

Ultrafast Charge Transfer Processes across the Potential Barrier of Core/Shell Quantum Dots

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For semiconductor nanocrystals charge transfer from excitonic to surface states is the defining property that determines the efficiency. If the property of interest is photoluminescence quantum yield (PL QY) or fluorescence intermittency of single particles, charge transfer needs to be mitigated; while for photovoltaics, electroluminescence, or photocatalysis the transfer process needs to be maximised. Charge transfer has successfully been controlled with the growth of epitaxial shells, which are paramount for passivating the nanocrystal surface or for band structure engineering by adjusting band offsets and spatial confinement of electrons and holes.

An especially interesting case are CdSe/CdS core/shell particles, in which the conduction band offset is small and the electron can reach the surface while still maintaining high PL QY. We have measured electron transfer (ET) dynamics from the $1S_e$ electron state to adsorbed methyl viologen (MV^{2+}) acting as electron scavenger using femtosecond transient absorption (TA) spectroscopy. The $1S_e$ electron was extracted efficiently from the CdSe core, even for CdS shells up to 20 Å thick, with an exponentially decreasing ET rate for increasing shell thickness with an attenuation factor $\beta \approx 0.13 \text{ \AA}^{-1}$. We observed that compared to the ground state exciton $1S_e1S_{3/2}$, the electron coupled to the $2S_{3/2}$ hot hole state exhibited slower ET rates for thin CdS shells. We attribute this behaviour to an Auger-assisted ET process (AAET), which depends on electron-hole coupling controlled by the CdS shell thickness (see Fig. 1). [1]

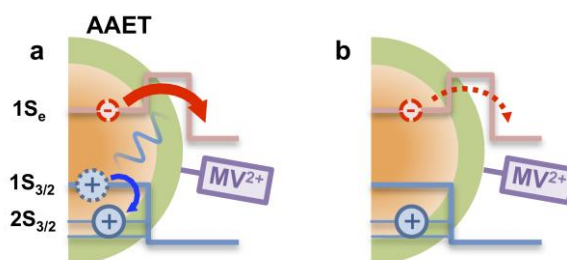


Fig. 1 The charge transfer of a conduction band electron to a surface-bound electron scavenger is aided by an Auger-like process that transfers energy to the hole. This pathway is less efficient if the hole is in an excited state.

The Auger process as well as the overall ET efficiency can be controlled by introducing a graded shell, in which the composition changes gradually from pure core to pure shell material. [2-4] Alloy formation mitigates crystal defects and reduces the Auger rate. [5] With prolonged exposure to high temperatures during shell growth or annealing, smoothing of the confining potential occurs [6], which is reflected by a 10-fold increase in ET rate in CdSe/CdS/ZnS core/shell/shell particles. A “sweet spot” between the two effects can be expected for intermediate grading. Using TA spectroscopy we are able to characterise the radial composition of graded shell nanocrystals by monitoring hot carrier cooling and ET rate. These results will allow a precise synthesis tailored to specific technological requirements.

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