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Radiative and Non-Radiative Lifetime Engineering of Quantum Dots in Multiple Solvents by Surface Atom Stoichiometry and Ligands

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Abstract

CdTe quantum dots have unique characteristics that are promising for applications in photoluminescence, photovoltaics or optoelectronics. However, wide variations of the reported quantum yields exist and the influence of ligand-surface interactions that are expected to control the excited state relaxation processes remains unknown. It is important to thoroughly understand the fundamental principles underlying these relaxation processes to tailor the QDs properties to their application. Here, we systematically investigate the roles of the surface atoms, ligand functional groups and solvent on the radiative and non-radiative relaxation rates. Combining a systematic synthetic approach with X-ray photoelectron, quantitative FT-IR and time-resolved visible spectroscopies, we find that CdTe QDs can be engineered with average radiative lifetimes ranging from nanoseconds up to microseconds. The non-radiative lifetimes are anticorrelated to the radiative lifetimes, although they show much less variation. The density, nature and orientation of the ligand functional groups and the dielectric constant of the solvent play major roles in determining charge carrier trapping and excitonic relaxation pathways. These results are used to propose a coupled dependence between hole-trapping on Te atoms and strong ligand coupling, primarily *via* Cd atoms, that can be used to engineer both the radiative and non-radiative lifetimes.

Keywords

cadmium telluride; fluorescence lifetime; infrared spectroscopy; surface states; ligand exchange; quantum dot synthesis

Introduction

Colloidal semiconductor nanocrystals (also called quantum dots, QDs) are showing great potential for a range of applications including photovoltaics¹, lasers², pH³ and chemical⁴⁻⁶ sensors and biophysical fluorescent probes.^{7,8} The commercialization of QDs as biological fluorescent probes is commonly based on CdSe, using a ZnS shelling procedure introduced in 1996.⁹ Shelling allowed subsequent water solubilization for biological labeling applications.^{7,8,10} In general, it is not possible to transfer CdSe to water using thiols and maintain a reasonable amount of fluorescence without using a shell.¹¹ If particularly small QDs are needed, such as for labeling small proteins, imaging small intracellular or

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Supporting Information Avaiable

Experimental Details, TEM images, linear plots of the radiative and non-radiative lifetimes as a function of surface atom ratio, ligand and solvent, FT-IR spectra, characterization and peak deconvolution analyses. This material is available free of charge via the internet at http://pubs.acs.org.

intercellular regions like mitochondria or neural synapses, or in quantitative FRET assays, CdTe may be a better choice, since they can retain their fluorescence in water using thiolated ligands without a shell.^{12,13} This effect was attributed to thiols acting as strong hole acceptors for CdSe but not for CdTe QDs.¹⁴ Furthermore, to use CdTe in photovoltaic applications where interfacial charge carrier transfer is necessary, a shell may reduce its efficiency.

CdTe QDs can be synthesized directly in water but typically require long reaction times under reflux,¹⁵⁻¹⁷ but can be shortened by the use of an autoclave¹⁸ or by a microwave-assisted procedure.¹⁹ Some of the reports of CdTe synthesized by aqueous routes are very promising, although the reported properties can be variable – even for those prepared by essentially identical procedures.^{16,20} Organometallic-based synthetic procedures for CdSe are, by far, the most prevalent due to high reproducibility and particle quality²¹ and have evolved to use more environmentally friendly and safer-to-handle precursors.^{22,23} CdTe can be synthesized by these same routes but the details have not been optimized as they have for CdSe.²⁴ Wuister *et al.* did use an organometallic approach for CdTe and have reported that thiol ligand-exchanged CdTe QDs in water can have higher luminescence than trioctylphosphine/dodecylamine-capped CdTe QDs in chloroform, while the opposite is true for CdSe.^{12,14} However, the degree of quantum yield (QY) enhancement for CdTe in water over organic solvents seems to be rather variable, which may be a result of different CdTe synthetic parameters.^{12,14,25,26}

Qu and Peng performed an in-depth study of synthesis parameters for the organometallic synthesis of CdSe, using CdO and elemental Se as precursors.²⁴ They found that using higher Se:Cd ratios in the reaction mixture resulted in a higher QY for organic-soluble QDs, which was attributed more to the organization of the passivating ligands on the surface rather than surface atomic stoichiometry. Jasienak and Mulvaney later found that post-preparative modifying of the surface atomic stoichiometry played a major role in determining the QY through the passivating ligands.²⁷ CdTe synthesized by Wuister et al. used the more difficult Cd(Me)₂ approach and only one Cd:Te synthesis ratio of ~1.2:1,¹² but these QDs had high fluorescence after transferring to water. In all these reports, it has not been clearly identified if the QY variations arise from changes in the radiative or non-radiative relaxation rates. Furthermore, there is a general lack of quantification of how the ligands bind to the QD surfaces and, in particular, their effect on the charge carrier relaxation processes.

The aim of this study is to evaluate the details underlying how the coupling of surface atoms to ligand binding affects the radiative and non-radiative relaxation pathways. We use the more accessible CdO precursor approach to organometallic CdTe synthesis and subsequent water solubilization by ligand exchange. We determine how the Cd:Te synthesis ratio affects the resulting surface atom ratio and, in turn, how they determine the binding of different ligands and, consequently, control the optical properties. These properties are investigated first with their native phosphonic acid/phosphine ligands and upon exchange with hydrophobic thiols in the same solvent, and then hydrophilic thiols in methanol and water. This systematic progression allows us to quantify the individual roles of the surface atoms, the coordinating and functional groups of the ligands, and the solvent in controlling the electronic relaxation pathways of CdTe QDs. Our results provide a deeper understanding of the relaxation pathways of the excited state so that one can optimize the synthetic conditions and ligand coupling to produce QDs tailored for specific applications.

Experimental Section

Chemicals

Cadmium oxide (CdO – Puratronic, 99.998%), 1-Tetradecylphosphonic acid (TDPA - 98%), 1-Octadecene (ODE – tech 90%), Tellurium powder (Te – 99.99%), Tri-n-butylphosphine (TBP – 95%, 1-Propanethiol (PPT – 98%), 3-Mercaptopropionic acid (MPA – 99%), and Tetramethyl ammonium hydroxyde pentahydrate (TMAH – 98%) were all purchased from Alfa Aesar. Hexanes, acetone and anhydrous diethyl ether were all ACS grade and purchased from EMD. Methanol was purchased from BDH through VWR Scientific. Fluorescein from the Reference Dye Sampler Kit (R14782, Invitrogen, Eugene, OR) was used for the photoluminescence quantum yield measurements.

QD Synthesis

The nanoparticles were prepared using 5 different Cd to Te molar ratios: 5:1, 2:1, 1:1, 1:2 and 1:5. As an example of the synthesis protocol for 5:1 Cd:Te with 0.2 mmol Cd was prepared as follows: 0.0256 g (0.2 mmol Cd) of CdO was mixed with 0.114 g of TDPA (0.41 mmol) and placed in 3.93 g of ODE in a three neck round bottom flask. This mixture was vacuum purged for ~30 minutes then, after turning off the vacuum, was placed under argon flow, and heated to 300°C with a heating mantle. At this temperature, the tellurium was injected, consisting of a mixture of 1.90 g of ODE and 0.10 g of a Te stock solution, prepared by dissolving 1.02 g of Te powder in 18.98 g tributylphosphine (0.04 mmol Te). After the Te was injected, the solution temperature was immediately reduced to 250°C and the nanocrystals grown to the desired size as monitored by their UV-Vis and PL spectra, usually within a couple of minutes. Once the nanocrystals had achieved the desired size, the heating mantle was removed and the reaction stopped by withdrawing a sample and dissolving into cold hexane. All synthesis times were controlled to produce similar sized QDs.

QD Ligand Exchange

Each of the samples was then split into 3 different aliquots; one aliquot was left as-prepared, one aliquot was ligand exchanged with propanethiol (PT), and the other aliquot was ligand exchanged with mercaptopropionic acid (MPA). The PT ligand exchange was performed as follows: 2 mL of the as-prepared nanocrystal solution was added to a vial and diluted with 2 mL of hexanes. To extract the unreacted starting materials, 4 mL of methanol were added and vigorously agitated. Then, to achieve efficient phase separation, the sample was centrifuged for 5 minutes. After centrifugation, the methanol layer containing the unreacted starting materials was removed from the hexane layer containing the QDs. The extraction was repeated. The hexane QD solution was precipitated with acetone and the solution was centrifuged for ~15 minutes until a pellet was formed at the bottom of the vial and only clear, colorless liquid remained above. The liquid was decanted and excess solvent was removed from the pellet by tapping the vial upside down. Immediately, the ligand solution was added to the pellet, which consisted of 200 μ L of PT dissolved in 10 mL of hexanes. Upon addition of the ligand solution to the pellet, the mixture was sonicated and placed in a three neck round bottom flask under argon and refluxed for 3 hours at $\sim 68^{\circ}$ C. After reflux, the heating mantle was removed and the solution was allowed to cool to room temperature. The same procedure was repeated for MPA ligand exchange, except that the QD sample was precipitated from hexanes with acetone, centrifuged to a pellet and decanted. Then a ligand solution, consisting of 200 μ l of MPA dissolved in 10 ml methanol adjusted to pH ~10.5 with tetramethylammonium hydroxide (TMAH), was added to the pellet. To obtain the MPA-QDs in water, a 2 mL aliquot of the MPA particles in methanol was precipitated by addition of diethyl ether and centrifuged for ~15 minutes until a pellet was obtained. The liquid was decanted and the vial was inverted and lightly tapped to remove any remaining

liquid. Following this, 2 mL of $18M\Omega$ Millipore water was added. The MPA-exchanged nanocrystals readily dissolved in the water.

Absorption and Fluorescence Spectroscopy

To measure the spectra and photoluminescence quantum yield (QY) of the as-prepared QDs in hexane, PT-QDs in hexane, MPA-QDs in methanol and MPA-QDs in water, aliquots from each of the samples were diluted with their respective solvents to an optical density of 0.01 at a wavelength of 450 nm, measured by a Hitachi U-3900H UV-VIS absorption spectrophotometer. Their photoluminescence spectra recorded with a Perkin-Elmer LS 55 luminescence spectrometer from 470 to 800 nm upon excitation at 450 nm. The QY was calculated by comparing the integrated area of the QD emission spectrum to that of a 0.01 O.D. (@450 nm) solution of fluorescein in 0.1M NaOH, which has a 92% QY.

To measure the fluorescence lifetime of the QDs, aliquots were diluted in their respective solvents to ~100 nM in a powder-coated stainless steel liquid cell into which a glass coverslip was sealed using a silicone O-ring seal. Time-correlated single photon counting (TCSPC) curves were obtained using a MicroTime 200 Confocal Fluorescence Lifetime Microscope (PicoQuant GmbH, Berlin, Germany), consisting of a 485 nm picosecond DPSS laser (LDH-P-C-485, Picoquant), controlled by the Sepia II software with 5 μ W power and 5 MHz repetition rate. The excitation laser was reflected from a dichroic mirror (DCXR500, Chroma) and passed through a water-immersion objective (Olympus UPLSAPO 60×w, 1.2N_A). The emitted fluorescence was collected by the same objective, transmitted through the same dichroic mirror, a 75 μ m pinhole, and a 605/55m emission filter (Chroma, Bellows Falls, VT) onto an avalanche photodiode detector (PDM, Microphoton Devices, Bolzano, Italy). The detector passed the signal to the TCSPC card (Picoharp 300, Picoquant) onto 4096 channels with 64 ps per channel, and the data was collected and analyzed with the SymphoTime software package. The width of the instrument response function was determined to be less than 0.3 ns, which greatly facilitated data fitting. The data was fit to the minimum number of exponentials, *i*, required until the chi-squared value was no-longer reduced and the residuals showed no systematic deviation (3 components were needed), and the average fluorescence lifetime, $\tau_{\rm fl}$, determined as follows:

$$\tau_{fl} = \frac{\sum\limits_{i=1}^{3} c_i \tau_i^2}{\sum\limits_{i=1}^{3} c_i \tau_i} \quad (1)$$

 c_i is the fractional amplitude of component *i*, where $\sum_{i}^{\sum c_i=1}$, and τ_i is the lifetime of component *i*.

FT-IR Spectroscopy

The FT-IR spectra were measured on a Bruker Vertex 70 FT-IR spectrometer equipped with a deuterated tri-glyceride sulfate (DTGS) detector, and the sample chamber purged with a steady stream of dry N₂. After measuring the background spectrum of a clean, dry CaF₂ window, 40 μ l of a solution of QDs with an exact OD of 0.1719 at the λ_{max} was placed in the exact center of the CaF₂ window, resulting in a drop smaller in diameter than the probe beam to ensure that the same amount of sample was measured for each sample, and then left in a horizontal position to dry overnight in the N₂-purged sample chamber. The FT-IR absorption spectrum was calculated by measuring and averaging 16 scans.

Transmission Electron Microscopy

TEM images were acquired on a JEOL 100cx transmission electron microscope (JEOL, Tokyo, Japan). QDs were washed of impurities by precipitating them from solution with methanol, centrifuging to a pellet and redissolving in pure hexane, which was repeated 2-3 times. A Formvar-coated copper TEM grid (Ted Pella, Redding, CA) was dipped into the well-washed QD hexane solution, and allowed to dry in air overnight. The acceleration voltage used during the measurement was 100 kV, and images were acquired on a CCD camera (low mount XR41, AMT, Danvers, MA).

X-Ray Photoelectron Spectroscopy

To measure the X-ray photoelectron spectra, QDs were precipitated using the same method as for ligand exchange; extraction with methanol 3 times followed by addition of acetone and centrifugation. The precipitate was placed on a carbon sticky tab, dried in a vacuum oven overnight before being inserted into the load lock of the XPS (Phi Versaprobe, Physical Electronic Inc., Chanhassen, MN) and allowed to dry for a further 24-48 hours prior to analysis. The XPS is equipped with a monochromated Al-Ka source (1486.6eV), dual-beam charge compensation and a spherical capacitance analyzer operated in fixed analyzer transmission mode. The Pass Energies used were 117eV and 23.5eV to 45eV for survey and quantification scans, respectively. Data was collected at a 45° take-off angle relative to the analyzer lens with between 100-500 ms collection time, depending on the peak. Data analysis was performed using Phi MultiPak (Physical Electronics Inc.). Charge referencing was made to the adventitious C1s peak. Data were smoothed by the Savitzky-Golay method prior to background subtraction via the iterated Shirley model. Peak areas were related to composition via the relative sensitivity factor method, which allows for multiple pass energies to be used in the same multiplex. Nanoparticles were assumed to be equally dispersed throughout the analysis volume and as such compositions were treated using the homogeneous quantification model. Data collection was performed using a collection angle of 45° is used to minimize errors associated with this assumption.

Results

It has previously been shown that 2 Cd-complexing ligands are needed to solubilize CdO.^{18,19,28} We performed all reactions using a constant 0.2 mmol Cd, 0.4 mmol TDPA, and vary the Te precursor amount. The sizes of the various CdTe QDs were controlled to be as equal as possible during synthesis by monitoring the absorption spectra. Details of the syntheses are provided in the supporting information. The resulting absorption spectra of the samples with different Cd:Te ratios are overlaid in figure 1(a). TEM images are shown in the supporting information, highlighting the similarity in size from Cd-rich to Te-rich, having an average of ~4nm and low size dispersion.

X-ray photoelectron spectra (XPS) of the Cd peaks for the 5:1 Cd:Te sample is shown in figure 2(a) and the Te peaks for the 1:5 Cd:Te sample is shown in figure 2(b), exhibiting excellent signal:noise ratios, thus allowing accurate integration of the peaks in figure 2(c). Using a 5:1 Cd:Te ratio in the reaction mixture led to an observed Cd:Te ratio of ~4:1 by XPS. With a 1:1 Cd:Te ratio, there observed ratio is ~1:1, and using 1:5 Cd:Te resulted in ~1:4 by XPS. It is important to note that these ratios are not absolute values of the surface composition, but provide comparisons between different samples of the same size. XPS is generally more sensitive to surface atoms than bulk atoms, although at these length scales, XPS does probe a significant fraction of the whole particle. However, if the particle bulk were significantly more Cd-rich or Te-rich, the bandgap energy, as measured from the absorption and emission spectra, would not be in agreement with their sizing curves as previously measured,²⁹ suggesting that the excess atoms lie preferentially on the QD

surface. This is not to say that the excess atoms are *exclusively* at the surface, and there is likely a radial "shell" of Cd-rich or Te-rich CdTe, as has been modeled for CdSe.²⁷ Also, the possibility of forming some pure Cd or Te nanoparticles cannot be excluded. However, in general, the atomic ratios shown here are in reasonable alignment with what was expected and primarily highlight that the surface of the samples are indeed Cd-Rich, CdTe neutral or Te-rich depending on the synthesis ratios.

Upon ligand exchange, the samples exhibited shifts in the fluorescence maximum and QYs. The fluorescence spectra for the 5:1 Cd:Te samples upon ligand exchange are shown in figure 3(a). Upon exchange of the TDPA/TBP with PT, there is a red shift in the emission maximum, whereas upon using MPA there is a blue-shift. The solvent also played a role, with MPA showing a larger blue-shift in water compared to methanol. The QY results as a function of surface atom ratio, ligand and solvent are summarized in figure 3(b). The inset of figure 3(b) shows an image of the PL as a function of surface atom ratio for the as-prepared samples, with native TDPA/TBP ligands. For the native QDs, the highest QY obtained was ~20% for QDs synthesized with a 5:1 Cd:Te molar ratio. As the ratio of Cd:Te decreased, so did the QY, with a rapid decrease occurring from 2:1 to 1:1 in which the QY decreased from \sim 17% to 3%, where it remains as the surface becomes Te-rich. Upon ligand exchange with PT, there is an increase in the QY for all particles as compared to the as-prepared CdTe, reaching up to 80% with 5:1 Cd:Te and decreasing with decreasing Cd:Te ratio. However, only when the surface becomes very Te-rich does the QY drop to negligible values; at 1:2, it is still at 30%. Upon exchange of the ligands with MPA, the QY is always smaller than for PT-QDs, but is higher than the original TDPA-QDs when the surface is Cd-rich. Interestingly, the solvent plays a significant role, where methanol quenches 5:1 Cd:Te less than water, but for 2:1 Cd:Te, methanol quenches them more than water does. However, we can obtain bright water-soluble CdTe QDs with QY between 45-50% by using either 5:1 or 2:1 Cd:Te ratios.

We used quantitative FT-IR absorption spectroscopy to investigate how the surface atom ratio determines the amount and type of ligand bound to each sample. We were extremely careful to remove excess ligands and to measure exactly the same concentration of QDs to allow quantitative comparisons of peak intensities to be made. The FT-IR absorption spectrum of the as-prepared 5:1, Cd:Te samples is shown in figure 4(a), and the 5:1 Cd:Te MPA-exchanged QDs in Figure 4(b), together with peak assignments. FT-IR spectra for all other samples are given in the supporting information. For the as-prepared samples, the FT-IR spectra show strong sp3 hybridized C-H stretching peaks between 2750 and 3000 cm⁻¹, which come from all bound ligands. From the synthetic conditions, 3 possible ligands are present; TDPA, TBP and ODE. TDPA is easy to identify and quantify from the double peak of deprotonated PO_3^{2-} between 1050 and 1250 cm⁻¹.³⁰ The peak at 1650 cm⁻¹ is characteristic of C=C stretching and those at 990cm⁻¹ and 910cm⁻¹ are characteristic of monosubstituted methylinic C-H bending modes (RHC=CH₂), each identifying the presence of bound octadecene (ODE) on the CdTe QDs, which is quite surprising since ODE is generally considered to be a non-coordinating ligand.³¹ TBP is more difficult to quantify due to the absence of characteristic peaks specific to this compound. However, the number of sp3 hybridized C-H bonds per TDPA, TBP and ODE are 29, 21 and 33 respectively, so can be indirectly inferred from the other peaks. Since the sp3 C-H peaks come from all these species, the integrated area between $2800 - 3000 \text{ cm}^{-1}$ allows us to assess the relative amount of total ligands bound as a function of Cd:Te surface atom ratio. Comparing the change in the C-H area from sample-to-sample to the TDPA and ODE intensities allows us to determine how the surface atoms affect native ligand binding (Figure 4(c)) and upon ligand exchange with PT (Figure 4(d)). The C-H peak area increases by $\sim 50\%$ from 5:1 Cd:Te to 1:1. Concomitantly, The TDPA peak decreases by ~50% and the ODE peaks increase by ~70%. This implies that there are more TBP ligands bound in the 1:1 sample

than the 5:1 sample, as one would expect. However, the large increase in the amount of ODE means that the increase in TBP is only ~30%. For 1:5 Cd:Te, the total C-H peak area is about half the value of the 1:1 Cd:Te, almost fully accounted for by the same relative decrease in the ODE peak area. It appears as though there is little-to-no extra TBP bound for the 1:5 Cd:Te compared to the 1:1. Comparing 1:5 to 5:1, there are about half the number of TDPA ligands bound to 1:5 than 5:1 and about the same amount of ODE, with about a 25% drop in the C-H peak area; the difference coming from TBP. Taken together, we can conclude that as the surface atom ratio moves from 5:1 to 1:1, ~50% less TDPA, ~70% more ODE and up to ~30% more TBP is bound. As the ratio moves from 1:1 to 1:5, about the same amount of TDPA, ~50% less ODE and about the same amount of TBP is bound.

After the 5:1 Cd:Te sample is exchange with PT, it was found that approximately 50% of the TDPA and ~30% of the ODE ligands remained on the QDs (Figure 4(d). The number of C-H bonds per PT molecule is far less than the native ligands, significantly lowering the extinction coefficient of this peak for PT. Therefore, inferring the amount of TBP that remains is much more difficult. Since the integrated C-H peak area for PT samples is significantly lower for PT samples than the as-prepared samples, it highlights that a significant number or ligands have been exchanged for PT. As the surface stoichiometry moves from 5:1 to 1:1, little of the TDPA remains, although about the same amount of ODE remains. The C-H peak does decrease by about 20% suggesting less PT per QD. For 1:5 Cd:Te PT-exchanges samples, no TDPA or ODE remains and the C-H peak is again reduced by a further 20-30%, implying less PT per QD for 1:5 than 1:1, showing its preference for Cd atoms, as one would expect.

After the samples are exchanged with MPA ligands, the broad O-H stretch covers the C-H stretch region, making this peak difficult to quantify. However there are no peaks associated with TDPA or ODE, suggesting complete removal of these ligands by MPA. There are characteristic strong C=O stretches for COOH at 1677 cm⁻¹ and COO⁻ at 1582 cm⁻¹ (asymmetric stretch) and at 1390 cm⁻¹ (symmetric stretch). The COOH peak is slightly lower in frequency than usually observed, which may indicate that the protonated COOH group is coordinated directly to the QD surface. The COOH and asymmetric COO⁻ peak areas can be used to estimate the relative number of MPA ligands bound for 5:1, 1:1 and 1:5 Cd:Te QDs, as well as the protonation state of such ligands in each solvent; methanol and water. This analysis requires peak deconvolution, which is described in detail in the supporting information. We must be careful when comparing the two peaks (COOH and COO⁻) directly to each other, since the extinction coefficient of COOH is about half that of COO^{-,32} In methanol, the COOH peak steadily decreases as the ratio of Cd:Te decreases, suggesting that they are bound primarily, although not exclusively, to the Cd atoms. The deprotonated COO⁻ peak is about 30% greater for 1:1 Cd:Te than 5:1, but reduces for 1:5, to about the same area as for 5:1. As the MPA-QDs are transferred to water, there is always a lower peak area of both COOH and COO⁻ peaks for all Cd:Te ratios compared to the same samples in methanol. There is significant ligand removal of protonated COOH for the 5:1 ratio, which becomes less pronounced as the Cd:Te ratio reduces. This strongly supports the conclusion that the protonated COOH ligands are weakly bound to the Cd atoms, while COO- ligands are more strongly bound; implying that the deprotonated COO⁻ ligands coordinate via the stronger thiol group to result in the charge groups protruding into the solvent. Both the COOH and COO- peaks decrease by about the same amount (~30-40%) for the 1:5 Cd:Te. Interestingly, in water, the COO- peak area does not change as the Cd:Te ratio decreases, although the COOH peak does increase slightly for the 1:5 ratio.

In order to investigate how the surface atoms and ligands affect the electronic processes underlying the variations in quantum yield, we performed fluorescence lifetime measurements to determine the radiative and non-radiative relaxation rates. The

fluorescence lifetime curve for the 5:1 sample is shown in figure 5(a). The lifetime data are fit to a series of exponentials until the residuals showed no deviation and the chi-squared value was reduced. Usually 3 were needed, and the average fluorescence lifetime, $\tau_{\rm fl}$, was calculated (see supporting information for further details). The average fluorescence lifetime values are plotted in figure 5 (b), and shows a dependence that does not directly correlate with the QY dependence, highlighting the fact that both the average radiative and average non-radiative rates are changing. These two rates (plotted as lifetimes) are calculated as follows:^{33,34}

$$\tau_r = \frac{1}{k_r} = \frac{\tau_{fl}}{QY} \quad (2)$$

and

$$k_{nr} = \frac{1}{\tau_{nr}} = \frac{1}{\tau_{fl}} - \frac{1}{\tau_r}$$
 (3)

Where τ_r is the average radiative lifetime and τ_{nr} is the average non-radiative lifetime. Strictly, equations (2) and (3) provide relationships between the radiative and non-radiative lifetimes from a single process. In our experiments, we do not separate excitonic emission from shallow trap emission, which is only slightly red-shifted and difficult to distinguish from the excitonic emission,^{34,35} due to using an emission filter in the microscopy setup. Therefore, this analysis provides average radiative and average non-radiative lifetimes that contain contributions from both excitonic and trap states, each of which will be discussed in detail below. The average radiative and non-radiative lifetimes are plotted in figures 5(c) and 5(d), respectively. The average radiative lifetimes span at least 2 orders of magnitude as the surface atom ratio varies from Cd-rich to Te-rich and so the data are plotted on a logarithmic scale to more clearly follow the effects. The data is also plotted on a linear scale in the supporting information to highlight the magnitude of the effect for Te-rich samples, and to more clearly see the changes in the non-radiative lifetimes. It is clear that a Te-rich surface significantly increases the average radiative lifetime compared to a Cd-rich surface with all ligands, but is more pronounced for QDs with MPA ligands. The solvent also affects the radiative lifetime, with MPA-QDs in methanol having a significantly longer radiative lifetime than in water. While the radiative lifetimes vary by 2 orders of magnitude, the nonradiative lifetimes vary by about 1 order. They do show a systematic decrease as the surface becomes more Te-rich, but show less of a ligand or solvent dependence.

Discussion

The much longer average radiative lifetime of Te-rich CdTe highlights that the reason for the QY change is due more to an average decrease in the electron-hole overlap integral than to an increase in non-radiative relaxation pathways. Phosphonic acid ligands bind very strongly to Cd atoms;^{36,37} in fact, phosphonic acid ligands are used to control the reactivity of Cd-monomers for better size and shape control during synthesis than phosphine oxides or amines.³⁸ The strong coupling of these ligands to the QD likely suppresses electron trapping at the Cd atoms, leaving hole trapping as the primary competing process. This suggests that the Te-atoms on the surface are less-passivated than Cd atoms, or Se atoms in the case of CdSe.³⁹ DFT calculations have shown that the trimethylphosphine-Te bond is about 70% the strength of the trimethylphosphine-Se bond, due to a smaller donation interaction energy involving less electrons per donation.⁴⁰ It is therefore more likely that Te-P bond would break during synthesis than Se-P to result in less-passivated Te atoms on CdTe QDs. This difference could explain the contrasting results observed between using chalcogenide-rich

precursor solutions when synthesizing CdSe²⁴ compared to CdTe, as shown here. If less ligand molecules are coordinated to the Te-rich QDs, it is reasonable to conclude that it would lead to increased hole trapping efficiency on the Te atoms due to the presence of dangling bonds. This conclusion is strongly supported by the FT-IR absorption spectra for the as-prepared CdTe, in which the integrated C-H peak area was lower for 1:5 than 1:1 and 5:1 Cd:Te ratio QDs. The calculated increase in the amount of TBP bound for 1:1 Cd:Te compared to 5:1 (~30%) is far less than the increase in the number of surface Te atoms measured by XPS (up to 250%), highlighting an overall higher fraction of unpassivated Te which results in an increased radiative lifetime. As the Cd:Te ratio changes from 1:1 to 1:5, the amount of bound TBP does not increase, while the number of Te atoms does so significantly, leading to an even greater increase in radiative lifetime, as we observe. To explain these effects we propose a model that connects the structural properties of the QD surface to the energy levels, shown schematically in figure 6. The details of this model will be explained below.

In addition to increasing the average radiative lifetime, there is a small but steady decrease in the non-radiative lifetime as the surface changes from Cd-rich to Te-rich. While holes have been shown to generally relax faster than electrons,^{41,42} the complexity of electron and hole relaxation pathways in colloidal QDs has been recently highlighted.⁴³ It was proposed that confining one of the charge carriers may enhance the ligand-induced nonadiabatic transition rate due to removing the Auger relaxation channel, which was used to explain the absence of a phonon bottleneck for both charge carriers. Recent TDDFT calculations also support this hypothesis.⁴⁴ For CdTe, it has been shown that the hole is trapped on the ~1ps timescale.^{45,46} Once trapped, it would be easier for the excess electronic energy to couple to the vibrations of the ligand molecule, resulting in a shorter non-radiative lifetime (faster rate). These processes are described in figure 6 as k₃ and k_{2 (non-rad)} respectively. We propose that it is the balance of the rates of these two processes that are responsible for the observed effects on the average radiative and non-radiative lifetimes shown in figure 5. The rate of the surface trapping process, R₃, is

$$R_3 = k_3 [Te]_s \lfloor h_x^+ \rfloor \quad (4)$$

Where $[Te]_S$ is the concentration of unpassivated surface Te atoms and $[h^+_x]$ is the density of holes, which at the (constant and low) laser power used in these experiments should be ~ 1 per QD. Since there are few Te atoms on Cd-rich QDs, this rate is relatively slow, and the competing process of excitonic radiative recombination ($R_{1(rad)}$) with the excitonic hole (h^+_x) leads to a relatively high QY. Once the hole is trapped, the rate of non-radiative relaxation of the excess electronic energy via the ligand-induced nonadiabatic transition is given by the product of the trapping rate and the ligand density

$$R_{2(non-rad)} = k_2 k_3 \lfloor e^{-} \rfloor [ligand] [Te]_s \lfloor h_x^+ \rfloor$$
(5)

The concentrations $[e^-]$ and $[h^+_x]$ are equal at time = 0, since the absorption of 1 photon creates 1 excitonic electron-hole pair. Since there is still some (although much reduced) overlap of the trapped-hole wavefunction with the electron, there is a competing radiative recombination process, $R_{2(rad)}$, which is expected to be relatively slow. The faster average radiative lifetime observed for Cd-rich QDs would be a result of the larger contribution from the fast excitonic emission ($R_{1(rad)}$) rather than the slower $R_{2(rad)}$ process). For Te-rich QDs, the larger [Te]_S in equation (4) leads to a faster R_3 process compared to $R_{1(rad)}$, resulting in a strong reduction in QY. The $R_{2(non-rad)}$ process described in equation (5) depends on both the ligand density and the number of hole-trap states. Since the ligands are largely bound to

the fewer Cd-atoms on the surface in Te-rich QDs, $R_{2(non-rad)}$ is low and there is a larger contribution of the slower $R_{2(rad)}$ to the observed average radiative lifetime. As the surface goes from Cd-rich to Te-rich, the decrease in the observed non-radiative lifetime (i.e. increase in $R_{2(non-rad)}$) suggests that k_3 [Te]_S increases at a faster rate than k_2 [ligand] decreases in equation (5). $R_{2(rad)}$ is determined by the overlap integral and is thus expected not to change. Additional non-radiative processes due to point defects within the crystal may also play a role, and will be investigated in future work. In any case, the proposed model in figure 6 is strongly supported by the FT-IR data; Cd-rich QDs are much more passivated by ligands than Te-rich QDs, especially by the strongly Cd-binding TDPA. The increased C-H peak area observed for 1:1 Cd:Te compared to 5:1 shows that some of the additional Te atoms are indeed passivated by ligands (most likely TBP).

It is not only the density of ligands that are important for the observed relaxation dynamics, but also their identity. This is evident from the strong dependence of ligand on QY. Upon ligand exchange of the native ligands with PT ligands, the average radiative lifetime decreased for all surface atom ratios, suggesting that the trapping process is significantly reduced by the thiol, in agreement with previous observations.^{12,14} Even though thiols preferentially bind to Cd, they also bind to Te, as demonstrated by FT-IR; as Cd:Te varies from 5:1 to 1:5, the total intensity of the C-H peak of PT-QDs and the C=O peaks of MPA-QDs decease by only a factor of ~2. Due to the smaller footprint of PT over TBP, more of the Te atoms would likely be passivated compared to the as-prepared CdTe, resulting in less trap states and a reduced average radiative lifetime. Furthermore, it has been proposed that the energy of thiol traps states is lower in energy than the valence band edge of CdTe.¹⁴ This lowering of trap energy may open up a new pathway in which the trapped holes may be thermally de-trapped (R_{-3} in figure 6(d)), which competes with both $R_{2(rad)}$ and $R_{2(non-rad)}$ to increase the probability of excitonic recombination $(R_{1(rad)})$, and thus increase QY, the process of delayed fluorescence. The relative rates of $R_{-3} R_{2(rad)}$, and $R_{2(non-rad)}$ would determine the overall contribution of delayed fluorescence vs the ligand-dependent nonradiative pathways on quantum yield and average lifetime, but it is reasonable to assume that R-3 would be faster than R_{2(rad)}. This is supported by the fact that the average radiative lifetime of the PT-capped QDs is lower than the TDPA/TBP capped QDs for all Cd:Te ratios. However, the trend of increased radiative lifetime with decreasing Cd:Te ratio is still evident, supporting the model of figure 6. Again this interpretation is supported by the FT-IR data, which shows a decrease in PT ligand binding between Cd-rich and Te-rich. The thiol group also increases the non-radiative lifetime compared to TDPA/TBP (i.e. decreases $R_{2(non-rad)}$ in equation (5)), and the trend of non-radiative lifetime decreasing with increasing Te-richness persists. A weaker coupling of the ligand to the QD would serve to decrease k_2 in equation (5) while a stronger coupling would increase it. However, since thiol ligands are much smaller than TDPA or TBP, one can expect that the density of ligands would be much higher for ligand-exchanged QDs, compared to the as-prepared samples. Based on the observations of Fig. 5(d), the increase in non-radiative lifetime (decrease in R_{2(non-rad)}) of Cd-rich samples upon ligand exchange suggests that the decrease in k₂ between thiol ligands and TDPA ligands is larger than the increase in [ligand]. The "noise" in the non-radiative lifetime trend may arise from variations in obtaining the same level of ligand exchange from sample-to-sample. It is common knowledge that the ligand exchange process is prone to variability. Furthermore, the overall trend of decreasing non-radiative lifetime with increasing Te-richness is stronger for PT ligands than for TDPA. Again, this can be explained as k_3 [Te]s increasing at a faster rate than k_2 [ligand] decreasing but, in addition to the ligand density, may also result from differences in k_2 upon ligand exchange. TDPA is a strongly coordinated ligand whereas TBP is much weaker, therefore replacing TDPA with thiols would reduce k₂ more than replacing TBP (on Te-rich QDs) with thiols.

The effect of the carboxylic acid group on the MPA ligand and the solvent also play significant roles in the charge carrier relaxation pathways, particularly for Te-rich surfaces, which seems to be additive to the effect of the thiol group. It was previously found that thiolated carboxylic acid ligands quench the fluorescence of CdSe-ZnS core-shell QDs more so than the hydroxyl analogues in water.⁴⁷ Here we have shown that the average radiative lifetime for Te-rich CdTe increases to several µs for MPA-QDs in methanol, which we have suggested to result from increased hole-trapping, but the same QDs in water have radiative lifetimes similar to the as-prepared QDs. This longer radiative lifetime correlates to the FT-IR data showing that the both forms of the MPA ligand are bound far less efficiently to the QD in the more polar solvent. The FT-IR data also suggests that the MPA ligands coordinate to the QD not just with the thiol groups (as is the case with PT), but also with their carboxylic acid groups, evidenced by the relatively low frequency of the COOH peak. This is particularly prevalent for the QDs in methanol. The carboxylic acid groups could increase the hole-trapping lifetime compared to the thiol (i.e compared to PT), to result in similar average radiative lifetimes as for the TDPA ligands. We envision this as a reduction in the R_{-3} process in figure 6(d). This is reasonable considering the chemical similarity of the carboxylic acid to the phosphonic acid. Even though phosphonic acids bind stronger than carboxylic acids, the smaller size of the MPA relative to TDPA, may lead to a larger number of ligands on the OD in both orientations (coordinated by the thiol group or the carboxylic acid group). Furthermore, the FT-IR data suggests that the protonated form preferentially binds to Cd atoms, as the peak was larger for Cd-rich CdTe in methanol, and it is this form that is more efficiently removed upon transfer to water. As the Te-rich QDs are transferred to water, there is a large decrease in average radiative lifetime, consistent with the view that the R₋₃ process may be largely recovered by the preferential removal of COOH-bound ligands. As was the case for TDPA/TBP- and PT-functionalized ODs, the non-radiative lifetime for MPA-functionalized QDs decreases steadily as the Cd:Te ratio decreases, concomitant with the FT-IR data showing that [ligand] is reduced. Similar to the TDPA/TBP and PT ligands, it appears that k_3 [Te]_S increases at a faster rate than k_2 [ligand] decreases in equation (5).

In addition to the effects of the ligand on the relaxation dynamics, the fluorescence spectra were red shifted for PT ligands, but blue-shifted for MPA ligands (figure 2(a)), suggesting electronic effects from both the thiol group and the carboxyl group, and further supporting the multi-functional-group binding observed by FT-IR. The red-shift for PT-QDs must be directly related to the thiol binding, since the solvent is unchanged between PT-QDs and TDPA-QDs. However, the extent of blue-shifting for MPA-QDs was larger in water than in methanol. It may initially seem contradictory that the blue-shift is larger for MPA-QDs in water than in methanol, considering that there are less MPA ligands bound to the QD in water than in methanol. However, recent work has identified the role of the dielectric constant of the solvent on the spectral shifts in CdTe using both experimental and TDDFT calculations.⁴⁸ It appears that there are competing effects in play; roles involving the coordinating group of the ligands and roles involving the dielectric constant of the solvent. Our systematic progression from hydrophobic thiol to hydrophilic thiol in methanol and then in water allowed us to separate some of these effects. The thiol group both helps to suppress hole trapping and causes a red-shift in the emission spectrum. Transfer of the QD into a higher dielectric constant medium is accompanied by a greater degree of deprotonation of the carboxylic acid, and so these effects cannot be directly uncoupled. However, as the QD is transferred from methanol into water, the additional blue-shift is mainly due to the increased dielectric constant. A previous report of thioglycolic acid (TGA)-capped QDs of similar emission peak position to ours and synthesized with a 5:1 Cd:Te ratio, identical to the QDs shown in figure 3 above, estimated an inverse dependence of wavelength shift with dielectric constant, with an ~7 nm blue shift as the dielectric constant changes from 40 to 68.⁴⁸ The blue shift observed here as the dielectric constant is changed from 32 (methanol)

to 78 (water) is only ~3 nm, which may be due to the fact that MPA is a slightly longer ligand than TGA, thereby screening the solvent effect from the QD more. In any case, it appears that the dielectric constant of the solvent is responsible for reversing the red-shift caused by the thiol group. There may also be some effects from the solvent on the radiative and non-radiative rates between MPA-QDs in methanol and water and may not *just* be a result of differences in how many ligands are bound, and in which orientation, as we have identified here, but other factors may come into play. Future work will attempt to decouple these factors.

We would like to point out that, while shell-free water-soluble quantum dots have strong advantages over core-shell quantum dots, especially concerning their size and ease of synthesis, adding a shell may still provide other advantages. For example, the shell material is usually less toxic than the core material, which reduces the fluorophore's toxicity for in vivo applications. Furthermore, blinking is a problem for single molecule fluorescence applications and it has been shown that adding a thick shell reduces, or may even eliminate, this effect.^{49,50} However, it is important to pay close attention to the core-shell interface as shells with large lattice mismatches to the core do not appear to reduce the blinking.⁵¹ Finally, adding a shell may reduce the effect of external conditions such as pH on the optical properties of cores,^{15,52} although pH effects have also been reported for core-shell ODs as well.⁵³⁻⁵⁵ More work is needed to fully understand the role of the external environment, especially aqueous environments, on shell-free QDs with different surface compositions to take full advantage of small and bright water-soluble QDs. It was previously shown that the coordinating group and the water-soluble functional group of the ligand plays an important role in fluorescence quenching of CdSe-ZnS core-shell QDs.⁴⁷ We have shown here that these effects depend on whether the surface is Cd-rich or Te-rich, which significantly affects the ligand binding and, in turn, can be used to engineer the radiative and non-radiative lifetimes. The underlying mechanisms for the lifetime variations are complex, being related to coupled effects of charge carrier trapping and ligand-induced nonadiabatic transitions affecting both radiative and non-radiative lifetimes and originating on different surface atoms.

In summary, the brightest shell-free QDs that we have synthesized have ~80% QY, with a Cd-rich surface coated with propanethiol ligands. These conditions provide the optimal balance between surface atom passivation and ligand binding strength and are among the highest QY CdTe particles reported. The QY of the same QDs with MPA ligands in polar solvents such as methanol and water show \sim 70% and 50%, respectively, highlighting the consistent high brightness across a range of solvents. This result is promising as MPA ligands provide a route to water solubility that results in minimal size increase but provide bright, shell-free water-soluble quantum dots. The synthesis uses the cheap, easy to handle CdO and elemental Te as precursors, and has the ability to reproducibly synthesize them without long refluxing times and, using a simple ligand exchange procedure, can be completed in less than an hour. Most importantly, we can use these results to tune both solubility and the optical properties by knowing how the coupled relaxation processes affect both radiative and non-radiative lifetimes. We have quantified that a Cd-rich surface shows higher quantum yield than a Te-rich surface primarily because the radiative lifetime is significantly increased by uncoordinated Te atoms causing hole trapping processes. In addition, strongly coordinating ligands, primarily on the Cd-atoms, increases the nonradiative lifetime. We postulated a model in which a balance between trapping rate and subsequent ligand-mediated non-radiative relaxation is controlled by surface atom stoichiometry and ligand density and coupling strength, which allows us to engineer both average radiative and non-radiative lifetimes. Quantitative FT-IR spectroscopy, together with systematic synthesis and ligand exchange, has provided strong support for this model. The implications of this study in gaining a deeper understanding of the connection between

the ligand binding chemistry and the physics underlying charge carrier relaxation processes will allow one to tailor QDs for a wide variety of applications by engineering these two lifetimes. For example, photovoltaic applications will likely benefit from a system with a long radiative lifetime combined with strong chemical coupling to conducting environments, while light emitting devices benefits from having a short radiative lifetime and weak external coupling. For near-field energy transfer processes, such as FRET, it is important to gain a more complete knowledge of how the local environment affects both the radiative and non-radiative lifetimes in order to accurately calculate the energy transfer rate, and ultimately the distance between the donor and acceptor molecules.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) Absorption spectra of CdTe QDs with varying Cd:Te ratios.





(a) XPS spectra of Cd peaks from 5:1 Cd:Te QDs. (b)XPS spectra of Te peaks from 1:5 Cd:Te QDs. (c) Integrated peak areas of Cd and Te, normalized to a total fraction of 1, for 5:1, 1:1 and 1:5 Cd:Te.



Figure 3.

(a) Fluorescence spectra of 5:1 Cd:Te QDs for as-prepared TDPA/TBP, and after ligand exchange with PT or MPA. The MPA-QDs are shown in both methanol and water. (b) Quantum yield as a function of Cd:Te surface atom ratio, ligand and solvent. Inset: fluorescence image of TDPA-QDs in hexanes under a 366 nm UV lamp with Cd:Te ratios varying from, left to right, 5:1, 2:1, 1:1, 1:2, 1:5.



Figure 4.

(a) FT-IR absorption spectrum of as-prepared CdTe synthesized with a Cd:Te ratio of 5:1. (b) FT-IR absorption spectrum of MPA-exchanged CdTe in methanol, synthesized with a Cd:Te ratio of 5:1. (c, d) Integrated peak areas of the sp3 C-H peak (black), PO_3^{2-} peak from TDPA (red), and 2 peaks that are representative of ODE ligands, C=C (blue) and the sp2 C-H (magenta) for as-prepared and PT-exchanged CdTe, respectively, as a function of Cd:Te ratio. (e, f) COOH (black) and COO⁻ (red) for MPA-exchanged CdTe in methanol and water, respectively, as a function of Cd:Te ratio.



Figure 5.

(a) Fluorescence lifetime decay (TCSPC) curve of a typical QD (5:1 with native TDPA ligands shown here) with multiexponential fit (red) and residuals. (b) Average fluorescence lifetime measured by the fit to (a), then using equation (3), as a function of Cd:Te surface atom ratio, ligand and solvent. (c) Radiative lifetime calculated using equation (2) as a function of Cd:Te surface atom ratio, ligand and solvent. (d) Non-radiative lifetime calculated using equation (3) as a function of Cd:Te surface atom ratio, ligand and solvent.





Figure 6.

Proposed model showing the relationship between surface structure and excitonic emission, trapping and non-radiative processes in (a) Cd-Rich and (b) Te-rich CdTe, respectively. (c) and (d) Energy level diagrams showing the various radiative and non-radiative processes for high-energy trap states such as from TDPA/TBP ligands and lower-energy trap states such as from thiol ligands, respectively. Rates, R_i , and rate constants, k_i , are related in equations (4) and (5).