Synthesis of CdSe/CdTe Nanobarbells

Jonathan E. Halpert, Venda J. Porter, John P. Zimmer, and Moungi G. Bawendi*

Massachusetts Institute of Technology, Department of Chemistry, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Received March 23, 2006; E-mail: mgb@mit.edu

Recently, considerable research has focused on the synthesis, shape control, and physics of heterostructured nanocrystals. Non-core/shell heterostructures using group II−VI nanocrystals, such as CdSe, have been of particular interest.[1−3] For example, CdSe rods have been used to nucleate the growth of gold nanocrystals (dots) onto one or both ends. These CdSe/Au nanobarbells have shown unique physical properties relating to the interaction between the two materials.[1] The method of their synthesis suggests that it may be possible to nucleate many other types of materials on the tips of semiconductor nanorods.

Conjoining two materials with a type-II band gap offset in a nanostructure spatially separates photogenerated carriers (Figure 1) within the nanostructure such that the wave function of the electron largely resides in one material and the wave function of the hole in the other.[4,5] Indeed, recent works have predicted that CdSe/CdTe heterostructures are ideal for separation of 1D excitons (1DEs), despite their large binding energies,[6] when the structure lies within the "wide wire" regime (where the rods and dots are of comparable thickness).[4] These materials could find potential applications in photovoltaic devices, including solar cells and photodetectors, by reducing the applied voltage required to turn excitons into free charge carriers.

Previous studies have produced type-II structures such as CdTe/CdSe core/shell nanocrystals[5] and CdTe branches grown off of CdSe tetrapods.[7] However, these structures are not ideal for photoconduction because once the excitons are separated, the charges cannot easily move through the film. Tetrapods leave empty volume when deposited into a film, while core/shell particles trap one of the carriers in the core. Here we present a synthesis for CdSe/CdTe rod/dot nanobarbells (Figure 2) designed to be of interest for photoconduction or photovoltaic applications, since the type-II electronic structure separates the exciton and the rodlike particles pack tightly into a film.[8] These nanobarbells should both allow exciton separation within the nanocrystal and separate conduction of electrons through CdSe rods and holes through CdTe dots.

The CdSe nanorods are prepared by injecting a room-temperature solution of trioctylphosphine (TOP) and trioctylphosphine selenide (TOP−Se) into a mixture containing trioctylphosphine oxide (TOPO), octadecylphosphonic acid (ODPA), and cadmium oxide (CdO) at 320 °C, as adapted from previously reported methods.[9,10] The rods are then purified in hexane by selective precipitation[11] and added to a mixture containing TOPO, hexadecylamine (HDA), and hexylphosphonic acid (HPA). After degassing and removing residual hexane by vacuum, the mixture is heated to 260 °C, and a room-temperature solution of cadmium 2,4-pentanedionate, 1,2-hexadecanediol, TOP, and 1.0 M trioctylphosphine telluride (TOP−Te) is added dropwise. Apart from the presence of the rods, these conditions are identical to those used in the preparation of CdTe dots. Any free CdTe dots formed during the synthesis of the nanobarbells (<10% of nanocrystals after reaction, as estimated by TEM) are extracted using toluene and hexane, in which the
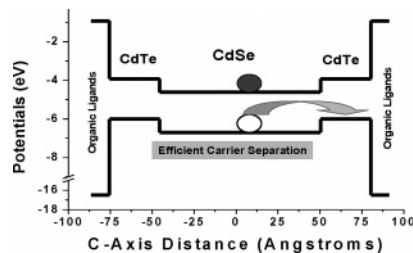

Figure 1. Band offsets of more than 500 meV in the bulk between valence (4.6 eV, 4.1 eV) and conduction (6.7 eV, 5.9 eV) bands of CdSe and CdTe driving exciton separation in the nanocrystal.[5]
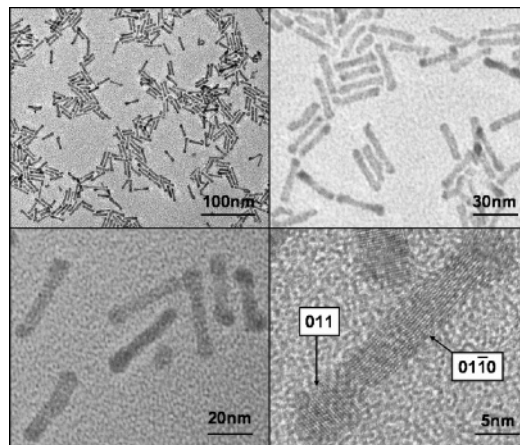
Figure 2. Transmission electron microscope images taken on a JEOL 200 TEM and expanded (top) and JEOL 2010 HR-TEM (bottom) showing CdSe/CdTe nanobarbells. HR-TEM images show that the CdTe dots are neither wurtzite nor oriented along the c-axis of the rod.

nanobarbells are insoluble. The nanobarbells can be purified in chloroform by selective precipitation using methanol. CdSe/CdTe nanobarbells appear to be light sensitive (precipitating out of solution) but stay dispersed in solution for several weeks if stored under nitrogen in the dark.

The mechanism for the formation of nanobarbells is similar to that suggested by Banin et al.[3] to explain the formation of gold tipped CdSe rods. The higher reactivity facets, the [000 ± 1] facets perpendicular to the crystalline c-axis, serve as nucleation points for the formation of a gold "dot" attached to the rod. By adding the CdTe precursor slowly and below nucleation temperature, the precursors in solution obtain the necessary free energy, as their concentration increases, to overcome the thermodynamic barrier to nucleation at the ends of a CdSe rod well before any appreciable homogeneous nucleation. Given an adequate number of nucleation sites in solution, nucleation on the end of a CdSe rod becomes the dominant pathway for CdTe dot formation, as only a small number of "free" dots are produced. After nucleation, growth then occurs primarily on the CdTe dots because of the preferential reactivity of the precursor. Evidence for this mechanism can be found in the
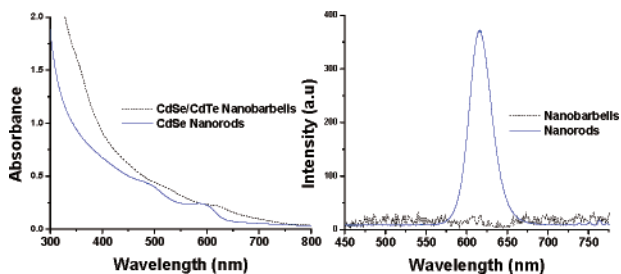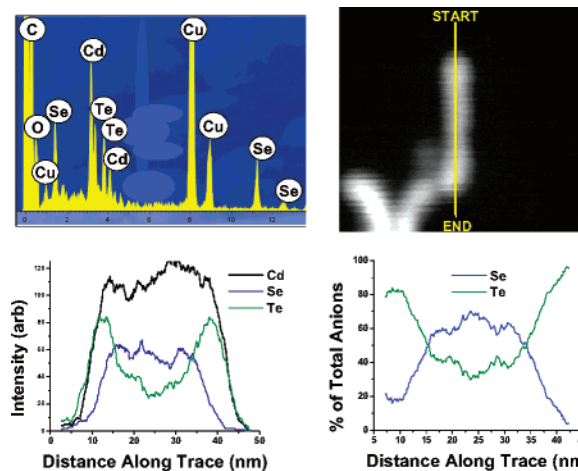
Figure 3. The absorption (left) and emission (right) spectra of a sample of nanobarbells before (nanorods) and after the addition of CdTe tips (nanobarbells).

Figure 4. Electron energy loss data (example top left) from a scanning transmission electron microscope (STEM) trace of a single CdSe/CdTe nanobarbell (image top right). Concentration is plotted for all three elements (bottom left), and the anion ratio is assessed (bottom right).

formation of CdTe dots attached to defect sites along the body of imperfectly shaped rods and in the minimal overcoating of the rod with CdTe seen in STEM measurements of CdSe/CdTe nanobarbells. It is noteworthy that the formation of these heterostructures simply requires modifying the CdTe dot synthesis only by (1) the presence of rods that serve as nucleation sites and (2) adding precursors dropwise at a temperature high enough for growth, but low enough to suppress homogeneous nucleation. This synthesis shows that the mechanism of rod nucleated growth may be generally applicable for creating other non-core/shell heterostructures with unique physical properties.

Nanobarbells exhibit absorption spectra (Figure 3) typical of type-II heterostructures,[5] with significant absorption across the visible spectrum. This is expected as the photon can be absorbed either by the CdSe rod, the CdTe dot, or intermediate states that exist at the junction between the two materials. Unlike in core/shell type-II heterostructures, however, there is no observed emission. Since the carriers are spatially well separated and the nanobarbell is not overcoated with a higher band gap material (such as ZnS), it is presumed that recombination occurs primarily through nonradiative pathways involving surface trap states.

Figure 2 is a TEM image showing multiple nanobarbells highlighting the uniformity of the material. The CdTe dots grow symmetrically on either end without branching or other deviations that may increase "empty" volume in a film. Nanobarbells synthesized in this manner should show packing properties similar to CdSe rods.[8] As transport in nanocrystal films is generally limited by a carrier tunneling mechanism,[12−14] obtaining good conductivity and high photocurrent requires minimizing the distance between adjacent particles. This requires the particles to form close-packed films, which in turn illustrates the need for well formed rodlike nanocrystals. Using a two step synthesis significantly improves the quality of the heterojunction by minimizing contamination of the CdTe dots with Se. A low growth temperature minimizes overcoating of the CdSe rods with CdTe. STEM measurements confirm this in Figure 4. Although the spatial precision of the instrument is limited, spots measured in the center of the rod indicate a concentration of CdTe that is less than 30%, which corresponds to a CdTe thickness of about two monolayers around a rod with radius ∼3 nm. However, the proximity of the Cd and Te peaks in the X-ray spectrum leads to overcounting of tellurium, and no discernible shell can be seen in HR-TEM images (Figure 2).

This synthesis demonstrates the power and utility of facet-selective nucleation for the creation of nanoheterostructures and provides another tool for the production of novel materials. This mechanism may be applicable to other heterostructures with materials chosen to allow a favorable interaction of properties, whether optical, electronic, or magnetic.

Supporting Information Available: Synthesis of the CdSe/CdTe rod/dot nanobarbells. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Steiner, D.; T. Mokari; U. Banin; O. Millo. *Phys. Rev. Lett.* **2005**, *95* (5) 056805(4).
(2) Kudera, S.; Carbone, L.; Casula, M. F.; Cingolani, R.; Falqui, A.; Snoeck, E.; Parak, W. J.; Manna, L. *Nano Lett.* **2005**, *5* (3), 445−449.
(3) Mokari, T.; Rothenberg, E.; Popov, I.; Costi, R.; Banin, U. *Science* **2004**, *304*, 1787−1790.
(4) Franceschetti, A.; Lang, L. W.; Bester, G.; Zunger, A. *Nano Lett.* **2006**, *6* (5), 1069−1074.
(5) Sungjee, K.; Fisher, B.; Eisler, H.-J.; Bawendi, M. G. *J. Am. Chem. Soc.* **2003**, *125 38*, 11466−11467.
(6) Shabaev, A.; Efros, Al. L. *Nano Lett.* **2004**, *4* (10), 1821−1825.
(7) Milliron, D.; Hughes, S. M.; Cui, Y.; Manna, L.; Lin-Wang, J. L.; Alivisatos, A. P. *Nature* **2004**, *430*, 190−195.
(8) Li, L.-S.; Alivisatos, A. P. *Adv. Mater.* **2003**, *15* (5), 408−411.
(9) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 1389−1395.
(10) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 3343−3353.
(11) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
(12) Drndic, M.; Jarosz, M. V.; Morgan, N. Y.; Kastner, M. A.; Bawendi, M. G. *J. Appl. Phys.* **2002**, 92 (12), 7498−7503.
(13) Jarosz, M. V.; Porter, V. J.; Fisher, B. R.; Kastner, M. A.; Bawendi, M. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *70*, 195327.
(14) Leatherdale, C. A.; Kagan, C. R.; Morgan, N. Y.; Empedocles, S. A.; Kastner, M. A.; Bawendi, M. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62* (4), 2669−2680.

JA0616534