Supplemental Information

A tandem dye sensitized photoelectrochemical system for light driven hydrogen production

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Experimental Details

All materials used in this study were used as received unless otherwise stated and purchased from either Sigma Aldrich or Alpha Aesar. Fluorine doped tin oxide (FTO) was purchased from Hartford Glass.

Photoelectrode preparation

Colloidal TiO$_2$ (Kang et al. Sol. Energ. Mat. Sol. C. 2003, 75: 475) and SnO$_2$ (Chappel and Zaban Sol. Energ. Mat. Sol. C. 2002, 71: 141) sol-gel pastes were prepared using literature protocols. For the FTO-TiO$_2$ electrodes, a compact TiO$_2$ blocking layer was first prepared. The blocking layer was formed via spray pyrolysis of 0.2 M titanium disopropoxide bis(acetylacetonate) in ethanol onto the conductive face of the FTO electrodes that were heated to and maintained at 400 °C during the deposition. The FTO was then heated at 450 °C for 30 min after deposition of the blocking layer, and prior to the application of the sol-gel paste. The colloidal paste was applied to the FTO electrodes using a doctor-blade method with tape spacers used to set the thickness of the sol-gel layer. Once spread, the films were allowed to dry in air and then annealed at 450 °C for 45 min. After annealing, the electrodes underwent an overnight soak in a 40 mM solution of TiCl$_4$ in water. Finally, they were dried and cured for an addition 30 min at 450 °C. For the FTO-SnO$_2$ electrodes, a compact SnO$_2$ blocking layer was first established by spin coating (2000 rpm, 1 min) a solution of 15 wt% SnO$_2$ in water on the FTO face, followed by heat treatment at 450 °C in air for 45 min. The SnO$_2$ sol-gel paste was then applied, again using the doctor blade method. After drying the films were annealed at 450 °C for 45 min. Finally, the FTO-SnO$_2$ were soaked in a 40 mM solution of TiCl$_4$ in water overnight to introduce a TiO$_2$ surface coating which has been shown to improve device performance (Snaith Nano Lett. 2010, 10: 1259). The films were annealed at 450 °C after the TiCl$_4$ treatment for 30 min. The FTO-TiO$_2$ electrode were soaked in a 400 μM solution of 2 or 3 in ethanol and the FTO-SnO$_2$ electrodes in a 400 μM solution of 1 in ethyl acetate overnight, and rinsed with ethanol for the former or ethyl acetate for the latter to form the fully prepared photoelectrodes used in this study.

Photochemical experiments

A custom made photoelectrochemical cell was used to prepare the dye sensitized photoelectrochemical cell (DSPEC) with a nafion membrane separating the anodic and cathodic sides of the cell. Each side of the cell consisted of a threaded glass opening (ace-thread #15, Ace Glass) with custom machined Delrin bushing. Each bushing contained
three drilled and taped ports allowing introduction of electrode leads or gas lines which could be secured using threaded nuts (IDEX Health and Science) allowing for a complete gas-tight seal on either side of the cell. Unless otherwise noted, the electrolyte for the DSPEC consisted of 0.1 mM Na$_2$SO$_4$ and 25 mM SiF$_6$ buffer with the pH adjusted to 5.8 using a concentrated solution of NaHCO$_3$. Additionally the anodic solution of the DSPEC contained 20 mM hydroquinone. To form the dye sensitized solar cells (DSSCs) used here, the FTO-TiO$_2$ photoanode described above was attached to a FTO-Pt cathode using a heat shrink gasket (Solaronix). The Pt coating was applied to the FTO by applying a solution of chloroplatinic acid in ethanol and heating to 450 °C for 30 min. The electrolyte used for the DSSC consisted of 1:1 acetonitrile:valeronitrile with 0.2 M lithium iodide, 0.05 M iodine, 0.2 M tetrabutylammonium iodide, and 0.5 M 4-tertbutylpyridine. The electrolyte was introduced inside the DSSC via ports drilled through the FTO-Pt cathode after assembling the cell.

For the light driven experiments, a 350 W Xe light source (Osram) was used with a 400 nm long pass filter (Thor Labs) as well as an AM 1.5 filter (Oriel) with the DSPEC photoanode placed to receive 100 mW cm$^{-2}$ light intensity. For the tandem cell photocurrent measurements, a Keithley 2400 source meter was connected between the photoanode of the DSPEC and the FTO-Pt cathode of the DSSC to monitor the current flow in the cell. A separate wire connected the DSSC photoanode to the Pt cathode of the DSSC to complete the series connection. The DSSC was placed directly behind the DSPEC photoanode for the tandem configuration to receive light that had passed through the DSPEC photoanode. For the voltage vs. time traces, a fresh prepared silver/silver chloride reference (in saturated KCl) was prepared and placed in the cathodic chamber of the DSPEC. A CH Instruments 650C potentiostat was used to monitor the open circuit voltage between the Pt counter and the Ag/AgCl reference during the course of the experiment. The incident photon to current efficiency (IPCE) measurement used a Jobin-Yvon monochromator and a Keithely 2400 source meter and custom written software (LabVIEW). The light intensity at each wavelength was calibrated using a photodiode (Newport).

**Hydrogen measurements**

An SRI Instruments 310C gas chromatograph was used for detection of photogenerated hydrogen. In order to measure the evolved hydrogen gas, a Pt cathode assembly was constructed in order to both minimize the headspace volume above the cathode (1.2 mL) and seal off the headspace from the atmosphere with a septa port for extracting samples for GC analysis. The assembly consisted of an insulated wire lead placed inside a 1/8” Teflon tube with a Pt wire soldered to the end of the lead, extruding from the end of the tube. The Pt wire end was then place inside a piece of glass cylinder (internal diameter 3.5 mm) with an epoxy seal applied between the tube and the top of the glass cylinder. A second piece of glass cylinder was epoxied to the top of the Teflon tube with the wire and a second piece of tubing extending out the top through an epoxy seal. Completing the assembly, the end of the second tube was connected to one side of a ¼”-28 threaded union (IDEX Health and Science) with a ferrule and nut with the opposite side of the union containing a ¼”-28 threaded to female Luer fitting. A Luer cap with a drilled hole
through the top and a septa placed inside the cap was fastened over the female Luer fitting. To measure a gas sample, a 100 µL syringe was filled with Ar, inserted through the septa, mixed with the head space gas by plunging (causing noise in the current trace of the measurement due to electrolyte flow across the Pt counter as the syringe was moved back and forth), extracted from the septa, and injected into the GC.

**Synthesis**

![Diagram of a molecule](image)

5-(4-Carboxyphenyl)10,15,20-tri(4-methylphenyl)porphyrin (1). Porphyrin 1 was prepared by the Adler-Longo porphyrin condensation method (Adler, A.D., et al. *J. Am. Chem. Soc.* 1964, 86, 3145). By adjusting the stoichiometry of the two aldehydes one can change the ratio of different substituted porphyrins formed from the condensation. Using a stoichiometry of 1, 5, and 6 of methyl 4-formylbenzoate, 4-methylbenzaldehyde and pyrrole, respectively, compound 1 is preferentially formed. After treatment with potassium hydroxide, followed by washing with water the target mono-carboxyphenyl porphyrin is obtained. Characterization of compound 1 was achieved by ¹H NMR and MALDI-TOF-MS. All values were consistent with literary values.

4-(Oxybenzoic acid)hydroxy-1,4,8,11,15,18,22,25-octabutoxyphthalocyaninatosilicon(IV) (2): Into a dry 10 ml round bottom flask was placed SiPc(OH)₂ (20 mg, 0.017 mmol), 4-hydroxybenzoic acid (12 mg, 0.087 mmol), dry dichloromethane (4 ml), and pyridine (4 drops). This solution was allowed to stir at room temperature for 4 days. The solution was evaporated under reduced pressure and the crude solid was taken up in dichloromethane and washed with deionized water, dried with sodium sulfate and
concentrated. The crude product was purified via silica gel column chromatography using toluene/ethyl acetate (65:35) as eluent to afford a green solid. Yield 5.3 mg (24%). $^1$H-NMR (400 MHz; CDCl$_3$; 0.03% Me$_4$Si): $\delta$H, ppm 7.63 (s, 8H), ppm 6.40 (d, 2H, J=8.8Hz) ppm 4.78 (m, 16H), ppm 2.86 (d, 2H, J=8.8Hz), ppm 2.14 (p, 16H), ppm 1.63 (sex, 16H), ppm 1.04 (t, 24H, J=7.4Hz). MS (MALDI-TOF): $m/z$ calcd. for C$_{71}$H$_{86}$N$_8$O$_{12}$Si 1271.57, obsd. 1272.43 (M+H), 1149.58 (M-benzoic acid).

2-(Oxyacetic acid)hydroxy-1,4,8,11,15,18,22,25-octabutoxyphthalocyaninato-silicon(IV) (3). A portion of SiPc(OH)$_2$ (30 mg, 0.026 mmol) was dissolved in dry pyridine and the solution was degassed for 5 min with argon. Glycolic acid (9.8 mg, 0.13 mmol) was added and the resulting solution was stirred at 55 $^\circ$C, under argon for 3 days. The pyridine was evaporated under reduced pressure and the resulting residue was taken up in dichloromethane and washed with deionized water (20 mL). The organic phase was dried over sodium sulfate and evaporated under reduced pressure. Column chromatography was done using silica gel in two purification steps; first, toluene/ethyl acetate/methanol (60:38:2) was used as eluent followed by a second column using chloroform/ethyl acetate/methanol (78:20:2) as eluent, which afforded a green solid. Yield 7 mg (22%), $^1$H-NMR (400 MHz; CDCl$_3$; 0.03% Me$_4$Si): $\delta$H, ppm 7.63 (s, 8H, Pc-H) ppm 4.86 (t, 16H, -CH$_2$-CH$_2$-CH$_2$-CH$_3$, J=7.4Hz), ppm 2.20 (p, 16H, -CH$_2$-CH$_2$-CH$_2$-CH$_3$), ppm 1.66 (sex, 16H, -CH$_2$-CH$_2$-CH$_2$-CH$_3$), ppm 1.08 (t, 24H, -CH$_2$-CH$_2$-CH$_2$-CH$_3$), ppm -1.40 (s, 2H, CH$_2$-Glycolic acid). MS (MALDI-TOF): $m/z$ calcd. for C$_{66}$H$_{84}$N$_8$O$_{12}$Si 1209.50, obsd. 1209.49, 1149.58 (M-glycolic acid).

**Supplemental Figures**
Figure S1. GC traces used for determination of the amount of light generated H$_2$ as shown in Figure 4 of the paper. The peaks starting at 0.4 min and centered at 0.55 min of the trace were assigned to H$_2$ and verified using a hydrogen standard.

Figure S2. Photocurrent (upper) and voltage vs. time (lower) as measured at the platinum cathode for a tandem cell (solid trace, same as Figure 3 of the paper) consisting of (electrode 1) SnO$_2$-1, (electrode 2) Pt, (electrode 3) TiO$_2$-2, and (electrode 4) Pt and DSPEC cell (dashed trace) without the DSSC wired in series (electrode 1 directly connected to electrode 4). No H$_2$ is observed in the case of the DSPEC without the DSSC connected in series by GC, consistent with the lack of photocurrent and insufficiently negative potential observed at the Pt cathode (dashed traces). The spikes in the photocurrent correspond with the sampling of the headspace for analysis by GC (data shown in Figure 4).
**Figure S3.** Photocurrent vs. applied bias for the tandem cell (black trace) and DSPEC without the DSSC connected in series (grey trace).

**Figure S4.** Potential diagram for the tandem DSPEC–DSSC system (A) and for the DSSC alone (B). The photochemical and electrochemical events occurring in the tandem cell consist of (1) excitation of the porphyrin dye at the DSPEC photanode; (2) sensitization of SnO$_2$ by the excited state porphyrin; (3) regeneration of the ground state porphyrin by oxidation of the sacrificial donor, hydroquinone; (4) the photovoltage produced by the DSSC increases the potential of electrons supplied to the cathode of the DSPEC; and (5) with the additional potential from the series connected DSSC, the production of H$_2$ occurs at the Pt cathode of the DSPEC. The excitation and electron transfer steps comprising step 4 of (A) are shown in (B) and consist of (4a) excitation of the phthalocyanine dye, (4b) sensitization of TiO$_2$, and (4c) regeneration of the ground state phthalocyanine by oxidation of I$^-$. The voltage generated by the DSSC ($\Delta V_{\text{DSSC}}$) is dependent on the difference between the TiO$_2$ conduction band and potential of the I$_3^-$/I$^-$. 
mediator. It is the magnitude of the voltage, and not the relative energy levels of the semiconductor conduction band or mediator species, that promotes current flow in the tandem cell. The upward arrows indicating energy increase by light absorption in the DSSC are of different lengths in (A) and (B) to reflect that a portion of the absorbed energy is lost in driving the internal reactions of the DSSC. The potential for the water oxidation half reaction is indicated in part (A) for reference.

**Figure S5.** Photograph of the tandem cell experimental setup. The electrode numbers correlate with those in Fig. 1. The arrow indicates the direction of illumination (photo taken from behind-right of the setup, cardboard shutters are blocking the Xe lamp). The DSSC is placed immediately behind the DSPEC photoanode. The Pt-wire assembly used for the H\textsubscript{2} measurements (described above) is not shown in the photo, and a wire-mesh Pt cathode is shown instead.