Synthesis and Characterization of Colloidal *β*-HgS Quantum Dots

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High-quality colloidal mercury sulfide quantum dots (QDs) are synthesized at room temperature using a strategy combining the effects of strongly binding Hg(II) ligands and metal/chalcogen precursor phase separation. This combination prevents both the rapid precipitation of bulk HgS in preparations involving only weak Hg(II) ligands and the reduction of mercury that takes place when only strongly binding ligands are used to slow the growth kinetics. Both the linear absorption and complementary band edge emission of the synthesized HgS QDs exhibit narrow, size-dependent transitions between 500 and 800 nm for sizes ranging from 1 to 5 nm in diameter. The metastable zinc blende phase of HgS is verified by wide-angle X-ray diffraction experiments and suggests potentially large tunable band edges if larger HgS nanocrystals that approach the bulk (zero energy) gap can be made. Growth of HgS QDs can be arrested by subsequent addition of Cd or Zn to the surface, after which the QDs can be stabilized with long-chain thiols or amines.

Introduction

Bulk mercury chalcogenides are narrow gap semiconductors widely used in infrared sensing applications. A technologically important feature of these materials is that solid solutions exist with other group IIB metal chalcogenides, such that the band edge energy in many cases increases continuously with the fraction of the wider gap component. This compositional control gives engineering access to an enormous spectral region: from the far-infrared to the visible.[1] At the same time, however, a different and perhaps more versatile approach to achieving this electronic tunablity is to exploit the quantum confinement effects intrinsic to colloidal nanocrystals, or quantum dots (QDs), made of mercury chalcogenides. In these systems, the band gap energy can, in principle, be varied from zero or small negative values to positive ones by simply reducing the physical dimensions of the particle.[2] Such materials are attractive for infrared[2] and biological imaging applications as well as for more fundamental studies about the physics of low dimensional materials. In this paper, a general strategy for colloidal nanocrystal fabrication is outlined which combines the concepts of precursor ligand stabilization and two-phase growth control. For HgS, it was found that this dual approach was necessary in order to produce small HgS QDs emitting in the visible region of the spectrum.

Despite tremendous progress in the synthesis of CdSe and other II−VI semiconductor QDs by the pyrolysis of organometallic precursors such as dimethylcadmium,[3] the synthesis of mercury chalcogenide QDs by this route has not been reported, due in part to the toxicity and volatility of corresponding organomercury compounds. Other preparations, involving the reaction of aqueous solutions of mercury salts with hydrogen chalcogenide gases have been developed. In particular, small 3−6 nm diameter HgTe QDs emitting in a broad wavelength range between 800 and 1400 nm have been made using this approach.[2,4] Other solvent-based procedures[5] involving sonochemistry, microwave assisted heating, thermal decomposition of mercury precursors, and Langmuir−Blodgett films have also been developed, but these lack the narrow size distribution and controlled growth characteristics of the more mature procedures such as those for CdSe QDs.

Recent synthetic work on CdSe,[6] CdTe,[6] and PbSe[7] illustrates a more universal approach for making high quality QDs, namely that an appropriate metal ion complexing agent can be used to separate crystal nucleation from growth by controlling the local concentration of reactive species.[8] In these procedures, metal ions are stabilized by surfactants such as long-chain fatty acids or alkylphosphonic acids. Control over the growth rate is achieved by slowing the effective mass transfer of reactive ions to the nanocrystal by either retarding the heterogeneous reaction rate with a more strongly binding metal ligand[6] or by altering the diffusion rate using bulkier, more sterically hindering ligands.[3a,6] This technique yields similarly low size polydispersities as in the aforementioned organometallic preparations in which crystal nucleation is separated from growth by the fast injection and decomposition of organometallic precursors.[3]

In the case of mercury, although many coordinating surfactants are available, we have found that the ligand binding strength alone does not adequately control the growth kinetics of HgS QDs. Representative ligands covering a large range of stability constants,[9] K, were investigated. Using those with K values less than 10^{17}, such as fatty acids (log $K \approx 6$ to 9) and amines (log $K \approx 10$ to 18), results in rapid precipitation of the mercury chalcogenide after addition of the chalcogen precursor. Increasing the surfactant chain length marginally slows the reaction, but not enough to prevent uncontrolled growth. At the other limit, more strongly binding ligands such as polyamines (log $K \approx 17$ to 28), phosphines (log $K \approx 30$ to 37), phosphine oxides, or thiols (log $K > 30$) appear to favor the reductive elimination of mercury metal[10] at temperatures necessary to react these complexes with common chalcogen precursors.

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Given the above constraints, an approach was undertaken to confine the mercury and sulfur precursors in different phases of the reaction medium, expanding early techniques of II−VI QD synthesis[11] to accommodate the reactivity of mercury. In this paper, a general procedure for the production of mercury chalcogenide QDs is outlined. For the case of HgS, room temperature absorption/emission, wide-angle X-ray diffraction, and transmission electron microscopy results are presented and discussed below.

Experimental Section

The following chemicals were purchased from Aldrich[12] and used without further purification: bis(2-ethylhexyl)sulfosuccinate (AOT), cyclohexane, mercury(II) acetate ($HgAc_2$), mercury-(II) chloride ($HgCl_2$), mercury(II) perchlorate ($Hg(ClO_4)_2$), zinc acetate, cadmium acetate, bis(trimethylsilyl)sulfide (($TMS)_2S$) and thioglycerol. For $Hg(ClO_4)_2$, the degree of hydration was estimated based on the listed formula weight. Deionized water was obtained from a Millipore MilliQ unit. Dimethylcadmium ($CdMe_2$) and diethylzinc ($ZnEt_2$) were purchased from Strem Chemicals, and filtered with a 0.2 μm PTFE filter prior to use. (Caution: $CdMe_2$ and $ZnEt_2$ are pyrophoric and should be handled with care. Further care should be exercised to avoid unintentional exposure to mercury compounds.)

In a typical procedure, 3.4 g of AOT ($\approx$ 0.01 mol) is dissolved in 20 mL cyclohexane. Additional drying of the AOT was found not to be important, and the amount of organic solvent can also be varied over a large range with no adverse effects on the crystal growth, being limited only by the solubility of the AOT in cyclohexane. A mercury stock solution is prepared by combining 100 mg $HgAc_2$ with 27 μL thioglycerol and 3 mL deionized water. Thioglycerol should be added last as it reacts immediately with $HgAc_2$ to form an insoluble black precipitate. The stock solution keeps over a period of weeks with eventual discoloration and slight precipitation of a black powder determined to be HgS from energy-dispersive X-ray spectroscopy (EDXS) measurements. Of this stock solution, 0.11 mL (1 × 10^{-5} mol Hg(II)) is added to the flask containing AOT/cyclohexane and stirred until clear. In a glovebox, 2.4 μL of ($TMS)_2S$ (1 × 10^{-5} mol) is mixed with 10 mL of hexanes and loaded into a disposable syringe. The chalcogen solution is then delivered at a rate of $\approx$1 mL/min with a syringe pump. Sharp color changes occur over the course of several minutes, progressing from yellow to pink to purple to green to olive and brown before flocculation.

To passivate the surface of HgS QDs, aqueous solutions of cadmium (zinc) acetate or hexane solutions of dimethylcadmium (diethylzinc) are used. For the organometallic precursors, 2 μL of $CdMe_2$ or $ZnEt_2$ (about 2 or 3 × 10^{-5} mol) are mixed with 10 mL of hexanes. The solution is then loaded into a disposable syringe and brought out of the glovebox. At a desired size (energy), HgS growth is stopped by replacing the ($TMS)_2S$ solution with the Cd (or Zn) solution and the metal precursors are subsequently introduced using the same syringe pump.

Once HgS QDs have been passivated with Cd or Zn, organic surface modifying ligands can be added to extract the particles from the reaction mixture. For Cd-passivated QDs, adding thiophenol to the reaction vessel causes the particles to precipitate from solution, whereupon they can be resuspended in polar aprotic solvents, such as DMF, pyridine, DMSO, and THF, with DMF being the preferred solvent. Dodecylamine and hexadecanethiol can also be used to stabilize Cd-passivated HgS QDs. Following addition of about 5 × 10^{-3} mol of either compound, butanol and methanol are added to precipitate the

QDs from solution. The recovered precipitate is then resuspended in toluene. In the case of Zn-passivated HgS QDs, only hexadecanethiol and octanethiol were found to effectively stabilize the particles. After adding 2 mL of either thiol, the particles are precipitated from solution with butanol/methanol and the recovered precipitate is resuspended in toluene.

Absorption experiments are carried out during particle growth by connecting the reaction flask to a 1 cm path length (Spectrocell Inc.) UV−vis cell mounted to a diode array UV−vis spectrometer HP8453 (Hewlett-Packard). The solution is continuously circulated between the cell and the flask using a gear pump with absorption spectra collected periodically. Wide-angle X-ray diffraction scans were taken using a high-resolution powder diffractometer with Cu Kα radiation, λ = 1.54 Å, derived from a 12 kW rotating anode X-ray generator (Rigaku). Powdered samples were mounted onto Si(001) substrates, offset by 3 degrees in omega to eliminate the Si(004) peak at 2θ = 69.128. Peak positions and their full width at half-maximum (fwhm) were determined using commercial peak fitting software. EDXS measurements were conducted using the EDAX energy-dispersive X-ray spectrometer attachment of a Leo 1550 scanning electron microscope (SEM) operated at an accelerating voltage of 10 kV.

Photoluminescence spectra and quantum yields (QY) were measured using a Spex fluorolog fluorimeter. A Xenon arc lamp was used as the incident light source. Samples were excited at right angles to the emission monochromator with a Hammamatsu R928 photomultiplier tube or CCD used as the detector. QY measurements were conducted relative to Rhodamine 610 in methanol. Optical densities were 0.1 or smaller, and 1 cm optical path length cells were used for both sample and standard. The wavelength-dependent instrument response was taken into account to correct raw quantum yields. Further corrections were made to account for differences in the sample/standard absorbance and refractive index.

Results and Discussion

The combination of a strongly binding ligand (thioglycerol) for Hg(II) and precursor phase separation makes it possible to grow HgS nanocrystals at controllable rates. An equimolar ratio of thioglycerol to mercury was found to be optimal for QD preparation. Increasing or decreasing this ratio adversely affects the reaction, with noticeable degradation of the HgS absorption spectra. During the course of the synthesis, the reaction mixture progresses through a striking range of colors, from yellow to purple to green and eventually brown. As shown in Figure 1, these colors arise, in part, from the large separation between the first and second absorption features, resulting in high transmission through this spectral window. The UV−vis absorbance indicates a narrow band edge absorption, as well as structure at higher energies, and the band edge fluorescence follows the same size dependence as the absorption with little deep trap emission observed.

Although $HgAc_2$ was found to be the most reliable precursor for the synthesis of HgS QDs, other mercury(II) salts can be used. Mercury/thioglycerol solutions based on $Hg(ClO_4)_2$ and $HgCl_2$ were made with identical concentrations based on listed formula weights. In the case of $Hg(ClO_4)_2$, similar results as with the acetate were obtained. $HgCl_2$ readily dissolves in water, but the subsequent addition of thioglycerol results in an immediate reaction evolving vapor and a white precipitate. This precipitate eventually redissolves in water over the course of several days, and the resulting solution can be used in the above synthesis, yielding a low concentration of QDs (i.e., the overall
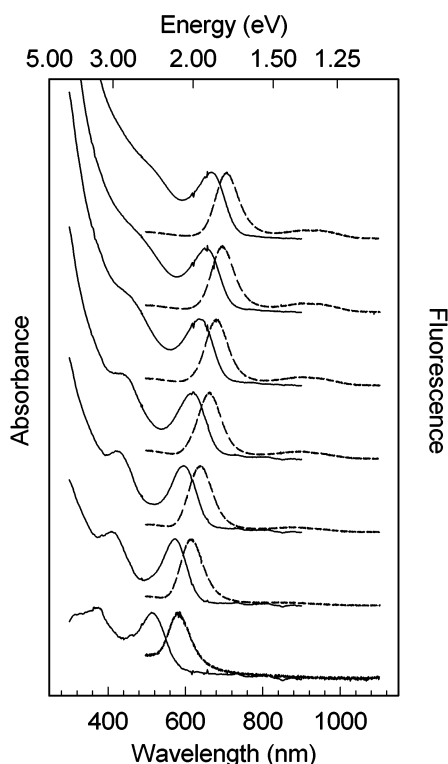
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Figure 1. Linear absorption and corresponding band edge emission of HgS QDs. The solid line denotes the absorption and the dashed line the emission.
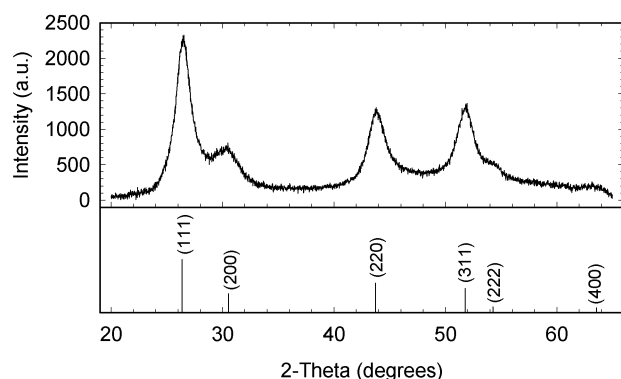

Figure 2. WAXS pattern of HgS QDs showing the zinc blende phase of the material. For comparison, a stick pattern of β-HgS is shown.

Figure 3. TEM micrograph of β-HgS QDs. Inset is an image of a single QD showing lattice with multiple twins.

Figure 4. Color photograph showing the emission of β-HgS QDs after Cd or Zn passivation. The inset is a photograph of the solutions as they appear to they eye under normal illumination.

absorbance of the solution is low) and poorly resolved features in the UV−vis spectra.

The band edge absorption of HgS QDs occurs over a range of energies between 2.1 and 1.5 eV. In contrast, the common HgS allotrope at room temperature and pressure is cinnabar (α-HgS, hexagonal unit cell) with a band gap of about 2.2 eV.[13] Wide-angle X-ray scattering (WAXS) measurements performed on particles grown to the point of flocculation (Figure 2) indicate that these QDs possess the cubic zinc blende (metacinnabar) structure of β-HgS, a metastable phase that is of technological interest because of its (bulk) zero energy band gap.[13]

Unlike other QDs grown using reverse micelle media, the size of the recovered material does not depend on the water content, $W = [H_2O]/[AOT]$. Preliminary particle sizing through WAXS[14] and transmission electron microscopy (TEM) shows that during the synthesis, the diameter of the β-HgS QDs ranges from approximately 1 nm for the smallest sizes to 5 nm (about 800 nm band edge) at the point of precipitation. Figure 3 is a TEM micrograph of material recovered midway through the
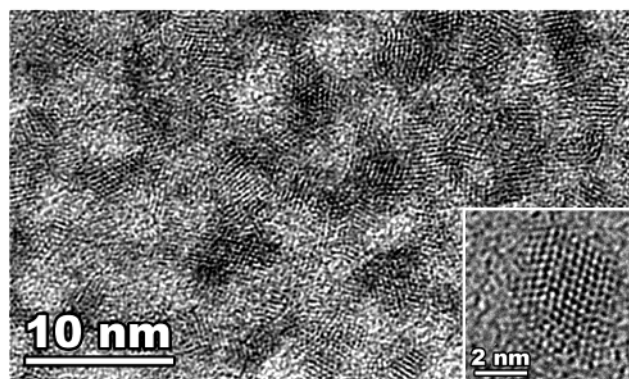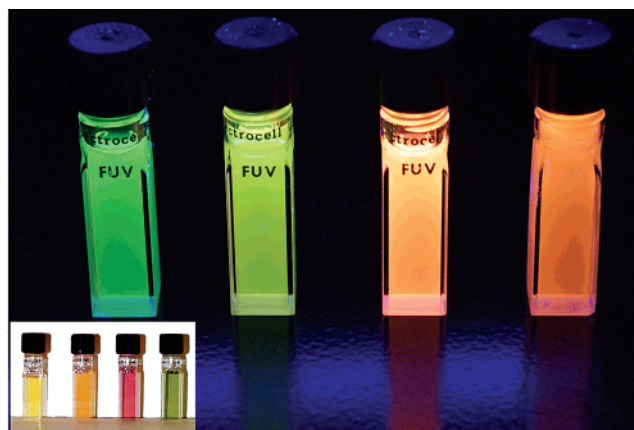
growth. In all cases, the observed QDs are substantially larger than the diameter of the micellar water pools expected for these $W < 1$ values,[15] suggesting that the QD growth is not exclusive to the aqueous phase of the nearly "dry" micelles.

Without intervention, β-HgS QDs grow unabated until they precipitate from solution for both stoichiometric and nonstoichiometric (10:1 or 1:10 Hg:S) sulfide additions. Nanocrystal growth can, however, be halted by adding Cd or Zn to the surface. In early studies, a similar approach has been used to demonstrate the concept of epitaxial layer growth,[11] but not to actively arrest crystal growth. In the present case, aqueous solutions of cadmium (zinc) acetate or hexane solutions of dimethylcadmium (diethylzinc) are directly added to the growth solution, stopping the growth by altering the surface reactivity of the QDs. As an added benefit, HgS nanocrystals treated with organometallic Cd or Zn precursors have noticeable room temperature quantum yields (5 to 6%), while the emission of those passivated using aqueous precursors is difficult to observe (QY < 1%). Figure 4 is a photograph of the room temperature emission from a size series of Cd- and Zn-passivated β-HgS QDs illustrating the enhanced QYs. The inset is a photograph of the solutions as they appear to the eye under room light.

After Cd or Zn addition, there is a noticeable broadening of the absorption spectrum. Preliminary measurements as well as comparisons to absorption/emission widths of more developed systems such as CdSe yield size distributions between 20 and 30%, with smaller values prior to surface modification suggested by the narrow, resolved, transitions in Figure 1. Cd-passivated QDs show no further evidence of growth over a period of months, but Zn-passivated particles undergo gradual etching of

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the surface over the course of several days, as evidenced by a gradual blue shift of both the absorption and emission spectra. The surface modification also allows the subsequent stabilization of β-HgS QDs with common ligands. For example, when modified with long-chain aliphatic amines or thiols (e.g., dodecylamine or hexadecanethiol), these QDs can be precipitated from solution and resuspended in a variety of nonpolar solvents.

In summary, this strategy combining Hg(II) ligand stabilization and precursor compartmentalization is envisioned as a general method for obtaining mercury chalcogenide QDs. Although the current work shows only the synthesis of small β-HgS QDs, these results should provide the foundation for future improvements in the synthesis of these materials, allowing the development of infrared emitting species. In this respect, work to extend the emission into the infrared with larger HgS QDs as well as with HgSe, HgTe, and their ternary alloys (e.g., $Hg_xCd_{1-x}Te$) is currently underway.

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