Nitroxide Radicals for Highly Efficient Redox Mediation in Dye-sensitized Solar Cells

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A robust nitroxide radical, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and its 4-subsituted derivatives (R-TEMPO) exhibit electrochemically reversible redox properties with tunable half-wave potentials ($E_{1/2}$) based on the substituent effect. Dye-sensitized solar cells using R-TEMPO as mediators with electron-withdrawing R groups showed significantly enhanced photovoltages compared with those obtained using iodides. The linearity between the open-circuit voltage (V_{oc}) and $E_{1/2}$ revealed that V_{oc} was dominated by the energy gap between the Fermi level of TiO_2 and the SOMO level of R-TEMPO.

The development of dye-sensitized solar cells (DSSC) has been held back by the limited range of redox mediators which typically rely on the use of iodides.[1] In this report, we describe that an electrochemically reversible one-electron redox couple of nitroxide radicals ($R_2N–O^\bullet/R_2N^+=O$)[2] provides a novel type of mediation system to produce the highly efficient photovoltaic effect, especially in terms of photovoltage enhancement.

DSSCs have been attracting significant interest over the past decades because of their high performance and yet low production costs.[3] Dye sensitization involves the injection of photoexcited electrons into the conduction band of TiO_2, followed by the dye regeneration by a redox system. Typical DSSCs using the I^-/I_3^- redox mediator have allowed an efficient energy conversion,[4] but they have several inherent problems, such as a limited V_{oc}, concomitant corrosion of the electrode metals, and the undesired dark color that reduces the external photon conversion efficiency, which have prompted studies on alternative mediators, such as cobalt complexes.[5]

A nitroxide radical, TEMPO, is almost robust under ambient conditions and has been employed as pendant redox sites bound to aliphatic backbones to develop the so-called "radical polymers" as charge-transporting and/or storage materials in electrochemical devices such as secondary batteries,[6] electrochromic cells[7] and sensors, and in memory devices and OLEDS.[8] We anticipated that nitroxide radicals are desirable as mediators in DSSC, based on their (i) rapid and reversible redox properties, (ii) suitable redox potentials which are susceptible to substituent effects, (iii) large diffusion coefficients and heterogeneous electron-transfer rate constants, and (iv) the rapid electron self-exchange reactions.[9] Grätzel et al. reported TEMPO as the mediator in DSSC,[10] but advantages over the conventional iodides have not been pursued because of the limited types of nitroxide molecules. In this study, we used several nitroxides, R-TEMPO, different in their redox potentials based on their substituent effect, as the mediator in the DSSC. Emphasis is placed on the capabilities of tuning the V_{oc} by the $E_{1/2}$ of the R-TEMPO, which suggested that the photovoltage is dominated by the energy gap between the Fermi level (E_F) of TiO_2 and the SOMO (singly occupied molecular orbital) level (E_{SOMO}) of R-TEMPO as the mediators. The observed $V_{oc}–E_{1/2}$
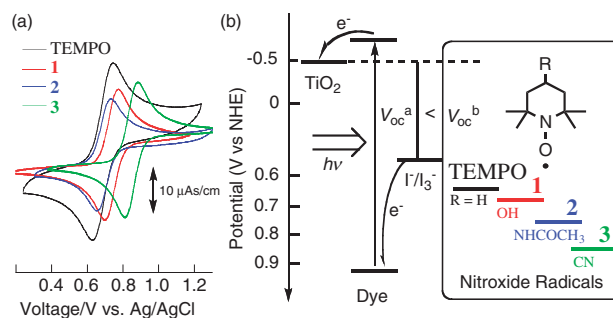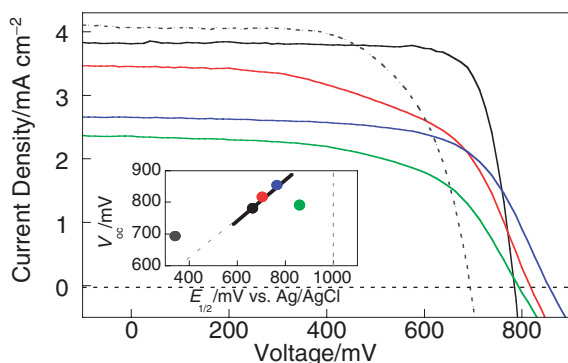

Figure 1. (a) Normalized cyclic voltammogram ($I/D_o^{1/2}$ vs. E) of the nitroxide radicals. (b) Energy diagram of DSSC using the nitroxide radicals as the mediators.

linearity and comparison with iodides gave insight into the nature of a back electron-transfer process, which influences the overall photovoltaic process.

Cyclic voltammograms of TEMPO and R-TEMPO with R = OH (**1**), NHCOCH$_3$ (**2**), and CN (**3**) all displayed reversible electrochemical responses at $E_{1/2}$ = 0.66, 0.70, 0.76, and 0.86 V vs. Ag/AgCl, respectively (Figure 1a). Diffusion coefficients evaluated from the slope of the Levich plots were D_0 = 12, 4.7, 3.5, and 5.2 × 10^{-5} cm s^{-1}, for TEMPO, **1**, **2**, and **3**, respectively. Heterogeneous rate constants for the electrode reactions evaluated by the Nicholson method were k_0 = 16, 1.8, 1.3, and 2.2 × 10^{-2} cm s^{-1}, for TEMPO, **1**, **2**, and **3**, respectively. These transport properties of the nitroxide radicals were comparable to those of the iodide ($D_0 = 2.0 \times 10^{-5}$ cm^2 s^{-1}, $k_0 = 3.1 \times 10^{-3}$ cm s^{-1}) and thus presumed to be suitable for the charge diffusion and dye regeneration in the DSSCs.

Test cells were fabricated as follows: A TiO_2 nanoparticle layer (1.5 μm) and a light-scattering layer were fabricated on a fluorine-doped tin oxide-coated glass substrate.[11] The resulting layer was heated at 450 °C for 2 h in air. Dye adsorption was carried out by immersing the TiO_2 electrode into a 0.3 mM solution of a dye (D131)[5b] in *tert*-butyl alcohol/CH$_3$CN (1/1 v/v) for 20 h at room temperature. The counter electrode consisted of a platinum-coated glass plate. Into the fabricated cell assembly was then introduced a solution of the nitroxide mediator which was a CH$_3$CN solution of 0.25 M R-TEMPO, 0.05 M NOBF$_4$, 1.6 M lithium bis(trifluoromethanesulfonyl)-imide, and 0.25 M N-methylbenzimidazole. The reference cell using the I^-/I_3^- mediator was fabricated with a CH$_3$CN solution of 0.6 M 1-methyl-3-propylimidazolium iodine, 0.06 M I$_2$, 0.1 M LiI, and 0.5 M 4-*tert*-butylpyridine, according to the previous papers.[3c] The photovoltaic performances were measured using a Keithley 2400 source meter and an AM 1.5 solar simulator (YSS-40S, Yamashita Denso Co.) as the light source.

The current density–photovoltage (*J–V*) curves are shown in Figure 2, and their characteristics are summarized in Table 1.

the forward electron-transfer rate when the R-TEMPO–dye potential gap was narrowed. Indeed, preliminary electrochemical impedance spectroscopy revealed that the resistance component that originated from the mediation process increased with the positive shift of $E_{1/2}$, which most likely dominated the overall resistance and thus short-circuit current density (J_{sc}) of the cell.

Additional advantages of R-TEMPO over the I^-/I_3^- mediator have been provided by the less corrosive properties of the nitroxide radicals against base metals and the much lower absorptivities with an ε_{max} value less than $10\,M^{-1}\,cm^{-1}$ in the range of 300–900 nm (cf. $\varepsilon_{max} = 786\,M^{-1}\,cm^{-1}$ for I_2 at $\lambda_{max} = 461\,nm$). The proposed characteristics of R-TEMPO offered design principles for an efficient DSSC by introducing multiple negative charges to the R-TEMPO to suppress the back electron transfer and employing dyes with deeper HOMO levels to maintain the energy gap with the mediator, which are the topics of our continuous investigation.

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11 We used in this paper 1.5 μm-thick TiO_2 layer which was thinner than 3–5 μm-thick layer typically employed in previous reported studies.

Figure 2. Current density–voltage (*J–V*) characteristics for the D131-sensitized solar cells using 0.1 M TEMPO (black) and R-TEMPO with R = OH (**1**, red), NHCOCH₃ (**2**, blue), and CN (**3**, green) as the redox mediators and a 1.5 μm thick TiO_2 layer on the FTO as the electron-transport layer, measured under an AM1.5 full-sunlight (100 mW cm⁻²) irradiation. The reference data obtained with I^-/I_3^- under the same conditions is shown as the gray dashed curve. Inset: Plots of V_{oc} vs. $E_{1/2}$ for TEMPO, R-TEMPO, and I^-/I_3^-. The dotted line represents $E_{1/2}$ for the oxidation of D131 which corresponds to the HOMO level to accept electrons from the mediator after the photo electron transfer to TiO_2.

Table 1. Photovoltaic parameters for DSSCs based on nitroxide radical electrolyte under an AM1.5 full-sunlight (100 mW cm⁻²) irradiation[a]

Mediator	J_{sc}/mA cm⁻²	V_{oc}/V	FF (—)	η/%
TEMPO	3.8	0.78	0.79	2.4
1	3.5	0.82	0.55	1.6
2	2.7	0.86	0.65	1.5
3	2.4	0.79	0.58	1.1
Iodide	4.1	0.69	0.65	1.8

[a]J_{sc}, short-circuit photocurrent density; V_{oc}, open-circuit voltage; FF, fill factor; η, light-to-power conversion efficiency.

All the R-TEMPO mediators examined in this study produced the photovoltaic effect. The $E_{1/2}$ of R-TEMPO shifted positively with the electron-withdrawing substituent R, but the energy diagram for the SOMO levels estimated from $E_{1/2}$ (Figure 1) suggested that the forward electron transfer to the dye was still downhill, allowing the regeneration of the dye cation. A higher V_{oc} could be obtained by the more positive potentials of R-TEMPO than that of the iodide.

An intriguing aspect of the R-TEMPO mediators is the unexpected apparent linearity of V_{oc} vs. $E_{1/2}$ observed for TEMPO, **1**, and **2** (Figure 2 inset), which indicated that the SOMO level changes dominated the variation of V_{oc}. This may be surprising because the effect of the back electron-transfer process to the positively charged mediators, approximated as $E_{SOMO} - E_F - V_{oc}$, was suggested to be almost equal, despite the difference in the energy levels. Moreover, the upward deviation of the V_{oc}–$E_{1/2}$ plot for the iodide from the linearity suggested that the negative charge of I_3^- suppressed the back electron-transfer process from the negatively charged TiO_2 surface, which has long been discussed to be the origin of the relatively large photovoltage observed for the I^-/I_3^- mediator. The V_{oc}–$E_{1/2}$ plot for **3** deviated downward from linearity, which suggested that the forward electron transfer to the dye cation may have been limited by the very small potential gap (140 mV) between **3** and the dye (Figure 1b). A comparison of the three R-TEMPOs, which satisfy the V_{oc}–$E_{1/2}$ linearity, revealed that J decreased with the increase in V_{oc}. This undesired trade-off relationship would result from the decrease in