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Microsecond Dye Regeneration Kinetics in Efficient Solid State Dye-Sensitized Solar Cells Using a Photoelectrochemically Deposited PEDOT Hole Conductor

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Abstract: Microsecond dye-regeneration kinetics was observed in efficient solid state dye-sensitized solar cells using photoelectrochemically deposited poly(3,4-ethylenedioxythiophene (PEDOT) hole conductors using transient absorption spectroscopy. The dye-regeneration rate is orders of magnitude slower than the case using the I^-/I_3^- redox couple or commonly used small molecule hole conductor and is attributed to the low dye to PEDOT ratio within the films.

Solid state dye-sensitized solar cells (ssDSSCs) utilizing conducting polymer (CP) hole conductors may offer significant technological advantages over the commonly used I^-/I_3^- redox couple used in organic or ionic liquid electrolyte solutions.[1] The CP plays the important role of regenerating dye-cations produced by the injection of electrons from photoexcited dyes to TiO_2 and transporting the positive charge to the cathode. Herein we show that the kinetics of dye regeneration in a 3% efficient ssDSSC using photoelectrochemically deposited poly(3,4-ethylenedioxythiophene (PEDOT) is orders of magnitude slower than either the I^-/I_3^- redox couple[2] or the frequently used small molecule hole conductor spiro-OMeOTAD (2,2′7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenyl-amine)-9,9′-spiro-bifluorene).[3] The slow dye regeneration kinetics limits the short circuit current of these devices, which is thought to originate from the low dye to CP ratio.

Mesoporous TiO_2/dye/PEDOT samples were prepared by a published photoelectrochemical deposition procedure[4] in which PEDOT deposition is initiated by the photo-oxidation of the sensitizing dyes anchored to TiO_2. This procedure was shown[5] to yield orders of magnitude better performance (best efficiency is ~3%) than chemical or electrochemical deposition of the CP in the dark. This enhanced performance is attributed to the creation of a better CP/dye interface.[5] Despite considerable efforts being focused on the development of CPs for ssDSSCs over the past decade, there is currently no report on the dye regeneration kinetics.

The working electrode was a TiO_2 film (5.5 μm, Solaronix-T) sensitized with Z907 ((*cis*-bis(isothiocyanato)(2,2′-bipyridyl-4,4′-dicarboxylato)(4,4′-dinonyl-2′-bipyridyl)ruthenium(II))) dye, deposited on a transparent conductive glass coated with an approximately 100 nm dense TiO_2 layer. The photoanodes were immersed into 0.1 M $LiClO_4$ and 0.01 M bis-EDOT in acetonitrile and illuminated from the TiO_2 side by a 25 mW/cm^2 broad-band light using a 485 nm long-pass filter. A constant 0.2 V was applied versus a Ag/AgCl reference electrode, and a Pt mesh was used as the counter electrode. The amount of PEDOT within the TiO_2 pores was varied by controlling the polymerization time as shown in Supporting Information SI 1. Assuming all the charge passed during the polymerization is consumed for the oxidative coupling of bis-EDOT, the calculated Z907 dye to bis-EDOT (contained in the PEDOT polymer) ratio at various deposition times is approximately 1.2 at 30 min and decreases logarithmically at shorter times (SI 1B).

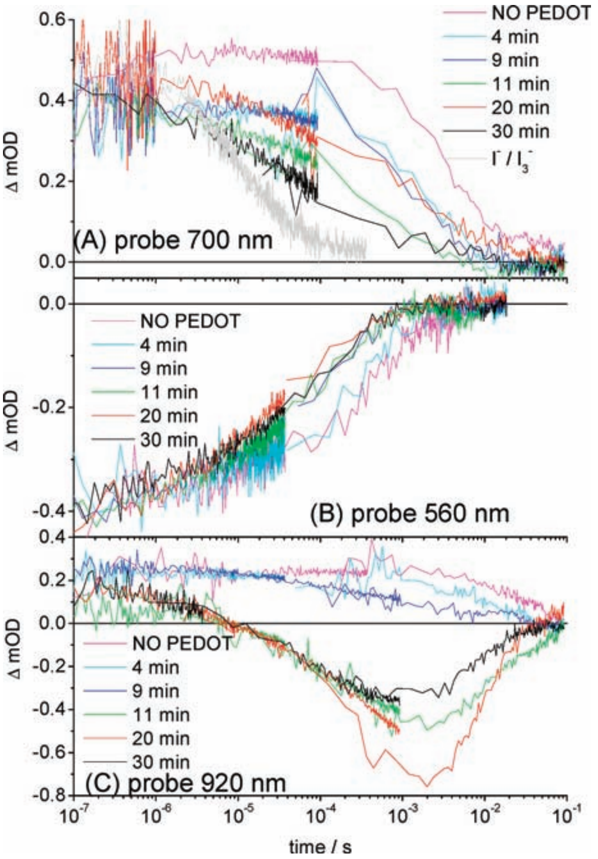

Figure 1. Transient absorption traces recorded at (A) 700, (B) 560, and (C) 920 nm as function of PEDOT growth time.

Figure 1 shows transient absorption (TA) signals of TiO_2/Z907 films containing PEDOT deposits grown for various times at three different probe wavelengths. The samples were treated with 1-ethyl-3-methylimidazolium bis-trifluoro-methanesulfone

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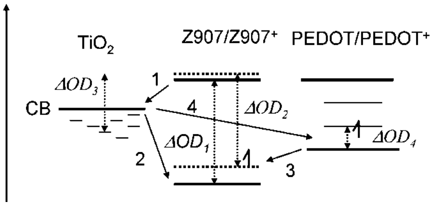

Figure 2. Schematics of electron transfer steps in ssDSSCs.

amide containing 0.2 M lithium bis-trifluoro-methanesulfone amide and 0.2 M 4-*tert*-butylpyridine for 24 h, a treatment reported to dramatically improve solar cell efficiency.[5]

Photons at the 532 nm pump wavelength are absorbed by Z907 leading to electron injection into the TiO$_2$ (step 1 in Figure 2) and Z907 cations (Z907$^+$). The TA signal at 700 nm corresponds to the absorption of Z907$^+$ (ΔOD$_2$ in Figure 2, TA spectrum of TiO$_2$/Z907 is shown in SI 2). The TA signal without PEDOT decays on the 1 to 10 ms time scale. The decay is gradually shifted to shorter times (1 μs to 1 ms) by depositing an increasing amount of PEDOT. The accelerated Z907$^+$ signal decay indicates Z907$^+$ regeneration by electron injection from PEDOT (step 3 in Figure 2). A 10% decrease in the initial signal amplitude is also observed in the presence of PEDOT. This cannot be explained by pump light absorption by PEDOT (see SI 3) and may be related to either a reduced electron injection rate (step 1 in Figure 2) or a fast component of the dye-regeneration kinetics that is not monitored within the time resolution of the setup (100 ns). Figure 1B shows TA signals recorded at 560 nm, which corresponds to the ground state bleaching of Z907 (ΔOD$_1$ in Figure 2). Similarly to Figure 1A, an increasingly faster Z907 ground state absorption recovery with longer PEDOT deposition time is observed. The signals in Figure 1B have been normalized to the TiO$_2$/Z907 signal (ΔmOD = -0.4) to aid comparison.

Figure 1C shows the transient absorption traces recorded at 920 nm. The initial positive ΔOD signal is attributed to light absorption by electrons injected into TiO$_2$ (ΔOD$_3$).[6] The decay of this initial absorption signal is accelerated by depositing PEDOT for up to 9 min. When PEDOT is deposited longer than that, the ΔOD absorption signal changes sign at ~10 μs to a strong bleaching signal, extending up to 10 to 100 ms. This negative signal is attributed to the bleaching of the intermediate absorption band of PEDOT (ΔOD$_4$) as the polymer attains higher doping levels, as previously assigned by detailed spectroelectrochemical measurements.[7] The rise time of the bleaching signal corresponds to the decay of the Z907$^+$ signal observed in Figure 1A and, therefore, is attributed to the oxidation of a "moderately doped" to high doping level PEDOT. The decay of the signal on the ms time scale corresponds to electron lifetime measurements performed by photovoltage decay[5] and, therefore, is attributed to the recombination step of the excess PEDOT holes with the excess electrons in the TiO$_2$ (step 4 in Figure 2).

The TA measurements indicate that Z907$^+$ regeneration in the TiO$_2$/Z907/PEDOT samples occurs on the 1 to 100 μs time scale, which is orders of magnitude slower than the typically observed ps to ns kinetics[2] using spiro-OMeTAD or the ns to μs kinetics using the I$^-$/I$_3$$^-$ redox couple (see Figure 1 A). The slow regeneration kinetics competing with recombination reactions between electrons in TiO$_2$ and Z907$^+$ (step 2 in Figure 2) may limit the short circuit current J_{sc}.

Table 1 compares the photovoltaic parameters of TiO$_2$/Z907/PEDOT ssDSSCs to those of TiO$_2$/Z907 photoanodes prepared using a standard I$^-$/I$_3$$^-$ electrolyte. The 3% conversion efficiency of an ssDSSC is one of the highest reported using CP hole conductors. The J_{sc} is 25% lower than that observed using the I$^-$/I$_3$$^-$ electrolyte, which cannot be explained by the difference in the light harvesting efficiency between the samples (see SI 3). Although a 10% reduction in the electron injection yield from Z907 to TiO$_2$ cannot be ruled out, the correlation between the J_{sc} and gradually faster dye regeneration kinetics with increasing PEDOT growth time suggests that the J_{sc} is limited by the slow dye regeneration kinetics.

Table 1. Photovoltaic Parameters and Total Polymerization Charge (*Q*) of ssDSSCs with Various Amounts of PEDOT Deposits

PEDOT growth time	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	Eff [%]	*Q* [mC cm^{-2}}
30 min	6.4	700	0.67	3	14.8
15 min	4.7	625	0.65	2	13.8
8 min	3.8	610	0.64	1.5	12.5
4 min	0.21	345	0.35	0.26	4.1
I$^-$/I$_3$ $^-$	8.42	755	0.63	4	N.A.

Electron injection from CP to the dye$^+$ may be controlled by the driving force as determined by the difference in oxidation potentials of the CP and the dye.[3] The oxidation potential of EDOT oligomers decreases with the number of EDOT units, e.g. 1.50 V, 0.84 V, 0.49 V versus Ag/AgCl for 1, 2, and 3 units.[8] At shorter growth times, the driving force for charge regeneration by shorter oligo-EDOT chains may be smaller, leading to a slower regeneration. Preliminary experiments indicate that the use of a small conjugated dye P257 (see SI 5) with an ~0.4 V higher oxidation potential than Z907 does not lead to significant acceleration of the regeneration kinetics. A more detailed study involving a wide range of sensitizers (porphyrins, indolines, and phenyl-conjugated oligoene dyes) is underway to determine the effect of driving force on the regeneration kinetics.

The calculated Z907 to bis-EDOT ratio is only 1:1.2 in the most efficient 3% ssDSSC. Yanagida et al. calculated[5] that PEDOT pore filling is only 20% after 30 min photoelectrochemical deposition, which may be responsible for the slow dye regeneration. Given this low pore filling, the efficient performance of the ssDSSCs is rather surprising and can be explained by the slow recombination between excess electrons in TiO$_2$ and excess holes in PEDOT, coupled to high electron diffusion coefficients.[5] Although improved pore filling is crucial for further performance enhancement, a large asymmetry between regeneration and recombination rates can also lead to high efficiency and is an important design rule for next generation redox couples intended to replace the corrosive I$^-$/I$_3$$^-$ couple.[9]

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Supporting Information Available: PEDOT polymerization; TA and UV−vis absorption spectrum of TiO$_2$/Z907 and TiO$_2$/Z907/PEDOT films, respectively; and photovoltaic device fabrication and testing. This material is available free of charge via the Internet at http://pubs.acs.org.

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