Supporting Information

Photosystem I-Polyaniline/TiO₂ Solid-State Solar Cells: Simple Devices for Biohybrid Solar Energy Conversion

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Materials

All materials were used as received without further purification. Aniline (99.9%, Certified ACS grade), sodium phosphate monobasic monohydrate (99.6%, Certified ACS grade), sodium phosphate dibasic anhydrous (laboratory grade), ferricyanide (99.8%, Certified ACS grade), dithiothreitol (99%, BioReagents grade) were purchased from Fisher Scientific. Hydrochloric acid (37%, ACS Grade), acetone, isopropyl alcohol, ethanol, and titanium (IV) chloride (99.9%, ReagentPlus®) were purchased from Sigma Aldrich and Triton X-100 (98%) was purchased from Acros Organics. Regenerated cellulose dialysis tubing (10 kDa molecular weight cut off) was purchased from Spectrum Labs.

FTO coated glass substrates (TEC 7, 1"x1" 6-8 Ω /sq) were purchased from MTI Corp. Commercial TiO₂ paste (Dyesol 90-T) was purchased from Dyesol Inc. Gold, silver, and aluminum evaporation sources (\geq 99.99%, pellets) were purchased from Ted Pella.

PSI Extraction

PSI was extracted and purified from commercially available spinach leaves (*Spinacia oleracea*) as previously described elsewhere.¹ In short, baby spinach leaves were homogenized, crudely filtered, and centrifuged at 8000 RCF for 1 min to isolate intact thylakoid membranes. The purified thylakoids were then lyzed in buffer containing 1% (w/v) Triton X-100. Following lysis, components were separated via centrifugation at 20,000 RCF for 15 min. The resulting supernatant was then loaded on a chilled hydroxylapitite column in a dark room. The column was washed with copious volumes of 20 mM phosphate buffer (PBS) (pH = 7.00) to remove loose chlorophylls and other non-protein components. Purified PSI was eluted in 200 mM PBS (pH = 7.00) with 0.05% (w/v) Triton X-100. Prior to use, 5 mL PSI samples were dialyzed (10 kDa cutoff tubing) for 12 hours against 4000 mL of 20 mM PBS to reduce buffer salt concentration and remove excess surfactant. PSI was characterized by the Baba assay using ferricyanide and dithiothreitol as the oxidizing agent and reducing agent, respectively, to determine the active P700 concentration of each sample.²

Device Fabrication

*TiO*₂ *Electrode Preparation*³:

FTO coated glass substrates were cleaned with three 20-minute sonication cycles in 3% Triton X-100 in DI-water, acetone, and isopropanol, respectively. Cleaned FTO substrates were placed in a 50 mM TiCl₄ bath at 70 °C for 30 min. Following the bath, substrates were annealed in a tube furnace at 500 °C for 60 min. 0.155 g commercial TiO₂ paste (Dyesol 90-T) was diluted with 0.47 g ethanol and vortexed until fully dissolved. A spin coating procedure was then utilized in which 10 drops of the diluted paste were applied to the TiCl₄-treated FTO electrodes, while stationary, and allowed to spread. The electrode was then spun at 300 RPM for 5 seconds, followed by 1500 RPM for 45 seconds. After removing from the spin coater, an ethanol-soaked cotton swap was used to clear a corner of TiO₂ coating for an eventual contact to the underlying FTO. These electrodes were then placed on the center of a hotplate, set to 390 °C, for 30 min. A final TiCl₄ bath, identical to one previously mentioned, was used to treat the electrodes for 30 min at 70 °C. The electrodes were then washed thoroughly with DI water and dried under stream of nitrogen. The samples were once again annealed with the same 500 °C tube furnace and stored for later use: up to 1 week outside of the glovebox, or indefinitely inside of the glovebox

PAni-PSI Deposition:

PAni-PSI films were prepared electrochemically from a single aqueous solution of 1 M aniline, 0.94 M HCl, 4 mM sodium phosphate, and 1.3 μ M PSI. The stock polymerization solution was prepared immediately before use. Using a CH Instruments 660A potentiostat, potentiostatic polymerization was carried out at +6.5 V for 120 seconds. In the three-electrode setup, the TiO₂ substrate was set as the working electrode (area = 1.54 cm²) with a Pt mesh counter electrode and Ag/AgCl (3 M KCl) reference electrode. Following electrochemical film formation, the modified TiO₂ substrates were rinsed with copious amounts of water and dried under a stream of nitrogen.

Cathode Evaporation:

The PAni-PSI modified devices were then placed face down in a custom mask for cathode evaporation that yields 0.071 cm2 contact areas. The devices were loaded into an evaporator chamber of an Åmod deposition system (Ångstrom Engineering). Ag and Au deposition was achieved in a resistive evaporator chamber, while the Al deposition was performed with electronbeam ablation. For the Ag-only contacts, a 20 nm layer of Ag deposited at 0.2 Å/s was formed first, followed by a 280 nm Ag layer at 2.0 Å/s. For the Au contacts, a 20 nm layer of Au deposited at 0.2 Å/s was formed first, followed by a 280 nm Ag layer at 2.0 Å/s. For the Au contacts, a 20 nm layer of Al deposited at 0.2 Å/s, followed by a 280 nm Al layer at 2.0 Å/s.

Device Testing

I-V data was measured in ambient air with a custom LabView program run through a Keithley 2400 source-meter. The solar spectrum at AM1.5 was provided by a SolarTech xenon solar simulator to within class A spectral matching (less than 25% spectral mismatch). The lamp was calibrated to 1-sun with an NREL certified photovoltaic standard. An aperture was used to

ensure illumination of only the contact being measured, while a multiplexer filtered all cathodic leads but that of the illuminated contact.

Film Thickness Optimization

In order to enhance the photocurrent output of the solid-state device the active layer thickness was increased by extending the polymerization time of the PAni-PSI film. With the increased polymerization time, films with higher optical density are observed, as depicted in Fig. S1.



Fig. S1 Left) Images of PAni-PSI films deposited on TiO2/FTO/glass substrates. Samples were prepared from potentiostatic polymerization at +6.5 V, for A) 90 s, B) 120 s, and C) 240 s. Right) Photovoltaic efficiency of Ag/PAni-PSI/TiO2 devices prepared with active layer thicknesses polymerized for 90, 120, or 240 s.

As observed in Fig. S1, the increasing film thickness that results from the increasing polymerization time, increases the device external quantum efficiency as a thicker light absorbing active layer (with more PSI) is produced. However, as the film thickness increases beyond that of 120 s, a diminishing efficiency is observed. Thus 120 s was used as the ideal polymerization time in this work.

Scanning Electron Microscopy

Device cross-sections were prepared by mechanically breaking a completed device. A suitable piece was positioned vertically on the SEM sample holder with copper tape. Imaging was performed on a Hitachi S4200 SEM at 5 keV accelerating voltage.



Fig. S2 Scanning electron microscope image of a typical Ag/PAni-PSI/TiO₂ device cross-section. Glass, FTO, TiO₂, PAni-PSI, and silver layers are labeled. Scale bar represents 1 μ m.

From the Fig. S2, the PAni-PSI layer was approximated to be 350 nm. The TiO₂ layer and FTO layer were determined to be 450 and 400 nm, respectively, which are consistent with the substrate preparation methods used in this study and elsewhere.

Additionally, elemental mapping was performed using energy-dispersive X-ray spectroscopy with a Zeiss Merlin scanning electron microscope. Shown in Fig. S3 are the SEM-EDS maps for the composite device cross-section, and for elements indicative of each device layer.



Fig. S3 SEM-EDS maps of a typical Ag/PAni-PSI/TiO₂ device: A) Composite image of device, and elemental maps for B) silver, C) nitrogen, D) titanium, E) tin, and F) silicon. All scale bars represent 10 μ m.

The device architecture was confirmed through the use of SEM-EDS mapping. Fig. S3B clearly presents silver, which comprises the silver cathode of this solid-state device. Also shown Fig. S3C is the presence of a strong nitrogen-rich layer, corresponding to the presence of the nitrogen-containing polymer and the PSI protein. Below the PAni-PSI layer is the TiO₂ layer

and FTO layer shown in Fig. S3D and S3E, respectively. Finally, Fig. S3F presents a silicon-rich sample indicative of the thick borosilicate glass layer of the device.

Internal Quantum Efficiency Action Spectrum:

In order to validate the role of PSI in the solid-state devices, action spectra were prepared by plotting the relationship between internal quantum efficiency (IQE%) and excitation wavelength. Using a Fianium SupercontinumTM laser source, a Ag/PAni-PSI/TiO₂ device was illuminated using monochromatic wavelengths raging from 383.5 - 740 nm, while i-V curves were collected at each wavelength selection. IQE% was calculated using Equation S1 according to Ref. 4:

$$IQE\% = \frac{Current (A) \left(\frac{6.022 \times 10^{23} e^{-}}{mol}\right) \left(\frac{1 \ mol}{96,485 \ C}\right)}{\Theta_{\lambda} \cdot P (W) \cdot \frac{1}{E_{\lambda}} \left(\frac{photons}{J}\right)} x \ 100$$
(S1)

Where θ_{λ} is the ratio of photons absorbed by the PAni-PSI film at the wavelength, λ , determined by the absorbance (A_{λ}) using the relationship, $\theta_{\lambda} = 1 - 10^{-A}$. P is the power of the laser in Watts at that specific wavelength, and E_{λ} is the energy of each photon at the same wavelength.



Fig. S4 Solid-state device action spectra relating the IQE% to incident wavelength.

As observed in the action spectrum, a localized quantum efficiency minimum is found at between 550-625 nm, as is intrinsic of the poor absorption coefficient of PSI's antenna chlorophyll network in that range. Local IQE maxima are observed near the 680 and 430 nm excitation wavelengths corresponding to the Q_y transition and Soret band of Chlorophyll a/b. Thus indicating both the presence of PSI in the PAni-PSI solid-state films, and its active role in the sensitization and generation of charge separation in the device. A representative absorption spectrum for spinach PSI is presented in Figure S4 (shown in green). For clarity, the spectrum was normalized to the IQE% curve near 430 nm.

Storage Stability Testing:

As an additional method to evaluate the performance stability of Ag/PAni-PSI/TiO2 devices, the photocurrent output of a device was recorded once daily and stored under ambient conditions of open atmosphere at room temperature for 20 days.



Fig. S5 Long term storage stability of Ag/PAni-PSI/TiO₂ device. Data points represent the average and standard deviation of four independent devices tested daily under 1-sun illumination.

After 20 days, 85% of the photocurrent is retained, indicating long-term stability of PSIbased devices, under ambient storage conditions.

References:

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