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Efficient Light Harvesting Polymers for Nanocrystalline TiO_2 Photovoltaic Cells†

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ABSTRACT

Carboxylated polythiophenes were found to be alternative photo sensitizers for nanocrystalline TiO_2 photovoltaic (PV) cells. The overall solar-to-electric energy conversion efficiency found was ~1.5% in these regenerative electrochemical photovoltaic cells without any dye sensitizer. These initial and promising results are believed to be due to the presence of the carboxylic group which provides enhanced adsorption and transport of the photoinduced charge. Further optimization is expected to result in even higher PV performance.

Silicon-based solar cells have been used only for limited applications due to their lack of flexibility, heavy weight, and high cost, regardless of their high solar-to-electric energy conversion efficiency. Several approaches have been applied in order to overcome these limitations, including investigation on fully organic and organic/inorganic hybrid solar cells. Organic/inorganic hybrid solar cells have been considered as a favorable alternative to inorganic solar cells since Grätzel and co-workers had reported efficient dye sensitized nanocrystalline TiO_2 photovoltaic (PV) cells, showing overall energy conversion efficiency of 7~10%. The sensitizer used is a ruthenium complex [Ru(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(NCS)$_2$] (N3).[1–4] Variations on this PV cell have been extensively investigated to increase overall energy conversion efficiency and to understand the photophysical properties.[5–13] The role of the dicarboxylic groups on the sensitizer to form an efficient ligand to chelate onto TiO_2 surface is also of great interest. The covalent Ti–O–C bond formed can help to transfer photoinduced charge from ruthenium to TiO_2 via the ligand [metal-to-ligand charge transfer, MLCT]. Computer simulation and other instrumental analyses have provided evidence for anchoring of the carboxylic group in the ligand onto the surface of TiO_2.[2,4,5,7]

Conjugated polymers such as polythiophenes and poly (*p*-phenylene vinylene)s (PPVs) have also been considered as promising light sensitizers and/or charge mediators for realization of efficient photovoltaic performances.[14–19] Especially, polythiophene is more attractive for nanocrystalline TiO_2 PV cells due to its environmental stability and tailorable electrochemical properties.[14,15,17] Recently, polythiophenes have been reported as sensitizers and charge-transfer mediators as well as solid electrolytes in nanocrystalline TiO_2 PV cells.[15] Though the photovoltaic efficiencies of these devices are not high, the approach is advantageous to fabricate efficient solid-state PV cells. Efficient photoinduced charge transfer[16] and well-matched energy levels[19] among polythiophenes and the other components in nanocrystalline TiO_2 PV cells are considered essential requirements to produce efficient solar-to-electric energy conversion efficiency in organic molecule sensitized nanocrystalline TiO_2 PV cells.

This paper investigates the effects of carboxylic groups on polythiophenes and the resulting photovoltaic performance of this system in nanocrystalline TiO_2 PV cells. Photovoltaic performances of carboxylated polythiophenes are compared to those of poly(3-hexyl thiophene) (PHT) which does not have the preferred carboxylic chelating group. The fabrication of the devices using dipping as well as spin coating of the polythiophene solution has been carried out to adsorb the polymer onto nanocrystalline TiO_2.

PTAA, PURET, H–PURET, and PHT were synthesized as described earlier.[20–22] The structures of the polymers are shown in Figure 1. The monomers 3-hexyl thiophene and 2-(3-thienyl) ethanol were purchased from Aldrich and ethyl-(3-thiophene acetate) from Fisher Scientific. The monomers were used without further purification. Poly(3-thiophene acetic acid) (PTAA), poly[2-(3-thienyl) ethanol butoxy carbonyl methyl-urethane] (PURET), and PHT have been synthesized from each monomer ethyl-(3-thiophene acetate), 2-(3-thienyl) ethanol, and 3-hexyl thiophene by chemical dehydrogenation method using anhydrous ferric chloride.

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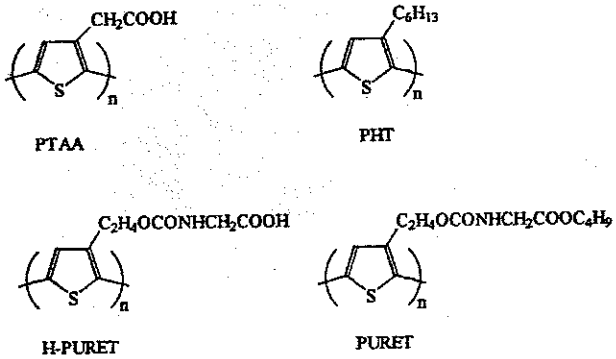

Figure 1. Structures of polythiophenes considered in this study.

Hydrolysis of PURET in sodium hydroxide aqueous solution leads to poly[2-(3-thienyl) ethanol hydroxyl carbonyl-methyl urethane] (HPURET) that bears carboxylic acid and urethane groups.

All devices were fabricated on fluorine-doped tin oxide (SnO_2:F) covered glass substrates with an active area of 0.25 cm^2. Films of nanocrystalline TiO_2 (P25, Degussa) on SnO_2:F coated glass substrates (TEC 15, sheet resistance of 15 Ω/□) were prepared by spin coating a TiO_2 paste which was made according to ref 2 (method B). Sintering was carried out at 450 °C for 30 min followed by cooling to 120 °C and then dipping into the polythiophene solutions for 1 day. The thickness of the TiO_2 film was 4.5 μm. Polymer solutions were prepared at a concentration of 7.5×10^{-2} mol/L (3.1×10^{-2} mol/L for HPURET) using their good solvents and the calculation of the concentration was based on the molecular weight of repeating units in the polymers. The solvents used for dissolving and washing the polymers were THF for PTAA and PURET, DMF for HPURET, and chloroform for PHT. Polymer-coated TiO_2 films were rinsed in good solvents and then dried under argon flow. Platinum-coated (thickness of 50 nm) TEC 15 glass substrates were used as a counter electrode. Iodine (0.05 M) and lithium iodide (0.5 M) in acetonitrile were applied as electrolytes.

The current−voltage ($I-V$) characteristics were measured with a Keithley SMU 2400 source measurement unit under light intensity of 100 mW/cm^2 with an AM 1.5 filter. UV−visible absorption spectra were obtained by using a GBC UV-vis 916 spectrophotometer. Semiempirical quantum chemical calculations were performed on various thiophene oligomers using computational programs (Cerius^2 4.6, MOPAC 6, and ZINDO 1.0 from Accelrys Inc., CA) to obtain the information of geometrically optimized structures and HOMO−LUMO energies.

As shown in Figure 2, we observed a red shift (50~60 nm) of the absorption peak of PTAA on the nanoporous TiO_2 film. The red shift of the UV-vis absorption peak implies that the carboxylic group in the branch of the polythiophene and TiO_2 interact with each other, shifting energy levels of the polymer. This interaction can expedite photoinduced charge transfer from the polymer to TiO_2. In the case of PHT, the peak shift of the UV-vis absorption depends on the concentrations of polymer solution. Thus, when large amounts of polymer are adsorbed onto TiO_2 film, it results

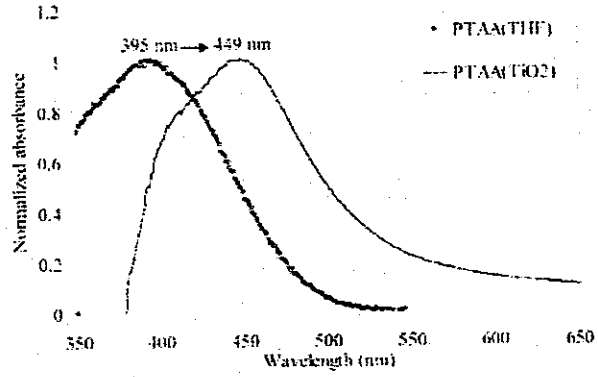

Figure 2. Absorption spectra of PTAA on nanoporous of TiO_2 film (solid line) and in THF solution (open circle).

Table 1. HOMO−LUMO Energies and Band Gap Values Obtained from Semiempirical Quantum Chemical Calculations

samples	HOMO (eV)	LUMO (eV)	band gap (eV)
N3[a]	−6.71	−1.9	4.81
HPURET[b]	−6.52	−1.53	4.99
PHT[b]	−6.50	−0.88	5.63

[a] Reference 24. [b] Four monomer units.

in a red shift of the absorption peak. When we dilute the polymer solution and decrease the amounts of adsorbed polymer, a blue shift of the absorption peak is observed. The overall peak shifts of the UV-vis absorption are in the order of PTAA > HPURET > PURET > PHT. This indicates that the carboxylic group contributes to the shifting of absorption peaks toward lower energy (longer wavelength), which can induce efficient light harvesting efficiency of the polymer and lower the energy band gap. One of the important requirements for being an efficient photosensitizer is to have a low energy band gap. N3 has been known to have a relatively low energy band gap of ~1.7 eV and can be oxidized even at a very low energy of incident light.[2] Energy band gaps of PHT are extensively changed by modifying the degree of regioregularity of the polymer.[23] The band gaps of these polymers are in the range of 1.7~2.1 eV depending on the regioregularity (head-to-head:head-to-tail = 0.9:0.1−0.5:0.5).[23] However, the overall energy conversion efficiencies of the PHTs are only in the range 0.18~0.42% (regioregular ~ regiorandom PHTs) in nanocrystalline TiO_2 PV cells. The photovoltaic performances of these PHTs suggest that in addition to band gap values, the positions of the LUMO levels of the polymers are also very important.

Table 1 shows gas-phase energy levels of four monomer units of polythiophenes, which have been calculated by semiempirical quantum chemical methods. The semiempirical quantum chemical calculation has been done after optimization of the structure of the molecules. The energy band gap and energy levels of HOMO and LUMO of N3 have been known as an ideal and well matched for wide band gap semiconductor TiO_2 PV cells. In the case of HPURET, the calculations show the band gap and HOMO levels similar to that of N3. The LUMO levels of HPURET are much closer to that of N3 compared to PHT.

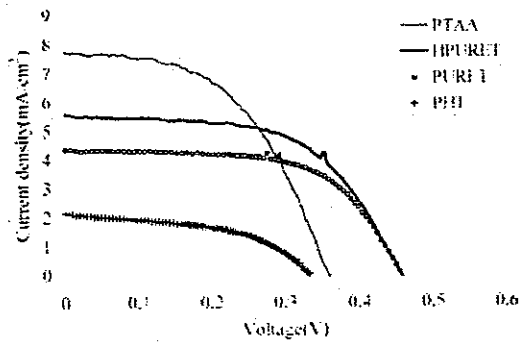

Figure 3. *I*−*V* characteristics of polythiophenes.

As shown in Figure 3, the trend of photocurrent−voltage curves of PURET and HPURET are similar, showing over 1% of overall energy conversion efficiencies. The carboxylic group containing polythiophenes shows significantly higher overall energy conversion efficiencies of 1.4 and 1.5% with high short circuit currents of 8.0 and 5.7 mA/cm^2 for PTAA and HPURET, respectively. These values are much higher compared to those reported previously.[14,15,17] The carboxylic group containing polythiophenes (PTAA and HPURET) show better PV performances than those containing ester groups (PURET) due to their efficient adsorption on the surface of TiO_2. However, lack of adsorption makes alkyl side chain polythiophene (PHT) show much smaller overall energy conversion efficiencies (0.18~0.42%) with a low short circuit current of 2 mA/cm^2. In the case of N3 dye, the carboxylic group of the ligand can anchor the surface of TiO_2. The anchoring can help to enhance metal-to-ligand charge transfer in nanocrystalline TiO_2 PV cells. In the case of these carboxylated polythiophenes, we observed enhanced PV performances as well when an ester group is present.

In previous work, spin coating was selected as a typical process of polymer adsorption. The thicker polymeric film obtained with this process, however, probably blocks liquid electrolytes from entering the nanoporous TiO_2 and results in relatively low PV performances (PTAA, energy conversion efficiency of 0.27%). Color differences observed on both sides (front and back) of the spin-coated polymer-TiO_2 films were apparent, which suggests that the polymer molecules had not permeated through the entire mesoporous TiO_2 films using the spin coating technique. However, dipping the TiO_2 thin film in polymer solutions resulted in higher efficiency (PTAA, 1.4%) due to a larger area of contact between the polymer and TiO_2. The homogeneous permeation of polymer into the mesoporous TiO_2 films was confirmed as the same polymer color was observed on both sides of the dipped polymer−TiO_2 films. Dipping followed by spin coating also seemed to block the electrolytes and thus showed smaller efficiency (PTAA, 0.53%).

In conclusion, we have demonstrated that carboxylated polythiophenes adsorbed by the dipping process in dilute solution can give significantly larger efficiencies than earlier reported. These results suggest that polythiophene may be an efficient sensitizer for nanocrystalline TiO_2 PV cells.

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