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Ultrafast charge cooling and carrier multiplication in semiconductor nanocrystals and superlattices

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ABSTRACT

We studied charge carrier photogeneration, cooling, carrier multiplication (CM) and charge mobility and decay in: a) isolated PbSe nanocrystals in solution, b) films of PbSe nanocrystals coupled by organic ligands, and c) 2D percolative networks of epitaxially connected PbSe nanocrystals. The studies were performed using ultrafast pump-probe spectroscopy with optical or terahertz/microwave conductivity detection.

The effects of electronic coupling between the nanocrystals on charge mobility were characterized by frequency-resolved microwave and terahertz photoconductivity measurements. Reducing the size of ligand molecules between nanocrystals in a film strongly increases the charge mobility. Direct connection of nanocrystals in a percolative network yielded a sum of electron and hole mobilities as high as $270 \pm 10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. We found that a high mobility is essential for multiple electron-hole pairs formed via CM to escape from recombination.

The coupling between the nanocrystals was found to strongly affect the competition between cooling of hot charges by phonon emission and CM. In percolative networks of connected nanocrystals CM is much more efficient than in films with ligands between the nanocrystals. In these networks CM occurs in a step-like fashion with threshold near the minimum photon energy of twice the band gap.

Keywords: Nanocrystal, charge generation, charge cooling, carrier multiplication, charge mobility

1. INTRODUCTION

Absorption of energetic photons in a bulk semiconductor leads to hot electrons and holes that usually cool to the band edge by thermal relaxation; *i.e.* phonon emission. This cooling can be intercepted by excitation of additional electrons across the band gap, see Figure 1. In this way, one absorbed photon generates multiple electron-hole pairs via Carrier Multiplication (CM), which is of interest for development of highly efficient photovoltaics.¹⁻⁴ In bulk semiconductors such as silicon the energetic threshold for CM is too high to be of practical use in solar cell applications. However, CM in nanometer sized semiconductor quantum dots (NCs) offers prospects for exploitation in photovoltaics. CM leads to formation of two or more electron-hole pairs that are initially in close proximity. For solar cell applications these charges must escape from recombination.

This paper highlights our research on generation of free mobile charges that result from CM in nanomaterials composed by assembly of colloidal PbSe quantum dots.^{3, 5-8} PbSe quantum dots are of particular interest, since their size can be adjusted to realize a band gap near 1 eV which is optimal for exploitation of CM in solar cells. Our studies on the efficiency of charge carrier photogeneration and mobility were carried out using (ultrafast) time-resolved pump-probe spectroscopy with optical or ac conductivity detection.

For device applications the charges produced *via* CM must be sufficiently mobile to prevent Auger recombination and to enable their extraction at external electrodes. Charge mobilities in the range $1 - 40 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ have been found for thin film solids of PbSe nanocrystals (NCs) that are connected by short organic ligands.^{5, 9, 10} Interestingly, a PbSe NC solid with 1,2-ethanediamine ligands has shown a lower threshold for CM than for the same NCs in dispersion.^{5, 11} In this PbSe NC solid the NCs are to some extent also coupled directly by thin atomic necks.¹² Hence, electronic coupling appears not only to be beneficial to charge mobility, but also to reduce the threshold energy of CM. The coupling has been further enhanced by facet-specific oriented attachment of NCs.^{7, 13-15} In the latter case, further thermal annealing of

the formed superlattice results in the formation of a percolative PbSe network, in which the NCs are connected *via* strong crystalline bridges in the in-plane directions. There are on average less than 4 connections per nanocrystal in this system. Hence, the percolative network can be considered as a planar system with a dimensionality between 2 and 1 with straight segments in orthogonal directions, see Figure 2.⁸ The short-range mobility of charge carriers was found to attain values as high $270 \pm 10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for a probing electric field oscillating in the terahertz (THz) frequency range.^{8, 15}

As discussed below CM in percolative PbSe networks has lower threshold energy and is more efficient than in films of PbSe NCs coupled by organic ligands.^{5, 8} Interestingly, the CM efficiency follows a step-like dependence on photon energy and reaches a value of about 1.4 at the minimum required photon energy of twice the band gap. According to detailed-balance calculations the CM efficiency realized in the percolative PbSe network would enhance the power conversion efficiency of a solar cell by $\sim 8\%$ over the Shockley-Queisser limit for a band gap of 0.7 eV at 1-sun. The results are of great promise for development of highly efficient third-generation solar cells.⁸

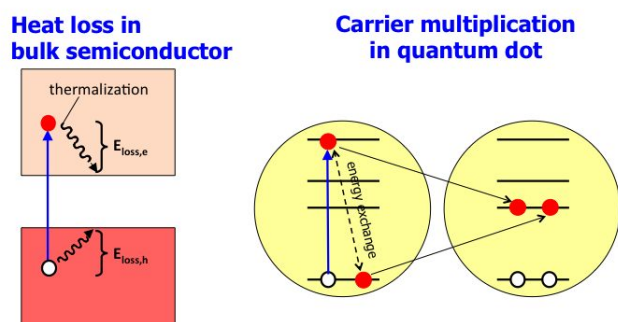


Figure 1. Left: Photoexcitation of a bulk semiconductor leads to formation of a hot electron and hole that usually lose their excess energy as heat due to phonon emission. Right: carrier multiplication in a quantum dot results in excitation of additional electrons across the band gap. Figure taken from ref. 3.

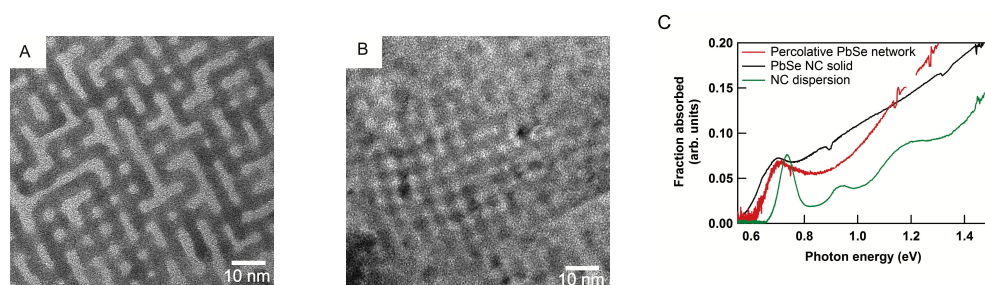


Figure 2. Structure and optical absorption. (A) TEM image of a monolayer percolative PbSe network (scale bar represents 10 nm). (B) TEM image of a PbSe NC solid with 1,2-ethanediamine ligands (scale bar represents 10 nm). (C) Optical absorption spectra of a percolative PbSe network, the PbSe NC solid and a NC dispersion in tetrachloroethylene. Figure taken from ref. 8.

2. RESULTS AND DISCUSSION

2.1. Carrier multiplication in NC solids

We studied effects of the charge mobility in NC solids on the efficiency of generating free mobile electrons and holes that are produced via CM. The mobility was systematically varied in solids of identical PbSe NCs (6.0 nm diameter), so that the initial CM efficiency is the same.⁵ The mobility was adjusted by varying the anchor group or length, using 1,2-ethanedithiol (2DT) and 1,2-*n*-alkanediamines (*n*DA) with *n*=2, 3, 4 or 6 ligand molecules. Figure 3A shows the optical absorption spectra of PbSe NC solids with 2DA, 4DA and 6DA ligands against the left axis. The peak at low energy is due to the first excitonic transition and shows that quantum confinement effects are still present after coupling of the NCs in the solid. We studied the efficiency of charge carrier generation by time-resolved microwave photoconductance measurements.^{5, 16} Charges were generated by photoexcitation with a 3 ns laser pulse at variable photon energy. The photoconductance increases during the laser pulse and reaches a maximum (with quantum yield $\phi_{\max}$) at a time that is determined by the competition between charge photogeneration and their decay by recombination or trapping.

The photoconductance at the end of the 3 ns laser pulse is plotted in Figure 3A against the right axis. For photon energies below ~ 1.5 eV the photoconductance follows the absorption spectrum. This simply reflects that the number of charges is proportional to the number of absorbed photons. Interestingly, at higher photon energies the photoconductance increases faster with photon energy than the fraction of absorbed photons. This is a signature of an increasing quantum yield due to CM. Above the CM threshold, the photoconductance deviates more from the optical absorption for shorter ligands. The higher mobility of charges for shorter ligands, facilitates charge escape from Auger recombination and enhances the quantum yield.

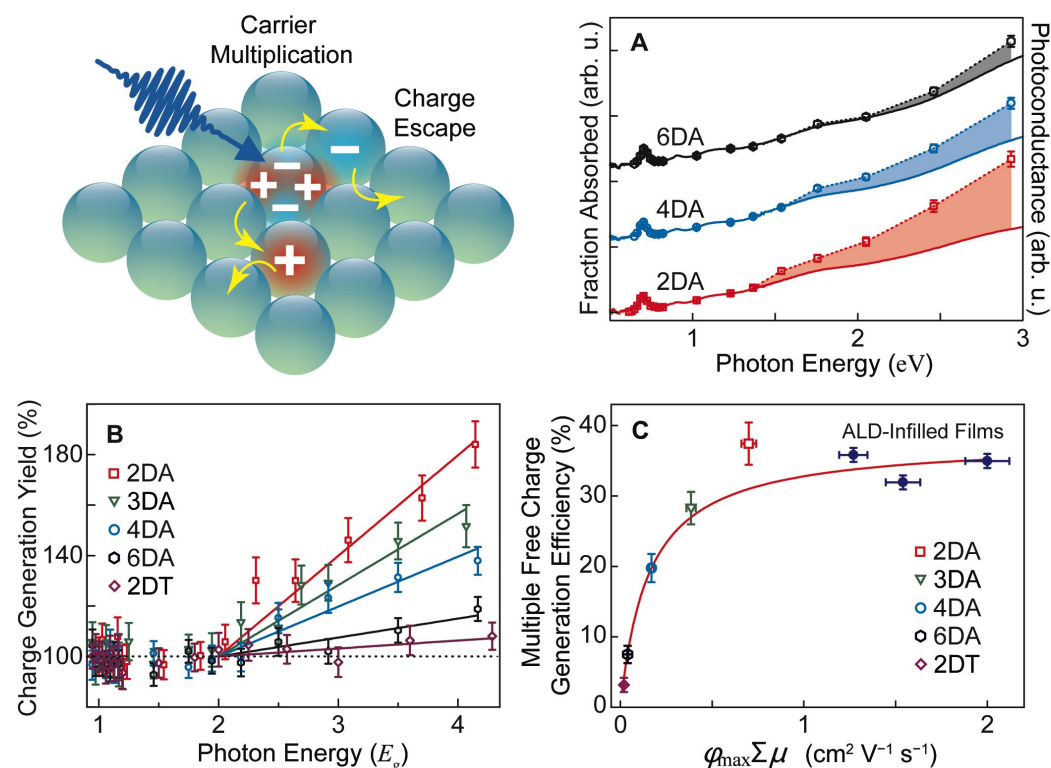


Figure 3. Carrier multiplication produces multiple charges in close proximity. The charges must be sufficiently mobile to escape from Auger recombination. (A) Fraction of absorbed photons (solid lines, offset for clarity) and microwave photoconductance per incident photon (markers) for PbSe NC solids with 2DA, 4DA and 6DA ligands; shaded areas indicate quantum yields exceeding one. (B) Charge generation yield versus photon energy; straight lines are linear fits to determine the quantum yield. (C) Charge carrier generation efficiency versus $\phi_{\max} \Sigma \mu$ for PbSe NC solids with organic ligands (open markers) and for ALD-infilled films from ref. 17 (solid blue markers). The data can be described by a theoretical model (red curve) of charge escape and Auger recombination.⁵ Figure taken from ref. 3.

Figure 3B shows the quantum yield as a function of photon energy for different ligands. The quantum yield depends strongly on the nature of the ligand. For n DA ligands the quantum yield rises faster with photon energy for shorter ligands (smaller n). However, for 2DT ligands (purple diamonds) there is hardly any effect of CM on the quantum yield. This is due to the low mobility of charges in a PbSe NC solid with 2DT ligands.⁵ We define the charge carrier generation efficiency as the slope of the linear fits in Figure 3B. The *efficiency* obtained in this way is the increase in quantum yield per unit photon energy normalized to the band gap of the material, analogous to the well-known CM efficiency.^{18, 19} Figure 3C shows the efficiency versus the product of $\phi_{\max}\Sigma\mu$, with $\Sigma\mu$ the sum of the electron and hole mobility. It is clear that the efficiency increases strongly with the charge mobility for the organic ligand series 2DT, 6DA, 4DA, 3DA and 2DA. The experimental results can be reproduced by a theoretical model (red curve) with the initial CM efficiency taken as 0.4 (as in solution) and multiple electron-hole pairs escaping from Auger recombination with a rate that scales linearly with the sum of the electron and hole mobilities. According to ref. 12 2DT binds to the NC surface much more strongly than amine ligands. Amine ligands were found to result in necking of NCs, with the effect becoming more significant for shorter ligands. Hence, the increase of the charge mobility for the ligand series mentioned above is at least partially due to enhanced necking.

To more strongly establish the relation between the charge mobility and the CM quantum yield we further enhanced the charge mobility by infilling PbSe NC solids with 2DT ligands with Al_2O_3 or $\text{Al}_2\text{O}_3/\text{ZnO}$.¹⁷ The efficiency of multiple free charge carrier generation for infilled samples is also shown in Figure 3C. The efficiency saturates at ~ 0.35 for a charge mobility near $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The saturation value is close to the initial CM efficiency value of 0.41, as measured for solution-dispersed PbSe NCs on picosecond timescale prior to Auger recombination.⁵ This similarity implies that most charges produced via CM in PbSe NC solids with higher mobility can escape from Auger recombination.

2.2. Carrier multiplication in 2D percolative networks

We studied CM in planar percolative PbSe networks with structure as shown in the transmission TEM image of Figure 2A.⁸ The attached NCs form straight segments with average length of about 20 nm. For comparison we also studied a thin film solid of PbSe NCs connected by 1,2-ethanediamine ligands with relatively thin atomic necks between part of the NCs, see TEM image in Figure 2B. Figure 2C shows that the optical absorption spectra of the percolative PbSe network and the NC solid show a broadened peak at around $0.70 \pm 0.01 \text{ eV}$. The peak is slightly red shifted from the first excitonic transition of PbSe NCs dispersed in tetrachloroethylene, which is due to the electronic coupling between NCs in the percolative network and the solid. The sum of the electron and hole mobilities for the percolative PbSe network is $270 \pm 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, in agreement with the previous result.¹⁵

The initial quantum yield for charge carrier photogeneration was determined from the measured THz conductivity at 2.0–2.5 ps after the pump laser pulse for different pump photon energies.⁸ In Figure 4 we show the quantum yield as a function of photon energy, $h\nu$ (top axis), and as a function of photon energy normalised to the band gap, $h\nu/E_g$ (bottom axis).

Figure 4 shows that the onset of CM is near twice the band gap for both the percolative PbSe network and the PbSe NC solid. Also, distinct step-like features appear in the quantum yield for the percolative network with plateaus at photon energies in the range $1.5 \text{ eV} - 2.0 \text{ eV}$ ($2.1E_g - 2.9E_g$) and $2.0 \text{ eV} - 2.6 \text{ eV}$ ($2.9E_g - 3.7E_g$). At higher energies the CM efficiency increases linearly. The PbSe NC solid exhibits a lower quantum yield with plateaus in the range $1.5 \text{ eV} - 1.9 \text{ eV}$ and $2.0 - 2.4 \text{ eV}$.

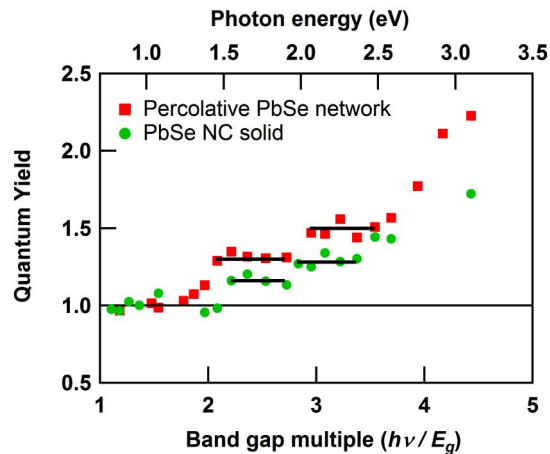


Figure 4. Quantum yield as a function of band gap multiple ($h\nu/E_g$, bottom axis) and as a function of photon energy ($h\nu$, top axis) for the percolative PbSe network and the PbSe NC solid. Figure taken from ref. 8.

CM at twice the band gap implies that the photon energy in excess of the band gap is fully converted to either the photoexcited electron or the hole, as shown in the lower panel of Figure 5. The plateaus in the quantum yield *versus* photon energy in Figure 4 can be due to fast cooling of the electron (or hole) from higher energy in a series of electronic states to a lower state from which CM takes place prior to further cooling. The fact that the quantum yield does not increase up to 2.0 at photon energy of $2E_g$ can have different origins. Firstly, it could be that not all photon absorption processes result in a fully asymmetric distribution of the photon energy. Possibly, part of the photons distribute their energy in excess of the band gap in a more symmetric way over the electron and the hole, as indicated in the upper panel of Figure 5. Secondly, decay by phonon emission competes with CM. Interestingly, for PbS nanosheets the CM threshold was found to be at much higher band gap multiple⁶ than for the percolative PbSe network of the present work. It appears that the continuous nanosheets behave more like the bulk crystal in which CM has a higher threshold energy due to restrictions imposed by conservation of crystal momentum of the electrons involved in CM.

Insight into the occurrence of asymmetric electronic excitations, as shown in the lower panel of Figure 5, can be obtained from electronic structure calculations. To this end we considered a percolative network of 12x12 coupled NCs taken from the TEM image in Figure 2A. Electronic states of this network were calculated using $k\cdot p$ theory.⁸ This four band model did not yield a significant amount of asymmetric electronic excitations. Apparently, the electronic states resulting from mixing of the four band-edge states in the percolative network are to a large extent still resembling the almost symmetric energy dispersion of the valence and conduction bands in bulk PbSe. Hence, the four band-edge states at the L-point are insufficient to describe asymmetric excitations. A next step would be to include states along the Σ -path in the 1st Brillouin zone, or states at higher energy at the L-point. A proper description of CM in the percolative networks requires a more advanced theoretical approach, such as $k\cdot p$ theory with more electronic bands, or density functional theory with modern exchange/correlation functionals.

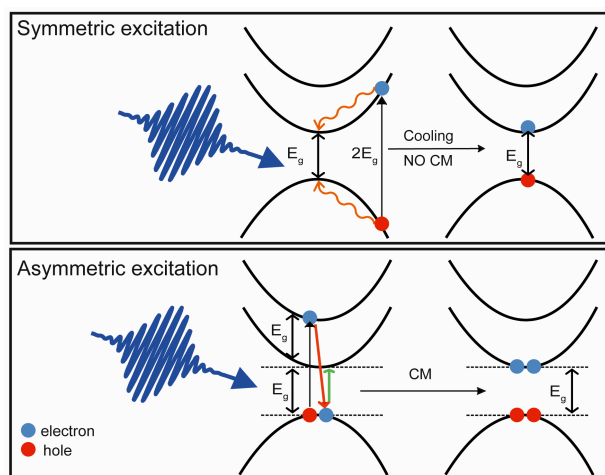


Figure 5. Photoexcitation and charge relaxation pathways. Upper panel: in a fully symmetric excitation at photon energy of twice the band gap, the excess energy is initially equally distributed between the electron (blue dot) and the hole (red dot), which subsequently relax by cooling to the band edges. Lower panel: in a fully asymmetric excitation the excess photon energy can be transferred to excite another electron *via* CM. In the example of this Figure the electron in the second conduction band acquires the excess photon energy and subsequently relaxes *via* CM. Figure taken from ref. 8.

3. CONCLUSIONS

We studied the efficiency of the photogeneration of free mobile charges in PbSe NC solids and percolative networks. Charges were generated by irradiation with short laser pulses and detected by microwave or terahertz conductivity measurements. In the PbSe NC solids the NCs were connected by organic ligand molecules. The mobility of charge carriers was found to increase for smaller ligands. The increase of the charge mobility enhances the yield of free mobile charges resulting from CM. This was explained as follows. CM initially leads to generation of two or more electron-hole pairs in close proximity. These electrons and holes can more easily escape from Auger recombination at higher charge mobility. Connection of NCs via atomic bonds reduced the threshold photon energy of CM to the minimum value of twice the band gap. In addition, step-like features in the CM quantum yield versus photon energy were observed with the effect being most pronounced in percolative PbSe networks. Further theoretical research is needed to explain the effects of coupling between NCs on the CM threshold energy and quantum yield.

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