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## Efficient dye-sensitized solar cells based on an iodine-free electrolyte using L-cysteine/L-cystine as a redox couple†‡

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A new iodine-free electrolyte based on amino acids L-cysteine/L-cystine as a redox couple has been designed and synthesized. DSSCs fabricated with the conventional  $I^-/I_3^-$  redox couple gave efficiencies of 8.1% and 6.3% under optimized experimental conditions based on ruthenium dye, N719, and metal-free organic dye, TH202, respectively. Based on the same dyes, the DSSCs employing the new L-cysteine/L-cystine redox couple showed comparable efficiencies of 7.7% and 5.6%, respectively. However, higher incident-photon-to-electron (IPCE) conversion efficiencies and larger  $J_{sc}$  values were found for devices with the L-cysteine/L-cystine redox couple than with  $I^-/I_3^-$ . From an electrochemical impedance spectroscopic study, we found that the charge recombination between the conduction band electrons in the  $TiO_2$  film and the electrolyte containing the L-cysteine/L-cystine redox couple is restrained.

Dye-sensitized solar cells (DSSCs) have attracted growing attention since O'Regan and Grätzel reported them first in 1991, due to their

low cost and great potential in large-scale applications.<sup>1,2</sup> In conventional systems, the electrolytes used in DSSCs are mainly based on the iodide/triiodide ( $I^-/I_3^-$ ) redox couple. However, many drawbacks have been identified for this redox couple, including the strong light absorption, corrosion of the metal current collectors, sublimation of iodine *etc.* Moreover, the large energy gap between the iodide/triiodide redox couple and the HOMO levels of the dyes resulted in a large waste of energy during dye regeneration.<sup>3</sup> Therefore, many attempts have been made to explore alternative redox couples and some good results have been reported recently,<sup>4–16</sup> such as metal complexes,<sup>5–8</sup> hole conductors,<sup>9,10</sup> halogens,<sup>11,12</sup> and some redox active organic compounds.<sup>13–16</sup> Herein, we formulate a new electrolyte involving the amino acids L-cysteine/L-cystine as a redox couple. L-cysteine and L-cystine were treated with KOH and 1,2-dimethyl-3-propyl-imidazol-bromide (DMPBrI) to remove the protons, which are harmful to the performance of the DSSCs. The synthetic route and the structure of the organic redox couple are shown in Scheme 1 with the quantitative yield. No impurity was detected in the sample by <sup>1</sup>H NMR and elemental analysis. The redox couple was applied to DSSCs sensitized with ruthenium dye N719 and organic dye TH202, which have been reported by our group previously<sup>17</sup> (Fig. 1), and relatively high efficiencies were achieved. This novel electrolyte system contains neither iodine nor iodide, it is non-corrosive to the metal current collector in large-area DSSCs, which is crucial for the commercialization of DSSCs in the future.

Cyclic voltammetry (CV) was employed to study the electrochemical properties of the amino acid based redox couple with 0.2 M lithium perchlorate ( $LiClO_4$ ) as a supporting electrolyte. The measurements were carried out at 20 °C at a scan rate of 50 mV s<sup>−1</sup> in

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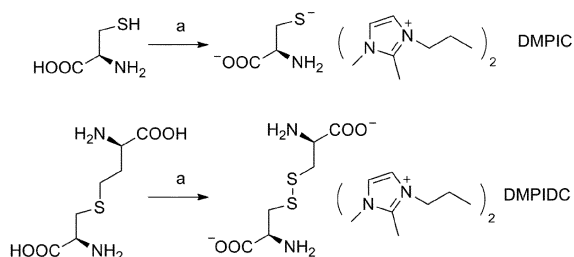
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## Broader context

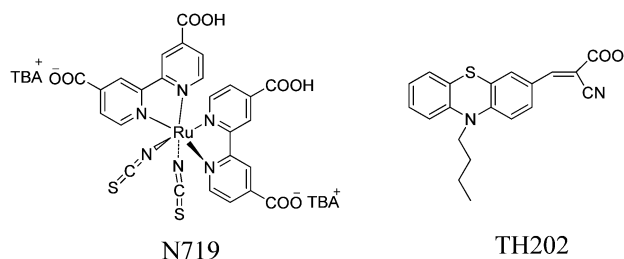
Dye-sensitized solar cells are currently attracting a great deal of both scientific and industrial interest due to their advantages towards solar energy conversion applications: these devices are in fact low cost, easily fabricated, and environmentally benign and, characteristically, have relatively high energy conversion efficiencies. Thus far, a sensible combination of a panchromatic ruthenium dye and an iodine electrolyte has respectably yielded a certified record solar-to-electricity conversion efficiency of 11.1%. Moreover, recognition of the drawbacks of the iodide/triiodide redox couple has translated into a strong impetus in the development of new, efficient, non-corrosive and stable redox couples. Herein, by employing a L-cysteine/L-cystine redox couple, we have prepared electrolytes and applied them in DSSCs sensitized by N719 and TH202. Efficiencies of 7.7% and 5.6% were achieved, respectively. This novel electrolyte system contains neither iodine nor iodide, it is non-corrosive to the metal current collector in large-area DSSC panels, which is critical for commercialization of DSSCs.



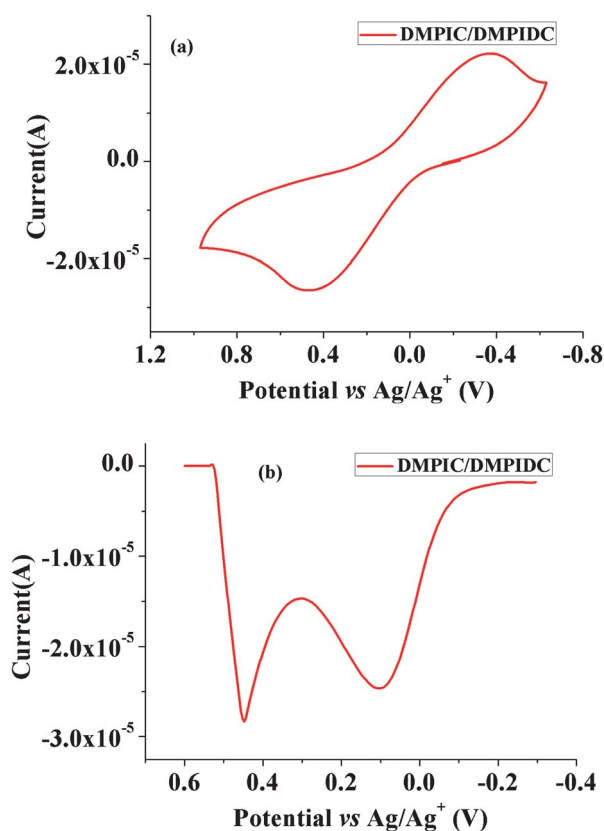
a: 1) 2 equivalent KOH, 25 °C, 12h; 2) 2 equivalent DMPBrI, 25 °C, 12h. Yield: DMPIC, 96%; DMPIDC, 97%.

**Scheme 1** The synthetic route and structures of the organic redox couple components.

an acetonitrile (AN) solution, which contained 6 mM DMPIC and 0.2 mM DMPIDC. The CV curve (Fig. 2a) showed a pair of redox peaks, which can either be one reversible redox process or two



**Fig. 1** The structures of the photosensitizers.

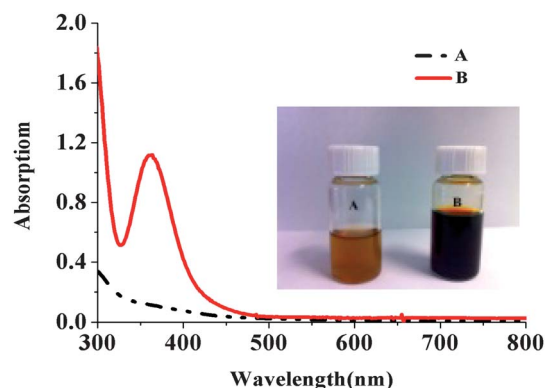


**Fig. 2** CV (a) and DPV (b) curves of DMPIC/DMPIDC.

irreversible redox processes. Under the same conditions, differential pulse voltammetry (DPV) was performed and two peak potentials at 0.103 V and 0.450 V *versus* Ag/Ag<sup>+</sup> were obtained (Fig. 2b), with a corresponding standard potential of 0.453 V and 0.800 *versus* a normal hydrogen electrode (NHE). The assignment of these two peaks can be difficult. They could be related to the oxidation processes of the DMPIC/DMPIC radical and the DMPIDC radical/DMPIDC. The involvement of other redox processes can, however, not be excluded. Under the same experimental conditions, the potential of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> (6 mM DMPIC, 0.2 mM I<sub>2</sub> in AN) gave a potential of 0.109 V *versus* Ag/Ag<sup>+</sup> (Fig. S1†), with a corresponding standard potential of 0.459 V *versus* NHE. The average redox potential of DMPIC/DMPIDC is only 0.006 V less than that of I<sup>-</sup>/I<sub>3</sub><sup>-</sup>.

The electrolytes with different ratios of DMPIC and DMPIDC were prepared for DSSC application. The corresponding experimental data are shown in the supplementary information (Fig. S2, Fig. S3, Table S1 and Table S3†). Under the optimized conditions, electrolyte A, containing 0.6 M DMPIC, 0.02 M DMPIDC, 0.1 M LiClO<sub>4</sub> and 0.4 M TBP in AN, gave the best efficiency among all the non-iodine based electrolytes. For comparison, an iodine-based electrolyte B, containing 0.6 M DMPIC, 0.02 M I<sub>2</sub>, 0.1 M LiClO<sub>4</sub> and 0.4 M TBP in AN, was employed. As seen from the UV-vis spectra and photo (Fig. 3), the DMPIC/DMPIDC based electrolyte A shows very weak absorption under 500 nm. However, the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolyte B exhibits a quite strong absorption in the same region. Therefore, the dyes can capture more sunlight in the system with electrolyte A than with electrolyte B in this region, which will be of great benefit to the solar energy conversion efficiency of DSSCs.

The DSSC devices, fabricated with N719-sensitized porous TiO<sub>2</sub> and electrolyte A, gave an average efficiency of 7.7% with an open-circuit photovoltage (*V*<sub>oc</sub>) of 0.72 V, a short-circuit photocurrent (*J*<sub>sc</sub>) of 17.0 mA cm<sup>-2</sup> and a fill factor (FF) of 64.2% under standard global AM 1.5 illumination. The detailed test data of the devices employing electrolyte A are shown in Table S2†. The integral current density calculated from the IPCE spectrum is 16.7 mA cm<sup>-2</sup>, which is in good agreement with the *J-V* test result (Fig. S4†). Comparably, the average efficiency of the devices employing electrolyte B is 7.0%, which is about a 10% decrease from those using electrolyte A. Although an efficiency of 8.1% is achieved with an optimized I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolyte C (0.6 M DMPIC, 0.053 M LiI, 0.03 M I<sub>2</sub>, 0.28 M TBP, and 0.05 M GuSCN in AN), an efficiency of 7.7% from the L-cysteine/L-cystine based electrolyte A is still remarkable when compared to other reported iodine free electrolytes. The test data are



**Fig. 3** UV-vis spectra and photo (inset) of electrolytes A and B.

**Table 1** Photovoltaic performances<sup>a</sup> of N719 based DSSCs with different electrolytes

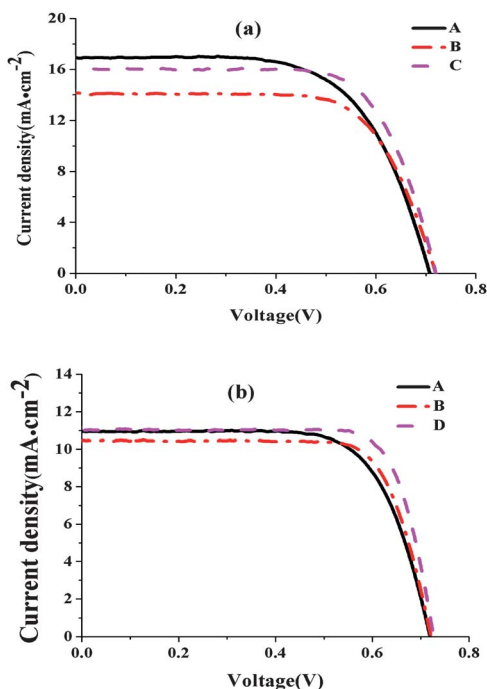
Electrolyte <sup>b</sup>	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF (%)	$\eta$ (%)
A	17.0	0.72	64.2	7.7
B	14.1	0.72	69.1	7.0
C	16.0	0.72	70.1	8.1

<sup>a</sup> The performances of the DSSCs were measured with a 0.159 cm<sup>2</sup> working area under 100 mW cm<sup>-2</sup> (AM 1.5) illumination. The concentration of the dye bath was  $2 \times 10^{-4}$  M in EtOH. <sup>b</sup> Electrolyte A: 0.6 M DMPIC, 0.02 M DMPIDC, 0.1 M LiClO<sub>4</sub> and 0.4 M TBP in AN. Electrolyte B: 0.6 M DMPII, 0.02 M I<sub>2</sub>, 0.1 M LiClO<sub>4</sub> and 0.4 M TBP in AN. Electrolyte C: 0.6 M DMPII, 0.0653M LiI, 0.03 M I<sub>2</sub>, 0.28 M TBP and 0.05 M GuSCN in AN.

**Table 2** The photovoltaic performances<sup>a</sup> of TH202 based DSSCs with different electrolytes

Electrolyte <sup>b</sup>	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (V)	FF (%)	$\eta$ (%)
A	11.3	0.72	70.1	5.6
B	10.4	0.72	74.5	5.6
D	11.1	0.73	78.0	6.3

<sup>a</sup> The performances of the DSSCs were measured with a 0.159 cm<sup>2</sup> working area under 100 mW cm<sup>-2</sup> (AM 1.5) illuminations. The concentration of the dye bath was  $2 \times 10^{-4}$  M in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Electrolyte A: 0.6 M DMPIC, 0.02 M DMPIDC, 0.1 M LiClO<sub>4</sub> and 0.4 M TBP in AN. Electrolyte B: 0.6 M DMPII, 0.02 M I<sub>2</sub>, 0.1 M LiClO<sub>4</sub> and 0.4 M TBP in AN. Electrolyte D: 0.6 M DMPII, 0.06 M LiI, 0.04 M I<sub>2</sub> and 0.4 M TBP in AN.

**Fig. 4**  $J$ - $V$  curves of DSSCs sensitized by N719 (a) and TH202 (b) with different electrolytes.

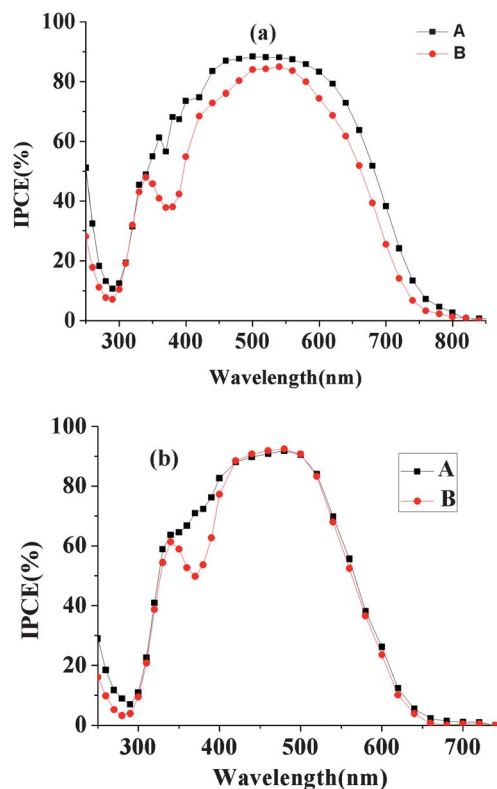
listed in Table 1 and the  $J$ - $V$  curves are shown in Fig. 4a. One can see that electrolyte A exhibits a  $J_{sc}$  value increased by 2.8 mA cm<sup>-2</sup> relative to electrolyte B, which corresponds to the higher incident photon-to-current conversion efficiencies (IPCE) in the wavelength region from 350 to 800 nm.<sup>4</sup> The  $V_{oc}$  for electrolyte A, however, is around 10 mV lower than that of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolytes (B and C).

Electrolyte A was also applied to DSSCs sensitized with the metal-free organic dye TH202. The test data are listed in Table 2 and Table S4†. The  $J$ - $V$  curves and IPCE spectra are shown in Fig. 4b and Fig. 5b, respectively. The devices sensitized with TH202 showed almost the same efficiencies with electrolyte A and B. The devices employing electrolyte A gave higher  $J_{sc}$  values mainly because of the higher IPCE under a wavelength of 350–450 nm. Based on the state-of-the-art composition of the iodine electrolyte, an efficiency of 6.3% was achieved using TH202 as a photosensitizer.

The current density transients of the DSSCs sensitized with N719 and TH202 employing electrolyte A were measured with intermittent

AM 1.5G illumination. The results are displayed in Fig. S6† and Fig. S7†, respectively. A current density of 16.9 mA cm<sup>-2</sup> was steadily obtained for the device sensitized with N719 after the first illumination (Fig. S6a†). After successive detection, the current density decreased gradually from 16.9 mA cm<sup>-2</sup> to 16.6 mA cm<sup>-2</sup> (Fig. S6b†). This is only about a 1.8% decrease in 1 h. The current density of the TH202 sensitized device reduced from 11.4 mA cm<sup>-2</sup> to 11.1 mA cm<sup>-2</sup> gradually over 1 h (Fig. S7†). This phenomenon is possibly due to the instability of the redox couple during continuous light irradiation.

Electrochemical impedance spectroscopy (EIS) analysis was used to study the interfacial charge transfer processes in the DSSC devices. The measurements were scanned from 10<sup>-2</sup> to 10<sup>6</sup> Hz at

**Fig. 5** The IPCE spectra of the DSSCs sensitized with N719 (a) and TH202 (b) with different electrolytes.

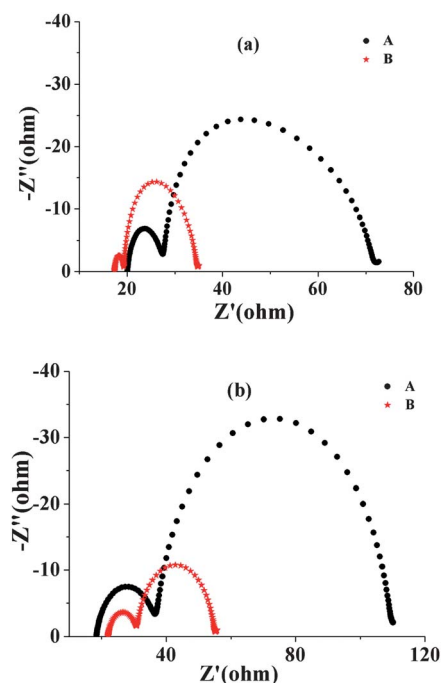


Fig. 6 EIS of DSSCs sensitized with N719 (a) and TH202 (b).

room temperature in dark conditions with a bias voltage of  $-0.75$  V (Fig. 6). The small arc located in the 10–20 kHz range reflects the charge-transfer resistance at the counter electrode. The devices sensitized with N719 (Fig. 6a) shows  $R_{ct} = 7.6 \Omega \text{ cm}^{-2}$  when electrolyte A is used. While  $R_{ct} = 1.9 \Omega \text{ cm}^{-2}$  was found for electrolyte B. The higher  $R_{ct}$  value for the electrolyte A system indicates that the oxidized species of the redox couple is regenerated slowly on the surface of the counter electrode compared to electrolyte B and probably causes the lower fill factor recorded for the device employing electrolyte A. The diameter of the medium frequency semicircle, corresponding to the recombination resistance ( $R_{rec}$ ), varies considerably. One can see that the  $R_{rec}$  value increased from  $15.2 \Omega \text{ cm}^{-2}$  to  $43.4 \Omega \text{ cm}^{-2}$  when electrolyte B was replaced by electrolyte A, implying that the recombination reaction between the conduction band electrons in the  $\text{TiO}_2$  film and electrolyte A is better inhibited than with electrolyte B. Although the potential of the DMPIC/DMPIDC system is a little more negative than that of  $\text{I}^-/\text{I}_3^-$ , similar  $V_{oc}$  values were found. Also, similar test results were obtained for TH202 based DSSCs (Fig. 6b), where  $R_{ct} = 18.6 \Omega \text{ cm}^{-2}$ ,  $8.9 \Omega \text{ cm}^{-2}$  and  $R_{rec} = 72.0 \Omega \text{ cm}^{-2}$ ,  $23.8 \Omega \text{ cm}^{-2}$  for electrolyte A and B, respectively.

In summary, an efficient and easily available iodine-free electrolyte based on the amino acids L-cysteine/L-cystine as a redox couple was applied in N719 and TH202 sensitized DSSCs, and efficiencies of 7.7% and 5.6% were achieved under  $100 \text{ mW cm}^{-2}$  (AM 1.5G) illumination, respectively. Although efficiencies of 8.1% and 6.3% were obtained, respectively, for the above two dyes with an optimal  $\text{I}^-/\text{I}_3^-$  based electrolyte, the high efficiencies of the DSSCs from the L-cysteine/L-cystine redox couple are still remarkable compared to other reported iodine free electrolytes. Further study on this redox couple to improve the fill factor is currently in progress.

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