

## Managing wetting behavior and collection efficiency in photoelectrochemical devices based on water electrolytes; improvement in efficiency of water/iodide dye sensitised cells to 4%.

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### Supporting Information

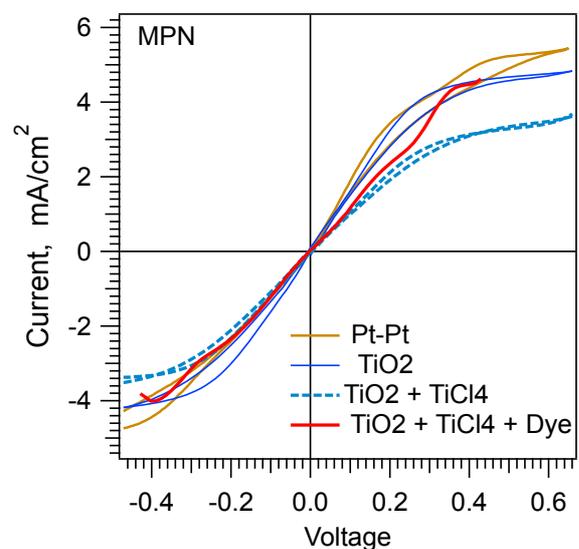
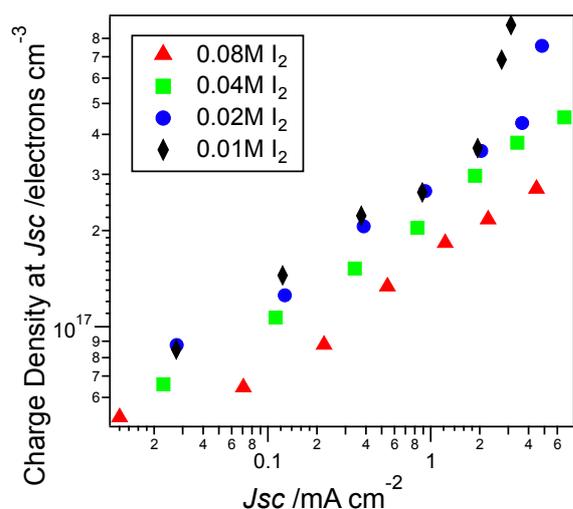


Figure S1. Current-voltage curves of different symmetrical cells with methoxypropionitrile electrolyte containing 0.1M NaI and 0.01M iodine. Label, e.g. Pt-TiO<sub>2</sub>, refers to the symmetric structure Pt-TiO<sub>2</sub>-gap-TiO<sub>2</sub>-Pt (see experimental). Total cell thickness ~75  $\mu\text{m}$  for all cells. TiO<sub>2</sub>: DyeSol 7  $\mu\text{m}$ .

We found that our standard Pt counter electrodes gave quite variable transfer resistance in the sodium iodide MPN electrolytes, although they were excellent in both PMMI/MPN, and NaI/Water electrolytes. Due to this, the data in figure S1 has been normalised along the voltage axis for better comparison of the plateau current. Despite some noise in the data, it can be seen that the addition of the Z907 to the TiO<sub>2</sub>+TiCl<sub>4</sub> film does not cause any significant decrease in the diffusion limited current.



**Figure S2.** Charge density at short circuit,  $n$  vs  $J_{sc}$  graph of Z907-based DSSCs with varying iodine concentration. ( $\text{TiO}_2$  film: G24i paste  $8.9\mu\text{m}$ ; Dye: Z907 1:100 cheno; Electrolytes: Water with 2M NaI, 0.5M GuSCN, ~saturated cheno, and iodine as noted in legend.)

Cells with lower iodine show  $\text{TiO}_2$  electron density vs  $J_{sc}$  that is deflected higher at high current levels. (See black diamonds, upper right, compared to green squares) The higher than expected charge at high light levels is a consequence of the lower diffusion limited current. When the current output of the  $\text{TiO}_2$ /dye film reaches the diffusion limited current, the tri-iodide gradient across the cell reaches its maximum. In other words the tri-iodide concentration at the platinum counter electrode reaches effectively zero. When the light level is increased above this, the excess electrons reaching the external circuit cannot escape through the platinum, so the electrons charge the platinum/electrolyte capacitance, causing a voltage drop across the platinum/electrolyte junction. This voltage drop causes the electrons to "back up" in the  $\text{TiO}_2$  film, increasing the electron density as seen in the data. The electron density in the  $\text{TiO}_2$  increases until the increased recombination rate from the film to the electrolyte, plus the current across the counter electrode, equal the injected flux. Essentially the  $\text{TiO}_2$  film is operating at some forward bias point along the  $JV$ . From the increase in charge at high light  $J_{sc}$ , we can be certain that the diffusion limited current concerns tri-iodide rather than iodide. If the limiting carrier was iodide, the concentration inside the  $\text{TiO}_2$  film would go to near zero and regeneration would decrease. The increased recombination caused by poor regeneration would decrease the charge stored in the  $\text{TiO}_2$ , rather than increasing it, as actually occurs.