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Exciton Multiplication and Relaxation Dynamics in Quantum Dots:  
Applications to Ultrahigh-Efficiency Solar Photon Conversion†

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Received May 24, 2005

Huge amounts of carbon-free energy will be required during the coming decades in order to stabilize atmospheric CO<sub>2</sub> to acceptable levels. Solar energy is the largest source of non-carbonaceous energy and can be used to produce both electricity and fuel. However, the ratio of the areal cost to the conversion efficiency for devices converting solar photons to electricity or fuel must be reduced by at least 1 order of magnitude from the present values; this requires large increases in the cell efficiency and large reductions in the cost per unit area. We have shown how semiconductor quantum dots may greatly increase photon conversion efficiencies by producing multiple excitons from a single photon. This is possible because quantization of energy levels in quantum dots slows the cooling of hot excitons, promotes multiple exciton generation, and lowers the photon energy threshold for this process. Quantum yields of 300% for exciton formation in PbSe quantum dots have been reported at photon energies 3.8 times the HOMO–LUMO transition energy, indicating the formation of three excitons/photon for all photoexcited quantum dots. Similar high quantum yields have also been reported for PbS quantum dots. A new model for this effect that is based on a coherent superposition of multiple excitonic states has been proposed.

## Introduction

According to recent analyses,<sup>1–3</sup> from 10 to 30 TW-yr of carbon-free energy will be required globally by the year 2050; this prediction is based on an estimated world population in 2050 of 10–11 billion people (it is presently 6 billion people) and an annual average global economic growth rate of 1.6%. More recent estimates of the world population indicate a lower level of 8–9 billion people by mid-century, but this factor may be counterbalanced by higher economic growth rates, especially in Asia. In any case, considering that the world currently uses a total of about 12–13 TW-yr annually, the amount of carbon-free energy that will be required in the coming decades is enormous and daunting.

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† This manuscript is a review of previously published work by the author and his colleagues and is based on several references listed below (refs 11, 20, 38, 52, and 53).

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The actual amount of carbon-free energy needed depends on the level of atmospheric CO<sub>2</sub> that can be tolerated with respect to its impact on global climate change. The present concentration of CO<sub>2</sub> is 378 ppm, up from 275 ppm before the industrial revolution 100 years ago. According to ref 1, if a maximum CO<sub>2</sub> level of 750 ppm could be tolerated (a level considered extremely dangerous and seriously disruptive by many climatologists) and if carbon sequestration is not considered, then about 10 TW-yr of carbon-free energy would be required annually by 2050. If the CO<sub>2</sub> level needs to be stabilized at 400 ppm, then 30 TW-yr of carbon-free energy would be required annually by 2050. These enormous levels of carbon-free energy that will have to be introduced by the middle of the century are from 1 to 3 times the total level of energy consumed today from all sources (fossil fuel, nuclear power, and renewable energy). Although fossil fuels (coal, oil, and natural gas) could provide the estimated total global energy required until the end of this century, they cannot be consumed at the present rate because this will generate unacceptable levels of atmospheric CO<sub>2</sub>; furthermore, in the case of oil and natural gas, the availability of secure supplies is decreasing and costs are escalating.

The solar constant at the top of the earth's atmosphere is  $1.7 \times 10^5$  TW; after passing through the atmosphere, more solar energy falls on the earth's surface in 1 h than is used in 1 year globally, but it is dilute ( $1 \text{ kW/m}^2$  at noon); about 600–1000 TW strikes the earth's terrestrial surfaces at practical sites suitable for solar energy harvesting. Solar energy is the largest renewable carbon-free resource, but in order for solar energy to provide a major fraction of the required levels of carbon-free energy in the future, the ratio of areal cost to conversion efficiency has to be improved from the present values by over 1 order of magnitude.

The present cost of photovoltaic (PV) modules is about \$3.50/peak watt; considering the additional balance of system costs (support structure, land, maintenance, power conditioning, etc.), this translates to an energy cost of about \$0.30 to 0.35/kWh. The grand challenge for solar photon conversion to either electricity or solar fuels (like hydrogen) is to discover and develop systems (either PV, photoelectrochemical, or photochemical) that exhibit combinations of efficiency and capital cost per unit area that result in a total cost of about \$0.40/peak watt; this corresponds to electricity at \$0.02/kWh or hydrogen produced by PV electrolysis at \$0.11/kWh using present day electrolyzers. Major advances in electrolyzer technology could bring this hydrogen cost down to \$0.04/kWh,<sup>4</sup> which is about the present cost of  $\text{H}_2$  from steam reforming of natural gas. Thus, a cost level of \$0.40/peak watt would make solar photon conversion very attractive, lead to widespread application, and avoid major economic disruption in a transition to a sustainable energy economy. However, such a cost goal requires solar conversion at a total cost of \$125/m<sup>2</sup> combined with a cell conversion efficiency of about 50%. Such combinations of cost and efficiency require truly disruptive technologies that do not exist at the present time. However, the attainment of these goals does not conflict with nor violate any fundamental scientific principles and is theoretically feasible. Here we discuss one approach that could lead to ultrahigh efficiencies using a single-band-gap semiconductor; it is based on utilizing high-energy photons in the solar spectrum to create multiple electron–hole pairs and hence enhance the photocurrent in solar photon conversion devices.

## Approach

For many years, we have been investigating the possibility of achieving ultrahigh conversion efficiency in single-band-gap cells by utilizing high-energy electrons (termed hot electrons and holes created by absorption of solar photons larger than the band gap) before these hot electrons and holes relax and convert their excess kinetic energy to heat through phonon emission.<sup>5–9</sup> This is very difficult in the case of bulk semiconductors because hot electrons relax very rapidly (sub-

picosecond time scale). However, in semiconductor nanocrystals (also termed quantum dots, QDs), discrete quantized energy levels are formed that dramatically affect the relaxation dynamics of hot electrons and holes and allow other relaxation channels to compete with phonon emission.

As is well-known, the maximum thermodynamic efficiency for the conversion of unconcentrated solar irradiance into electrical or chemical free energy in the radiative limit, assuming detailed balance, a single threshold absorber, and thermal equilibrium between electrons and phonons, was calculated by Shockley and Queisser in 1961<sup>2</sup> to be about 31%. This efficiency is attainable in semiconductors with band gaps ranging from about 1.25 to 1.45 eV.

However, the solar spectrum contains photons with energies ranging from about 0.5 to 3.5 eV. Photons with energies below the semiconductor band gap are not absorbed, while those with energies above the band gap create charge carriers with a total excess kinetic energy equal to the difference between the photon energy and the band gap. This excess kinetic energy creates an effective temperature for an ensemble of photogenerated carriers that can be much higher than the lattice temperature; such carriers are called “hot electrons and hot holes”, and their initial temperature upon photon absorption can be as high as 3000 K with the lattice temperature at 300 K.

In the Shockley–Queisser analysis, a major factor limiting the conversion efficiency to 31% is that the excess kinetic energy of hot carriers is lost as heat through phonon emission. The approach to reduce this loss and increase efficiency above the 31% limit has been to use a stack of cascaded multiple p–n junctions in the absorber with band gaps better matched to the solar spectrum; in this way, higher energy photons are absorbed in the higher band gap semiconductors and lower energy photons in the lower band gap semiconductors, thus reducing the overall heat loss due to carrier relaxation via phonon emission. In the limit of an infinite stack of band gaps perfectly matched to the solar spectrum, the ultimate conversion efficiency at one-sun intensity increases to about 66%. For practical purposes, the stacks have been limited to two or three p–n junctions; actual efficiencies of about 32% have been reported in PV cells with two cascaded p–n junctions.<sup>10</sup>

For a single-band-gap system, there are two fundamental ways that hot carriers can be converted to useful work to enhance the efficiency of photon conversion. One way produces an enhanced photovoltage, and the other way produces an enhanced photocurrent. The former requires that the hot carriers be extracted from the photoconverter before they cool,<sup>5,6,11</sup> while the latter requires the hot carriers to produce two or more electron–hole pairs.<sup>12,13</sup> This process is well-known in bulk semiconductors and is termed impact ionization (I.I.); it is the inverse of the Auger process

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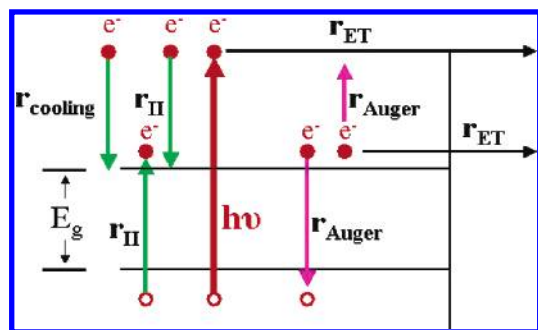
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**Figure 1.** For  $e^-$  multiplication by I.I. (from ref 52),  $r_{\text{I.I.}} > r_{\text{ET}}^{\text{hot}}$ ,  $r_{\text{cooling}}$ ,  $r_{\text{Auger}} < r_{\text{I.I.}}$ , and  $r_{\text{ET}} > r_{\text{radiative}} > r_{\text{Auger}}$ .

whereby two electron–hole pairs recombine to produce a single highly energetic electron–hole pair. To achieve higher photovoltages, the rates of photogenerated carrier separation, transport, and interfacial transfer across the semiconductor interface must all be fast compared to the rate of carrier cooling.<sup>6,7,14</sup> The achievement of higher photocurrent requires that the rate of I.I. ( $r_{\text{I.I.}}$ ) or electron–hole pair multiplication is greater than the rate of carrier cooling ( $r_{\text{cooling}}$ ), the rate of electron transfer ( $r_{\text{ET}}$ ) of hot electrons, and the rate of the forward Auger processes ( $r_{\text{Auger}}$ ) (see Figure 1). Also, the rate of electron transfer of cooled electrons must be faster than the radiative recombination rate ( $r_{\text{radiative}}$ ) and  $r_{\text{Auger}}$ .

**Cooling Dynamics in QDs.** Although the hot-carrier cooling rates are very fast in bulk semiconductors, the rates can be slowed in quantized semiconductor structures (termed quantum dots, QDs) because of the formation of discrete quantized energy levels. In QDs, photogenerated electrons and holes become bound to each other because of strong quantum confinement, and these correlated electron–hole pairs are called excitons. The slowed cooling of energetic excitons can enhance the photon conversion efficiency by allowing electrical or chemical free energy to be extracted from the energetic excitons before they relax to their lowest electronic state and produce heat.

The proposal of slowed hot-carrier cooling in quantized semiconductor structures, including quantum wells, quantum wires, QDs, and superlattices,<sup>6,8,14–17</sup> has been experimentally verified.<sup>11,18–20</sup> When the carriers in the semiconductor are confined by potential barriers to regions of space that are smaller than or comparable to their deBroglie wavelength or to the Bohr radius of excitons in the semiconductor bulk, the relaxation dynamics can be dramatically altered; specifically, the hot-carrier cooling rates may be dramatically reduced, and the rate of exciton multiplication could become competitive with the rate of carrier cooling (see below).

In QDs, slowed hot exciton cooling is theoretically possible even at arbitrarily low light intensity; this effect is

called a “phonon bottleneck”. This slowed cooling could make the rate of multiple exciton generation (MEG) an important process in QDs.<sup>11,20</sup> The first prediction of slowed cooling at low light intensities in quantized structures was made by Nozik and co-workers.<sup>6,8,14</sup> They anticipated that cooling of carriers would require multiphonon processes when the quantized levels are separated in energy by more than phonon energies. They analyzed the expected slowed cooling time for hot holes at the surface of highly doped n-type semiconductors, where quantized energy levels arise because of the narrow space charge layer (i.e., depletion layer) produced by the high doping level. The multiphonon relaxation time was estimated from

$$\tau_c \sim \omega^{-1} \exp(\Delta E/kT) \quad (1)$$

where  $\tau_c$  is the hot-carrier cooling time,  $\omega$  is the phonon frequency, and  $\Delta E$  is the energy separation between quantized levels. For strongly quantized electron levels, with  $\Delta E > 0.2$  eV,  $\tau_c$  could be  $> 100$  ps, according to eq 1.

Recently, more complete theoretical models for slowed cooling in QDs have been proposed by Bockelmann and co-workers<sup>16,21</sup> and Benisty and co-workers.<sup>15,17</sup> All models for slowed hot-electron cooling and phonon bottleneck in QDs require that cooling occurs only via longitudinal optical (LO) phonon emission. However, there are several other mechanisms by which hot electrons can cool in QDs. Most prominent among these is the Auger mechanism.<sup>22</sup> Here, the excess energy of the electron is transferred via an Auger process to the hole, which then cools rapidly because of its larger effective mass and smaller energy level spacing. Thus, an Auger mechanism for hot-electron cooling can break the phonon bottleneck.<sup>22</sup>

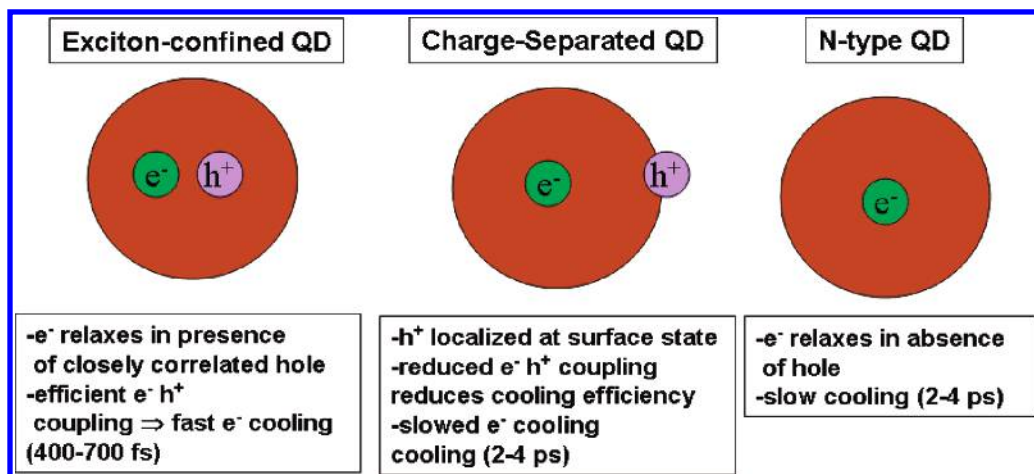
Studies of carrier cooling and relaxation have been performed on II–VI CdSe colloidal QDs by Klimov et al.,<sup>23,24</sup> Guyot-Sionnest et al.,<sup>25</sup> Ellingson et al.,<sup>18,26</sup> and Blackburn et al.<sup>19</sup> These results support the Auger mechanism for electron relaxation, whereby the excess electron energy is rapidly transferred to the hole, which then relaxes rapidly through its dense spectrum of states. When the hole is rapidly removed and trapped at the QD surface, the Auger mechanism for hot-electron relaxation is inhibited and the relaxation time increases.

Recent results were reported<sup>18,19,26</sup> for the electron cooling dynamics in InP QDs, where the QD surface was modified to permit hole trapping but not electron trapping and also where only electrons were injected into the QD from an external redox molecule (sodium biphenyl) so that holes necessary for the Auger cooling mechanism were not present in the QD.<sup>19</sup> If the electron and hole remain the QD core,

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**Figure 2.** Different electron–hole configurations in a QD and the resulting relaxation/cooling dynamics (from ref 53).

strong electron–hole interaction leads to efficient, fast relaxation via the Auger mechanism, but in QDs where the hole is localized at the surface, the increased spatial separation inhibits the Auger process and results in slower relaxation.

To further investigate the mechanisms involved in the intraband relaxation, we conducted experiments in which only electrons were present inside the QDs and holes were absent. Sodium biphenyl is a very strong reducing agent that has been shown to successfully inject electrons into the conduction band of CdSe QDs,<sup>27,28</sup> effectively bleaching the  $1S_h$  to  $1S_e$  transition and allowing an IR-induced transition to the  $1P_e$  level. Sodium biphenyl was therefore used to inject electrons into the  $1S$  electron level in InP QDs.<sup>19</sup> This  $1S_e$  electron was then excited to the  $1P_e$  level with an IR pump, and its relaxation dynamics back to the ground  $1S$  state was monitored. Time-resolved, IR-induced transitions in n-type (electron-injected) InP QDs showed that the relaxation of the excited electrons from the  $1P_e$  to  $1S_e$  level could be fit to a single exponential, with an average time constant ranging from 2 to 4 ps; in neutral 50-Å trioctyl phosphine/trioctylphosphine oxide-capped InP QDs, the relaxation showed a large 400-fs component indicative of fast electron cooling. These experiments confirmed that, in the absence of a core-confined hole, electronic relaxation is slowed by about an order of magnitude. A summary of the results of these experiments investigating the effects of electron–hole separation on electron cooling is shown in Figure 2.

**Electron–Hole Pair Multiplication in QDs.** The formation of multiple electron–hole pairs per absorbed photon in photoexcited bulk semiconductors is a process typically explained by I.I. In this process, an electron or hole with kinetic energy greater than that of the semiconductor band gap produces one or more additional electron–hole pairs. The kinetic energy can be created either by applying an electric field or by absorbing a photon with energy above the semiconductor band-gap energy. The former is well studied and understood.<sup>29–31</sup> The latter process is less well

studied but has been observed in photoexcited p–n junctions of Si, Ge, and InSb.<sup>32–35</sup>

However, I.I. has not contributed meaningfully to improved quantum yield (QY) in working solar cells primarily because the I.I. efficiency does not reach significant values until photon energies reach the ultraviolet region of the spectrum. In bulk semiconductors, the threshold photon energy for I.I. exceeds that required for energy conservation alone because, in addition to conserving energy, crystal momentum must be conserved. Additionally, the rate of I.I. must compete with the rate of energy relaxation by electron–phonon scattering. It has been shown that the rate of I.I. becomes competitive with phonon scattering rates only when the kinetic energy of the electron is many times the band-gap energy ( $E_g$ ).<sup>29–31</sup> The observed transition between inefficient and efficient I.I. occurs slowly; for example, in Si the I.I. efficiency was found to be only 5% (i.e., total QY = 105%) at  $h\nu \approx 4$  eV ( $3.6E_g$ ) and 25% at  $h\nu \approx 4.8$  eV ( $4.4E_g$ ).<sup>35,36</sup> This large blue shift of the threshold photon energy for I.I. in semiconductors prevents materials such as bulk Si and GaAs from yielding improved solar conversion efficiencies.<sup>13,36</sup>

However, in QDs, the rate of electron relaxation through electron–phonon interactions can be significantly reduced because of the discrete character of the electron–hole spectra, and the rate of Auger processes, including the inverse Auger process of exciton multiplication, is greatly enhanced because of carrier confinement and the concomitantly increased electron–hole Coulomb interaction (see Figure 3). Furthermore, crystal momentum need not be conserved because momentum is not a good quantum number for three-dimensionally confined carriers. Indeed, very efficient multiple electron–hole pair (multiexciton) creation by one

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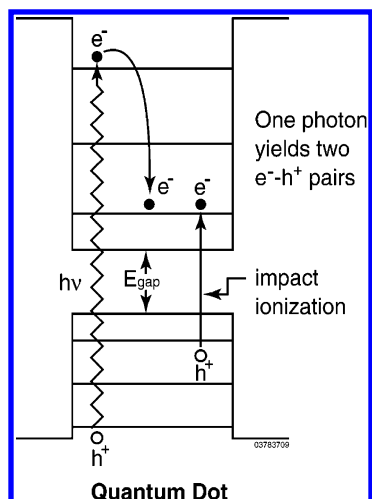
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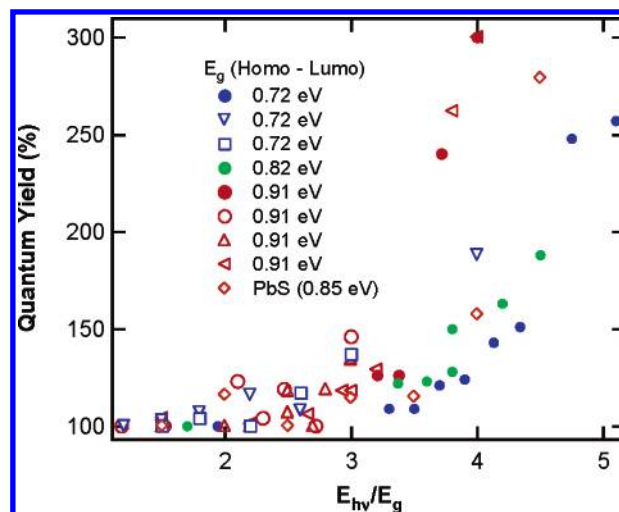


**Figure 3.** Enhanced PV efficiency in QD solar cells by electron–hole pair multiplication (from ref 20).

photon was reported recently in PbSe nanocrystals by Schaller and Klimov.<sup>37</sup> They reported an excitation energy threshold for the formation of two excitons per photon at  $3E_g$ , where  $E_g$  is the absorption energy gap of the nanocrystal (HOMO–LUMO transition energy). Schaller and Klimov reported a QY value of 218% (118% I.I. efficiency) at  $3.8E_g$ ; QYs above 200% indicate the formation of more than two excitons per absorbed photon. We have recently reported<sup>38</sup> a QY value of 300% for 3.9-nm-diameter PbSe QDs at a photon energy of  $4E_g$ , indicating the formation of three excitons per photon for every photoexcited QD in the sample. We also provided evidence that the threshold for MEG by optical excitation is  $2E_g$ ,<sup>38</sup> not  $3E_g$  as reported previously for PbSe QDs,<sup>37</sup> and we showed that comparably efficient MEG occurs also in PbS nanocrystals.<sup>38</sup> We also introduced a new possible mechanism for MEG that invokes a coherent superposition of multiple excitonic states, meaning that multiple excitons are essentially created instantly upon absorption of high-energy photons,<sup>38</sup> our new model also explains the lower threshold energy for MEG.

We detected multiexcitons by monitoring the signature of multiexciton decay dynamics using transient absorption (TA) spectroscopy; this is the same approach as that used by Schaller and Klimov.<sup>37</sup> The magnitude of the photoinduced absorption change at the band edge is proportional to the number of electron–hole pairs created in the sample. The transients are detected by probing either with a band edge (energy gap or HOMO–LUMO transition energy  $\equiv E_g$ ) probe pulse or with a mid-IR probe pulse that monitors intraband transitions in the newly created excitons. Although both the band-edge and mid-IR probe signals would incorporate components from excitons with energy above the  $1S_h-1S_e$  exciton, our multiple exciton Auger recombination analysis relies only on data for delays  $>5$  ps, by which time carrier multiplication and cooling are complete.

The dependence of the MEG QY on the ratio of the pump photon energy to the band gap ( $E_{hv}/E_g$  varied from 1.9 to 5.0) for PbSe QD samples with  $E_g = 0.72$  eV (diameter =



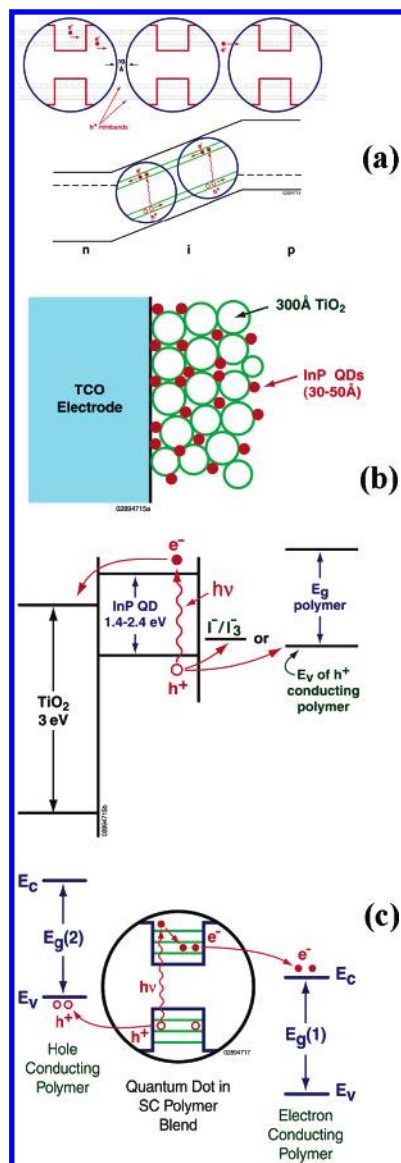
**Figure 4.** QY for exciton formation from a single photon vs photon energy expressed as the ratio of the photon energy to the QD band gap (HOMO–LUMO energy) for three PbSe QD sizes and one PbS (diameter = 3.9, 4.7, 5.4, and 5.5 nm, respectively, and  $E_g = 0.91$ , 0.82, 0.73, and 0.85 eV, respectively). Solid symbols indicate data acquired using a mid-IR probe; open symbols indicate band-edge probe energy. QY results were independent of the probe energy utilized (from ref 38).

5.7 nm),  $E_g = 0.82$  eV (diameter = 4.7 nm), and  $E_g = 0.91$  eV (diameter = 3.9 nm) is shown in Figure 4. For all three samples, the sharp rise in the QY begins at about 3 times the energy gap, a result in agreement with that reported by Schaller and Klimov.<sup>37</sup> Our data show that, for the 3.9 nm QD ( $E_g = 0.91$  eV), the QY reaches a remarkable value of 300% at  $E_{hv}/E_g = 4.0$ , indicating that the QDs produce three excitons per absorbed photon. For the other two PbSe samples [ $E_g = 0.82$  eV (4.7 nm diameter) and 0.72 eV (5.7 nm diameter)], it is estimated that a QY of 300% is reached at an  $E_{hv}/E_g$  value of 5.5. It was noted that the  $2P_h-2P_e$  transition in the QDs is resonant with the  $3E_g$  excitation, corresponding to the sharp onset of increased MEG efficiency. If this symmetric transition ( $2P_h-2P_e$ ) dominates the absorption at  $\sim 3E_g$ , the resulting excited state provides both the electron and hole with excess energy of  $1E_g$ , in resonance with the lowest exciton absorption (at  $1E_g$ ). Our data also showed that the QY begins to surpass 100% at  $E_{hv}/E_g$  values greater than 2.0 (see Figure 4). We carefully measured 16 QY values between  $2.1E_g$  and  $2.9E_g$  (mean value = 109.8%) and 11 QY values between  $1.2E_g$  and  $2.0E_g$  (mean value = 101.3%). Application of statistical  $t$  tests shows that the QY values for photon energies between  $1E_g$  and  $2E_g$  were not statistically different from 100% ( $P$  value = 0.105), while the differences in the QYs between  $1.2E_g-2.0E_g$  and  $2.1E_g-2.9E_g$  were very statistically significant with a  $P$  value of 0.001. Also, simple visual inspection of Figure 4 indicated a significant difference in the QY values between  $1E_g-2E_g$  and  $2E_g-3E_g$ .

**QD Solar Cells.** The two fundamental pathways for enhancing the conversion efficiency (increased photovoltage<sup>5,6,11</sup> or increased photocurrent<sup>11–13</sup>) can be accessed, in principle, in three different QD solar cell configurations;

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**Figure 5.** Configurations for QD solar cells. (a) A QD array used as a photoelectrode for a photoelectrochemical or as the i region of a p-i-n PV cell. (b) QDs used to sensitize a nanocrystalline film of a wide-band-gap oxide semiconductor (viz., TiO<sub>2</sub>) to visible light. This configuration is analogous to the dye-sensitized solar cell where the dye is replaced by QDs. (c) QDs dispersed in a blend of electron- and hole-conducting polymers. In configurations a-c, the occurrence of MEG could produce higher photocurrents and higher conversion efficiency. In a, enhanced efficiency could be achieved either through MEG or hot-carrier transport through the minibands of the QD array, resulting in a higher photopotential (from ref 53).

these configurations are shown in Figure 5, and they are described below. However, it is emphasized that although we measured 300% QY for exciton formation in the QDs, we have not yet reported enhanced photocurrent with photocurrent QYs greater than 100% in any QD-based photon conversion device, where the multiple excitons are dissociated and the electron and holes separated and collected in an external circuit. Such experiments are currently in progress. The QD cell configurations are as follows:

**Photoelectrodes Composed of QD Arrays.** In this configuration, the QDs are formed into an ordered 3-D array with inter-QD spacing sufficiently small such that strong electronic coupling occurs and minibands are formed to allow

long-range electron transport (see Figure 5a). The system is a 3-D analogue to a 1-D superlattice and the miniband structures formed therein.<sup>11</sup> The delocalized quantized 3-D miniband states could be expected to slow the carrier cooling and permit the transport and collection of hot carriers to produce a higher photopotential in a PV cell or in a photoelectrochemical cell where the 3-D QD array is the photoelectrode. Also, I.I. might be expected to occur in the QD arrays, enhancing the photocurrent. However, hot-electron transport/collection and I.I. cannot occur simultaneously; they are mutually exclusive, and only one of these processes can be present in a given system.

**QD-Sensitized Nanocrystalline TiO<sub>2</sub> Solar Cells.** This configuration is a variation of a recent promising new type of PV cell that is based on dye sensitization of nanocrystalline TiO<sub>2</sub> layers.<sup>39-41</sup> In this latter PV cell, dye molecules are chemisorbed onto the surface of 10–30-nm-size TiO<sub>2</sub> particles that have been sintered into a highly porous nanocrystalline 10–20- $\mu$ m TiO<sub>2</sub> film. Upon photoexcitation of the dye molecules, electrons are very efficiently injected from the excited state of the dye into the conduction band of TiO<sub>2</sub>, affecting charge separation and producing a PV effect. The cell circuit is completed using a nonaqueous redox electrolyte that contains I<sup>-</sup>/I<sub>3</sub><sup>-</sup> and a Pt counter electrode to allow reduction of the adsorbed photooxidized dye back to its initial nonoxidized state (via I<sub>3</sub><sup>-</sup> produced at the Pt cathode by reduction of I<sup>-</sup>).

For the QD-sensitized cell, QDs are substituted for the dye molecules; they can be adsorbed from a colloidal QD solution<sup>42</sup> or produced in situ<sup>43-46</sup> (see Figure 5b).

Successful PV effects in such cells have been reported for several semiconductor QDs including InP, CdSe, CdS, and PbS.<sup>42-46</sup> Possible advantages of QDs over dye molecules are the tunability of optical properties with size and better heterojunction formation with solid hole conductors.

Experiments on the dynamics of electron transfer (ET) from QDs of CdS and InP adsorbed onto nanocrystalline TiO<sub>2</sub> have been conducted.<sup>19,47</sup> The time scales for ET were determined by femtosecond TA spectroscopy. For CdS, the ET was found to proceed from the QD LUMO level and was biphasic with ET times of 10 and 50 ps.<sup>19</sup> For InP, hole transfer to a hole acceptor (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine) in solution was found to occur within 4 ps. However, ET was found to occur from surface states rather than from the LUMO level, and a time scale could not be established from the experiments.<sup>47</sup> These initial results indicated that the rate of ET can be adjusted to be in the range where it is optimum for enhancing carrier multiplication followed by charge separation.

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**QDs Dispersed in Organic Semiconductor Polymer Matrixes.** Recently, PV effects have been reported in structures consisting of QDs forming junctions with organic semiconductor polymers. In one configuration, a disordered array of CdSe QDs is formed in a hole-conducting polymer: MEH-PPV [poly[2-methoxy-[5-(2'-ethyl)hexyl]oxy-*p*-phenylenevinylene]].<sup>48</sup> Upon photoexcitation of the QDs, the photogenerated holes are injected into the MEH-PPV polymer phase and are collected via an electrical contact to the polymer phase. The electrons remain in the CdSe QDs and are collected through diffusion and percolation in the nanocrystalline phase to an electrical contact to the QD network. Initial results show relatively low conversion efficiencies,<sup>48,49</sup> but improvements have been reported with rodlike CdSe QD shapes<sup>50</sup> embedded in poly(3-hexylthiophene) (the rodlike shape enhances electron transport through the nanocrystalline QD phase). In another configuration,<sup>51</sup> a polycrystalline TiO<sub>2</sub> layer is used as the electron-conducting phase, and MEH-PPV is used to conduct the holes; the electron and holes are injected into their respective transport media upon photoexcitation of the QDs.

A variation of these configurations is to disperse the QDs into a blend of electron- and hole-conducting polymers (see Figure 5c). This scheme is the inverse of light-emitting-diode structures based on QDs. In the PV cell, each type of carrier-transporting polymer would have a selective electrical contact to remove the respective charge carriers. A critical factor for success is to prevent electron-hole recombination at the interfaces of the two polymer blends; prevention of electron-hole recombination is also critical for the other QD configurations mentioned above.

All of the possible QD-organic polymer PV cell configurations would benefit greatly if the QDs produce multiple electron-hole pairs. This is also true for all of the QD solar cell systems described above. The various cell configurations simply represent different modes of collecting and transporting the photogenerated carriers produced in the QDs.

## Conclusion

The relaxation dynamics of photoexcited excitons (bound electron-hole pairs) in semiconductor QDs can be greatly

modified compared to the relaxation dynamics of free electron-hole pairs formed in bulk semiconductors. Specifically, the cooling dynamics of highly energetic (hot) excitons created by absorption of supra-band-gap photons can be slowed by at least 1 order of magnitude (2–7 ps vs 400–700 fs). This slowed cooling is caused by a so-called “phonon bottleneck” when the energy spacing between quantized levels in the QD is greater than the LO phonon energy, thus inhibiting hot-exciton relaxation (cooling) by electron-phonon interactions. To produce the slowed hot-electron cooling via the phonon bottleneck, it is necessary to block an Auger process that could bypass the phonon bottleneck and allow fast electron cooling. The Auger cooling process involves the transfer of excess electron energy to a hole, which then cools rapidly because of its higher effective mass and closely spaced energy levels. Blocking the Auger cooling is achieved by rapidly removing the photogenerated hole before it undergoes Auger scattering with the photogenerated electron or by injecting electrons into the LUMO level (conduction band) of the QD from an external electron-donating chemical species and then exciting these electrons with an IR pulse. Slowed electron cooling in QDs offers the potential to use QDs in solar cells to enhance their conversion efficiency. In bulk semiconductors, the hot electrons (and holes) created by absorption of supra-band-gap photons cool so rapidly to the band edges that the excess kinetic energy of the photogenerated carriers is converted to heat and limits the theoretical Shockley-Queisser thermodynamic conversion efficiency to about 31% (at one sun). Slowed cooling in QDs could lead to their use in solar cell configurations, wherein MEG (the formation of two or more electron-hole pairs per absorbed photon, and called I.I. in bulk semiconductors) or hot-electron separation, transport, and transfer can become significant, thus producing enhanced photocurrents or photovoltages and corresponding enhanced conversion efficiencies with thermodynamics limits of 66% (one sun). Very efficient exciton multiplication in PbSe and PbS QDs has now been observed, and up to 3 excitons/photon have been reported at photon energies greater than about 3.8 times the QD band gap (HOMO-LUMO energy separation). Three configurations for QD solar cells have been described here that could produce either enhanced photocurrent or photovoltage.

**Acknowledgment.** This work was funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences. A.J.N. acknowledges the vital contributions to the work reviewed here by Randy Ellingson, Matt Beard, Justin Johnson, Olga Micic, Jeff Blackburn, Pingrong Yu, Alexander L. Efros, and Andrew Shabaev.

IC0508425

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