## **Quantum Dots Based Photo-Electrochemical Solar Cells**

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Quantum dot sensitized solar cell (QDSSC) is considered to be a simple analogue of dye sensitized solar cell (DSSC). The only apparent difference involves the replacement of the organometallic or organic dyes with QD sensitizers such as CdS, CdSe, PbS, PbSe and InP. Otherwise the basic cell mechanisms, including charge separation by the sensitizer, charge transport in both the mesoporous electrode and the electrolyte, and the recombination paths seem to be similar to those of DSSC. The replacement of dye sensitizers by QDs is motivated by their absorption coefficient which is higher than most dyes, and the size confinement that allows tailoring of their absorption spectrum. Moreover the use of QDs opens new possibilities for third generation solar cell configurations such as multiple carrier generation (MEG) and hot electron injection. However, in spite of their great potential, the conversion efficiency of QDs sensitized solar cells has reached only ~6%, a low value compared with the DSSC analogue. The rather low efficiencies of QDSSC were attributed mainly to the charge separation and recombination processes at the TiO<sub>2</sub>/QD/electrolyte junctions.

Recently we reported on the use of a pure QDs photoactive electrode to form a tandem photo-electrochemical solar cell. The half cell arrangement of this QD solar cell (entitled QD<sub>FTO</sub> in the following) contained a QD layer deposited directly on Fluorine doped Tin Oxide (FTO) glass, polysulfide electrolyte (based on 1M Na<sub>2</sub>S, 0.1M S and 0.1M NaOH) and a Pt counter electrode as shown in Fig 1. Under one sun illumination,  $QD_{FTO}$  exhibit photovoltages up to 650mV and short circuit currents of ~2mA/cm<sup>2</sup>, which implies that QDs can build up chemical potential in the presence of the liquid electrolyte. This understanding opens a discussion on the mechanisms of QDSSCs which also utilize a QD layer as the photoactive component.

Here we report on new measurements of  $QD_{FTO}$  which point toward conceptual differences between DSSC to QDSSC. The  $QD_{FTO}$  configuration, in which a QD layer is deposited directly on FTO glass, enables direct photo-electrochemical study of the QDs without interference of the mesoporous TiO<sub>2</sub> electrode. We show that solar cell based solely on QDs can generate photovoltaic activity when immersed in polysulfide electrolyte. Advanced characterization, utilizing charge extraction and open circuit voltage (Voc) decay techniques, quantify the charge accumulated in the QDs layer and the rate at which it recombines with the surrounding electrolyte. The results provide new insight of a fundamental difference between DSSC and QDSSC which is critical for further improvement of QD sensitized solar cell.



**Figure 1**. Energy band diagram showing the charge transfer processes in (a) DSSC: electron injection from the excited dye state to the  $TiO_2$ -CB while holes are removed by the electrolyte. The major path for recombination is from the  $TiO_2$ -CB to the electrolyte. (b) QDSSC: fast electron injection from the QD excited state directly to the  $TiO_2$ -CB or through the QD surface states (slower injection process), while holes are removed by the electrolyte. The main recombination paths are (1) from the  $TiO_2$ -CB to the electrolyte, (2) from the QD (CB or surface states) to the electrolyte and (3) internal recombination within the QD. (c) QD<sub>FTO</sub>: photo-generated holes are removed by the electrolyte while the excited electrons diffuse within the QDs layer. The major recombination paths in QD<sub>FTO</sub> are (1) from the QD (CB or surface states) to the electrolyte and (2) internal recombination within the QD.