

Effect of sensitizer adsorption temperature on the performance of dye-sensitized solar cells

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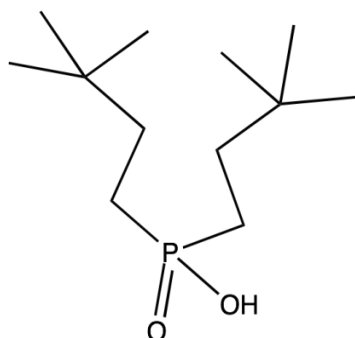
Experimental section

Materials

All solvent and reagents were of puriss grade quality and were used as received. Guanidium thiocyanate (GuNCS) was purchased from Fluka. 1,3-dimethylimidazolium iodide (DMII) was prepared accordingly to the reported procedure in ref.¹. The purity was confirmed by ¹H NMR analysis. The Dineohexyl phosphinic acid or bis-(3, 3-dimethyl-butyl)-phosphinic acid was synthesized as reported ².

Device fabrication

A screen-printed double layer film of interconnected TiO₂ particles was used as photo-anode on NSG10 TCO glass (Nippon Sheet Glass). 75 µM of dineohexyl phosphinic acid (DINHOP) was used as a co-adsorbent (structure represented below) together with 300 µM of C101 in a mixture of tert-butanol and acetonitrile solvent (1:1 by volume). The photo-anodes were sensitized for 14 hours.



After being washed by acetonitrile and dried in dry air, the sensitized electrodes were sealed using a 25 μm thick Surllyn gasket, melted by heating with the Pt-modified TEC15 TCO counter electrode. The latter was prepared by spreading out a drop of 5 mM $(\text{H}_2\text{PtCl}_6)_{\text{EtOH}}$ solution onto the counter electrode before treating it at 400°C during 15 min under air. The internal space between the two electrodes was filled with acetonitrile-based electrolyte using a vacuum back filling system. A hole, was introduced in the counter electrode by sand-blasting, and was sealed with a thin glass sheet. The electrolyte's composition was 0.6 M DMII, 50 mM LiI, 30 mM I_2 , 0.5 M *tert*-butylpyridine and 0.1 M GuNCS in a solvent mixture of 85 % acetonitrile with 15 % valeronitrile by volume.

The printed photo-anode had a square geometry of 4 x 4 mm and prior to measurements the cell was masked by a square black tape that has a 5 x 5 mm large aperture. Anti-reflecting coating on the NSG10 glass was also used to prevent reflection losses. An Al foil was taped at the back side of the counter electrode to reflect unabsorbed light back to the photo-anode. The size of the photo-anode has been determined by two means: profilometry and SEM.

Photovoltaic measurements and TiO_2 characterization

A 450 W xenon light source (Oriel, USA) was used to provide an incident irradiance of 100 mW/cm^2 at the surface of the solar cells. The spectral output of the lamp was filtered using Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) that enables passing through light from 350 to 750 nm and hence to reduce light mismatch between real solar illumination and the simulated one to less than 2%. Light intensities were regulated with wire mesh attenuators. The (*J-V*) measurements were performed using a Keithley model 2400 digital source meter (Keithley, USA) by applying independently external voltage to the cell and by measuring the photo-generated current out from the cell. Incident photon-to-current conversion measurements were realized using a 300 W xenon light source (ILC Technology, USA). A Gemini-180 double monochromator Jobin Yvon Ltd. (UK), was used to select and increment

wavelength irradiation to the cell. Impedance measurements were performed in dark at 20°C using an autolab impedance-meter. Difference in ohmic drop has been corrected before measurements. The measurements were conducted by applying a voltage superimposed by a sinusoidal perturbation of 10 mV from 100 kHz to 10 mHz.

Specific surface area was evaluated by the Brunauer, Emmett, Teller (BET) multi-point method from N₂ physisorption at 77 K using a Micromeritics ASAP 2000 apparatus. Prior to these measurements, the sample was degassed at 250 °C under vacuum during 4 hours. The films morphology and size of the photo-anode was investigated using a High Resolution Scanning Electron Microscope FEI XL-30 SFEG coupled to a TLD detector (Through the Lens Detector). The ATR-FTIR spectra for all the samples were measured using a Digilab FTS 7000 FTIR spectrometer fitted with aDTGS detector. All the data reported here were taken with the “GoldenGate” 45 diamond anvil ATR accessory. Spectra were derived from 64 scans with a resolution of 0.2 cm⁻¹. Accurate value for the position of the bands was obtained by fitting their profile with a Gaussian function suited to the spectrometer’s software and the baseline subtracted from the total spectrum.

References

- [1] K.K. Bando, Y. Mitsuzuka, M. Sugino, H. Sugihara, K. Sayama, H. Arakawa, *Chem. Lett.* **1999**,853.
- [2] M. Wang, X. Li, H. Lin, P. Pechy, S.M. Zakeeruddin, M. Grätzel, *Dalton trans.* **2009**, 45, 10015-10020.

Table S1: Reproducibility of the PV characteristics recorded on sensitized square electrodes (4 x 4 mm²) at 60°C, 20°C and 4°C.

	60°C				20°C				4°C			
	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>ff</i>	<i>PCE</i>	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>ff</i>	<i>PCE</i>	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>ff</i>	<i>PCE</i>
<i>Cell 1</i>	20.54	706.2	0.704	10.3	21.10	715.5	0.704	10.8	21.4	765.9	0.72	11.9
<i>Cell 2</i>	19.83	731.2	0.705	10.3	20.81	762.8	0.707	11.3	19.86	761.7	0.729	11.1
<i>Cell 3</i>	21.21	706.3	0.715	10.8	20.00	750.9	0.714	10.9	20.78	772.9	0.717	11.6
<i>Cell 4</i>	21.29	704.6	0.696	10.6	21.57	756.1	0.698	11.6	21.06	765.1	0.731	11.9
<i>Cell 5</i>	20.64	705.6	0.703	10.3	20.83	762.7	0.703	11.3				
<i>Cell 6</i>	21.62	736.0	0.704	11.3	20.91	754.1	0.686	11.0				
<i>Cell 7</i>					19.55	763.9	0.739	11.2				

Table S2: Average PV parameters obtained with 10 cells using sensitized spot electrodes (0.283 cm² area masked with an aperture of 0.159 cm²) at 60°C, 20°C and 4°C.

	60°C				20°C				4°C			
	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>ff</i>	<i>PCE</i>	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>ff</i>	<i>PCE</i>	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>ff</i>	<i>PCE</i>
<i>Average</i>	17.35	724.7	0.705	8.9	18.10	730.6	0.714	9.4	18.40	754.8	0.731	10.2
<i>Δx</i>	±0.10	±1.2	±0.009		±0.18	±5.0	±0.012		±0.2	±9.0	±0.009	

Table S3: ATR-FTIR absorption band position of the C101 dye anchored onto 7 μm thick mesoporous TiO_2 transparent layer at different temperatures.

	60°C	20°C	4°C
$\nu(\text{COO}^-)_{\text{sym}}$	1382.6 cm^{-1}	1381.9 cm^{-1}	1381.7 cm^{-1}
$\nu(\text{bpy ring})$	1433.8 cm^{-1}	1435.2 cm^{-1}	1433.3 cm^{-1}
	1537.3 cm^{-1}	1540.0 cm^{-1}	1536.7 cm^{-1}
$\nu(\text{bpy-COO}^-)_{\text{asym}}$	1608.6 cm^{-1}	1608.5 cm^{-1}	1608.5 cm^{-1}
$\nu(\text{C}\equiv\text{N})$	2102.0 cm^{-1}	2100.0 cm^{-1}	2100.0 cm^{-1}
$\nu(\text{C-H})_{\text{CH}_2}$	2858.7 cm^{-1}	2859.1 cm^{-1}	2857.8 cm^{-1}
	2930.0 cm^{-1}	2930.4 cm^{-1}	2928.6 cm^{-1}
$\nu(\text{C-H})_{\text{CH}_3}$	2958.6 cm^{-1}	2958.1 cm^{-1}	2958.1 cm^{-1}

Table S4: PV characteristics recorded at room temperature and low temperature (4°C) for Z907Na, N719 and N749 dyes on sensitized spot electrodes (0.283 cm² area masked with an aperture of 0.159 cm²).

	20°C				4°C			
	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>ff</i>	<i>PCE</i>	<i>J_{sc}</i>	<i>V_{oc}</i>	<i>ff</i>	<i>PCE</i>
Z907Na	15.1	734.9	0.707	7.9	15.6	746.3	0.712	8.3
N719	17.3	740.2	0.677	8.8	16.7	718.9	0.732	8.9
N749	16.0	706.4	0.699	8.0	14.9	663.0	0.675	6.8

Fig. S1: Evolution of cell capacitance as a function of photo-voltage for films sensitized with C101 at 60°C (red curve), 20°C (green curve) and 4°C (blue curve).

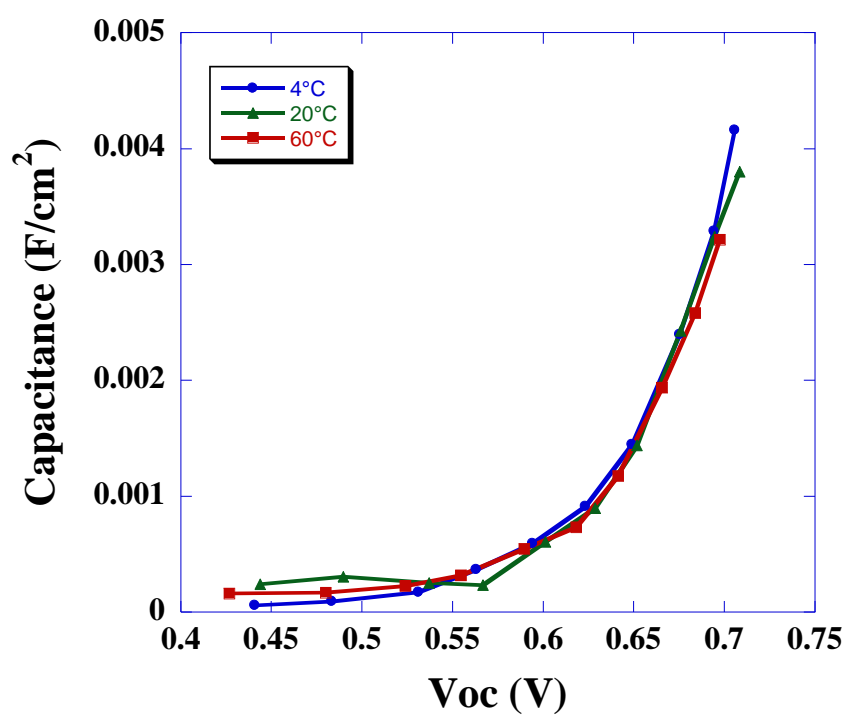


Fig. S2: ATR-FTIR spectra comparison of TiO₂ nanocrystalline film sensitized in a solution of 4:1 ratio of C101/DINHOP (red curve) and C101 alone (blue curve).

