

## Project 04: Metal Oxide/Organic Hybrid Solar Cells

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### Introduction

Organic PV solar cells offer exciting possibilities for low-cost solar energy harvesting, especially in terms of energy payback time. Their solar power conversion efficiencies are now experiencing a plateau of ~5% under standard solar illumination conditions, with the record now at 6%<sup>1</sup> using carefully-designed low-bandgap electron donors with fullerene derivatives. Bulk carrier mobilities in such systems are low, especially electron mobilities, which imposes a fundamental limit to the efficiencies that these devices can reach. To address the shortcomings of organic PV devices, we propose hybrid organic/inorganic PV structures where the electron acceptor/transport layer is replaced with a semiconducting transparent metal oxide thin film. Candidate metal oxides include TiO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and ZnO, as well as mixed-oxide films. These materials are attractive because they can exhibit electron mobilities as high as 100 cm<sup>2</sup>/Vs<sup>2</sup> – about 100-1000 times higher than the best organics – in amorphous, room temperature deposited films. They are therefore compatible with the large-area, low-cost paradigm envisioned for organic electronics. Furthermore, the electron affinities (EA) of these materials span a significant range (4.2 eV for ZnO to 3.7 eV for In<sub>2</sub>O<sub>3</sub>), which is suitably matched to those of prospective organic donor materials, and allows some degree of EA<sub>Acceptor</sub>-EA<sub>Donor</sub> tuning.

This approach has been studied by others<sup>3</sup>, but thus far, planar heterojunction polymer/inorganic hybrid devices typically achieve power conversion efficiencies significantly below 1%. In contrast, planar heterojunction purely organic devices routinely exceed 1%, and have been reported in excess of 4%<sup>4</sup>. This is quite surprising, considering the numerous apparent advantages of a metal oxide electron acceptor layer. As previously noted, their electron mobilities are orders of magnitudes higher than organics. N-doping levels can be controlled through the background pressure of oxygen present during deposition<sup>5</sup>. These factors should enable both increased conductivity compared to an organic layer, as well as the creation of space charge fields to enhance charge carrier separation following exciton dissociation.

Comparing the illuminated J-V characteristics of planar heterojunction organic<sup>6</sup> and hybrid devices<sup>7</sup>, it is evident that the hybrid devices suffer from lower short-circuit current densities and fill-factors compared to their purely organic counterparts. Short-circuit current density is proportional to the efficiencies of exciton dissociation and charge separation/collection. Low fill-factors are usually interpreted as evidence of high internal series resistance, as the J-V curve becomes more resistor-like, and less diode-like, but can also be evidence of interfacial carrier recombination. Because the internal fields are highest (when operating in the 4<sup>th</sup> quadrant) under short-circuit conditions, the charge separation/collection efficiency is highest at V=0. As the bias is increased towards the open-circuit voltage, the internal fields are decreased, a higher density of electrons and holes are found in the vicinity of the donor/acceptor interface, and interfacial carrier recombination, if present, will play a more significant role, reducing the measured current density, and therefore the fill-factor. Given the much higher electron mobilities and conductivities of the metal oxide films compared to organic electron acceptors, we can rule out resistance in the electron transport layer as the source of the reduced fill factor (although we cannot rule out microstructural differences in the donor layer deposited on the oxide impacting its resistance), and we therefore suggest that limited exciton dissociation and carrier recombination dynamics at the hybrid heterojunction are the likely cause of the lower efficiencies observed in these devices. The proposed Network research program will study these phenomena, and methods for modifying exciton and carrier dynamics through a combination of photovoltaic device characterization, direct ultrafast probing of excitons and carriers, and photoelectron spectroscopic (UPS and IPES) studies of interfacial electronic structures.

In order to achieve the highest efficiencies, it has been demonstrated that nanoporous (as opposed to planar) oxide acceptor films, infiltrated with polymer donor materials, are necessary<sup>8</sup>. Ideally these films have pores with smooth edges, are oriented perpendicular to the substrate, and have radii matched to the exciton diffusion length of the organic. Such a system should simultaneously maximize exciton dissociation and charge transport in both films. Complications arise, however, when the microstructure of the polymer film is altered in the pores compared to the bulk, reducing both the carrier mobility and exciton diffusion length. In this project, we will initially fabricate and study simple planar heterojunction systems to establish benchmarks against which the nanostructured acceptor layers will be evaluated. Bilayer systems will be fabricated for both device and ultrafast laser characterization, and oxide films will be supplied for UPS studies.

We will begin with regioregular poly(3-hexylthiophene) (P3HT) as the organic donor system, as this is standard for such devices. Systematic studies of the effect of varying the EA and mobility of the acceptor, through choice of oxide and fabrication conditions, will be studied using P3HT as the donor. Other candidates, such as fluorine-thiophene copolymers and small-molecule organics, such as various phthalocyanines, subphthalocyanines and pentacene will be studied following the initial stages of this project. This will allow systematic study of the effects of altering the organic donor EA and hole mobility relative to that of the inorganic acceptor.

Self-assembled monolayers (SAMs) intermediate between the oxide and organic films have been shown to affect the wetting of the organic film, and to introduce interfacial dipoles that alter the alignment of the organic HOMO/LUMO with the inorganic VBM/CBM<sup>9</sup>. I. Hill has extensive experience in the use of SAMs to alter the electronic structures and hydrophobicities of organic/inorganic interfaces<sup>10,11,12,13</sup>. We anticipate that in addition to changes in the band alignment and organic film morphology at the interface, SAMs will also alter both exciton dissociation and charge recombination dynamics at the interface. In particular, the passivation of oxide surface states, which act as recombination centres, and the increase of the physical separation of the organic donor and oxide acceptor should alter the dynamics. Systematic effects of phosphonic acid-based SAMs on device efficiencies and exciton/charge dynamics at the interface will be studied. Effects of altering the organic moieties (aliphatic and aromatic), intrinsic dipole moment, and the chain length (spacer thickness) will be studied.

#### **Device Fabrication and Characterization (I. Hill)**

Amorphous oxide films will be prepared by RF sputter deposition in a custom three-source system capable of producing pure, binary, and ternary oxide systems<sup>14,15</sup>. Oxygen vacancy concentration in these films (dopant density; resistivity) will be controlled by background O<sub>2</sub> pressure during sputtering, and/or post deposition annealing in O<sub>2</sub>.

Polymer films will be deposited by spin-coating in inert atmosphere, while small-molecule films will be deposited by thermal vacuum deposition. In both cases, top contact metals will be deposited by vacuum deposition.

Dark and illuminated device current-voltage characteristics will be measured using Keithley source-measure units and simulated solar irradiation (AM 1.5G 0-10 suns Newport Oriel and Sciencetech simulators). Monochromatic incident photon-to-charge-carrier efficiencies (IPCE) will be measured. Metrics will include the power-conversion efficiency, open-circuit voltage, fill factor and quantum efficiency. These results will be interpreted in the context of the measurements of exciton dynamics and energetic alignment detailed below.

#### **Ultrafast Charge Dynamics (C. Silva)**

To understand further the important factors that limit the power conversion efficiency, we will explore in detail the mechanism of carrier photogeneration in organic/inorganic heterojunctions (e.g.

P3HT/TiO<sub>2</sub>). It is understood that following photoinduced charge transfer in polymer distributed heterostructures, Coulomb interactions between electrons and holes confine these geminate charge pairs at the heterojunction<sup>16</sup>. They may stabilize to form either charge-transfer excitons or they may remain in a fully charge-separated state. Carrier generation requires that these overcome their Coulomb potential under the influence of an electric field<sup>17</sup>; charge recombination has been found to be a limiting factor in photovoltaic quantum efficiencies in polymer-based systems<sup>18</sup>. The composite carrier generation efficiency thus depends on two independent processes as follows:

- Excitons produced in the bulk of either component must be transported to the heterojunction and dissociate on a fast timescale compared to competing radiative and nonradiative processes. We will determine the efficiency of charge generation by means of ultrafast spectroscopies on picosecond timescales<sup>19</sup>.
- Geminate pairs must dissociate to produce mobile carriers. If back-electron-transfer to the polymer donor produces a singlet exciton, we will observe delayed fluorescence during all timescales in which this process occurs. Measurement of the decay of the delayed fluorescence signal up to millisecond windows will provide information on the lifetime of geminate pairs.

To achieve these objectives we will implement methodologies already in place at the U. de Montréal. We will excite either the organic or inorganic component selectively in composite films with a tunable femtosecond laser source (230—2600 nm) and measure time-resolved photoluminescence (PL) spectra spanning time windows from picoseconds to milliseconds. We will also carry out femtosecond transient absorption spectroscopic measurements to probe the polaron absorption signal in the organic, and interfacial charge recombination efficiencies over fast timescales. We will measure as a function of temperature (down to 4 K) and external electric field to unravel detailed mechanistic information.

### **Photoelectron Spectroscopies (A. Kahn)**

Photoelectron spectroscopies can be used to measure directly most of the energetic offsets and interfacial dipoles discussed earlier. These techniques have been extremely influential in the field of purely organic electronic devices, where they have been used to measure energetic alignment at metal/organic interfaces<sup>20</sup>, HOMO/HOMO alignment at organic donor/acceptor interfaces<sup>21</sup>, and exciton binding energies in OPV materials<sup>22</sup>. Furthermore, by monitoring the density of states at the interface between the donor and acceptor, localized interface states, resulting from chemical interactions, dangling bonds, or simple charge transfer can be identified as potential exciton recombination sites, and the efficacy of passivating these states can be precisely quantified.

Ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES) will be used to measure directly the ionization potentials and electron affinities at surfaces and interfaces. Furthermore, in the case of small-molecule donors deposited on metal oxide acceptors, the molecular HOMO/oxide VBM offset can be measured directly using UPS, and the LUMO/CBM offset using IPES. Excitonic binding energies can be determined by comparing the HOMO/LUMO splitting with UV-vis determined optical bandgaps. Interface dipoles induced by SAMs on metal-oxide surfaces and their influence on the energetic alignment of organic overlayers can be directly measured<sup>23</sup>.

The combination of direct device measurements, time-resolved measurements of charge and exciton dynamics, and direct measurement of the energetic states of the organic and bulk oxide films responsible for charge transport and exciton dissociation, *all performed on the same oxide/organic systems*, demonstrates both the unique strengths of the proposed Network approach to optimizing hybrid organic inorganic interfaces for solar cell applications, and the unique opportunities for HQP to access the Network Collaborators' facilities.

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