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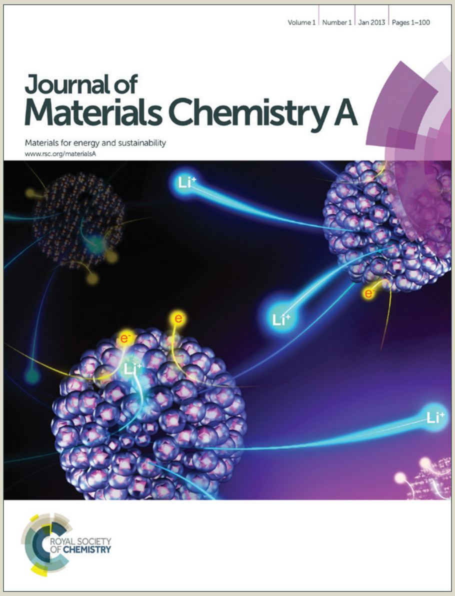

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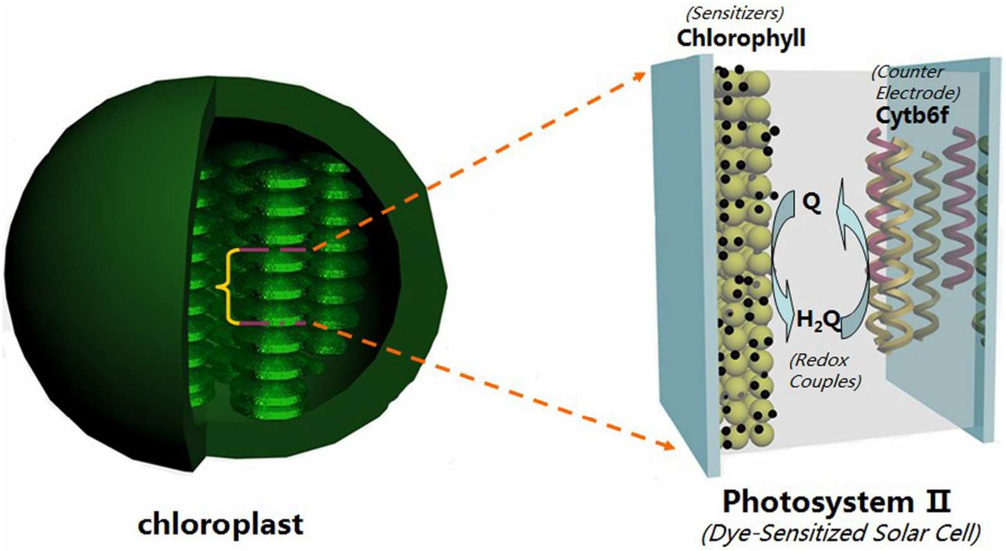

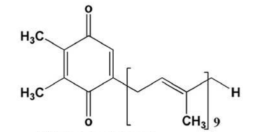

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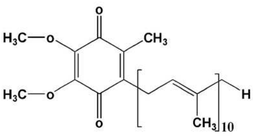
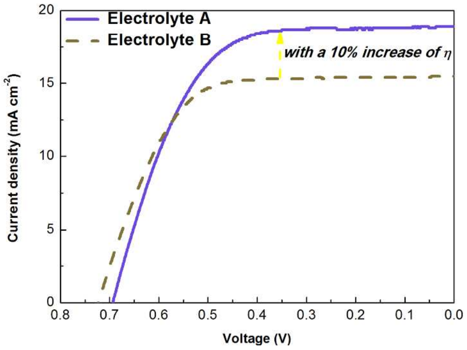


ubiquinone 10



# Efficient Dye-sensitized Solar Cells Employing Highly Environment-friendly Ubiquinone 10 based $I_2$-free Electrolyte Inspired From the Photosynthesis

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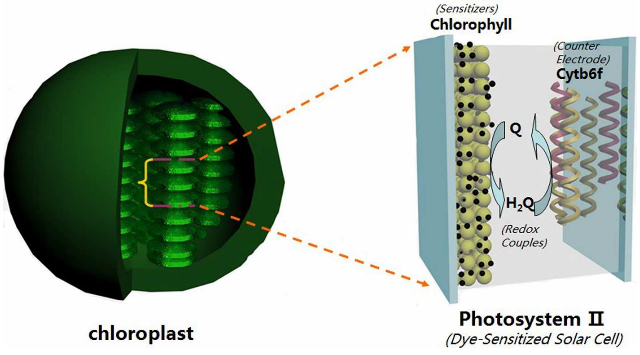
**A highly environment-friendly ubiquinone 10 ($UQ_{10}$) based $I_2$-free electrolyte, which is inspired from the photosynthesis, is employed in dye-sensitized solar cells (DSSCs) under 100 mW $cm^{-2}$ (AM 1.5 G) illumination. Profitting from this $UQ_{10}$ based electrolyte, A 10% increased power conversion efficiency of 8.18% is achieved compared with the traditional one containing $I_2$ (7.44%). The superior performance of this $UQ_{10}$ based electrolyte is mainly from the less visible light wastage and high catalytic activity to the counter electrode as revealed by photoelectrochemical characterizations. Moreover, being widely adopted in cardiovascular medicine and cosmetics, $UQ_{10}$ is a very safe and low-cost choice to DSSCs. With advantages of high power conversion efficiency, bio-safety, universal dye compatibility and diversity of molecular designing, $UQ_{10}$ is very promising to be widely applied in DSSCs, and perovskite based solar cells.**

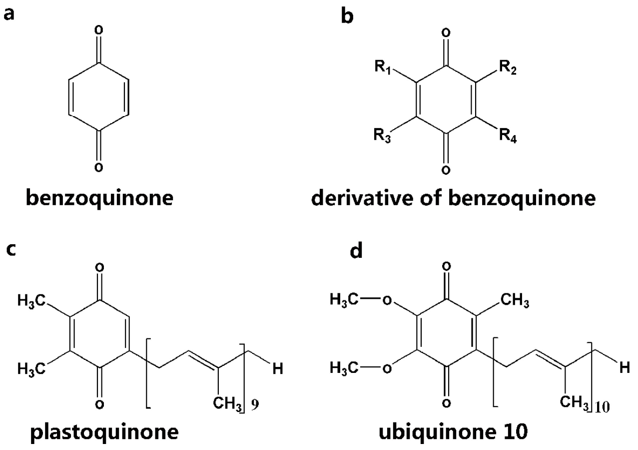
As energy shortage is gradually turning to be a severe crisis, various of solar cells have attracted intensive investigations[1-8]. By contrast, the most original and efficient light power conversion device is the chloroplast which converts the captured-light to electrons (or ions) through photosystem Ⅰ (PS Ⅰ) and photosystem Ⅱ (PS Ⅱ) and then turns such kind of electric energy into storable chemical energy[9,10]. Based on a very similar mechanism of photosynthesis, O'regan and Gr□tzel reported a prototype of the dye-sensitized solar cells (DSSC) in 1991[2] which has achieved a power conversion efficiency of 12.3%[11] in last two decades. And the process of photosystem Ⅱ in photosynthesis which the DSSC was inspired from can be simply described as that: 1) the chlorophyll (as dye in DSSC) on thylakoid membrane (nanostructure photoanode) turns to be high energy state (or excited state) after capturing the light; 2) the excited chlorophyll losses the energy (loss electron) which is used to decompose the water; 3) the electron lost chlorophyll is regenerated by reacting with Q (redox couple) and the Q turns to be H2Q; 4) the H2Q obtains electron from cytb6f (counter electrode).

Playing a significant part of regenerating the photo-oxidized dye and facilitating the charge transport[12] in DSSC, the electrolytes (liquid or solid) have been researched in abundance, and several good results have been obtained[13-30]. However, cobalt-complex based electrolytes, by which the highest energy conversion efficiency was achieved[11] and most of the other organic redox couples are restricted in further industrial application for that they are just compatible with circumscribed sensitizers[31]. Refering to the traditional electrolyte based on iodide/triiodide ($I^-/I_3^-$) which performances well with the most widely-used Ru-complex dyes and most other sensitizers, it also owns drawbacks of considerable visible light absorption, corrosion to counter electrode and high sublimability of $I_2$[32,33]. In view of these, the superior alternative electrolytes have been urgently desired.

Inspired by the PS Ⅱ of photosynthesis illustrated in **Scheme 1**, plastoquinone (PQ) (**Scheme 2c**) which plays a very similar role with redox couples in PS Ⅱ has appealed to us much as a promising alternative in DSSC. Before this, Cheng et al. had reported a preliminary research on an electrolyte based on benzoquinone[34] (**Scheme 2a**) which is the simplest molecular structure of quinones. However, the reported redox couple is unstable and unable to be prepared in open environment[35]. Aiming to overcome this drawback, we had developed a more facile and stable method to prepare benzoquinone based electrolyte in an open environment via acetic acid treatment in a previously reported work[36]. And a slightly lower power conversion efficiency of 5.82% compared with the traditional electrolyte had been obtained which suggests that quinones are of very potential to be applied in DSSC. What's more, several kinds of simple derivetives of benzoquinone (**Scheme 2b**) had been studied in the same work trying to find out the optimal quinone adopted in DSSC. Based on these, natural quinones such as PQ and ubiquinone 10 （$UQ_{10}$） presented in **Scheme 2d** have recently drawn our attention inspired by PS Ⅱ. As the PQ is



**Scheme 1** the basic mechanism of photosystem Ⅱ in photosynthesis and dye-sensitized solar cell (DSSC).



**Scheme 2** molecular structure of **a** benzoquinone, **b** derivative of benzoquinone, **c** plastoquinone and **d** ubiquinone 10.

not easy to obtain, a very similar quinone of $UQ_{10}$ has been employed as electrolyte A in DSSC compared with the common one based on $I_2$ (electrolyte B) in this paper. Herein, we assembled DSSCs employing electrolyte A and electrolyte B, and measured their performance. A high power conversion efficiency of 8.18% by electrolyte A has been achieved which is 10% higher than electrolyte B (7.44%) and about 40% increased in contrast to the previously studied benzoquinone. As a frequently-used component in cardiovascular medicine and cosmetics,[37,38] $UQ_{10}$ has high bio-safety to human bodies. Apart from this merit, other advantages such as high power conversion efficiency, universal dye compatibility and diversity of molecular designing of $UQ_{10}$ contribute to its promising application in DSSCs and perovskite based solar cells[4,5].

$UQ_{10}$ is an unctuous and plastoquinone-like component of the electron transport chain, therefore a liposoluble solvent ethyl acetate was used to prepare the $UQ_{10}$ based electrolyte. The main redox process of $UQ_{10}$ (**Scheme 2d**) is a two step reaction which is the same with benzoquinone (**Scheme 2a**)[36,39,40]. Though the certain redox process in system of electrolyte A can not be determined in our current work, the relative redox potentail of electrolyte A compared with electrolyte B is able to be derived from the confirmed value reported formerly.[39] Reported by Damien Marchal et al.[39], the standard redox potential of $UQ_{10}$ is about 0.105 V *vs* NHE at PH7 which is more negative than $I^-/I_3^-$ (0.45V *vs* NHE)[41]. The relatively negative redox potential tends to lead to a low open-circuit voltage ($V_{OC}$) of DSSC using $UQ_{10}$ based electrolyte. To optimize the ingredient of electrolyte employing $UQ_{10}$, a series of electrolytes with different concentration of $UQ_{10}$ ranging from 0 to 0.1 M were prepared and applied in DSSCs (details of experimental sections are listed in the Electronic Supplementary Information (ESI)). The resluts shown in **Fig. 1a** which exhibitates that the conversion efficiency of DSSCs firstly rises and then descends with the concentration of $UQ_{10}$ increasing suggestes that the mixing of $UQ_{10}$ leads to an enhancement of the performance of $I_2$-free electrolyte in devices and the optimal amount of $UQ_{10}$ is 0.01 M. The decline of the power conversion efficiency when the amount of $UQ_{10}$ increases further may be ascribed to the precipitation of $UQ_{10}$ in the solvent under high concentration. Anyway what is the most noteworthy is that the introdunction of moderate $UQ_{10}$ contributes significantly to the performance of DSSCs.

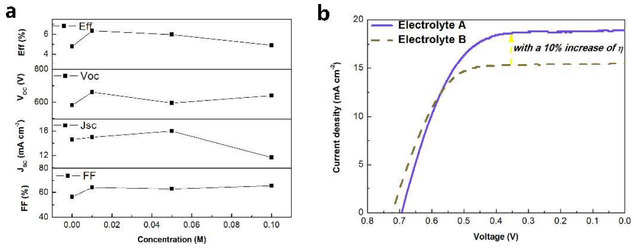


**Fig. 1** **a)** Photovoltaic performance of DSSCs based on N719 sensitized electrode A employing electrolytes with different concentration of UQ10; **b)** J-V characteristics of DSSCs based on N719 sensitizers with electrolyte A and electrolyte B.

When comparing $UQ_{10}$ based electrolyte (electrolyte A) with traditional one containing $I_2$ (electrolyte B) electrode B was employed under the same condition (one sun illumination) to assemble the DSSCs. The result displayed in **Fig. 1b** indicates that the short-circuit current density ($J_{SC}$) of DSSC based on electrolyte A increases from 15.5 to 18.9 mA $cm^{-2}$ with an approximate $V_{OC}$ and fill factor (FF) compared with electrolyte B (detailed data is listed in **Table 1**). And the power conversion efficiency reaches to 8.18% from 7.44% with a 10% increasing which is a significant result to explore the alternative to frequently-used electrolyte. Through analysising the properties of $UQ_{10}$, this enhanced performance of DSSC using electrolyte A could be attributed to results of its high ion mobility, faster reaction rate and function of elelctron transfer ladder between dye and iodide ion.

In order to investigate the visible light absorption of electrolyte A and electrolyte B, UV-vis spectra were measured as shown in **Fig. 2a**. It is clearly exhibited in the photogragh insetting in **Fig. 2a** that the frequently-used electrolyte B presents to be dark mulberry while the electrolyte A is transparent yellow. By quantitative analysing, electrolyte B has a strong absorption below 500nm in contrast to electrolyte A which means the latter almost do not contend with dyes for incident light and thus contributes to the validly utilized light. And as we know, more valid light utilizing will naturally result in higher $J_{SC}$ which is in conformity with the results in **Fig. 1b** and **Table 1**.

Open-circuit voltage decay (OCVD) measurements were employed to explore the electron lifetime of DSSCs with electrolyte A and electrolyte B. After turning off the illumination in a steady state, the $V_{OC}$ will subsequently decay and the decay curves are presented in **Fig. 2b**. The electron lifetime ($\tau_n$) is a

**Table 1** Photovoltaic parameters[a] of DSSCs based on electrolyte A and electrolyte B[b].

| | $V_{OC}$ (mV) | $J_{SC}$ (mA $cm^{-2}$) | FF (%) | η (%) |
|---|---|---|---|---|
| Electrolyte A | 693 | 18.9 | 62.5 | 8.18 |
| Electrolyte B | 723 | 15.5 | 66.4 | 7.44 |

[a] The photovoltaic parameters were measured under simulated AM 1.5 G illumination intensity of 100 mW $cm^{-2}$ and a temperature of 293 K, and all the DSSCs were fabricated in the way shown in the Experimental Section (shown in EIS). [b] The compositions of electrolyte A and B are as follows: Electrolyte A: 0.6 M PMII, 0.1M LiN(CF3S02)2, 0.4 M TBP, 0.01M UQ10 solved in EA and PC (vol: vol= 1: 1); Electrolyte B: 0.6 M PMII, 0.05M lithium iodide (LiI), 0.4 M TBP, 0.1 M Guandine thiocyanate (GITC), 0.03 M iodine ($I_2$) solved in Acetonitrile (ACN) and PC (vol: vol= 1: 1).

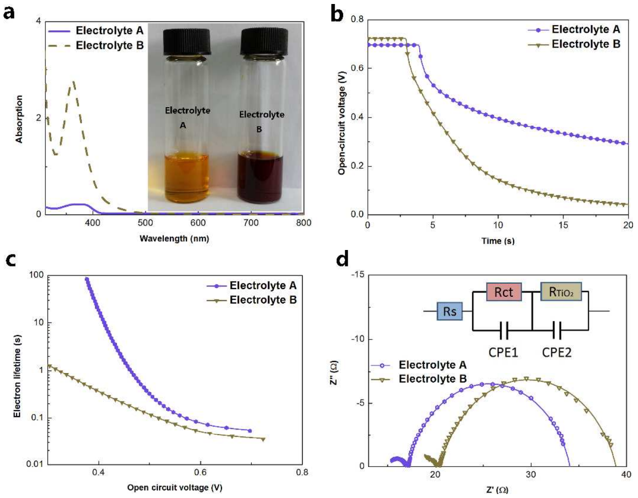


**Fig. 2** **a)** UV-vis spectra of absorption of electrolyte A and electrolyte B; **b)** Open-circuit voltage decay for DSSCs based on electrolyte A and electrolyte B; **c)** Electron lifetime as a function of open-circuit voltage for DSSCs with electrolyte A and electrolyte B; **d)** Nyquist plots and corresponding fitted curves of the electrolyte A and electrolyte B measured under 100 mW cm$^{-2}$ irradiation. The symbols are the experimental date, and solid lines are the fitted results.

function of decay rate of Voc which is described as the following equation:[42]

$$\tau_n = -\frac{k_B T}{e}\left(\frac{dV_{OC}}{dt}\right)^{-1}$$

where $k_BT$ is the thermal energy, and e is the electron charge. **Fig. 2c** shows the electron lifetime (in log-linear representation) for the DSSCs using electrolyte A and electrolyte B. It is obvious that the $V_{OC}$ decay rate of electrolyte A is slower and its electron lifetime is longer than that of electrolyte B which demonstrates that excited electrons in deviecs employing electrolyte A transport longer and more electrons enter into external circuit. So taken as a whole, a higher perfmance of the devices are achieved profitted from the longer electron lifetime of electrolyre A.

Attempting to clarify the charge transfer process in devices employing electrolyte A and electrolyte B respectively, electrochemical impedance spectroscopy (EIS) analysis was investigated under one sun illumination at open circuit condition. By fitting the experimental data with an equivalent circuit model presented as the inset in **Fig. 2d**, the internal impedance can be determinated including series resistance ($R_S$), charge recombination resistance ($R_{TiO2}$) and charge transfer resistance ($R_{CT}$) at the counter electrode/electrolyte interface (detailed data is shown in **Table 2**). As generally known, $R_{CT}$ is the most direct and valuable information when discussing the influence on DSSCs from the electrolytes. A much smaller first-semicircle in high frequency region and about one third $R_{CT}$ (1.98 Ω) of the fill factor of the devices. And the $R_S$ (15.2 Ω) of electrolyte A is a little bit higher than electrolyte B (14.6 Ω) which corresponds to the slightly lower FF of electrolyte A. With a larger second electrolyte A based device compared with electrolyte B ($R_{CT}$=5.9 Ω) powerfully demonstrate that catalytic activity of $UQ_{10}$ on platinum is much more superior than $I_2$ which is coincided to the 10% increased $J_{SC}$ of electrolyte A employed device presented in **Fig. 1b**. $R_S$ read from the onset of the first semicircle in **Fig. 2d** means ohmic series resistance of DSSCs which is correlated with semicircle in low frequency region compared with electrolyte B, electrolyte A based DSSC is deduced to have a lower $R_{TiO2}$ (16.9Ω) which contributes to its slightly lower $V_{OC}$ (693 mV). In conclusion, the J-V properties can be expained adequately by these electrical impedance analysis. In the other hand, the electron lifetime can be estimated from the frequency of minimum Z'' ($\omega_{min}$) at the low frequency semicircle by the following equation:[43]

$$\tau_e = \frac{1}{2\pi\omega_{min}}$$

**Table 2** Impedance parameters of devices based on electrolyte A and electrolyte B.

| | $R_S$ (Ω) | $R_{CT}$ (Ω) | $R_{TiO2}$ (Ω) | $\omega_{min}$ (Hz) | $\tau_n$ (ms) |
|---|---|---|---|---|---|
| Electrolyte A | 15.2 | 1.98 | 16.9 | 3.742 | 42.5 |
| Electrolyte B | 14.6 | 5.9 | 18.4 | 4.52 | 35.2 |

Electrochemical impedance spectroscopy (EIS) was performed with the frequency ranging from 100 KHz to 0.1 Hz at open circuit conditions under 100 mW cm$^{-2}$ irradiation. The compositions of the electrolytes are the same in **Table 1**.

As revealed in **Table 2**, the calculated value of the electron lifetime of device basing on electrolyte A (42.5 ms) is longer than electrolyte B (35.2 ms) which is in good agreement with the results measured by OCVD shown in **Fig. 2b** and **2c**. Typically longer electron lifetime corresponds to higher $V_{OC}$ in DSSC. However, the result is abnormal for the electrolyte A which has longer electron life time but a slightly lower Voc compared with electrolyte B. And this discrepancy can be ascribed to the complex multi-step redox behavior of $UQ_{10}$ which may retard the electron transport processes, so the electron relaxation of each reaction step lengthens the whole electron relaxation time which leads to a high measured electron lifetime without the recombination decreasing.

In summary, a bioinspired $I_2$-free electrolyte based on $UQ_{10}$ has been investigated in this work. A high power conversion efficiency of 8.18% by $UQ_{10}$ based electrolyte was achieved which is 10% increased compared with the traditional one and about 40% enhanced to the previously mentioned benzoquinone[34]. Several characterization methods have been applied to expound its superior performance, and less incident light wastage and high catalytic activity to the counter electrode are considered to be the main factors determining the results. With advantages of high power conversion efficiency, bio-safety, universal dye compatibility and diversity of molecular designing, $UQ_{10}$ is very promising to be the alternative to the traditional $I_2$ based electrolyte and even widely applied in perovskite based solar cells. However, there are still several challenges such as long-term stability, solvent selecting and PH value adjusting requiring further exploration.

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## Notes and references

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