Investigation of ligand effects on exciton recombination in PbS nanoparticles

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Abstract: Multiple exciton generation (MEG) and exciton recombination were studied by femtosecond transient absorption spectroscopy in PbS nanoparticles (NPs) capped with oleic acid (PbS–OLA) and 2,3-dimercaptopropane sulfonate (PbS–DMPS) ligands. Analysis of the transient absorption data showed that the PbS–DMPS nanoparticles exhibit increased rates of multi- and single-exciton recombination compared with the PbS–OLA nanoparticles; however, the MEG yield for both sets of particles was the same within experimental error. The origin of the differences in the exciton recombination decay rates is unknown, but it is speculated that it may be due to the ionic functionality of DMPS or to the different ligating atoms of the OLA and DMPS ligands. The PbS–DMPS nanoparticles were highly sensitive to the presence of oxygen, which caused a dramatic increase in nonradiative decay pathways, which can be mistaken for multiexciton absorbance and decay. Removal of oxygen eliminated the nonradiative decay pathways. Overall, this study showed that the dynamics of MEG can be modified by changing the NP ligand shell, a result that may be useful in the development of NP-based thin-film solar devices.

Key words: multiple exciton generation, surface modification of nanoparticles, exciton recombination, nanoparticle ligand exchange.

Introduction

Semiconductor nanoparticles (NPs) are favorable candidates for integration into cost-effective solar devices. This is primarily due to their broad optical tunability and ease of processing. In particular, lead chalcogenide (PbS, PbSe, or PbTe) NPs provide tunability through the near-infrared (NIR) portion of the electromagnetic spectrum while exhibiting quantum-confined properties, two desirable qualities for matching the solar spectrum in photovoltaic devices.1–5

Because of quantum confinement, an NP has a discrete energy spectrum. In semiconductor NPs, this spectrum is split by a forbidden energy gap much like in bulk semiconductors. However, owing to the discretized energy states, NPs exhibit very different properties from the bulk.6 Most importantly, bulk semiconductors waste excess solar energy as heat. In semiconductor NPs, however, a process called multiple exciton generation (MEG) can lead to more efficient solar energy transduction. In the MEG process, multiple excitons are created per photon absorbed, provided energy and momentum requirements are met. For semiconductor NPs, the incident photon energy required to create...
multiple excitons is $2E_g$ or greater (where $E_g$ is the NP bandgap energy).\textsuperscript{7–11} In contrast, much greater excitation energies are needed for bulk semiconductor MEG.\textsuperscript{12} In principle, if MEG occurs and charge separation and (or) transport is faster than or competitive with recombination, MEG can appreciably enhance the photocurrent of solar devices.

To attain efficient marketable NP-based devices, the lifetimes of single and multiple excitons, and what governs these lifetimes, must be understood. For this reason, substantial effort has gone into quantifying MEG decay times in various NP systems. It is well-documented that multiple excitons recombine through an Auger-type process much more quickly (tens to hundreds of picoseconds) than the long-lived (nanosecond to microsecond) radiative recombination of single excitons and that this process is dependent on the size, shape, and composition of the NPs studied.\textsuperscript{7–11,13–18}

Because of the large surface-to-volume ratio inherent to NPs, it is hypothesized that the NP surface plays a significant role in the electronic dynamics of the system.\textsuperscript{19,20} Thus, a key component in designing NP-based solar cells is understanding the role of the stabilizing ligand shell. Provided that electron dynamics are not influenced by a large density of surface trap states,\textsuperscript{21} it is hypothesized that by controlling the type of ligand on the NPs the MEG efficiency, multixciton lifetime, and charge transport through a device can be optimized. Additionally, it was shown for PbSe that preparation techniques and post-treatment of NP films with various ligands and solvents yield very different recombination dynamics and MEG efficiencies.\textsuperscript{22} The authors of this study suggested that the differences they observed are most likely attributable to the chemical species present on the NP surface or to the changes observed in average interparticle distance.\textsuperscript{22} These results prompted our curiosity regarding using the structure of the ligand shell to control MEG, and we began a study to investigate ligand effects on MEG. In this paper we report the results of our first study. Specifically, oleic acid-capped PbS NPs (PbS–OLA) and 2,3-dimercaptopropanesulfonate capped PbS NPs (PbS–DMPS) were investigated with femtosecond transient absorption spectroscopy to determine if there is a ligand effect on MEG and exciton recombination dynamics.

Before presenting the results of our study, a few more introductory notes are necessary. Recently, there has been some controversy over MEG in NP systems. In particular, it has been argued that MEG is less efficient than what was previously reported\textsuperscript{11,23–25} (Note, however, that the controversy is not about the existence of MEG). For example, a re-examination of CdSe and CdTe NPs led to the conclusion that MEG efficiency is negligible in these systems, contrary to prior results and contrary to the general idea that MEG is enhanced in quantum-confined systems.\textsuperscript{23} In our view, much of the controversy stems from the fact that numerous experimental variables can affect the apparent MEG dynamics. For example, differences in apparent MEG efficiencies have been reported in different preparatory batches of supposedly identical nanoparticles.\textsuperscript{26,27} Because of this, controversy has developed over the existence of photocharging of the NPs leading to a misinterpretation of true MEG yields; however, stirring of the solutions to sample a fresh volume of NPs with each laser pulse greatly reduces the probability of photoinization and allows for the observation of true MEG yields.\textsuperscript{26} Additionally, the extent of ligand coverage and oxidation of a NP surface may lead to increased carrier trapping, thus requiring additional considerations in analyzing the carrier dynamics.\textsuperscript{27} All of these points serve to emphasize that to efficiently exploit MEG in working devices it is essential to understand the properties of the NPs, including elucidating the direct effect of the ligand shell.

**Experimental section**

**Synthesis of PbS NPs**

All reagents and solvents were obtained from Sigma-Aldrich except D$_2$O, which was purchased from Cambridge Isotope Laboratories. Lead sulfide NPs were synthesized by preparing a lead precursor solution according to the method of Hines and Scholes.\textsuperscript{1} To synthesize the parent OLA-capped particles, a solution consisting of 4 mL octadecene and 4 mL OLA was prepared and 0.3 g PbO was added to the mixture. The solution was heated under vacuum to 100 °C for 30 min to dissolve the PbO and to drive off H$_2$O. The solution was subsequently heated to the appropriate injection temperature (100–150 °C) for the desired particle size and held at that temperature for at least 30 min.

While the lead solution was heating, a sulfur precursor solution of 0.167 mM hexamethylidisilathiane and 4 mL octadecene was degassed under nitrogen. When the lead solution reached the desired injection temperature, the sulfur precursor was quickly injected into the flask and allowed to cool to room temperature. Removal of excess ligand and octadecene was completed by repeated precipitation in acetone, centrifugation of the particles, and dispersion in small amounts of toluene.\textsuperscript{1} NIR characterization of the particles was accomplished using a PerkinElmer Lambda 19 UV–vis–NIR spectrophotometer. Particle size and monodispersity were measured using a FEI Titan 80-300 TEM in STEM mode (PbS–OLA NP $d = 5.0 \pm 0.7$ nm).

Ligand exchange on the PbS–OLA particles was accomplished according to literature precedent.\textsuperscript{28} D$_2$O was chosen as the solvent over H$_2$O because of its suppressed NIR absorption. Equal volumes of PbS–OLA solutions (25 mg/mL) and the 2,3-dimercaptopropanesulfonate sodium salt dissolved in D$_2$O (78 mmol/L) were stirred until phase transfer of the particles was complete (~1 h). The ionically functionalized NPs were centrifuged to break emulsions formed during stirring and phase transfer. The PbS–DMPS particles were then precipitated from D$_2$O using acetonitrile, centrifuged, and resuspended in D$_2$O. The particles were characterized by NIR absorbance spectroscopy and TEM imaging (PbS–DMPS NP $d = 5.2 \pm 0.9$ nm).

**Femtosecond laser system**

The optical setup used for obtaining the pump–probe transient absorption data included a passively mode-locked Ti:Sapphire oscillator (SpectraPhysics Tsunami, 750 mW) pumped by a solid-state Nd:YAG laser (SpectraPhysics Millennia Pro., 5 W). This source yielded 100 fs pulses centered at 800 nm. The pulses were seeded into a regenerative am-
plifier (SpectraPhysics Spitfire Pro) pumped by a q-switched intracavity-doubled Nd:YLF laser (SpectraPhysics Empower, 15 W).

**Optical layout**

The beam from the amplifier (3.1 W, 1 kHz) was split into pump and probe components as shown in Fig. 1. The pump component was frequency doubled to 400 nm for MEG experiments (for non-MEG experiments it remained at 800 nm) and was chopped at 500 Hz, half the rate of the probe, with an optical chopper. The probe component was tuned in an optical parametric amplifier (OPA) to match the NIR first exciton absorbance of the nanoparticle samples. The probe pulses were delayed with respect to the pump by a micron resolution delay stage. The probe signal was detected on a fast biased InGaAs photodiode (Thorlabs DET 410), whereas the pump signal was indexed by a biased silicon photodiode (Thorlabs DET 210). The signal intensities were amplified and sampled using a fast preamplifier (SRS-SR445A) and boxcar integrator (SRS-SR250). The output from the boxcar integrator was connected to an analog-to-digital converter and then input into a PC. Transient absorption data was calculated using the probe pulse intensity with and without pump pulse excitation. IgorPro software was used for data analysis.

**Sample preparation and handling**

Solvents were degassed with nitrogen prior to use. Samples were prepared by dispersing NPs in an appropriate solvent at a desired concentration. Sample solutions were placed in cuvettes equipped with stir bars and PTFE stoppers. To ensure removal of oxygen, PbS–DMPS solutions were degassed a second time before transferring to a cuvette in the latter studies. The headspaces of all cuvettes were filled with nitrogen, and the cuvettes were taped and sealed for the duration of the femtosecond experiments.

As a special note, transients taken for stirred and static solutions of both PbS–OLA and PbS–DMPS sometimes showed an appreciable difference in the ratio of early to late population components. Also, as previously mentioned, there have been recent reports outlining the observation of ligand-dependent photocharging of NP solutions.26 For these reasons, all of the samples used for MEG determination in this study were stirred.

**Results and discussion**

**Choice of ligands**

Because we are trying to elucidate the direct effect of the ligand on MEG, we determined that solution-phase samples were of interest primarily owing to the fact that, in solution, the effective concentration of NPs is less than in a film, which decreases the likelihood that interparticle distance is affecting MEG. During our initial investigations of NP ligand–shell substitution reactions, we found that substitution of PbS–OLA NPs by neutral organic thiol ligands led to precipitation of the NPs or to opaque solutions in a wide variety of solvents, rendering the NPs unsuitable for our transient absorption measurements. It was necessary, therefore, to find a ligand, other than one of the neutral thiols, which would allow the NPs to remain suspended in a transparent solution. A literature search revealed that substitution of OLA-capped nanoparticles by DMPS yielded stable NPs in solution, particularly under anaerobic conditions.28 This same study suggested that, once the DMPS is coordinated to the NP, the ionic ligands repel one another, thereby maintaining a minimum interparticle distance that reduced the probability of precipitation brought on by agglomeration. Most importantly, this study determined that thin-film devices made with the PbS–DMPS NPs showed enhanced photoresponse in the NIR compared with PbS–OLA films, where no photocurrent was detected under the same conditions. This enhanced photoactivity was primarily attributed to the reduced interparticle spacing in the PbS–DMPS films over PbS–OLA films. Transient absorption studies of the PbS–OLA and PbS–DMPS NPs could reveal additional information regarding the differences in photoresponse of the films, such as enhancements of MEG quantum yields or longer exciton lifetimes. The synthetic ease of the DMPS-for-OLA substitution reaction, combined with the encouraging thin-film photocurrent results, was a strong incentive to carry out this study using the DMPS and OLA NP systems.

**Transient absorption of OLA-capped NPs**

Two fractions of OLA-capped NPs (from the same synthetic batch) with a first exciton absorbance at 1340 nm were excited with 800 and 400 nm laser pulses in toluene solution. In all transient absorption measurements, the probe wavelength was tuned to the maximum of the exciton absorbance in the NIR spectrum. The particles were excited under low-fluence excitation to prevent nonlinearities and to ensure that the average number of photons absorbed per NP ($N_{abs}$) was kept to a minimum. The value for $N_{abs}$ is given by eq. [1].

$$[1] \quad N_{abs} = \frac{J(0)}{cL} \left(1 - e^{-\alpha L}\right)$$

where $L$ is the path length of the cuvette, $J(0)$ is the photon fluence at the front face of the cuvette, $c$ is the sample concentration, and $\alpha L = OD \ln{10}$ as calculated from the optical density (OD) of the NP absorbance spectrum.

Raw transient absorption traces at varied pump fluences obtained for 800 nm excitation (Fig. 2a) were fit using a global least-squares fitting routine. The subsequent analysis was performed according to the procedure outlined by Ellingson et al.8 Within this analysis, the time constants for
single exciton ($t_X$) and biexciton ($t_{MX}$) recombination were global parameters and were varied for at least four kinetic traces until the best fit results were obtained. The resulting time constants revealed a single exciton lifetime of 80 ns and a faster biexciton time constant of 436 ps. The amplitudes for these variable fluence traces at 800 nm excitation ($<2E_g$) are the Poisson amplitudes, which are influenced by $N_{abs}$. Upon extracting the amplitudes and exciton lifetimes in the case where MEG does not occur ($h\nu < 2E_g$), raw transients for MEG excitation can be analyzed. Figure 2b shows the variable fluence traces for the excitation of PbS–OLA at 400 nm ($3.35E_g$). In this case, the curves were fit by constraining $t_X$ and $t_{MX}$ to the extracted values obtained above; however, the amplitudes of these curves are no longer strictly Poissonian and now contain components of MEG. Extraction of the MEG quantum yield will be detailed later.

Fig. 2. Transient decay curves for PbS–oleic acid (OLA) nanoparticles (NPs) excited at (a) 800 nm (1.55 eV, 1.68$E_g$, where $E_g$ is the NP bandgap energy) and (b) 400 nm (3.11 eV, 3.35$E_g$), with various pump intensities.

Fig. 3. Example NIR absorbance spectra showing the first exciton absorption ($1S_h–1S_e$) for parent PbS–oleic acid (OLA) (blue line) nanoparticles (NPs) vs ligand-exchanged PbS–2,3-dimercaptopropanesulfonate (DMPS) particles (red line).

Ligand exchange and transient absorption of PbS–DMPS NPs

Ligand-exchange reactions were carried out on PbS–OLA NPs with DMPS (PbS–MPS). The PbS–DMPS NPs were characterized by TEM imaging and NIR absorption spectroscopy to confirm their size and exciton absorbance (see Experimental section). The red shift in the NIR spectrum for the PbS–DMPS NPs compared with PbS–OLA NPs (Fig. 3) is accounted for by the change in dielectric constant of the solvent$^{28}$ and not by a change in particle size, as confirmed by TEM imaging.

Ultrafast decay curves for a single batch of PbS–DMPS particles were obtained for 800 and 400 nm excitation (1.69 and 3.38 times the bandgap energy, respectively) at various pump fluences. The raw traces for both excitation wavelengths are shown in Fig. 4. It is interesting to note that the transient dynamics recorded for PbS–DMPS at 400 nm excitation (Fig. 4b) are very different from the OLA-capped particles under MEG conditions. At first glance, it appears that the PbS–DMPS nanoparticles excited under MEG conditions have a greatly enhanced MEG signature compared to the PbS–OLA NPs (the ratio of populations at early and late times; 2.5 and 3.4, respectively). However, experiments showed that the enhanced MEG in the PbS–DMPS nanoparticles excited under MEG conditions have a greatly enhanced MEG signature compared to the PbS–OLA NPs (the ratio of populations at early and late times; 2.5 and 3.4, respectively). However, experiments showed that the enhanced MEG in the PbS–DMPS NPs is likely attributable to NP decomposition leading to enhanced trapping. After 1–3 days in the sealed cuvettes, the particles precipitated out of solution. The precipitation time was loosely correlated to the care taken to remove oxygen in the samples. To investigate this phenomenon further, a second ligand exchange was performed from the same PbS–OLA parent batch but with care taken to remove O$_2$ from the PbS–DMPS product before sealing it in the sample cuvettes. Additionally, the PbS–DMPS and PbS–OLA NPs were monitored by NIR absorbance spectroscopy throughout the MEG laser experiments to ensure that the laser experiments were not carried out on decomposed NPs.
In the case of PbS–OLA NPs, shown in Fig. 5a, there is no change in the 1S\textsubscript{h}−1S\textsubscript{e} (first exciton) absorbance over the course of the femtosecond experiments. (It should be noted that there is a blue shift of the exciton absorbance in these NPs compared with freshly prepared NPs. This change is most likely due to some oxidation of the NP core\cite{29} causing a change in size of the nanoparticles. Nevertheless, there is no evidence of the particles changing during the course of the MEG data collection.) In contrast to the PbS–OLA solution, the PbS–DMPS NPs do change during the MEG experiment (Fig. 5b): the first exciton absorbance peak narrows and appears almost multimodal within 1 day.

To eliminate the effects of NP decomposition during the MEG experiments, only transient spectra taken within the first 8 h following sample preparation were used in the data analyses. Additionally, the samples were degassed a second time prior to sealing the cuvettes. Results of the MEG experiments on PbS–DMPS NPs prepared under these anaerobic conditions are shown in Fig. 6. Note there is no apparent decomposition in the spectra of the PbS–DMPS NPs.

The global fitting procedure described previously was used to fit the raw transient data for PbS–DMPS. Time constants extracted from the non-MEG curve fits are listed in Table 1 and compared with those obtained for PbS–OLA. Also shown in Table 1 are the MEG quantum yields (QYs) for the PbS–DMPS and PbS–OLA particles. In determining QY, the ratio of short and long time signal (A/B) is plotted as a function of \( N_{\text{abs}} \) (Fig. 7). Fits for the curves for 800 nm excitation assume Poisson statistics for the absorption of

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**Fig. 4.** Variable fluence transient curves and curve fits for PbS–2,3-dimercaptopropanesulfonate (DMPS) under (a) 800 nm and (b) 400 nm excitation.

**Fig. 5.** Time-lapse absorbance spectra of (a) parent PbS–oleic acid (OLA) nanoparticles (NPs) and (b) ligand-exchanged PbS–2,3-dimercaptopropanesulfonate (DMPS) particles throughout the transient absorption experiments.
photons by the NPs. The curves for 400 nm excitation are non-Poissonian, but are fit by allowing for the adjustment of the QY, which accounts for the enhanced amplitudes owing to MEG. By extrapolating these fits back to vanishing photon fluence and dividing out the contribution of the 800 nm excitation curves, the MEG QY for each particle set was determined. Note in Table 1 that even the more rigorously deoxygenated PbS–DMPS NPs experience faster decay dynamics than their PbS–OLA parent batch; however, the MEG QY for each particle set is the same within experimental error. The time constants for multi- and single-exciton decay for the PbS–DMPS particles are less than half that of the PbS–OLA particles, indicating that the ligand has an effect on MEG and exciton recombination.30

The origin of the ligand effect on decay dynamics is unknown. One suggestion is that the faster decay rates for exciton recombination in the DMPS system are due to the

Table 1. Characteristic lifetimes of multiple (\(t_{MX}\)) and single (\(t_X\)) exciton recombination and extracted multiple exciton generation (MEG) quantum yields (QYs) for PbS–oleic acid (OLA) and PbS–2,3-dimercaptopropionate (DMPS).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(t_{MX}) (ps)</th>
<th>(t_X) (ns)</th>
<th>MEG QY</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS–OLA</td>
<td>436±45</td>
<td>80</td>
<td>1.4±0.1</td>
</tr>
<tr>
<td>PbS–DMPS</td>
<td>223±65</td>
<td>36</td>
<td>1.5±0.1</td>
</tr>
</tbody>
</table>
negative charge on the ligand. It is suggested that the electron is electrostatically repelled by the anionic ligand shell. This would prevent delocalization of the electrons over the surface of the NP, spatially confining them to the core, which causes them to recombine with holes more quickly. A related hypothesis is that the ligand effect can be attributed to the different ligating atoms in the two ligands. The DMPS ligand binds through sulfur instead of oxygen. Because oxygen is more electronegative than sulfur, it is more likely to accept electron density and, therefore, more likely to delocalize the electronic wave function over the surface of the NP, which would lead to slower electron–hole recombination rates. A final suggestion is that the differences in the decay dynamics may be due to a solvent effect. Previous studies suggested that the solvent can affect electron dynamics in NPs that have significant trap state densities, but does not play as significant a role in passivated NPs. The NPs used in this investigation are passivated by the ligands, leading to the conclusion that solvent effects may not be of great consequence. Investigations are underway in our laboratory to further probe these ligand effects and to provide insight into their origin.

Key insights and conclusions

PbS NPs with OLA and DMPS ligands were investigated to determine how the NP ligand shell affects MEG and exciton recombination dynamics. Experiments showed striking differences between the PbS–DMPS samples prepared in the presence of oxygen and those prepared anaerobically. With oxygen present in the samples, the kinetic decay curves exhibited large false MEG-type signatures and enhanced recombination rates owing to the photooxidation and degradation of the NPs and the ensuing increase in the number of nonradiative decay pathways. Rigorous removal of oxygen from the samples produced kinetic decay curves with time constants for PbS–DMPS NPs that were significantly shorter than those of the PbS–OLA NPs. The origin of the differences in the exciton recombination decay rates is unknown, but it is speculated that it may be due to the ionic functionality of the DMPS ligand or to the different ligating atoms of the OLA and DMPS ligands. This study shows that MEG dynamics can be tuned by changing the NP ligand shell, which may have implications for the development of NP-based efficient thin-film solar devices.

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References

Whereas the PbS–OLA particles did not exhibit signs of photooxidation during the laser studies, it is possible they might have undergone oxidation prior to the laser studies and prior to ligand exchange. It is also possible that having pre-oxidized particles during the ligand exchange facilitates the oxidation of the ligand or prevents satisfactory passivation of the NPs, leading to the precipitation of the NPs. During the course of our investigation, it was reported by Klimov and co-workers that oxidation of the NP core has a slight effect on MEG dynamics. In the same manner, if oligosulfide formation of the DMPS ligand occurs because of oxidation then a coordination site (or dangling bond) can open up on the surface of the particle. Both the oxidation of the NP core and the presence of dangling bonds can contribute to electron-trapping states on the NP surface. Correcting for a trapping factor in such a case provides a better assessment of true MEG yields.

References: