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

Linfeng Liu1*, Xiong Li1,2*, Jiangzhao Chen1, Yaoguang Rong1, Zhiliang Ku1 & Hongwei Han1

1Michael Grätzel Center for Mesoscopic Solar Cells, Wuhan National Laboratory for Optoelectronics, School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China, 2College of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China.

A supramolecular lithium cation assemblies of crown ether, [LiC12-crown-4]1, has been used to replace conventional tetraalkylammonium counterion in thiolate/disulfide (ET2/BET) mediated dye-sensitized solar cells (DSCs), which exhibit high stability and efficiency of 6.61% under 100 mW·cm−2 simulated sunlight illumination.

Dye-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 efficiency1–3. The electrolytes used in high-performance DSCs are usually based on the I-/I3− redox couple4,5. Despite its superior performance, the I-/I3− 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 DSCs6. 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-/I3−7,8. 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-/I3−) system in DSCs9–12. However, the photovoltaic properties of these redox couples are still barely satisfactory compared to conventional I-/I3− 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 electrocatalysts8,13–18 were adopted to decrease the charge transfer resistance (Rct) at the counter electrode (CE)/electrolyte interface. On the other hand, in order to finetune the redox potential and enhance the open-circuit voltage ( Voc), significant efforts have also been made in optimizing the molecular structure of this organic redox system19–21. 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 degradation22,23. 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 length22,23, resulting in low short-circuit current density (Jsc). 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 TiO2 surface24. We also noted the same fading phenomenon of dye sensitized TiO2 film in the organic sulfide system, thus resulting in serious decline of Jsc. 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 [1]. 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 ([Li12-crown-4]⁺) were used as counterion of ET⁺, respectively. The redox potentials (E_redox) of ET⁺/BET in acetonitrile with [Li12-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 [Li12-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 (Li₂CO₃) 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 researchers demonstrated, the tetraalkylammonium cations always prejudice photoelectron injection and electron diffusion process. On the contrary, the adsorption or intercalation of Li⁺ on TiO₂ 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).

| 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   |
| [Li12-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⁺, [Li12-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 [Li12-crown-4]⁺ than Li⁺, primarily measurements were carried out to distinguish the effect caused by [Li12-crown-4]⁺ and Li⁺ on the TiO₂/electrolyte interface. From intensity modulated photovoltage spectroscopy (IMVS) (Figure 2), the electron lifetime of ET⁺/BET in acetonitrile with [Li12-crown-4]⁺ and Li⁺ 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.

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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 TiO₂ was increased to 12 μm. Eventually the
DSC based on [Li12-crown-4]+ ET+/BET exhibited an η of 6.61% with a JSC value of 14.3 mA/cm², a VOC value of 670 mV, and an FF of 0.69, while TMA+ only exhibited an η of 5.73% with a JSC value of 11.2 mA/cm², a VOC value of 669 mV, and an FF of 0.76 under 100 mW/cm² 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 [Li12-crown-4]+ counterion could produce stable photovoltaic properties (Figure 5b), and no obvious decrease of VOC, JSC, FF, or η was observed during 126 h. It could be concluded that the ET+/BET redox couple with [Li12-crown-4]+ as counterion shows better stability than that of TMA+.

In summary, the [Li12-crown-4]+ is demonstrated to be an efficient alternative of the conventional tetraalkylammonium cation in thiolate/disulfide mediated DSCs. By encapsulating Li+ in the 12-crown-4 cavity, the supramolecular counterion, [Li12-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 [Li12-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 [Li12-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 TiO2 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 TiCl4 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 TiO2 were printed layer by layer. The electrodes coated with the TiO2 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 TiO2, “triple-layer” film thus produced is once again treated with 40 mM LiClO4 solution, as described previously, then rinsed with water and ethanol and sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO2 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 by electrochemical polymerization 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 (I–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 photovoltage spectroscopy (IMVS) experiment was carried out using high-intensity green LEDs (530 nm) driven by a ZAHNER Eta frequency response analyzer. A charge extraction setup identical to that in the work of Duffys 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 Hz with 10 mV AC amplitude.

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**Figure 5** The stability tests of DSCs with TMA+/ET+/BET (a) and [Li12-crown-4]+ ET+/BET (b) based electrolytes and PEDOT CEs during 126 h storage under short-circuit at dark conditions and room temperature.
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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.

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