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Effect of electronic structure on carrier multiplication efficiency: Comparative study of PbSe and CdSe nanocrystals

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Recently, we demonstrated that PbSe nanocrystal quantum dots can efficiently produce multiple electron-hole pairs (excitons) in response to a single absorbed photon. To address the generality of this carrier-multiplication phenomenon to other materials, we perform a comparative study of multiexciton generation in PbSe and CdSe nanocrystals that have distinctly different electronic structures. We find that both materials exhibit high-efficiency carrier multiplication and the activation threshold is lower in CdSe nanocrystals than in PbSe nanocrystals (~2.5 vs ~2.9 energy gaps). Furthermore, the efficiencies of multiexciton generation are nearly identical for both materials despite a vast difference in both energy structures and carrier relaxation behaviors, strongly suggesting that this phenomenon is general to quantum-confined semiconductor nanocrystals. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2142092]

Carrier multiplication (CM) is a process in which absorption of a single photon produces multiple electron-hole pairs (excitons).[1,2] This effect has the potential to significantly increase the efficiency of solar cells[2–4] and has other applications ranging from low-threshold lasing[5] to single-photon splitting of water molecules. In our first paper on high-efficiency CM in PbSe nanocrystals (NCs),[6] we demonstrated that absorption of a single photon could produce up to 2.2 excitons per NC, which translates into 220% internal quantum efficiency (QE) for converting light quanta into charge carriers. Ellingson *et al.* recently confirmed these results in similar studies of PbSe NCs and NCs of another lead-salt compound, PbS.[7] These observations raise questions regarding the generality of CM to other materials and the potential limits on photon-to-exciton conversion efficiency. Specifically, how important are the unique features of lead salts (such as mirror symmetry between the conduction and valence bands resulting from nearly identical electron and hole masses) for obtaining highly efficient CM?

To address this issue, here we perform comparative studies of CM in NCs of PbSe and CdSe, which are characterized by significant differences in electronic structures and carrier relaxation behaviors. Despite these differences, both compositions show comparable CM efficiencies (defined in terms of differential QE; see below), which is indicative of the generality of this phenomenon to quantum-confined, semiconductor NCs. Our data indicate that CdSe NCs show a lower CM threshold than PbSe NCs ($\sim 2.5E_g$ vs $\sim 2.9E_g$; E_g is the NC energy gap), which can be explained via simple carrier effective-mass arguments. We observe a monotonic increase in QE with increasing photon energy above the CM threshold up to 690% in PbSe NCs and 165% in CdSe NCs.

To detect CM and measure its efficiency, we exploit significant differences in the recombination dynamics of single excitons and multiexcitons, which is the method first proposed by us in Ref. 6. Single excitons decay via relatively slow radiative recombination [tens and hundreds of nanoseconds in CdSe (Ref. 8) and PbSe NCs,[9,10] respectively], while multiexcitons decay on a much faster, picosecond time scale because of Auger recombination.[11–13] As a result of this difference, the generation of multiexcitons from a single absorbed photon can be detected via a fast decay component in NC population dynamics.

Carrier dynamics are monitored using femtosecond transient absorption (TA), in which pump-pulse-induced absorption changes ($\Delta\alpha$) are probed with a second time-delayed pulse that is tuned to the lowest $1S$ exciton transition, which approximately defines the position of the NC energy gap (pulsewidths were ~50 to ~200 fs depending on the laser source). When multiexcitons are generated by high intensity pump pulses via absorption of multiple photons (no CM), NC exciton populations exhibit a Poissonian distribution,[13] for which the average number of excitons excited per NC, $\langle N_0\rangle$, is simply proportional to the pump fluence, j_p: $\langle N_0\rangle = j_p\sigma_a$, where σ_a is the NC absorption cross section.[13] In the analysis below, we also utilize the average exciton multiplicity in photoexcited NCs, $\langle N_x\rangle$, which can be used as a measure of the CM efficiency: $QE = 100\%\langle N_x\rangle$. In the case of the Poissonian distribution of carrier populations (no CM), $\langle N_x\rangle$ is determined solely by the pump fluence (i.e., by $\langle N_0\rangle$): $\langle N_x\rangle = \langle N_0\rangle(1-e^{-\langle N_0\rangle})^{-1}$. At low pump intensities ($\langle N_0\rangle \ll 1$), this expression yields $\langle N_x\rangle \approx 1$ so that the $1S$ absorption change ($\Delta\alpha_{1S}$) is determined only by $\langle N_0\rangle$ ($\Delta\alpha_{1S} \propto \langle N_0\rangle$), i.e., it provides a measure of the fraction of the photoexcited NCs in the NC ensemble.

An interesting feature of the electron-hole system produced by CM is that it is *non-Poissonian*. Specifically, at low excitation intensities ($j_p\sigma_a \ll 1$) for which the probability of generating multiexcitons via sequential absorption of multiple photons is negligibly small, $\langle N_x\rangle$ is determined not by the pump fluence but rather by the pump photon energy. Furthermore, in this case, the maximum possible exciton multiplicity ($N_{x,\max}$) is not infinite (as in the case of the Poisson distribution generated using high-intensity excitation) but instead is limited by $\hbar\omega_p/E_g$, ($\hbar\omega_p$ is the pump photon energy) due to the energy conservation requirement. If $N_{x,\max}$ does not exceed the $1S$ electron-state degeneracy, G (which is the case in our experiments with both CdSe and PbSe

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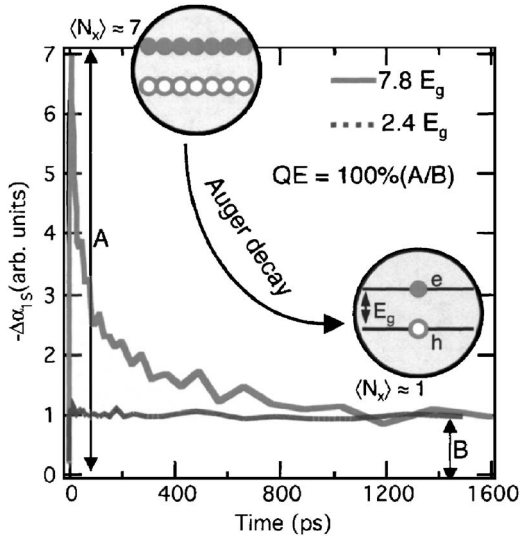

FIG. 1. Calculations of CM QE from time-resolved TA data illustrated using two traces measured for PbSe NCs at low pump intensity ($\langle N_0\rangle < 0.1$) with photon energies $2.4E_g$ (no CM; dashed line) and $7.8E_g$ (CM producing ~7 excitons per NC; solid line).

NCs, for which G is 2 and 8, respectively), $\Delta\alpha_{1S}$ is determined by both the fraction of the photoexcited NCs and the average *exciton multiplicity* produced by CM: $\Delta\alpha_{1S} \propto \langle N_0\rangle \times \langle N_x\rangle$. In this case, time-resolved $\Delta\alpha_{1S}$ traces allow one to directly measure $\langle N_x\rangle$ without the need for any additional calibration. Specifically, the amplitude of the long-lived background (B), which is associated with the single remaining exciton in a NC following Auger recombination of multiexcitons, provides a scale bar for calculating exciton multiplicity at early times after excitation, $\langle N_x\rangle = A/B$ (A is the amplitude of the TA time transient measured at short times after excitation), as well as the CM efficiency as illustrated in Fig. 1 using a TA trace measured for PbSe NCs.

In our initial report on high-efficiency CM in PbSe NCs,[6] we measured CM QEs of 220% at $\sim 3.8E_g$. Since then, we have extended the range of pump energies up to $\sim 8E_g$ and observe that, starting at the CM threshold of $\sim 2.9E_g$, QE gradually increases up to 690% [see Fig. 1 and Fig. 2(a) inset], which indicates direct generation of ~7 excitons by a single absorbed photon. In the spectral range studied [the inset in Fig. 2(b)], the CM efficiency does not show any saturation and likely increases even further with increasing $\hbar\omega_p$ and/or decreasing E_g.

We also observe significant CM efficiencies in CdSe NCs. Figure 2(b) (main frame) shows $1S$ TA dynamics measured at low intensities ($\langle N_0\rangle = 0.1$) using pump photons of 3.1 or 6.2 eV for two NC samples with energy gaps of 2.0 and 2.1 eV. Because of the energy conservation requirement, the generation of biexcitons via CM cannot occur for 3.1 -eV photons, whereas it becomes possible at 6.2 eV. From TA dynamics measured for these samples at high excitation intensities ($\langle N_0\rangle > 1$) with a 3.1-eV pump, we infer that the biexciton decay constants (τ_2) are 300 ps ($E_g = 2.0$ eV) and 150 ps ($E_g = 2.1$ eV) [inset in Fig. 2(b)]; the smaller value of τ_2 for NCs of a wider gap (i.e., smaller NC size) is the typical trend observed for Auger recombination of multiexcitons in NCs.[11,13] Importantly, the fast component with essentially *identical* relaxation constants (300 and 160 ps) can be generated at low pump levels ($\langle N_0\rangle = 0.1$) but using 6.2

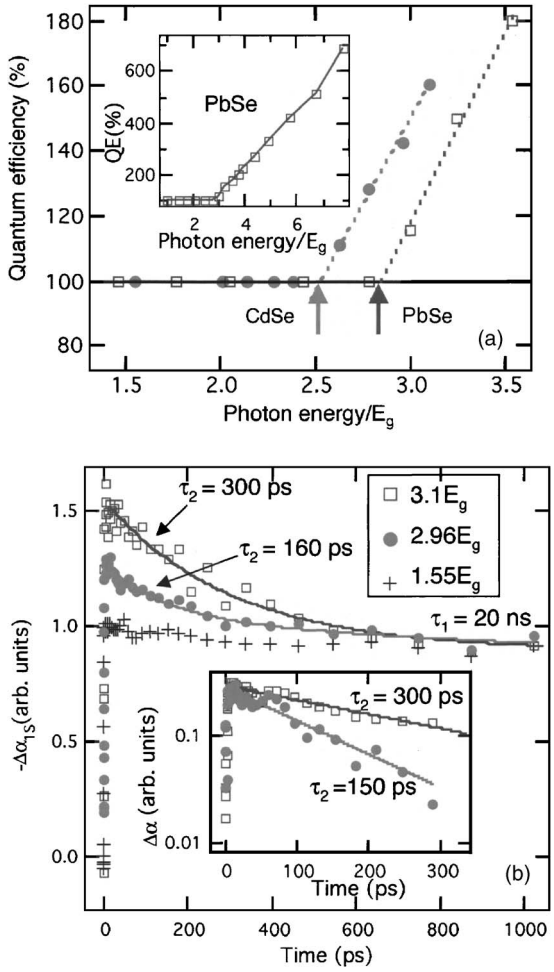

FIG. 2. (a) CM QEs for CdSe (circles) and PbSe (squares) NCs as a function of excitation photon energy divided by E_g. Arrows mark the onsets of CM. The dashed lines are linear fits used to calculate differential QEs. Inset: CM QEs for PbSe NCs measured over a wide range of excitation photon energies up to $7.8E_g$. (b) Main frame: TA time traces normalized at long time delays for CdSe NCs with energy gaps of 2.0 eV (crosses and squares) and 2.1 eV (circles) measured at low pump intensity ($\langle N_0\rangle = 0.1$) using photon energies of 3.1 eV (no CM; crosses) and 6.2 eV (CM possible; squares and circles). Lines are double exponential fits obtained using τ_2 as a fitting parameter and $\tau_1 = 20$ ns (single-exciton lifetime from Ref. 8). Inset: biexciton dynamics extracted from the TA traces (Ref. 13) measured with a 3.1 -eV pump at $\langle N_0\rangle = 1.3$ for the same samples: $E_g = 2.0$ eV (squares) and $E_g = 2.1$ eV (circles).

-eV photon energy [squares and circles in Fig. 2(b); main frame]. This result indicates a direct generation of biexcitons in CdSe NCs. From comparison of the amplitudes of the fast (biexciton) and the slow (single-exciton) TA components, we quantify the spectral dependence of QE, which is plotted as a function of $\hbar\omega_p/E_g$ in Fig. 2(a). In CdSe NCs, the onset of CM occurs at $\sim 2.5E_g$, and QE gradually increases up to 165% at $3.1E_g$.

Because of the continuous increase of QE with increasing $\hbar\omega_p/E_g$, exciton multiplicity cannot be used to compare the CM efficiency in CdSe and PbSe NCs. As a measure of this efficiency, we introduce a new quantity, "differential QE" (DQE), which we define from the slope of QE vs $(\hbar\omega_p/E_g)$ dependences at the onset of CM. Using this definition, we find that DQEs are nearly identical in CdSe and PbSe NCs (112% and 114% per E_g, respectively). This result is surprising given the vastly different electronic structures of the cadmium salts and lead salts and indicates that CM is

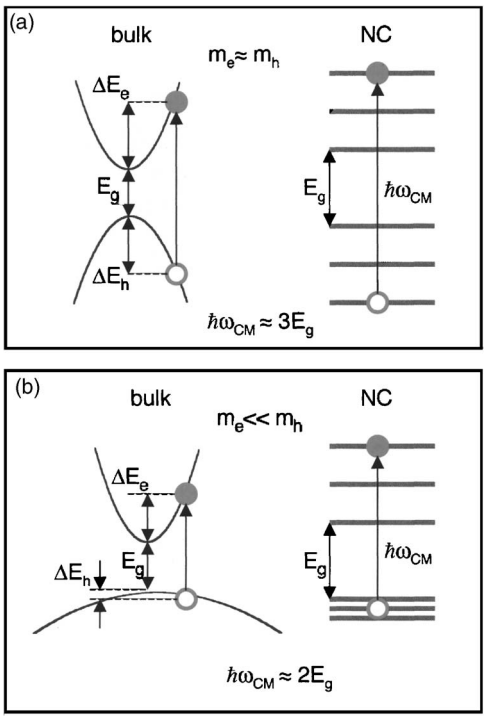

FIG. 3. (a) Bulklike, carrier effective-mass considerations indicate that in the case of similar electron and hole masses ($m_e \approx m_h$) the onset of CM is $\sim 3.0E_g$ (a), whereas it approaches $\sim 2.0E_g$ (b) in the case for which the electron and hole masses are very dissimilar ($m_e \ll m_h$).

likely general to NCs and does not rely on any specific arrangement of energy states (e.g., the mirror symmetry between the conduction and valence bands in the lead salts).

It is interesting that the difference in CM thresholds observed in CdSe and PbSe NCs can be understood in terms of simple bulk-semiconductor, effective-mass arguments without invoking a precise structure of quantized states in these two NC materials. From energy conservation, the minimum photon energy required to produce CM ($\hbar\omega_{\mathrm{CM}}$) is determined from the condition $\Delta E_{e(h)} = E_g$ [$\Delta E_{e(h)}$ is the electron (hole) energy in excess of E_g] , which yields $\hbar\omega_{\mathrm{CM}} = (2 + m_e/m_h)E_g$ (it is assumed that $m_e \leqslant m_h$). In lead salts, $m_e \approx m_h$ and hence $\hbar\omega_{\mathrm{CM}} \approx 3E_g$ [Fig. 3(a)], which is in agreement with the $\sim 2.9E_g$ threshold observed experimentally for PbSe NCs. Because in CdSe holes are heavier than electrons, $\hbar\omega_{\mathrm{CM}}$ should be smaller than $3E_g$ [Fig. 3(b)], which is again consistent with results of our measurements indicating, a CM threshold of approximately $2.5E_g$. The rationale for the "bulklike" behavior of the CM thresholds in NCs is that these thresholds occur high above the energy gap where the electronic structures and optical selection rules in NCs become reminiscent of those in bulk materials.[13,14]

CM is conventionally explained in terms of impact ionization,[1,2,4,15] for which the CM efficiency is determined by the competition between Auger-type, carrier-carrier interactions, and intraband relaxation. In this picture, CM is expected to be more efficient in PbSe NCs compared to NCs of CdSe because of the lower intraband relaxation rates[16] and stronger Auger-type interactions (as evaluated from Auger recombination rates) (Ref. 12) of PbSe NCs. However, the above statement is not consistent with our experimental results indicating that DQE values are comparable in CdSe and PbSe NCs. Our results are also difficult to explain in terms of the "coherent-CM" picture originally discussed briefly in our paper[6] and recently elaborated by Ellingson *et al.*[7] The coherent-CM mechanism requires very large Coulomb coupling and also predicts an oscillatory buildup of the multiexciton population, which is observed neither in our initial report on CM (Ref. 6) nor in Ref. 7, in which the authors were explicitly looking for this effect. Recently, we introduced a new mechanism that describes CM in NCs in terms of direct, *instantaneous* generation of multiexcitons via *virtual* single-exciton states.[17] This process can be treated using second-order perturbation theory, which predicts high multiexciton generation rates without the need for either precise resonance between single-exciton and multiexciton states or very large Coulomb coupling. This mechanism is consistent with the existing experimental data reported to date (this paper and Refs. 6 and 7) and would imply broad generality of this phenomenon of highly efficient CM in different types of semiconductor NCs.

In conclusion, we observe extremely large absolute QEs (up to 690%) and high differential QEs (from 112% to 114% per E_g) in both PbSe and CdSe NCs, which strongly indicate the generality of high-efficiency CM to NC materials. This phenomenon has numerous potential applications ranging from nonlinear optics and lasing to photovoltaics and photochemistry. For example, population inversion requires $>G/2$ excitons per NC, and therefore, it normally can only be produced at high pump intensities.[12] Utilizing CM, population inversion can be obtained with a single-photon, which can reduce optical gain thresholds significantly.

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