Carrier multiplication yields in PbS and PbSe nanocrystals measured by transient photoluminescence

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We report here an assessment of carrier multiplication (CM) yields in PbSe and PbS nanocrystals (NCs) by a quantitative analysis of biexciton and exciton dynamics in transient photoluminescence decays. Interest in CM, the generation of more than one electron and hole after absorption of one photon, has renewed in recent years because of reports suggesting greatly increased efficiencies in nanocrystalline materials compared to the bulk form, in which CM was otherwise too weak to be of consequence in photovoltaic energy conversion devices. In our PbSe and PbS NC samples, however, we estimate using transient photoluminescence that at most 0.25 additional e-h pairs are generated per photon even at energies $\hbar \omega > 5E_g$, instead of the much higher values reported in the literature. We argue by comparing NC CM estimates and reported bulk values on an absolute energy basis, which we justify as appropriate on physical grounds, that the data reported thus far are inconclusive with respect to the importance of nanoscale-specific phenomena in the CM process.

I. INTRODUCTION

The process of carrier multiplication (CM) consists of the generation of more than one electron and hole after absorption of a single photon in a semiconductor, its effectiveness determined by a rich interplay of the interactions between charge carriers, phonons and light. From a practical perspective, though, its chief potential as an enabler of more efficient solar spectrum harvesting in energy conversion devices has been limited by the very weak CM of bulk materials. The topic of CM has however reemerged in recent years due to reports of very strong enhancements of the CM process in nanocrystalline semiconductors.

Enhanced CM was first reported for PbSe and PbS nanocrystals (NCs) by Schaller et al. and Ellingson et al. using the transient absorption (TA) technique. Work on this material system has been extended, with one report inferring the creation of up to 7 e-h by a single high energy photon based on pump-probe data, and a study suggesting that the enhancement occurs not only for NCs in solution but also in close-packed films relevant for potential device applications. Other material systems have also been explored, with work initially showing evidence for strong CM as well in CdSe, InAs, and Si NCs.

Since then, there have been several reports observing little or no CM. Using a transient photoluminescence experiment, we found no evidence for CM in CdSe NCs at energies well above previously reported thresholds. More recently, Pijpers et al. have reported difficulty in reproducing their observation of CM in InAs, and a new study has reported no observable CM in InAs/CdSe/ZnSe (core/shell/shell) NCs. In addition, there remain several unresolved questions pertaining to CM in lead chalcogenide NCs. For instance, there are significant qualitative and quantitative differences between the Schaller et al. report of strong CM following a universal trend with $\hbar \omega / E_g$ and the Ellingson et al. results which appear to show a distinct particle size dependence and smaller yields, in some cases by factors of 2-3. Second, considerable theoretical debate about CM in NCs remains, mostly due to a lack of information about intraband relaxation processes deep in the exciton and biexciton manifolds. Recognizing this deficiency, Allan and Delerue have allowed for a wide range of intraband relaxation rates in their flexible theoretical framework, but still find the largest CM yields reported by Schaller et al. difficult to accommodate. Overall, these outstanding issues suggest the need for continuing the assessment of CM in lead chalcogenide NC samples.

In this work we study carrier multiplication in PbSe and PbS NCs using transient photoluminescence (tPL), a technique that more specifically informs on the e-h pair population within NCs than the pump-probe methods commonly employed. We first characterize the exciton and multiexciton PL signatures in these materials using low photon-energy excitation. We find that PbSe and PbS NCs, when adequately surface passivated, have flat exciton population dynamics over a 1ns window. At higher excitation power, strong features appear with fast 50-200ps decay lifetimes attributed to biexcitons. After these calibration steps, we measured tPL decays to look for evidence of CM using excitation at 3.1eV, well above previously reported CM energy thresholds for the NC materials in this study. Although we distinctly observe a signal consistent with CM for all of our PbS and PbSe NC samples, the CM yields we estimate, defined as the average number of additional e-h pairs generated per absorbed photon, reach only $y_{cm} \approx 25\%$ even when $\hbar \omega > 5E_g$. These values are significantly lower than those of previous reports.

In the final section we explore the issue of comparing CM yields between NCs of different sizes and with the bulk. We show that if nanoscale-specific physics, such as potentially slowed intraband relaxation, are not a priori assumed, one would expect CM yields to depend only on the incident photon energy, regardless of the particle's size.
optical density
0.6 0.8 1 1.2 1.4
energy (eV)
0
0.2
0.4
0.6
0.8
1

FIG. 1: Absorption spectrum of a typical PbSe NC sample used in this study. The NC bandgap $E_g = 0.84eV$ is determined as the peak of the first absorption feature.

size. This suggests that CM yields be compared on an absolute photon energy basis. Revisiting the literature in this framework shows that the reports on PbS and PbSe NCs to date do not uniformly suggest very large enhancements of the underlying CM physics when compared to what has been reported for bulk PbS.

II. EXPERIMENTAL

PbSe and PbS NCs were prepared by high temperature pyrolysis of Pb and Se/S precursors in an oleic acid/octadecene mixture. The growth solutions were purified by a single precipitation, redispersed in hexane, and transferred to 1mm path length quartz cuvettes in a nitrogen glovebox. The resulting samples, with optical densities of $∼ 1-3$ at 1.55eV, were sealed and taken out into air for subsequent measurements. As will be described below, some samples of larger particles (first absorption feature $< 0.8eV$) were treated with Cd$^{2+}$ by adding a few drops of cadmium oleate to the hexane NC dispersions at room temperature. All samples were magnetically stirred during acquisitions, and PL decays under weak 1.55eV excitation were periodically monitored to check for any degradation. A typical sample’s absorption spectrum is shown in Fig. 1

Transient photoluminescence decays of the samples were collected using a fluorescence upconversion apparatus based on an amplified Ti:sapphire system operating at 250kHz. A portion of the pulse train was passed through a BBO crystal to generate excitation sources at 3.1 eV and 1.55 eV which were separated with two dichroic mirrors and focused on the sample to spot sizes of roughly $\sim 100\mu m$ and $\sim 50\mu m$ diameter respectively. Emission was collected in a front-face geometry using off-axis parabolic mirrors and focused onto another BBO crystal. Following a variable delay, the rest of the 1.55eV pulse train was overlapped with the collected emission and the resulting sum frequency generation was separated spatially and spectrally using interference filters and a monochromator. The signal was detected with a cooled PMT and amplified using a lock-in amplifier. For these experiments, the pulse width was maintained relatively long by tweaking the amplifier compressor away from its optimal short-pulse configuration to avoid excess noise from continuum generation in the mixing crystal. We have nevertheless maintained a time resolution better than $\sim 15$ ps as measured from the rise time of the tPL signal. Because the peaks of the exciton and multiexciton PL were not found appreciably different within our spectral resolution, all decays for a given sample were acquired at a fixed wavelength.

III. RESULTS AND DISCUSSION

A. Exciton decay dynamics

We began by characterizing the PL dynamics of single excitons (X) in PbS and PbSe NCs using weak 1.55eV excitation. In general, samples of small and moderate sized NCs had flat PL dynamics over the full temporal range of our instrument (see Fig. 2). In contrast, as-prepared CdSe core particles almost invariably show significant sub-nanosecond dynamics, attributable to trapping by defects. The flat decays we observe in these PbSe and PbS samples suggest good surface passivation of NCs prepared by these methods and are consistent with the very high luminescence quantum yields reported in the literature. In addition, we also measured the PL dynamics over a much longer window for one of our PbS samples using an InGaAs amplified photodiode and found a nearly single exponential fluorescence decay with a $\sim 660ns$ lifetime, consistent with previous studies.

The PL dynamics of larger as-prepared particles, those with $E_g < 0.8eV$, typically showed multiexponential X decays with large sub-nanosecond components, suggesting poor surface passivation. Moreover, these dynamics steepened irreversibly upon exposure to 3.1eV radiation. In an attempt to remove non-radiative pathways and to stabilize the particles, we chose to apply a mild Cd$^{2+}$ treatment to the NCs. Addition of cadmium oleate to hexane dispersions of $E_g = 0.73eV$ PbS and $E_g = 0.60eV$ PbSe NCs resulted in nearly flat single-exponential X decays and robustness to prolonged 3.1eV irradiation, while causing no noticeable changes in the absorption spectra and emission wavelength of the samples. Our measurements also suggest that surface treatment of these samples does not have much effect on CM yields. We studied one sample of fairly large $E_g = 0.68eV$ PbSe NCs that did not require Cd$^{2+}$ treatment, and found that its estimated CM yields were similar to the other large NC samples that were treated with Cd$^{2+}$. We also checked
the effect of the Cd\textsuperscript{2+} treatment by applying it to NC samples that already exhibited adequate surface passivation and found no significant change of the biexciton lifetime or estimated CM yield.

We have chosen to carry out further studies only on samples that show flat tPL decays over our experimental timescale, whether as-prepared or Cd\textsuperscript{2+}-treated, because the interpretation of subsequent results is considerably simplified. A multieponential X decay entails an inhomogeneous distribution of NC surface passivation which can then support a nontrivial distribution of multiexciton lifetimes\cite{12,21}, complicating both the isolation of MX features in tPL decays and the quantification of the underlying exciton and multiexciton populations. The second and more serious problem was that the X decays of samples with poor surface passivation tended to change irreversibly when exposed to 3.1eV for the lengths of time necessary to obtain adequately clean data with our apparatus. For these reasons we focused only on well-passivated samples. It is conceivable that CM yields might depend on the details of the NC surface. If so, the results of this work may be difficult to generalize beyond the constraints of our particular sample preparation and selection methods.

**B. transient PL of the BX state**

Strong excitation pulses can create biexcitons (BX) and further multie excitons in NCs by sequential photon absorption. An excitation power series for our \( E_g = 0.84\)eV PbSe sample is presented in Fig. 3a, showing the growth of a large fast feature, which we attribute to the BX, on top of the single X dynamics. These decays are well described as the sum of a slow X component and a fast BX component, \( a_{BX} e^{-t/\tau_{BX}} + a_X e^{-t/\tau_X} \) with fixed lifetimes \( \tau_X > 1\)ns and \( \tau_{BX} \approx 60\)ps. Under strong excitation, additional faster components appear, attributable to emission from higher multie excitons\cite{37}. The rapid \( \tau_{BX} \) decay times are due to an Auger-like relaxation mechanism\cite{26} and the rates we measure are consistent with those measured by pump-probe techniques\cite{38}.

Our method for estimating CM yields\cite{12} described in the next section, relies importantly on an accurate calibration of the link between observed tPL decays and the underlying BX and X populations soon after excitation. This information can be summarized in the quantity \( (a_{BX}/a_X)_{sat} \), the ratio of the sizes of the BX and...
X tPL decay components expected in the hypothetical case that all NCs are initially excited to the BX state, i.e. when the BX is saturated. In Fig. 3b, we fit the observed exponential components, \( a_X \) and \( a_{BX} \), to population profiles assuming poissonian photon absorption statistics. The power series of X and BX features are found consistent with this assumption, and we are able to estimate sample-dependent \( (a_{BX}/a_X)_{sat} \) values in the range of 2.5-4. This implies that the radiative rate of the biexciton, \( k_{rad}^{BX} \), is \( \approx 3.5 - 5 \) times greater than \( k_{rad}^{X} \). Interestingly, the numbers are similar to those observed for CdSe NCs, where we proposed that the enhanced \( k_{rad}^{BX} \) could be due to spin substructure since the lowest X fine structure state in CdSe is known to be dark.

Because our best estimates of \( (a_{BX}/a_X)_{sat} \) are in the range 2.5-4, we fit the BX to CM. The CM yield, \( y_{cm} \), for the sample is then given by

\[
y_{cm} = \left( \frac{a_{BX}}{a_X} \right)_{P \rightarrow 0} / \left( \frac{a_{BX}}{a_X} \right)_{sat}
\]

Because our best estimates of \( (a_{BX}/a_X)_{sat} \) are in the range 2.5-4, CM yields are smaller by a factor of \( \approx 2 \) than the simple ratio \( a_{BX}/a_X \) would suggest. For this \( E_g = 0.84 \)eV sample, \( y_{cm} \approx 9\% \) at \( \hbar \omega/E_g = 3.7 \). Fig. 4b and 4d display similar data for a sample of larger \( E_g = 0.68 \)eV PbSe NCs. The sample exhibits a bigger fast component in the \( P \to 0 \) limit, and therefore a larger CM yield of \( \approx 23\% \) at \( \hbar \omega/E_g = 4.6 \).

We have studied a number of PbS and PbSe NC samples in this way and find \( y_{cm} \) always in the range of 10 - 25\% even in samples for which \( \hbar \omega > 5E_g \). As is summarized in Fig. 3, our CM yield estimates are significantly lower than those previously reported by other researchers for their PbS and PbSe NC samples. Schaller et al. report a universal dependence of CM yields on \( \hbar \omega/E_g \), predicting CM yields of up to 2 additional e-h pairs at \( \hbar \omega = 5E_g \). Ellington et al. do not observe such structure in their data, but instead report CM yields that appear to depend on particle size. The data fall below the universal curve of Schaller et al. by a factor of roughly two, while our own best estimates of the CM yields are an additional factor of 2-3 smaller. It should also be noted that the findings of Schaller et al. predict not only BX formation, but also triexciton (TX) yields of 0.5 and 1 for our largest samples when excited at 3.1eV. However, our data fits very well to only a BX and an X component. Any appreciable TX would have been evidenced in our measured decays since the TX decay dynamics are within our experimental time resolution and the TX emission peak is expected to be close to that of the X and BX because of the approximate 8-fold degeneracy of the lowest lead chalcogenide NC electron and hole states.

Since our numerical results are in disagreement with the previous reports based on TA techniques, we consider here possible sources of error in our CM estimates. In Fig. 5 we show estimated 95\% confidence intervals for \( (a_{BX}/a_X)_{P \rightarrow 0} \) related to noise in the experimental decays. These uncertainties in \( y_{cm} \) are all smaller than \( \pm 0.06 \) and are likely unbiased. The part of our methodology most susceptible to a systematic error is the saturation ratio of the BX to X tPL components, \( (a_{BX}/a_X)_{sat} \). Any multiplicative error in this quantity translates directly into a multiplicative error in the CM yield. In our study, we have estimated \( (a_{BX}/a_X)_{sat} \) by fitting the sizes of X and BX decay components under 1.55eV excitation to a population profile and then assuming that this saturation ratio should apply as well to biexcitons created by a CM process. Using these \( (a_{BX}/a_X)_{sat} \) values of \( \approx 2.5-4 \), we have determined CM yields in the range of 10-25\%. For our results to roughly match the magnitudes of CM reported by Ellington et al. we would have had to use much smaller values \( (a_{BX}/a_X)_{sat} \approx 1 \), with an even further reduction to \( (a_{BX}/a_X)_{sat} < 1 \) required to achieve agreement with the Schaller et al. reports. However, using such small \( (a_{BX}/a_X)_{sat} \) would be inconsistent with our direct observation of \( a_{BX} > 2a_X \) under sufficiently strong excitation conditions. We are therefore confident in our principal conclusion that the CM yields in the PbSe and PbS NC samples we have studied are significantly smaller than those previously reported for the PbX material system.
D. Comparison with bulk CM

In this section we seek to establish a basis for comparison of CM yields between NC samples of different sizes and with the bulk material. It has been common to compare CM yields at the same scaled energies $\hbar \omega/E_g$. This practice follows precedent from the bulk impact ionization literature and is useful when considering device applications. However, aside from providing a convenient way to show data from different materials on a single plot, the physical basis for such comparisons is not obvious. It may not transparently lead to answers of some basic questions, like whether or not nanoscale-specific phenomena have a large effect on CM. In general, the CM yield for a material system (for example, CdSe or PbS) is expected to be determined both by particle size and the photon energy, $y_{cm} (r, \hbar \omega)$, which can be recast as $y_{cm} (E_g, \hbar \omega)$, where $E_g$ is the size-dependent bandgap. Much of the existing NC CM literature infers an important role for nanoscale physics from the fact that their estimates of $y_{cm}$ are much larger than reports for $y_{cm}^{bulk}$ when compared at the same relative energy $\hbar \omega/E_g$. This assumes that without enhancement $y_{cm} (E_g, \hbar \omega) = y_{cm}^{bulk} \left( E_g^{bulk}/E_g \right) \hbar \omega$, or, in other words, that at a given $\hbar \omega$, NCs would exhibit only the CM that would be present in the bulk at the lower photon energy ($E_g^{bulk}/E_g$). To our understanding, though, the only property of $y_{cm} (E_g, \hbar \omega)$ that a priori scales with $E_g^{bulk}/E_g$ is the energy conservation requirement, $y_{cm} (E_g, \hbar \omega) = 0$ for $\hbar \omega < 2E_g$, but this does not seem sufficient to justify the assumption that $y_{cm} (E_g, \hbar \omega) = y_{cm}^{bulk} \left( E_g^{bulk}/E_g \right) \hbar \omega$ in general as an adequate description of CM physics in the absence of NC enhancement.
To construct a more appropriate reference for comparison with NC results, we consider bulk material physics and explore how \( y_{cm}(r, \hbar \omega) \) behaves if all phenomena exclusive to the nanoscale are neglected. In the bulk limit it is intuitively clear that \( y_{cm}(r, \hbar \omega) \) is independent of \( r \). The competing processes of intraband relaxation and impact ionization have the same rates for crystals of, say, 1\( \mu \)m and 0.5\( \mu \)m, resulting in the same CM efficiency. To understand why the impact ionization rate remains constant one can start from the first-order perturbation theory formulation:

\[
k_{1e1h \rightarrow 2e2h} = \frac{2\pi}{\hbar} |\langle 2e2h|V_{\text{coul}}|1e1h\rangle|^2 \rho_{2e2h}(E)
\]

Where \( V_{\text{coul}} \) is the coulomb interaction and \( \rho_{2e2h}(E) \) is the density of two electron, two hole states (corresponding to a BX) at the energy \( E \) of the initial one electron, one hole configuration (which corresponds to \( X \) in an NC). A reduction in volume has two effects. First, the average coulomb coupling is enhanced, with \( |\langle 2e2h|V_{\text{coul}}|1e1h\rangle|^2 \propto V^{-4} \). However, this is fully balanced by the reduction in average density of states (DOS), since \( \rho_{2e2h}(E) \propto V^4 \). If no new physics are introduced, this process of shrinking the bulk can be continued into the nanoscale with the important conclusion that for \( \hbar \omega \) above the \( 2E_g(r) \) energy conserving threshold, \( y_{cm}(r, \hbar \omega) = y_{cm}^{\text{bulk}}(\hbar \omega) \). It must be kept in mind that even though the spacing between energy levels is certainly larger in NCs, the DOS averaged over sufficiently wide intervals is the same as in the bulk, with volume scalings \( \rho_X(E) \propto V^2 \) and \( \rho_{BX}(E) \propto V^4 \). We should only expect a divergence from \( y_{cm}(E_g, \hbar \omega) = y_{cm}^{\text{bulk}}(\hbar \omega) \) if new physics appear in the nanoscale that have a strong influence on the CM process.

This suggests that comparisons between NC and the bulk should be made on an absolute photon energy basis as long as \( \hbar \omega \) is well above the energy-conserving limit. Then the difference \( y_{cm}(E_g, \hbar \omega) - y_{cm}^{\text{bulk}}(\hbar \omega) \) would be attributable specifically to nanoscale phenomena. In contrast, the usual literature comparison at fixed \( \hbar \omega/E_g \) can significantly exaggerate enhancement over the bulk simply because \( E_g(r) > E_g^{\text{bulk}} \), so that, for instance, even without novel NC physics, PbSe and PbS NCs with \( E_g(r) > E_g^{\text{bulk}} \) will appear to show at least a two-fold CM threshold reduction. It is noted that from a practical perspective, bulk-like CM in NCs does indeed present a real advantage because the extra carriers can be extracted at a higher voltage difference \( E_g(r) \). Also, a \( \hbar \omega/E_g \) basis is useful in comparing a sample’s actual CM to the maximum possible imposed by energy conservation. However, it is not obvious that a comparison of how near two different samples are to their separate energy-conserving limits can usefully inform on differences in their underlying physics. For that, we argue that the absolute photon energy basis appears to be more appropriate.

In light of these considerations, we show in Fig. 7 a summary of literature data on PbS and PbSe NCs replotted on an absolute energy axis along with values of CM yields in bulk PbS films reported by Smith and Dutton. These authors studied the photoconductivity of commercial PbS films and found an increase in photocurrent response at shorter wavelengths which they attributed to a CM process, emerging from a threshold \( \hbar \omega \approx 2\mathrm{eV} \) and rising approximately linearly to \( y_{cm} \approx 2 \) at \( \hbar \omega = 6\mathrm{eV} \). It should be kept in mind that there are numerous potential sources of error in this bulk CM determination, some of which we detail later, but it is nevertheless interesting to note that the CM yields for NCs reported in the literature appear only modestly enhanced over these bulk values. Except in the case of very large (small \( E_g \)) NCs following the universal curve of Schaller et al., CM yields are within a factor of \( 2 \) of the bulk report, and exhibit a similar CM energy threshold between 2-3eV. Figure 7 shows our own estimates compared to the NC and bulk literature data at \( \hbar \omega = 3.1\mathrm{eV} \) plotted against \( E_g(r) \). Our results are below the bulk CM reported value, those of Ellingson et al appear consistent with it, and the Schaller et al. results fall well above for larger NCs.

Reaching a robust conclusion at this stage on the relative strengths of CM in bulk and NC forms is difficult because of potential uncertainties in the bulk values reported Smith and Dutton. First, the authors did not present a characterization of the commercial PbS films studied, and it is possible that significant oxidation may have taken place since no protective coating was used. This is important since exposure to O\(_2\) is known to cause significant changes in bulk PbS photoconductivity. Second, the reported yields are very sensitive to any sys-
that nanoscale phenomena are responsible for strong CM enhancement, as we have discussed in the previous paragraph and in Fig. 7.

Given the possibility that CM in NCs might follow largely bulk-like physics, it is interesting to examine what is known about the NC-specific physical mechanisms that could affect the multiplication process. The most commonly cited rationalizations of CM enhancement in NCs are the possibility of strong coulomb interaction and slow intraband relaxation. It could be argued, for example, that coulomb couplings are significantly enhanced in the nanoscale based on the much faster Auger relaxation rates of band-edge multie excitons compared to the bulk. This enhancement of Auger rates at the band edge is thought to be due to a relaxation of momentum conservation requirements brought about by the finite nature and abrupt surface of NCs. However, because momentum conservation is not a limiting constraint on impact ionization in the bulk at high excess kinetic energies and it is not clear that the nanocrystalline form should still exhibit significant enhancement. Calculations by Allan and Delerue suggest that $k_1e_1h \rightarrow 2e_2h$ is if anything smaller in PbSe NCs than for the bulk.

Similarly, there is still no evidence of a phonon bottleneck for intraband relaxation at high electron and hole kinetic energies. Due to practical considerations relating to experimental time resolution, most studies on NCs have focused only on relaxation from some of the lowest excited states to the band edge. Even then, they find very fast picosecond relaxation times. Moreover, at the high excess kinetic energies required for CM, the X manifold is much denser and it seems less likely that a phonon bottleneck effect could play a very large role.

The remaining potential nanoscale CM enhancement mechanisms have to do with the discrete state structure. Certainly, the discrete nature of states in a NC is critical near the energy conservation threshold, as no CM can occur when $\hbar \omega < 2E_g(r)$ even though the bulk $2e-2h$ DOS is finite. However, if we restrict our attention to $\hbar \omega$ well over $2E_g(r)$, as has been the case when large CM yields have been reported, it is plausible that the BX manifold is sufficiently dense that bulk-like behavior could result. Further, even if there were deviations, we would not expect them to be monotonic in either $E_g(r)$ or $\hbar \omega$. Finally, it is possible that there could be strong coupling between X and BX, but not enough is known about phase and population relaxation mechanisms of carriers with high kinetic energies to conclude that such effects would be important for CM.

All these arguments above should not be taken as proof or justification that $y_{\text{CM}}(E_g, \hbar \omega) = y_{\text{CM}}^{\text{bulk}}(\hbar \omega)$ for NCs, but simply to show that such a conclusion would not be inconsistent with what is experimentally known about NC photophysics. Too little is understood about the physics of highly energetic carriers in NCs to make strong a priori predictions of the role of nanoscale phenomena in CM.
IV. CONCLUSIONS

The principal experimental conclusion of this work is that CM yields in our PbSe and PbS NC samples estimated by transient photoluminescence are well below the values that have been reported in the literature for PbSe and PbS NCs using transient pump-probe techniques. It should be noted that these previous reports themselves show significant numerical disagreement between each other even though they employ nominally similar methods. In broad terms, the variation between the reports of Schaller et al., Ellingson et al., and our own must ultimately stem from either systematic differences in data acquisition procedures, variation in the way CM is determined from observed decays, or actual sample-to-sample differences of the CM efficiency. The fact that Ellingson et al. and Schaller et al. use nearly equivalent methods for estimating CM but find conflicting results suggests that their samples are inherently different, or that the two groups handled these samples differently during the course of their experiments. In our own work there is a possibility of systematic error related to the calibration method we use, but we have argued above that this alone cannot readily account for the contrast with the existing literature. The answer may yet lie in sample-to-sample CM variation, and if so would suggest that CM in NCs is strongly affected by defects or surface ligand type and coverage.

The second effort of this work has been to establish a basis for comparing CM efficiencies in NCs and the bulk that more clearly isolates the effects of changes in underlying physics. We have argued that an absolute photon efficiency is more suitable for this purpose, and by comparison to values reported for the bulk, we found that the CM yields reported for NCs do not immediately suggest a very large role for nanoscale-specific phenomena. Because these bulk values themselves could be beset by large errors, it is difficult to reach a definitive conclusion. A modern, robust, assessment of CM in bulk PbS and PbSe will be necessary for this to be possible. Similarly, understanding the variation in the NC CM literature will require applying multiple experimental methodologies to identical NC samples or, more importantly, the development of new spectroscopic techniques that are more specifically tailored to multiexciton detection than the population-dynamics based measurements in use at this time. A clear picture of the CM process in the transition from the bulk to the nanoscale will have to wait for experimental efforts on these two fronts.

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APPENDIX A: POPULATION MODELING

As has been described in detail in our previous work on CdSe NCs the exponential components in a tPL decay can be related to the MX and X populations immediately following excitation through the following approximate expressions:

\[ a_X \propto k_{rad}^X p_1 \]
\[ a_{BX} \propto \left( k_{rad}^{BX} - k_{rad}^X \right) p_2 \]

where \( p_1 \) and \( p_2 \) are the population of NCs that start with at least an exciton or a biexciton respectively at time 0. These populations are given by \( p_{n, m} = \sum_{k \geq m} I_k \), where the population of the \( k \)-th multiexciton state, \( I_k \), is determined by poisson statistics, taking into account excitation beam inhomogeneity and position dependent collection efficiency:

\[ I_k = \int \phi(x) n(x)^k \frac{e^{-n(x)}}{k!} dx \]

where \( j(x) \) and \( \phi(x) \) are the photon flux and collection efficiency at position \( x \), and \( \sigma \) is the absorption cross section. \( n(x) \) is the average number of photons absorbed per pulse by an NC located at \( x \). If \( j(x) \) and \( \phi(x) \) were known, it would be possible to compute the \( I_k \) up to a common proportionality constant and obtain, by comparison with experiment, the saturation ratio \( a_{BX}/a_X \), the value of \( a_{BX}/a_X \) when \( p_2 = p_1 \). However, both \( j(x) \) and especially \( \phi(x) \) are difficult to determine accurately in our apparatus. Instead, we exploit the fact that the shape of \( p_1 \) as a function of excitation power fully determines the shape of \( p_2 \). To see this, we note that during any of our experimental power series \( n(x) \) only changes in magnitude while retaining its shape. Setting \( n(x) = n_0 h(x) \), where \( h(x) \) is a fixed shape and \( n_0 \) is a constant parameter, one can show that:

\[ p_2(n_0) = p_1(n_0) - n_0 \frac{\partial p_1}{\partial n_0} \]

In the above, \( n_0 \) can be replaced with any quantity proportional to it, such as average excitation power, so knowledge of the absorption cross section is not required. Therefore, if one finds any \( h(x) \) and \( \phi(x) \) so that the calculated \( p_1(n_0) \) closely fits the shape of the observed \( a_X \) excitation series, then the \( p_2(n_0) \) calculated with the same \( h(x) \) and \( \phi(x) \) will be proportional to \( a_{BX} \). The results of this procedure, shown in Fig. [3], demonstrate that the \( a_{BX} \) we observe match very well the trend we independently predict from the \( a_X \) evolution, further supporting our assignment of this fast component in the tPL
to the biexciton. Our estimate of \((a_{BX}/a_X)_{sat}\) is then obtained as the ratio of the proportionality constants relating \(a_X\) to \(p_1\) and \(a_{BX}\) to \(p_2\). We find saturation values \((a_{BX}/a_X)_{sat}\) of 2.5-4 using this method. Since \((a_{BX}/a_X)_{sat} = k_{BX}^{rad}/k_X^{rad} - 1\), the corresponding values of \(k_{BX}^{rad}/k_X^{rad}\) are in the range 3.5-5.

**APPENDIX B: BX AND X RADIATIVE RATES**

We present here a calculation of \(k_{BX}^{rad}/k_X^{rad}\) for a simple model of the lead chalcogenide ground state. The 1S\(_a\) and 1S\(_b\) states in lead chalcogenide are eight-fold degenerate. There are four equivalent valleys in the band structure and two-fold spin degeneracy. The possible X electronic configurations can be labeled \(i,m,h\), and the BX configurations \(i,j,m,n,h\), where \(i,j,m,n \in 1\ldots8\). Because total momentum and spin must be conserved during an optical interaction, only the recombination of an electron and hole with the same \(k\) and same spin is allowed. Assuming that particle momentum and spin remain good quantum numbers, each electron state is connected by a dipole transition to exactly one of the eight hole states. By symmetry, these transition dipole moments all have the same magnitude \(|\mu|\). We can then calculate the radiative square transition dipole of each X and BX microstate. In the case of X, there are 8 configurations of type \(1_{e}h_{i}\), with \(k_{rad} = \mu^{2}\), and \(8 \cdot 7\) of type \(1_{e}3_{h}\) with \(k_{rad} = 0\). Similarly, for the BX, there are \(3 \choose 2\) configurations like \(1_{e}2_{e}1_{h}2_{h}\) with \(k_{rad} = \mu^{2} + \mu^{2}\), \(8 \cdot 7 \cdot 6\) configurations of type \(1_{e}2_{e}1_{h}3_{h}\) with \(k_{rad} = \mu^{2}\), and \(3 \choose 2\) \(2\) dark \(1_{e}2_{e}3_{h}4_{h}\)-type states. Taking the thermal average, one finds \(k_{X}^{rad} = \mu^{2}/8\) and \(k_{BX}^{rad} = \mu^{2}/2\), and therefore \(k_{BX}^{rad} = 4k_{X}^{rad}\). This result should remain approximately valid even in the presence of perturbations that mix states with different quantum numbers or couple the electrons and holes, as long as the width of the resulting energy fine structure is sufficiently smaller than the available thermal energy, \(kT\).
In the literature CM yields are often reported as an internal quantum efficiency (IQE), which is related to our $y_{cm}$ by IQE = 100%($y_{cm} + 1$).

As in our previous work, we delay fitting of the 1.55eV-excited decays by a time $\sim \tau_{BX}/2$ to minimize unwanted interference from higher MX tPL components in the determinations of $a_{X}$ and $a_{BX}$.

For example, we find $\tau_{BX} \approx 58$ps and $\tau_{BX} \approx 140$ps for $E_g = 0.84$eV and $E_g = 0.68$eV PbSe NCs respectively, while Beard et al. have determined $\tau_{BX} = 67$ps for $E_g = 0.84$eV and Schaller et al. report $\tau_{BX} = 149$ps for $E_g = 0.64$eV.

The steep volume dependence $|\langle 2e2h|V_{coul}|1e1h\rangle|^2 \propto V^{-4}$ might appear surprising at first. It should be kept in mind that this square matrix element is averaged over all 2e2h configurations of nearby energy. However, for $\langle 2e2h|V_{coul}|1e1h\rangle \neq 0$, conservation of momentum and spin must be satisfied and one of either the initial electron or hole must not change state. The proportion of final 2e2h states that violate these conditions and thus have $\langle 2e2h|V_{coul}|1e1h\rangle = 0$ increases with volume, ultimately resulting in a stronger volume scaling of $|\langle 2e2h|V_{coul}|1e1h\rangle|^2$ than would be expected from averaging only the non-zero terms.