

Supporting Information

Bright and Compact Alloyed Quantum Dots with Broadly Tunable Near-Infrared Absorption and Fluorescence Spectra through Mercury Cation Exchange

Andrew M. Smith and Shuming Nie*

Departments of Biomedical Engineering and Chemistry, Emory University and Georgia Institute of Technology, 101 Woodruff Circle, Suite 2001, Atlanta, GA 30322, USA

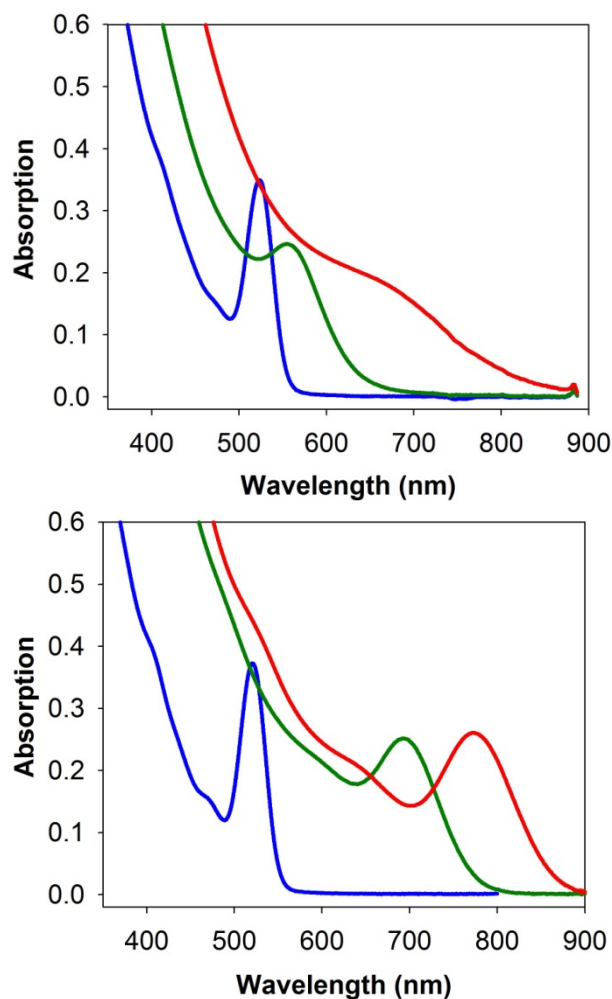
Materials. Cadmium oxide (99.99%), cadmium acetate hydrate (99.99%), mercury acetate (99.999%), sulfur (99.998%), 1-thioglycerol, 1-octanethiol, dimethylsulfoxide (DMSO), potassium hydroxide, octylamine, dodecylamine, acetone, chloroform, methanol, and hexane were purchased from Sigma. Tetradecylphosphonic acid (TDPA), tellurium (99.999%), and 1-octadecene (technical grade, 90%, ODE) were obtained from Alfa Aesar. Dimethylcadmium, trioctylphosphine oxide (99%) and trioctylphosphine (TOP) were from Strem. Oleylamine was from Acros Organics.

Nanocrystal Synthesis. CdTe synthesis was performed in a high temperature solvent using previously published procedures.¹ Cadmium oxide (25.7 mg, 0.2 mmol), tetradecylphosphonic acid (122 mg, 0.44 mmol), and ODE (2 mL) were added to a three-necked flask and heated to 250°C under argon until complete dissolution of CdO. After cooling to room temperature, oleylamine (1 g, 3.74 mmol) and additional ODE (6.5 mL) were added. The solution was heated to reflux under vacuum (~20 Pa, ~100°C) for 1 hour and then heated to 300°C under argon flow. A second solution, containing tellurium (12.76 mg, 0.1 mmol), trioctylphosphine (TOP, 2 mL), and ODE (3 mL), previously dissolved at ~280°C and then cooled to room temperature, was injected into the cadmium precursor solution, and the growth temperature was set to 250°C. Using this method, highly monodisperse nanocrystals were grown between 2.0 and 3.5 nm diameter after reaction times between 20 seconds and 10 minutes. To grow larger nanocrystals, additional cadmium and tellurium precursors were sequentially injected dropwise into the reaction solution, starting at 4 minutes after the first injection. The 0.02 M tellurium solution used for the first injection was also used for subsequent injections, and a 0.02 M cadmium oxide-tetradecylphosphonic acid solution in ODE was used as a cadmium precursor. After reaching the desired size, the reaction mixture was cooled to room temperature, diluted 1:1 with hexane, and centrifuged to remove unreacted cadmium precursor. The QDs were then purified with repeated hexane-methanol extractions and stored in decane under inert gas. It is important to avoid precipitation of these QDs, which may result in irreversible aggregation that may not become evident until colloidal destabilization occurs during high-temperature shell growth. CdSe and CdS nanocrystals were prepared and purified using similar protocols, adapted from previous reports.²

Mercury Exchange. Mercury thiolate precursors were prepared by mixing a solution of mercury acetate (1 eq.) with a solution of mercaptan (e.g. 1-octanethiol, 3 eq.) and KOH (3 eq.) in methanol at room temperature. The mercury thiolate precipitate was isolated via filtration, washed twice with methanol and once with ether, and then dried under vacuum. In a typical mercury exchange reaction, CdTe QDs were diluted to 20 µM with chloroform and mixed with octylamine (0-5% v/v). A chloroform solution of the mercury thiolate (0.1 M) was added as a single fast injection under intense stirring. The extent of the kinetically-limited mercury exchange reaction was determined by both the amount of mercury added and by the duration of the reaction. The bandgap was monitored through absorption spectrophotometry. Mild heating (50°C) and the use of octylamine can increase the reaction rate. The reaction was halted by the addition of an equal volume of ODE, followed by centrifugation or filtration to remove excess mercury precursor, and repeated hexane-methanol extractions (at least 3). The elemental composition was determined using XPS or ICP-MS (see below). For reactions using amines in solution, it is critical to perform this procedure under inert gas for smaller QDs, which are prone to oxidative etching. Addition of ligands such as phosphines, phosphonic acids, or thiols result in inhomogeneous cation exchange (see **Supporting Figure 1**). Removal of the excess mercury precursor prior to shell growth is necessary in order to prevent a significant red-shift in the spectra during heating and to avoid homogeneous nucleation of HgTe nanocrystals. For CdSe and CdS nanocrystals, mercury acetate dissolved in neat octylamine was used as the mercury precursor.

Shell Growth. A purified hexane solution of Hg_xCd_{1-x}Te nanocrystals (200 nmol) was diluted in a mixture of trioctylphosphine oxide (2 g) and octadecene (7.5 mL), and hexane was removed under vacuum at 60°C. The solution was further evacuated for at least 30 minutes at 100°C and purged with argon. After heating to 160°C, a CdTe shell was grown on the nanocrystals using alternating dropwise injections of a solution of 0.1 M tellurium

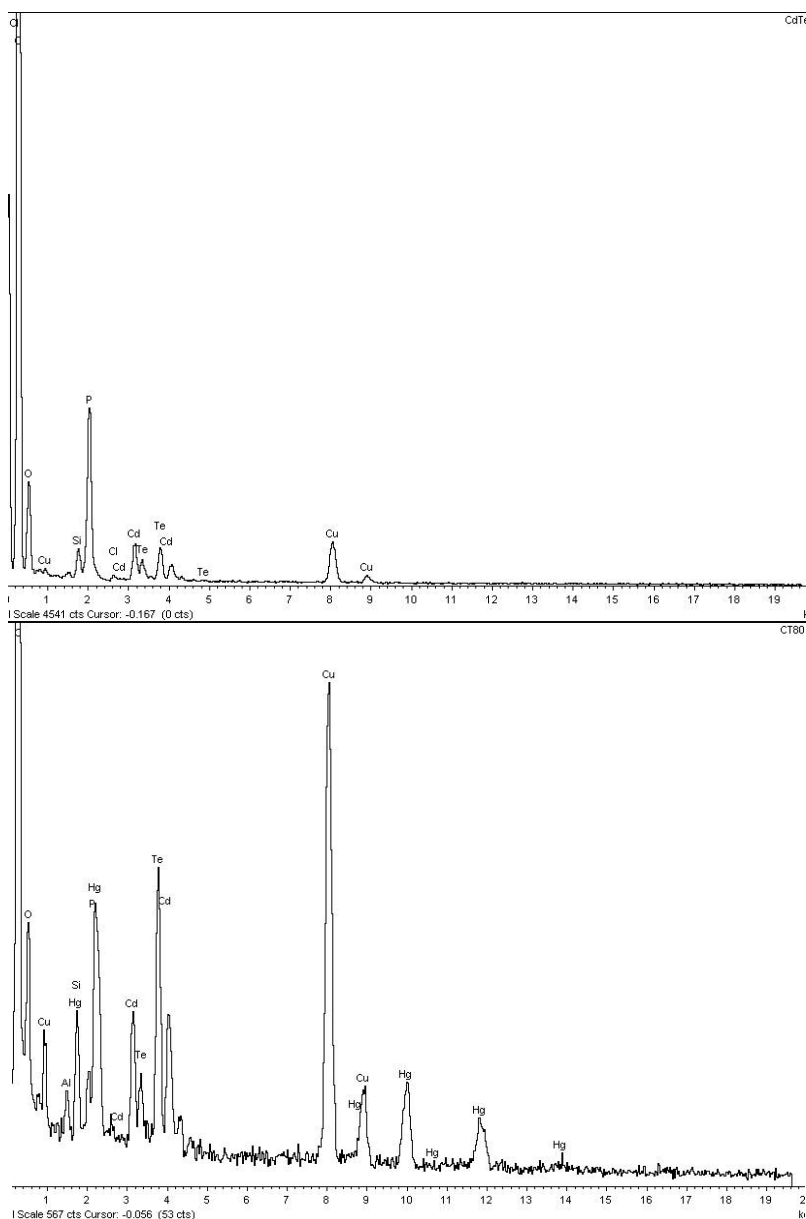
(with 0.25 M trioctylphosphine in ODE, previously dissolved at 160°C overnight), and a 0.1 M solution of dimethylcadmium in oleylamine. The QDs were annealed at 185°C for 20 minutes, and 10 mL of air-free oleylamine was added. The $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ shell was then grown on the nanocrystals at 210°C through the SILAR process³ using dimethylcadmium and diethylzinc in oleylamine, and elemental sulfur in octadecene. The nanocrystals were annealed at 230°C for 30 minutes after shell growth, and then cooled to room temperature and isolated through precipitation from excess acetone. We have also found that alternative precursors may also be used for shell growth, including cadmium ethylxanthate and zinc ethylxanthate.^{4,5} It is important to note that $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ QDs are labile due to weak binding between surface mercury atoms and ligands, and should not be precipitated prior to shell growth. In addition, $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ QDs are readily etched when exposed to high concentrations of phosphines, carboxylic acids, or phosphonic acids, until overgrowth of a CdTe shell. The $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ nanocrystals were found to be most resistant to etching in TOPO, in the absence of amines, however primary amines were important for maximizing quantum yield during the growth of the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ shell.



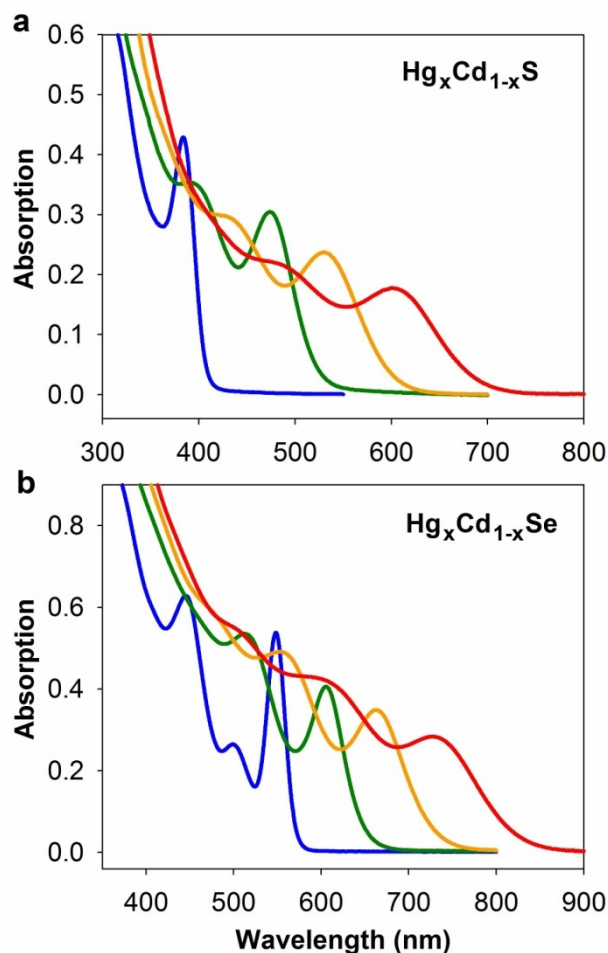
Supporting Figure 1. Examples of inhomogeneous (top) and homogeneous (bottom) cation exchange reactions in nonpolar solution. Absorption spectra of the QDs are shown at three time points: 0 minutes (before the addition of mercury) in blue, after roughly 30 minutes in green, and after overnight reaction in red. Inhomogeneous exchange was induced through the addition of a small amount of octanethiol, as free thiols substantially deteriorate the resulting QD alloys.

Characterization and Instrumentation. Absorption spectra in the range 300-900 nm were measured on a Shimadzu UV-2401PC scanning spectrophotometer. Absorption spectra from 850-1700 nm were measured using a NIR-512 spectrometer from Ocean Optics with a tungsten halogen lamp. Photoluminescence spectra were acquired using a spectrofluorometer from Photon Technology International with a xenon excitation lamp with

a photomultiplier tube detector for the spectral range 400-850 nm, and an InGaAs detector for the range 850-1600 nm. Quantum yield was measured by comparison to Atto dyes (520, 565, 610, or 680) dissolved in ethanol. All samples and standards were diluted to an optical density of 0.05 at the excitation wavelength, the emission spectra were integrated, and quantum yield was calculated after correcting for solvent refractive indices. For transmission electron microscopy, 5 μ L of sample was dropped onto formvar/carbon 200 mesh TEM grids. Basic transmission electron microscopy was performed by Dr. Hong Yi using a Hitachi H-7500 TEM at the Electron Microscopy Core Facility at Emory University. High resolution TEM was performed by Dr. Amar Kumbhar using a Hitachi H-9500 equipped with energy dispersive X-ray spectrometer at the Clemson University Electron Microscopy Facility. For quantitative elemental analysis, chloroform solutions of purified QDs were dried under vacuum, and the nanoparticle film was dissolved in aqua regia at 80°C for ~ 4 hours. The solution was then diluted in deionized water and analyzed for cadmium, mercury, and tellurium using inductively coupled plasma mass spectrometry (ICP-MS, VG PlasmaQuad 3, Center for Applied Isotope Studies at the University of Georgia).



Supporting Figure 2 Energy dispersive X-ray spectrum of CdTe (top) and Hg_xCd_{1-x}Te (bottom) nanocrystals. The Hg: Cd: Te proportions were 0:1.05:1 and 0.43:0.45:1, respectively.



Supporting Figure 3. Absorption spectra of $\text{Hg}_x\text{Cd}_{1-x}\text{S}$ (a) and $\text{Hg}_x\text{Cd}_{1-x}\text{Se}$ (b) nanocrystals prepared in organic solution and exchanged using mercury acetate and amines.

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