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Charge Relaxation, Localization, and Separation in Colloidal Semiconductor Nanocrystals

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Semiconductor nanocrystals, or quantum dots, have unique potential for optical and opto-electronic applications, because the energies of optical transitions can be tuned simply by changing the dimensions of the nanocrystals. Colloidal synthesis provides a low-cost, flexible route for the production of nanocrystals with precisely controlled dimensions, made of a variety of semiconductor materials. Recent advances in chemical synthesis have enabled the production of complex nanocrystals, including highly anisotropic structures and nanocrystal heterostructures that incorporate more than one semiconductor material, enabling an even greater degree of control over photophysical processes. In order for these nanocrystals to be used in applications, it will be necessary to understand, and ultimately to control, the processes that occur in the nanocrystals following the absorption of a photon. For example, in order for the nanocrystals to be used in solar energy conversion, they must efficiently absorb solar photons, and the excitons that result must be efficiently split into spatially separated electrons and holes before energy is lost through recombination. In this talk, I will discuss recent experiments that investigate carrier relaxation, localization, and separation processes in semiconductor nanocrystals and the relationship between the dynamics of these processes and the structure of the nanocrystals.

As a first example, I will discuss charge separation in heterostructures consisting of CdSe nanorods with CdTe tips [1]. CdSe and CdTe have a type-II band alignment, with an electron at the conduction band edge having lower energy in CdSe, and a hole at the valence band edge having lower energy in CdTe. Absorption of a photon by one of the materials therefore leads to ultrafast charge separation, on time scales less than 1 ps, into the two materials. We have shown that the structure of the nanocrystal affects charge separation rates: charge separation is slower in highly strained, curved nanorod heterostructures, most likely due to a strain-induced potential barrier at the CdSe/CdTe interface. In addition, the charge separation rate depends on the band offset between the two materials, with a smaller offset leading to more rapid charge separation. The dynamics of charge separation thus have much in common with those of epitaxially grown semiconductor heterostructures. On the other hand, the nanocrystals are synthesized in macroscopic quantities as colloidal suspensions, making them resemble in many ways molecular charge-separation complexes.

This intermediate state between molecules and bulk solid-state materials is also occupied by small metal clusters. 44-atom silver clusters stabilized by thiolate ligands exhibit optical spectra with discrete peaks characteristic of molecular transitions, rather than the broad plasmonic resonances characteristic of larger silver nanoparticles. Using ultrafast transient-absorption measurements, we verified that these transitions all occur within the same species, and we observed the presence of a long-lived charge-separated state in the clusters [2]. The unexpectedly long lifetime of this state and the broad optical absorption spectrum of the clusters mean that ligand-stabilized silver clusters are promising materials for solar energy harvesting.

Unexpected charge separation was also observed in CdSe/CdS core/shell nanorods [3,4]. These nanocrystals consist of a small, nearly spherical CdSe core surrounded by a much larger, rod-shaped CdS shell. CdSe and CdS have a type-I band alignment, with both the band-edge electron and hole having lower energy in CdSe. Creation of an electron-hole pair in the CdS shell is therefore expected to be followed by trapping of both carriers in the CdSe core. Typically, this happens rapidly, on picosecond or sub-picosecond timescales, similar to the ultrafast charge separation observed in CdSe/CdTe nanocrystal heterostructures. We found that, contrary to this expectation, the electron remains delocalized in the shell over the entire recombination lifetime of the electron-hole pair, on the order of 10 ns. Experiments and calculations indicate that this delocalization is due to unusually slow relaxation from the second-lowest to the lowest-energy electron state in the nanocrystal. This inhibited relaxation provides a mean of controlling the spatial location of photoexcited electrons by excitation energy, and suggests that a simple picture of band alignment is insufficient for understanding charge separation in semiconductor nanocrystal heterostructures. Finally, it demonstrates that carrier relaxation processes in semiconductor nanocrystals can be strongly affected by the nanocrystal structure.

Another example of the relationship between carrier relaxation dynamics and structure is provided by CdSe nanoplatelets. Recently, methods have been developed for the colloidal synthesis of thin, flat semiconductor platelets with lateral dimensions in the range of 10 – 100 nm, and with thicknesses of only 5 – 7 monolayers. Absorption and emission spectra suggest that carriers in these platelets are confined in only one dimension, as compared to the two- or three-dimensional confinement that has previously been achievable in colloidal systems. Using time-resolved measurements of photoluminescence spectra from these nanoplatelets, we confirmed that carrier relaxation in these systems is consistent with one-dimensional confinement, meaning that these platelets are the colloidal equivalent of epitaxial quantum wells, and we showed that carrier relaxation occurs rapidly, on time scales of a few picoseconds [5]. This rapid relaxation, together with the high photoluminescence efficiency of the structures, make them promising as optical gain materials.

References

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