SUPPLEMENTAL INFORMATION

Self-Powered Ion Detectors Based on Dye-Sensitized Photovoltaics

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Methods

Device Fabrication: 8 - 9 µM thick transparent TiO₂ films were prepared by doctor blading commercially available Ti-Nanoxide T/SP paste (Solaronix Inc.) on 2.2 mm thick fluorine doped tin oxide with a sheet resistance of 7 ohm/square. The substrates were cleaned using organic solvents and pre-treated in 40 mM aqueous TiCl₄ solution at 70 °C for 30 minutes prior to film deposition. After coating with TiO₂ paste, the substrates were fired for 30 minutes at 450 °C to allow a porous nanocrystalline film to form. (see Supplementary Fig. 6) This step was followed up with a TiCl₄ post-treatment and additional sintering at 450 °C for 15 minutes. The prepared films were allowed to cool down to approximately 50 °C and immersed in a 0.5 mM solution of commercial N3 dye (Sigma Aldrich). The dye solution was prepared by dissolving N3 in an 8/2 (v/v) mixture of tetrahydrofuran and t-butanol. The films were soaked in dye solution for 24 hours after which they were removed from solution, rinsed with isopropanol and dried under a stream of compressed N₂. For device assembly, a 25 µM Surlyn gasket (Solaronix, Inc.) was placed between the working electrode and the counter electrode following which, the device was placed on a hotplate at 100 °C and pressed down on for ~ 30 seconds to ensure a good seal is obtained. The counter electrode was prepared by sputtering 50 nm Pt on FTO. Additionally, screen printed TiO₂ films consisting of a 10 µM transparent film of 15 - 20 nm diameter particles followed by a 3 - 4 µM scattering layer of 400 nm diameter particles obtained from Solaronix Inc. were also tested. (see Supplementary Fig. 7)

Electrolyte & Analyte Preparation: Electrolyte solutions were introduced into the device through a 0.5 mm diameter drilled hole in the counter electrode using a Vac’n’Fill syringe (Solaronix, Inc.). The ideal electrolyte solution contained 0.6 M 1,2-dimethyl-3-propyl-
imidazolium iodide (DMPII), 0.1 M Lithium Iodide (LiI), 0.05 M Iodine (I$_2$) and 0.5 M 4-tert-
butylpyridine (tBP) in acetonitrile. Analyte solutions were prepared by dissolving AgNO$_3$
concentrations ranging from 1 nM to 1 mM in acetonitrile.

**Solar Cell Characterization:** Current-Voltage (JV) characteristics were recorded using a
Solartron Analytical Modulab MTS Materials Test System. The cells were illuminated with a
Newport solar simulator (model# 91191-1000) calibrated to AM1.5 (100 mW/cm$^2$) using an
NREL Si reference cell (Model PVM233 KG5).

**Electrochemical Impedance Spectroscopy:** EIS measurements were recorded using the
Solartron Analytical Modulab MTS Materials Test System. The cells were scanned over a
frequency range of 100 kHz to 0.1 Hz with 10 mV amplitude, at open-circuit conditions, under 1
sun illumination. The obtained Nyquist plots were fit using an equivalent circuit model to extract
relevant parameters.

**Energy Dispersive X-ray Spectroscopy:** SEM and EDS measurements were made using a
Hitachi SU8000 scanning electron microscope. The spectra and images shown in Figure 5 were
obtained by applying an acceleration voltage of 10 kV and a working distance of 15.3 mm.
Fitting electrochemical impedance spectroscopy (EIS) data:

A sample of the data obtained from EIS measurements is shown below along with the definition of each internal resistance identified. Since our data does not show a distinct semi-circle corresponding to the low-frequency resistance $R_D$, typically arising from electrolyte diffusion, we do not include this parameter in our model. The fits were performed using ZView software (Solartron Analytical). Here, $R_{FTO}$ corresponds to the sheet resistance of the fluorine doped tin oxide (FTO) substrate, $R_R$ is the resistance corresponding to recombination at the TiO$_2$/dye/electrolyte interface, $R_{CT}$ is the resistance to charge transfer at the counter electrode and CPE1 and 2 are constant phase elements.

**Fig. 1.** EIS data of a typical device under AM 1.5 (100 mW/cm$^2$) simulated sunlight at open-circuit conditions. Shown here are the resistances corresponding to the high, mid and low-frequency regions on the Nyquist plot. Inset: Equivalent circuit model used to fit the data.
Modeling device current density-voltage (JV) characteristics:

To model the JV characteristics of the system, we consider a modified equivalent circuit model as described by Han et al. [1]

![Diagram of equivalent circuit model](image)

**Fig. 2.** Here, \( J_{ph} \) is the photocurrent, \( R_S \) is the series resistance, \( R_{SH} \) is the shunt resistance, and \( V \) is the bias voltage, while \( R_{FTO} \) corresponds to the sheet resistance of the FTO, \( R_R \) is the resistance corresponding to recombination at the TiO\(_2\)/dye/electrolyte interface, \( R_{CT} \) is the resistance to charge transfer at the counter electrode, \( R_D \) (Warburg element) corresponds to the electrolyte diffusion resistance and CPE1 and 2 are constant phase elements.

For JV modeling, the capacitances associated with \( R_R \) and \( R_{CT} \) may be ignored since these measurements are performed under DC conditions, while \( R_R \) may be treated as a diode. We lump the other three internal resistances into one fitting parameter \( 'R_s' \). The JV curve can now be modeled as per the generalized Shockley equation. [2].
\[ J = \frac{R_{SH}}{R_s + R_{SH}} \left\{ J_s \left[ \exp \left( \frac{q(V - J_s R_s)}{n k T} \right) - 1 \right] + \frac{V}{R_{SH}} \right\} - J_{ph}(V) \]

where \( J_s \) is the reverse dark saturation current and \( n \) is the ideality factor. To obtain the trends seen in Fig. 4, we set \( J_{ph} = J_{SC} \) and \( R_{SH} = 0.1 \text{ M}\Omega \cdot \text{cm}^2 \) (estimated from dark current data) with \( R_s, J_s, \) and \( n \) as fitting parameters.

**Fig. 3.** (a) Changes in fill factor as a function of \([\text{Ag}^+]\). No noticeable trend is seen here (b) The ideality factor \((n)\) obtained from fitting our data to a Shockley model as a function of \([\text{Ag}^+]\). (c) Changes in the saturation current in the dark plotted as a function of \([\text{Ag}^+]\). (d) Changes in series resistance plotted as a function of \([\text{Ag}^+]\).
**Fig. 4.** An image showing silver clusters formed on the TiO$_2$ film after sensor tests were performed, directly underneath the filling hole.
Fig. 5. The left hand side y-axis shows the normalized values of $R_s$ that are obtained from fitting the JV data to a Shockley model as seen in Fig. 4(d). The right-hand side y-axis shows the normalized values of $R_s$ that are obtained by plugging in the resistance values obtained from EIS measurements into the following equation: $R_s = R_{FTO} + R_{CT}$. It must be noted that $R_D$ was not taken into account, since we could not fit this resistance, as previously mentioned. The discrepancy between the two sets of $R_s$ values, especially at higher concentrations of Ag$^{+}$ most likely arises from this omission. Consequently, it appears that $R_D$ becomes larger at higher concentrations of Ag$^{+}$, which is consistent with the hypothesis that the mobility of triiodide ions is reduced as the Ag$^{+}$ content in the electrolyte becomes larger.
Fig. 6. (a) An SEM image of a TiO₂ electrode prepared by doctor blading 9 µM thick film of T/SP paste. (b) SEM image of a screen printed TiO₂ electrode consisting a 10 µM transparent film of 15 - 20 nm diameter particles followed by a 3 - 4 µM scattering layer of 400 nm diameter particles obtained from Solaronix Inc.
Fig. 7. J-V characteristics of a device with a screen-printed TiO$_2$ electrode (transparent + scattering films) under AM 1.5 (100 mW/cm$^2$) simulated sunlight. The area of the dye coated TiO$_2$ region was 0.36 cm$^2$. Inset: Obtained performance parameters for one such device. Based on literature, the scattering layer should facilitate a current enhancement by increasing light absorption within the device. However, we did not find such an improvement to occur perhaps because the screen-printed films were not freshly prepared.
Notes and references
