

Quantum Dot Sensitized Solar Cells: Materials and Mechanisms

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Quantum dot sensitized solar cells (QDSSCs) are gaining attention as they show promise toward the development of next generation solar cells. They consist of a mesoporous wide band gap semiconductor (usually TiO_2), which is sensitized with low band gap semiconductor nanocrystals, polysulfide redox couple and a counter electrode. Upon excitation, electrons are injected from the semiconductor nanocrystals to the TiO_2 followed by diffusion to the front contact, while holes are transferred to the electrolyte for regeneration at the counter electrode.

Quantum dots (QDs) have attracted much attention because of their large absorption coefficient and the possibility to tune their absorption spectrum by quantum size confinement. Despite their great potential, however, the conversion efficiency of quantum dot sensitized solar cells is still very low compared to that of conventional dye sensitized solar cells (DSSCs). The factors limiting the power conversion efficiencies of QDSSCs include the recombination pathways formed at the TiO_2 /QD/electrolyte triple junction, low photo-voltages compared to the standard DSSCs and the absorption spectrum of the efficient sensitizers. In recent years, we focus on acquiring better physical understanding of the fundamental mechanisms of QDSSCs aiming at methods to overcome some of the performance limiting factors.

A significant part of our research has been devoted to the basic understanding of QDSSCs mechanisms. In order to gain deeper insights about the factors limiting the performance of QDSSCs, we have developed a unique electrochemical characterization method that offers the possibility of separating the contribution of each cell component to the overall cell operation. This method utilizes the novel concept of a photoreference electrode for electrochemical measurements in a three-electrode mode. Using this technique, we were able to provide quantitative information regarding the potential losses associated with the counter electrode. Moreover, the method enabled a direct calculation of a recombination current, which arises from insufficient regeneration of the redox electrolyte by the counter electrode. Consequently, it became clear that an improvement in the catalytic nature of the counter electrode will not only reduce potential losses in the photoelectrochemical cell, but will also improve the charge collection efficiency, resulting in significant improvement of the overall cell performance. Additionally, to explore the intrinsic electronic properties of the QDs, we designed a solar cell structure consisting only of QDs and liquid electrolyte. Using these cells, we applied characterization tools, such as transient photovoltage and charge extraction, to study the nature of the surface states, the Fermi level and the effect of charge within the QDs. The changes in the Fermi level position with respect to the

electrolyte and the buildup of chemical potential in both the n and p type QDs resulted in significant insight about the electronic properties of the QDs. Finally, we confronted a basic question: Is a QDSSC a simple analogue of a DSSC? Until recently, it was assumed that QDs act as a simple analogue of the conventional dye with no conceptual difference between the operation mechanisms of both types of cells. However, intensive physical analysis of our cells revealed fundamental differences between QDSSCs and DSSCs. Using electrochemical impedance spectroscopy, we have explored the electrical properties of the $\text{TiO}_2/\text{QDs}/\text{electrolyte}$ triple junction formed at the sensitized electrode. We showed that a fingerprint of QDs is present in the device capacitance, indicating that QDs surface states take part in the electrode's density of states alongside the well-known contribution of TiO_2 . This discovery provided an important proof for the major role played by QDs in the recombination processes in the cell.

To reduce the recombination rate in these cells, we introduced a new type of MgO coating that dramatically increases the lifetime of electrons and consequently improves the cell efficiency. Coated at the TiO_2/QD interface the MgO slows back transfer of electrons to the electrolyte via the QDs. This study emphasized that in QDSSCs electrons can recombine both from TiO_2 and from the QDs to the electrolyte.

Unlike in DSSCs, the QD sensitizer layer can be modified in order to alter the relative energetics within the cell, thus affecting both charge injection and recombination mechanisms. To improve the injection of electrons from the QDs to the TiO_2 , we modified the QDs with dipoles. This modification leads to the adjustment of the energy level of the QDs with respect to the mesoporous TiO_2 bands and those of the TiO_2 with respect to the electrolyte, thus increasing both the photocurrent and photovoltage of the cells.

Finally, we examined the wide bandgap electrode material and morphology. The use of thick QD sensitizing layer opens the path for investigation of flat systems as models. Using combinatorial methods we conduct a search of new metal oxides aiming mostly at higher photovoltages in QDSSCs. Preliminary results suggest that materials operating better than TiO_2 can be found.