

Co-sensitization of N719 with an Organic Dye for Dye-sensitized Solar Cells Application

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The co-sensitization of N719 with a cyclic thiourea functionalized organic dye, coded AZ5, for dye-sensitized solar cells (DSSCs) was demonstrated. Due to its intensive absorption in ultraviolet region, AZ5 could compensate the loss of light harvest induced by triiodide, thereby the short-circuit photocurrent density (J_{sc}) was increased for co-sensitized (N719+AZ5) DSSC. Moreover, the electron recombination and dye aggregation were retarded upon N719 cocktail co-sensitized with AZ5, thus the open-circuit voltage (V_{oc}) of co-sensitized device was enhanced as well. The increased J_{sc} ($17.9 \text{ mA}\cdot\text{cm}^{-2}$) combined with the enhanced V_{oc} (698 mV) ultimately resulted in an improved power conversion efficiency (PCE) of 7.91% for co-sensitized DSSC, which was raised by 8.6% in comparison with that of N719 (PCE = 7.28%) sensitized alone. In addition, co-sensitized DSSC exhibited a better stability than that of N719 sensitized device probably due to the depression of dye desorption.

Key Words : Co-sensitization, N719, Cyclic thiourea, Organic dye, Dye-sensitized solar cells

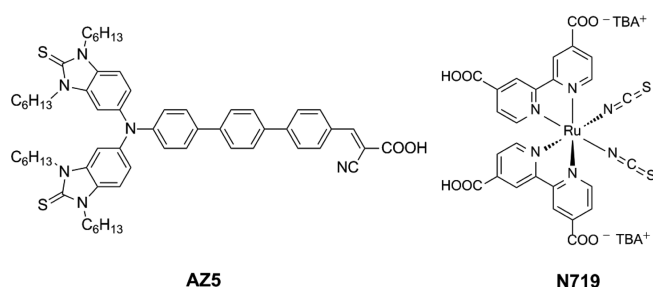
Introduction

Dye-sensitized solar cells (DSSCs) have received considerable scientific research attentions in recent years because of their easy fabrication process, low price and high energy conversion efficiency.^{1,2} Usually, a typical DSSC is composed of four components, including a photoanode, a sensitizer, an electrolyte, and a counter electrode. Among these constituents, the sensitizer directly affects the power conversion efficiency (PCE) since it plays a critical role in light-harvesting and the subsequent charge injection into the conduction band of TiO₂.³⁻⁵ So far, various kinds of sensitizers, such as ruthenium complexes,⁶⁻⁸ porphyrin compounds,^{9,10} and organic dyes¹¹⁻¹⁴ have been developed in the past two decades. An ideal sensitizer should harvest the sunlight as much as possible to achieve panchromatic absorption, for example, the ruthenium complex N749 (black dye) can harvest photons below a threshold wavelength of 920 nm and yielded a remarkably high PCE of 11.1%.¹⁵ However, it is a very tough work to design a panchromatic sensitizer that absorbs photons over the entire sunlight spectrum. In addition, the charge injection process will be jeopardized by lowering the lowest unoccupied molecular orbital (LUMO) energy to expand the absorption spectral into the near-infrared region, thus resulting in a lower PCE.¹⁶

On the other hand, co-sensitization using two or multiple sensitizers with complementary absorption spectra is another practical approach to achieve DSSCs panchromatic light harvesting.¹⁷⁻⁴⁰ Many co-sensitization systems have been proposed and demonstrated improved photovoltaic performance, such as ruthenium complex co-sensitized with an organic dye,¹⁷⁻²⁶ porphyrin²⁷⁻³⁰ or phthalocyanine³¹⁻³⁴ co-sen-

sitized with an organic dye, and organic dye co-sensitized with another organic dye.³⁵⁻⁴⁰ The co-sensitizers generally have a suitable molecular structure to avoid competitive adsorption and effectively suppress dye aggregation.¹⁷⁻³⁹ Additionally, they have a large molar extinction coefficient in the red-shifted region^{18,26,29,36,37} or around 400 nm to compensate for the light-harvest loss by electrolytes (Γ^-/I_3^-),^{20,23-25,32} moreover, they usually could form a compact molecule monolayer with the main sensitizer under co-sensitization condition to depress electron recombination.^{20,22,24,35}

Recently, we reported a series of cyclic thiourea/urea functionalized triphenylamine-based organic sensitizers for high-performance DSSCs.⁴¹ Among them, AZ5 (Scheme 1, left), which took cyclic thiourea functionalized triphenylamine as the electron donor, biphenyl as the π -conjugation linker and cyanoacrylic acid as the acceptor, exhibited a broad UV-vis absorption band with a high molar extinction coefficient ($66\ 000 \text{ M}^{-1} \text{ cm}^{-1}$ in acetonitrile) around 350 nm. And this characteristic can be used to recover the photocurrent loss induced by the absorption (below 400 nm) of electrolytes (Γ^-/I_3^-).⁴² Furthermore, the bulky cyclic thiourea functionalized triphenylamine donor in AZ5 could efficiently suppress the unfavourable electron recombination processes, additionally, the long alkyl chains substituted at cyclic thiourea groups may be helpful to reduce dye aggregation.^{20,23,43} On the other hand, as a typical ruthenium complex sensitizer, N719 (Scheme 1, right) has wide spectral response over visible to near infrared spectrum but relatively weaker absorption over ultraviolet spectrum.⁴⁴ Therefore, AZ5 could be a good candidate for co-sensitization with N719 due to their complementary absorption spectra as well as different molecular



Scheme 1. Molecular structures of **AZ5** and **N719**.

sizes and anchoring groups. Here, the co-sensitization of **N719** with **AZ5** *via* a cocktail approach was presented, and the co-sensitized DSSC exhibited an improved *PCE* (7.91%) with respect to that of the individual devices sensitized with **N719** (*PCE* = 7.28%) or **AZ5** (*PCE* = 4.37%), which is mainly attributed to the comparatively higher J_{sc} coupled with an enhanced V_{oc} .

Experimental

N719 was synthesized following the reported procedure,⁴⁴ and the synthesis procedure of **AZ5** was published elsewhere.⁴¹

Fabrication of DSSCs. The glass plates (F-doped SnO_2 , 14 Ω/sq , > 90% transparency in the visible region, Geao Co.) were sequentially cleaned in a detergent solution for 30 min, acetone solution for 15 min, deionized water for 15 min using an ultrasonic bath. Then were coated a paste of TiO_2 (20 nm, Geao Co.) by screen-printing method. The nanoporous TiO_2 working electrodes were then sequentially heated at 325 $^\circ\text{C}$ for 5 min, 375 $^\circ\text{C}$ for 5 min, 450 $^\circ\text{C}$ for 15 min, and finally 480 $^\circ\text{C}$ for 15 min. The thickness of TiO_2 film was measured by SEM (Quanta 200) and the result was about 12 μm . Upon cooling to room temperature, the TiO_2 electrodes were immersed in the following *tert*-butanol-acetonitrile (1/1, v/v) solutions at room temperature for 24 h: (a) 0.3 mM **AZ5**; (b) 0.3 mM **N719**; (c) 0.3 mM **N719** and 0.2 mM **AZ5**. The counter electrode was prepared by screen-printing a paste of Pt (Geao Co.) on an FTO substrate and sintering at 400 $^\circ\text{C}$ under air for 30 min. The dye-adsorbed TiO_2 working electrode and a counter electrode were then assembled into a sealed DSSC with a sealant spacer (25 μm , Surlyn 1702) between the two electrode plates. A drop of electrolyte solution [0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M LiI, 0.03 M I_2 , and 0.5 M 4-*tert*-butylpyridine in acetonitrile and valeronitrile (15/85, v/v)] was introduced into the cell through a drilled hole *via* vacuum back-filling. Finally, the hole was sealed using the sealant and a cover glass.

Measurement. UV-Vis absorption spectra were obtained on Hitachi U-3900/3900H UV-Vis spectrometer. Photocurrent-density-voltage (*J-V*) characteristics of the DSSCs were measured under illumination with AM 1.5G solar light from a 300 W xenon lamp solar simulator (94022A, Newport Co., USA). The incident light intensity was calibrated to 100

$\text{mW}\cdot\text{cm}^{-2}$ with a standard silicon solar cell. *J-V* characteristics were recorded with a digital source meter (Keithley 2400) controlled by a computer. The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cells were tested on a commercial setup (QTest Station 2000 IPCE Measurement System, Crowntech, USA). Electrical impedance spectra (EIS) for DSSCs under dark with bias -0.7 V were measured with CH Instruments 660C electrochemical workstation at frequencies of 0.1–100000 Hz. The magnitude of the alternative signal was 10 mV. Charge-transfer resistances were determined by fitting the impedance spectra using Z-view software. The DSSCs for stability test were stored under ambient illumination and temperature conditions.³⁸

Results and Discussion

UV-vis Absorption. The UV-vis absorption spectra of **AZ5**, **N719**, and **N719+AZ5** in acetonitrile-butanol (1/1, v/v) were displayed in Figure 1(a). Dye **AZ5** exhibited a broad and intensive absorption at 346 nm ($\epsilon = 64\ 860\ \text{M}^{-1}$

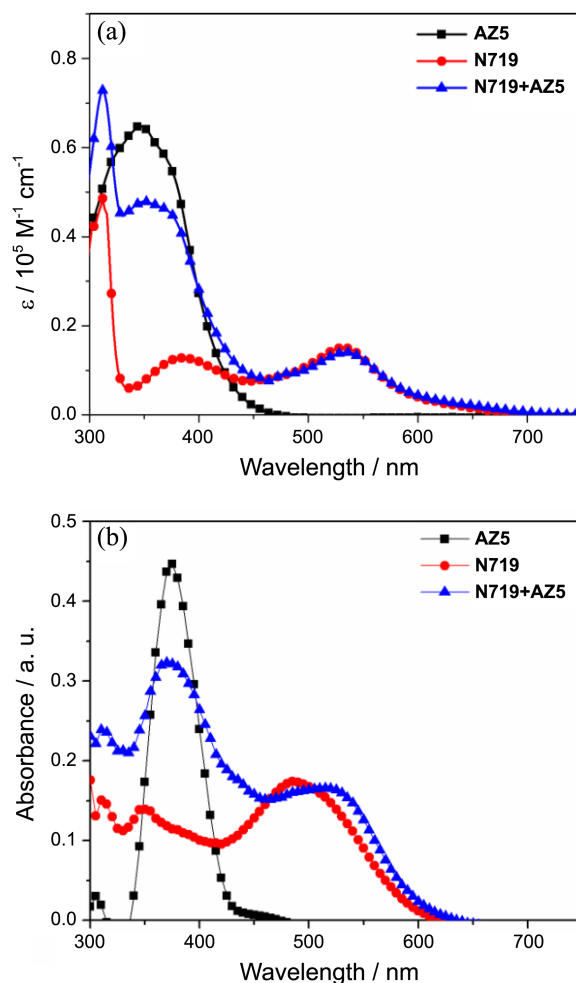


Figure 1. (a) UV-vis absorption spectra of **AZ5** (10^{-5} M), **N719** (10^{-5} M), and **N719** (10^{-5} M) + **AZ5** (0.67×10^{-5} M) in acetonitrile-butanol (1/1, v/v) solution. (b) UV-vis absorption spectra of **AZ5**, **N719**, and **N719+AZ5** on TiO_2 films (4 μm).

cm^{-1}), which was assigned to the localized π - π^* transitions of the conjugated systems.⁴¹ So the loss of light absorption originating from triiodide dissolved in the electrolyte could be suppressed by **AZ5** as the latter has a relatively higher molar extinction coefficient than triiodide.^{20,24} On the other hand, dye **N719** showed two broad visible bands at 534 nm ($\epsilon = 14\,600\text{ M}^{-1}\text{ cm}^{-1}$) and 390 nm ($\epsilon = 12\,800\text{ M}^{-1}\text{ cm}^{-1}$) as well as a UV absorption band at 312 nm ($\epsilon = 48\,700\text{ M}^{-1}\text{ cm}^{-1}$), the former two absorption bands were attributed to the metal-to-ligand charge transfer (MLCT) transitions while the latter at UV region was assigned to intraligand (π - π^*) charge-transfer transitions.⁴⁴ In addition, the cocktail solution of **N719**+**AZ5** showed much more intensive absorption in ultraviolet region relative to dye **N719** alone.

The UV-vis absorption of **AZ5**, **N719**, and **N719**+**AZ5** on TiO_2 films were showed in Figure 1(b). The maximum absorption peak of **AZ5** on TiO_2 films was red shifted to 374 nm with respect to that in solution due to the J aggregation and interaction with the surface of TiO_2 .¹⁹ For **N719**, the maximum absorption peak on film was significantly blue shifted to 487 nm compared to that in solution, which indicated that H aggregation occurred for **N719** adsorbed on TiO_2 film.²⁸ However, upon co-sensitization with **AZ5** on TiO_2 film, the maximum absorption of **N719** was red shifted to 519 nm in comparison with that of only **N719** on film, but still blue shifted compared with that of **N719** in solution. This observation implied that both H aggregation and J aggregation were occurred for **N719** under co-sensitization condition.²⁸

Photovoltaic Performance. The current density-voltage (J - V) characteristics of DSSCs sensitized/co-sensitized by **AZ5**, **N719**, and **N719**+**AZ5** were plotted in Figure 2(a) and the corresponding photovoltaic data including short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and PCE were listed in Table 1.

Under a standard AM 1.5G simulated sunlight irradiation, the **AZ5** sensitized DSSC gave a J_{sc} of $9.3\text{ mA}\cdot\text{cm}^{-2}$, a V_{oc} of 678 mV, and a FF of 69.3%, resulted in a PCE of 4.37%. Moreover, the **N719** sensitized DSSC yielded a J_{sc} of $16.9\text{ mA}\cdot\text{cm}^{-2}$, a V_{oc} of 666 mV, a FF of 64.6%, and a PCE of 7.28%. Encouragingly, compared with the devices sensitized by **N719** or **AZ5** alone, the co-sensitized (**N719**+**AZ5**) DSSC exhibited a significantly improved PCE of 7.91% mainly attributed to the relatively higher J_{sc} ($17.9\text{ mA}\cdot\text{cm}^{-2}$) accompanied with an enhanced V_{oc} (698 mV).

The incident photon to current efficiency (IPCE) spectra of the DSSCs sensitized with **AZ5**, **N719**, and **AZ5**+**N719** were displayed in Figure 2(b). The DSSC based on **AZ5**

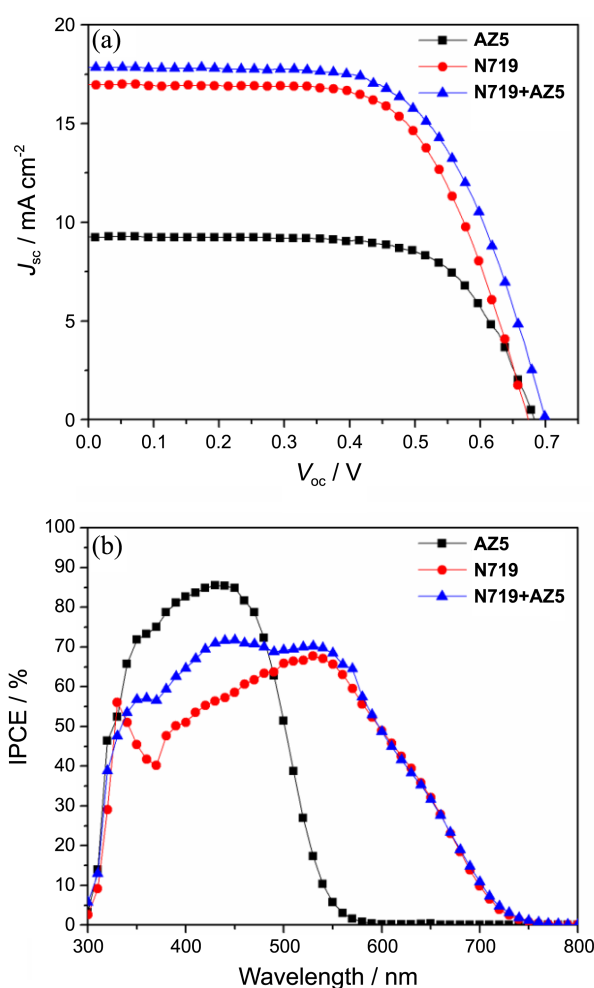


Figure 2. (a) J - V curves of DSSCs sensitized with **AZ5**, **N719**, and **N719**+**AZ5** under AM 1.5G irradiation. (b) IPCE spectra of the DSSCs sensitized with **AZ5**, **N719**, and **AZ5**+**N719**.

alone showed an IPCE band ranged from 300 nm to 600 nm, and attaining maximum of 86% at 435 nm. The DSSC sensitized with **N719** had a broad IPCE spectrum across the entire visible region extending up to 800 nm and exhibited the highest IPCE value 68% at wavelength 530 nm. While the IPCE of co-sensitized DSSC was clearly lower than that of **AZ5**-based DSSC in the UV region, which may attributed to relatively lower concentration of **AZ5** in co-sensitization solution.²⁴ However, it should be noted that IPCE spectrum of co-sensitized DSSC was evidently higher than that of **N719** sensitized DSSC at the range of 350 nm to 580 nm, which indicated that the loss of the light absorption induced by triiodide in electrolyte may be compensated by the

Table 1. Photovoltaic Performance Data of the DSSCs^a

Dye	$J_{\text{sc}}/\text{mA}\cdot\text{cm}^{-2}$	V_{oc}/mV	$FF/\%$	$PCE/\%$	Amount of N719 / $10^{-7}\text{ mol cm}^{-2}$	Amount of AZ5 / $10^{-7}\text{ mol cm}^{-2}$
AZ5	9.3	678	69.3	4.37		1.2
N719	16.9	666	64.6	7.28	1.5	
N719 + AZ5	17.9	698	63.3	7.91	1.3	0.7

^aMeasured under AM 1.5G irradiation (100 mW cm^{-2}) with 0.25 cm^2 working area.

addition of co-sensitizer **AZ5**. These results are consistent with UV-vis absorption in solution as well as on TiO₂ films. Furthermore, the IPCE spectrum of co-sensitized DSSC did not change in the spectral region 580 nm to 800 nm with respect to that of **N719**-based DSSC. This phenomenon implied that the adsorption of **N719** under co-sensitization condition was almost not affected by **AZ5**.^{20,33} In addition, it can be derived that a better dye coverage on the surface of TiO₂ was formed upon co-sensitization from the IPCE spectra.²⁴ Therefore, the co-sensitized DSSC increased light-harvesting and yielded a relatively higher J_{sc} than **N719**-based DSSC.

To quantify the amounts of adsorbed dyes on the TiO₂ films, the single dye sensitized photoanode was dipped into acetic anhydride (for desorption of **AZ5**) or 1.0 M NaOH solution (for desorption of **N719**), while the co-sensitized photoanode was dipped into acetic anhydride and 1.0 M NaOH sequentially.¹⁷ The amounts of desorbed dyes were evaluated and the results were provided in Table 1. Compared with only **N719** sensitized photoanode, the amounts of **N719** adsorbed on co-sensitized photoanode was decreased slightly from 1.5×10^{-7} mol cm⁻² to 1.3×10^{-7} mol cm⁻², however, 0.7×10^{-7} mol cm⁻² of **AZ5** was additionally adsorbed on co-sensitized photoanode, so the total adsorbed dye amount was significantly increased to 2.0×10^{-7} mol cm⁻². These results are in line with IPCE and UV-vis absorption on TiO₂ films.

Electrochemical Impedance Spectroscopy Research.

To clarify the enhancement in V_{oc} , electrochemical impedance spectroscopy (EIS)^{45,46} in the dark was carried out to investigate the interfacial charge transfer processes in DSSCs. Two semicircles were located in the Nyquist plots (Figure 3(a)), and the smaller semicircle at high-frequency region reflected the impedances of the charge transfer (R_{ct}) on the Pt counter electrode while the larger semicircle at intermediate-frequency region represented charge-transfer resistance (R_{rec}) at the TiO₂/dye/electrolyte interface. A larger R_{rec} indicated slower or less electron recombination and resulted in an increased V_{oc} . The R_{rec} of co-sensitized (**N719**+**AZ5**) DSSC (72.2 Ω) was significantly larger than that of the individually sensitized **N719** (41.8 Ω) and **AZ5** (53.1 Ω) devices. Moreover, the electron lifetime can be calculated using the equation $\tau = 1/(2\pi f_c)$,⁴⁷ where f_c is the peak frequency of intermediate-frequency region in the Bode phase plots (Figure 3(b)). And the calculated electron lifetime increased in the order of **N719** (6.7 ms) < **AZ5** (8.7 ms) < **N719**+**AZ5** (12.2 ms). Both R_{rec} and electron lifetime were well in line with V_{oc} . Three plausible mechanisms may account for the significantly increased V_{oc} : (1) a more compact and ordered monolayer of **N719** with **AZ5** was formed on the photoanode surface, leading to prolonged electron lifetime;¹⁹ (2) electron recombination between the injected electrons and the electrolyte was suppressed owing to the bulky cyclic thiourea functionalized triphenylamine donor in **AZ5**;^{28,41} (3) aggregation of individual dyes was effectively inhibited due to the long alkyl chains substituted at cyclic thiourea groups, therefore the electron injections were improved.^{23,24}

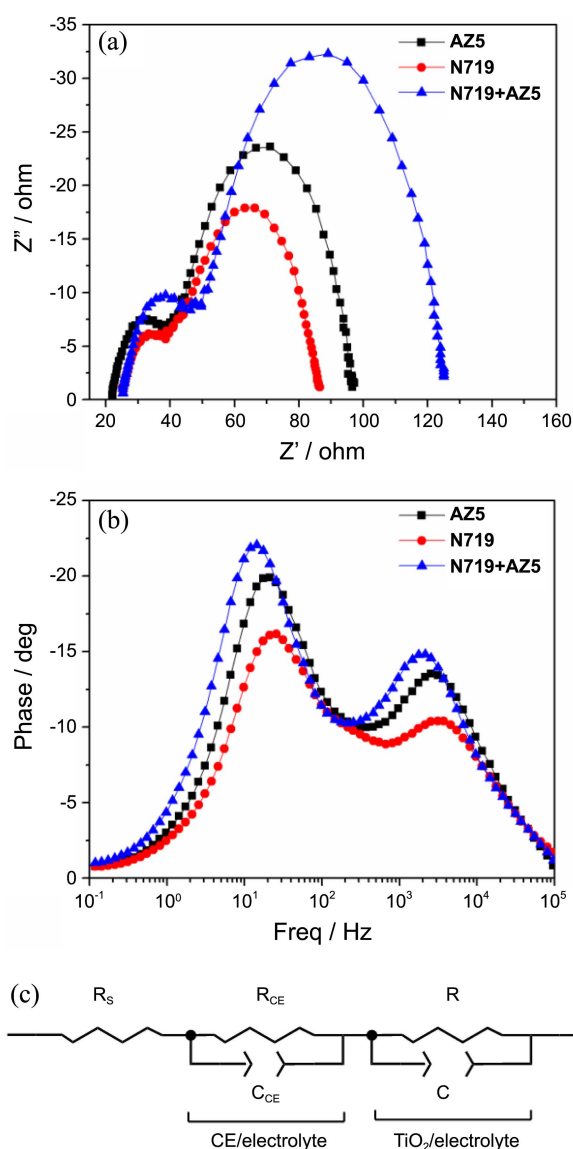


Figure 3. EIS spectra of DSSCs tested at -0.7 V forward bias in the dark: (a) Nyquist; (b) Bode phase plots; (c) equivalent circuit.

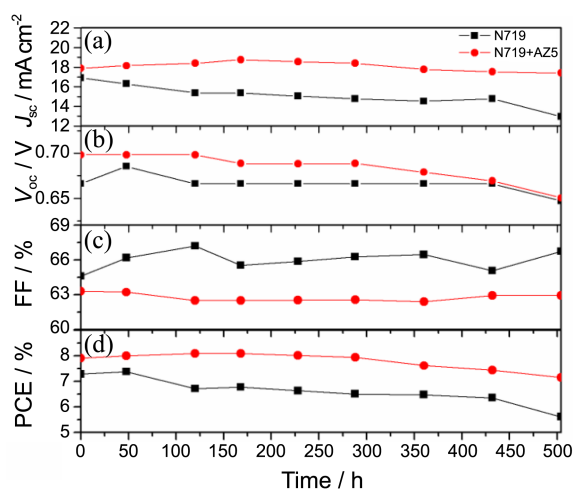


Figure 4. A test of stability of DSSCs sensitized/co-sensitized by **N719** and **N719**+**AZ5**: (a) short-circuit photocurrent density (J_{sc}); (b) open-circuit voltage (V_{oc}); (c) fill factor (FF); (d) power conversion efficiency (PCE).

Stability Test. The stability of DSSCs sensitized/co-sensitized by N719 and N719+AZ5 was tested and the results were plotted in Figure 4. The PCE of N719-based DSSC was slightly increased to 7.37% during the first 50 h, but then decreased to 6.70% at 120 h and further to 6.50% at 290 h. The main reason for the degraded performance was due to the decreased J_{sc} , which implied that some of N719 molecules desorbed from the TiO₂ surface thus decreasing light absorption.²⁸ In contrast, the PCE of co-sensitized DSSC was slightly increased to 7.99% during the beginning 50 h, and further increased to 8.08% at 170 h then slowly decreased to the initial value (7.91%) at 290 h. This results was attributed to the constant J_{sc} , which suggested that a more compact and ordered monolayer of dyes was formed so the desorption of N719 was suppressed to some extent owing to the presence of AZ5.

Conclusion

In conclusion, N719 co-sensitized with a cyclic thiourea functionalized organic dye AZ5 was investigated, and an improved PCE up to 7.91% was obtained due to the increased J_{sc} coupled with an enhanced V_{oc} relative to that of N719 (PCE = 7.28%) or AZ5 (PCE = 4.37%) sensitized alone. The J_{sc} was increased because the light absorption loss induced by triiodide could be suppressed by AZ5 since it has a relatively higher molar extinction coefficient in ultraviolet region than triiodide. While the V_{oc} was enhanced because the electron recombination and aggregation were significantly inhibited as N719 co-sensitized with AZ5. Moreover, the stability of DSSCs was improved as well under co-sensitization condition.

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