

Electronic Supplementary Information

Passivation of Nanocrystalline TiO₂ Junctions by Surface Adsorbed Phosphinate Amphiphiles Enhances the Photovoltaic Performance of Dye Sensitized Solar Cells

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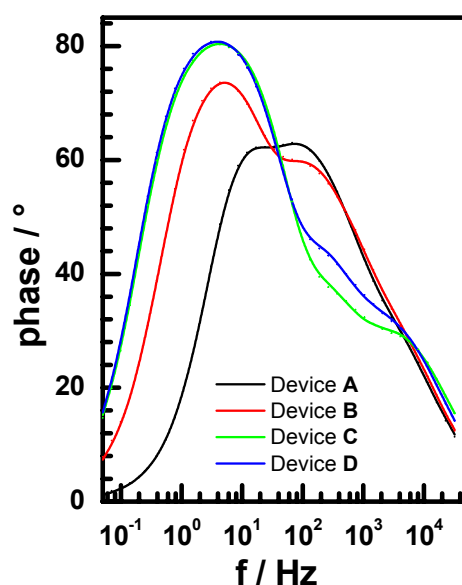


Figure S1. Impedance measurement results. Bode plot of the different devices at forward bias of -0.525 V under dark conditions: device **A**, the bare TiO₂; device **B**, the TiO₂ coated with DINHOP; device **C**, the TiO₂ sensitized with Z907Na; device **D**, the TiO₂ co-sensitized with Z907Na/DINHOP (molar ratio 1:1). The electrolyte composition is as follows: 1.0 M DMII, 0.15 M I₂, 0.5 M NBB, and 0.1 M GNCS in MPN.

Figure S1 shows the maximum phase angle having a large shift towards lower frequency for device **A** to **D**, revealing an increase in the apparent recombination lifetime (τ_n) at forward bias of -0.525 V from 38 ms (device **A**) to 254 ms (device **B**), 607 ms (device **C**), and 622 ms (device **D**).

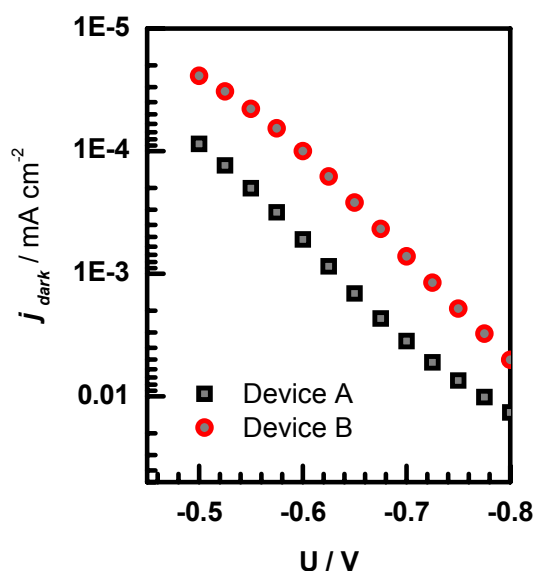


Figure S2. Dark current measurement. The dark current from impedance measurement as a function of the forward bias for different devices under dark conditions: device **A**, the bare TiO₂; device **B**, the TiO₂ coated with DINHOP. The electrolyte composition is as follows: 1.0 M DMII, 0.15 M I₂, 0.5 M NBB, and 0.1 M GNCS in MPN.

Figure S2 shows that adsorption of DINHOP (device **B**, red) at the surface of the mesoscopic titania film reduces substantially the dark current than that of the bare electrode (device **A**, black) under forward bias, increasing the electron diffusion length by a factor of two to four.

Transient Photoelectrical Measurements In the transient photovoltage decay experiment, different steady-state lights were supplied with a home-made white light-emitting diode array by tuning the driving voltage, and a red light-emitting diode array controlled with a fast solid-state switch was used to generate a perturbation pulse with a width of 50 ms. The pulsed red- and steady-state white-lights were both incident on the photoanode side of a testing cell. The pulsed red lights were carefully controlled by the driving potential of the red diode array to keep the modulated photovoltage below 10 mV. We used red light as a probe to generate a photovoltage perturbation near the V_{oc} of the cell under the white light and measured the voltage decay process thereafter. Normally, the decay follows closely a monoexponential form, thus the recombination rate constant can be extracted from the slope of the semi-logarithmic plot. Film II was used as the photoanode.

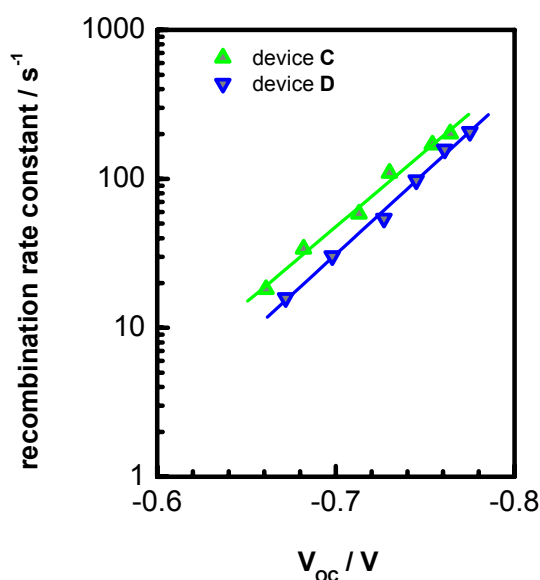


Figure S3. Transient photoelectrical measurements. Apparent Recombination rate constants of devices using Z907Na dye alone (device C) or Z907Na in conjunction with a DINHOP as coadsorbent (device D) as a function of the open circuit voltage adjusted by varying the intensity of the light bias. Double

layer films (film II) were used in the devices. The electrolyte composition is as follows: 1.0 M DMII, 0.15 M I₂, 0.1 M guanidinium thiocyanate (GSCN), and 0.5 M *N*-butylbenzimidazole in MPN.

The transient decay experiment is a useful technique to understand the surface states of sensitized mesoporous titania film and the charge recombination at the titania/electrolyte interface. Figure S3 shows that the logarithmic plot of recombination rate constant (k) versus V_{oc} for devices with and without DINHOP. A global fit to the recombination rate gives a common slope of 10.5 ± 0.4 , corresponding to ~ 92 mV/decade. [1, 2] The passivation of surface states due to DINHOP adsorption retards the electron recapture by triiodide at the TiO₂/electrolyte interface as indicated in Figure S3.

[1] Van de Lagemaat, J.; Park, N. G.; Frank, A. J. *J. Phys. Chem. B* **2000**, *104*, 2044.

[2] Zhang, Z.; Evans, N.; Zakeeruddin, S. M.; Humphry-Baker, R.; Graetzel, M. *J. Phys. Chem. C* **2007**, *111*, 398.