# **Electronic Supplementary Information**

#### Fabrication of Stable Photovoltachromic Cell using Solvent-free Hybrid Polymer

### Electrolyte

Ming-Che Yang, Hsun-Wei Cho and Jih-Jen Wu\*

Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan

## Experimental

The patterned WO<sub>3</sub>/Pt electrodes were formed on FTO substrates using screen printing technique. Peroxopolytungstic solution was prepared by the dissolution of tungsten powders in hydrogen peroxide and deionized (DI) water. After adding acetic acid, the solution was refluxed for 12 h. White particles were obtained after the vacuum drying of the solution at  $60^{\circ}$ C.<sup>1</sup> The powders were dissolved in ethanol and then the ethyl cellulose and terpineol were added in the solution to form the WO<sub>3</sub> paste. The Pt paste was prepared by adding the chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) into the ethyl cellulose/terpineol solution. The patterned WO<sub>3</sub>/Pt film was prepared by first screen printing of WO<sub>3</sub> paste on the FTO substrate with an area of 8 mm X 8 mm and then another screen printing of Pt paste encircling the WO<sub>3</sub> region followed by respectively annealing at 100°C and 350°C for 3 h and 1 h. The thickness of WO<sub>3</sub> film is 800 nm. The TiO<sub>2</sub> NP film with a thickness of 1.5 µm was deposited on the FTO substrate by screen printing followed by calcination at 450 °C. The area of TiO<sub>2</sub> anode was 12 mm X 12 mm. The TiO<sub>2</sub> paste was prepared by the sonication of the mixture of

P25, acetylacetone, triton X-100, and DI water. Dye adsorption was conducted by immersing the TiO<sub>2</sub> NP electrode in ethanolic solution of N719 dye at 50 °C for 8 h. The photoelectrode and electrochromic electrode were sandwiched together with 60  $\mu$ m-thick hot-melt Surlyn spacers. The electrolyte was introduced between the two electrodes by capillary action. The liquid electrolyte solution (named as EL electrolyte) is composed of 0.5 M LiI and 5 mM I<sub>2</sub> in propylene carbonate. To prepare the solvent-free polymer electrolyte, 3 g of PEG (Mw=600) was first dissolved in 10 ml of 2-propanol followed by adding 0.06 ml of titanium tert-isopropoxide (TTIP). The mixture was kept stirring at 50 °C for 3h and then was left at room temperature for 24 h to complete the hydrolysis and condensation.<sup>2</sup> 0.87 mM LiI, 87  $\mu$ M I<sub>2</sub> and 1,2-dimethyl-3-propylimidazolium iodide (DMPII) with various concentrations were added into the PEG-Ti hybrid systems to form solvent-free polymer electrolyte. For simplicity, the solvent-free polymer electrolytes without DMPII as well as with 0.8, 1.6, and 3.2 mM DMPII are named as E1, E2, E3, and E4 electrolytes, respectively.

### References

- W.-T. Wu, W.-P. Liao, L.-Y. Chen, J.-S. Chen and J.-J. Wu, Phys. Chem. Chem. Phys., 2009, 11, 9751-9758.
- 2. L. Hechavarría, N. Mendoza, P. Altuzar and H. Hu, *Journal of Solid State Electrochemistry*, 2010, **14**, 323-330.

Cell	Voc	Jsc	F.F.	η	Rsh	Rs
	(V)	$(mA/cm^2)$		(%)	$(k\Omega cm^2)$	$(k\Omega cm^2)$
PVCC-E1	0.48	1.07	0.14	0.07	192	769
PVCC-E2	0.52	1.32	0.21	0.14	208	303
PVCC-E3	0.57	1.55	0.26	0.23	189	178
PVCC-E4	0.56	1.47	0.34	0.28	455	192
PVCC-E1-a <sup>§</sup>	0.45	1.30	0.17	0.10	185	555

Table S1 Photovotalic properties of PVCCs

<sup>§</sup>The concentration of LiI in the DMPII-free electrolyte of the cell is twice higher than that in E1 electrolyte.



**Fig. S1** Photovoltaic performances of PVCC-E1and PVCC-E1-a. The concentration of LiI in the DMPII-free electrolyte of PVCC-E1-a is twice higher than that in PVCC-E1.