

Multiple Exciton Generation in Quantum Dots, Quantum Dot Arrays, Quantum Dot Solar Cells, and via Molecular Singlet Fission: Application to Next Generation Solar Photon Conversion to PV and Fuel

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Abstract

In quantum dots (QDs), quantum rods (QRs) and unique molecular chromophores that undergo singlet fission (SF) the relaxation pathways of photoexcited states can be modified to produce efficient multiple exciton generation (MEG) from single photons. We have observed efficient MEG in PbSe, PbS, PbTe, and Si QDs and efficient SF in molecules that satisfy specific requirements for their excited state energy levels. We have studied MEG in close-packed QD arrays where the QDs are electronically coupled in the films and thus exhibit good transport while still maintaining quantization and MEG. We have developed simple, all-inorganic QD solar cells that produce large short-circuit photocurrents and respectable power conversion efficiencies via both nanocrystalline Schottky junctions and nanocrystalline p-n junctions. These solar cells also showed for the first time external quantum yields (QYs) for photocurrent that exceed 100% in the photon energy regions of the solar spectrum where MEG is possible (i.e., energy conservation is satisfied); the photocurrent internal QYs from MEG as a function of photon energy match those determined via time-resolved spectroscopy and the results settle controversy concerning MEG.

We have also observed very efficient SF in thin films of molecular crystals of 1,3-diphenylisobenzofuran with quantum yields of 200% at the optimum SF threshold of $2E_g$ (HOMO-LUMO for T_1-S_0), reflecting the creation of two excited triplet states from the first excited singlet state. Various possible configurations for novel solar cells based on MEG in QDs

and SF in molecules that could produce high conversion efficiencies will be presented, along with progress in developing such new types of solar cells.

Recent analyses of the dramatic effects of solar concentration combined with MEG or SF on the conversion efficiency of solar cells will also be discussed. The properties required for

nanocrystals and SF molecules to achieve the high solar conversion efficiencies predicted by theory will be presented.

Regarding production of solar fuels, all viable systems must have the following features: (1) two photosystems arranged either in a Z-scheme analogous to biological photosynthesis, or two tandem *p-n* junctions connected in series where sufficient photopotential (1.23 V + overvoltage for H₂O splitting) is generated to drive the redox reactions; (2) strong absorption of solar photons; (3) efficient separation of the photogenerated e-h pairs, (4) efficient transport to and collection of the separated carriers at electrocatalytic surfaces; (5) low overvoltages; (6) appropriate alignment of the redox potentials in the photoelectrodes with those of the fuel-producing reactions; and (7) resistance to dark- and photo-corrosion achieving long-term photostability. Cells with buried junctions in a tandem p-n configuration or a Z-scheme can achieve these requirements, and assuming an overvoltage of 0.4V the optimal bandgaps are 0.8 eV and 1.5 eV, and the maximum PCE is 33%. The structure is similar to a tandem PV structure with an SQ limit of ~44-45%. Requirements (6) and (7) are very problematic but can be met using buried junctions so that the electrochemical redox reactions occur on highly conducting (viz. metal) electrodes ensuring the e- and h+ energy levels automatically align with the redox potentials of the two oxidation and reduction half-reactions as photopotential generated in the cell drops across the Helmholtz double layer at the metal-aqueous electrolyte interface, and not across the semiconductor depletion layer, and the photoactive regions are encapsulated with corrosion resistant material to isolate them from aqueous electrolyte, preventing photocorrosion and avoiding a major problem that plagues the conventional photoelectrochemical approach.

One issue with buried junctions is that when scaling the systems up to large areas it is necessary to ensure that the performance and PCE of the system is not limited by ohmic losses due to rate-

limiting H^+ diffusion from the anode region to the cathode region of the cells. This issue can be readily solved by perforating the planar cell structure with liquid electrolyte channels containing barriers or membranes that allow H^+ transport but not molecular H_2 or O_2 transport. Another approach is make electrical contact between the outer conductive layer of the cathode (anode) and a separate catalytic metal cathode (anode) that is placed directly opposite the anode region, such that the gas evolving anode and cathode surfaces face each other and the H^+ diffusion path can thus be made very short.