bulk CdS crystal(513nm), the blue shift of absorption peak can be attributed to the quantum size effect. Figure 5b is the room-temperature photoluminescence spectrum of the same sample. There are two emission bands in the spectrum. The green emission band around 523nm can be ascribed to near-band-edge emission, and the red emission band around 641nm is thought to be due to surface states emission, which may be caused by the structural defects on the surface of CdS nanowires [13].

Conclusion

In summary, single crystalline CdS nanowires have been synthesized successfully on a large scale in the presence of PEG through a solvothermal route. On the basis of comparative experiments, a possible growth mechanism was proposed that the length of nanowires can be controlled by adjusting the number of nucleus. The synthesis of CdS nanowires by substituting PVA for PEG confirmed the applicability of the growth mechanism. The mechanism for nanowire formation may be extended to produce other 1D semiconductor materials by selecting appropriate reagent to reduce nuclear number.

Acknowledgements. The work is supported by Shandong Provincial Foundation of National Science (No. Y2005B10) and Shandong Provincial Supported Foundation of Excellent Young Scientist (No. 2006BS04008 and 2006BS01106).

References

[1] An CH, Tang KB, Liu XM, Qian YT (2003) Eur J Inorg Chem 25: 3250
[2] Yang Q, Tang KB, Wang CR, Qian YT, Zhang SY (2002) J Phys Chem B 106: 9227
[3] Lu QY, Gao F, Komarneni S (2006) Chem Mater 18: 159
[4] Hirai T, Bando Y, Komasawa I (2002) J Phys Chem B 106: 8967
[5] Zhao J, Bardecker JA, Munro AM, Liu MS, Niu Y, Ding IK, Luo J, Chen B, Jen AK, Ginger DS (2006) Nano Lett 6: 463
[6] Matsune K, Oda H, Toyama T, Okamoto H, Kudriavysevand Y, Asomoza R (2006) Sol Energ Mat Sol C 90: 3108
[7] Routkevitch D, Bigioni T, Moskovits M, Xu JM (1996) J Phys Chem 100: 14037
[8] Anikin KV, Melnik NN, Simakin AV, Shafeev GA, Voronov VV, Vitukhnovsky AG (2002) Chemical Physics Letters 366: 357

[9] Barrelet CJ, Wu Y, Bell DC, Lieber CM (2003) J Am Chem Soc 125: 11498
[10] Xiong YJ, Xie Y, Yang J, Zhang R, Wu CZ, Du GA (2002) J Mater Chem 12: 3712
[11] Xu D, Liu Z, Liang J, Qian Y T (2005) J Phys Chem B 109: 14344
[12] Yang J, Zeng JH, Yu SH, Yang L, Zhou GE, Qian YT (2000) Chem Mater 12: 3259
[13] Butty J, Peyghambarian N, Kao YH, Mackenzie JD (1996) Appl Phy Lett 69: 3224