Formation and dynamics of multiple electron-hole pairs in quantum dots, nanorods and nanoplatelets

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The generation of two or more electron-hole pairs for the absorption of a single energetic photon is of interest for development of highly efficient (up to 44%) solar cells. This process of carrier multiplication is schematically shown in Figure 1 for a thin film array of semiconductor quantum dots (QDs). Using ultrafast pump/probe laser spectroscopy, it has been established previously that a single energetic photon can generate multiple excitons in PbSe QDs in colloidal solution.[1,2] We also studied carrier multiplication in PbSe/PbS core/shell QDs and PbSe/$PbSe_yS_{1-y}$ core/alloy-shell QDs.[3] The optical absorption exhibits a red-shift upon the introduction of a shell around a PbSe core, which increases with the thickness of the shell. According to electronic structure calculations this can be attributed to charge delocalization into the shell. Remarkably, the measured quantum yield of MEG, the hot exciton cooling rate and the Auger recombination rate of biexcitons are similar for pure PbSe QDs and core/shell QDs with the same core size and varying shell thickness. The higher density of states in the alloy and core/shell QDs provide a faster exciton cooling channel that likely competes with the fast MEG process due to a higher biexciton density of states.

We have extended studies on carrier multiplication to PbSe quantum dot arrays. The studies were carried out using (ultrafast) time-resolved optical, terahertz and microwave detection. Photoexcitation of an array of PbSe QDs with ethanediamine ligands was found to directly yield free mobile charges with 100% quantum yield.[4] The charges move according to a band-like mechanism with an almost temperature independent mobility, which is as high as 3 cm^2/Vs. On increasing the photon energy above twice the band gap carrier multiplication was found to occur. For photoexcitation at six times the band gap energy the yield of charges is as high as 300%.[5] These charges are readily available for use in optoelectronic devices without employing a donor/acceptor architecture or an electric field.

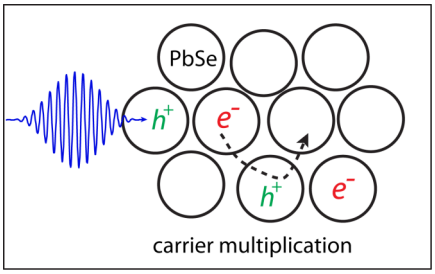

Figure 1. A single energetic photon can produce multiple pairs of free charge carriers in a thin film of quantum dots.

Thin blend films of the polymer poly(3-hexyl thiophene) (P3HT) and the electron acceptor PCBM (a C_{60} derivative) attract a great deal of attention as the light-absorbing and charge transporting material in plastic solar cells, see Figure 2. The absorption of the infrared part of the solar spectrum can be enhanced by adding PbS quantum dots to a P3HT:PCBM film. We studied charge transfer from photoexcited PbS quantum dots to P3HT and PCBM, as shown in Figure 2. While charges undergo transfer from the quantum dots to the organic components, they do not contribute to the terahertz photoconductivity. The absence of formation of free mobile charges can be explained by coulomb interaction with charge-induced dipoles in the highly polarizable quantum dots.

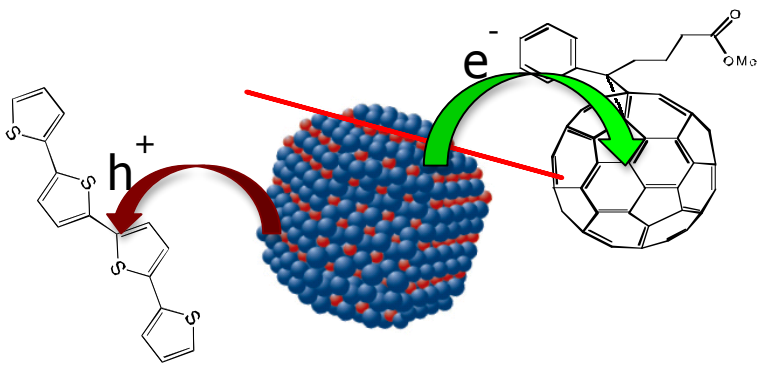

Figure 2. We studied the dynamics of excitons in blends of the conjugated polymer P3HT with the electron acceptor PCBM and infrared sensitizing PbS quantum dots.

Photoexcitation CdSe/CdS core/shell nanorods or PbSe nanorods was found to result in formation of charges that can freely move within a rod. At higher photoexcitation density the terahertz photoconductivity becomes independent on the number of charges in a nanorod. On basis of results from computer simulations of charge motion this peculiar behavior can be attributed to effects of Coulomb interactions between multiple electrons and holes within a nanorod. To reproduce the experimental results with simulations it is necessary that the delocalization of charges over the cross section of the nanorod is taken into account.

Recently Dubertret et al. reported the synthesis of highly fluorescent two-dimensional nanoplatelets consisting of CdSe.[6] The nanoplatelets are a few monolayers thick and have lateral dimensions of tens of nanometers. Photoexcitation at high fluence leads to formation of multiple electron-hole pairs within a nanoplatelet. A single electron-hole pair has a lifetime as long as ~ 4 ns, while multiple electron-hole pairs undergo decay on a timescale of ~ 100-200 ps. Surprisingly the ultrafast kinetics of charge recombination is only weakly dependent on the number of electron-hole pairs (up to 200) within a nanoplatelet. The terahertz photoconductivity is typical for charges that move partly in- and out-of-phase with the oscillations of the terahertz electric field. The magnitude of the terahertz photoconductivity due to multiple electron-hole pairs is hardly dependent on the charge density, similar to results for nanorods. This unexpected behavior will be discussed on basis of computer simulations of multiple electrons and holes that move in each other's Coulomb field within a nanoplatelet.

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