ADVANCED MATERIALS

Supporting Information

for

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Quantum Dot Synthesis

Tri-n-octylphosphine (TOP), tri-n-octylphosphine oxide (TOPO), hexadecylamine (HDA), oleylamine and hexamethyldisilane (HMDS) were purchased from Fluka. Diethylxinc (Et_2Zn) and dimethylcadmium [Me_2Cd] were purchased from Strem Chemicals. Selenium pellets were obtained from Alpha Aesar. CdO and ZnO powder, sulfur granules, oleic acid and octadecene (ODE) were purchased from Sigma-Aldrich. All reagents were used as purchased with no additional purification.

QD CdSe cores were synthesized by first degassing 3g of TOPO under vacuum at 90°C for approximately 30 min. To perform the injection of QD precursors in this solvent, the temperature was raised to 310°C under inert Ar gas overpressure. This injection usually consisted of 4 ml from a solution of 1 M Se dissolved in TOP, 150 μl of Me_2Cd and additional TOP to fill a 20 ml syringe. After a swift injection to cool down the reaction mixture below the nucleation threshold, the temperature was maintained at 200°C to allow the QDs to grow in size until the desired emission wavelength was reached. This was controlled by regularly extracting aliquots during the growth phase. Once the solution was cooled to approximately 90°C, butanol was added and the QD cores were purified by repeated precipitation with methanol to rinse any residual TOPO. They were subsequently dispersed in 15 ml of hexane.

To prepare core-shell CdSe/ZnS QDs, 15g of TOPO and 15g of HDA were degassed under vacuum at 95°C for 30 min. 1 ml from a ~70 μM stock solution of QD CdSe cores was also precipitated with methanol. Collection of the precipitate was done by centrifugation and the cores were re-suspended in 1 ml of hexane to which 1 ml of TOP was then added. This solution was combined with the TOPO-HDA solvents at a reduced temperature of 60°C under Ar overpressure. Degassing was carried on for another 20 min at this temperature to allow hexane evaporation as well as other undesired materials of low vapor pressure. The temperature was raised to 140°C and the solution of ZnS precursors was injected slowly dropwise while stirring vigorously. This solution consisted of 75 ml of Et_2Zn, 75 ml of HMDS and 5 ml of TOP. Once the injection was completed, cooling, addition of butanol, QD core-shell purification and dispersion was performed the same way than previously for the QD core synthesis.

A different approach with the SILAR (successive ion layer adsorption and reaction) method was taken to synthesize CdSe/CdS/CdZnS/ZnS multishell QDs. First, stock solutions of cadmium oleate, zinc oleate and dissolved sulfur were prepared under inert Ar atmosphere after degassing the solvents at 75°C for an hour. The latter solution was obtained at a concentration of 0.1 M by mixing 481 mg of sulfur granules with 150 ml of ODE at 105°C for 2 hours. The former two stock solutions were made by complexing the relevant metal oxide with oleic acid. This was accomplished at 190°C with 1.926g of CdO in 30 ml of oleic acid to produce cadmium oleate ([Cd] $\sim$ 0.5 M) and at 250°C with 1.221g of ZnO in 30 ml of oleic acid for zinc oleate ([Zn] $\sim$ 0.5 M). Before starting the multishell growth, diluted 0.1 M Cd and Zn precursor solutions were prepared by adding oleic acid after melting the original stock solutions. A Cd : Zn 1 : 1 precursor solution ([Cd : Zn] $\sim$ 0.1 M) was also prepared to grow the alloy $Cd_{0.5}Zn_{0.5}S$ shell.

Second, the QD cores were put in a solvent mixture suitable for SILAR shell growth. 30 ml of ODE and 20 ml of oleylamine were loaded in the reaction vessel and heated to 70°C under vacuum for 30 min and then cooled to 60°C. 10 ml from a ~60 M stock solution of QD CdSe cores were transferred as is into the reaction flask under Ar overpressure via syringe. Hexane was then pumped off under vacuum at 70°C during 20 min. Back under Ar atmosphere, heating was increased to reach the chosen growth temperature of the CdS shell at 230°C.

Finally, SILAR shell growth was done by alternating the injection of either Cd, Cd : Zn or Zn precursor solutions with the sulfur solution, starting with the Cd precursors since the first shell was made of CdS and since the core synthesis was carried out with excess Se relative to Cd. The amount used for each injection was calculated from the respective volumes of concentric spherical shells with a thickness of a half hypothetical monolayer (ML), taking into account the increase in QD radius caused by each additional ML. On QD cores having a radius of 1.56 nm, the 3 MLs CdS shell was grown with 0.82 ml, 1.22 ml and 1.70 ml injections of each Cd and sulfur precursors (0.1 M). Successive Cd : Zn and sulfur 0.1 M precursor injections of 1.84 ml, 2.42 ml and 3.07 ml each were done to obtain the 3 MLs $Cd_{0.5}Zn_{0.5}S$ shell. The final ZnS outer shell also having a thickness of 3 MLs was grown with 4.15 ml, 5.00 ml and 5.93 ml injections of each Zn and sulfur precursors. The growth

temperatures were 260°C and 310°C for the $Cd_{0.5}Zn_{0.5}S$ shell and ZnS shell respectively. We waited at least 10 min between each injection to give sufficient time for the deposition of the injected reagents on the QDs. This time was increased to 20 min for the first ML of a different semiconductor shell. At the end, the multishell QDs were cooled down below 90°C and purified by precipitation, first with a 1 : 1 solution of ethanol and methanol and then at least twice with ethanol only, separated and redispersed in 15 ml of hexane.