Hot Electron Transfer from Semiconductor Nanocrystals[1]

David J. Norris
Optical Materials Engineering Laboratory
ETH Zurich, Zurich Switzerland

The maximum theoretical efficiency of a standard single-junction silicon solar cell is limited to ~31%, in part by the loss of any photon energy that exceeds the semiconductor bandgap.[2] Absorption of high-energy photons creates hot electrons and holes that cool quickly (within ~1 ps) to the band edges by sequential emission of phonons. There the carriers remain for hundreds of picoseconds or longer before slower processes such as radiative or nonradiative recombination occur. The goal of standard solar cells is to extract these band-edge electrons and holes to produce electrical current. However, because of the initial cooling process, a substantial amount of solar energy has already been irreversibly lost. If instead, all of the energy of the hot carriers could be captured, solar-to-electric power conversion efficiencies could be increased, theoretically to as high as 66%.[3] One can envision the realization of such a hot carrier solar cell in a semiconductor device where scattering among photoexcited electrons and reabsorption of additional photons in the conduction band is faster than hot-electron cooling, resulting in a quasi-equilibrium characterized by an electron temperature much higher than the lattice temperature. This is coupled with equally fast hot-electron transfer to an electron conductor in a narrow energy window (to minimize additional energy loss in the latter). The same argument applies to the holes.

A potential route to the above hot-carrier solar cell is to use semiconductor nanocrystals, or quantum dots.[4] In these materials, the quasi-continuous conduction and valence energy bands of the bulk semiconductor become discretized owing to confinement of the charge carriers. Consequently, the energy spacing between the electronic levels can be much larger than the highest phonon frequency of the lattice, creating a "phonon bottleneck" in which hot-carrier relaxation is only possible via slower multiphonon emission.[5] For example, hot-electron lifetimes as long as ~1 ns have been observed in quantum dots grown by molecular beam epitaxy.[6] Even in colloidal quantum dots, which are coated with surfactant molecules that provide additional high-frequency vibrations for carrier relaxation, long lifetimes have been demonstrated through careful design of core-shell structures and control of interfaces.[7] Such slowing of electron relaxation in core-shell quantum dots has recently been shown to allow the tunneling of hot electrons through the shells to surface trap states.[8]

Because of their ability to slow electronic relaxation, quantum dots can in principle enable extraction of hot carriers (to electron or hole conductors) before they cool to the band edges, leading to more efficient solar cells.[9] However, hot-carrier transfer from nanocrystals to an electron or hole conductor had not been observed until

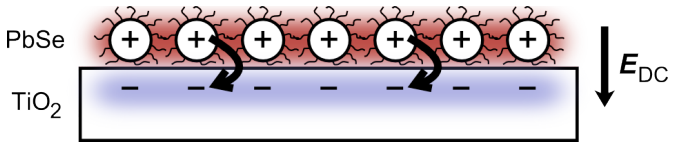

Fig. 1 We will discuss hot-electron extraction from colloidal PbSe quantum dots to a single-crystalline TiO_2 substrate. The dc electric field induced by the electron transfer was detected via time-resolved second harmonic generation.

recently. Here, we will discuss experiments (Fig. 1) that show that electron transfer from the higher excited states of a colloidal semiconductor nanocrystal (PbSe) to a common electron acceptor (TiO_2) is indeed possible and, with appropriate chemical treatment of the nanocrystal surface, occurs on an ultrafast time scale (<50 fs).

We utilized optical second harmonic generation (SHG)[10] to probe the transfer process. This technique offers femtosecond time resolution with sufficient sensitivity for well-defined crystalline interfaces. In a centrosymmetric semiconductor such as rutile TiO_2, the second harmonic response originates only from the first few atomic layers near the surface. Thus, SHG should be extremely sensitive to changes in the local electronic environment resulting from interfacial electron transfer.

The SHG signal shows a sudden rise due to hot electron transfer from the quantum dots to the substrate. In addition, we observed oscillations due to coherent surface phonons in the TiO_2 substrate that resulted from the sub-50 fs charge separation across the PbSe-TiO_2 interface.

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