

Supplementary Information

Effects of Water Intrusion on the Charge-Carrier Dynamics, Performance, and Stability of Dye-Sensitized Solar Cells

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Experimental

The procedure for fabricating dye-sensitized solar cells (DSSCs) are described elsewhere.¹ In brief, a thin compact layer of TiO₂ was deposited on a cleaned transparent conducting glass (TCO) plate (Pilkington, 2.3 mm thick, 8 Ω/sq) by spraying 0.2 M titanium diisopropoxide bis(acetylacetonate) in isopropanol onto the TCO substrate, followed by heating at 450 °C for 30 min. The paste of 22 nm-sized TiO₂ nanoparticles was deposited on the TCO substrate by the doctor blade technique and then sintered at 500 °C following a published temperature ramp profile.² The average film thickness was about 10 μm as determined with a surface profiler (KLA Tencor Alpha-Step 500). The sintered TiO₂ films were soaked in 0.02 M TiCl₄ solution at room temperature for 6 h, rinsed with distilled water, and then annealed again at 500 °C in air for 30 min. After cooling the samples from 500 °C to 80–100 °C, the TiO₂ films were immersed in a solution of acetonitrile and *tert*-butyl alcohol (1:1, v/v) containing 0.3 mM Ru(4,4'-dicarboxylic acid-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)₂ (Z907 dye) and 0.5 mM chenodeoxycholic acid (CDCA) for 15 h. The semitransparent counter electrodes were prepared by spreading a droplet of 7 mM H₂PtCl₆ in 2-propanol onto the TCO plates (Pilkington, 2.3 mm thickness, 15 Ω/sq) and subsequently firing them at 400 °C for 20 min. The TiO₂ working electrode and the Pt-coated counter electrode were then sandwiched together using the 25-μm thick Surlyn (Dupont grade 1702). The electrolytes consisted of 1.0 M 1-propyl-3-methylimidazolium iodide (PMII), 0.15 M I₂, 0.1 M guanidinium thiocyanate (GNCS), and 0.5 M N-butylbenzimidazole (NBB) in either methoxypropionitrile or acetonitrile/valeronitrile (85:15, v/v) containing either 0 or 10 vol% water.

Transport and recombination were characterized by electrochemical impedance spectroscopy (EIS). A potentiostat/frequency analyzer (PARSTAT 2273) was used for the EIS measurements. The cells were biased at open circuit under 680 nm light at different intensities.

The modulation frequencies were in the range of $0.05\text{--}10^5$ Hz, and the modulation voltage was fixed at 10 mV. Z-view 2.9c (Scribner Associates) was used to analyze the EIS spectra according to the transmission line model.³

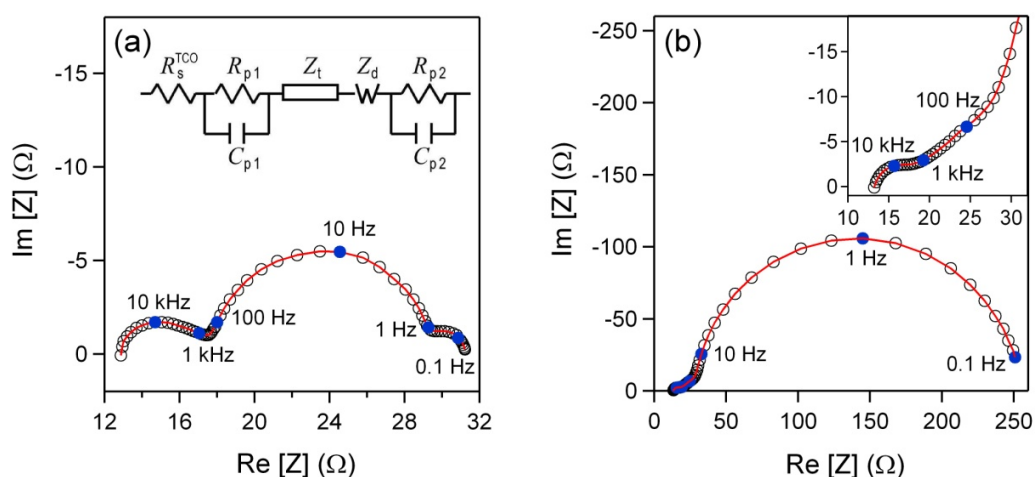


Fig. S1 (a) Nyquist plot of the impedance spectrum under 680 nm illumination measured at an open-circuit voltage (V_{oc}) of 655 mV. The inset shows the equivalent circuit model. (b) The Nyquist plot of the impedance spectrum measured at $V_{oc}=565$ mV. The inset shows the high-frequency region of the Nyquist plot.

Fig. S1 shows the typical EIS spectra under 680 nm illumination at different open-circuit voltages. In the equivalent circuit model, R_s^{TCO} is the sheet resistance of TCOs, R_{p1} and C_{p1} are the respective charge-transfer resistances and interfacial capacitance at the TCO/ TiO_2 /electrolyte interface, Z_t is the transmission line element, Z_d is the Warburg impedance associated with ion diffusion in the electrolyte, and R_{p2} and C_{p2} are the respective charge-transfer resistances and interfacial capacitance at TCO/Pt/electrolyte interface. The transmission line element Z_t contains the distributed transport resistance R_t of electrons in the TiO_2 film, the recombination resistance R_{ct} , and the chemical capacitance C_μ at the TiO_2 /electrolyte interface. Three distinct features of the impedance response can be identified in Fig. S1a: (1) a small semicircle at low frequencies (<1 Hz), which is associated with ion diffusion with a Warburg impedance Z_d ; (2) a large semicircle at intermediate frequencies (ca. 1–100 Hz), which corresponds to the charge-transfer process at the TiO_2 /electrolyte interface with a charge-transfer (recombination) resistance R_{ct} ; and

(3) the small semicircle at high frequencies (>1 kHz), which is associated with the charge-transfer processes at the counter electrode and/or the TCO/TiO₂/electrolyte interface. Fig. S1b shows the EIS response at an intermediate open-circuit voltage, from which a linear region with 45° slope (100–1000 Hz) can be identified. This feature is a characteristic for the transmission line element Z_t .³

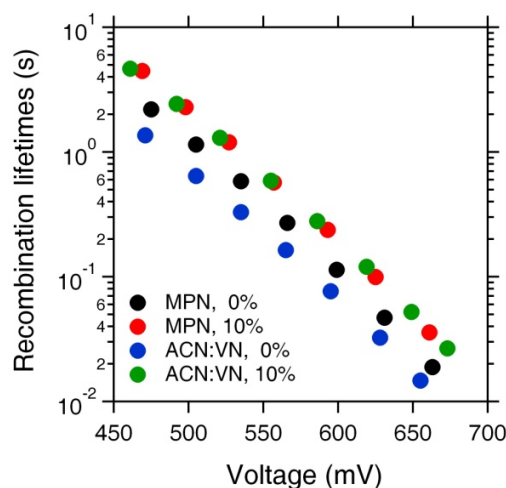


Fig. S2 Dependence of the recombination lifetime on the open-circuit voltage for DSSCs with different combinations of the solvents (MPN or ACN:VN) and water percentages (0% or 10%).

Fig. S2 shows the dependence of the recombination lifetime ($\tau_{ct} = R_{ct}C_{\mu}$) on the open-circuit voltage for DSSCs used in this study. Adding 10 vol% water to the DSSCs containing either MPN or ACN:VN leads to longer electron lifetimes relative to the cells without added water.

References

1. N. R. Neale, N. Kopidakis, J. van de Lagemaat, M. Grätzel and A. J. Frank, *J. Phys. Chem. B*, 2005, **109**, 23183-23189.
2. P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker and M. Grätzel, *J. Phys. Chem. B*, 2003, **107**, 14336-14341.
3. F. Fabregat-Santiago, G. Garcia-Belmonte, J. Bisquert, A. Zaban and P. Salvador, *J. Phys. Chem. B*, 2002, **106**, 334-339.