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Interfacially Treated Dye-Sensitized Solar Cell with in Situ Photopolymerized Iodine Doped Polythiophene

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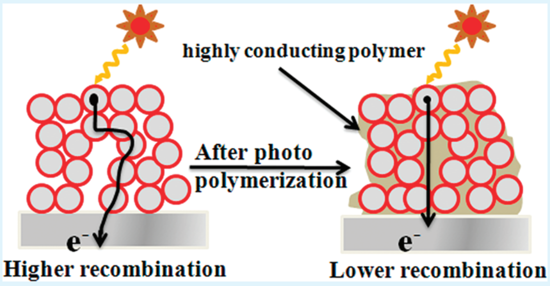
Supporting Information

ABSTRACT: A thin film of iodine doped polythiophene was grown photoelectrochemically around the dye-sensitized TiO_2 nanoparticles in a Grätzel cell, and the effect of iodine doping level on the cell performance was investigated using X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, and photovoltage decay. At an optimum doping level, the cell demonstrated the enhanced energy conversion efficiency by 27.52% compared to the cell without polythiophene.



KEYWORDS: *photopolymerization, polythiophene, iodine doping, interfacial treatment, enhanced energy conversion, dye sensitized solar cell*

1. INTRODUCTION

Dye-sensitized solar cell (DSSC) was introduced over a decade ago as a technically and economically viable alternative way for traditional p−n junction silicon solar cells.[1,2] Thereafter, various attempts have been made to enhance the performance of the cell.[3−10] A doctor bladed mesoporous film of TiO_2 nanoparticles is generally used as an n-type wide band gap material which is sensitized with a Ru dye. Among various factors, the nanoscale morphology of interfaces of such devices is always crucial for their performance. As a result of poor contact among TiO_2 nanoparticles, the mesoporous structure contains a large number of interfacial centers with a high interfacial resistance which traps the photogenerated electrons and delays the transportation of these electrons into the electrode side. This phenomenon enhances the unwanted charge carrier recombination. In order to reduce the recombination, in situ polymerized polythiophene is proposed here as an interfacial contact modifier to increase an intimate contact between TiO_2 nanoparticles in the mesoporous film. This polymer modifier layer can also adjust the hydrophobicity of the dyes sensitized TiO_2 particles to match well with the hydrophobic organic electrolyte.

It is already known that iodine doping can increase the electrical conductivity of polythiophene ranging from semiconductor to metallic regime, depending upon the level of doping.[11] Therefore, in the present study, a thin film of iodine doped polythiophene with different doping level was grown photoelectrochemically around the TiO_2 nanoparticles as an interfacial modifier layer. This modifier layer certainly has an additional advantage to further suppress the charge carrier recombination by collecting the scattered electrons from the grain boundary of TiO_2 particle film and accelerating the unidirectional electron transportation in TiO_2 film.

2. EXPERIMENTAL DETAILS

A ca. 12 μm thick mesoporous film of TiO_2 nanoparticles was doctor bladed on a FTO glass substrate using TiO_2 paste. The film was sintered at 450 °C, and it was sensitized with N3-ruthenium complex dye (Ru(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$(NCS)$_2$)). For photopolymerization, the above FTO/TiO_2/dye was used as a working electrode which was pressed against a Pt counter to construct a sandwich type cell with a polyimide tape as a spacer. A freshly prepared solution containing 0.1 M thiophene monomer, 0.1 M LiI, and various concentration of I_2 (0.0125 M = I-1:1/4, 0.05 M = I-1:1, 0.2 M = I-1:4) in acetonitrile was injected into the space between two electrodes, and polymerization was performed by illuminating with a white light source (50 mW) under the bias of +200 mV.

3. RESULTS AND DISCUSSION

Polythiophene is always synthesized by oxidative polymerization, and the chemical and electrochemical wet oxidative

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processes are the most widely used for growing conductive polymers. The electrochemical process initiates polymerization at the electrode surface, and hence, it creates the poor contact problem between TiO_2 film and the conducting glass electrode when the polymerization is performed on the electrode covered with the TiO_2 film. On the other hand, chemical oxidation for polymerization is not a very controllable process to deposit a homogeneous and thin film of polymer just around the TiO_2 nanoparticles in the mesoporous film. Therefore, in situ photopolymerization was preferred in the present study to deposit a very thin film of polythiophene homogeneously around the TiO_2 nanoparticles. Figure 1 shows the potentiostatic current transient at +200 mV bias potential during the polymerization of thiophene. In the dark condition, the current transient is almost constant, indicating no nucleation of polythiophene. However, it should be noted here that when the TiO_2 film was illuminated after a certain lapse of time, a sudden rise in current for the activation of polythiophene nucleation can be observed. With the illumination time, the current decreased and settled down after a certain time. This type of trend is the typical current transient for the nucleation and growth of polymer.[12] As revealed by the current transient under dark condition, the bias potential of +200 mV applied here cannot initiate the polymerization. This bias potential is just to drive the photogenerated charge carriers which prevents them from recombining and assists the polymerization. Upon white light illumination, dye gets excited and the excited electrons transfer to the TiO_2 conduction band. The excitation leaves holes on the HOMO level of the dye which has the key role to initiate polymerization. These holes are filled up by electrons from thiophene which leads thiophene to undergo oxidation and finally to the polymerization. In this way, the polythiophene layer grows only on the dye surface. In other words, the present technique deposits polytiophene only around the dye sensitized TiO_2 nanoparticles. Figure 2 shows the SEM images of the dye sensitized TiO_2 film before and after the in situ polymerization of thiophene. After the polymerization, a thin film of polythiophene can be seen only in a very few areas. However, when the time of polymerization was extended longer than 15 min, the top surface coverage of TiO_2 film by the polymer increased gradually and finally covered the whole surface. Therefore, the time of polymerization was optimized as 15 min.

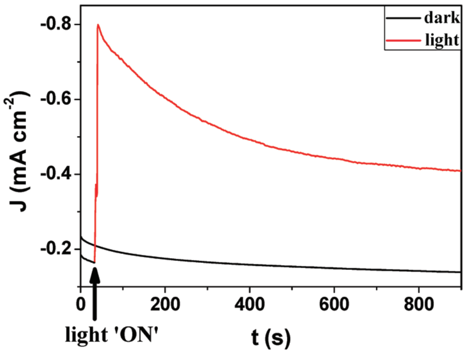

Figure 1. Potentiostatic current transient during in situ polymerization of 0.1 M thiophene in acetonitrile containing 0.1 M LiI and 0.1 m I_2 under the bias of +200 mV.

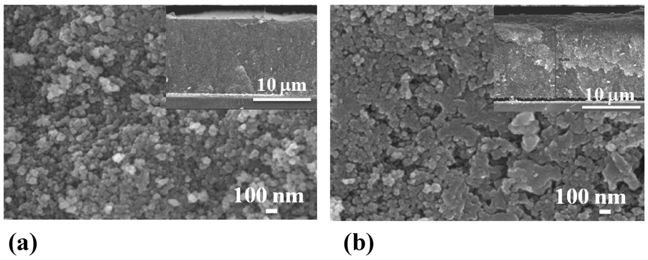

Figure 2. SEM top and cross sectional views of dye sensitized TiO_2 film (b) before and (c) after photopolymerization under illumination of 50 mW white light.

LiI and I_2 are the essential ingredients of electrolyte in DSSCs because, apart from just the function of an electrolyte, the I^-/I_3^- redox pair of the electrolyte also regenerates the oxidized dye.[4−6] Therefore, polymerization was performed in an electrolyte containing LiI and I_2 as a source of iodine for doping in the growing polymer matrix, and the doping level was varied with the concentration of iodine. An EDX investigation of the film after polymerization showed 0.02, 0.08, and 0.07 at % of iodine for the samples I-1:1/4, I-1:1, and I-1:4, respectively. More or less similar results were obtained when the above samples were further investigated using XPS. The XPS spectra exhibited by I 3d core of the iodine doped polythiophene with various level of doping in a dye sensitized TiO_2 films are shown in Figure 3 which shows the location of I $3d_{5/2}$ and I $3d_{3/2}$ peaks at the binding energy of 620.75 and 632.25 eV, respectively. The location of these peaks and the peak separation of 11.5 eV strongly suggest the characteristic of iodine doped polymer.[13,14] On the basis of EDX result and the peak area in I 3d XPS spectra, clearly, the doping level in polythiophene was high when the concentration of LiI and I_2 in the electrolyte was 0.1 M (i.e., I-1:1 sample). The thermogravimetry analysis (TGA) also showed the maximum weight loss up to 14% for this sample I-1:1, indicating the higher amount of polymer content and the doping level (Figure S1, Supporting Information).

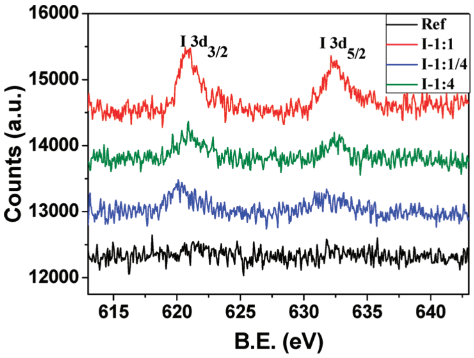

Figure 3. I 3d XPS spectra of an iodine doped polythiophene film.

Since an electrolyte is needed to drive the in situ photopolymerization of thiophene under the external bias potential (Figure S2, Supporting Information), ions from the electrolyte always are incorporated into the growing polymer layer. Therefore, it was not possible to photopolymerize thiophene without doping. Attempts to undope iodine from the doped polymer layer by electrochemical reduction process destroyed the dye and the TiO_2 film. As a result, photopolymerization without iodine doping could not be investigated in the present work. When all the samples with different doping level were examined for the photovoltaic performance, the sample I-1:1 with the highest doping level demonstrated the best cell performance with the energy conversion efficiency of 6.44%. It is the enhancement factor by 27.52% compared to the cell without polythiophene interfacial modifier (ref) which exhibited only 5.05% of the energy conversion efficiency (Figure 4). The details of photovoltaic parameters of the polythiophene modified DSSCs with different doping level are summarized in Table 1.

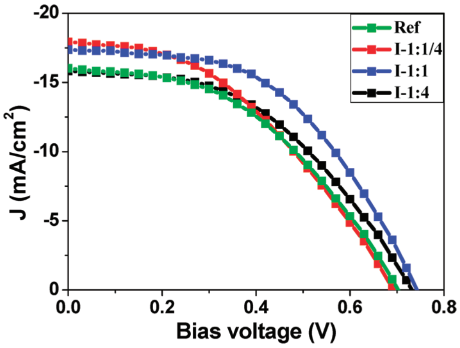

Figure 4. $J-V$ characteristic curves of DSSCs with and without (ref) polythiophene interfacial film.

Table 1. Photovoltaic Performance Parameters of DSSCs without (Ref) and with in Situ Polymerized Iodine Doped Polythiophene Layer as an Interfacial Modifier under Illumination of Simulated Solar Radiation (50 mW cm^{-2})

sample	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	eff (%)
ref	0.70	16.03	0.45	5.05
I-1:1/4	0.69	17.92	0.42	5.16
I-1:1	0.74	17.37	0.50	6.44
I-1:4	0.73	15.83	0.46	5.38

To understand the role of iodine doping on the cell performance, electrochemical impedance spectroscopy (EIS) was studied. Figure 5a shows the Nyquist plots of DSSCs with and without polythiophene modification (ref), and Figure 5b is the equivalent circuit model employed to fit the impedance data. Here, Rs denotes the series resistance, R1 stands for the charge transfer resistance of the FTO/TiO$_2$, and R2 is the charge transfer resistance of TiO$_2$/dye/polythiophene/electrolyte.[15] Considering all other interfacial resistances constant under the same experimental conditions, the R2 value is mainly influenced by the doping level of iodine which is the focal point of the present investigation. Table 2 summarizes the quantitatively fitted results of the Nyquist plots using the equivalent circuit. The Nyquist plots before and after fitting were found to be very close (Figure 5a), and the error limits on various impedance parameters were within 1%. Here, higher R2 value indicates the higher electronic resistance of the in situ plolymerized polymer film, and such a film with high R2 value hardly collects the scattered electrons from the grain boundary of TiO$_2$ film. As a result, an increase in charge carrier recombination takes place which leads to the reduction of the fill factor (FF) of the cell. In other words, increasing conductivity of the interfacial polymer film accelerates the unidirectional transportation of electrons in the TiO$_2$ film which reduces the recombination and increases the FF. Therefore, it is noteworthy to correlate R2 values in Table 2, the fill factor (FF) value in Table 1, and the doping level of iodine in polythiophene layer. Here, the cell with the highest doping level (i.e., I-1:1) exhibited the lowest R2, highest FF, and the highest energy conversion efficiency (Eff). Surprisingly, the cell with the lowest doping level (i.e., I-1:1/4) exhibited the higher R2 and lower FF values than the cell without polymer interfacial modifier (i.e., ref). It is probably due to very low doping level which might not be enough to reduce the interfacial resistance. Instead, compared to the ref cell, it might have increased the interfacial resistance as a nonconducting electron blocking layer in TiO$_2$ film. However, irrespective of the iodine doping level, the presence of polytiophene film checks the back electron transport into electrolyte which also assists to reduce the recombination, although this contribution is very low compared to the contribution from the unidirectional fast electron transportation.

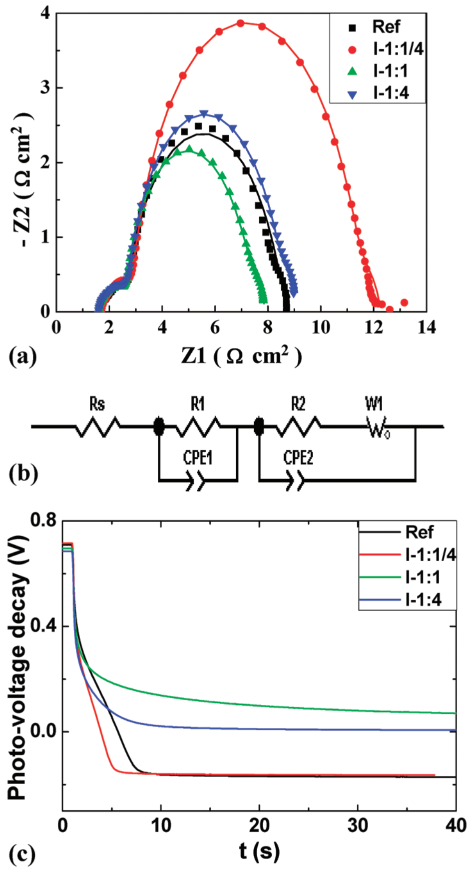

Figure 5. (a) Nyquist plots: triangles, squares, and circles are the data points; solid lines represent the fitted data using an equivalent circuit shown in (b), (b) equivalent circuit model, and (c) photovoltage decay, of DSSCs with and without polythiophene interfacial film.

Apart from FF, open circuit voltage (V_{oc}) is another factor which determines the cell performance. As expected, the cell with high open circuit voltage (V_{oc}) and high FF demonstrated the high Eff (Table 1). Therefore, it is noteworthy to investigate how the V_{oc} decays with the time when the light source is switched off, which is a measure of an indirect way to know the lifetime of photogenerated electron in the cell being investigated. In other words, it indicates the kinetics of charge carrier recombination[16,17] and reveals that the high recombination rate kills the hot electrons faster, resulting in the faster V_{oc} decay. Figure 5c reveals that the V_{oc} decay in the cell I-1:1 with the highest iodine doping is the slowest followed by the cell I-1:4 with the second highest doping level, the ref cell, and

Table 2. Parameters Obtained by Fitting the Impedance Spectra of DSSCs without (Ref) and with in Situ Polymerized Iodine Doped Polythiophene Layer as an Interfacial Modifier

sample	Rs ($\Omega\cdot m^2$)	R1 ($\Omega\cdot m^2$)	CPE 1−T (mF/cm^2)	CPE 1−P	R2 ($\Omega\cdot m^2$)	CPE2−T (mF/cm^2)	CPE 2−P	W1−R ($\Omega\cdot m^2$)	W1−T (F/cm^2)	W1−P
ref	1.72	0.95	0.67	0.73	5.72	3.47	0.87	0.54	9.42	0.39
1:1/4	1.67	1.31	1.81	0.64	8.28	3.167	0.94	0.97	10.40	0.41
1:1	1.59	1.12	1.13	0.68	4.47	3.23	0.96	0.72	3.38	0.42
1:4	1.56	1.18	1.32	0.67	5.63	3.55	0.95	0.77	4.58	0.50

the cell I-1:1/4 with the lowest doping level. These results are in good agreement with the R2 and electron lifetime demonstrated by the EIS and V_{oc} decay studies. Compared to the cell without the interfacial polythiophene modifier layer, the incident photon to current efficiency (IPCE) of the cell with the interfacial polythiophene modifier layer was found to be higher (Figure S3, Supporting Information) which also supports that the interfacial modifier layer suppresses the recombination.

4. CONCLUSIONS

Introduction of a thin film of iodine doped poythiophene around the dye-sensitized TiO_2 nanoparticles in a DSSC helps to suppress the recombination by accelerating unidirectional electron transportation in TiO_2 film which enabled one to enhance the power conversion efficiency by the factor of 27.52%, leading to the final efficiency of 6.44%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Thermogravimetry analysis (TGA), additional potentiostatic current transient and incident photon to current efficiency (IPCE). This material is available free of charge via the Internet at http://pubs.acs.org.

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