Carrier multiplication and free charge generation in quantum dot solids

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Introduction

In a conventional solar cell the photon energy in excess of the semiconductor band gap is lost as heat. This heat loss is the main reason that the theoretical efficiency of a conventional solar cell is limited to ~33%. The efficiency can be increased if the excess energy is utilized to excite additional electrons across the band gap via carrier multiplication (CM), see Figure 1. CM leads to formation of two or more electron-hole pairs for the absorption of one photon.

In bulk semiconductors such as silicon the energetic threshold for CM is too high to be of practical use. However, CM in nanometer sized semiconductor quantum dots (QDs) offers prospects for exploitation in photovoltaics. CM leads to formation of two or more electron-hole pairs that are initially in close proximity. For photovoltaic applications these charges must escape from recombination. This talk outlines our recent progress in the generation of free mobile charges that result from CM in thin films of QDs. We studied PbSe QDs, since their band gap can be tuned to 1eV, which is optimal for exploitation of CM in a solar cell.

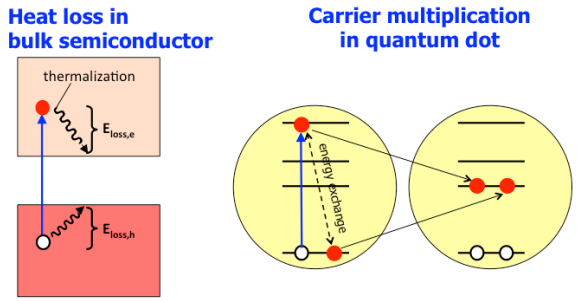

Figure 1. Left: Photoexcitation of a bulk semiconductor leads to formation of a hot electron and hole that usually lose their excess energy as heat due to phonon emission. Right: carrier multiplication in a quantum dot results in excitation of additional electrons across the band gap.

Generation of free mobile charges via carrier multiplication in thin film quantum dot solids.

CM produces multiple electron-hole pairs that are initially in close proximity. The charges must be sufficiently mobile to escape from Auger recombination. We increased the mobility by replacing the bulky oleic acid surface ligands by smaller ligands, including 1,2-ethanedithiol (2DT) and 1,2-*n*-alkanediamines (*n*DA) with *n*=2, 3, 4 or 6.[1-3] The microwave photoconductance, or equivalently the multiple free charge carrier generation (MFCG) yield, for QD solids with these ligands is plotted in Figure 2A against the right axis. For photon energies below ~ 1.5 eV the photoconductance follows the absorption spectrum. This reflects that the number of charges is proportional to the number of absorbed photons. At higher photon energies the photoconductance increases faster with photon energy than the fraction of absorbed photons, which is a signature of CM. The effect is more pronounced for shorter ligands. The higher mobility of charges for shorter ligands facilitates escape from Auger recombination and enhances the MFCG yield.

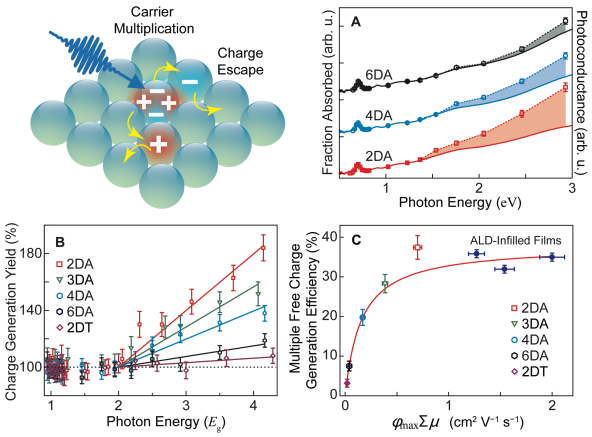

Figure 2. (A) Fraction of absorbed photons (solid lines, offset for clarity) and microwave photoconductance per incident photon (markers) for PbSe QD solids with 2DA, 4DA and 6DA ligands; shaded areas indicate MFCG yields exceeding one. (B) Charge generation yield versus photon energy; straight lines are linear fits to determine the MFCG efficiency. (C) MFCG efficiency versus $\phi_{max}\Sigma\mu$ for PbSe QD solids with organic ligands (open markers) and for ALD-infilled films from ref. [4] (solid blue markers).

Fig. 2B shows the MFCG yield as a function of photon energy for different ligands. For *n*DA ligands the MFCG yield rises faster with photon energy for shorter ligands. However, for 2DT ligands there is hardly any effect of CM on the MFCG yield. This is due to the low mobility of charges in a PbSe QD solid with 2DT ligands.[5] Fig. 3C shows the MFCG *efficiency* (the slope of the linear fits in Fig. 2B) versus $\phi_{max}\Sigma\mu$, with ϕ_{max} the charge yield at the end of the laser pulse and $\Sigma\mu$ the sum of the electron and hole mobility. It is clear that the MFCG efficiency increases with mobility and saturates at a value near 1 $cm^2\ V^{-1}\ s^{-1}$.

Competition between carrier multiplication and cooling of hot charge carriers

We found that the CM efficiency in PbSe QD solids is independent of temperature.[6] Apparently phonons do not notably affect the cooling rate of charges nor compensate energetic mismatches in electronic transitions.

References

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(5) Footnote: *The higher mobility for ligands with amine groups is possibly associated with their weaker binding on the QD surface than thiol groups. The weaker binding leads to partial absence of amine ligands, resulting in necking and stronger coupling of adjacent QDs.*

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