Surfactant-assisted synthesis of semiconductor nanotubes and nanowires

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Nanotubes and nanowires of CdSe and CdS have been obtained from solutions containing a surfactant such as Triton 100-X. They have been characterized by x-ray diffraction, electron microscopy, and optical spectroscopy. © *2001 American Institute of Physics.*
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Several methods have been employed for synthesizing semiconductor nanowires in the literature.[1–4] These methods include laser ablation, electrochemical fabrication, and high temperature reactions. We have been exploring relatively simple chemical methods of preparing semiconductor nanowires and have been able to synthesize these materials by employing surfactants such as t-octyl-$(OCH_2CH_2)_xOH$, $x=9$, 10 (Triton-X) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Thus, nanowires of sulfides and selenides of Cu, Zn, and Cd with high aspect ratios can be prepared by using Triton 100-X.[5] It was of great interest to explore whether surfactant-assisted synthesis under suitable conditions can yield nanotubes of II–VI semiconductors, since nanotubes of II–VI semiconductor materials are not known to date. We have indeed found it possible to obtain both nanotubes and nanowires of CdSe and CdS by surfactant-assisted synthesis. We have characterized these nanostructures by various means.

In a typical preparation of CdSe nanotubes, a suspension of a fine powder of cadmium oxide (10 mmol) was prepared in 20 ml of Triton 100-X ($\sim$24 mmol). A solution of NaHSe ($NaBH_4$/Se in 40 ml water) was added dropwise under constant stirring, to the suspension at 40 °C in an argon atmosphere. The resulting mixture was refluxed for 12 h and left overnight. The product was washed repeatedly with cyclohexane and diethyl ether and dried. Much of the surfactant was removed in the washing process. When AOT was used as a surfactant, the procedure was as follows. To a solution of AOT (4.5 mmol) in 25 ml cyclohexane, cadmium oxide (10 mmol) was added and stirred rigorously to form a good suspension. The rest of the procedure was similar to that with Triton 100-X. In order to obtain nanowires of CdSe the same procedure was followed except that the surfactant concentration was lower (10 mmol of Triton 100-X or 2.25 mmol of AOT). Nanotubes and nanowires of CdS were obtained by using an aqueous solution of thioacetamide in basic medium in place of the NaHSe solution. The products were examined by EDX analysis, x-ray diffraction (XRD), and transmission electron microscopy (TEM). EDX analysis of the nanostructures showed them to have Cd:Se (S) ratios of 1:1.

XRD patterns of the nanowires and nanotubes of CdSe and CdS showed patterns characteristic of the hexagonal structure with $a=4.307$ Å, $c=7.046$ Å in the case of CdSe, and $a=4.140$ Å, $c=6.695$ Å in the case of CdS. The lines were somewhat broad due to the small dimensions of the nanostructures. It is noteworthy that CdS, which is ordinarily cubic, occurs in the hexagonal structure in the nanowires and the nanotubes. In Figs. 1(a) and 1(b) we show typical TEM images of CdS nanowires. The diameter and length of the nanowires are in the ranges of 40–160 nm and 3–4 μm, respectively. Most of the nanowires appear to be polycrystalline as shown from the electron diffraction (ED) pattern in the inset of Fig. 1(b). The innermost ring in the ED pattern corresponds to $d(100)$ of 3.66 Å. In Fig. 1(c) we show TEM images of polycrystalline CdSe nanowires. The diameter of these nanowires is in the range of 30–40 nm and length goes up to a micron.

Figure 2 shows the TEM images of the CdSe nanotubes, to demonstrate their tubular nature. The nanotubes are generally long, with lengths up to 5 μm. The outer diameter of the nanotubes is in the 15–20 nm range while the diameter of the central tubule is in the 10–15 nm range. The wall thickness is therefore around 5 nm. The ED pattern of the nanotubes, given as an inset in Fig. 2(b), shows diffuse rings indicating the polycrystalline nature of the material. The rings corresponding to $d(101)=3.25$ Å and $d(110)=2.10$ Å are clearly seen.

In Fig. 3(a) we show a high-resolution TEM (HREM) image of a nanotube after annealing the as-obtained material to 300–400 °C under high vacuum. The image clearly reveals the tubular space and the presence of some ordered CdSe layers surrounding the central tubule. The interlayer spacing is 3.23 Å, just as in multiwalled carbon nanotubes. It appears that annealing the nanotubes removes the remaining surfactant and also improves the crystallinity of the nanotube.

We have also been able to prepare nanotube structures of CdS by employing a high concentration of the surfactant, by a procedure similar to that employed with CdSe. Figure 3(b) shows a typical TEM image of a CdS nanotube. The ED pattern given in Fig. 3(b) shows diffuse rings with the innermost ring corresponding to $d(100)=3.66$ Å. The CdS nanotubes have a central tubule diameter of $\sim$15 nm and an outer diameter of $\sim$50 nm, with a length of a few microns.

The electronic absorption spectrum of the CdSe nanotubes shows a broad band with the highest intensity maximum around 550 nm compared to the bulk polycrystalline

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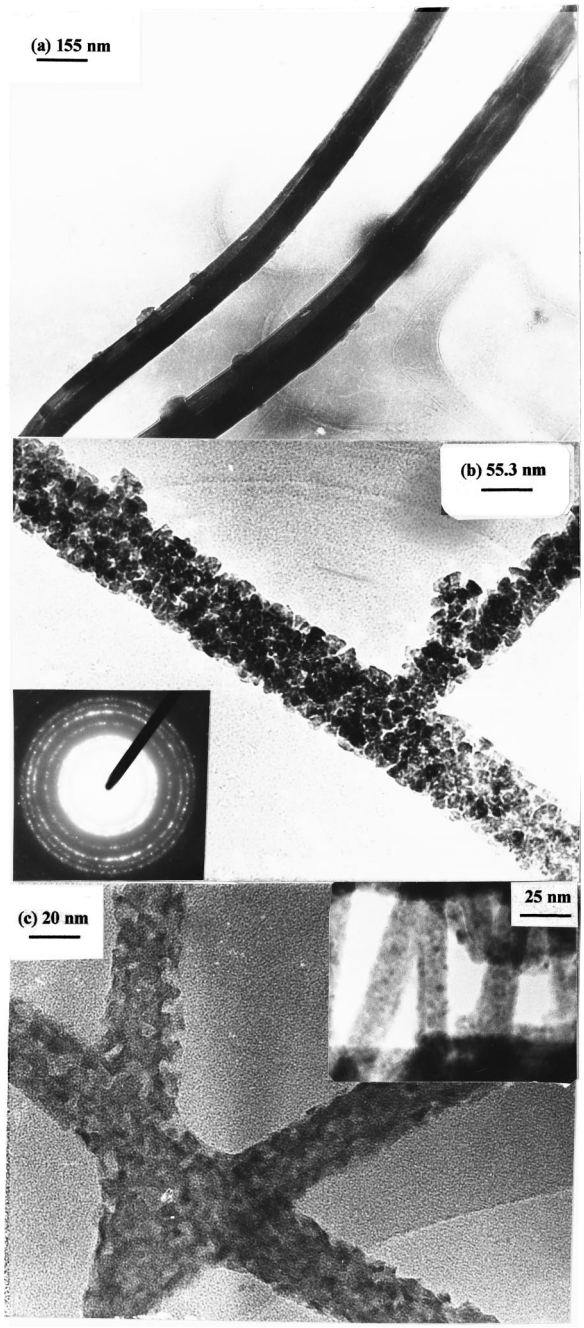

FIG. 1. (a) and (b) TEM images of CdS nanowires obtained by using Triton 100-X as the surfactant. Inset (b) shows the electron diffraction pattern of the CdS nanowires; (c) shows TEM images of CdSe nanowires obtained by using Triton 100-X as the surfactant.

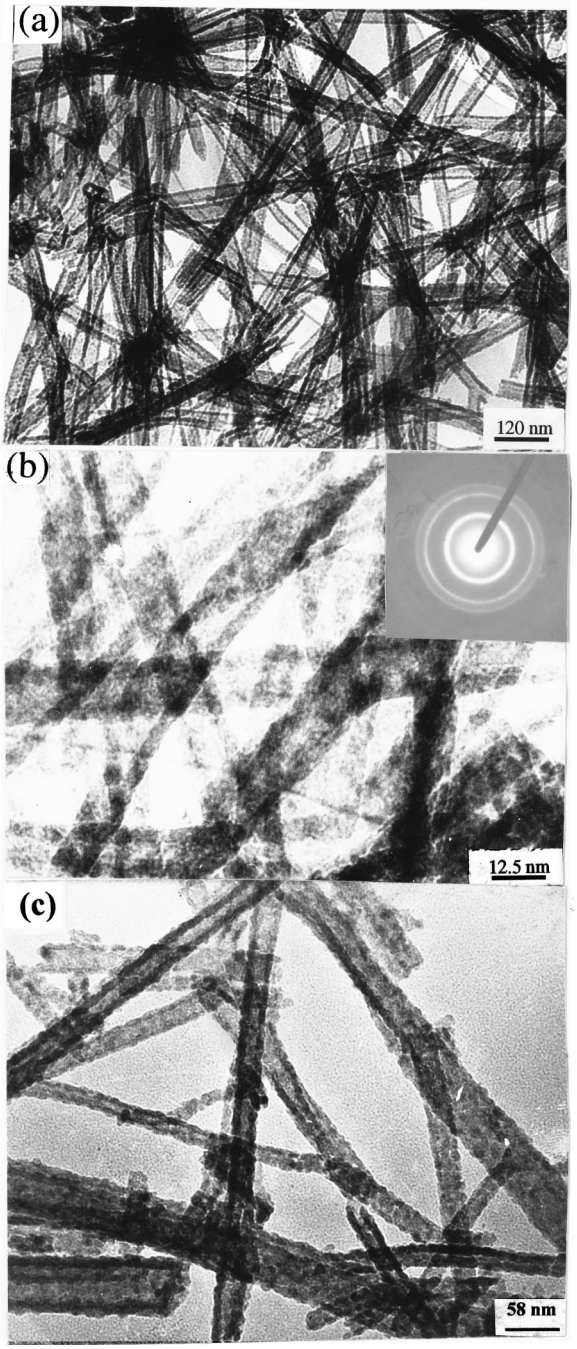

FIG. 2. (a) and (b) TEM images of CdSe nanotubes obtained by using Triton 100-X as the surfactant. The TEM image of CdSe nanotubes obtained by using AOT as the surfactant is shown in (c). The inset (b) shows the electron diffraction pattern of the nanotubes.

sample which has a maximum around 650 nm. It is interesting that the nanotubes show a blueshift due to quantum confinement, even though they are extended along one dimension. The electronic absorption spectrum of the CdS nanotubes also shows a similar blueshift of the absorption maxima due to quantum confinement. Quantum confinement effects in the nanotubes are also seen in the photoluminescence (PL) spectra. In Fig. 4 we show the PL spectrum of CdSe nanotubes. The spectrum of the nanotubes shows a

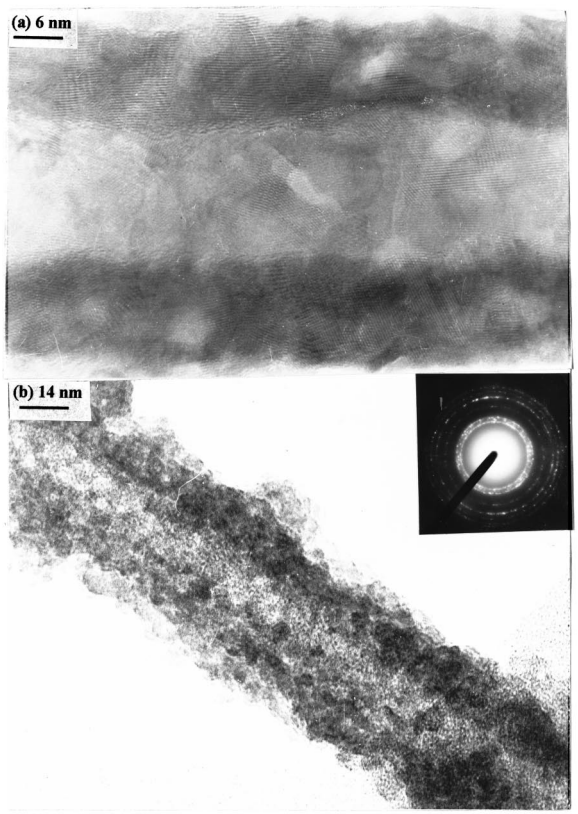

FIG. 3. (a) HREM image of a vacuum annealed nanotube of CdSe; (b) shows the TEM image of a CdS nanotube; (b) shows the electron diffraction pattern.

broad maximum around 560 nm while the bulk sample does not show such a feature in this region. The band around 750 nm in the PL spectrum of the bulk sample is blueshifted in the case of the nanotubes.

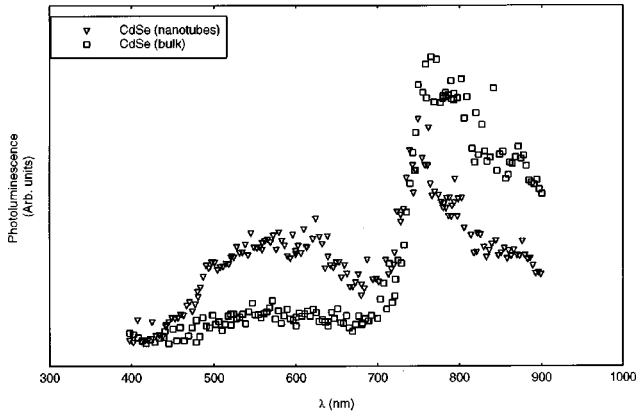

FIG. 4. Photoluminescence spectra of nanotube and bulk samples of CdSe.

In conclusion, we have obtained semiconductor nanotubes and nanowires by surfactant-assisted synthesis. These nanostructures show quantum confinement effects. It appears that at the high concentrations employed, the surfactant molecules aggregate, providing a template for the growth of the nanotubes of the chalcogenides.

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[1] C. R. Martin, Science **266**, 1961 (1994).
[2] X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, and A. P. Alivisatos, Nature (London) **404**, 59 (2000), and references therein.
[3] D. Xu, Y. Xu, D. Chen, G. Guo, L. Gui, and Y. Tang, Adv. Mater. **21**, 520 (2000), and references therein.
[4] C.-C. Chen, C.-Y. Chao, and Z.-H. Lang, Chem. Mater. **12**, 1516 (2000), and references therein.
[5] A. Govindaraj, F. L. Deepak, N. A. Gunari, and C. N. R. Rao, Isr. J. Chem. (2000) (special issue on Nanotechnology), (in press).