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Link Foundation Energy Fellow (2009-2012) - Final Report

Link Energy Fellowship Research Summary

Introduction

Significant technological advances will be required to economically utilize photovoltaic (PV) technology at the terawatt scale. So called "third generation" PV technologies will retain the low cost of emerging thin film solar cells but, through the use of new materials and device architectures, they will achieve power conversion efficiencies comparable to or even exceeding silicon cells available today.

Organic semiconductors, including small molecules and polymers, are promising candidate materials for realizing third generation PV technology. They possess very high absorption coefficients relative to inorganic semiconductors and are compatible with low-cost deposition techniques that could enable inexpensive scaling of manufacturing. However, due to poor charge transport characteristics and the fact that absorption in these materials is limited to visible wavelengths, power conversion efficiencies for organic photovoltaic (OPV) devices are generally too low to be economically viable.

It may be possible to increase the efficiency of OPVs without sacrificing their inherent low cost by incorporating artificially nanostructured materials into device structures. Of particular interest are chemically synthesized nanocrystal quantum dots (QDs). QDs are compatible with the same low-cost deposition techniques available for organic semiconductors and have a broad optical response that can be tuned from visible to infrared wavelengths by selection of the type and physical size of the nanocrystals. This tunability may enable multi-junction solar cells of high efficiency in which each layer is sensitized to a different part of the solar emission spectrum.

A second material system of interest includes J-aggregating dyes. J-aggregates represent a unique class of organic semiconductor that has a tendency to form supramolecular structures with optical properties that can be very different from their monomer constituents. In particular, J-aggregates exhibit extremely intense and narrow absorption peaks that can enable almost 100% of incident light to be absorbed in a film that is on the order of 10 nm thick. This unique property makes J-aggregates attractive for use as active layers in multi-junction solar cells.

The aim of the work conducted during my tenure as a Link Foundation Energy Fellow was (1) to investigate the fundamental excitonic and charge transport processes that are relevant in nanostructured photovoltaic structures, and (2) to demonstrate photovoltaic structures that incorporate novel nanostructured materials (QDs and J-aggregates) toward realizing high efficiency and low cost solar cells.

Results

One of the key challenges associated with utilizing colloidal QDs as an active layer material in photovoltaic structures pertains to the need for organic ligands to passivate electronic defects on the QD surfaces and to prevent the aggregation of the QDs in solution. When dispersed into a thin film, the presence of these organic ligands mediates the inter-particle spacing of the QDs and acts as an insulating barrier that impedes charge transport. This results in very low mobility of charge carriers, which is highly undesirable in a solar cell structure. A promising approach toward overcoming this problem is to employ ligand exchange treatments to QD thin films in order to replace long and bulky native ligands with ones that are much shorter. This facilitates a shorter inter-particle spacing and higher carrier mobility. We demonstrated several QD-based solar cell architectures that incorporate PbS QD films treated with ethanedithiol (EDT) ligands, including a hybrid organic structure (Zhao et al, 2010) and a hybrid metal oxide structure with a power conversion efficiency (PCE) > 3% (Brown et al, 2011).

Despite considerable progress in this field, aspects of charge transport in QD films remain poorly understood. In particular, a rapid bias-stress effect, or shift in threshold voltage (ΔV_T) with the application of a gate bias, was observed in several studies of lead chalcogenide QDs in field-effect transistor (FET) structures. The instability associated with bias stress precludes practical applications of QD FETs, but more critically, makes the interpretation of their characteristics very complicated. This, in turn, complicates the characterization of QD materials that are of interest for solar cells. To address this problem, we investigated the origin of this phenomenon in EDT-treated PbS QD FETs by studying the dynamics of the stressing process as a function of dielectric material, drain bias, gate bias, temperature, and QD size. We determined that bias stress in this system indeed originates from charge trapping in the bulk QD film and not at dielectric interface states. Moreover, our investigation suggests that the instability may in part be due to charge-induced ionization of the EDT ligands themselves (Osedach et al, 2012).

Finally, we sought to incorporate J-aggregate materials into a photovoltaic structure that would take advantage of their unique optical characteristics. We demonstrated a near-infrared photodetector that consists of metal oxide charge transport layers and J-aggregates of the cyanine dye, U3, as the photoactive layer. Optimization of optical interference effects within the structure to maximize optical absorption in an ultrathin J-aggregate film resulted in an external quantum efficiency (EQE) of 16.1%.

Significance and Impact

Our investigation of the charge trapping mechanisms and bias-stress effect in PbS QD FETs is of direct relevance to researchers studying QD-based photovoltaic structures, where the occurrence of charge trapping can significantly affect device performance. The techniques that we employed to characterize the bias-stress effect in QD FETs may be useful for assessing the quality of surface passivation achieved by new ligand exchange treatments in the future. The demonstration of a high-performance photodiode based on an ultrathin film of J-aggregating dye serves as a proof-of-concept for the use of this unique type of organic semiconductor in optoelectronic devices. The obtained EQE of 16.1% is the highest reported in a photosensitive device that incorporates a neat film of J-aggregating dye. The exploration of new materials for renewable energy undertaken here, with the support of the Link Foundation Energy Fellowship, directly supports ongoing global efforts to realize a competitive third-generation solar cell technology.

Future Directions

Two important directions for the improvement of QD photovoltaic performance include (1) engineering the chemistry of QD films through the exploration of new ligands and surface modification techniques, and (2) the development of more sophisticated devices structures that incorporate QD films. For example, structures with textured transport layers to improve carrier collection efficiency from QD films may achieve this aim. With regard to J-aggregates, the primary shortcoming of the U3 material used in our work is a low transverse exciton diffusion length that substantially reduces internal quantum efficiency. This problem may be overcome by means of chemical modification of the U3 film to enable increased electronic interaction between adjacent layers of the J-aggregate molecules or by the exploration of entirely different material systems characterized by higher exciton diffusion lengths. The ultimate maturity of photovoltaic structures consisting of either of these material systems would be a multi-junction cell in which each sub-cell is specifically tuned to a different part of the solar spectrum. In the case of QDs, this would simply involve the incorporation of QDs of varying sizes (bandgaps). In the case of J-aggregates, a suite of dyes that are sensitive across the visible and infrared would need to be identified and successfully integrated into photodiode structures. Such a highly engineered multijunction structure may enable power conversion efficiencies exceeding those of conventional single-junction inorganic solar cells to be realized. Since both of these material systems involve low-temperature synthesis and processing, such structures may potentially also be less expensive than their conventional inorganic counterparts.

Publications with Acknowledgement of Link Foundation Support

1. **T. P. Osedach**, A. Iacchetti, R. R. Lunt, T. L. Andrew, P. R. Brown, G. Akselrod, V. Bulović. Near-Infrared Photodetector Consisting of J-Aggregating Cyanine Dye and Metal Oxide Thin Films, Submitted.

2. **T. P. Osedach**, N. Zhao, T. L. Andrew, P. R. Brown, D. B. Strasfeld, D. D. Wanger, L.-Y. Chang, M. G. Bawendi, V. Bulović. Bias Stress in 1,2-Ethanedithiol-Treated PbS QD Field Effect Transistors. *ACS Nano*, **2012**, 6, 3121-3127.

3. R. R. Lunt, **T. P. Osedach**, P. R. Brown, J. A. Rowehl, V. Bulović. Practical Roadmap and Limits to Nanostructured Photovoltaics. *Adv. Mater*. **2011**, 23, 5712-5727.

4. P. R. Brown, R. R. Lunt, N. Zhao, **T. P. Osedach**, D. D. Wanger, L.-Y. Chang, M. G. Bawendi, V. Bulović. Improved Current Extraction from ZnO/PbS Quantum Dot Heterojunction Photovoltaics Using a MoO_3 Interfacial Layer. *Nano Lett.* **2011**, 11, 2955-2961.

5. **T.P. Osedach**, N. Zhao, S.M. Geyer, L.-Y. Chang, D. D. Wanger, A.C. Arango, M.G. Bawendi, V. Bulović, Interfacial Recombination for Fast Operation of an Infrared Organic/QD Photodetector. *Adv. Mater.* **2010**, 22, 5250-5254.

6. N. Zhao, **T.P. Osedach**, L.-Y. Chang, S.M. Geyer, D. D. Wanger, M.T. Binda, A.C. Arango, M.G. Bawendi, V. Bulović. Colloidal PbS Quantum Dot Solar Cells with High Fill Factor. *ACS Nano* **2010**, 4, 3743-3752.

Usage of Discretionary Funds

During my first year, I used my Link Fellowship discretionary funds to purchase a high speed / low noise current amplifier. This directly facilitated my study of carrier recombination at a QD/organic heterointerface, which resulted in a publication in *Advanced Materials*. During my first year, the travel component of my fellowship also enabled me to present this work at the *International Conference on Organic Electronics* in Paris (June 2010). During the second year of my fellowship, I used my discretionary funds to purchase glass substrates patterned with gold electrodes. These substrates were used to fabricate QD-based field-effect transistors, resulting in my communication in *ACS Nano* on the bias-stress effect in this system.

Value of the Link Fellowship

The Link Foundation Energy Fellowship was a vital source of support to my graduate studies. I believe it was especially useful to be supported during my latter years of graduate school. The fellowship gave me the liberty to freely pursue project ideas and research directions during my most creative and productive stage of doctoral study. The available of discretionary and travel funds were also very useful and substantially contributed to my graduate school experience. The former enabled me to make decisive equipment and research material investments that opened up new project directions and accelerated my progress. The availability of funds for travel enabled me to attend and present my work at an international conference that I would otherwise have not been able to attend. My Link Foundation Energy fellowship was a tremendously valuable source of support during my doctoral study and I am truly grateful to have been the recipient of this honor.