

Pushing the Band Gap Envelope: Mid-Infrared Emitting Colloidal PbSe Quantum Dots

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Efficient mid-infrared (mid-IR) light sources and lasers are important enablers for a variety of technologies, including gas analysis, remote sensing, and atmospheric monitoring.¹ Among current sources, organic laser dyes are poor fluorophores (quantum yields (QYs) in emission <0.5%) that are confined to the near-IR, while mid-IR emitting rare-earth doped crystals offer limited emission wavelengths and small absorption cross sections. Alternatively, epitaxial quantum wells provide the possibility for efficient, continuously tunable mid-IR emission,² but these are not chemically processible. Here, we report the synthesis of the first *colloidal* quantum dots (QDs) with efficient, particle-size-tunable, narrow-bandwidth mid-IR photoluminescence (PL) at energies as low as 0.30 eV (4.1 μm). Colloidal QDs, or semiconductor nanocrystals, have properties similar to molecular emitters, which are soluble and processible in a range of organic and inorganic chemical matrices. Previously, colloidal QDs have been reported that emit from the ultraviolet, e.g., ZnSe,³ through the visible, e.g., CdSe,⁴ and into the near-IR, e.g., small-size PbSe (<8 nm in diameter).⁵ Bulk PbSe has a band gap of 0.26 eV (4.7 μm) at room temperature (RT); therefore, PbSe QDs have the potential to provide PL in the mid-IR energy range (>2.5 μm). We describe the synthetic routes to large-size PbSe QDs (>8 nm) that have allowed us to realize this potential.

The QDs discussed in this communication were synthesized via chemical routes according to two distinct variations of literature methods.^{5c} Both a low-⁶ and a high-temperature⁷ route were utilized to produce QDs emitting over the entire energy range reported herein. After synthesis, QDs were collected by precipitating by addition of methanol, followed by centrifugation. No additional size-selection techniques were employed for either route. All QDs were characterized by PL and absorption spectroscopy, as well as by transmission electron microscopy (TEM).

Both routes demonstrate excellent tunability in PL and narrow size distributions, with peak fwhm values of typical spectra consistently <70 meV over the entire energy range reported (Figure 1). The absorption spectra of the smaller QDs (PL peak >0.45 eV) synthesized by these methods show characteristic features with small Stokes shifts. Typical values are ~10 meV, for example, in the case of 0.49 eV-emitting QDs. Broadening of absorption features for energies <0.45 eV and strong ligand absorptions (C–H stretches from 0.35–0.37 eV or 2850–3000 cm^{-1}) complicate analysis of Stokes shifts for larger dots.

QD sizes were determined by TEM imaging (Figure 2) and correlated with the lowest optical transition energies (Figure 3), as determined from the PL maxima.⁸ The experimental energies are systematically lower than values predicted by a literature model (Figure 3). Further, TEM reveals not only the expected increase in size as PL energy decreases, but also a shape change. Figure 2

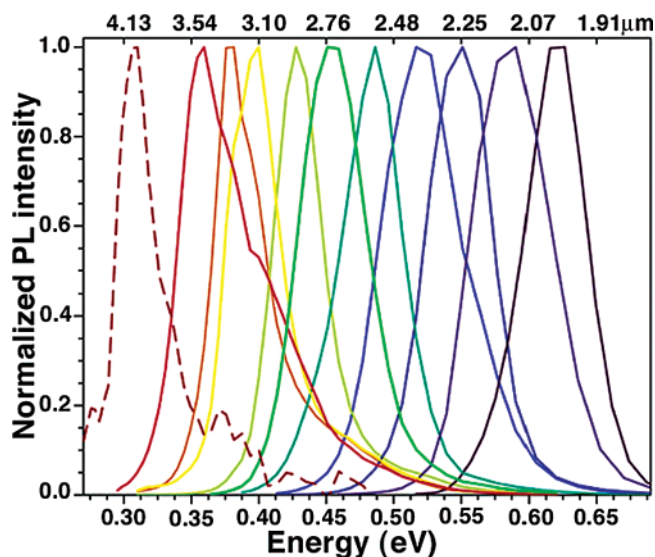


Figure 1. Normalized PL spectra⁸ of a series of PbSe QDs at RT, showing excellent tunability and narrow size distributions ($\sigma \approx 10\%$). The dashed spectrum was collected at 77 K from a sample with a peak at 0.34 eV at RT, exhibiting a red shift and narrowing.

depicts aliquots taken during growth using the high-temperature route, which shows a transition from spherical- to cubic-shaped QDs. The shape change also manifests itself in a switch from hexagonal close packing for spherical QDs, to a cubic arrangement for the larger cubic QDs upon drying on a TEM grid.

At small sizes, it is well established that PbSe QDs are spherical in shape.⁵ With the minimum surface-to-volume ratio, spheres are the lowest-energy shape when nanoparticles are small and surface energy considerations are dominant. At larger sizes, where bulk volume contributes more strongly to overall particle energetics, the crystal structure has a greater impact on particle shape. The underlying rock-salt crystal structure of PbSe favors a cubic shape for relatively large QDs. Further, the QD size at which this shape transition occurs is reaction-temperature dependent, occurring at a smaller size during low-temperature, slower growth (at sizes as small as 12 nm), where slower growth favors the thermodynamically preferred shape.⁹ Neither growth temperature nor the transition from sphere to cube produces a discernible change in the PL of QDs of a given size.

QYs were measured¹⁰ for QDs emitting at a wide range of energies and were found to decrease with increasing QD size, from values near unity for near-IR QDs (not shown) to 0.5% for QDs emitting at 0.35 eV (Figure 3, inset). A possible explanation for the diminution of both PL and absorption features in the mid-IR involves strong electronic coupling between a QD and its organic ligand layer, either through direct wave function mixing or energy transfer. Exciton relaxation may, therefore, take place nonradiatively

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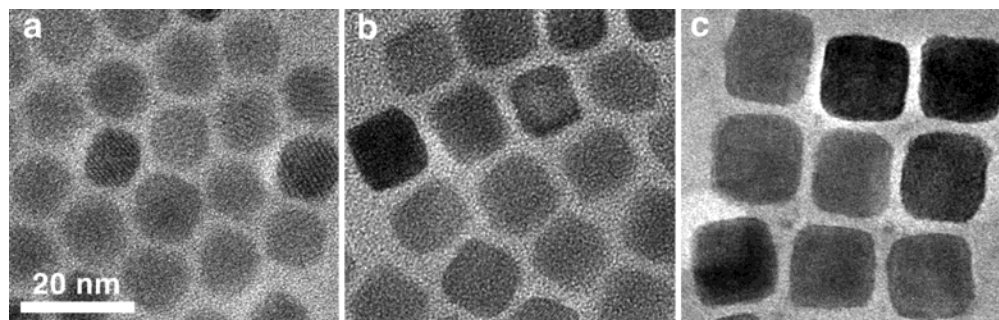


Figure 2. TEM images of PbSe QDs from aliquots removed during a single synthesis showing a shape transition: (a) 11 nm, (b) 13 nm, and (c) 16 nm.

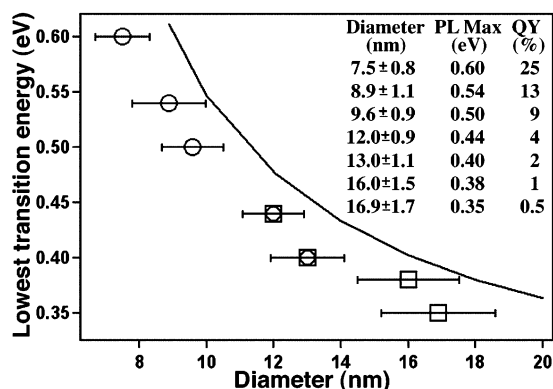


Figure 3. Correlation of the lowest transition energy with QD size (\pm size dispersion) and shape (\circ = spheres, \square = cubes). Solid curve represents calculation of the same by the four-band envelope-function formalism.¹¹ Inset: size, PL maximum, and QY for a series of PbSe QDs. “Diameter” of cubic QDs is edge length.

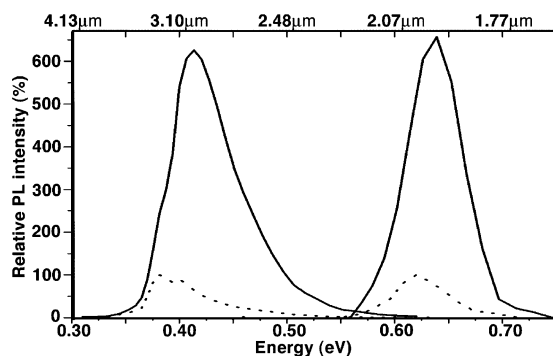


Figure 4. Relative PL intensity before (dotted line) and after (solid line) CdSe coating for QDs of two emission energies.

through coupling to the vibronic system of the ligands, reducing QYs and “smearing” transition features in absorption. In addition, QDs that emit near 0.35–0.37 eV (2850–3000 cm^{-1}) lose a significant amount of intensity to reabsorptive excitation of C–H stretches in their organic passivation layer. This can be observed as an asymmetrical narrowing of the lower energy peaks in Figure 1. Although these effects result in reduced QD PL efficiencies in the mid-IR, there are no equivalent organic or solution-phase inorganic phosphors in this energy range.

Figure 4 shows the preliminary results of attempts to improve QY through inorganic passivation. A shell of a higher band gap

material such as CdSe has been shown to enhance PL intensity of less-than-ideal QD samples in distinct size and shape regimes as much as 6-fold. Already, core/shell QDs have demonstrated QYs above 1% at 0.35 eV. Benefits to QD stability and substitutional flexibility of the surrounding organic ligands have also been observed.

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Supporting Information Available: Corresponding absorption and PL spectra for near-IR and mid-IR QDs and additional TEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- For 0.34 eV QDs: lead(II) acetate trihydrate (2.55 mmol) and oleic acid (7.9 mmol) in trioctylphosphine (TOP, 10 mL) and phenyl ether (1 mL) are heated under vacuum (65 °C, 1 h), and 4.5 mL of the solution is removed. To the remaining solution is added TOP selenium (TOPSe, 1.7 mmol in TOP), and this mixture is injected into rapidly stirring phenyl ether (10 mL) at 200 °C. The solution is returned to 200 °C over 3.5 min. The 4.5-mL portion of the original solution is then mixed with TOPSe (0.85 mmol in TOP) and added dropwise over 8.5 min. After 3 min, the solution is rapidly cooled.
- For 0.34 eV QDs: lead(II) acetate trihydrate (1.7 mmol) and oleic acid (4.7 mmol) in TOP (7 mL) and phenyl ether (1.5 mL) are heated under vacuum (65 °C, 1 h). TOPSe (1.7 mmol in TOP) is added, and the mixture is injected into rapidly stirring phenyl ether at 250 °C. After 4 min, the solution is rapidly cooled.
- PL collected on a cooled InSb detector from dilute samples in hexane or CDCl_3 excited at 808 nm.
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- QY is calculated relative to IR26, and includes corrections for grating and detector efficiencies.
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