

Polymer:TiO₂ bulk heterojunction photovoltaic cells

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Polymer based photovoltaic (PV) cells are extensively studied since they offer a low-cost approach to the production of photovoltaic cells. One of the concepts of polymer PV cells is based on sensitized nanoporous TiO₂ in which a p-type conjugated polymer is used that combines the functions of absorption and hole transport. The short exciton diffusion length in conjugated polymers prohibits the use of pore diameters in the TiO₂ network larger than 20 nm. Larger pores would reduce the charge separation efficiency. However, the small pore diameter makes it difficult to fill the pores of the TiO₂ network with polymer.

We present a new and simple procedure for preparing bulk-heterojunction (BHJ) hybrid organic-inorganic solar cells, in which a continuous interpenetrating network of TiO₂ is created inside a thin conjugated polymer film.

The cells were fabricated in the following way. First a PEDOT:PSS layer was spun onto ITO-coated glass at 1500 rpm. Next, the TiO₂/polymer BHJ was deposited by spincoating a mixture of titanium(IV) isopropoxide, as the TiO₂ precursor, and poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylenevinylene) (MDMO-PPV) or poly(3-octylthiophene) (P3OT) in tetrahydrofuran (THF). Several concentrations (2.5-5.5 mg polymer per ml THF) and different spin speeds (500-5000 rpm) were used to study the influence of the layer thickness on the cell performance. After spin coating, the films were stored in the dark in air overnight in order to form the TiO₂ via hydrolysis of the titanium(IV) isopropoxide. Additionally they were put into vacuum (10⁻⁶ mbar) overnight before evaporating the LiF/Al counter-electrode. Some films were prepared on quartz substrates for x-ray photon spectroscopy (XPS), photoluminescence quenching, photo-induced absorption (PIA) and UV-VIS experiments.

XPS spectra of a titanium(IV) isopropoxide film without the polymer present were taken and compared to the XPS spectrum of a film baked at 400 °C. Both spectra are very similar. From these spectra the TiO₂ conversion efficiency can be determined, resulting in a conversion between 87 % and 91 % for the film treated at 400 °C and between 77 % and 91 % for the film converted at room temperature. For a BHJ film of 1:1 (v/v) MDMO-PPV:TiO₂ analysis of the XPS spectrum results in a minimum TiO₂ conversion of 65%.

After absorption of a photon charge separation is necessary in order to generate power in a photovoltaic cell. Photo-induced absorption experiments at 80 K with excitation

at 488 nm, were performed to study if charge separation takes place between the polymer and TiO₂. The results for a 1:1 (v/v) MDMO-PPV:TiO₂ blend show an absorption at 0.42 and 1.32 eV that can be attributed to the radical cation of MDMO-PPV which resides after electron transfer to the TiO₂. This shows that charge separation takes place.

To visualise the structure of these BHJ SEM images were taken of the P3OT:TiO₂ BHJ cells. Prior to taking the SEM image, the polymer phase was removed by an UV-ozone treatment. The SEM images show a continuous TiO₂ structure with pores of about 50 nm in diameter.

I-V measurements on the PPV:TiO₂ BHJ cells showed an V_{oc} of about 500 mV which was almost independent of the PPV:TiO₂ ratio. The I_{sc} increased with increasing TiO₂ concentration up to a maximum of 0.6 mA/cm² (0.7 sun equivalent) at a TiO₂ concentration of 20 % (v/v), after which the current decreased again. This maximum can be explained by the fact that both holes and electrons have to be transported through the cell, electrons via the TiO₂ and holes via the polymer. So both phases have to be present and provide a continuous pathway for the charge carriers. Besides that, also the dimension of the two phases is important and should ideally be on the order of the exciton diffusion length, which is 10-20 nm. One can imagine that for low TiO₂ contents the PPV phase is too large or that the TiO₂ does not yet form a continuous network. This is also supported by luminescence quenching measurements, which show that the luminescence of the PPV is more and more quenched for increasing TiO₂ content and is almost completely quenched at TiO₂ concentrations above 25 % (v/v). Fill factors (FF) for these cells are about 40 % The initial power conversion efficiency at roughly 0.7 sun equivalent is around 0.2 % for a cell with 20 % TiO₂. Cells with a BHJ of P3OT and TiO₂ show a V_{oc} of about 400 mV that is independent of the TiO₂ concentration. The I_{sc} shows a maximum of 0.7 mA/cm² for a TiO₂ concentration of 10 % (v/v). This concentration is lower compared to the PPV blends. The FF is comparable to that for the PPV cells. The initial power conversion efficiency for the 10 % TiO₂ cell is 0.2 % (0.7 sun equivalent).

The performance of both the PPV and P3OT cells increases during the first day after the deposition (when stored in the dark) of the LiF/Al electrodes, which is mainly due to an increase in the I_{sc}. After this initial increase the P3OT BHJ cells show a 10% decrease in the efficiency over 3 weeks (storage in dark) resulting from a decrease in FF. The PPV BHJ cells on the other are less stable. For these cells the efficiency decreases to almost zero within a few days.