

Dipolar Capping of Quantum Dots: Opportunities and Challenges for Solar Energy Conversion

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Achieving efficient surface passivation schemes in quantum dot (QD) nanocrystals is essential for their implementation in novel optoelectronic devices. The passivation of QD surfaces is commonly achieved by capping the semiconducting nanocrystals with molecular agents, inorganic shells or even atomic treatments. All these treatments aim for the suppression of non-radiative relaxation paths for photo-excited charge carriers. Beyond obtaining an effective QD surface passivation treatment, the synergy between QDs and their capping agents offers a plethora of opportunities for controlling nanocrystal stability and QD optoelectronic properties, including bandgap, doping and work-function tuning.

One appealing path for tuning QD work-function is based on exploiting molecular dipoles as a QD passivation shell[1-6]. Applying QD dipolar capping (QD-DC) treatments represents a desirable route for improving the performance of solar cell device geometries, where the QD-DC treatments, apart from providing a reliable passivation scheme for the QDs, may improve charge collection at contacts (by generating a cascaded energy level architecture [1-3]), or be employed for minimizing thermal losses at the electrodes (aiming establishing Ohmic contacts [4-5]). These aspects have the potential of enhancing short circuit currents and open circuit voltage in QD based solar cells.

QD-DC treatments have been analyzed previously in QD sensitized architectures [4,5]. In these reports the QD-DC treatment recipe was expected to tune QD-oxide donor-acceptor energetics; such treatments should improve solar cell output voltage in devices by reducing interfacial thermal losses at the QD-oxide electrode [6]. These reports exploiting QD-DC treatments found that the QD sensitized solar cell performance was optimized upon dipolar treatments, with a reported induced gain in photo-voltage onset (PV) of $\Delta PV/\mu \sim 20$ meV/Debye. Remarkably, these findings appear to be very modest when compared with those obtained in QD-DC solids, where changes in the QD work-function as large as 400meV/Debye were reported [1]. The reason for the weaker work-function tunability in QD

sensitized oxides upon QD-DC treatments when compared with QD solids remains an open question.

In this contribution [7], we analyze interfacial dynamics in QD sensitized oxides as a function of QD-DC treatments. We resolve that interfacial ET rates, which are directly correlated with donor-acceptor energetics in QD sensitized oxides [8], are invariant to QD-DC treatments; this occurs despite an efficient molecular capping of the QDs (as revealed by THz spectroscopy, XPS and theoretical modelling). Photoelectron Spectroscopy reveals that the QD work-function remains invariant towards the sign and magnitude of the analyzed QD dipolar capping treatments; consistent with the invariance of the monitored donor-to-acceptor electron transfer rates by THz spectroscopy. These findings are rationalized by Fermi level pinning at the strongly coupled QD-oxide interface; this interfacial feature, which has been previously resolved in QD sensitized systems based on TiO₂, ZnO and SnO₂ electrodes [9,10,11], precludes tuning of donor-acceptor energetics by QD-DC at QD sensitized oxide interfaces.

Finally, we will show how a simple approach consisting on placing an insulating layer between donor and acceptor might enable the tuning of donor-acceptor energetics in QD sensitized oxides by QD dipolar molecular capping. These findings may open the path for establishing Ohmic contacts between the QD LUMO and CB electrode contacts in device architectures. Reducing the energy cost of exciton dissociation at the QD-oxide interface have the potential of boosting open circuit voltages and hence improving efficiencies in sensitized solar cell devices.

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