Synthesis of CdSe/CdTe Nanobarbells – Supporting Information

To synthesize the CdSe/CdTe rod/dot nanobarbells, CdSe rods were first synthesized by heating 0.2054g cadmium oxide (CdO), 1.2946g octadecylphosphonic acid (ODPA) and 2.500g trioctylphosphine oxide (TOPO) to 300°C in a 3-neck 25ml flask, until solution is clear, heating to 320°C and injecting a solution of 0.300g toluene, 1.290g trioctylphosphine (TOP) and 0.410g of 3.5M trioctylphosphine selenide (TOP-Se), and growing the rods at 260°C for fifteen minutes. The rods are then precipitated from solution twice by adding ~5ml butanol and ~20ml methanol, centrifuging the solution at 3900 RPM and redispersing in hexane. After the second precipitation rods are redispersed in hexane with a few drops of octylamine and allowed to sit for several days until a significant increase in quantum yield has occurred. Introducing a mild etchant to the solution of nanorods, such as octylamine, at room temperature and letting it sit over a period of ~ 1 week prior to the introduction of CdTe precursors reduced the number of CdTe “warts” grown along the shaft of the rods. Rods were then precipitated as above, redispersed in hexane and filtered.

To create CdSe/CdTe nanobarbells, 3.125g TOPO, 2.875g hexadecylamine (HDA) and 0.2825g hexylphosphonic acid (HPA) are degassed at 140°C in a 4-neck 50ml flask with an attached addition funnel, cooled to 80°C at which time rods, containing approximately 1 mmol of Cd total as estimated by optical absorption, that are dispersed in hexane are added to the pot and the hexane removed under vacuum. Meanwhile a solution of 0.078g cadmium 2,4-pentadionate, 0.285g 1,2-hexadecanediol, and 4ml TOP is degassed at 110°C in a separate vial. After degassing the solution is cooled to room temperature and 2ml of 1.0M trioctylphosphine telluride (TOP-Te) is added to the vial, the contents of
which are transferred to the addition funnel and added to the pot at 260ºC dropwise at a rate of 1drop/3seconds, conditions identical to, excepting the presence of the rods, the dropwise addition and the temperature, the formation of CdTe dots. The total reaction time after the start of the addition of the precursor solution did not exceed 15 minutes after which the resulting solution is cooled to room temperature and transferred under argon to a nitrogen glovebox to avoid oxidization of the CdTe tips.

It may be noted that the temperature at which the tips are grown is not high enough to cause the CdSe nanorods to become spherical. This is probably because they are not kept at this temperature long enough to achieve the thermodynamically lowest energy state (a sphere) and also because the addition of CdTe precursor in solution drives the general reaction towards the deposition of material onto the ends, and thus away from the “ripening” effect of material leaving the ends and being deposited on the sides. Furthermore, were deposition of CdSe on the side of the rod favorable at this temperature, it seems unlikely that tip formation would occur at all, since most CdTe would also form isotropically. At higher temperatures (or given more time and no precursors), the CdSe rods would be expected to deform and become spheres.

After formation, the CdSe/CdTe nanobarbells are then precipitated from the growth solution by the addition of toluene, and centrifuged at 3900RPM, after which the supernatant, containing CdTe dots (usually accounting for less than 10% of total CdTe added in second step) is discarded. The resulting precipitate is sonicated into a suspension in hexane from which it will immediately precipitate and can be centrifuged. Once again the supernatant is discarded. These steps extract, in the supernatant, any CdTe dots formed during the synthesis from the solid CdSe/CdTe nanobarbells. After
this CdSe/CdTe nanobarbells can be redispersed in chloroform and precipitated several times using butanol/methanol in order to remove any excess organic material from the solution. CdSe/CdTe nanobarbells appear to be light sensitive and stay dispersed in solution for several days only if stored under nitrogen in the dark.

Figure 1: Transmission electron microscope (TEM) images of CdSe/CdTe nanobarbells taken on a JEOL 200 TEM (top) and high resolution TEM images of same structures taken on a JEOL 2010 HRTEM.