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Time-resolved photoluminescence spectroscopy of ligand-capped PbS nanocrystals

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Abstract

PbS nanocrystals are synthesized using colloidal techniques and have their surfaces capped with oleic acid. The absorption band edge of the PbS nanocrystals is tuned between 900 and 580 nm. The PbS nanocrystals exhibit tuneable photoluminescence with large non-resonant Stokes shifts of up to 500 meV. The magnitude of the Stokes shift is found to be dependent upon the size of PbS nanocrystals. Time-resolved photoluminescence spectroscopy of the PbS nanocrystals reveals that the photoluminescence has an extraordinarily long lifetime of 1 μ s. This long fluorescence lifetime is attributed to the effect of dielectric screening similar to that observed in other IV–VI semiconductor nanocrystals.

1. Introduction

Semiconductor nanocrystals (NCs) have become immensely popular due to the ability to tailor their optical and energetic properties by varying the size [1–4], shape [5, 6] and material [7–11]. Quantum confinement of charge carriers in nanocrystals whose size is comparable to their excitonic Bohr radius results in discrete energy levels and narrow optical transitions. Nanocrystals are currently exploited in a range of applications ranging from biological imaging, quantum computing, and solar cells to electroluminescent devices [12–17].

An increase in the quantum confinement of charge carriers generally leads to more atomic-like behaviour in nanocrystals and this is appealing for almost all applications. PbS nanocrystals have charge carriers with equal effective masses and an exciton Bohr radius of 18 nm [18]. Strong quantum confinement of both charge carriers can be easily achieved by synthesizing PbS nanocrystals with radius less than 18 nm using many of the existing colloidal techniques [19, 20]. Thus PbS nanocrystals offer the unique opportunity of studying semiconductor nanocrystals in the strong confinement regime.

A recent rapid rise in the research interests of colloidal PbS nanocrystals has been spawned by the ability to generate high

photoluminescence yields [21–26]. Hines *et al* used organic ligands to control PbS nanocrystal growth in organic solvents and also passivate the surface [21]. The passivation of the PbS nanocrystal surface states enabled photoluminescence from the PbS nanocrystal band edge with quantum yields of up to 20% [21].

The high photoluminescence yields and the ability to tune the size have led to PbS nanocrystals being incorporated into novel electroluminescence devices consisting of blended nanocrystals and conducting polymers [23, 24]. These devices hold great promise for being efficient emitters in the near-IR region, especially the telecommunications region [23, 24]. Improvements in the performance of such opto-electronic devices require a detailed understanding of the energy relaxation mechanisms in the PbS nanocrystals.

Here we present a method for tuning the band edge of oleic-acid-capped PbS nanocrystals from 900 to 580 nm, with a size change from 2 to 1 nm respectively. The PbS nanocrystals with an absorption band edge at 580 nm exhibit photoluminescence with a peak at 770 nm and this has allowed time-resolved photoluminescence spectra for oleic-acid-capped PbS nanocrystals to be obtained. Time-resolved photoluminescence spectroscopy provides information about the nature of energy relaxation in the system,



Figure 1. (a) Image of a vial of oleic-acid-capped PbS NCs prepared at 40 °C, (b) fluorescence image of a vial of oleic-acid-capped PbS NCs excited by a UV lamp.

helping distinguish between direct exciton recombination and relaxation with the assistance of trap states or phonons. Steady state absorption and photoluminescence spectroscopy is also used to examine the changes in the non-resonant Stokes shift as a function of nanocrystal size.

2. Experiment

PbS nanocrystals were prepared in a similar manner to Hines *et al*, but with H_2S gas used instead of bis(trimethylsilyl)sulfide (TMS). This enabled synthesis temperatures as low as 40 °C and consequently smaller PbS nanocrystals were formed.

A typical reaction is as follows: in a continuously stirred sealed flask, a lead oleate precursor solution containing 0.1 g lead acetate, 10 ml of n-decane and 0.4 ml oleic acid was heated to 130 °C for 20 min under a continuous flow of argon. Next the solution was cooled to 40 °C and 1 ml of H₂S gas was injected at a rate of 1×10^{-4} l s⁻¹ into the gas phase of the sealed flask. PbS nanocrystal formation occurred within seconds of the complete injection of the H₂S gas and after 1 min the reaction was complete and the solution was subsequently cooled back to room temperature. This procedure produced a colloidal suspension of oleic-acid-capped PbS NCs with a mean size of approximately 1–2 nm (as determined by HRTEM) and a band edge at 580 nm. Such NC solutions can be readily diluted in a non-polar solvent such as toluene or hexane.

Fine control of the mean NC size was achieved by adjusting the temperature between 40 and 130 °C, before the H_2S gas was added to induce NC formation. This allowed the absorption band edge to be tuned between 580 and 900 nm.

The CdSe semiconductor nanocrystals used in the time-resolved photoluminescence spectra were commercial (Qdot company) 5 nm CdSe/ZnS core-shell NCs with a room temperature quantum yield of up to 50% and a photoluminescence lifetime of 10 ns.

Room temperature optical absorption spectra were obtained with a Perkin Elmer Lambda 40 UV/vis spectrometer



Figure 2. (a) Absorption spectra of oleic-acid-capped PbS nanocrystals prepared at 50, 75, 100 and 130 $^{\circ}$ C. (b) Fine tuning of the absorption spectra of oleic-acid-capped PbS nanocrystals as the temperature is varied between 40 and 130 $^{\circ}$ C.

operating with the slits set to a 2 nm band pass and 1 nm grating steps. Room temperature photoluminescence spectra were collected perpendicular to an excitation laser beam (532 nm CW) using a single lens, coupled into a single-grating (1200 g mm⁻¹) monochromator (Acton Research) with a silicon photodiode detector. Time-resolved photoluminescence decays were obtained using a time-correlated single-photon counting spectrometer (Picoquant Fluotime 200) with 400 nm wavelength 100 fs pulses sourced from a frequency-doubled mode-locked Ti:sapphire laser (Spectra Physics Tsunami). Pulse repetition rates of 1 Hz were used and the limit of the apparatus's observation window was 1 μ s.

3. Results and discussion

Figure 1(a) shows an image of a vial of the smallest oleicacid-capped PbS nanocrystals and figure 1(b) shows this vial fluorescing red when excited with a UV lamp. The absorption band edge of this solution was at 580 nm and the striking green colour is remarkable for a colloidal suspension of PbS nanocrystals.

In figure 2(a) we see the absorption spectra for four PbS nanocrystal solutions synthesized with increasing temperature. The standard deviation of the position of the band edge peak for a specific synthesis temperature was typically 5%. This is mainly due to the difficulties in the control of the addition rate of H₂S. Figure 2(b) shows the ability to tune the band



Figure 3. (a) Photoluminescence spectra of oleic-acid-capped PbS nanocrystals prepared at 50, 75, 100 and 130 °C. (b) Fine tuning of the photoluminescence spectra of oleic-acid-capped PbS nanocrystals as the temperature is varied between 40 and 130 °C.

edge of the absorption spectrum anywhere between 580 and 900 nm as the temperature is varied between 40 and 130 °C. The band edge remains a clearly defined peak that suggests the size distribution remains narrow even as the mean size is reduced. Clearly the band edge shifts to lower energies as the synthesis temperature is increased. This suggests that lower synthesis temperatures yield the smallest PbS nanocrystals.

Figure 3(a) shows the absorption and photoluminescence spectra of PbS nanocrystal solutions synthesized at 50, 100 and 130 °C. We see that, as the absorption spectrum is tuned, so too is the photoluminescence. The spectral bandwidths of the photoluminescence spectra in figure 3(a) are comparable to the absorption peaks, suggesting that the emission is from a single state rather than an ensemble of trap states [2]. Trapped state emission from an NC solution typically has a full width at half maximum (FWHM) significantly larger than the FHWM of a Gaussian fitted to the band edge peak in the absorption spectrum. The photoluminescence spectra presented in figure 3(b) show the ability to tune the emission from 770 to 1000 nm as the temperature is increased from 40 to 130 °C. The spectral width of the photoluminescence remains fairly constant as the peak shifts from 770 to 1000 nm.

The clearly defined band edge peaks in the absorption spectra of the oleic-acid-capped PbS nanocrystals allowed relatively precise measurements of the non-resonant Stokes shift. Figure 4 shows the variation of the non-resonant Stokes shift as a function of the absorption band edge peak. It is well known that in PbS NCs the absorption band edge depends



Figure 4. Variation of Stokes shift as a function of the absorption band edge of oleic-acid-capped PbS nanocrystals.

upon the nanocrystal size, with the band edge shifting to higher energies as the size of the nanocrystal decreases [18, 21, 27]. At these extremely small nanocrystal sizes, tiny deviations in the mean size of the PbS NCs lead to a large shift in the absorption band edge [27]. TEM analysis also correlated this but could only be used to show size shifts between the smallest and largest nanocrystal samples. Thus by correlating the Stokes shift with the absorption band edge we have a more accurate description of how the Stokes shift might change with the size and energy level structure of the oleic-acid-capped PbS NCs.

In figure 4 we see that the Stokes shift increases linearly as the band edge increases in energy. This means that as the size of the PbS nanocrystal decreases the Stokes shift increases. Non-resonant Stokes shifts have also been reported for other NCs, such as PbSe [2] (90 meV), CdSe [28] (300 meV) and ZnSe [29], which are comparable with the 100–500 meV measured here for the PbS NCs. For CdSe and ZnSe, the Stokes shift is attributed to a dark exciton state whereby phonons assist excitons from the excited state to a normally spin forbidden state of lower energy, from which they relax to the ground state, emitting a photon of lower energy than the initial absorbing state [28, 29]. However, for PbSe and PbS no such state has been theoretically predicted and the nature of the Stokes shift requires further investigation.

The smallest PbS nanocrystals, synthesized at $40 \,^{\circ}$ C, displayed an absorption band edge at 580 nm and a photoluminescence peak at 770 nm. Figure 5(a) shows a transmission electron microscopy (TEM) image of the oleic-acid-capped PbS NCs synthesized at $40 \,^{\circ}$ C and figure 5(b) shows a TEM image of PbS NCs synthesized at $130 \,^{\circ}$ C. The TEM images in figure 5 show 1 and 2 nm PbS nanocrystals for 40 and 130 $\,^{\circ}$ C respectively with a relatively narrow size distribution. The size of these PbS nanocrystals is extremely small and this leads to a high degree of quantum confinement in these structures. The ability to tune the emission of the oleic-acid-capped PbS nanocrystals into the near visible regime allows conventional time-resolved photoluminescence spectroscopy measurements to be performed and compared directly to other semiconductor nanocrystals such as CdSe.

Figure 6 shows the time-resolved photoluminescence spectra from a colloidal solution of 1 nm oleic-acid-capped PbS NCs, synthesized at 40 °C, and as a comparison a colloidal solution of 5 nm CdSe/ZnS nanocrystals. The fluorescence decays in figure 6 were recorded at the respective peaks in the emission of the two samples. The lifetime of the PbS



Figure 5. Transmission electron microscopy image of oleic-acid-capped PbS nanocrystals synthesized at (a) 40 $^{\circ}$ C and (b) 130 $^{\circ}$ C.



Figure 6. Time-resolved photoluminescence lifetime spectra of 1 nm oleic-acid-capped PbS nanocrystals and 5 nm CdSe nanocrystals.

nanocrystals has a single-exponential time constant measured to be 1 μ s and is two orders of magnitude longer than the CdSe/ZnS nanocrystals. The observed decay time of the PbS NCs is longer than expected for a dipole transition, but shorter than expected for emission related to trap states [30].

Colloidal PbSe semiconductor nanocrystals have also shown long fluorescence lifetimes of up to 0.88 μ s, similar to the PbS nanocrystals measured here [30]. The long radiative lifetimes in the PbSe nanocrystals were attributed to the effects of dielectric screening and there was no need to invoke a triplet or quasi-forbidden transitions, such as a dark exciton state, to explain the results [30]. The screening of the radiating field inside the nanocrystal has the effect of weakening the internal field and consequently increases the radiative lifetime by a factor of $[3\varepsilon_1/(\varepsilon_2+2\varepsilon_1)]^{-2}$, where $\varepsilon_1 \sim 1.88$ and $\varepsilon_2 \sim 23$ are the optical dielectric constants of the solvent host (hexane) and the nanocrystal material (PbS) respectively [30, 31]. This leads to an increase of the radiative lifetime by a factor of 22, which is a 15% increase in this factor as compared to PbSe NCs in chloroform in [30]. This also correlates with the 1 μ s lifetime of the PbS NCs being 12% longer than the 0.88 μ s lifetime of the PbSe NCs. The long lifetimes associated with the effect of dielectric screening is predicted for all the IV-VI semiconductor nanocrystals with high dielectric constants [30]. Thus the long lifetimes measured in the colloidal PbS nanocrystals are not unexpected.

4. Conclusion

In conclusion, we have shown the ability to tune the PbS NC absorption band edge from 900 to 580 nm with decreasing temperature. The photoluminescence from the PbS NCs also shifted with the absorption band edge from 1000 to 770 nm. TEM confirmed the size shifts in the PbS NCs and the photoluminescence lifetime of 1 nm oleic-acid-capped PbS nanocrystals was measured to be 1 μ s. This long fluorescence lifetime was two orders of magnitude longer than CdSe nanocrystals. The extremely long lifetimes in the PbS nanocrystals are expected due to the effect of dielectric screening. Steady-state spectroscopy of the oleic-acid-capped PbS NCs revealed large non-resonant Stokes shifts that increased as the nanocrystal size decreased.

Further work to measure the fluorescence lifetimes as a function of nanocrystal size is underway. This should provide more information about the nature of the relatively large nonresonant Stokes shifts observed in these PbS nanocrystals.

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