Probing the operation mechanism within quantum dot-based solar cells

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Colloidal quantum dots (QDs) provide a unique material platform for a wide variety of applications due to new physics that comes into play at the nanoscale. Additionally, the ease of synthesis allows for well-controlled uniform samples while using cost effective precursors. The processing of QDs into films and optoelectronic devices has seen vast improvements over the past few years. In particular, QDs can be used in photovoltaic devices as light sensitizers for wider bandgap semiconductors, electron or hole conductors within composite films, an absorber layer that acts to both absorb light and transport charge within a quantum-confined yet electronically coupled array (here termed quantum dot solar cells (QDSCs)), or simply as an ink to provide a new route toward bulk materials (here termed ink-based solar cells). In this talk, I will discuss recent developments made on the latter two applications of QDs for photovoltaics.

Devices with PbSe QDs have been optimized to provide measured external quantum efficiencies greater than 100% attributed to multiple exciton generation, thus greatly motivating more research on this type of solar cell. The power conversion efficiency of QDSCs is rapidly increasing from improved device architectures that allow for enhanced and selective charge extraction interfaces within the device stack. To date, the *p*-*n* depleted heterojunction model is often used to describe the operation of QDSCs. The state of the art (highest overall efficiency) optimized structure involves ohmic contacts to an *n*-type transparent window layer (TiO_2, ZnO nanocrystals, and others) and a thin film of an array of electronically coupled ~1.3 eV PbS quantum dots (QDs). It has been reasoned that band bending in the PbS QD layer at the heterojunction interface

creates a space charge region in the presumably *p*-type film, such that all photogenerated charge carries are transported and collected through drift currents. It is not known how band bending that occurs in traditional bulk semiconductors will develop within the QD layer that possess quantized yet coupled energy levels. Advancements in device efficiency can likely follow if better understanding of interfacial energetics and how photogenerated carriers are collected at the electrodes, through either drift or diffusion currents. Utilizing scanning Kelvin probe microscopy (SKPM), we have correlated the contact potential difference between a conductive AFM tip and the layers within an operating CQDSC cross-section to effectively map the potential throughout the device as a function of bias applied to the electrodes. This allows us to directly visualize regions of localized band bending and space charge. We find a lack of band bending, indicating a minimal space-charge region at the ZnO/PbS hetero-interface. Rather, our SKPM profiles suggest that photogenerated charge carriers are transported in field free layers likely *via* diffusion. We compare the SKPM data to an in-depth capacitance-voltage study, highlighting differences between the operating principles of CQDSCs vs. the traditional *p-n* junction model. This work challenges the notion of the depleted heterojunction architecture in the effort to develop a more accurate model for CQDSC device operation.

Additionally, we have developed the use of CdTe QDs to create bulk, sintered films for ink-based solar cells. Here, respectable efficiencies of >12% have been achieved in devices where CdTe tetrapods are spincoated from pyridine onto ITO, treated with $CdCl_2$ and briefly annealed (20 s on a hotplate set to 350 C). ZnO sol-gel is deposited on top of the CdTe layer. The devices show enhanced performance after a short light soak in forward bias. We have inserted these QD-based CdTe layers into more than seven device geometries with various contact layers. We determine that there is a unique interface that forms between the ITO layer and CdTe layer that provides excellent ohmic hole contact after this light soak in forward bias. Moreover, the devices have an impressive blue-response in comparison to standard CdTe solar cells despite having the junction at the back of the optical path rather than as a window layer. The operational

mechanism of these ink-based CdTe devices will be discussed in comparison to traditional CdTe technology.