Supporting information

Efficient aqueous dye-sensitized solar cell electrolytes based on TEMPO/TEMPO⁺ redox couple

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Details of solar cell fabrication and characterization

Solar cell fabrication

The details of fabrication of solar cells were reported previously.¹ FTO substrates (TEC15, Pilkington) were cleaned in an ultrasonic bath by use of 2 wt % detergents (60 min), water (60 min), ethanol (60 min), and acetone (60 min) in order. A compact TiO₂ layer (~ 160 nm) was first deposited on FTO glass by spray pyrolysis of Ti-precursor solution (0.2 M Ti-isopropoxide and 2 M acetylacetone in isopropanol) at 450 °C. The substrates were then screen printed with around 4 µm transparent TiO₂ nanoparticles (NR 18 Dyesol) and about 4 μ m scattering TiO₂ nanoparticles (~ 200 nm). The resulting films (active area 0.25 cm²) were treated by a heating process: 180 °C (10 min), 320 °C (10 min), 390 °C (10 min), and 500 °C (60 min) in an oven (Nabertherm Controller P320) at air atmosphere. After sintering, the samples were treated in 40 mM aqueous TiCl₄ at 70 °C for 30 min. A final heating step (500 °C for 60 min) was performed. After sintering, when temperature cooled to be around 100 °C, the electrodes were immersed into dye bath containing 0.2 mM LEG4 in acetonitrile overnight for sensitization. The counter electrodes were prepared by dropping 10 μ l 5 mM H₂PtCl solution in ethanol on the top of glass followed by heating in air at 400 °C for 30 min. The sensitized films and the counter electrodes were then assembled into a sandwich-type structure using a 50 µm hot-melt Surlyn frame. The electrolytes were then introduced into the cells through predrilled hole on the counter electrode by vacuum injection. At least three solar cells were fabricated and the averaged results were reported.

Solar Cell Characterization

The details of solar cell characterization were reported before.² Briefly, current–voltage characteristics were measured by use of a Keithley 2400 source/meter and a Newport solar simulator (model 91160) giving light with AM 1.5 G spectral distribution, which was calibrated with a certified reference solar cell (Fraunhofer ISE) to an intensity 1000 W/m². A black mask ($0.5 \times 0.5 \text{ cm}^2$) was applied on top of the cells which have the same active area. The apparatus for incident photon to current conversion efficiency (IPCE) consists of a computer-controlled setup with a xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM 110) and a Keithley 2700 multimeter. The same certified reference solar cell was used for calibration as previously mentioned.



Figure S1. Cyclic voltammogram of 5 mM TEMPOBF₄ in 0.1 M KCl aqueous solution with different scan rates: 5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s and 200 mV/s. K₃Fe(CN)₆ (0.47 V vs NHE³) was used to calibrate the reference electrode potential before and after experiments, shown as black curves (only the latter shown here). The diffusion coefficient was calculated by utilizing the relationship between scan rate and peak current as shown in the insert graph, which is fitted with equation: $i_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} C_0^* v^{1/2}$.



Figure S2. (a) Extracted amount of charges under various Voc for 0, 2 and 6 wt% SDS in the electrolytes. (b) Dependence of electron lifetime on accumulated charges under open circuit situation for 0, 2 and 6 wt% SDS in the electrolytes, calculated from (a) and electron lifetime measurement under Voc.⁵ The detailed setups were detailed described previously.²



Figure S3. Differential pulsed voltammetry (DPV) of 5 mM TEMPOBF₄ in 0.1 M KCl solution taken at different days, with the same experimental setup as in Figure S1. The scan range was 0.8 V-0 V at 10 mV/s scan rate. The reference electrode was not calibrated and could explain the observed shift in peak position. The relative intensity of the peak was found to decrease 2.5 % for 3 days and 5 % for 15 days, which is proportional to the concentration of TEMPO⁺ in the electrolyte⁴, while the intensity at above 0.6 V was found to increase, probably from the redox chemistry of the degraded compound.

Reference

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