Solar Cells

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Efficient Dye-Sensitized Solar Cells Based on Hydroquinone/Benzoquinone as a Bioinspired Redox Couple**

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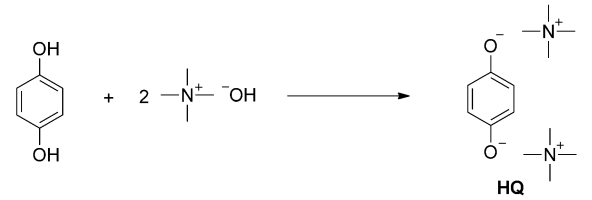
Dye-sensitized solar cells (DSSCs), which provide a more economical and effective method to carry out the energy conversion from solar light to electricity, were first reported by Grätzel et al. in 1991.[1,2] As one of crucial components in DSSCs, the electrolyte has attracted ever-increasing attention in recent years. In conventional systems, the electrolytes used in DSSCs are usually based on the iodide/triiodide (I^-/I_3^-) redox couple. However, many drawbacks have been identified for this redox couple, including the light absorption, corrosion of metal current collectors, and sublimation of iodine. Also, the potential mismatch between I^-/I_3^- redox potential and the HOMO level of photosensitizer leads to a decrease in photovoltage.[3,4] Therefore, many attempts have been made to explore effective and practical redox couples, and some good results have been reported,[3,4] such as metal complexes,[5–8] hole conductors,[9–11] halogens,[12–14] and some electroactive organic compounds.[15–19] Inspired by the redox relays of photosystem II, herein we formulate a new type of hybrid electrolyte involving the tetramethylammonium hydroquinone (HQ)/benzoquinone (BQ) redox couple. The synthesis and structure of HQ are shown in Scheme 1, using tetramethylammonium hydroxide and hydroquinone as raw material (details of the synthetic methods are given in the Experimental Section). No impurity was detected by ^{1}H NMR spectra and elemental analysis after the synthesis. The benzoquinone was purified by recrystallization as yellow needles.



Scheme 1. Synthesis and structure of the organic redox couple components.

The differential pulse voltammetry (DPV) was employed to study the electrochemical properties of the HQ/BQ-based electrolytes with 0.2 M lithium perchlorate ($LiClO_4$) as supporting electrolyte. The measurements were carried out at 20 °C at a scan rate of 50 mV s^{-1} in acetonitrile solution that contains 3 mM HQ and 2 mM BQ. HQ and BQ can form a charge-transfer complex together, called quinhydrone.[21,22] HQ is very strong reductant, and it can lose two electrons to form BQ. Potentials of −0.196 V and 0.204 V versus Ag/Ag$^+$ were obtained (Figure 1), with a corresponding standard potential of 0.194 V and 0.594 versus NHE.[23] The potentials of 0.194 V and 0.594 V correspond to the oxidation processes (Scheme 2). HQ loses one electron to form quinhydrone radicals, corresponding to the potential of 0.194 V. The quinhydrone radicals are active and they can lose one more electron to form BQ. The potential of the oxidation process is 0.594 V. Under the same conditions, the potential of I^-/I_3^- is 0.109 V versus Ag/Ag$^+$ (Supporting Information, Figure S1), corresponding to 0.499 V versus NHE.

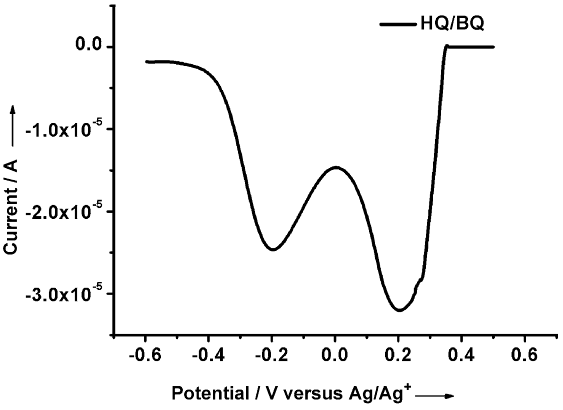


Figure 1. Differential pulse voltammetry curves of HQ/BQ versus Ag/Ag$^+$.

We applied the redox couple HQ/BQ to form the hybrid electrolyte. Different concentration of HQ/BQ and an optimized amount of the other compounds (0.60 M 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M $LiClO_4$,

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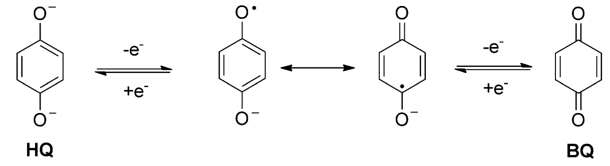

Scheme 2. Oxidation processes of HQ/BQ.

0.4 M 4-*tert*-butylpyridine (TBP)) were used, and four hybrid electrolytes **A**, **C**, **D** and **E** were formulated and investigated in the DSSC devices (Supporting Information, Figure S2) in comparison to electrolyte **B** based on I^-/I_3^- (Table 1).

Table 1: Photovoltaic performances of N719-based DSSCs with different electrolytes.

Electrolyte[a]	A	B[b]	C	D	E
Conc. HQ/BQ [mol L^{-1}]	0.06/ 0.04	0/0	0.12/ 0.08	0.12/ 0.04	0.06/ 0.03
V_{oc} [mV][c]	750	720	742	746	754
J_{sc} [mA cm^{-2}][c]	17.2	16.0	16.6	15.7	14.3
FF [%][c]	66.3	69.8	65.9	69.1	65.1
η [%][c]	8.4	8.0	8.1	8.0	7.0

[a] Electrolytes **A**, **C**, **D**, and **E** contain a different amount of HQ/BQ and an optimized amount of the other solutes: 0.60 M DMPII, 0.1 M $LiClO_4$, 0.4 M TBP were employed. Electrolyte **B**: 0.60 M DMPII, 0.03 M I_2, 0.053 M LiI, 0.28 M TBP, and 0.05 M GuSCN. [b] The device containing electrolyte **B** was optimized for the pure iodine-based redox couple. [c] All of the devices contained a 4 μm scattering layer on top of the transparent TiO_2 layer (12 μm). The cells were investigated using a metal mask with an active area of 0.159 cm², and photovoltaic data were recorded under AM 1.5 G illumination.

As shown in UV/Vis spectra of the electrolytes (Figure 2), the hybrid electrolyte **A** in absence of I_3^- is more transparent and shows a negligible absorption in the visible region, in contrast to a I^-/I_3^--based redox electrolyte **B** displaying a strong absorption up to more than 450 nm. Negligible absorption of electrolyte **A** in the short-wavelength region reduces optical losses in DSSC application, which is expected to improve the overall light-to-electricity conversion efficiency.

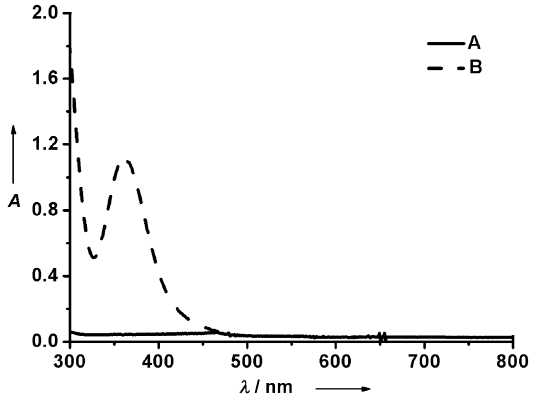

Figure 2. UV/Vis spectra of different electrolytes. Electrolyte **A**: 0.6 M DMPII, 0.06 M HQ, 0.04 M BQ, 0.1 M $LiClO_4$, 0.4 M TBP in MeCN. Electrolyte **B**: 0.6 M DMPII, 0.063 M LiI, 0.03 M I_2, 0.28 M TBP, 0.05 M GuSCN in MeCN. The spectra of both electrolytes were recorded with a thin layer of electrolyte **A** or **B** confined between two conducting glass substrates sealed by Surlyn sheet (25 μm thick). DMPII = 1,2-dimethyl-3-propylimidazolium iodide, TBP = 4-*tert*-butylpyridine, GuSCH = guanidine thiocyanate.

The devices fabricated with dye N719-sensitized porous TiO_2 and electrolyte **A** gave an average efficiency of 8.4% with an open-circuit photovoltage (V_{oc}) of 750 mV, a short-circuit photocurrent (J_{sc}) of 17.2 mA cm^{-2}, and a fill factor (FF) of 66.3% under standard global AM 1.5 illumination (Figure 3, Table 1). Integral current density calculated from the incident photon conversion efficiency (IPCE) spectrum is 17.1 mA cm^{-2}, which is in good agreement with the *J*–*V* test result (Figure 4). The device employing the electrolyte **B** based on I^-/I_3^- has $V_{oc} = 720$ mV, $J_{sc} = 16.0$ mA cm^{-2}, and FF = 69.8%, yielding 8.0% of conversion efficiency; the integral current density calculated from the IPCE spectrum is 16.1 mA cm^{-2} (Figure 3, Figure 4, Table 1). This is the highest efficiency we can obtain with the I^-/I_3^--based electrolyte. The devices employing hybrid electrolytes **A**, **C**, **D**, and **E** gave a higher V_{oc} than that of the device employing purely iodine-based electrolyte **B**. Two reasons can explain this significant difference: one is the tetramethylammonium cation, which

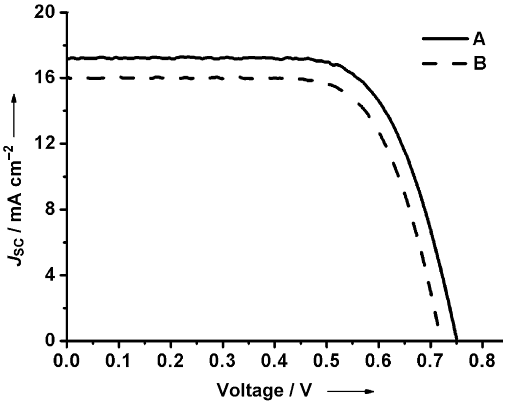

Figure 3. *J*–*V* curves of DSSCs sensitized by N719 with electrolyte **A** and **B**.

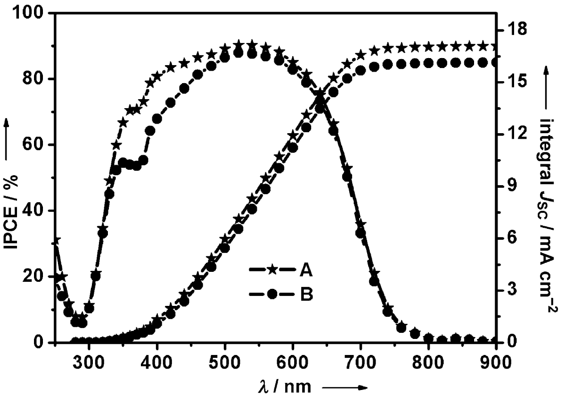

Figure 4. Incident photon conversion efficiency (IPCE) spectra of DSSCs sensitized by N719 employing electrolyte **A** and **B**.

can prevent the charge recombination[20] and lead to a higher voltage. This effect can be observed in electrochemical impedance spectra and electron-lifetime in TiO_2 of the corresponding devices (Figure 6, Figure 7). The other is the larger gap between the quasi-Fermi level of TiO_2 and the potential of redox couple HQ/BQ than that of between the quasi-Fermi level of TiO_2 and the potential of I^-/I_3^-.[3,4] The potential of the redox couple HQ/BQ is 95 mV more positive than that of I^-/I_3^-, but the conduction band of TiO_2 with the I^-/I_3^- based electrolyte is around 20 mV negative than that of with HQ/BQ-based electrolyte (Figure 5). Correspondingly, the value of V_{oc} for the devices employing HQ/BQ-based electrolyte is much higher. The devices employing electrolyte **A** gave much higher J_{sc} than that of the devices employing electrolyte **B** owing to the higher conversion efficiency in the region from 300 to 500 nm (Figure 4).

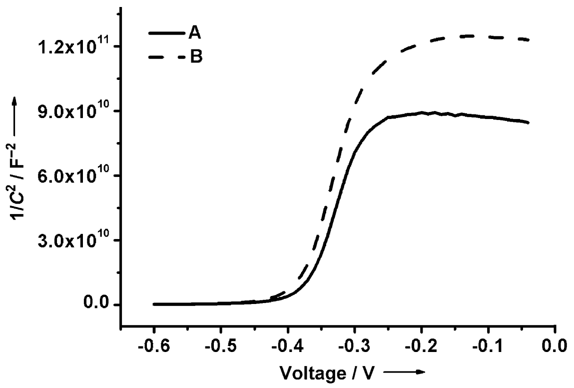

Figure 5. Evolution of cell capacitance as a function of photovoltage for films with different electrolytes.

Current-density transients of DSSCs sensitized by N719 employing hybrid electrolyte **A** were measured with intermittent illumination under AM 1.5 G (Supporting Information, Figure S3). A current density of $17.1\,mA\,cm^{-2}$ was steadily obtained for devices sensitized by N719.

Electrochemical impedance spectroscopy (EIS) analysis was employed to study the interfacial charge transfer processes in DSSCs. The measurements were performed by scanning from 10^{-2} to 10^6 Hz at room temperature under dark conditions with the bias voltage corresponding to V_{oc}. Nyquist plots and Bode phase plots for the devices fabricated with electrolyte **A** and **B** are shown in Figure 6. Some important parameters can be obtained by fitting the EIS spectra to an electrochemical model (Table 2).[24] R_S, R_{rec}, and R_{CE} represent the series resistances, charge-transfer resistances at the dye/TiO_2/electrolyte interface, and counter electrode (CE), respectively. From the EIS measurements, the electron lifetime (τ_e) expressing the electron recombination between the electrolyte and TiO_2 may be extracted from the angular frequency (ω_{rec}) at the mid frequency peak in the Bode phase plots using the relation $\tau_e = 1/\omega_{rec}$. The small arc located in the 10–20 kHz range reflects the charge-transfer resistance at the counter electrode. The devices sensitized by N719 shows $R_{CE} = 3.9\,\Omega\,cm^{-2}$ with electrolyte **A** and $R_{CE} = 3.5\,\Omega\,cm^{-2}$ were found for electrolyte **B**. The R_{CE} is nearly the same, indicating that the electrolyte can regenerate effectively on the CE. The diameters of the medium-frequency semicircle, corresponding to the recombination resistance (R_{rec}), vary considerably. We can see that the R_{rec} value increased from $19.5\,\Omega\,cm^{-2}$ to $41.1\,\Omega\,cm^{-2}$ when the I^-/I_3^- based electrolyte **B** was replaced by HQ/BQ-based hybrid electrolyte **A**. The electron lifetimes (τ_e) extracted from ω_{rec} at the mid frequency peak in the Bode phase plots are 0.18 ms and 0.11 ms for the devices with electrolyte **A** and **B**, respectively. These results all imply that the recombination reaction between the conduction band electron in TiO_2 film and electrolyte **A** is better inhibited than that with electrolyte **B**. This is also supported by our preliminary electron-lifetime studies (Figure 7). Comparing the electron lifetimes as a function of V_{oc}, DSSCs based on electrolyte **A** showed significantly longer electron lifetimes compared to that of with electrolyte **B**. This provides support for preventing electrons in TiO_2 from recombining with redox species yielding a high V_{oc}.

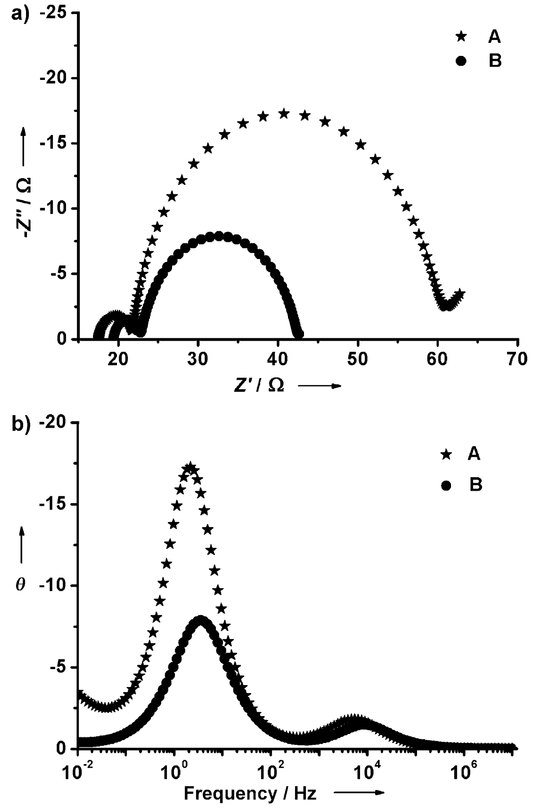

Figure 6. a) Nyquist and b) Bode phase plots of DSSCs employing electrolyte **A** and **B**.

Table 2: Parameters obtained by fitting the EIS spectra to an electrochemical model.

Electrolyte	R_S [Ω]	R_{rec} [Ω]	R_{CE} [Ω]	τ_e [ms]
A	17.5	41.1	3.9	0.18
B	19.3	19.5	3.5	0.11

In summary, when the new redox couple HQ/BQ is applied to a hybrid electrolyte, the system was demonstrated

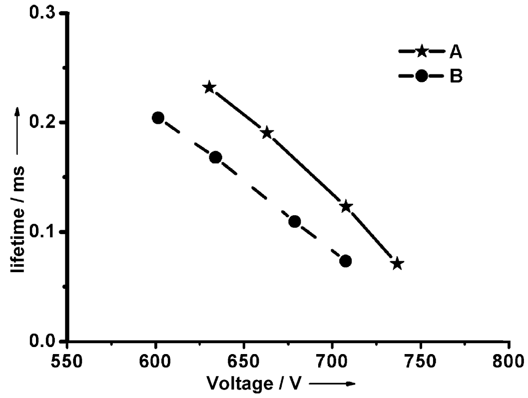

Figure 7. Electron lifetime as a function of extracted charge under open-circuit conditions for DSSCs based on electrolyte **A** and **B**.

to outperform the well-known I^-/I_3^- redox system. An efficiency of 8.4 % was achieved in our lab under AM 1.5 G illumination (100 mW cm^{-2}) using the N719 as photosensitizer that is higher than the recorded efficiency of 8.0 % of the corresponding system employing a pure iodine-based electrolyte. The device employing hybrid electrolytes gave a higher value of V_{oc} because of the larger gap between the quasi-Fermi level of TiO_2 and the potential of redox couple HQ/BQ and the increase of the resistance for recombination of the conduction-band electron with electrolyte. Work in progress is focused on the stability of the electrolytes and the application of purely HQ/BQ-based electrolyte in DSSCs.

Experimental Section

Synthesis of tetramethylammonium hydroquinone (TMAHQ): A 25 wt % solution of tetramethylammonium hydroxide in water (16.00 g, 44 mmol; Sinopharm Chemical Reagent Co., Ltd.) was added to a flask under a nitrogen atmosphere, and nitrogen was passed through for about half an hour to keep off the air in water. Hydroquinone (2.42 g, 22 mmol; Yizhong Chemical plant in Tianjin Dagang) was then added to the flask. The mixture was stirred at 25 °C for 10 h and then the water was evaporated and the resulting solid was dried under vacuum at 50 °C. ^{1}H NMR (CD_3OD, 400 MHz): $\delta = 3.20$ (s, 24H), 6.60 ppm (s, 4H) MS (API-ES): negative ion: $m/z = 108.0$ [hydroquinone]$^{2-}$, calculated 108.0; positive ion: $m/z = 74.1$ [TMA]$^+$, calculated 74.1. Elemental analysis(%) calcd for $C_{14}H_{28}N_2O_2$: C 65.59, H 11.01, N 10.93, O 12.48; found: C 65.01, H 10.95, N 11.01, O 12.64.

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Keywords: benzoquinone · dye-sensitized solar cells · hybrid electrolytes · hydroquinone · redox couples

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