

Bandgap-limited open-circuit voltage in planar heterojunction photovoltaics using printed colloidal quantum dots as a photosensitive layer

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Although shipments of solar photovoltaic (PV) modules are at record levels, higher conversion efficiencies and higher-throughput manufacturing processes are critically needed in order for solar PV to become a significant part of energy production in the US. Nanostructured PV utilizing small molecule organics or conjugated polymers offer processing advantages, but efficiencies have remained low due in large part to low open-circuit voltages (V_{oc}). Using printing methods, we deposit a layer of colloidal cadmium selenide (CdSe) quantum dots (QDs) onto a wide band-gap organic hole-transporting thin film of N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-9,9-spiro-bifluorene (spiro-TPD) in order to form a unique planar heterojunction PV device that produces much higher V_{oc} than previously predicted for nanostructured heterojunction PVs. Absorption and charge generation occur primarily in the QD layer and indium-tin-oxide (ITO) provides the top contact, allowing for exceptional device stability and full transparency below the QD bandgap of 2.0 eV. Overall power conversion efficiencies remain low at 0.04% because only a small percentage of the incident light is absorbed (4% at the first QD excitonic peak of 2.1 eV) and fill factors are near 0.4, yet V_{oc} is 1.3V. The internal quantum efficiency (IQE) exhibits a strong dependence on QD film thickness and reaches a maximum of 30% at a thickness of 3-4 monolayers, indicating that resistive losses dominate photocurrent generation for QD thicknesses above 4-5 monolayers. The high V_{oc} is remarkable for an architecture with symmetric electrodes and far exceeds the offset between the highest occupied molecular orbital (HOMO) of the acceptor (near 5.2 eV) and the lowest unoccupied molecular (LUMO) orbital of the QDs (near 4.6 eV). From the bias-dependence of quantum efficiency, we identify an intensity-independent built-in photovoltage of 1.5 V that sets an upper limit on the maximum attainable V_{oc} . Investigation of the photocurrent transients reveals a vast discrepancy between the time constant associated with charge extraction (0.6 μ s, measured at 0V) and that of recombination (0.7 ms, measured at 2 V). We conclude that suppression of non-radiative recombination in the QD film and across the heterojunction interface produces the condition where V_{oc} is limited by the optical gap of the QD film rather than the HOMO/LUMO offset. Because the device architecture is straightforward and fabrication techniques are facile, tandem cells are easily attained, furthering the prospect for high conversion efficiencies coupled with the potential for scaleable manufacturing.