

# Engineering Thermal Losses on Quantum Dot Sensitized Oxides

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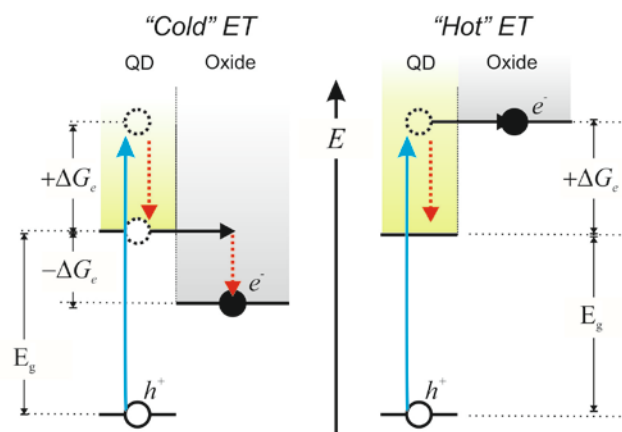
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While metal oxides constitute robust and relatively cheap semiconductor materials that are finding increasing applications in opto-electronics, their band gaps are typically prohibitively wide for the generation of electron–hole pairs through the absorption of visible light. Several approaches have been developed to circumvent this drawback. Specifically, the sensitization of mesoporous oxides by semiconductor quantum dot (QD) nanocrystals represents a promising route for the development of low-cost solutions for energy production (i.e., in QD sensitized solar cells) and storage (i.e., photo-catalysis for water splitting).

Under conventional operating conditions (see figure 1 left), sunlight is absorbed by a semiconductor quantum dot which is anchored to the surface of a semiconducting oxide nanoparticle. Any excess energy of the impinging photon vs the QD absorption onset ( $+\Delta G_e$  in fig. 1) is primarily dissipated as heat within the QD (intra-band relaxation in the QD). Afterwards, the exciton contained in the QD can be dissociated into free electrons at the oxide metal contact following electron transfer (ET, see fig. 1). The excess energy between QD LUMO and the bottom of the oxide CB ( $-\Delta G_e$  in fig. 1) constitutes a second thermalization process (now in the oxide CB) which reduces the available energy in the system to produce work (with a maximum value given by  $E_g - \Delta G_e$  in fig.1). In order to prevent the latter, an Ohmic contact should be established between sensitizer and an oxide electrode,  $-\Delta G_e \rightarrow 0$ , however one should take into account that the delicate charge kinetic balance of the system can be dramatically affected (e.g. reduced  $-\Delta G_e$  implies slower ET, then radiative relaxation within the QD could compete kinetically). This kinetic competition is at the core of the



**Figure 1:** (Left) Sketch of a QD sensitized oxide after photo-induced electron transfer (ET) to the oxide,  $+\Delta G_e$  and  $-\Delta G_e$  represent thermalization processes taking place in the QD and oxide respectively. (Right) Sketch of a QD sensitized oxide after photo-induced hot electron transfer; intra-band thermalization processes are circumvented.

tradeoff between sensitized solar cells showing low voltage and high current or vice versa. To circumvent this problem, we have shown before that the coupling between QD-oxide can be boosted by properly tuning interfacial chemistry; furthermore, a novel approach based on exploiting molecular dipoles at QD surface has been suggested to both been able to reduce  $\Delta G_e$  and speed up ET simultaneously. Furthermore, in the quest towards photo-conversion efficiencies beyond the Shockley-Queisser limit, one can aim to extract electrons from the sensitizer even before thermalization within the QD takes place ( $\pm\Delta G_e$  losses are prevented, see figure 1 right). All together engineering thermal losses in QD-oxide systems seems a mandatory route for optimizing technical applications aiming low cost solar energy conversion.

In this work, photo-induced electron transfer (ET) processes in PbS/SnO<sub>2</sub> based electrodes grown by successive ionic layer adsorption and reaction (SILAR) are investigated using optical pump-THz probe (OPTP) spectroscopy. The QD sensitization of a mesoporous oxide matrix by SILAR is achieved by repeated cycles of 4 successive dipping steps of an oxide film into beakers containing: (i) a cation solution (ii) pure solvent to remove the excess of unbound cations, (iii) an anion solution and (iv) pure solvent to remove the excess of unbound anions. Following the growth of PbS dots, molecules with gas phase dipolar moments between  $-3$  and  $+5$  Debyes are used to functionalize the QDs, with the aim of reducing thermal losses at the QD/oxide contact by tuning QD-oxide relative work-functions. Independently of QD surface capping, we found that ET rates are invariant, implying negligible influence of the molecular capping on  $-\Delta G_e$ ; this is rationalized by Fermi level pinning of the QD LUMO states at the QD/oxide interface. On the other hand, back electron transfer from the oxide to the dot is modulated by the dipole moment of capping molecules; Indicating that certain degree of tunability of the QD HOMO states is doable by exploiting molecular dipoles at QD-oxide interfaces (e.g. useful to prevent thermal losses for hole extraction in complete solar cells). From these results we conclude that decoupling between the QD and the oxide is a mandatory request for reducing thermal losses at the oxide metal contacts. Furthermore, the ET rates in SILAR based QD sensitized oxides are found to be highly dependent on excitation photon energy. Up to 100% hot electron transfer yields are resolved at room temperature for excess energy exceeding  $+\Delta G_e \sim 1\text{eV}$ . This onset can be reduced with reducing the temperature of the system, illustrating the kinetic competition between QD intra-band relaxation and hot electron transfer towards the oxide.