Vol. 8, No. 10

3174-3181

Carrier Multiplication in Semiconductor Nanocrystals: Theoretical Screening of Candidate Materials Based on Band-Structure Effects

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Received May 21, 2008; Revised Manuscript Received July 3, 2008

ABSTRACT

Direct carrier multiplication (DCM) occurs when a highly excited electron—hole pair decays by transferring its excess energy to the electrons rather than to the lattice, possibly exciting additional electron—hole pairs. Atomistic electronic structure calculations have shown that DCM can be induced by electron—hole Coulomb interactions, in an impact-ionization-like process whose rate is proportional to the density of biexciton states ρ_{XX} . Here we introduce a DCM "figure of merit" $R_2(E)$ which is proportional to the ratio between the biexciton density of states ρ_{XX} and the single-exciton density of states ρ_X , restricted to single-exciton and biexciton states that are coupled by Coulomb interactions. Using $R_2(E)$, we consider GaAs, InAs, InP, GaSb, InSb, CdSe, Ge, Si, and PbSe nanocrystals of different sizes. Although DCM can be affected by both quantum-confinement effects (reflecting the underly electronic structure of the confined *dot-interior* states) and *surface* effects, here we are interested to isolate the former. To this end the nanocrystal energy levels are obtained from the corresponding *bulk* band structure via the truncated crystal approximation. We find that PbSe, Si, GaAs, CdSe, and InP nanocrystals have larger DCM figure of merit than the other nanocrystals. Our calculations suggest that high DCM efficiency requires high degeneracy of the corresponding *bulk* band-edge states. Interestingly, by considering band structure effects we find that as the dot size increases the DCM critical energy E_0 (the energy at which $R_2(E)$ becomes ≥ 1) is *reduced*, suggesting improved DCM. However, whether the normalized E_0/ε_g increases or decreases as the dot size increases depends on dot material.

I. Introduction. Phenomenology of Carrier Multiplication in Nanocrystals. One of the proposed routes to increase the efficiency of solar cells over the Shockley–Queisser limit¹ is to utilize high-energy photons from the blue end of solar spectrum to produce multiple electron–hole pairs.² In conventional solar cells, each absorbed photon generates only one electron–hole pair, and the excess photon energy ΔE $= \hbar \omega - \varepsilon_g$ (where ω is the photon frequency and ε_g is the semiconductor band gap) is lost to heat. If the excess photon

energy could instead be used to generate additional carriers—in a process known as direct carrier multiplication (DCM)—the solar-cell current could be increased without reducing the open-circuit voltage, thereby increasing the solar-cell efficiency.

Carrier multiplication has been observed in bulk semiconductors,^{3–6} where it occurs via impact ionization. In this process (Figure 1a), a high-energy electron—hole pair, created by photon absorption, decays toward the band edges by transferring its excess energy to the creation of additional electron—hole pairs. However, the efficiency of DCM in bulk semiconductors^{3–6} is too low to be beneficial for solar-cell applications, because the cross section for DCM is low on account of the stringent momentum conservation rule it needs to fulfill,² and because competing processes, such as phononassisted decay (Figure 1b), are very efficient in bulk semiconductors.⁷ Hopes were recently expressed that impact ionization might be more efficient in semiconductor nanocrystals,² because momentum conservation rules would be relaxed by the lack of translational symmetry. Furthermore, it was suggested^{2,8} that the competing process of phononassisted carrier relaxation (Figure 1b) might be inhibited in nanocrystals, due to the sparse density of electronic levels.

Carrier multiplication has been recently reported in a variety of semiconductor nanocrystals: PbSe⁹⁻¹³ PbS,^{10,13} PbTe,¹⁴ CdSe,^{11,12} InAs,^{15,16} and Si.¹⁷ The quantum efficiency (QE) of the DCM process is conventionally expressed in percent as QE($\hbar\omega$) = 100 $N_{\rm eh}(\hbar\omega)$,¹¹ where $N_{\rm eh}(\hbar\omega)$ is the average number of electron—hole pairs generated per absorbed photon of energy $\hbar\omega$. Phenomenologically, $N_{\rm eh}(\hbar\omega)$ was found to follow a linear scaling law above a certain energy threshold $E_{\rm th}$:

$$N_{\rm eh}(\hbar\omega) = \theta(\hbar\omega - \varepsilon_{\rm g}^{\rm dot}) + \lambda_{\rm CM}(\hbar\omega - E_{\rm th})\theta(\hbar\omega - E_{\rm th}) \quad (1)$$

The first term on the right-hand side represents the conventional photogeneration process, where an absorbed photon of energy $\hbar \omega > \varepsilon_{\rm g}^{\rm dot}$ creates a single electron—hole pair, and the second term corresponds to the DCM process, where each absorbed photon of energy $\hbar \omega > E_{\rm th}$ produces, on average, $\lambda_{\rm CM}(\hbar \omega - E_{\rm th})$ additional electron—hole pairs. Energy conservation dictates that the maximum value of $N_{\rm eh}$ is given by the steplike function

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Figure 1. Schematic diagram of carrier relaxation and excitation processes in semiconductor nanocrystals. (a) Impact ionization (II) process: An absorbed photon of energy $\hbar \omega > 2\varepsilon_g^{\text{dot}}$ creates an excited electron-hole pair. The hot carrier transfers its excess energy to excite another electron-hole pair. (b) Phonon-assisted decay (PAD): The hot carrier (electron) relaxes by emitting phonons. (c) Auger recombination (AR): One of two electron-hole pairs recombines and transfers its energy to excite a carrier (electron) to higher energy.

Table 1. Experimental Values of the Carrier Multiplication Threshold Energy $E_{\rm th}/\varepsilon_{\rm g}^{\rm dot}$ and the Multiplication Factor $\lambda_{\rm CM}\varepsilon_{\rm g}^{\rm dot}$ (eq 2)

material	$E_{ m th}/arepsilon_{ m g}{ m dot}$	$\lambda_{ m CM} arepsilon_{ m g}^{ m dot}$
PbSe	$2.9^a, 2.1^b$	1.14^{a}
PbS	2.9^{a}	1.1^{a}
CdSe	$2.5^{a}, > 3.1^{c}$	1.12^a
Si	2.4^d	1.6^{c}
InAs	$2.0^{e}, > 3.7^{f}$	0.35^d

 a Reference 12. b Reference 10. c Reference 18. d Reference 17. e Reference 16. f Reference 19.

$$N_{\rm eh}^{\rm max}(\hbar\omega) = [\hbar\omega/\varepsilon_{\rm g}^{\rm dot}]$$
⁽²⁾

where the square bracket denotes the integer part of $\hbar\omega/\varepsilon_g^{\text{dot}}$. If we extract E_{th} and λ_{CM} from the energy-conservation function of eq 2 by taking the lower edge of each step, we obtain the simple expectation that $E_{\text{th}} = 2\varepsilon_g^{\text{dot}}$ and $\lambda_{\text{CM}} = 1/\varepsilon_g^{\text{dot}}$.

Experimentally,^{10,12,16,17} the DCM energy threshold E_{th} and the DCM coefficient λ_{CM} were found to be material dependent, but for a given material to be nearly independent of the nanocrystal band gap ε_g^{dot} , or, equivalently, of the nanocrystal size. Table 1 summarizes the values of the scaled quantities $E_{th}/\varepsilon_g^{dot}$ and $\lambda_{CM}\varepsilon_g^{dot}$ obtained from experiment. Surprisingly, the experimentally determined values of λ_{CM} for PbSe, PbS, CdSe, and Si (Table 1) are larger than those predicted by the energy-conservation rule (eq 2), although the condition $N_{\rm eh}(\hbar\omega) < N_{\rm eh}^{\rm max}(\hbar\omega)$ is satisfied by virtue of the relatively large values of E_{th} . The coefficients E_{th} and λ_{CM} of eq 1 provide a measure of the efficiency of the DCM process in different semiconductor nanocrystals. Recent experiments have questioned the existence of DCM in CdSe¹⁸ and InAs¹⁹ nanocrystals. Tuan Trinh et al.20 recently confirmed the occurrence of DCM in PbSe nanocrystals, although with much lower efficiency than previously reported.^{10,12}

We wish to isolate in this work bulk band structure effects from surface effects. Thus, we will model here the electronic levels of the dot by an approach that eliminates surface effects. The questions we wish to address are as follows: (i) Is the lack of translational symmetry in nanocrystals the reason for high carrier-multiplication efficiency and is strong quantum confinement necessary for efficient carrier multiplication? (ii) Competing processes: Can impact ionization outperform the inverse process of Auger recombination (Figure 1c), thereby creating a net carrier multiplication effect? Can DCM be faster than competing decay processes, such as phonon-assisted relaxation? (iii) Which property of the band structure of a bulk material is most conducive to DCM in dots made of such a material?

In order to address these three issues, we introduce a DCM "figure of merit" $R_2(E)$ which is proportional to the ratio between the biexciton density of states $\rho_{XX}(E)$ and the singleexciton density of states $\rho_{\rm X}(E)$, restricted to single-exciton and biexciton states that are coupled by Coulomb interactions. Thus, $R_2(E)$ is proportional to the ratio between the impact ionization rate and the Auger recombination rate (inverse process).²³ Using $R_2(E)$, calculated via the atomistic pseudopotential method, we screen different dot materials and sizes for those that have the largest DCM figure of merit. We find that (i) lack of translational symmetry in dots does not play an important role in enhancing DCM relative to bulk. (ii) For $2\varepsilon_g^{\text{dot}} < E < 3\varepsilon_g^{\text{dot}}$ (the energy window most useful for DCM), we find that dots made of PbSe, Si, GaAs, CdSe, or InP have a significantly higher (2-3 orders of magnitude) DCM figure of merit than other dot materials, such as GaSb, InSb, InAs, or Ge. (iii) For a given material, we find that $R_2(E)$ trends to decrease with decreasing size, suggesting that the DCM rate may actually become smaller upon quantum confinement. We conclude that any increases in the DCM efficiency in nanocrystal versus the corresponding bulk materials should be attributed to the suppression of competing relaxation mechanisms for the photoexcited carriers, rather than the rate of the intrinsic DCM process itself.

In order to provide a rigorous definition of the figure of merit $R_2(E)$, we next move from a phenomenological description to a microscopic description of the DCM process.

II. Microscopic Scaling of Carrier Multiplication Rates. Different theoretical models have been proposed in the literature to explain the high efficiency of DCM in semiconductor nanocrystals.^{8,10,11,21,23} Ellingson et al.¹⁰ and Shabaev et al.8 proposed a coherent multiexciton model in which absorbed photons instantaneously generate a coherent superposition of excited single-excitons and biexcitons. The efficiency of the DCM process is then determined by the dephasing rates of the excited single-exciton (γ_1) and the biexciton (γ_2) and by the coupling U between single-exciton and biexciton states. In the model of refs 8 and 10, efficient DCM requires that $\gamma_1 \ll \gamma_2$ and that $\gamma_1 \ll U/\hbar$. In the strongcoupling limit $U/\hbar > \gamma_2$, the model predicts quantum beats in the bleaching of the first absorption peak, which however have never been observed experimentally,^{10,11} suggesting that strong coupling may not be realized. In the opposite weakcoupling limit $U/\hbar < \gamma_2$, the model of ref 8 still predicts efficient DCM, provided that $\gamma_1 \ll \gamma_2$. However, the underlying condition $\gamma_1 \ll U/\hbar$ —which according to ref 8 is a prerequisite to have efficient DCM-has not been verified experimentally.11 Indeed, it is not clear that the "window of opportunity" $\gamma_1 \ll U/\hbar < \gamma_2$ required by the coherent superposition model exists in real systems.

Schaller et al.¹¹ proposed a second-order perturbationtheory approach, where multiexcitons are directly formed upon light absorption via transitions to virtual single-exciton states. Using a model consisting of a single virtual exciton state coupled with a biexciton state, they showed that DCM efficiencies of the order of 130% can be achieved for $U \approx$ Γ_x , where Γ_x is the line width of the excitonic transition.

Both theoretical models of "coherent multiexciton superposition"^{8,10} and "generation via virtual single-excitons",¹¹ have not attempted a microscopic calculation for actual nanocrystals, so their quantitative predictions and appropriateness remain unknown. Recently, using atomistic modeling, Allan and Delerue^{21,22} and Franceschetti, An, and Zunger²³ presented actual electronic structure calculations of the rates of several exciton-decay processes in nanocrystals. These calculations are in substantial agreement and showed that the impact-ionization mechanism-which had been previously dismissed as the source of carrier multiplication in nanocrystals^{10,11,17}—leads to very fast (much less than picoseconds) DCM rates.

Atomistic calculations²¹ showed that, for sufficiently large excitation energy, the impact ionization rate of PbSe nanocrystals is comparable to that of bulk PbSe. This result suggests that the superior impact ionization efficiency in nanocrystals is not due to the relaxation of the momentumconservation rule, as initially proposed,² but instead to the ineffectiveness of competing relaxation mechanisms (e.g., phonon-assisted decay, Figure 1b) for the photoexcited electron-hole pair. Indeed, Allan and Delerue²¹ showed that the number of electron-hole pairs $N_{\rm eh}(E)$ generated by impact ionization decreases rapidly as the phonon-assisted decay rate increases. Thus, the competition between impact ionization (Figure 1a) and phonon assisted decay (Figure 1b) determines the net efficiency of carrier multiplication: In bulk solids phonon-assisted decay wins, whereas in nanocrystals impact ionization could be more effective.

Using atomistic pseudopotential calculations, Franceschetti, An, and Zunger²³ showed that in PbSe nanocrystals the impact ionization rate (Figure 1a) is much faster than the Auger recombination rate (Figure 1c), despite the fact that the Coulomb matrix elements that describe the two processes are the same. This asymmetry is due to the much larger density of final states in the impact ionization process (single-exciton \rightarrow biexciton) than in the Auger recombination process (biexciton \rightarrow single-exciton). Specifically, ref 23 showed that for energies $E > 2.3\varepsilon_g^{dot}$ the density of biexciton states $\rho_{XX}(E)$ becomes larger than the density of singleexciton states $\rho_{\rm X}(E)$.

The impact ionization rate was calculated in refs 21 and 23 using the Fermi golden rule, which is valid if $U/\hbar < \gamma_2$. This weak-coupling scenario is consistent with experimental results, namely, the absence of quantum beats in the bleaching of the absorption peak.^{10,11} Note that in the impact ionization model the DCM rate is proportional to the product $|U|^2 \rho_{XX}(E)$, so even for relatively small values of U the DCM process can be very efficient, if $\rho_{XX}(E)$ is large. As the size of a nanocrystal increases, U becomes smaller in magnitude,

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but $\rho_{XX}(E)$ increases, thereby compensating for the reduced Coulomb interaction between carriers. This may explain why efficient DCM has been observed in nanocrystals as large as two times the bulk exciton Bohr radius,¹⁷ suggesting that strong quantum confinement is not required to achieve efficient DCM.

III. Method.

A. DCM Figure of Merit. From the above discussion, it is apparent that the ratio

$$R_1(E) = \rho_{XX}(E) / \rho_X(E) \tag{3}$$

is an important parameter in determining the efficiency of carrier multiplication in nanocrystals. According to ref 23, large values of $\rho_{XX}(E)$ indicate a large density of final states for the DCM process, while small values of $\rho_{\rm X}(E)$ indicate a small density of final states for the Auger recombination process. In addition, small values of $\rho_{\rm X}(E)$ may lead to a reduced efficiency of phonon-assisted carrier relaxation, which is the main competing process for carrier multiplication.²¹ However, it is important to take into account that, for a given energy E, not all single-exciton and biexciton states of that energy are coupled. The reason is that the Coulomb potential only couples X and XX states that differ by no more than two particles. Thus, a more relevant quantity is the ratio $\rho_{XX}(\varepsilon, E)/\rho_X(\varepsilon, E)$ between the biexciton and singleexciton densities of states when one particle (electron or hole) is *fixed* in a single-particle level of energy ε . This leads us to introduce the following DCM "figure of merit":

$$R_2(E) = \frac{1}{N(E)} \int_{\varepsilon_{\min}(E)}^{\varepsilon_{\max}(E)} \rho(\varepsilon) \frac{\rho_{XX}(\varepsilon, E)}{\rho_X(\varepsilon, E)} \,\mathrm{d}\varepsilon \tag{4}$$

Here $\rho(\varepsilon)$ is the single-particle density of states (DOS) of the nanocrystals:

$$\rho(\varepsilon) = \sum_{n} \delta(\varepsilon - \varepsilon_n^{\text{dot}}) \tag{5}$$

If $\varepsilon = \varepsilon_v$ is in the valence band, then:

$$\rho_{\rm X}(\varepsilon_{\rm v}, E) = \rho(\varepsilon_{\rm v}) \int_{\varepsilon_{\rm F}}^{\infty} d\varepsilon_{\rm c} \rho(\varepsilon_{\rm c}) \delta(E - \varepsilon_{\rm c} + \varepsilon_{\rm v}) \tag{6}$$

and

$$\rho_{XX}(\varepsilon_{v}, E) = \rho(\varepsilon_{v}) \int_{-\infty}^{\varepsilon_{\rm F}} d\varepsilon_{v'} \rho(\varepsilon_{v'}) \int_{\varepsilon_{\rm F}}^{\infty} d\varepsilon_{c} \rho(\varepsilon_{c}) \times \int_{\varepsilon_{\rm c}}^{\infty} d\varepsilon_{c'} \rho(\varepsilon_{c'}) \delta(E - \varepsilon_{\rm c} - \varepsilon_{c'} + \varepsilon_{\rm v} + \varepsilon_{v'})$$
(7)

Similar expressions apply if ε is in the conduction band. The integration limits ε_{\min} (E) and ε_{\max} (E) in eq 4 are the minimum and maximum single-particle energies of a carrier belonging to an electron-hole pair of energy $E > \varepsilon_g^{dot}$.

and

$$\varepsilon_{\min}(E) = \varepsilon_{\rm VBM} - E + \varepsilon_{\rm g}^{\rm dot} \tag{8}$$

$$\varepsilon_{\max}(E) = \varepsilon_{\text{CBM}} + E - \varepsilon_{g}^{\text{dot}} \tag{9}$$

where ε_{CBM} and ε_{VBM} are the energies of the conductionband minimum (CBM) and valence-band maximum (VBM), respectively. Finally, N(E) in eq 4 is a normalization factor given by

$$N(E) = \int_{\varepsilon_{\min}(E)}^{\varepsilon_{\max}(E)} \rho(\varepsilon) \,\mathrm{d}\varepsilon \tag{10}$$

B. Calculating Dot Energy Levels from the Truncated **Crystal Approximation.** The figure of merit $R_2(E)$ is a

(0)



Figure 2. Illustration of truncated-crystal approximation (TCA) to calculate the single-particle density of states (DOS) of a cubic InP nanocrystal (c). The single-particel energy levels of a InP nanocrystal (b) is obtained from the energy bands of the corresponding bulk InP (a), calculated at special $\bar{\mathbf{k}}$ points (indicated by vertical dashed lines) in the bulk Brillouin zone, such that the envelope function vanishes at the surface of the nanocrystal. In the figure we show only the special $\bar{\mathbf{k}}$ points located on the Γ -L line in the Brillouin zone.

functional of the single-particle density of states $\rho(\varepsilon)$, so a correct determination of $\rho(\varepsilon)$ is crucial to accurately determine $R_2(E)$. As shown by eqs 6 and 7, the calculation of $R_2(E)$ may require a very large number of nanocrystal energy levels ε_n , if the multiexciton energy *E* is large. Thus, a direct calculation of $R_2(E)$ using first-principles methods or atomistic semiempirical methods (such as tight-binding or pseudopotential) would be costly. Here we want to calculate $R_2(E)$ for several nanocrystal materials and nanocrystal sizes. So we resort to an approximation for calculating the nanocrystal energy levels.

Although DCM can be affected by both quantum-confinement effects (reflecting the underlying electronic structure of the confined dot-interior states) and surface special effects, we are interested in isolating the former.

To do so, we use here the truncated-crystal approximation (TCA) to calculate the single-particle DOS (eq 5), the singleexciton and biexciton densities of states (eqs 6 and 7), and the DCM "figure of merit" $R_2(E)$ (eq 4). The idea behind the TCA²⁴⁻²⁸ is to obtain the single-particle energy levels of a nanocrystal (containing many atoms) from the energy bands of the corresponding bulk material (containing only a few atoms per cell), calculated at special \mathbf{k} points in the bulk Brillouin zone, such that the envelope function $F(\mathbf{r}) = \sum_{\bar{\mathbf{k}}} e^{i\bar{\mathbf{k}}\cdot\mathbf{r}}$ vanishes at the surface of the nanocrystal (Figure 2). This approach was used over 30 years ago to predict the energy levels of finite graphene strips from the band structure of (infinite periodic) graphite or boron nitride^{24,25} and to approximate the levels of finite slabs of Si from the Si bulk band structure.^{26,28} The TCA approach was later refined and improved²⁷ to include the effects of a finite potential barrier. While this does bring about an improvement, we judge that in the present survey of many materials the trends are not affected much by this correction. Indeed, the valence-band and conduction-band offsets between semiconductors and its the surrounding organic molecules are large in colloidal nanostructures,²⁹ and the effective mass discontinuity at the dot surface further enhances the electronic states localization.³⁰ Consequently, for a rapid screening of materials, we will use the infinite-barrier TCA described above instead of the finite-barrier TCA.²⁷ Also note that the TCA includes multiple band edge valleys (e.g., Γ , *X*, and *L*) but not their coupling. The inclusion of the effect of higher valleys on the density of states has been shown²⁷ to be important.

In the TCA the DOS of a nanocrystal is given by

$$\rho^{\text{TCA}}(\varepsilon) = \sum_{n=1}^{N_{\text{bands}}} \sum_{\bar{\mathbf{k}}} \delta(\varepsilon - \varepsilon_{n,\bar{\mathbf{k}}}^{\text{bulk}})$$
(11)

where $\varepsilon_{n,\mathbf{k}}^{\text{bulk}}$ is the energy of the bulk band *n* calculated at the special TCA point \mathbf{k} (Figure 2). In this work we consider cubic nanocrystals, a choice that simplifies the use of the TCA, compared to other nanocrystal shapes. As shown in Figure 2 for a cubic nanocrystal of edge L, the set of special \mathbf{k} points is given by

$$\overline{\mathbf{k}}_{ij,k} = \mathbf{k}_0 + \frac{\pi}{L}(i,j,k) \tag{12}$$

that are located inside the bulk Brillouin zone. Here \mathbf{k}_0 is the \mathbf{k} point of the band edge (CBM or VBM) and *i*, *j*, *k* are positive integers. For direct-gap III–V semiconductors, such as GaAs and InP, both the VBM and the CBM have $k_0 = \Gamma$. In the case of Ge, $\mathbf{k}_0 = \Gamma$ for the VBM and $\mathbf{k}_0 = L$ for the CBM. In the case of Si, $\mathbf{k}_0 = \Gamma$ for the VBM and $\mathbf{k}_0 = \Delta_0$ (0.85X) for the CBM.

As is evident from eq 11, the truncated-crystal approximation assumes that the nanocrystal introduces no new physics with respect to the bulk, except the discretization of the energy levels stemming from quantum confinement. It serves therefore to map the properties of a given bulk band structure—degeneracy of band edges, effective masses, and detailed electronic structure—into the properties of the nanocrystal electronic structure.

The TCA based on EPM is an approximation to the direct solution of the Schrödinger equation using the same pseudopotential, and is not recommended here as a substitute for the latter. In this paper we use the TCA to isolate DCM effects in different dot materials due to differences in their underlying bulk band structure (degeneracies, band topology, effective masses, etc.).

C. Calculation of the Bulk Band Structure. Since the TCA requires the solution of the Schrödinger equation for a small bulk unit cell (albeit for many **k** points in the Brillouin zone), first-principles methods, as well as semiempirical atomistic methods, can be used to calculate the density of states. The band structure of the infinite, periodic bulk crystal is calculated here using (i) the empirical pseudopotential method (EPM) and (ii) density-functional theory in the localdensity approximation (LDA). Figure 3 shows a comparison of the TCA electronic structure of InP nanocrystals calculated using EPM and LDA. The EPM pseudopotentials were fitted to experimental transition energies, deformation potentials, and effective masses of bulk InP.³⁰ The LDA calculations, including spin-orbit interaction, were performed using the VASP code with the projector augmented wave (PAW) pseudopotentials.³¹ The LDA calculation (including spin-orbit



Figure 3. Comparison of the electronic properties of cubic InP nanocrystals as obtained from the truncated crystal approximation in conjunction with the empirical-pseudopotential bulk band structure (EPM/TCA) and the corrected LDA bulk band structure (C-LDA/TCA). The nanocrystal size is denoted as $N \times N \times N$ (in units of the lattice constant a_0), where N = 6, N = 8, and N = 10. (a) Nanocrystal energy gap, (b) single-particle density of state (DOS).

interaction) underestimates the band gap by $\approx 60\%$ and the conduction band effective mass by $\approx 40\%$. The approach followed here is to shift the LDA conduction band up to correct for the band gap error. However, this does not solve the entire problem because the LDA effective masses are still incorrect. As a result, the LDA band gap (Figure 3a) and DOS (Figure 3b) are systematically shifted relative to EPM. Furthermore, the LDA-predicted band gaps of narrow-gap semiconductors (e.g., InAs, InSb, GaSb, and Ge) are negative, so the band-edge states are spuriously coupled. This significantly complicates the use of LDA within the TCA approximation. Therefore, in the following we will use EPM/TCA rather than C-LDA/TCA. The EPM calculated single-particle density of states as obtained from TCA is given in Figure 4 for a few materials and a few sizes.

IV. Results: DCM Figure of Merit.

A. Initial Material Choice. Figure 5 shows the experimentally determined band gaps of 27 III–V,^{33,34} II–VI,^{34,35} IV,³² and IV–VI³² bulk semiconductors. For each III–V, II–VI, or IV semiconductor, we show the direct Γ – Γ gap, as well as the indirect Γ –X and Γ –L gaps. For each IV–VI semiconductor, we show the lowest L–L gap, as well as the $E_1(\Sigma-\Sigma)$ and $E_2(\Delta-\Delta)$ gaps. In the following, we will consider representative nanocrystals made of GaAs, InAs, InP, GaSb, InSb, CdSe, Ge, Si, and PbSe, for which accurate semiempirical pseudopotentials are available.^{31,36,37}

B. Direct-to-Indirect Band Gap Transition vs Dot Size. The TCA-calculated band gaps of the nanocrystals considered in this work are shown in Figure 6 as a function of the nanocrystal effective radius. We observe that nanocrystals that have a direct band gap at large sizes—namely, GaAs, InP, GaSb, InAs, InSb (Γ point band gap), and PbSe (*L*-point band gap)—become indirect at small sizes, as indicated by the vertical red arrows in Figure 6. For example, the band gap of GaAs nanocrystals becomes indirect below R = 40 Å, while the band gap of GaSb nanocrystals becomes indirect below R = 90 Å. Such direct/indirect transition occurs because the effective mass of the conduction-band Γ valley is lighter than the effective mass of other valleys such as *X* and/or *L*, and the energy difference between the Γ level and those higher-energy valleys is relatively small (see Figure 5). Because TCA is a single-band method which neglects interband and intraband interaction effects, the direct/indirect transition may be different from all band calculations. In the case of GaAs, we predicted a Γ -to-*X* transition at R = 16 Å via direct semiempirical pseudopotential calculations.³⁵ The existence of such high-energy conduction-band valleys is important for DCM efficiency (even when the nanocrystals are sufficiently large that the band gap is direct), because the presence of states derived from the bulk *X* and *L* valleys tends to significantly increase the single-particle DOS, due to the high multiplicity and large effective mass of those valleys.

C. Selecting nanocrystals via $R_2(E)$. The calculated DCM figure of merit $R_2(E)$ of the nine nanocrystal semiconductors considered here is shown in Figure 7 as a function of the reduced energy $E/\varepsilon_g^{\text{dot}}$. In each case we give in the heading the CBM and VBM valley degeneracies. For each material, we show the results for three different dot sizes described as $N \times N \times N$ multiples of the bulk cubic unit cell. The effective dot radius is related to $N \operatorname{via}^{39} R = (3/4\pi)^{1/3} \times N \times a_0$.

We see from Figure 7 that for all nanocrystal materials and sizes, $R_2(E)$ increases monotonically with energy *E*. The steepness of the figure of merit $R_2(E)$ correlates well with the experimentally measured values of λ_{CM} (see Table 1). For example, we find that Si and PbSe nanocrystals, which have a large λ_{CM} , also have a large $R_2(E)$, while InAs nanocrystals, which have a small λ_{CM} , also have a rather flat $R_2(E)$. According to ref 12, PbSe and CdSe nanocrystals have a similar values of λ_{CM} , 1.14 and 1.12 (see Table 1), respectively. Their $R_2(E)$ values are also very close. Figure 8 shows the value of $R_2(E)$ calculated at $E = 2.6\varepsilon_g^{dot}$ for nanocrystals of the same size but different materials. Larger values of $R_2(E)$ indicate larger DCM efficiency.

Interestingly, the figure of merit R_2 of eq 4 (Figure 7) is rather similar to the DOS ratio R_1 of eq 3 (Figure 9), which does not consider the Coulomb selection rule.

D. DCM Critical Energy E_0 . The value $R_2(E) = 1$ is relevant to DCM because it establishes the threshold E_0 above which the impact ionization rate becomes faster than the Auger recombination rate.^{21,23} Furthermore, according to the multiexciton superposition model of refs 8 and 10, if $R_2(E)$ > 1, it is more likely that a superposition of photogenerated single-excitons and biexcitons of energy E will decay into a biexciton rather than into a single-exciton. Thus, the lower the value of E_0 , the more efficient DCM is. We find that the DCM critical energy E_0 depends on both the nanocrystal size and the nanocrystal material, ranging from $\sim 2.2\varepsilon_g^{dot}$ for PbSe nanocrystals (R = 3.7 nm) to $\sim 3.2\varepsilon_g^{\text{dot}}$ for InAs nanocrystals (R = 2.2 nm) (Figure 10b). E_0 should not be confused with the DCM threshold $E_{\rm th}$ of eq 1. $E_{\rm th}$ is determined by the optical absorption spectrum of the nanocrystals. In fact, we can write $E_{\text{th}} = \max(E_0, E_{\text{opt}})$, where E_{opt} is the minimum photon energy such that the photogenerated electron or the photogenerated hole have sufficient excess energy to initiate the carrier multiplication process.²³

Figure 10a shows, for all of the nanocrystals considered here, the calculated value of the DCM critical energy E_0 as



Figure 4. Calculated single-particle density of states of cubic nanocrystals of size $(N \times N \times N)a_0$ for N = 6 (green), N = 8 (blue), and N = 10 (red). Vertical arrows indicate the CBM and VBM energies of the nanocrystals.



Figure 5. The bulk band gaps of 12 III–V semiconductors (GaAs, AlAs, InAs, GaP, AlP, InP, GaSb, AlSb, InSb, GaN, AlN, and InN),^{33,34} 9 II–VI semiconductors (CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe, and HgTe),^{34,35} 3 IV semiconductors (Ge, Si, and Sn),³⁴ and 3 IV–VI semiconductors (PbS, PbSe, and PbTe).³⁴ For zinc blende III–V and II–V and diamond IV semiconductors we show three band gaps: $\varepsilon_{g}(\Gamma-\Gamma)$ (blue circle), $\varepsilon_{g}(\Gamma-X)$ (red circle), and $\varepsilon_{g}(\Gamma-L)$ (green circle). For IV–VI semiconductors with the NaCl crystal structure have band gaps $\varepsilon_{g}(L-L)$ (green circle), $E_{1}(\Sigma-\Sigma)$ (blue circle), and $E_{2}(\Delta-\Delta)$ (red circle). The right-hand side panel shows the solar spectrum.⁴⁰ The black solid line indicates the maximum band gap for efficient DCM process.

a function of the nanocrystal band gap ε_g^{dot} showing three sizes for each dot. There is an overall linear increase of E_0 with the band gap, which is evident from Figure 10a. To remove this linear background, in Figure 10b, we show E_0/ε_g^{dot} as a function of the band gap ε_g^{dot} . We see from Figure 10b that PbSe, Si, GaAs, CdSe, and InP nanocrystals have a significantly lower DCM critical energy than GaSb, InSb, Ge, and InAs nanocrystals. Figure 10a shows that as the dot size increases, E_0 decreases, so larger dots are better than smaller dots. Figure 10b shows that the *normalized* E_0/ε_g^{dot} sometimes increases (e.g., Si) and sometimes decreases (e.g., InAs) as the dot size increases.

The application of nanocrystals as light absorber in solarcell devices requires a good match of the nanocrystal absorption spectrum with the solar spectrum.⁴⁰ Using a detailed balance model, Hanna and Nozik⁴¹ found that, in the presence of carrier multiplication, the optimal value of the nanocrystal band gap is around 0.7–0.9 eV. We find that PbSe nanocrystals, having sufficiently small band gaps and sufficiently low DCM threshold, are the best candidates for DCM-based solar-cell applications. Although Si has low DCM critical energy and large DCM figure of merit, its

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absorption spectrum for small nanocrystal size does not match the solar spectrum.⁴⁰

V. Conclusions. The DCM process involves the creation of two or more electron—hole pairs as a result of exciting a nanostructure by one photon with energy at least two times larger than the band gap ε_{g}^{dot} . We explained high carrier-multiplication efficiency in nanocrystals as follows: (i) The lack of translational symmetry is not the reason for high carrier-multiplication efficiency. Strong quantum confinement is not necessary for efficient carrier multiplication. (ii) If the biexciton DOS is larger than the single-exciton DOS, impact ionization outperforms the inverse process of Auger recombination. (iii) Efficient DCM requires a reduced phonon assisted relaxation rate, which may be realized in nanocrystals.

Using the TCA approach to the electronic structure of nanocrystals—based on the atomistic, semiempirical pseudopotential approach—we calculated the DCM figure of merit $R_2(E)$ of GaSb, InAs, InP, GaSb, InSb, CdSe, Ge, Si, and PbSe nanocrystals. We found that PbSe, Si, GaAs, CdSe, and InP nanocrystals have larger DCM figure of merit than the other nanocrystals. We explained these results as follows:



Figure 6. Calculated TCA band gap of nanocrystals as a function of effective radius for the semiconductors GaAs, GaSb, InAs, InP, InSb, Si, Ge, and PbSe. Vertical red arrows indicate direct—indirect electronic phase transitions.



Figure 7. The DCM figure of merit R_2 (eq 4) of cubic nanocrystals of size $(N \times N \times N)a_0$ for N = 6 (green), N = 8 (blue), and N = 10 (red) for different semiconductors as a function of the reduced photon energy. The insets give the nanocrystal band gap (in eV).



Figure 8. The DCM figure of merit $R_2(E)$ at photon energy $E = 2.6\varepsilon_g^{\text{dot}}$ for different nanocrystals of size N = 6.



Figure 9. Same as Figure 7 but using the figure of merit R_1 of eq 3, which does not consider the Coulomb selection rule.

(i) The degeneracy of the CBM and VBM is the most important factor for DCM efficiency. Not including spin degeneracy, the conduction-band is nondegenerate at Γ , 3-fold-degenerate at X, and 4-fold-degenerate at the *L*-point. PbSe (Figure 7i), for which both the CBM and VBM are located at the *L*-point, has the highest DCM figure of merit among the semiconductors calculated here.

(ii) The energy spacing between the Γ -, *X*-, and *L*-valleys is also important for direct Γ - Γ semiconductors. Although the CBM state of *bulk* GaAs (Figure 7a), InSb (Figure 7e) and GaSb (Figure 7b) is Γ -derived, the electron states of the corresponding small *nanocrystals* derive from the 4-fold *L*-point Bloch state, because in these materials there is an electronic Γ -to-*L* transition (Figure 6) due to the small Γ -*L* valley-spacing in the bulk (Figure 5). Notably, from this point of view InAs is worse for DCM because there is no Γ -to-*L* transition at any nanocrystal size on account of the very large Γ -*L* spacing in bulk InAs (Figure 5).



Figure 10. The DCM critical energy E_0 , i.e., the photon energy at which $R_2(E) = 1$, is shown as a function of nanocrystal band gap. In (a) we show E_0 in absolute units (eV), while in (b) we show $E_0/\varepsilon_g^{\text{dot}}$. For each material we show three points corresponding to three sizes (the smaller the nanocrystal gap, the larger the dot size). Part a shows that as the dot size increases E_0 decreases, whereas part b shows that the *normalized* $E_0/\varepsilon_g^{\text{dot}}$ sometimes increases (e.g., Si) and sometimes decreases (e.g., InAs) as the dot size increases.

(iii) Relative to properties (i) and (ii), the importance of the effective masses for the DCM process is small.

We see from Figure 7 that for all nanocrystal materials and sizes, $R_2(E)$ increases monotonically with energy *E*. The "steepness" of the figure of merit $R_2(E)$ correlates well with the experimentally measured values of λ_{CM} (see Table 1). For example, we find that Si and PbSe nanocrystals, which have a large λ_{CM} , also have a large $R_2(E)$, while InAs nanocrystals, which have a small λ_{CM} , also have a rather flat $R_2(E)$. Larger values of $R_2(E)$ indicate larger DCM efficiency.

Interestingly, by considering band structure effects we find that as the dot size increases the DCM critical energy E_0 (the photon energy at which $R_2(E)$ becomes ≥ 1) is reduced, suggesting improved DCM. However, whether the normalized E_0/ε_g increases or decreases as the dot size increases depends on dot material.

Acknowledgment. This work was funded by the U.S. Department of Energy, Office of Science, Basic Energy Science, Materials Sciences and Engineering, under Contract No. DE-AC36-99GO10337 to NREL.

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NL801459H