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Improvement of Thiolate/Disulfide Mediated Dye-Sensitized Solar Cells through Supramolecular Lithium Cation Assembling of Crown Ether

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A supramolecular lithium cation assemblies of crown ether, $[Li \subset 12\text{-crown-}4]^+$, has been used to replace conventional tetraalkylammonium counterion in thiolate/disulfide (ET^-/BET) mediated dye-sensitized solar cells (DSCs), which exhibit high stability and efficiency of 6.61% under 100 mW·cm^{-2} simulated sunlight illumination.

D ye-sensitized solar cells (DSCs), as a promising type of solar energy-to-electricity conversion device, have attracted considerable interest because of their low cost, easy fabrication and promising efficiency[1–3]. The electrolytes used in high-performance DSCs are usually based on the I^-/I_3^- redox couple[4,5]. Despite its superior performance, the I^-/I_3^- redox couple also embraces many fatal flaws such as corrosive nature, substantial vapor pressure, visible light absorption and low redox potential, which limit both the practicality and the efficiency of DSCs[6]. Employing iodine-free redox couples should be a key solution to these problems. Most recently, through optimizing the working electrode as well as the photosensitizer, one of the iodine-free mediators, the cobalt complex, was identified as the first alternative redox couple that can outperform the conventional I^-/I_3^-[7,8]. In addition, due to its intrinsic characteristics of slow electron recombination, rapid dye regeneration and fast mass transport, another iodine-free system, the thiolate/disulfide mediators, has also been proven to be a promising candidate to replace the iodide/triiodide (I^-/I_3^-) system in DSCs[9–12]. However, the photovoltaic properties of these redox couples are still barely satisfactory compared to conventional I^-/I_3^- couple.

To further optimize the performance of DSCs based on the thiolate/disulfide redox couples, numerous researches are implemented from every aspect. Especially, in consideration of the poor fill factor (*FF*) with commonly used platinum CE, alternative electrocatalysts[8,13–18] were adopted to decrease the charge transfer resistance (R_{ct}) at the counter electrode (CE)/electrolyte interface. On the other hand, in order to finetune the redox potential and enhance the open-circuit voltage (V_{OC}), significant efforts have also been made in optimizing the molecular structure of this organic redox system[19–21]. Although these researches have achieved some exciting results, the photocurrent obtained by thiolate/disulfide redox cannot gain clearly enhancement, which hinders the further improvement in overall energy conversion efficiency (η) of the DSCs based on this redox couple. Moreover, the DSCs based on the organic sulfide electrolyte usually suffer from dye desorption and/or slow electrolyte degradation[12,14]. Accordingly, further works should be conducted to optimize and improve both of its efficiency and stability. Thereinto, tetraalkylammoniums are usually utilized as counterions along with thiolate/disulfide redox couples to help increase the solubility of reduced species in the organic solvent-based electrolyte. However, the utilization of these counterions always lead to unsatisfactory injection efficiency and short electron diffusion length[22,23], resulting in low short-circuit current density (J_{SC}). Meanwhile, tetraalkylammonium as a starting material may contain tetraalkylammonium hydroxide as a contaminant or undergo gradual thermal Hoffmann degradation, forming basic trialkylamine, and this basic product could induce desorption of the dye molecules from TiO$_2$ surface[24]. We also noted the same fading phenomenon of dye sensitized TiO$_2$ film in the organic sulfide system, thus resulting in serious decline of J_{SC}. Consequently, the replacement of the ubiquitous tetraalkylammonium counterions in thiolate/disulfide electrolyte would be a critical improvement.

It is well known that some small cations such as Li$^+$ could obviously improve J_{SC} of DSCs, but simultaneously result in large reduction of V_{OC}[25]. Moreover, the solubility of lithium thiolate is very low in the aprotic solvent, resulting in poor performance in the DSCs using thiolate/disulfide mediator. In this communication, we employed a supramolecular lithium complex as counterion to replace the traditional tetraalkylammonium. It was found that this replacement could not only increase the efficiency of DSCs, but also its stability.

Results

Dye N719 was employed as photosensitizer for DSC fabrication. A porous PEDOT film was utilized as CE. An organic redox couple consisting of the thiolate form (1-ethyl-1H-tetrazole-5-thiol, ET$^-$) and disulfide dimer (BET) was adopted as active species in electrolyte. Different cations, tetramethylammonium (TMA$^+$), lithium (Li$^+$), and a supramolecular complex ([Li⊂12-crown-4]$^+$) were used as counterion of ET$^-$, respectively. The redox potentials (E_{redox}) of ET$^-$/BET in acetonitrile with [Li⊂12-crown-4]$^+$ and Li$^+$ are identical, which is 0.30 V $vs.$ NHE determined by cyclic voltammetry. The synthesis routes and structures of TMA$^+$ET$^-$, Li$^+$ET$^-$, and [Li⊂12-crown-4]$^+$ET$^-$ are shown in Figure 1. BET was synthesized according to reported procedures. TMA$^+$ET$^-$ was prepared by neutralization of corresponding mercaptan (ET) with tetramethylammonium hydroxide (TBAOH) in methanol (MeOH) under reflux for 3 h. Li$^+$ET$^-$ was obtained by deprotonation of ET with lithium bicarbonate (Li$_2$CO$_3$). [Li⊂12-crown-4]$^+$ET$^-$ was synthesized by deprotonation of ET with lithium bicarbonate (Li$_2$CO$_3$) and 12-crown-4 in ethanol (EtOH).

Due to the varying solubility of ET$^-$ with different counterions, the concentration of the reduced components in all the electrolytes was kept relatively low, which resulted in devices with less than optimal performance, but allowed for comparisons in cell performance as a function of different counterions. The detailed photovoltaic parameters are summarized in Table 1. The TMA$^+$ET$^-$/BET electrolyte with TMA$^+$ as counterion shows an η of 3.5% with a V_{OC} of 656 mV, a J_{SC} of 7.9 mA·cm^{-2}, and an FF of 0.68 under standard global AM 1.5 illumination. As many researches demonstrated, the tetraalkylammonium cations always prejudice photoelectron injection and electron diffusion process[7]. On the contrary, the adsorption or intercalation of Li$^+$ on TiO$_2$ surface contributes to fast electron injection and transport rate, which have positive effect on J_{SC}. Therefore, to improve J_{SC}, Li$^+$ was introduced as counterion along with ET$^-$/BET.

Table 1 | The photovoltaic parameters of ET$^-$/BET (0.1 M/0.05 M in acetonitrile) based DSCs with different cations (0.1 M). Condition: TiO$_2$ consisting of an 8 μm transparent layer and a 4 μm scattering layer; activated area of the TiO$_2$ film, 0.42 cm^{-2}; black mask 0.13 cm^{-2}; tested under 100 mW·cm^{-2} simulated sun light illumination

Electrolyte	V_{OC}/mV	J_{SC}/mA cm^{-2}	FF	η%
TMA$^+$	656	7.9	0.68	3.5
Li$^+$	607	8.8	0.61	3.3
[Li⊂12-crown-4]$^+$	632	9.3	0.71	4.2

The J_{SC} of DSC based on Li$^+$ increases to 8.8 mA·cm^{-2}, much higher than that using TMA$^+$. However, the Li$^+$ based electrolyte only renders an efficiency of 3.3% because of an extremely lower V_{OC} of 607 mV together with an unexpected reduction of 10% in FF.

To remedy the weakness of Li$^+$ counterion and continue optimizing the performance of thiolate/disulfide redox couple, we employed the supramolecular derivative of Li$^+$, [Li⊂12-crown-4]$^+$, as the counterion. It was found that, besides a slightly higher J_{SC} (9.3 mA·cm^{-2}), this replacement endows remarkable increases both in V_{OC} (632 mV) and FF (0.71), finally resulting in large improvement of η (4.2%), much better than Li$^+$ as well as TMA$^+$. This result apparently indicates that encapsulating Li$^+$ into 12-crown-4 has profound effect on the performance of ET$^-$/BET mediated DSCs.

To illuminate the reason for the better performance of DSCs with [Li⊂12-crown-4]$^+$ than Li$^+$, primarily measurements were carried out to distinguish the effect caused by [Li⊂12-crown-4]$^+$ and Li$^+$ on the TiO$_2$/electrolyte interface. From intensity modulated photovoltage spectroscopy (IMVS) (Figure 2), the electron lifetime of devices adopting TMA$^+$ based electrolyte is slightly lower than that of [Li⊂12-crown-4]$^+$ and Li$^+$, but there is no significant difference in charge recombination kinetics when [Li⊂12-crown-4]$^+$ and Li$^+$ are used as counterions. It is well known that, under identical E_{redox}, the V_{OC} is determined by conduction band edge (E_{CB}) of TiO$_2$ and charge recombination in DSCs. Therefore, the dissimilarity in V_{OC} should be attributed to the shift of E_{CB} which is usually evoked by adsorbing cations onto TiO$_2$ surface. Extracted charge measurements were utilized to determine the E_{CB} shift in DSCs. The quasi Fermi level ($E_{F,n}$), which is given by the sum of measured cell potential and redox potential of the electrolyte, depends on both the E_{CB} and the extracted charge density (Q_{OC}) in TiO$_2$ film. Therefore, the lower and higher $E_{F,n}$ at the same Q_{OC} means a negative (upward)
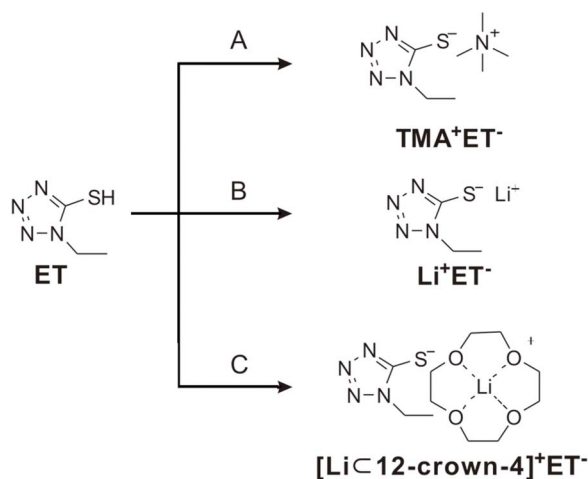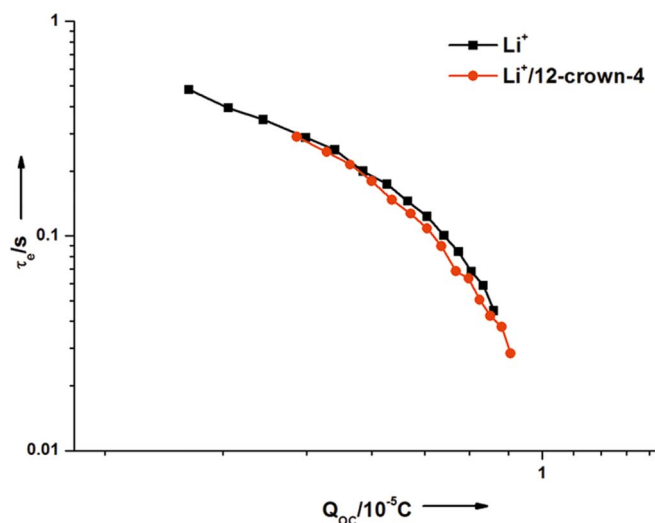

Figure 1 | Synthetic routes and structures of the thiolate/disulfide redox components. A) TBAOH, MeOH, reflux, 3 h; B) Li$_2$CO$_3$, EtOH, 45°C, 12 h; C) Li$_2$CO$_3$, 12-crown-4, EtOH, 45°C, 12 h.

Figure 2 | Electron lifetime as a function of extracted charge in DSCs with [Li⊂12-crown-4]$^+$ and Li$^+$ based electrolytes.

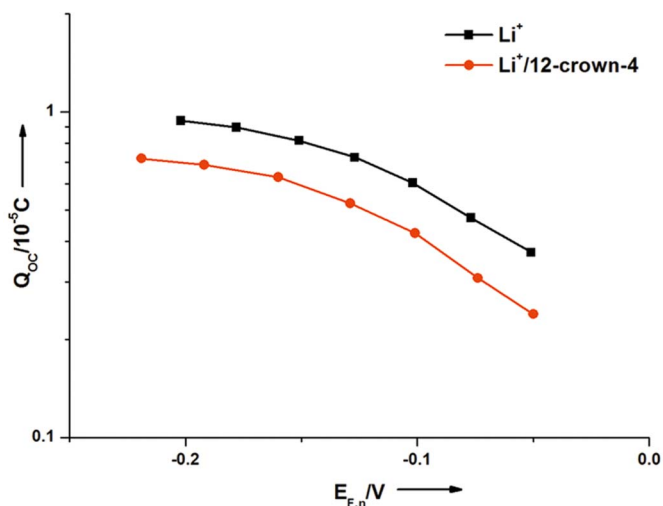**Figure 3 | Extracted charge as a function of the quasi-Fermi energy ($E_{F,n}$) levels of TiO$_2$ in DSCs with [Li⊂12-crown-4]$^+$ and Li$^+$ based electrolytes.**

and positive (downward) shift of the E_{CB}, respectively. Considering that the tetraalkylammonium cations do not interact with the TiO$_2$ surface, the E_{CB} of TiO$_2$ in TMA$^+$ based electrolyte can be noted as reference[26]. By contrast, the specific interaction between Li$^+$ and TiO$_2$ is known to induce the positive shift of its E_{CB} and results in a low V_{OC}[25]. Figure 3 clearly shows that, the [Li⊂12-crown-4]$^+$ based electrolyte causes the E_{CB} shift of about 60 mV less positive than Li$^+$ does, contributing to the main V_{OC} enhancement for [Li⊂12-crown-4]$^+$ based DSC. This rise might be due to the weakening of the adsorption or intercalation of Li$^+$ cations into the TiO$_2$ electrode by encapsulating Li$^+$ in the cavity of 12-crown-4.

As previously mentioned, the *FF* value is increased to 0.71 with [Li⊂12-crown-4]$^+$ relative to TMA$^+$ (0.61) and Li$^+$ (0.68). Herein electrochemical impedance spectroscopy (EIS) analysis of the dummy cell constructed by two identical PEDOT electrodes was employed. Figure 4 presents the EIS results in the form of Nyquist plot and the equivalent circuit upgraded by Roy-Mayhew et al.[27]. The

high-frequency semicircle (first semicircle) is regarded as the second Nernst diffusion impedance in the electrode pores (N_{pore}). The middle semicircle (second semicircle) represents the charge transfer resistance and the capacitance of the CE/electrolyte interface (R_{ct}, CPE). After fitting EIS data, the [Li⊂12-crown-4]$^+$ based electrolyte displays an average R_{ct} of 4.01 Ω, smaller than that of TMA$^+$ (6.94 Ω) and Li$^+$ (12.35 Ω). The lower R_{ct} of [Li⊂12-crown-4]$^+$ electrolyte implies that this novel electrolyte exhibits a higher electrochemical reactivity on PEDOT electrode. The PEDOT electrode contains abundant electronegative sulfur and oxygen atoms, and easily interacts with Li$^+$[28]. This interaction might strengthen the adsorption of ET$^-$ onto PEDOT, resulting in decrease of surface activity of PEDOT electrode. On the contrary, it should be difficult for TMA$^+$ to interact with PEDOT film. Therefore, we assumed that the Li$^+$ based electrolyte exhibits unfavorable charge-transfer process compared to TMA$^+$. When using supramolecular [Li⊂12-crown-4]$^+$ as counterion, Li$^+$ is encapsulated by 12-crown-4. This encapsulation weakens the interaction of [Li⊂12-crown-4]$^+$ with PEDOT, accordingly suppressing the adsorption of ET$^-$ on this polymer film, so the PEDOT electrode shows a higher catalytic activity for [Li⊂12-crown-4]$^+$ET$^-$/BET. To further elucidate the results, the Tafel measurement of symmetrical dummy cells was also performed and presented in Supporting Information Figure S1. The cathodic slope in the Tafel line of [Li⊂12-crown-4]$^+$ based electrolyte is apparently higher than that of Li$^+$. This result indicates that [Li⊂12-crown-4]$^+$ could yield a higher exchange current density (J_0) on PEDOT CE than Li$^+$ does, implying that the ET$^-$/BET redox couple with [Li⊂12-crown-4]$^+$ cation has higher interfacial charge-transfer activity on PEDOT.

Discussion

It is evident that this supramolecular counterion [Li⊂12-crown-4]$^+$ cooperating with ET$^-$/BET shows promise as a potential efficient cation for thiolate/disulfide based DSCs, where η increased by 20% in comparison to that of TMA$^+$ (as Table 1 shows). To fabricate [Li⊂12-crown-4]$^+$ET$^-$/BET based DSCs with more optimal performance, the concentration ratio between the reduced and oxidized species was optimized to 0.4 M/0.08 M ([Li⊂12-crown-4]$^+$ET$^-$/BET). A routine additive 0.5 M 4-*tert*-butylpyridine was added to the electrolyte, and the thickness of TiO$_2$ was increased to 12 μm. Eventually the
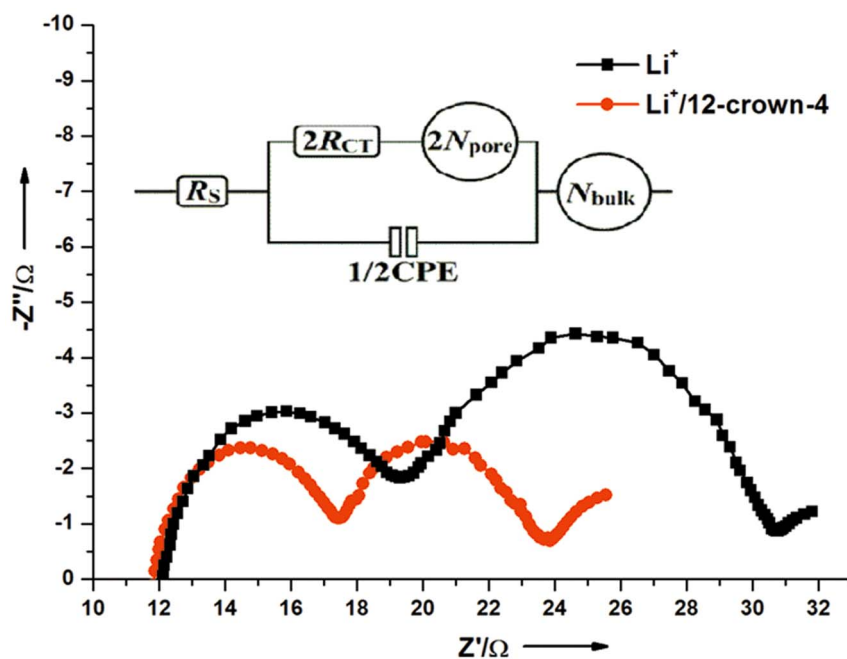

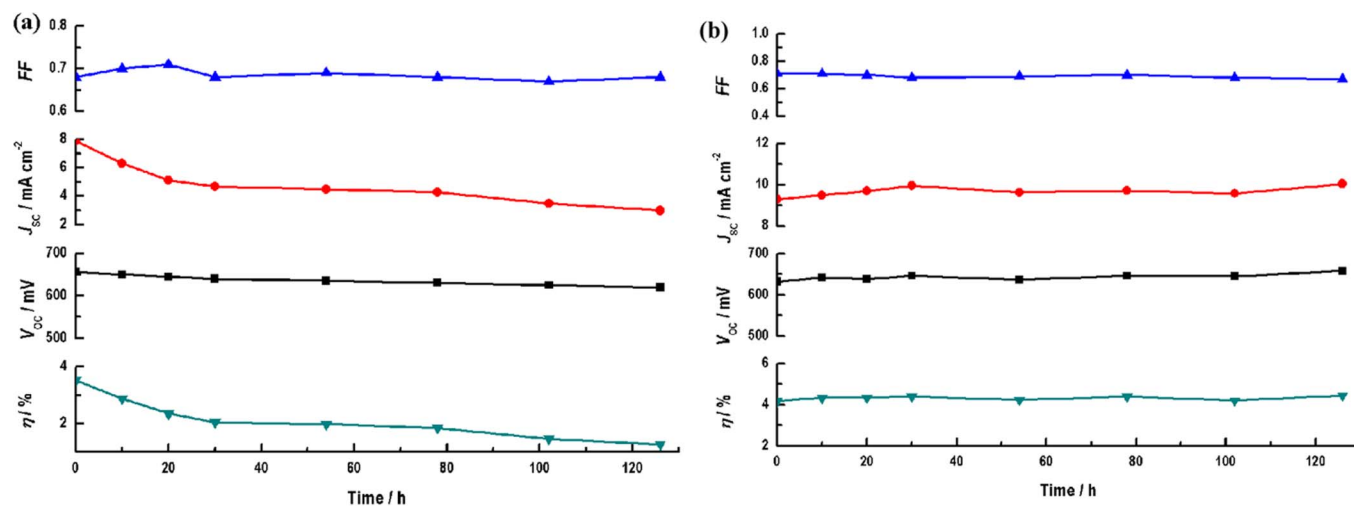**Figure 4 | Impedance spectra of ET$^-$/BET based symmetric cells using PEDOT CEs under 0 V bias voltage.**

Figure 5 | The stability tests of DSCs with TMA^+ET^-/BET (a) and $[Li \subset 12\text{-crown-4}]^+ ET^-/BET$ (b) based electrolytes and PEDOT CEs during 126 h storage under short-circuit at dark conditions and room temperature.

DSC based on $[Li \subset 12\text{-crown-4}]^+ET^-/BET$ exhibited an η of 6.61% with a J_{SC} value of 14.3 mA·cm^{-2}, a V_{OC} value of 670 mV, and an FF of 0.69, while TMA^+ only exhibited an η of 5.73% with a J_{SC} value of 11.2 mA·cm^{-2}, a V_{OC} value of 669 mV, and an FF of 0.76 under 100 mW·cm^{-2} simulated sunlight illumination.

Preliminary stability tests were performed at room temperature and showed in Figure 5. Contrary to the TMA^+ET^-/BET mediated DSC which underwent an obvious decomposition of dye and accordingly a serious decline of photovoltaic performance within 24 h (Figure 5a), the $[Li \subset 12\text{-crown-4}]^+$ counterion could produce stable photovoltaic properties (Figure 5b), and no obvious decrease of V_{OC}, J_{SC}, FF, or η was observed during 126 h. It could be concluded that the ET^-/BET redox couple with $[Li \subset 12\text{-crown-4}]^+$ as counterion shows better stability than that of TMA^+.

In summary, the $[Li \subset 12\text{-crown-4}]^+$ is demonstrated to be an efficient alternative of the conventional tetraalkylammonium counterion in thiolate/disulfide mediated DSCs. By encapsulating Li^+ in the 12-crown-4 cavity, the supramolecular counterion, $[Li \subset 12\text{-crown-4}]^+$, could not only inherit the advantage of Li^+ in the aspect of the photocurrent generation, but also retain the merit of TMA^+ in the aspect of the photovoltage output. Meanwhile, employing $[Li \subset 12\text{-crown-4}]^+$ as the counterion of the organic sulfide mediators also accelerates the charge-transfer process on the electrolyte/CE interface, leading to a considerable increase in FF. Moreover, the thiolate/disulfide mediated DSC using $[Li \subset 12\text{-crown-4}]^+$ exhibits improved stability compared to that using TMA^+. Consequently, this report emphasizes that screening the counterion should be a successful approach to optimize the performance of thiolate/disulfide electrolyte. In consideration of the large variety of metal cations and crown ethers, both higher efficiency and better stability could be expected via optimizing the collocation between metal cations and crown ethers, opening new avenues for the use of the organic sulfide based DSC devices.

Methods

Fabrication of DSCs. FTO glass plates with high transparency in the visible range purchased from Nippon sheet glass. It was first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. Photoelectrodes consisted of a TiO_2 film with a triple-layer structure. A compact blocking underlayer of dense titanium dioxide was deposited onto a cleaned FTO glass substrate by immersing the FTO glass plates into a 40 mM aqueous $TiCl_4$ solution at 70°C for 30 min, which was washed with water and ethanol. Successive depositions of 8 μm or 12 μm thick transparent layer (PST-18NR, JGC Catalysts and Chemicals Ltd., Japan) and 4 μm thick light-scattering layer (PST-400C, JGC Catalysts and Chemicals Ltd., Japan) of nanocrystalline TiO_2 were printed layer by layer. The electrodes coated with the TiO_2 pastes were gradually heated under an

airflow at 325°C for 5 min, at 375°C for 5 min, and at 450°C for 15 min, and finally, at 500°C for 15 min. After sintering, The TiO_2 "triple-layer" film thus produced is once again treated with 40 mM $TiCl_4$ solution, as described previously, then rinsed with water and ethanol and sintered at 500°C for 30 min. After cooling to 80°C, the TiO_2 electrode was immersed into a 0.5 mM N719 solution and kept at room temperature for 24 h to assure complete sensitizer uptake. To prepare the counter electrode, PEDOT film was obtained through electropolymerization using a bath solution consisting of 0.01 mol·L^{-1} bis-EDOT and 0.1 mol·L^{-1} LiTFSI in acetonitrile at a constant potential (0.6 V vs. Ag/AgCl). The charge capacity for the preparation of the PEDOT film was at 25 mC·cm^{-2}. Sensitized semiconductor films were washed with the same solvent as used in the dye-bath, dried and sealed with the prepared PEDOT counter electrode using a 45 μm thick hot-melt film (Surlyn, Solaronix) through heating the system at 120°C. The electrolyte solution in ACN was then introduced through two holes predrilled in the counter electrode, and the cell was sealed with thermoplastic Surlyn covers and a glass coverslip.

Characterization. Current–voltage (J–V) characteristics were measured using a Keithley 2400 source/meter and a Newport solar simulator (model 91192-1000) giving light with AM 1.5 G spectral distribution, which was calibrated using a certified reference solar cell (Fraunhofer ISE) with an intensity 100 mW·cm^{-2}. An intensity-modulated photovoltaic spectroscopy (IMVS) experiment was carried out using high-intensity green LEDs (530 nm) driven by a ZAHNER Xpot frequency response analyzer. A charge extraction setup identical to that in the work of Duffy[29] was used to determine the charge stored in the films. Electrochemical impedance spectroscopy (EIS) of the symmetric cell was carried out on ZAHNER ENNIUM Electrochemical Workstations in the frequency range 0.1 to 10^5 Hz with 10 mV AC amplitude.

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Acknowledgments

Author contributions

H.W.H. contributed to the conception and design of experiment, analysis of the data and correcting the manuscript with assistance of L.F.L., X.L., J.Z.C., Y.G.R. and Z.L.K. L.F.L. and X.L. carried out the DSC studies, participated in the sequence alignment and drafted the manuscript. J.Z.C., Y.G.R. and Z.L.K. participated in the design of the study and performed the statistical analysis.

Additional information

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