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Unusual Enhancement of Photocurrent by Incorporation of Brönsted Base Thiourea into Electrolyte of Dye-Sensitized Solar Cell

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Thiourea was used as an additive in the iodide/iodine redox electrolyte for dye-sensitized solar cell and its effect was investigated. Thiourea was found to have the simultaneous effect of a positive band edge shift and a decrease in charge recombination rate. Addition of 0.05 M thiourea in the electrolyte comprising 0.7 M 1-methyl-3-propylimidazolium iodide (MPII) and 0.05 M I_2 in acetonitrile enhanced significantly photocurrent density from 7.7 to 10.8 mA/cm^2, while voltage decreased from 0.78 to 0.71 V. As a result, overall conversion efficiency increased from 4.7% to 5.8%, corresponding to increment of 23%. The solution acidity was changed from $pK_a = 18.9$ (thiourea in acetonitrile) to $pK_a = 4.9$ (thiourea in iodide- and iodine-containing acetonitrile), corresponding to change in pH from 10.1 to 3.1, which was attributed to chemical reaction between thiourea and iodine. As a consequence of the reaction, protons were produced and triiodide concentration was slightly reduced. The generation of protons in the electrolyte, associated with a positive shift of conduction band edge, led to a significant increase in photocurrent density. The unexpectedly small voltage drop, however, was ascribed to a slow recombination rate due to the reduced triiodide concentration. A large increase in photocurrent density along with a small decrease in voltage was also demonstrated from the variation of thiourea concentration.

Introduction

A dye-sensitized solar cell (DSSC) composed of a dye-adsorbed mesoporous TiO_2 film, a redox electrolyte, and a platinum-coated counter electrode has been considered as a low-cost solar-to-electrical energy conversion device.[1] Compared to the conventional solar cell comprising n-type and p-type semiconductors, the use of electrolyte in DSSC makes a clear distinction between DSSC and the conventional pn junction device. The I^- and I_3^- in electrolyte play an important role in regeneration of the oxidized dye by reduction and oxidation reaction. Apart from the redox role of electrolyte, cations and additives in electrolyte have been known to influence photovoltaic performance since they affect conduction band edge energy of TiO_2 and/or charge recombination.[2,3] Among the studied additives, 4-*tert*-butylpyridine (TBP) has been typically used as a means of improving open-circuit voltage.[4] The increased voltage by TBP treatment was found to be related to recombination kinetics at TiO_2/electrolyte interface and TiO_2 conduction band edge displacement.[5−8] It was also reported that TBP prevented triiodide access to the TiO_2 surface by complexation with iodine, leading to decrease of the recombination of photoinjected electrons.[9−11] According to the previous studies on TBP, its role seems to be attributed to both the negative shift of the conduction band edge of TiO_2 and the suppression of charge recombination. There is another additive, guanidinium thiocyanate (GSCN), which has recently been used.[12−14] Contrary to TBP, GSCN was found to shift the conduction band of TiO_2 to positive direction. However, the addition of GSCN into the electrolyte led to an increase in voltage in spite of the positive shift of TiO_2 conduction band position. Detailed study showed that the significant decrease in charge recombination by a factor of about 20 compensated for the downward shift of band edge by 100 mV, which was responsible for the increased voltage.[15]

Compared to TBP that is neutral and Brönsted base, GSCN is ionic and guanidinium cation $(NH_2)_3C^+$ is the conjugate acid of guanidine $(NH_2)_2C = NH$ and has a pK_a of 13.[15] We have been interested in GSCN analog, thiourea $(NH_2)_2C{=}S$, as an additive in electrolyte because thiourea is neutral and Brönsted base. It is therefore interesting to investigate the effect of thiourea on photovoltaic property of dye-sensitized solar cell. Here we report photovoltaic property and transient photocurrent and photovoltage characteristics of dye-sensitized solar cells in the presence of thiourea in electrolyte.

Experimental Section

Anatase TiO_2 nanoparticles were synthesized by acetic acid catalyzed hydrolysis of titanium isopropoxide (97%, Aldrich), followed by being autoclaved at 230 °C for 12 h. Aqueous solvent in the autoclaved TiO_2 colloid solution was replaced by ethanol for preparation of non-aqueous TiO_2 paste. Ethyl cellulose (Aldrich), lauric acid (Fluka), and terpineol (Aldrich) were added into the ethanol solution of the TiO_2 particles, and then ethanol was removed from the solution using a rotary evaporator to obtain viscous pastes. For homogeneous mixing, the paste was further treated with a three-roll mill. The nominal composition of TiO_2/terpineol/ethylcellulose/lauric acid was about 1.25/4/0.3/0.1.

FTO glasses (Pilkington, TEC-8, 8 Ω/sq) were washed in ethanol using an ultrasonic bath for 10 min. The FTO layer was first covered with 0.1 M Ti(IV) bis(ethyl acetoacetato)-diisopropoxide (Aldrich) in 1-butanol (Aldrich) solution by the spin-coating method, on which the nanocrystalline TiO_2 paste was deposited using a doctor-blade technique. After the TiO_2

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films were heated at 550 °C for 1 h, the sides of TiO_2 films was trimmed to 9-mm wide and 5-mm long. The thickness of TiO_2 films was measured by an Alpha step profiler. The annealed TiO_2 electrodes were immersed in ethanol containing 0.5 mM N719 dye (Esolar, $TBA_2[RuL_2(NCS)_2]$, where L is 4-carboxylic acid-4′-carboxylate-2,2′-bipyridine and TBA is tetrabutylammonium) for 5 h at 40 °C. Pt counter electrodes were prepared by spreading a droplet of 0.7 mM H_2PtCl_6 in 2-propanol on top of a FTO substrate and heating heated at 400 °C for 20 min. The two electrodes were sealed with 25 μm-thick Surlyn (Solaronix). The redox electrolyte was introduced through a small hole drilled in the counter electrode. The electrolyte (E1) was composed of 0.7 M 1-methyl-3-propylimidazolium iodide (MPII) and 0.05 M I_2 in acetonitrile and the electrolyte (E2) consisted of 0.05 M thiourea, 0.7 M MPII and 0.05 M I_2 in acetonitrile.

Photocurrent−voltage measurements were performed using a Keithley 2400 source measure unit. A 1000 W xenon lamp (Oriel) was used as the light source and the light intensity was adjusted using an NREL-calibrated Si solar cell equipped with a KG-2 filter for approximating AM 1.5 G one sun light intensity (100 mW/cm^2). The incident photon-to-current efficiency (IPCE) spectra was measured as a function of wavelength from 300 to 800 nm under DC measurement mode using a specially designed IPCE system (PV Measurements, Inc.), where a 75 W xenon light source was used for monochromatic light. The absorbance of electrolytes was recorded by a UV−vis spectrophotometer (Agilent 8453) in the wavelength range of 300−800 nm. The pH of electrolytes was examined by a pH meter (Hanna instruments, HI 4222).

The time constants for photoinjected electron transport and recombination were measured by using a photocurrent and photovoltage transient setup. The cells were probed with a weak laser pulse at 532 nm superimposed on a relatively large, back ground (bias) illumination at 680 nm. The bias light was illuminated by a 0.5 W diode laser (B&W TEK Inc., Model: BWF1−670−300E/55370). The intensity of the bias light was adjusted using ND filters (neutral density filters). The 680 nm bias light is only weakly absorbed by the dye, and therefore the injected electrons are introduced into a narrow spatial region of the film, corresponding to where the probe light enters the film. A 30 mW frequency-doubled Nd:YAG laser (Laser-Export Co. Ltd. Model: LCS-DTL-314QT) ($\lambda = 532$ nm, pulse duration 10 ns) was used as probe light. The photocurrent transients were obtained by using a Stanford Research Systems model SR570 low-noise current preamplifier, amplified by a Stanford Research Systems model SR560 low-noise preamplifier, and recorded on Tektronics TDS 3054B digital phosphore oscilloscope 500 MHz 5GS/s DPO. The photovoltage transients were obtained by using SR560 preamplifier, which was recorded on oscilloscope combined with Keithley 2400 measure unit. The photocurrent- and the photovoltage−time curves were fitted with an exponential relationship, $y(t) = \exp(-t/\tau)$, where y represents photocurrent density or photovoltage, t is time and τ (τ_C for electron transport and τ_R for recombination) is constant.

Results and Discussion

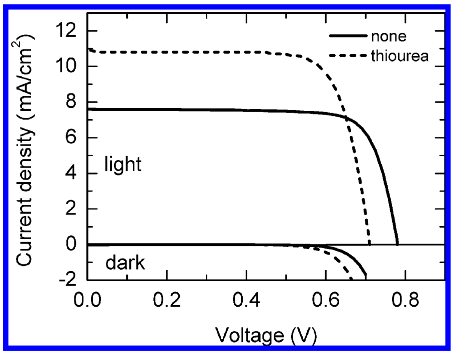


Figure 1. Photocurrent density−voltage characteristics of dye-sensitized solar cells with and without 0.05 M thiourea in electrolyte having 0.7 M MPII and 0.05 M I_2 in acetonitrile. TiO_2 film thickness was ~6 μm. Measurements were performed under AM 1.5 G light illumination (100mW/cm^2) and the cells were covered with aperture masks during measurement.

Figure 1 compares photocurrent density−voltage curves of DSSCs with and without thiourea and photovoltaic parameters are summarized in Table 1. The thiourea-containing electrolyte shows higher photocurrent density and lower voltage. For the 6-μm-thick TiO_2 film, the photocurrent density increases by about 40%, from 7.7 mA/cm^2 to 10.8 mA/cm^2 after incorporation of thiourea, while the voltage decreases from 0.78 to 0.71 V. As a result, overall conversion efficiency is increased from 4.7% to 5.8%, corresponding to increment of 23%. Similar tendency is observed for the thicker film of 11 μm, where the photocurrent density is improved from 11.9 mA/cm^2 to 13.4 mA/cm^2 and voltage is decreased from 0.76 to 0.71 V. As mentioned previously, nitrogen-containing Brönsted bases, such as TBP and other pyridine derivatives, in electrolyte generally increase photovoltage, associated with negative shift of TiO_2 conduction band, and has little or adverse effect on photocurrent.[16−18] When considering that thiourea is Brönsted base, the significant increase in photocurrent density is thus unusual. This unusual enhancement of photocurrent along with a slight decrease in voltage observed in the presence of thiourea is first thought to be probably due to an improved electron transport rate and/or an accelerated charge recombination rate.

Figure 2 shows time constants for electron transport (Figure 2a) and electron recombination (Figure 2b). Contrary to our expectation, there is little difference in electron transport kinetics but time constant for electron recombination is slightly longer for the thiourea-containing electrolyte. The increased photocurrent by incorporation of thiourea does not seem to correlate to electron transport kinetics. The longer recombination time constant means that the electron lifetime increases in the presence of thiourea, which is expected to increase voltage. However, the open-circuit voltage is turned out to decrease in spite of the reduced recombination rate, which underlines a positive shift of conduction band edge energy of TiO_2. Since the recombination kinetics and the band edge movement are in trade-off relationship, it is important to figure out which factor is predominant. For instance, the GSCN additive induced a positive shift of conduction band but reduced recombination rate at the same time. It came to conclusion that the increase in voltage observed in the presence of GSCN additive was mainly attributed to the reduced charge recombination.[15] It was reported that addition of 2-methyl-4-propoxypyridine improved photovoltage although the rate of interfacial charge recombination was enhanced.[19] In this case, the negative shift of conduction band of TiO_2 was a predominant factor affecting the increased voltage. To investigate the basis for the increased photocurrent and the decreased voltage in the presence of thiourea, spectroscopic analysis is performed.

Figure 3 shows IPCE spectra for the cells with and without thiourea in the electrolyte. As expected, the absolute IPCE is higher for the thiourea-containing electrolyte. Here, we had better pay attention to the IPCE at around 360 nm. Since I_3^- ions absorb 360 nm light,[10] N719 dye cannot absorb effectively

TABLE 1: Comparison of Short-Circuit Photocurrent Density (J_{SC}), Open-Circuit Voltage (V_{OC}), Fill Factor (FF), and Conversion Efficiency (η) of the Dye-Sensitized Solar Cells with and without Thiourea in Electrolyte[a]

sample	composition of electrolyte	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)	TiO_2 thickness (μm)
none	0.7 M MPII, 0.05 M I_2	7.7	0.78	0.78	4.7	6
		11.9	0.76	0.75	6.8	11
thiourea	0.05 M thiourea, 0.7 M MPII, 0.05 M I_2	10.8	0.71	0.75	5.8	6
		13.4	0.71	0.75	7.1	11

[a] Acetonitrile was used as a solvent for electrolyte. Data were obtained under the AM 1.5 G light illumination (100mW/cm^2). An aperture mask was used during measurement.

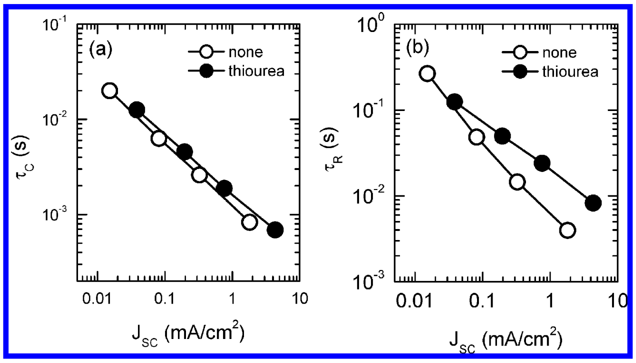


Figure 2. Time constants for (a) electron transport and (b) recombination as a function of light intensity, represented by photocurrent density. TiO_2 film thickness for transient study was 6 μm.

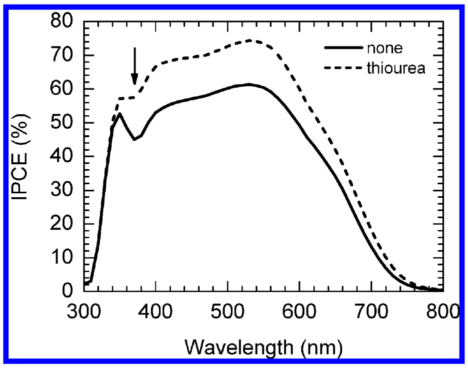


Figure 3. Incident photon-to-current conversion efficiency (IPCE) as a function of wavelength for dye-sensitized solar cells with and without thiourea in electrolyte. TiO_2 film thickness is ~11 μm. Arrow indicates that IPCE at around 360 nm competes with absorption by I_3^- ions in electrolyte.

at around 360 nm light because of competition with absorption by I_3^-. For this reason, relatively low IPCE is generally observed at around 360 nm. Compared to the IPCE at around 360 nm for the electrolyte without thiourea, the thiourea-containing electrolyte shows relatively high IPCE, which indicates that triiodide concentration is relatively lower for the thiourea-containing electrolyte than for the electrolyte without thiourea.

In Figure 4, we compare the UV−vis absorption spectra of the redox electrolyte with and without thiourea. Strong absorption at around 360 nm is due to I_3^- species, which is substantially reduced in the presence of thiourea. This decrease in I_3^- concentration suggests that iodine might be in part consumed by reaction with thiourea. Therefore, for the thiourea-containing electrolyte, the relatively high IPCE at around 360 nm as observed in Figure 3 can be explained by the reduced I_3^- concentration. In addition, the relatively longer time constant for recombination observed from transient photovoltage measurement in Figure 2 can be also explained by the reduced I_3^- concentration because the recombination rate increases in general with increasing I_3^- concentration.[20] Although the addition of thiourea retards the charge recombination by

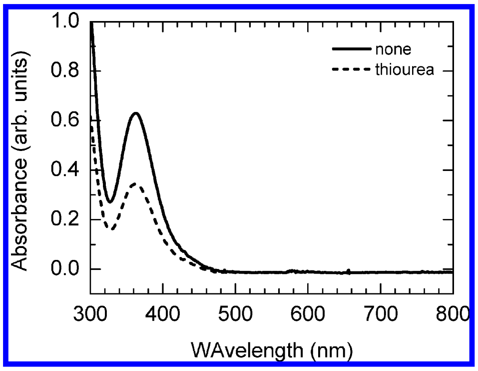
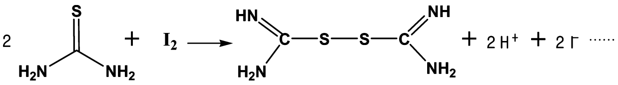


Figure 4. Absorption spectra of electrolyte (0.7 M MPII and 0.05 M I_2 in acetonitrile) with and without thiourea as a function of wavelength.

decreasing the amount of triiodide in electrolyte, it cannot be ruled out that the thiourea molecules themselves may physically and/or chemically adsorb on TiO_2 surface, thereby retarding the charge recombination.

Since we use the same amount of iodine for preparing E1 (without thiourea) and E2 (with thiourea) electrolytes, lower concentration of I_3^- in the E2 electrolyte is likely to result from chemical reaction between thiourea and iodine, as evidenced by the UV−vis absorption measurement. It has been known that formamidine disulfide forms when thiourea reacts with iodine,[21] as can be seen in eq 1.



(1)

If this reaction occurs in electrolyte, then triiodide concentration is expected to be lowered because iodine is consumed by reaction with thiourea. In addition, pH of the electrolyte is likely to be altered because the reaction produces protons. We measured the pH of the 0.05 M thiourea in acetonitrile and pH of the 0.05 M thiourea in redox electrolyte of 0.7 M MPII and 0.05 M I_2 in acetonitrile. When 0.05 M thiourea is added to aprotic acetonitrile (pK_a in aprotic solvent is described in reference[22]), pH of the solution exhibits 10.1, corresponding to pK_a of 18.9, indicating that the solution is basic. However, when thiourea is added to the iodide/iodine redox electrolyte, the solution becomes acidic characteristics with pH of 3.1 (pK_a = 4.9). The acidic property is ascribed to the probable reaction between thiourea and iodine as described in eq 1. On the basis of eq 1 and the measured pH, it can be deduced that about 2% ($= 10^{-3.1}/5 \times 10^{-2}$) of thiourea reacts with iodine. It was reported that increase in the number of proton increased photocurrent density and decreased photovoltage.[23] Therefore, the increased photocurrent density by thiourea additive is attributed to the generation of protons in electrolyte. Besides proton as a byproduct, the reaction also produces iodide ions according to eq 1. Therefore, the net iodide concentration is

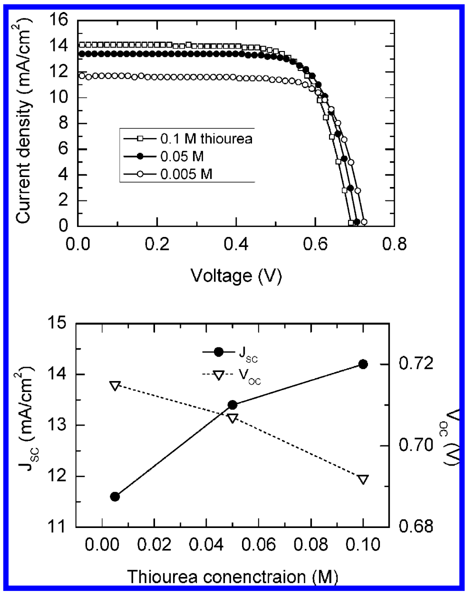


Figure 5. Effect of thiourea concentration in electrolyte on photovoltaic property. The electrolyte was composed of 0.7 M MPII, 0.05 M I_2 and x M thiourea in acetonitrile, where $x = 0.005$, 0.05, and 0.1 M. TiO_2 film thickness was about 11 μm.

expected to slightly increase in the thiourea-containing electrolyte. Iodide concentration was reported to affect photocurrent density as well,[24] where photocurrent density was found to increase with increasing the iodide concentration. The increased photocurrent density for the thiourea-containing electrolyte is thus associated with not only protons but also the increased iodide concentration. One can expect that photovoltaic property is probably dependent on thiourea concentration since the proton concentration, as well as iodide and triiodide concentration, can be changed by thiourea concentration.

Figure 5 shows dependence of photocurrent and voltage on thiourea concentration. Photocurrent and voltage are substantially affected by thiourea concentration, where photocurrent density increases significantly and voltage decreases slightly with increasing thiourea concentration. This is due to the fact that proton concentration is expected to increase with increasing thiourea concentration, leading to gradual shift of band edge toward positive direction, which results in gradual changes in both voltage and photocurrent. It is noticed that a large increase in photocurrent density is observed as thiourea increases from 0.005 to 0.05 M, while voltage decreases relatively to small extent. It can be expected that a significant increase in proton concentration from 10× increase in thiourea concentration leads to a large decrease in voltage. However, the observed small decrease in voltage is attributed to the reduced I_3^- concentration, associated with slow recombination rate as confirmed from photovoltage transient spectroscopy in Figure 2(b). This suggests that thiourea can simultaneously control band edge displacement and recombination kinetics by the way of doing positive shift of conduction band edge and suppression of recombination.

Conclusions

We studied thiourea as an additive in the iodide/triiodide electrolyte for dye-sensitized solar cells and investigated its effect on photovoltaic property. Unlike the reported TBP and pyridine derivatives that induced a negative shift of the band edge, associated with their basic property, leading to an increase in voltage and decrease or little change in photocurrent, thiourea in the redox electrolyte was found to decrease voltage and increase photocurrent of dye-sensitized solar cell despite that it is known to be a base. The studies on UV−vis absorption, IPCE and pH measurement confirmed that triiodide concentration was decreased in the presence of thiourea since iodine was consumed by reaction with thiourea. In addition, thiourea decreased the pH of the electrolyte from pH = ∼10 to pH = ∼3, which resulted in production of protons in the electrolyte. According to transient photovoltage study, a decrease in triiodide concentration reduces the charge recombination rate, with the expectation that the voltage would be improved. Nevertheless, the observed voltage was slightly decreased, which was related to pH (proton concentration) and the consequent positive shift of the band edge. It was noticed that the voltage was not significantly altered even in the presence of protons, which was due to a complementary effect of slow recombination rate. We suggest here that thiourea is a useful additive since it shows dual effects of positive band edge shift, associated with high photocurrent, and suppression of recombination, associated with prevention of a large decrease in voltage.

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