

Hierarchically Ordered Cadmium Sulfide Nanowires Dispersed in Aqueous Solution

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Received January 9, 2005. Revised Manuscript Received April 11, 2005

The paper reports on the preparation, characterization, and dispersion of cadmium sulfide (CdS) nanowires using ordered mesoporous silica, SBA-15, as a template. A homogeneous and stable dispersion of hierarchically ordered CdS nanowires in water solubilized with sodium dodecyl sulfate (SDS) has been obtained. Direct imaging of the nanoconnectors (templated by the micropores in SBA-15) between the bundled nanowires has been accomplished by high-resolution transmission electron microscope (HRTEM). Cryogenic-TEM (cryo-TEM) measurements carried out on the dispersed samples complemented by small-angle X-ray (SAX) diffraction and HRTEM examination of the dry CdS powder clarify the role played by the micropores in the formation of a hierarchically ordered array of nanowires in the meso- and atomic scale. The amount of nanoconnectors is controlled by varying the calcination temperature of SBA-15, which tunes the formation of either bundled or individual CdS nanowires. The effect of such organizations is discussed in view of optical absorption and fluorescence measurements.

Introduction

The potential of semiconductor nanostructures in various applications such as light-emitting diodes (LEDs), flat panel displays, thin film transistors, and lasers is the driving force behind the rapid progress in this research field.^{1–4} The fabrication of 1D nanostructures, namely nanowires,⁴ nanoribbons,⁵ nanorods,⁶ nanobelts,⁷ and nanotubes⁸ has attracted a great deal of attention. Among the semiconductor materials, metal sulfides occupy a special position as they have a unique combination of physical and chemical properties suitable for the applications mentioned above.⁹ These applications arise primarily due to three important controllable attributes of the semiconducting material, namely, crystallinity, size and shape, and stoichiometry. These properties depend on the synthesis routes adopted and the process parameters employed during their growth. Several approaches have been used for the preparation of metal sulfides nanowires. These include polymer-controlled growth,¹⁰ liquid crystal or micellar template approach,^{11,12} solvothermal approach,¹³ laser

assisted growth,¹⁴ chemical approach,^{15–17} and porous template approach.^{18–20} All these approaches with the exception of porous templates have yielded isolated nanowires. Very few reports have appeared on the preparation of ordered arrays of semiconductor nanowires.^{16,18–20} Development of future nanoscale devices depends to a large extent on overcoming the challenge of assembling nanowires in an orderly manner.

Ordered mesoporous silica (OMS) materials having a uniform pore size and narrow pore size distribution offer the possibility of preparing ordered arrays of nanowires. Initially, nanowires were synthesized using MCM-41 mesoporous material as hard-template.²¹ However, these attempts using MCM-41 resulted only in isolated nanowires of about 2–4 nm in diameter. The first successful effort to prepare an ordered array of nanowires was reported for carbon (CMK-3) using a class of OMS, SBA-15 as a hard-

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- (21) Since there are two templating processes taking place during the formation of the nanowires we have used the term *soft-template* (triblock copolymer) for the formation of SBA-15, which is a cooperative process between the amphiphiles and the silica source, and *hard-template* for the formation of CdS nanowires throughout the text.

template.²² SBA-15 was soft-templated by triblock copolymer, Pluronic, P123, (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$)).²³ It was found that in addition to the mesopores, there are also micropores in the walls of SBA-15, which template the nanoconnectors between the nanowires. Thus, the role of micropores in the formation of ordered arrays of nanowires is vital and needs careful examination. The experimental evidence for the existence of the connecting micropores was first provided on the basis of nitrogen adsorption and desorption measurements performed extensively on SBA-15 samples.²⁴ In the very same paper, it is mentioned that direct observation of the connecting micropores was possibly beyond the imaging capability of a transmission electron microscope (TEM). However, direct imaging of the connecting micropores had been reported for Pt nanowires prepared using SBA-15 as hard-template.²⁵

In the present work we attempt to probe the role of micropores in the synthesis of ordered arrays of CdS nanowires through the direct imaging of the nanoconnectors between the nanowires. We have also used SBA-15 to prepare CdS nanowires as reported by others previously.^{19,20} The use of SBA-15 with tunable pore size as hard template facilitates better control over size, shape, and size distribution of nanowires. The issue of nanowire's crystallinity has not been clearly addressed in previous studies although the degree and the quality of crystallinity of these nanowires have a direct significance on their optical properties.¹⁴ Structural and optical characterization of these nanowires is presented in this paper.

The uniqueness of the present endeavor is the preparation of a stable dispersion of CdS nanowires solubilized in water by sodium dodecyl sulfate (SDS) molecules. A recent report stated that polymer-stabilized CdSe nanoparticles could not be dispersed in water and therefore toluene and chloroform were needed to prepare stable dispersions.²⁶ However, in the successful preparation of nonordered CdS nanowires in aqueous solution, ethylenediamine served the twin purpose of structure-directing agent and stabilizer.²⁷ It may be difficult to optimize the reaction parameters with a single component having two roles. In contrast, our work employs SBA-15 as structure-directing template followed by independent preparation of aqueous dispersions of nanowires.

Hence, we are able to prepare ordered arrays of nanowires due to the presence of nanoconnectors, hard-templated by the micropores in silica walls. Moreover, the connectivity between the nanowires is tuned by suitably varying the calcination temperatures of SBA-15. As a result we are able to prepare stable and homogeneous aqueous dispersions of these nanowires either in ordered bundles or individually

dispersed. Thus the present work is carried out with two major objectives: (i) investigation of the importance of micropores in the formation of ordered arrays of nanowires, and (ii) preparation of stable and uniform dispersions of CdS nanowires in aqueous solutions.

Experimental Section

All chemicals were supplied by Sigma-Aldrich except Pluronic, received as a gift from BASF, and were used as received.

Hard-Template Preparation. Mesoporous silica SBA-15 was prepared using a triblock copolymer as a soft-template following the general procedure reported by Zhao et al.²³ The molar ratio of the reactants TMOS/P123/HCl/deionized (DI) water used in our work is 1:0.02:4.2:194, respectively. The reaction was carried out under acidic conditions (pH about 1–2) and followed by a hydrothermal treatment at 373 K for 144 h. The resulting precipitate was filtered, washed with DI water, dried, and then calcined in air at 773, 973, and 1173 K to obtain SBA-15. A stepwise calcination process was employed to remove the soft-template. A typical calcination process was as follows: ramp to 373 K at 2 K/min and dwell for 2 h, then ramp to 573 K at 1 K/min and dwell for 4 h, and finally a ramp to 773, 973, or 1173 K at 1 K/min and dwell for 6 h.

Nanowires Preparation. The experimental parameters reported earlier²⁰ for the preparation of CdS nanowires were slightly modified (the stirring duration and the heating treatment) to improve the incorporation of CdS precursors into the pores and enhance the crystalline quality. A mixture of cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), thio urea ($\text{CS}(\text{NH}_2)_2$), and ethanol ($\text{C}_2\text{H}_5\text{OH}$) with the molar ratio 1:1:174, respectively, was first stirred for half an hour. Typically, 0.308 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.076 g of $\text{CS}(\text{NH}_2)_2$, and 8 g of ethanol were used in our preparation. This was followed by the addition of 0.15 g of thermally calcined SBA-15 and stirring for 6 h. The reaction mixture was transferred to a Petri dish, dried, and heat-treated at 333 K for 16 h. The mixture was then heated very slowly at a rate of 0.2 K/min up to 423 K and then was maintained at this temperature for 24 h. The mixture revealed a distinct yellowish color indicative of the formation of CdS. The obtained solid powder was then soaked in 2 M NaOH for several hours to remove the silica template and then washed with DI water several times until the pH of the resultant solution was 7 (neutral) before finally washing with ethanol and drying at room temperature.

Dispersion of Nanowires. The following chemicals, in turn, were independently used for the stabilization of CdS nanowires: SDS, cetyltrimethylammonium chloride (CTAC), and pluronic F127 ($\text{EO}_{106}\text{PO}_{60}\text{EO}_{106}$, where EO and PO stand for ethylene oxide and propylene oxide units). The dispersions were prepared in glass vials and sonicated at an energy range of 5–30 W/cm² under ice-cooled environment (Sonics and Materials Inc). Centrifugation was performed at 1500 rpm for 5 min using a Megafuge 1.0 (Heraeus) to remove the precipitates. The solubility of CdS in water was calculated by drying the precipitate and subtracting the amount from the initial amount of CdS taken prior to dispersion. Thermogravimetric analysis (TGA) analysis was performed on the precipitate to check for CdS and SDS content using a Mettler Toledo Star System (Mettler TC 15) under N_2 (200 mL/min) at a heating rate of 5 K/min from room temperature to 573 K.

X-ray Diffraction. Small-angle X-ray (SAX) diffraction measurements were performed on SBA-15, the dry silica-free CdS, and the dispersed solutions of CdS nanowires using Ni filtered Cu K α radiation of 0.15418 nm operated at 40 kV, 40 mA (Seifert ID 3000 generator). A linear position-sensitive detector (MBraun) was used to record the diffraction patterns. Samples for SAX diffraction

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measurements were prepared by filling the powder or liquid into 1.5-mm-diameter thin glass capillaries (GLAS) and sealing them with epoxy. A direct method of beam height correction was used for desmearing.²⁸ Diffraction curves were normalized with respect to the attenuated main beam. Wide-angle X-ray (WAX) diffraction measurement was performed to determine the crystalline structure of silica-free CdS samples using a Philips X-ray diffractometer (PW 1050/70) operated at 40 kV, 28 mA. The mean particle size can be estimated from the X-ray diffraction position and the peak width using the Scherrer formula, $D = 0.941\lambda/B\cos\theta_B$, where D is the mean diameter of the particle, λ is the wavelength of the Cu K α line, θ_B is the angle between the incident beam and the reflection lattice planes, and B is the width of the diffraction peak expressed in radians.²⁹

Electron Microscopy. HRTEM images were recorded using a JEOL2010 microscope operated at 200 kV. The chemical composition was measured using the energy-dispersive X-ray spectrometer (EDS) attached to the HRTEM. The dry powder was dispersed in acetone using ultrasonication before placing a drop on a carbon-coated copper grid. Low-temperature, cryogenic-TEM (cryo-TEM) technique was employed to image the samples in liquid state. Sample preparation was carried out using a Vitrobot at room temperature.³⁰ A drop of the solution was deposited on a TEM grid coated by a holey carbon film (lacey carbon, 300 mesh, Ted Pella, Inc), automatically blotted with a filter paper, and plunged into liquid ethane at its freezing point. The vitrified samples were stored under liquid nitrogen before transfer to a TEM (Technai 12, FEI) operated at 120 kV using a Gatan cryo-holder for imaging at 98 K in low-dose mode and with a few micrometers underfocus to increase phase contrast. Images were recorded on a Gatan 794 CCD camera and analyzed using Digital Micrograph 3.6 software.

Optical Measurements. Optical absorption and fluorescence measurements were carried out on the liquid samples using a UV–Vis spectrometer (Jasco V-560) and fluorimeter (JY, Fluorolog 3).

Results and Discussion

In this section, characterization of SBA-15 and formation of CdS nanowires through SAX diffraction and HRTEM measurements are first described. Then the observations on the preparation, solubility, and stability of aqueous dispersions of CdS nanowires are detailed and discussed. The results from SAX diffraction and cryo-TEM examination of these aqueous dispersions are described subsequently. Finally, the optical properties determined from UV–Vis absorption and fluorescence measurements are presented.

SBA-15 Characterization and CdS Formation. The SAX diffraction curve of thermally calcined SBA-15 at 773 K (Figure 1a) shows four peaks indexed as (100), (110), (200), and (210) reflections, confirming the hexagonal symmetry of the ordered pores. After incorporation of CdS into the pore channels, a similar SAX diffraction pattern (Figure 1b) was obtained showing peaks at the same positions as those of the parent SBA-15, implying an excellent stability of the mesostructure framework during the hard-templating process. There is a significant decrease in the intensity of

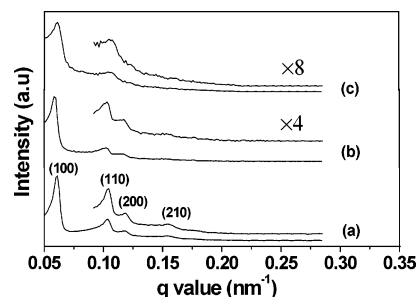


Figure 1. SAX diffraction curves of (a) parent SBA-15 calcined at 773 K, (b) SBA-15 incorporated with CdS, and (c) silica-free CdS nanowires. The intensity of curves b and c is magnified as indicated in the figure.

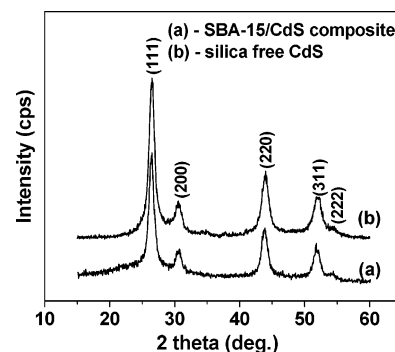


Figure 2. WAX diffraction curves of (a) CdS present in SBA-15 pore channels and (b) silica-free CdS samples showing cubic zinc blende symmetry.

all reflections, which is attributed to the reduced scattering contrast in the CdS–silica system (Figure 1b) in comparison with that of the air–silica system (Figure 1a). The SAX diffraction pattern of silica-free CdS nanowires (Figure 1c) reveals the formation of hexagonally packed nanoarrays, demonstrating the Babinet principle.³¹

The WAX diffraction patterns recorded before and after removal of SBA-15 (Figure 2) show the same peaks corresponding to the crystal structure of cubic zinc blende phase. The relatively broadened peaks suggest reduced dimension of CdS crystallites. There are three possible crystal structures for CdS: hexagonal wurtzite, cubic zinc blende, and high-pressure rocksalt phase.³² While the hexagonal phase can be observed in both the bulk and nanocrystalline CdS, the cubic and the rocksalt phases can be observed only in nanocrystalline CdS.³³ The crystal structure of previously reported CdS nanowires is only hexagonal symmetry^{6,7,10,19,34} except in the work by Liu et al.²⁰ where it is cubic zinc blende. In the present work, the average diameter of the CdS crystallites is found to be 8.5 nm. Thus, our ordered CdS nanowires array samples show a high degree of crystallinity in both meso- and atomic scales as indicated by SAX and WAX diffraction patterns. This demonstrates the formation of hierarchically well-ordered CdS nanowires with hexagonal mesostructure packing and cubic zinc blende crystallinity.

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Mesoporous Framework Stability at Different Calcination Temperatures. The parent SBA-15 samples were also calcined at higher temperatures of 973 and 1173 K. SAX diffraction measurements (not shown) of these samples reveal that the hexagonal symmetry of the mesopores remained intact in all calcination temperatures, although the lattice contracted for the sample calcined at temperatures above 773 K.^{35,36} Furthermore, it is reported that the amount of micropores in SBA-15 decreased with increasing calcination temperature.³⁷ We have used this parameter to tune the connectivity between the CdS nanowires. This fact can be exploited to either prepare ordered arrays of nanowires or exfoliate them to form individual nanowires.

HRTEM Imaging of CdS Nanowires. Bundles of dry silica-free CdS nanowires (prepared using SBA-15 calcined at 773 K) are a few hundreds of nanometers long as clearly imaged by TEM (Figure 3a). The diameter of each nanowire in the bundle is about 8 nm, which is in reasonable agreement with the mean particle size determined using the Scherrer formula. The average length of the nanowire extends to ~ 2000 nm. Thus, the aspect ratio of these nanowires is large: ~ 250 . Closer inspection reveals a high degree of crystallinity of CdS nanowires (Figure 3b). The slow heating rates used in this work are seen to induce a high degree of crystallinity with minimum crystal defects. Although the crystalline growth in different nanowires within each bundle is along different directions, the growth proceeds along one direction within a single nanowire as revealed by HRTEM micrographs. The measured d spacing for the (111) plane is 0.339 nm and is in close agreement with the value of 0.335 nm determined from the WAX diffraction pattern (Figure 2). The nanoconnectors between the wires (templated by the micropores) can be seen in Figure 3b and c (indicated by black circles). The nanoconnectors are disorderedly located between the nanowires and do not have a discrete diameter. It is remarkable that the crystallinity is maintained through the nanoconnectors between the wires. The thick black lines perpendicular to the lattice planes in Figure 3c are Moiré fringes. The elemental composition of the CdS nanowires via EDS at different points along the length and the diameter of the nanowire is homogeneous and nearly stoichiometric; Cd/S $\approx 1.05:1$ (see inset of Figure 3c). The absence of Si peak in the EDS spectrum also reveals that the CdS wires are silica-free. The presence of Cu peak is attributed to the copper grid used in TEM sample preparation.

Dispersion of CdS Nanowires. We prepared aqueous dispersions of CdS nanowires templated by a set of SBA-15 samples calcined at different temperatures (773, 973, and 1173 K). The silica-free nanowires were mixed in water and ethanol and sonicated. These dispersions were highly unstable. Thus, an alternate route to obtain stable dispersions in water was adopted from our previous work on nanotube stabilization in water. Bandyopadhyaya et al.³⁸ have devel-

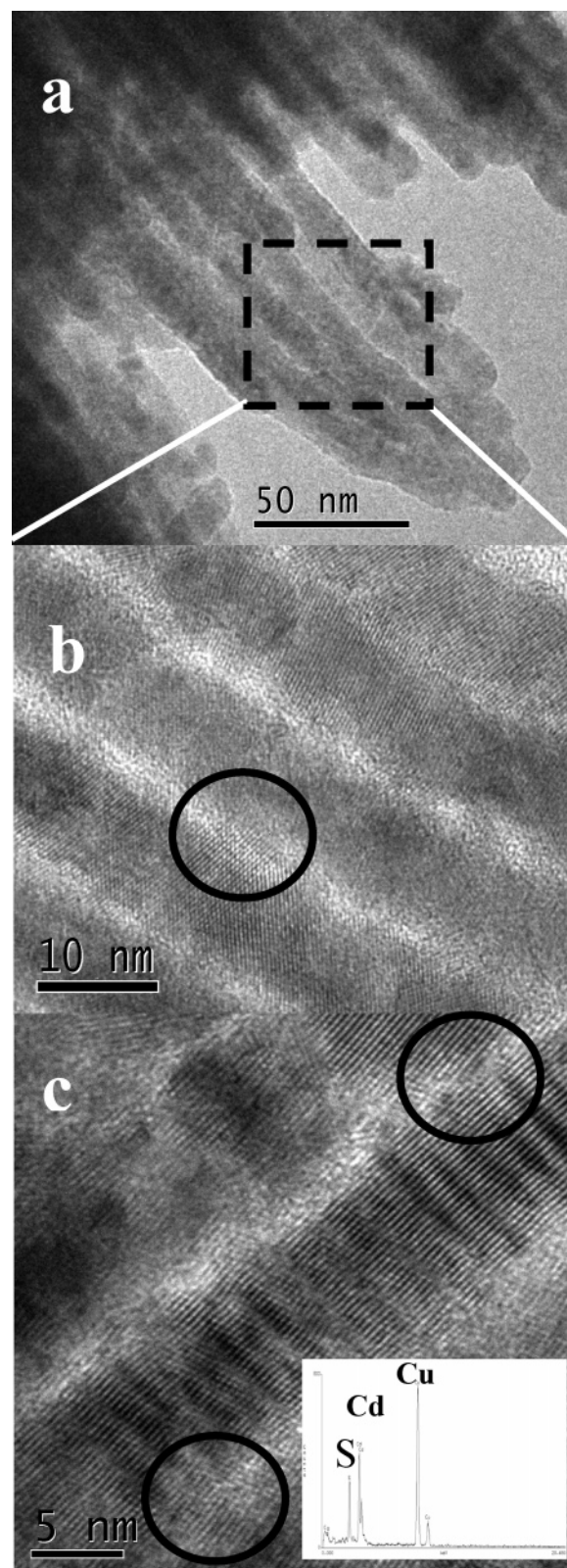


Figure 3. TEM image of silica-free CdS nanowires calcined at 773 K. The dashed zone in (a) is magnified in (b) and further in (c). The black circles indicate the presence of nanoconnectors between the crystalline nanowires. Inset in (c) shows EDS pattern recorded to determine the chemical composition of the CdS nanowires. The presence of Cu peak in the EDS spectrum is attributed to the Cu grid used in sample preparation.

oped a versatile method to exfoliate as-prepared single-walled carbon nanotubes (SWNT) bundles into individual nanotubes and disperse them in aqueous solution. This method is based on the physisorption of gum arabic (GA) on the surface

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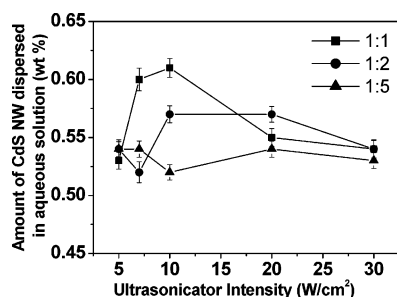


Figure 4. Concentration of CdS nanowires dispersed in aqueous solution vs ultrasonication intensity and CdS to SDS ratio.

of SWNT, which does not require any chemical modification of the nanotubes. Researchers have also reported on preparation of stable dispersions of SWNT with SDS as well.^{39,40} Taking a cue from these works on carbon nanotubes, we attempted to prepare stable dispersions of CdS nanowires in aqueous solutions using different surfactants.

Aqueous dispersions were prepared with a variety of dispersants, namely negatively charged SDS, positively charged CTAC, and neutral pluronics F127. For CTAC and F127 all the nanowires precipitated at the bottom of the vial within half an hour with a clear phase separation. On the other hand, the dispersions prepared with SDS are stable over a period of at least 8 months.

Furthermore, the amount of CdS nanowires in aqueous solution was investigated as a function of CdS/SDS ratio and ultrasonication intensity (Figure 4). The solubility of CdS nanowires in water is found to be rather low and varies between 0.52 and 0.61 wt. %. The highest value of 0.61 wt % is obtained for 1:1 (weight ratio of CdS to SDS) prepared at 10 W/cm². For a given CdS to SDS ratio, there is no systematic effect observed in the amount of CdS nanowires upon varying the intensity. The CdS solubility was calculated by weighing the dried precipitate. TGA was carried out on the precipitates to estimate its SDS content. These results (not shown) indicate that the amount of SDS settled at the bottom of the vial along with the CdS precipitates is insignificant. Therefore it can be assumed that the entire initial amount of SDS taken to prepare these dispersions is present in the solution phase.

A stable homogeneous aqueous dispersion of nanowires may enable facile preparation of nanocomposites with the possibility of using a wide spectrum of polymers. Preparation of novel nanocomposites of polymers and CdS nanowires has been recently reported via simultaneous monomer polymerization and formation of CdS nanowires.⁴¹ A precise tuning of the temperature and the concentration of the solvent may be a prerequisite in such a case. We believe that an independent synthesis of stable dispersions of nanowires in water and subsequent direct mixing with polymers may facilitate straightforward and more controllable preparation of nanocomposites.⁴²

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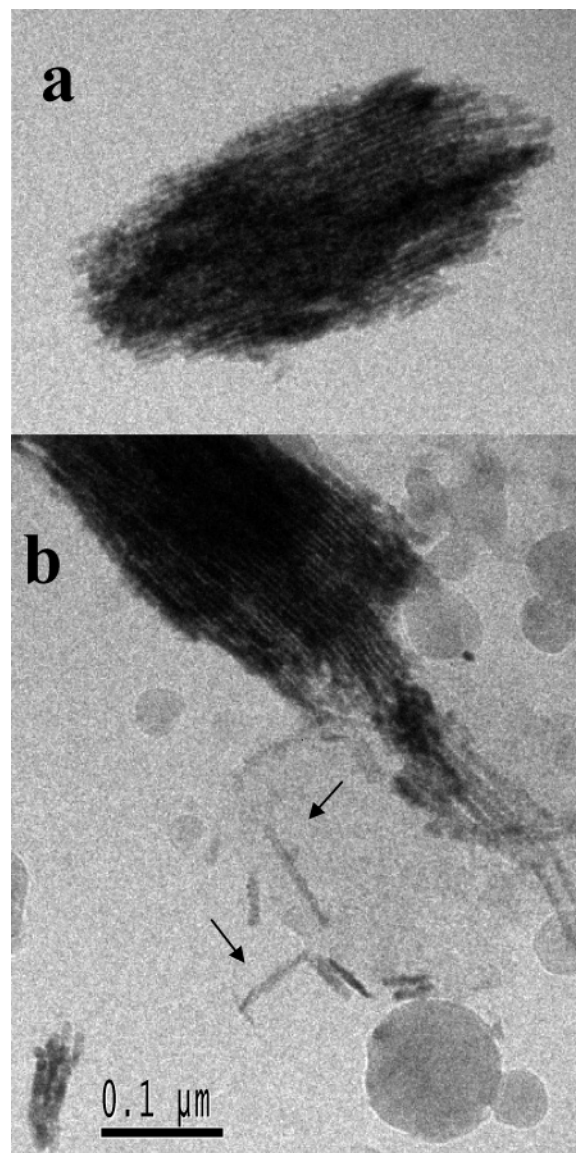


Figure 5. Cryo-TEM micrograph of 1:1 CdS/SDS dispersion using ultrasound intensity of 5 W/cm² for 20 min. The parent mesoporous template was calcined at (a) 773 K and (b) 973 K. Arrows indicate individual nanowires.

Cryo-TEM Investigation. Stable dispersions of template-free CdS nanowires were imaged by cryo-TEM. Nanowires (templated by SBA-15, calcined at 773 K) of about 8 nm are shown in Figure 5a. Here the nanowires are ordered in bundles, presumably due to the presence of CdS nanoconnectors templated by the micropores in SBA-15. These in turn prevented bundle exfoliation. However, at higher calcination temperature (973 K) individual nanowires were observed (Figure 5b). Since the number of nanoconnectors diminished for this sample in comparison to SBA-15 calcined at 773 K, partial exfoliation of the ordered bundles is noticed. This exfoliation behavior at higher calcination temperatures is currently being studied using HRTEM and cryo-TEM.

SAX Diffraction Measurements of Aqueous Dispersion of CdS Nanowires. SAX diffraction experiments were performed for the same template-free CdS nanowires prepared using SBA-15 calcined at 773, 973, and 1173K, dispersed in aqueous solutions (Figure 6). The strong reflection, corresponding to (100) peak, is observed at the

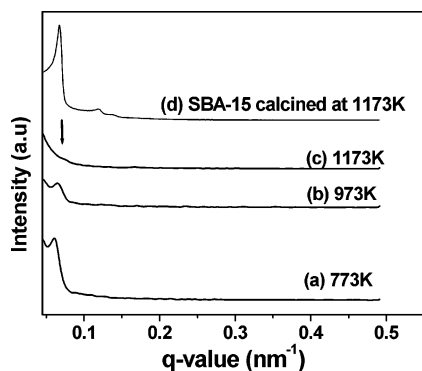


Figure 6. SAX diffraction curves of silica-free CdS nanowires with SDS (1:1 w/w) dispersed in water. The dispersion is sonicated at intensity of 5 W/cm² for 20 min. The parent SBA-15 is calcined at different temperatures, (a) 773 K, (b) 973 K, and (c) 1173 K, and (d) SBA-15 dry powder was calcined at 1173 K. The arrow in (c) indicates the absence of the (100) peak for this sample, confirming the collapse of the ordered array mesostructure.

same position for samples prepared using SBA-15 calcined at 773 and 973 K (Figure 6a and b). It indicates a periodicity of 10 nm, in agreement with HRTEM and cryo-TEM measurements (Figures 3 and 5). Thus the hexagonal mesostructure symmetry is preserved after sonication. The normalized intensity of the (100) peak of the sample calcined at 973 K (Figure 6b) is lower than the one calcined at 773 K (Figure 6a). This is most probably a result of a decreasing number of nanoconnectors between the nanowires leading to reduction in meso scale order, as has been demonstrated in the cryo-TEM micrographs (Figure 5). Interestingly, the SAX diffraction curve of the dispersed CdS nanowires prepared using the hard template SBA-15 calcined at 1173 K does not reveal any ordering (Figure 6c) although the dry SBA-15 calcined at 1173 K is highly ordered (Figure 6d). This clearly reveals that most of the micropores in the silica walls might have collapsed after calcination of the parent SBA-15 at 1173 K. Therefore, the bundles were easily exfoliated during sonication to prepare the aqueous dispersions. Complete collapse of micropores in SBA-15 calcined at 1243 K has been earlier observed by Ryoo and co-workers.³⁷ Hence, the bundles of ordered nanowires can easily exfoliate into individual wires after sonication even at a mild intensity. It is therefore established that the presence of micropores in the silica walls of SBA-15 controls the meso-scale ordering of nanowires. The SAX diffraction measurements on aqueous dispersions can be used as an effective characterization tool to probe the presence or absence of micropores qualitatively.

Optical Absorption and Fluorescence Measurements.

These measurements were carried out for aqueous dispersions of the nanowires. Figure 7 shows the absorbance spectra of silica-free CdS nanowires solution prepared using SBA-15 calcined at different temperatures. The inset shows the absorbance dependence on sonication intensity for samples prepared using SBA-15 calcined at 773 K. The absorbance increases gradually with increasing photon energy (decreasing wavelength). However, it increases sharply at around 520 nm and then a distinct shoulder appears at around 490 nm (as indicated by arrows in Figure 7) for samples prepared using SBA-15 calcined at 773 and 973 K. This shoulder at 490 nm emerges as a pronounced peak only in case of

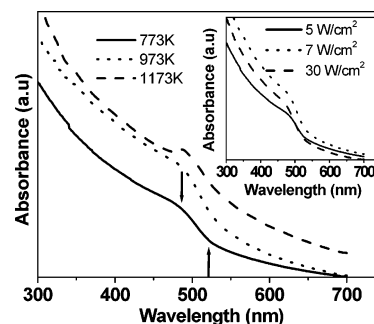


Figure 7. Absorbance spectra of silica-free CdS nanowires dispersed in water at 5 W/cm² prepared using SBA-15 calcined at different temperatures. The arrows indicate the sharp rise in absorption noticed at about 520 nm and the emergence of a clear shoulder at 490 nm in the spectra. The inset shows the spectra obtained for dispersed aqueous samples prepared using SBA-15 calcined at 773 K sonicated at different intensities.

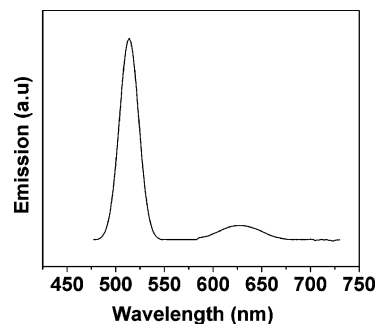


Figure 8. Typical fluorescence spectrum recorded for the aqueous dispersion of CdS nanowires with SDS (1:1 w/w) prepared at intensity 5 W/cm² for 20 min. The excitation wavelength is 400 nm.

nanowires prepared using SBA-15 calcined at 1173 K, namely fully exfoliated nanowires. The absorption spectra obtained for dispersed samples prepared at different ultrasonic intensities also exhibit a shoulder at 490 nm (inset of Figure 7). As mentioned earlier, the cubic phase of CdS is not existent in bulk form and hence the band gap for cubic phase in bulk form is unknown.³³

Fluorescence measurements were carried out for the CdS nanowires dispersed in aqueous solutions (prepared using SBA-15 calcined at 773 K). Usually two emissions are observed from semiconductor nanostructured materials: one is the sharp excitonic emission located near the absorption band edge and the other is the broad emission at longer wavelength due to surface states and/or defects.^{43,44} We observe a relatively sharp emission peaking at 513 nm with a full width half-maximum (fwhm) of 20 nm (Figure 8). The observed spectrum is similar to the spectrum recorded from a 25-nm diameter CdS nanowire excited at 400 nm.¹⁴ However, we also notice a relatively broad emission around 575–675 nm with a lesser intensity attributed to the surface defects (trap states). We did not observe any significant change either in the peak position or the peak width for CdS nanowires prepared using SBA-15 calcined at different temperatures. The nanoconnectors that, as seen, are important in forming stable ordered assemblies, appear not to affect the overall optical properties of the CdS nanowires. In fact, the preparation in the SBA-15 template produces nanowires

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(44) Oneil, M.; Marohn, J.; McLendon, G. *J. Phys. Chem.* **1990**, *94*, 4356.

of high spectroscopic quality: they possess narrow excitonic emission with almost insignificant surface/defect long wavelength emission, even when dispersed in water with SDS.

Conclusion

In summary, preparation of stable and homogeneous dispersions of CdS nanowires in aqueous SDS solutions has been successfully established. Direct imaging of nanoconnectors in hierarchically ordered arrays of CdS nanowires using HRTEM has been demonstrated. A clear insight on the importance of micropores in the formation of ordered array of nanowires is provided by cryo-TEM complemented by SAX diffraction measurements of CdS nanowires dispersed in aqueous solutions. The amount of nanoconnectors, which tunes the connectivity between nanowire bundles and individual nanowires, can be manipulated by suitably con-

trolling the calcination temperature of the hard template, SBA-15. Employing longer stirring time and slower heating rates facilitates better incorporation of CdS precursor into the pores of SBA-15 and ensures a high degree of crystallinity of the nanowires, respectively. The optical absorption measurements indicate sensitivity to these changes in ordering. The nanowires are characterized by a high-quality, narrow excitonic fluorescence almost clean of surface/defect emission, indicating only marginal surface traps or defects.

Acknowledgment. This study was supported by the Israeli Science Foundation, Center of Excellence (Grant 8003). We acknowledge Prof. D. Y. Zhao for fruitful discussions. We also thank Dr. Yael Levi-Kalishman and late Prof. Shlomo Efrima for their helpful suggestions in the preparation of this manuscript.

CM0500408