Synthetic Scheme for High Quality InAs Nanocrystals Based on “Self-Focusing” and One-Pot Synthesis of InAs-Based Core/Shell Nanocrystals

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Experimental Section

Materials:

1-octadecene (90%, Aldrich), Indium acetate (In(Ac), 99.99%) Tri-n-octylphosphine (TOP, 97%), tris-(trimethylsilyl)phosphine ((TMS)₃P, 98%), 1-octylamine (Alf 99%) Stearic acid (SA, 98%), Cadmium stearate and selenium powder (Se, 9.999%) were purchased from Alfa. Mercaptopropionic acid (MPA, 99%) Zinc Oxide (ZnO, 99.99%) and Octanoic Acid (98%) were purchased from Adrich. Indium stearate and Tris-(trimethylsilyl)arsine (As(TMS)₃) were synthesized in the lab respectively. Zinc precursor and Cadmium precursor were prepared by heating the mixture of ZnO and octanoic acid or CdO and Octanoic acid at 250 °C respectively, then Zinc and Cadmium precursors were purified by the addition of acetone, and the precipitation was dried under the vacuum respectively.

Stock Solution:

Cadmium stock solution. A solution of 0.2 M Cd in ODE was prepared as followed: 2mM cadmium precursor, 2mM octylamine (0.7 ml) and ODE (9.3ml) were loaded into flask and heated to 80 °C under argon. When the solution is clear, it was cooled down to room temperature.

Zinc stock solution. A solution of 0.2 M Zn in ODE was prepared as followed; 2 mM Zinc precursor (2mM octylamine (0.7ml) and ODE (9.3ml) were loaded into flask and heated to 80 °C under the argon. When the solution is clear, the solution was cooled down to room temperature.

Selenium stock solution. A solution of 0.2 M selenium was prepared by mixing 2mM selenium (0.158g) with TOP (10ml) in a glovebox.
Synthesis of InAs quantum Dots. In a typical synthetic reaction, 0.4mM Indium stearate, 0.5ml TOP and 3.5ml ODE were loaded into three-neck-flask. This mixture was heated to 150 oC under the argon flow. At this moment, As(TMS)3 solution made in glovebox (0.05-0.1 mmol) was injection into reaction solution, and then the solution was heated to a desired temperature for the growth of InAs with different size.

In Situ Synthesis of core/shell QDs based on the InAs core. (See supporting information)

Transmission Electron Microscopy (TEM) The low-resolution TEM images were taken on a JEOL 100CX transmission electron microscope with an acceleration voltage of 100kV. Carbon coated copper grids were dipped in the hexanes or toluene solutions to deposit nanocrystals onto the film. High-resolution TEM (HRTEM) pictures were taken using a Taitan microscope with an acceleration voltage of 300KV.

Optical Measurements. Absorption spectra were measured on a HP 8453 diode array spectrophotometer. Photoluminescence (PL) was measured on a Spex Fluorolog 3-111 using a PMT detector for spectra between 400 and 850 nm and a liquid-nitrogen-cooled InGaAs photodiode detector for emission in the NIR (700-1500 nm). PL quantum yields (QYs) of the samples were determined through comparison using organic dyes with known quantum yields as standards.

In Situ Synthesis of InAs/CdSe core/shell QDs. The growth solution of InAs quantum dots was set at 180°C, next, 0.04mM Se in TOP (0.2ml) was injected into reaction flask including InAs nanocrystals, waiting for 5minutes, the same amount of cadmium precursors was injected into reaction solution. After that, the temperature was increased to 190 °C for 30 min to allow the growth of CdSe shell.

In Situ Synthesis of InAs/InP core/shell QDs. InAs core synthesized in the previous section was cooled to 110 °C. 0.3mM Stearic acid (0.5ml in ODE) was injected into the reaction solution, then a mixture of 1mM octylamine (0.2ml ) and 0.2mM (TMS)3P in ODE (0.8ml) was added into reaction solution drop by drop. After the addition of P precursor, the mixture was heated to 178 °C and maintained 45minutes for the growth of InP shell onto the InAs core.
**In Situ Synthesis of InAs/ZnSe core/shell QDs.** The growth solution of InAs quantum dots was set at 180 °C, next, 0.04mM Se in TOP (0.2ml) was injected into reaction flask including InAs nanocrystals, waiting for 5minutes, the same amount of zinc precursors was injected into reaction solution. After that, the temperature was increased to 220 °C for 30 min to allow the growth of ZnSe shell.

**Water-solubility with mercaptopropionic acid (MPA).** The MPA-coated nanocrystals were synthesized by the phase transfer method. In the following manner hydrophobic nanocrystals were dissolved in about 2 mL of chloroform to give a high concentration solution (optical density about 1) and added under vigorous stirring to the same volume of a water solution containing MPA. The amount of MPA was adjusted to roughly 200% of the total Zn-atoms on the particle surface. After 2 h, the NCs transferred into the water phase. A clear solution (pH=8–10) was obtained by the addition of NaOH solution.

**Atomic absorption (AA) Measurements**
A purified InAs/CdSe core/shell nanocrystal sample was dried by gentle heating under argon, and then the sample was digested by 0.5 mL of king water. The digested sample was transferred into a volumetric flask to make an aqueous solution for the AA measurement. The concentration of cadmium, selenium, indium and arsenic was determined using a GBC 932 atomic absorption spectrometer. The obtained Arsenic concentration was converted into the nanocrystal particle concentration by dividing it by the number of As atoms in one nanocrystal, assuming that the nanocrystal particle has the same density as its bulk material.
Figure 1S. UV-Vis spectra of InAs nanocrystals synthesized in presence of octylamine

Figure 2S. The quantum yield of one set of InAs/CdSe core/shell nanocrystals with different number of monolayers of CdSe layers
Figure 3S. The quantum yield of InAs/CdSe core/shell nanocrystals before and after phase transfer.

![Quantum Yield Graph](image)

Figure 4S. TEM and high resolution TEM (HRTEM) images of InAs/CdSe core/shell particles and its electron diffraction patterns.

![TEM Images](image)