The Life and Fate of optical excitations in Quantum-Dot Solids

Arjan Houtepen
Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Films of colloidal semiconductor nanocrystals, so-called Quantum-Dot solids, are heavily investigated as candidates for photodetectors and solar cells. The operation of such devices requires efficient charge-carrier photogeneration, high charge-carrier mobilities and long charge-carrier lifetimes. For photovoltaic application Quantum Dots are of particular interest since it has been demonstrated in recent years that absorption of a single high-energy photon can result in the generation of multiple excitons (multiple exciton generation, MEG). If these excitons can be converted into mobile charge carriers this process will lead to an increased photocurrent and, hence, an increased power conversion efficiency in solar cells.

We have prepared QD solids composed of PbSe nanocrystals with very short interparticle distances that fulfill all of the above requirements. The processes of (multiple) carrier photogeneration, diffusion and decay have been studied by a combination of terahertz (THz) spectroscopy, transient absorption (TA) spectroscopy and temperature-dependent time-resolved microwave conductivity (TRMC).

Charge carrier mobility

Using the TRMC technique we demonstrate that the charge carrier mobility in QD solids can be as high as 3 cm^2/Vs. This mobility depends on several parameters such as the material of the QDs (CdSe has a three orders of magnitude lower mobility than PbSe), the interparticle separation (through the length of the ligands used) and the nature of the ligand anchor group (thiols result in a two orders of magnitude lower mobility than amines).[1]
The high diffusion rate of charge carriers can be visualized directly by spectrally-resolved transient absorption spectroscopy: ultrafast spectral diffusion is observed due to carriers hopping to lower energy sites in the Quantum-Dot solid; this spectral diffusion is complete in 2 ps, indicating that the hopping time is well below a ps. In addition we find that the rate of intraband relaxation (hot carrier cooling) is significantly higher in these quantum solids than it is for isolated quantum dots in dispersion.[2]

Photogeneration of (multiple) mobile charge carriers

We use a combination of transient absorption spectroscopy and Terahertz spectroscopy to demonstrate that all photogenerated excitons dissociate into mobile charge carriers, on a sub ps timescale.[3] This conclusion is confirmed by time-resolved microwave photoconductivity measurements that show that the yield of charge carrier generation is temperature independent. These measurements also show an Anderson transition from hopping-like transport to band-like transport as the charge density is increased.
The exciton dissociation rate is sufficiently high to allow even multiple excitons, created efficiently via MEG, to dissociate into mobile charge carriers. As a result, multiple carriers per absorbed photon, generated efficiently via MEG, are

directly available, without the aid of an electric field or interfaces that provide an additional driving force for exciton dissociation.[4]

Charge carrier recombination

At very low photoexcitation density the decay of the photoconductivity in these films reveals trapping of carriers on a ~10 ns timescale. However, even at excitation densities as low as 1 photoexcitation per 1000 QDs, charge recombination is dominated by Auger recombination, which is surprisingly fast and efficient in these films. Using Monte Carlo simulations we show that the high efficiency of Auger recombination is due to a combination of the very high carrier diffusion rates and energetic disorder. Disorder results in the focusing of charge carriers in low energy sites. These "Auger hot-spots" are responsible for the fast charge recombination.[5]

In the absence of Auger recombination charges are trapped in sub-bandgap states on a ~10 ns timescale. However this is not always the end of the story: when thiols are used as ligands for the quantum dots we find that these trapped charges have an appreciable mobility and a long lifetime. It has been suggested that this trap-to-trap transport is the main transport mechanism active in current QD solar cells.

The combination of the above results allows us to construct a coherent picture of the life and fate of optical excitations in quantum-dot solids. In addition these results demonstrate that Quantum-Dot solids are very promising candidates for simple and cheap optoelectronic devices.

1 Gao, Y. *et al.* Photoconductivity of strongly coupled PbSe Quantum-Dot solids: dependence on ligand anchor group and length. *Manuscript in preparation*.

2 Gao, Y. *et al.* Enhanced Hot-Carrier Cooling and Ultrafast Spectral Diffusion in Strongly Coupled PbSe Quantum-Dot Solids. *Nano Lett.* **11**, 5471-5476, (2011).

3 Talgorn, E. *et al.* Unity quantum yield of photogenerated charges and band-like transport in quantum-dot solids. *Nat. Nanotechnol.* **6**, 733-739, (2011).

4 Aerts, M. *et al.* Free Charges Produced by Carrier Multiplication in Strongly Coupled PbSe Quantum Dot Films. *Nano Lett.* **11**, 4485-4489, (2011).

5 Gao, Y., Schins, J. M., Houtepen, A. J. & Siebbeles, L. D. A. Energy disorder strongly enhances Auger recombination in Quantum-dot solids. *Manuscript in preparation*.