NEW PARADIGM FOR SOLAR ENERGY CONVERSION USING SEMICONDUCTOR NANOCRYSTALS

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The efficiency with which photons are converted into charge carriers determines the ultimate efficiencies of various photo-induced physical and chemical processes including photo-generation of electricity, production of solar fuels, optically pumped lasing, generation of nonlinear-optical responses, etc. Normally, it is assumed that the absorption of a single light quantum (a photon) by a semiconductor produces a single electron-hole pair (exciton), meaning that the quantum efficiency (QE) in generating charge carries is 100%. A potential approach to surpassing this limit is through carrier multiplication (CM), in which absorption of a single photon produces multiple excitons. Recently, we discovered, that while being low efficiency in bulk semiconductors, CM becomes extremely efficient in ultrasmall semiconductor nanocrystals (NCs) [1]. By utilizing a significant difference in dynamical behaviors of single excitons and multiexcitons in NCs [2], we demonstrated that two and even three excitons could be produced in a PbSe NC per single absorbed photon resulting in QEs of up to 220%. Recently, these results were confirmed in Ref. 3, where up to three excitons (QE up to 300%) were also observed for PbSe NCs using the same "dynamical" detection method; this paper also reported CM in NCs of another lead-salt compound, PbS.

These first experimental observations raise the questions regarding the mechanism for high-efficiency CM in NCs, the generality of this phenomenon and the limits of exciton multiplicity that can be obtained via CM. To address these issues, we perform a comparative study of CM in NCs of PbSe and CdSe that are characterized by a significant difference in both electronic structures and carrier relaxation behaviors. Despite these differences, both compositions show comparable CM efficiencies (defined in terms of the slope of the QE dependence on photon energy above the CM threshold), which is indicative of the generality of this phenomenon to quantum-confined, semiconductor nanoparticles. We demonstrate that CdSe NCs show a lower activation threshold for CM than PbSe NCs (~2.5 vs. ~2.9 energy gaps), which can be explained using simple carrier effective-mass arguments. For PbSe NCs, we observe a monotonic increase of QE up to ~700% with increasing excess energy above the CM threshold (Fig. 1). The latter value, which is observed for photon energy of 7.8 energy gap corresponds to the *ultimate limit* of exciton multiplicity allowed by energy conservation (Fig. 1).

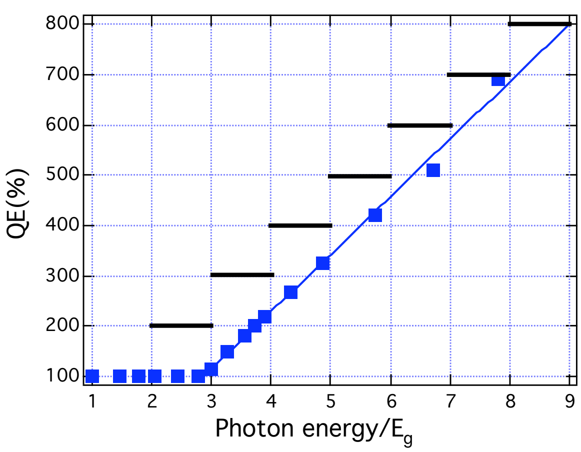

Figure 1. "Ideal" QEs derived from energy conservation (horizontal bars) and experimental QEs measured for PbSe NCs (solid squares) as a function of pump-photon energy, $\hbar\omega$, normalized by energy gap. Experimental QEs approach the limit determined by energy conservation at $\hbar\omega = 7.8E_g$, for which QE ≈ 700%. The line is a linear fit (slope = $115\%/E_g$) to experimental data in the range of energies $>3E_g$; it indicates that complete filling of the 1S quantized state (8 electron-hole pairs) produced by a single photon is expected at $\hbar\omega \approx 9E_g$.

We also perform detailed studies of buildup dynamics of multiexciton populations in CdSe and PbSe NCs. We do not detect any time delays (with better than 100 fs accuracy) that could be attributed to the CM process, which strongly suggests that multiexcitons are generated *instantaneously* by a single absorbed photon. To explain this specific observation as well as the results of previous experiments [1, 3], we propose a new model that describes CM in terms of direct generation of multiexcitons via *virtual* single-exciton states [4]. This process relies upon confinement-induced enhancement of Coulomb interactions in NCs and large spectral densities of high-energy single-exciton and multiexciton states.

High exciton multiplicity in response to a single light quantum observed in our experiments can find numerous applications in physics and chemistry ranging from high-efficiency photovoltaics and single-photon oxidation of water molecules (water splitting) to low-threshold lasing and generation of entangled photon pairs.

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