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Spectral Broadening in Nanocrystalline TiO_2 Solar Cells Based on Poly(*p*-phenylene ethynylene) and Polythiophene Sensitizers

Jeremiah K. Mwaura, Xiaoyong Zhao, Hui Jiang,
Kirk S. Schanze,* and John R. Reynolds*

*Department of Chemistry, Center for Macromolecular
Science and Engineering, University of Florida,
PO Box 117200, Gainesville, Florida 32611-7200*

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Since the breakthrough work by Grätzel and co-workers, dye-sensitized solar cells (DSSCs) have attracted considerable attention as organic/inorganic hybrids in the quest for alternatives to silicon-based solar cells.[1−3] With power conversion efficiencies just above 10%, DSSCs have been shown to exhibit potentially useful operating characteristics.[2] The conventional DSSC consists of a working electrode made of a sintered film of nanocrystalline and porous titanium dioxide (TiO_2) as the electron acceptor, whereas the dye sensitizer, for electron injection into the TiO_2 conduction band, is usually a layer of adsorbed ruthenium complex. A solution electrolyte containing a redox couple (typically iodine/triiodide) is used to regenerate the oxidized dye molecules, and a platinum counter electrode completes the cell. The complex Ru(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(NCS)$_2$ is frequently used as the sensitizer, although other dyes such as porphyrins, phthalocyanines, and coumarins have been evaluated.[4−6] The carboxylic acid functionality has been shown to be crucial for anchoring the dye molecules onto the TiO_2 surface.[7−9]

Given the versatile optical and semiconductor properties of conjugated polymers, it is possible that the properties of DSSC's could be improved by incorporating them into the cells as sensitizers. With their high absorption coefficients and tunable band gaps spanning a broad portion of the visible and near-infrared spectrum, along with the presence of multiple bound ionic sites, conjugated polyelectrolytes (CPEs)[10] serve as alternative light-harvesting and charge-transfer materials in these cells. DSSCs have recently been demonstrated using CPEs, especially using polythiophene derivatives.[11−16] For example, poly(3-thiophene acetic acid) was used to sensitize TiO_2 in devices with power conversion efficiencies up to 1.5%.[13,17,18]

Although the performance in terms of the overall power conversion efficiencies achieved to date with CPE sensitizers is lower than in conventional cells, prospects are high for rapid improvement. The highly ionic nature of CPEs provides multiple binding sites and, along with the ability to form active films using layer-by-layer self-assembly, will allow control of the amount of polymer adsorbed at a surface. The flexibility in preparing variable band gap polymers allows spectral broadening of the solar light absorbed, thereby potentially increasing the amount of charge injected into the TiO_2. In addition to the electronic band gap, the energies of the HOMO and LUMO levels of the polymeric chromophores can be adjusted to allow excited-state charge transfer to the TiO_2 acceptor while also ensuring that the photo-oxidized polymer is easily reduced by the electrolyte.

In this communication, we have utilized a dual-polymer system (see Figure 1) to demonstrate spectral broadening in the fabrication of CPE-DSSCs. The first polymer, a carboxylated poly(*p*-phenylene ethynylene) (PPE-CO_2), and its derivatives have been used before by our group to fabricate photovoltaic cells through layer-by-layer electrostatic adsorption with a water-soluble fullerene derivative.[19] PPE-CO_2 absorbs in the blue region of the spectrum, whereas a commercially available second CPE, a carboxylated polythiophene (PT-CO_2), has a more red-shifted absorption spectrum. For the cells reported here as a proof-of-concept, individual CPE cells gave relatively similar solar power conversion efficiencies (η) at AM 1.5 conditions, whereas the dual polymer cells more than doubled the η value.

PPE-CO_2 was synthesized as described elsewhere,[20] whereas PT-CO_2 was purchased from Rieke Metals, Inc., as the sodium salt and protonated to the acid form by dilute hydrochloric acid (both polymers have $M_n \approx 15-20$ kg mol^{-1}). Solutions of the polymers (1×10^{-3} M on the basis of polymer repeat) in anhydrous dimethylformamide (DMF) were used. To adsorb films for the dual sensitizer cells, we mixed equal volumes of the individual polymer solutions.

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* Corresponding authors. E-mail: kschanze@chem.ufl.edu (K.S.S.); reynolds@chem.ufl.edu (J.R.R.).

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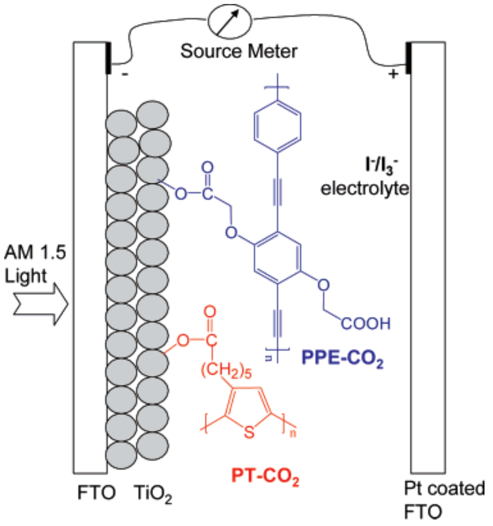

Figure 1. Schematic representation of the dual-polymer-sensitized DSCC, also showing the structures of the polymer repeat units.

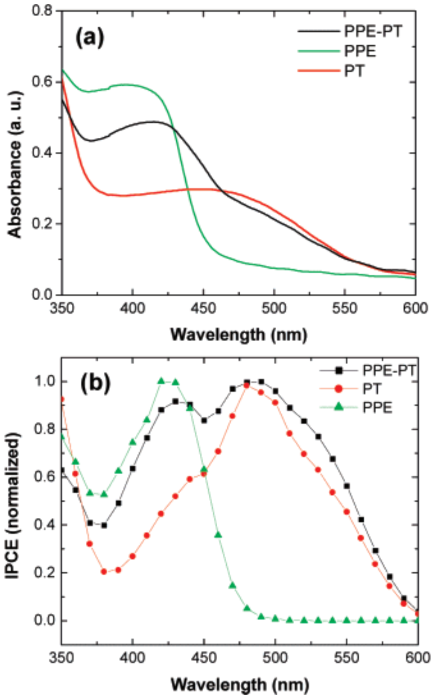

Figure 2. (a) UV−vis absorption and (b) IPCE spectra of the PPE-CO$_2$, PT-CO$_2$, and dual polymer PPE-CO$_2$/PT-CO$_2$ solar cells.

The films of nanocrystalline TiO$_2$ (15 nm particles, film ∼4 μm thick) were coated on fluorine-doped tin oxide (FTO) glass substrates (from Harford Glass, TEC 15) as described in the literature.[9] The TiO$_2$ films were sintered at 450 °C for 30 min, cooled to 80 °C, and then dipped in the polymer solutions for 12 h. The comparatively long adsorption time was used to allow a high degree of penetration of the polymer into the nanostructured titania. After adsorption, the polymer-coated films were rinsed with DMF and ethanol before being dried under a nitrogen flow. The counter electrode used was made of 50 nm Pt coated on FTO, whereas a propylene carbonate solution of iodine (0.05 M)/lithium iodide (0.5 M) was applied as the electrolyte to complete the cells.

Figure 2a shows the absorption spectra of the PPE-CO$_2$, PT-CO$_2$, and dual-polymer-coated TiO$_2$ films used to fabricate the solar cells. Both polymers form uniform coatings, as observed under an optical microscope. PPE-CO$_2$ has a λ_{max} of 420 nm, whereas PT-CO$_2$ has a λ_{max} of 460 nm with a broad tail extending to 600 nm. The combined PPE-CO$_2$/PT-CO$_2$ absorption encompasses both the polymers' absorption regions: 350 to near 600 nm. As there is a competitive deposition process between the two CPEs, the surface coverage, and thus the amount of light absorbed in a selected portion of the spectrum, can be controlled simply by varying the ratio of the CPEs in the adsorption solution.

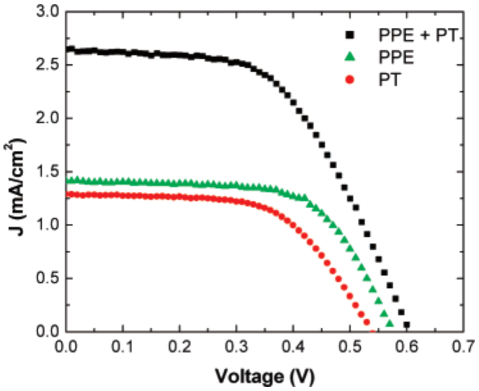

Figure 3. *J*−*V* characteristics of the PPE-CO$_2$, PT-CO$_2$, and PPE-CO$_2$/PT-CO$_2$ solar cells under AM 1.5 conditions.

The normalized photocurrent action spectra (IPCE) of the solar cells are shown in Figure 2b. The photocurrent matches well with the absorption spectra, showing that the combined PPE-CO$_2$/PT-CO$_2$ photocurrent is a contribution from both the individual polymers. At the maxima, the IPCE values are 11 and 14% for the PPE-CO$_2$ and PT-CO$_2$ components, respectively. Although these values are not as high as molecular adsorbed dyes, the fact that they are close to one another is important as we consider the ability of both polymers to contribute the photocurrent in the cell. Photocurrent is generated in the hybrid cells by photoinduced electron transfer at the interface between the sensitizer polymers and the acceptor, TiO$_2$.[13] The LUMO energy levels of PPE-CO$_2$ and PT-CO$_2$ are ca. 3.2 and 3.5 eV (below vacuum), respectively.[19,21] For both polymers, the LUMO levels are energetically higher than the conduction band of TiO$_2$ (4.3 eV), and consequently, charge injection into TiO$_2$ by the singlet excited-state of the polymers is energetically feasible. In support of this notion, transient absorption studies of PPE-CO$_2$/TiO$_2$ and PT-CO$_2$/TiO$_2$ films provide clear evidence for efficient charge injection and transient production of the oxidized polymers. As shown in the Supporting Information, nanosecond pulsed excitation of a CPE/TiO$_2$ film rapidly ($\tau < 5$ ns) produces spectral changes consistent with production of the oxidized polymer (a positive polaron state); the transients decay within a few microseconds, a time scale that is consistent with charge recombination.

The power conversion efficiencies (η) of the polymer-sensitized solar cells were evaluated under AM 1.5 conditions (100 mW/cm^2 incident radiation). The photocurrent density−voltage (*J*−*V*) curves for the PPE-CO$_2$, PT-CO$_2$ and PPE-CO$_2$/PT-CO$_2$ sensitized cells are shown in Figure 3 with the cells' performance in terms of short circuit current (J_{sc}), open

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Table 1. Summarized Solar Cell Performance Values

Device	J_{SC} (mA/cm^2)	V_{0C} (V)	FF	η%
PPE-CO_2, PT-CO_2	2.70	0.60	0.55	0.89
PPE-CO_2	1.41	0.57	0.63	0.51
PT-CO_2	1.30	0.54	0.60	0.41

circuit voltage (V_{oc}), fill factor, and AM 1.5 (η) summarized in Table 1.

Examining these results, we find that the concept of spectral broadening is clearly demonstrated. The photocurrent (2.7 mA/cm^2) and η (~0.9%) for the dual-polymer solar cells is essentially the sum of the response from each individual polymer. Qualitatively, the observed doubling of the efficiency is consistent with the broadened spectral coverage. Work in progress seeks to quantify the relationship between the polymer composition and the overall efficiency. At the same time, the V_{oc} of 600 mV and FF ca. 60% are independent of the composition of the CPE sensitizing layer and are a characteristic of the cell structure and not the individual polymers used. This is consistent with each polymer independently contributing to the cell performance in a similar manner. Relative to the single polymer CPE-DSSCs studied to date, the V_{oc} and FF are comparable to, or better than, those reported. Whereas the best reported AM 1.5 efficiency values are ~ 2.4% for a polythiophene-polyelectrolyte-sensitized DSSC, the performance of these cells was enhanced with ionic liquids[15] and suggests further improvements are possible with our cells.

In summary, we have demonstrated the concept of spectral broadening through the use of a dual-polymer system to enhance the performance of polymer-sensitized TiO_2 solar cells. By synthesizing CPEs with long wavelength absorption into the NIR, we can expand this spectral broadening and, as there is no conceptual limit to the number of polymers that might be co-adsorbed at any one time, this method can ultimately lead to a close matching of the full solar spectrum. Although the cells reported here are unoptimized with respect to polymer solution concentration, both polymer and TiO_2 film thickness, FTO sheet resistance, and electrolyte, we are working to optimize these conditions while also studying a variety of CPEs. In initial results, using FTO with 8 Ω/□ and commercial TiO_2 paste from Solaronix (see preparation details in the Supporting Information), we have been able to increase the dual-polymer cell performance in terms of photocurrent and η to ~7 mA/cm^2 and ~ 1.5%, respectively (see $i-V$ curve and cell characteristics in the Supporting Information). These results demonstrate the potential for CPEs as sensitizers in nanocrystalline TiO_2 solar cells.

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Supporting Information Available: Experimental procedures, $J-V$ curve, table of cell parameters, transient absorption spectra, decay kinetics. This material is available free of charge via the Internet at http://pubs.acs.org.

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