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Chemical Structure, Ensemble and Single Particle Spectroscopy of Thick-Shell InP-ZnSe Quantum Dots

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Abstract

Thick-shell (> 5 nm) InP-ZnSe colloidal quantum dots (QDs) grown by a continuous-injection shell growth process are reported. The growth of a thick crystalline shell is attributed to the high temperature of the growth process and the relatively low lattice mismatch between the InP core and ZnSe shell. In addition to a narrow ensemble photoluminescence (PL) line-width (~ 40 nm), ensemble and single particle emission dynamics measurements indicate that blinking and Auger recombination are reduced in these heterostructures. More specifically, high single dot ON-times (> 95%) were obtained for the core-shell QDs and measured ensemble bi-exciton lifetimes, $\tau_{2X} \sim 540$ ps represent a 7-fold increase compared to InP-ZnS QDs. Further, high-resolution energy dispersive X-ray (EDX) chemical maps directly shows for the first time significant incorporation of indium into the shell of the InP-ZnSe QDs. Examination of the atomic structure of the thick-shell QDs by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) reveals structural defects in sub-populations of particles that may mitigate PL efficiencies (~ 40% in ensemble), providing insight towards further synthetic refinement. These InP-ZnSe heterostructures represent progress toward fully cadmium-free QDs with superior photo-physical properties important in biological labeling and other emission-based technologies.

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Supporting Information

Experimental methods, EDX spectra and chemical maps, InP-ZnS characterization and additional blinking traces. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

Notes

The authors declare no competing financial interest.

Keywords

indium phosphide; blinking; chemical structure; cadmium-free; zinc selenide; coreshell quantum dots

Colloidal semiconductor nanocrystals, also known as quantum dots (QDs), offer great promise as ideal optical materials for a number of emission-based technologies. Indeed, QDs have recently been popularized by their use as phosphors in wide-gamut, high brightness displays.¹ In biology, QD labeling strategies developed for single molecule tracking allow detailed mapping of cellular and neuronal processes over extended periods.² QDs have also been developed for use in solid-state lighting,^{3,4} luminescent solar concentrators (LSCs),⁵ low threshold solution-processed lasers,⁶ and as single and entangled photon sources.^{7,8} However, the bulk of progress towards the commercialization of QD technologies has so far centered on the development of cadmium-based materials, which are optically active at visible wavelengths and are fairly easy to synthesize with high quality photo-physical properties.^{9,10} With concerns over the toxicity of cadmium¹¹ and recent restrictions on its use in consumer products, considerable effort has been devoted to developing copper-indium chalcogenides and indium phosphide (InP) QDs as cadmium-free alternatives.

InP is of particular interest due to its size-tunable emission over the visible and near infrared spectral range (band gap ~ 1.35 eV) and lower intrinsic toxicity.^{12,13} However, compared to ubiquitous cadmium selenide (CdSe) QDs, InP QDs suffer from synthetically induced broad size distributions, have relatively low photoluminescence (PL) quantum yields (QY) and poor environmental stability.¹⁴ While significant attention has been given to improving these aspects of InP QDs,^{15–17} InP QDs are further characterized by strong PL instability/blinking at the single dot level,¹⁸ where the intensity of the emission from individual nanocrystals cycles between high and low values under continuous excitation.¹⁹ PL blinking limits the use of QDs in single-molecule tracking experiments, as stable single-photon sources and in other emission-based applications. The most proven strategy to minimize blinking in QDs has been to encapsulate the QD core in a thick crystalline inorganic shell.^{20,21} In this way, excited charge carriers are decoupled from the nanocrystal surface and surrounding environment.

In this work, we encapsulate InP QDs in a thick (> 5 nm) crystalline zinc selenide (ZnSe) shell. Thick-shell growth is credited to slow continuous injection of the shell material at high temperature and to a small lattice mismatch²² (3.4%) between the core and shell material. Concomitantly, high-resolution chemical maps of the QDs provides evidence for alloying of indium into the shell, which could further facilitate thick shell growth. The resulting core-shell heterostructures exhibit significant room temperature blinking reduction, characterized by ON-time fractions that can exceed 95%. In addition, we achieve a 7 -fold increase in the bi-exciton lifetime compared to large lattice mismatched zinc sulfide (ZnS) shelled QDs. Longer bi-exciton lifetimes indicate suppression of non-radiative Auger recombination. The reduction of Auger processes in QDs has been noted as a key parameter in the performance of many emission-based devices.^{23,24} We further identify structural defects in the shells of sub-populations of QDs that potentially mitigate PL efficiencies in the thick-shell heterostructures.

Ensemble optical and structural characterization.

Figure 1a shows the absorbance and PL spectra of a sample of thick-shell InP-ZnSe QDs. Zinc (II) oleate and selenium dissolved in trioctylphosphine are employed as shell precursors. Shell growth is carried out at high temperature (300 °C) *via* a continuous injection route in an inert atmosphere. During the growth procedure the QDs develop a strong absorbance feature at photon energies in the blue part of the visible spectrum; the onset of which matches the band edge of bulk ZnSe (2.7 eV, 460 nm) and is consistent with the growth of a large shell. Additionally, both the absorbance and PL of the InP-ZnSe QDs significantly shift to lower energy (InP core emission peak ~ 590 nm) during the first 2 hours of shell growth, a signature of relaxed exciton confinement induced by the ZnSe shell.¹⁶ We remark that calculated conduction band offsets for bulk InP-ZnSe (~ 0.39 eV),²⁵ are comparable to accepted values for CdSe-CdS core-shell QDs (~ 0.32 eV)²⁶ in which photo-excited electrons delocalize into the CdS shell.²⁷ Similarly to these CdSe-CdS heterostructures, a larger valence band offset likely strongly confines excited holes to the InP core.²⁸ The InP-ZnSe heterostructures exhibit PL QYs of $\sim 40\%$ at room temperature (emission maximum ~ 2.0 eV, 620 nm) and a full width at half maximum (FWHM) of ~ 40 nm (~ 130 meV), which is among the highest color purities reported for InP QDs.²⁹

Imaging of the QDs using transmission electron microscopy (TEM) shows that following ZnSe shell growth, the average diameter of the particles increases from ~ 3.0 nm for the InP core (figure S4, supporting information) to 14.1 nm (figure 1b), corresponding to a shell thickness of ~ 5.5 nm (~ 17 monolayers). We note a slight degree of irregularity in the shapes and morphology of the QDs produced by our shell growth method, highlighting the challenges and complexities related to InP epitaxy. The possible implications of these irregularities on the optical properties of the QDs are discussed below. Despite this, we obtain size distributions comparable to similarly thick-shell CdSe-CdS QDs of $\sim 11\%$ (figure S1, supporting information).²⁰ Furthermore, high-resolution transmission electron microscopy (HR-TEM) (figure 1c) depicts the highly crystalline nature of the heterostructures, revealing that they can be uniform and faceted with lattice fringes throughout. The lattice spacing (~ 0.21 nm) depicted in the high-resolution image acquired in high annular angular dark-field (HAADF) mode (figure 1d, inset) corresponds to the

(220) plane of the zinc-blende (ZB) crystal structure. Powder X-ray diffraction (XRD) measurements (figure 1d) supports epitaxial growth of ZB-ZnSe on top a ZB-InP core (figure S4, supporting information), indicating a retention of the starting crystal phase.

Figure 2a shows a high-resolution energy dispersive X-ray (EDX) chemical map of a core-shell InP-ZnSe QD. The map reveals in great detail the location of the core and shell elements of the particle and clearly shows that the InP core tends to be centered in a symmetrically grown ZnSe shell. This is further confirmed by a line scan profile of the QD (figure 2b). Figure S2 (supporting information) provides additional chemical maps of the thick-shell QDs. Interestingly, the chemical maps also show that indium is distributed across the core-shell interface and into the ZnSe shell (figure 2c and figure S2) of the heterostructures. Specifically, a $\sim 2\%$ (atomic percent) incorporation of indium in the ZnSe shell was estimated from the EDX maps, (figure S3, supporting information) suggesting that during shell growth indium alloys into the shell of the core-shell structures. This incorporation of indium into the shell may have implications on interfacial strain and the growth of a defect-free shell as well as the optical properties of the QDs.^{30,31} Future experiments will be needed to determine the role that alloying plays in these thick-shell QDs. The EDX maps additionally provide information on the relative amounts of each element present throughout the entire QDs and indicate that the core-shell particles are predominantly ZnSe (96% by composition, figure S2, supporting information) as expected.

Ensemble photoluminescence dynamics.

To gain insight into the excited state dynamics of the thick-shell InP-ZnSe QDs, we performed time-resolved PL measurements on dilute concentrations of QD samples suspended in toluene. Samples were excited at low fluences ($\sim 1 \mu\text{J}/\text{cm}^2$) and their emission dynamics measured with a time-correlated single-photon counting (TCSPC) system (time resolution, $t_{\text{res}} \sim 35$ ps). At these low excitation fluences, we expect the majority of photo-excited QDs to contain a single electron-hole pair. Figure 3a shows the recorded PL dynamics for InP, InP-ZnSe and a sample of InP-ZnS QDs prepared by our shell growth strategy using the same starting InP core. The decay of the QD samples is clearly multi-exponential and can be fit to a tri-exponential function (table S1, supporting information). While the specific origin of the multi-exponential decay in InP QDs is not fully understood, we observe a fast decay (~ 2 ns) in the trace of the as synthesized InP cores often attributed to unpassivated surface bonds.³² This decay is absent from the traces of the core-shell QDs indicating that the ZnS and ZnSe shell sufficiently passivates the related surface traps. For the core-shell structures, the decay times and the average lifetime, $\tau_{\text{avg}} \sim 68$ ns, observed for the InP-ZnSe are longer than the decay times and the average lifetime, $\tau_{\text{avg}} \sim 47$ ns, observed for the InP-ZnS QDs grown here. This increase in the lifetime of thick-shell InP-ZnSe compared to InP-ZnS presumably results from the combined effect of a larger shell volume and weaker exciton confinement,²⁵ leading to a lower oscillator strength for the radiative transition and a longer decay lifetime.³³

By further increasing the intensity of the excitation source, it is possible to assess the decay dynamics of multi-excitonic states in the thick-shell InP-ZnSe QDs. Multi-exciton recombination is important in applications where QDs are illuminated under high flux, such

as optical pumping.³⁴ Figure 3b shows the excitation intensity-dependent PL decay of the InP-ZnSe QDs for a range of excitation fluences ($1\text{--}100\ \mu\text{J}/\text{cm}^2$). At higher excitation intensities, the decay develops a fast component that grows with the intensity of the excitation beam. This fast decay arises from the recombination of multi-excitons, which become dominant at high excitation densities due to the increased probability of multi-photon absorption from the same laser pulse. Rapid decay of this multi-excitonic component is consistent with decay *via* fast non-radiative Auger recombination, where the e-h (electron-hole) recombination energy is quickly transferred to another carrier (electron or hole) present within the QD.³⁵ These measurements indicate that Auger recombination is a primary decay pathway in our thick-shell InP-ZnSe QDs at high fluences.

The excitation intensity-dependent PL dynamics can be used to extract the bi-exciton lifetime, (τ_{2x}), associated with the decay of doubly excited InP-ZnSe QDs. To this end, the decay traces in figure 3b are normalized at long delay times ($t = 4\ \text{ns}$). Next, the PL decay collected at low excitation fluence ($1\ \mu\text{J}/\text{cm}^2$) is subtracted from the decay traces measured at higher fluences to reveal the dynamics due to multi-excitons. The extracted dynamics (example in inset, figure 3b) can be fit to a single-exponential, with an average $\tau_{2x} \sim 540\ \text{ps}$. Similar measurements on InP-ZnS QDs, yield a much shorter average τ_{2x} of $\sim 78\ \text{ps}$ (figure S6, supporting information). This increase (~ 7 fold) in the bi-exciton lifetime of InP-ZnSe compared to InP-ZnS QDs indicate a reduction in the efficiency of fast non-radiative Auger recombination,³⁶ likely due to a decrease in electron-hole overlap generated by the ZnSe shell.³⁷ Despite this reduction in the efficiency of Auger-related processes in the thick-shell InP-ZnSe QDs, according to the expected ‘statistical’ scaling of the radiative rate with exciton multiplicity³⁸, bi-exciton radiative recombination rates are expected to increase by a factor of 2-4 compared to single-exciton rates. The observed bi-exciton rate for the InP-ZnSe QDs represent an approximate 125-fold increase compared to the average single-exciton decay rate and suggests that non-radiative Auger recombination remains the dominant decay pathway of bi-excitons in these thick-shell InP-ZnSe QDs.

Single QD fluorescence microscopy.

In order to characterize the thick-shell InP-ZnSe structures at the single-dot level, blinking measurements were conducted on individual core-shell nanocrystals. The core-shell QDs were diluted to $\sim 1\ \text{nM}$ concentration and drop-cast onto glass cover-slips. The resulting films were sealed in a nitrogen dry-box in order to minimize the influence of photo-oxidative degradation on the blinking behavior of the QDs over the time period investigated. The emission from single dots was collected with a custom-built epi-fluorescence microscope using a $400\ \text{nm}$ ($3.1\ \text{eV}$), $76\ \text{MHz}$ laser for excitation.³⁹ The mean separation between QDs of around $4\ \mu\text{m}$, minimizes the possibility of observing emission from aggregates. Single-dot PL intensity-time traces were recorded using an electron-multiplying CCD (charge-coupled device) camera at $10\ \text{Hz}$ ($100\ \text{ms}$ per frame) for up to ten minutes. Intensity-time traces for the thick-shell InP-ZnSe QDs and corresponding intensity distribution are shown in figure 4a and figure S7 of the supporting information. The emission intensity can be seen to fluctuate between high (‘ON’) and low (‘OFF’) values. To quantify this blinking behavior, the time spent in high intensity periods (ON-time) during the course of the experiment was extracted from each QD studied ($n = 44$). A QD is considered

to be in the ON state when its emission intensity is above, $\langle BG \rangle + 4\sigma$, where $\langle BG \rangle$ is the mean background signal from a spot without QDs and σ is the standard deviation. The core-shell InP-ZnSe QDs studied have an average ON-time $\sim 80\%$ with several (15%) individuals having ON-time fractions in excess of 90% (figure 4b). Although our observations were conducted in a reduced-air environment, blinking measurements made in air using a lower energy excitation source indicate that the thick-shell dots can be stable under ambient conditions (figure S7, supporting information).

To understand the observed blinking reduction in the thick-shell InP-ZnSe QDs, we consider further the processes that lead to blinking. In QDs, blinking is commonly thought to originate from one of two processes; dubbed type A and type B blinking.⁴⁰ In A-type blinking - conventional charging/discharging model,⁴¹ a nanocrystal becomes charged following photo-induced Auger ionization or trapping (long-lived) of excited charge carriers and the emission is dominated by non-radiative Auger recombination. In B-type blinking, off events arise when excited 'hot' charge carriers become trapped at recombination centers that introduce non-radiative recombination channels other than Auger recombination.⁴² Independent of a particular model; PL blinking is initiated when excited charge carriers become trapped at defects typically situated at the surface of the nanocrystal or within the external environment. By encapsulating the InP QD core in a thick crystalline shell, these traps become less accessible to excited charge carriers. In this way, the thick ZnSe shell serves as a physical barrier that decouples excited carriers from the nanocrystal surface and surrounding environment.

In contrast to thick-shell InP-ZnSe QDs, single InP-ZnS dots are characterized by strong blinking, with typical ON-time values $< 25\%$ (figure S8, supporting information). This large amount of time spent in the off state can be attributed to poor shell growth during the overcoating process. In addition to producing a thin passivating shell layer (~ 1.7 nm, S5 supporting information) that leads to greater overlap of excited charge carriers with the nanocrystal surface, the large lattice mismatch between InP and ZnS ($\sim 7.7\%$ for zinc blende phases²²) can result in the formation of defects within the shell and at the interface of the core-shell heterostructures during growth.⁴³ Indeed, these defects can increase the availability of trap sites for charge carriers, inducing strong intermittent emission from individual QDs.³⁹

The PL intermittency of the single QDs can further be characterized by observing the statistics of the duration of OFF and ON times, $\tau_{off/on}$. This approach has been used extensively to study the long-time kinetics related to blinking in QDs and other systems.^{44,45} In figure 4c, the cumulative distribution of $\tau_{off/on}$, that is, the probability, $P_{off/on}(\tau_{off/on} > \tau)$, of observing an OFF or ON period greater than τ is plotted for InP-ZnSe QDs. In QDs this distribution follows a power-law distribution, $P_{off/on}(\tau_{off/on}) \sim \tau^{-\mu_{off/on}}$ where $\mu_{off/on}$ is the power-law exponent describing the statistics of OFF or ON periods. Previously reported values for $\mu_{off/on}$ in InP QDs with high blinking rates are close to 1.5.¹⁸ For the thick-shell InP-ZnSe QDs (trace shown in figure 3a), $P_{off/on}(\tau_{off/on} > \tau)$ can be fitted to a power-law distribution with $\mu_{off} = 2.1$ and $\mu_{on} = 1.05$. The values of the power-law exponents indicate that PL blinking is dominated by much shorter OFF events and longer ON periods, consistent with the observation of higher on-times. The departure of $\mu_{off/on}$ in InP-ZnSe QDs

from typical values is in good agreement with previous results obtained for CdSe-CdS^{10,20} and suggests that access of photo-excited charge carriers to trap sites is restricted in the InP-ZnSe heterostructures.

Imaging structural defects.

Despite successful thick-shell growth, several InP-ZnSe QDs have low ON-times and the ensemble PL QY (~ 40%) is relatively low compared to values that can be obtained for thin-shell InP heterostructures.¹⁷ These observations indicate that while a thick ZnSe shell may restrict access to surface-related trap states, moderate quantum efficiencies and incomplete blinking suppression possibly arise from imperfections in the internal structure of some particles within the synthetic batch, giving rise to a dim or dark population of QDs. Emission from these QD populations would be expected to be dominated by non-radiative processes. Indeed, our group has previously identified dim and dark defected sub-populations in thick-shell CdSe-CdS QDs afflicted by strong PL intermittency and contributing to low ensemble PL QYs.^{39,46}

Figure 5a shows a HR-TEM image of the thick-shell InP-ZnSe QDs. Besides some residual structural inhomogeneity, there are apparent regions of low contrast in some of the particles within the synthetic batch. We utilized HAADF-STEM in conjunction with a very low beam current to image the atomic structure of several of these particles without inducing damage. The HAADF-STEM images in figures 5b-d clearly show extended features in the shell structure near the core region of the particle that are likely one of the primary factors limiting the PL QY of the material. These unique features may be the result of a point defect propagating from the InP core, prohibiting proper shell growth. Additionally, in the case of InP QDs, it has been shown that high temperature (>250 °C) growth processes employing carboxylate precursors can lead to the formation of an irregular amorphous oxide layer at the surface of the InP core.⁴⁷ Uniform shell growth atop such a disordered surface layer would be expected to be difficult, if at all possible, and may be a plausible explanation for this non-uniform defected shell growth observed for some particles. In the future, direct investigations of the relationship between the atomic structure and optical properties of these thick-shell InP-ZnSe QDs will provide useful feedback to direct and refine syntheses of the QDs.

In summary, we have synthesized InP core-shell QDs with thick (> 5 nm) crystalline ZnSe shells. These cadmium-free QD heterostructures feature reduced blinking - characterized by high ON-time fractions. The observed blinking reduction is attributed to the large ZnSe shell volume, which isolates excited charge carriers from the nanocrystal surface and surrounding environment. Additionally, compared to InP-ZnS QDs, non-radiative Auger recombination of higher-order bi-excitons is reduced in our thick-shell InP-ZnSe QD system. Advanced high-resolution STEM and EDX imaging provide an unprecedented level of insight into the atomic and chemical structure of the thick-shell QDs. Following the submission of this manuscript, Chandrasekaran et al.⁴⁸ also reported the synthesis of thick-shelled InP-ZnSe with improved optical properties. Combined with the structural insight gained in the current work, further synthetic refinements will enable these cadmium-free dots for applications in challenging biological settings and in other emission-based technologies.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Optical and structural characterization of thick-shell InP-ZnSe QDs.

(a) Absorption (blue) and photoluminescence (PL) (red) spectra of a batch of thick-shell InP-ZnSe QDs. Dotted line corresponds to the absorption spectrum of the starting InP core. (b) TEM image of the InP-ZnSe core-shell heterostructures. (c) High-resolution TEM image of the QDs. (d) X-ray powder diffraction pattern obtained from the sample shown in b. Inset: High-resolution high-angle annular dark-field (HAADF) STEM image of a InP-ZnSe QD. The red (green) tick pattern show the reference XRD peak positions of bulk zinc-blende ZnSe (InP).

Figure 2. Elemental characterization of thick-shell InP-ZnSe QDs.

(a) Energy dispersive X-ray (EDX) chemical map of a core-shell InP-ZnSe QD. (b) Corresponding line scan showing the intensity profile of each element across the diameter of the particle. (c) Indium, (d) Phosphorus, (e) Zinc and (f) Selenum chemical maps from the particle in a.

Figure 3. PL dynamics of InP-ZnSe core-shell QDs.

(a) Low-pump fluence PL lifetime measurement for InP, InP-ZnSe and InP-ZnS samples in dilute toluene. Dashed lines represent fits to a tri-exponential decay function. (b) Pump-fluence-dependent PL dynamics of thick-shell InP-ZnSe QDs at different pump fluences ($1\text{--}100 \mu\text{J}/\text{cm}^2$). The traces are normalized at long delay times ($t=4$ ns) and show that the fast bi-exciton signal which emerges at higher pump fluences have decayed within 1.5 ns. At longer delay times the decay dynamics is dominated by single-exciton recombination. Next, the PL decay collected at the lowest pump fluence (black trace) is subtracted from the decay traces measured at higher fluences to reveal the dynamics due to multi-excitons only. The inset shows an example of the extracted multi-exciton decay component (red trace) fitted to a single-exponential decay (dashed line) with an average $\tau_{2X} \sim 540 \pm 30$ ps.

Figure 4. Photoluminescence blinking behavior of single thick-shell InP-ZnSe QDs.

(a) Intensity-time trace and distribution of the PL intensity from an individual InP-ZnSe QD (bin size is 100 ms). The background (red trace) was recorded from a region with no QDs. Dotted (red) line represents the ON-OFF threshold for analysis. (b) Distribution of the blinking ON-time fraction. (c) Distribution of ON (red) and OFF (blue) time durations plotted on a log-log scale. Dashed lines represent power-law ($\tau^{-\mu_{off/on}}$) fits to the data.

Figure 5. Imaging of structural defects in thick-shell InP-ZnSe QDs.

(a) HR-TEM image showing low-contrast features in the InP-ZnSe QDs (red arrows). (b-d) HAADF-STEM images of InP-ZnSe core-shell QDs with extended (bulk) shell defects propagating from the InP core region.