Single-Crystalline CdSe Nanostructures: from Primary Grains to Oriented Nanowires

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Nanostructured semiconductor materials are of great interest because of their novel physical, chemical, optical, and optoelectronic properties,[1] as well as their applications in fabricating nanoscale electronic, photonic, electromechanical, and biomedical devices.[2−5] Cadmium selenide (CdSe) is the most extensively studied compound semiconductor because of the versatile size-tunable properties of its nanostructures.[6] In particular, CdSe nanowires[7,8] and nanotubes[9] were applied in the fabrication of optoelectronic devices because the power conversion efficiency of nanowires has been demonstrated to be higher than that of quantum dots.[8] Moreover, nanowires with a preferred orientation may produce unique light-scattering and polarization effects, which are of considerable interest in the development of microemitters of polarized light and micrometer-scale polarization-sensitive photosensors.[10,11] It has been reported that invidual CdSe nanorods possess excellent optical properties and up to 100% polarized photoluminescence (PL).[10] Therefore, a technology that allows for the controllable fabrication of nanowires both arranged in the right place and with the appropriate orientation must be addressed. Shape-controlled synthesis of CdSe nanorods[11] and template-assisted synthesis of CdSe nanowires[7] and nanotubes[9] have been demonstrated through electrochemical and chemical approaches. However, these nanowires and nanotubes are composed of nanoscale grains and are of polycrystalline structure. The grain boundary scattering could greatly affect the optoelectronic performance. Thus, the synthesis of highly crystalline and preferentially oriented nanowires is still a challenge. In addition, the size and shape of inorganic nanocrystals widely affect their electrical and optical properties.[6] The systematic manipulation of the shapes of inorganic nanocrystals is therefore an important goal in materials chemistry. Prompted by the foregoing, we demonstrate in this paper the synthesis of shape-controlled CdSe nanostructures from nanoparticles over nanorods to single-crystalline nanowires using a template wetting approach.

Template wetting, employing porous matrices as molds, is a simple and versatile method for the preparation of one-dimensional (1D) nanostructures.[12] Nanowires and/or nanotubes with narrow diameter distribution and uniform depth have been obtained[13,14] with this approach. In this work, CdSe nanostructures were obtained by wetting of ordered porous alumina templates with an organochalcogenolate precursor, $Cd(SePh)_2{\cdot}TMEDA$ (TMEDA = tetramethylethylenediamine), which was synthesized according to the literature.[15] A porous alumina template with a pore diameter of 25 nm and a pore depth of 100 μm[16] was covered with a layer of precursor powder, heated to 160 °C at a rate of 2 °C/min, and kept at 160 °C for 2 h. At this temperature, the precursor melt infiltrated the pores. The wetted template was heated to 500 °C at a rate of 2 °C/min and held at this temperature for at least 2 h. This led to a complete decomposition of the precursor into CdSe nanostructures. Finally, the template was cooled to room temperature at a rate of 5 °C/min. All annealing procedures were performed in corundum crucibles under an argon atmosphere. The wetting−crystallization−cooling cycles can be repeated several times to customize the morphology. The templates were selectively removed by etching with a 30 wt % solution of potassium hydroxide at 70 °C. The resulting suspension was sonicated and subsequently washed with deionized water to neutrality.

In these experiments, the formation of a very thin shell of amorphous carbon[17] was observed. The removal of this shell became possible by addition of a small amount of a siloxane such as hexaphenylcyclotrisiloxane or stopcock grease to the precursor solution. In these cases, a brittle shell of amorphous Si/O/C was formed instead of the amorphous carbon shell, and sonication could be used for its complete removal, yielding pure nanostructures of CdSe (see the Supporting Information).

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(1) Xia, N. G.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, *15*, 353−389.
(2) Cui, Y.; Wei, Q.; Park, H. K.; Lieber, C. M. *Science* **2001**, *293*, 1289−1292.
(3) Huang, Y.; Duan, X.; Cui, Y.; Lauhon, L. J.; Kim, K.; Lieber, C. M. *Science* **2001**, *294*, 1313−1317.
(4) Gudiksen, M. S.; Lauhon, L. J.; Wang, J. F.; Smith, D. C.; Lieber, C. M. *Nature* **2002**, *415*, 617.
(5) Duan, X. F.; Huang, Y.; Agarwal, R.; Lieber, C. M. *Nature* **2003**, *421*, 241.
(6) Alivisatos, A. P. *Science* **1996**, *271*, 933−937.
(7) Xu, D.; Shi, X.; Guo, G.; Gui, L.; Tabg, Y. *J. Phys. Chem. B* **2000**, *104*, 5061−5063. Duan, X.; Lieber, C. M. *Adv. Mater.* **2000**, *12*, 298.
(8) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425−2427.
(9) Jiang, X. C.; Mayers, B.; Herricks, T.; Xia, Y. N. *Adv. Mater.* **2003**, *15*, 1740−1743.
(10) Artemyev, M.; Möller, B.; Woggon, U. *Nano Lett.* **2003**, *3*, 509−512.
(11) Hu, J. T.; Li, L. S.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Science* **2001**, *292*, 2060. Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.
(12) Martin, C. R. *Adv. Mater.* **1991**, *3*, 457.
(13) Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Schilling, J.; Choi, J.; Gösele, U. *Science* **2002**, *296*, 2002.
(14) Zhao, L.; Yosef, M.; Steinhart, M.; Göring, P.; Hofmeister, H.; Gösele, U.; Schlecht, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 311.
(15) Yosef, M.; Schaper, A. K.; Fröba, M.; Schlecht, S. *Inorg. Chem.* **2005**, *44*, 5890−5896.
(16) Masuda, H.; Hasegawa, F.; Ono, S. *J. Electrochem. Soc.* **1997**, *144*, L127−L130.
(17) Göring, P.; Pippel, E.; Hofmeister, H.; Wehrspohn, R. B.; Steinhart, M.; Gösele, U. *Nano Lett.* **2004**, *4*, 1121−1125.

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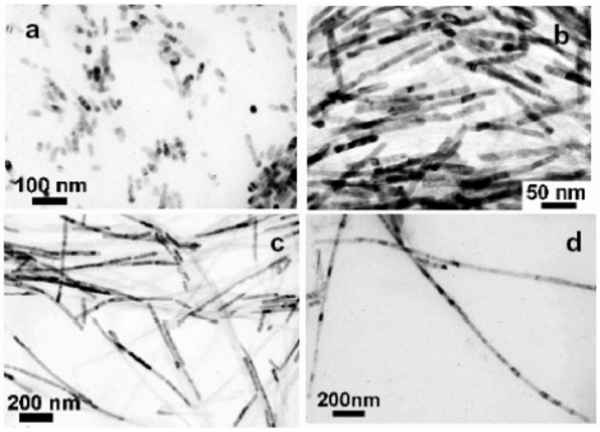

Figure 1. TEM images of CdSe nanostructures: (a) nanoparticles obtained after one wetting−crystallization−cooling cycle; (b) nanorods obtained by two cycles; (c) nanorods with higher aspect ratios prepared by three cycles; (d) nanowires obtained after four cycles.

Using transmission electron microscopy (TEM) images of samples taken at different numbers of wetting−crystallization−cooling cycles and at different annealing times, one can follow the shape evolution of the nanostructures (Figure 1a−d). The CdSe nanoparticles shown in Figure 1a were obtained by one wetting cycle and annealing at 500 °C for 5 h. Using two wetting cycles and annealing at 500 °C for 11 h total, nanorods were strongly favored (Figure 1b). Nanorods with a higher aspect ratio formed after three cycles and annealing at 500 °C for 35 h (Figure 1c).

Finally, nanowires with an aspect ratio up to 75 (Figure 1d) were produced by four wetting cycles and an overall annealing time of 83 h at 500 °C. All nanostructures have a diameter of 25 nm, corresponding to the pore diameter of the templates used. It is worth noticing that the overall annealing time adding up with the number of cycles plays an important role in controlling the shape of the nanostructures.

The investigation of the isolated semiconductor nanostructures by high-resolution transmission electron microscopy (HRTEM) showed single-crystalline wires without a common growth direction. A preference for the *c*-axis as the long axis of the wires was observed, but some other growth directions were also found for a minority of nanowires. For the CdSe nanowires with [001] as the long axis, an interplanar spacing (d_{hkl}) of 3.50 Å, corresponding to the (002) lattice planes of the hexagonal wurtzite phase of CdSe, was observed (Figure 2). Indexing of a typical SAED (selected area electron diffraction) pattern (Figure 2a, inset) of the single-crystalline CdSe wires could be done for this phase as well. The XRD pattern of the wires aligned within the pores and with the long axis parallel to the incident beam confirmed the presence of the wurtzite phase for the complete product (Figure 3). The relative intensity of the (002) reflection is higher than for polycrystalline CdSe powder, confirming that the *c*-axis of the hexagonal nanocrystals is preferentially aligned along the long axis of the pores rather than being randomly oriented.

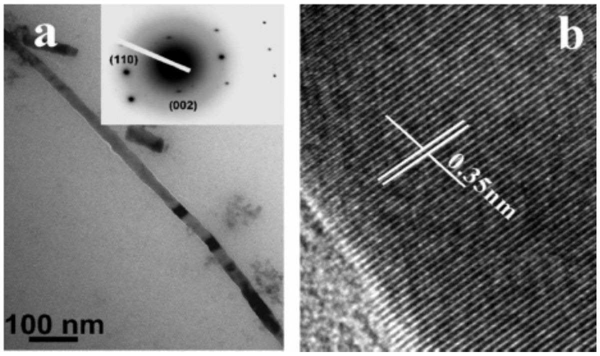

Figure 2. (a) TEM image of one individual CdSe nanowire with a diameter of 25 nm; inset: SAED pattern with indexed Bragg reflections; (b) HRTEM image of the nanowire showing (002) lattice planes with a spacing of d = 3.5 Å.

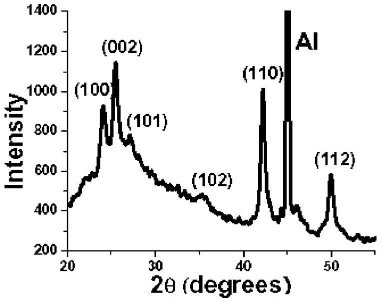

Figure 3. X-ray diffraction pattern of CdSe nanowires aligned in the porous template ($\theta/2\theta$ mode, indexing for wurtzite CdSe).

We propose that the formation mechanism of the CdSe nanostructures can be devided into two stages. In the first stage, many small primary grains form from the molecular precursor. These grains grow to nanoparticles with a certain size distribution. The smaller particles are then consumed by the further growth of the bigger ones, as the Gibbs−Thomson effect provides a thermodynamic driving force for large particles to grow at the expense of smaller ones.[18,19] This stage is a typical Ostwald ripening process[20] eventually leading to particles with a diameter close to the pore width. These particles are large enough to show distinct crystal facets so that a defined surface energy can be ascribed to the individual particle surfaces. In the second stage of particle growth, anisotropic structures such as rods and wires are formed. In contrast to solution systems where the nanocrystals have free mobility in the liqiud phase that allows them to get close and attach to each other (oriented attachment),[21−23] the CdSe nanocrystals in our system are confined in one-dimensional pore channels that hinder the nanocrystals from free movement and rotation. Thus, we believe that the growth mechanism of nanowires occurring in our system is substantially different from the one in solution. A tentative explanation may come from the idea that the transformation of nanoparticles to nanowires is associated with consecutive wetting steps, bringing new precursor material into the pores, and with the thermolysis of the precursor melt in the presence of a melt−nanoparticle interface. It can be expected that the formation of CdSe from the precursor melt will be facilitated at the interface that has the role of a seed for the formation

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(18) Pelce, P. *Dynamics of Curved Fronts*; Academic Press: San Diego, 1988.
(19) McLean, J. G.; Krishnamachari, B.; Peale, D. R.; Chason, E.; Sethna, J. P.; Cooper, B. H. *Phys. Rev. B* **1997**, *55*, 1811.
(20) Ostwald, W. *Z. Phys. Chem.* **1900**, *34*, 495.
(21) Penn, R. L.; Banfield, J. F. *Science* **1998**, *281*, 969−971.
(22) Alivisatos, A. P. *Science* **2000**, *289*, 736−737.
(23) Pradhan, N.; Xu, H. F.; Peng, X. G. *Nano Lett.* **2006**, *6*, 720−724.

of newly formed CdSe in the second wetting cycle (and in the following ones). It is known from earlier work[15] that the initial state of the degradation of the precursor is the formation of small amorphous grains at 351 °C. These crystallize at slightly higher temperatures. When the crystallization is induced by the interface with an neighboring nanoparticle, the crystallization is likely to be epitaxial, giving the newly grown part of the nanostructure the same orientation as the nanoparticle formed in the first thermolysis. This epitaxial growth can occur at every wetting step performed with the templates. Thus, anisotropic elongated nanostructures such as rods or wires can be made stepwise as single crystals starting from the products of the first thermolysis. The preference for the *c*-axis as the long axis of the resulting wires can be explained by the fact that the growth of a crystalline phase by attachment of nonaggregated building units is normally favored at the faces with a highest surface energy.[24] For wurtzite semiconductors such as CdSe, this is the {001} pair of facets.[24] When the presursor melt covers different nanoparticles with different orientation in a given template pore, growth will preferably occur at the ones with {001} surfaces, making this orientation the dominant one for the anisotropic products. The same principle holds true for a potential diffusive growth of the nanostructures during the long annealing step at 500 °C. This will also favor further crystal growth at {001} surfaces over other orientations.

The chemical composition of the CdSe nanowires was also determined independently by EDX spectroscopy. The EDX spectra revealed that the atomic ratio of Cd and Se is very close to 1:1 (see the Supporting Information for EDX spectra).

For optical characterization, photoluminescence (PL) measurements were performed at room temperature using a HeCd laser ($\lambda = 325$ nm, 15 mW) as an excitation source. The PL of CdSe nanowires that were transferred to a Si wafer was observed. As expected, the nanowires show a bulklike PL band centered at 703 nm (Figure 4). This value coincides with the center of the PL band of bulk CdSe.[25] The relatively narrow full width at half-maximum (fwhm) of 57 nm agrees well with the high crystallinity and purity of the CdSe nanowires produced by this approach.

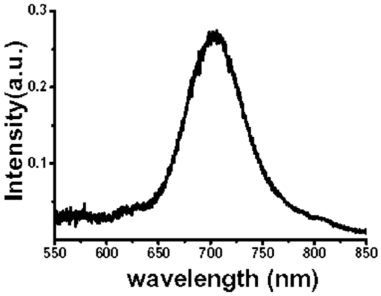

Figure 4. Room-temperature photoluminescence (PL) spectrum of CdSe nanowires on a silicon wafer ($\lambda_{\max} = 703$ nm).

In summary, we presented the preparation of CdSe nanostructures with tunable aspect ratio by a template wetting method. For an annealing temperature of 500 °C and varying annealing times, CdSe nanostructures from nanoparticles over nanorods to high aspect ratio nanowires were accessible. The nanowires display excellent uniformity in diameter. Different from other template-based approaches, the nanowires were single-crystalline and had their *c*-axis preferentially aligned with their long axis, not oriented randomly. A more elaborate investigation of a potentially polarized PL will be subject of future work.

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Supporting Information Available: EDX spectrum and additional PL spectra of CdSe nanowires and nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Jun, Y.; Choi, J.-S.; Cheon, J. *Angew. Chem., Int. Ed*. **2006**, *45*, 3414. Manna, L.; Wang, L. W.; Cingolani, R.; Alivisatos, A. P. *J. Phys. Chem. B* **2005**, *109*, 6183−6192.

(25) *Numerical Data and Functional Relationships in Science and Technology*; Madelung, O., Shulz, M, Eds.; Springer: New York, 1987; Group 3, Vol. 22, p 204.