

A molecular tandem cell for efficient solar water splitting

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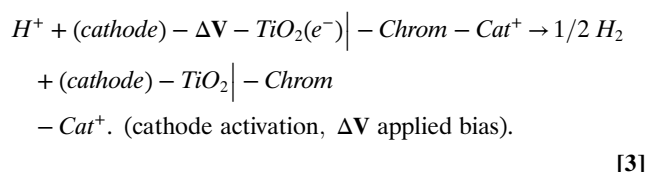
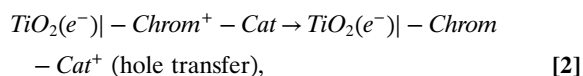
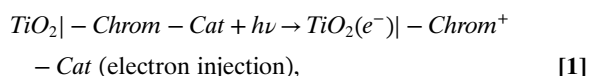
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Artificial photosynthesis provides a way to store solar energy in chemical bonds. Achieving water splitting without an applied external potential bias provides the key to artificial photosynthetic devices. We describe here a tandem photoelectrochemical cell design that combines a dye-sensitized photoelectrosynthesis cell (DSPEC) and an organic solar cell (OSC) in a photoanode for water oxidation. When combined with a Pt electrode for H₂ evolution, the electrode becomes part of a combined electrochemical cell for water splitting, 2H₂O → O₂ + 2H₂, by increasing the voltage of the photoanode sufficiently to drive bias-free reduction of H⁺ to H₂. The combined electrode gave a 1.5% solar conversion efficiency for water splitting with no external applied bias, providing a mimic for the tandem cell configuration of PSII in natural photosynthesis. The electrode provided sustained water splitting in the molecular photoelectrode with sustained photocurrent densities of 1.24 mA/cm² for 1 h under 1-sun illumination with no applied bias.

water splitting | molecular tandem cell | solar fuels | bias-free | organic cell

Artificial photosynthesis, inspired by oxygenic photosynthesis in nature, uses sunlight to perform water oxidation by transferring oxidative and reductive equivalents to reduce CO₂ to carbon-based compounds with glucose as a final product (1–4). Meeting the demands imposed by artificial photosynthesis, with solar water splitting or CO₂ reduction, presents a series of challenges. Water oxidation, with the sequential loss of four electrons and four protons, is especially demanding (5, 6). On an electrode surface, the initiating photon absorption/electron transfer steps typically require integration with a catalyst to complete water oxidation on the microsecond timescale to avoid back-electron transfer (7). Research improvements have led to more efficient core/shell photoanode materials, enhancements in water oxidation rates, and improved interfacial designs that use electron-transfer mediators to assist charge separation between photoanode, chromophore, and catalyst (8–11). It is still challenging to store solar energy in chemical bonds by artificial photosynthesis. In this application, water oxidation is coupled with a bias at the cathode to drive water reduction. A mechanism is shown in Eqs. 1–3 for the first step in a water oxidation cycle at a TiO₂-based photoanode.



There are few literature examples that report single-electrode water splitting without an applied bias (12, 13). Multijunction photoelectrochemical solar cell configurations that focus on hydrogen production have appeared in the literature (14, 15). They include: 1) photoanode/photocathode tandem cells with both reactions driven by light; 2) integrated photovoltaic (PV)/photoelectrochemical (PEC) cells, with one of the electrodes in the PEC driven by light and the other in the dark with a solar cell supplying the energy for the reaction, and 3) PV/electrolyzer hybrid devices that drive both reactions in the dark with all of the energy supplied by solar cells. In type 1 cells, the device configuration includes a two-sided light-absorptive component with both the photoanode and photocathode connected in series. In type 2 cells, a PEC cell (photoanode or photocathode) is integrated with a PV device and is used to form a PEC/PV tandem

Significance

A major challenge for artificial photosynthesis is creating a photoelectrode to split water without an added bias. Here, we demonstrate the value of combining of a dye-sensitized photoelectrosynthesis cell and an organic solar cell in a photoanode for water oxidation. With the two component electrodes, and a counter Pt electrode for H₂ evolution, the electrode becomes part of a combined electrochemical cell for unassisted water splitting, 2H₂O → O₂ + 2H₂. The results described here offer a major improvement in solar-to-hydrogen conversion efficiency (STH%) for a molecularly based solar fuel electrode. The STH% for water splitting was 1.5% for the tandem cell compared to ~1% for natural photosynthesis.

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cell. In type 3 cells, an electrolysis cell is combined with a PV cell with integrated PV and electrolyzers for water splitting.

For PEC/PV tandem cells, a good companion light absorber is an organic solar cell (OSC) with low-energy light-absorbing chromophores that does not compete with light absorption by the PEC electrode. Compared to conventional semiconductors, an OSC can feature easy fabrication with low-cost, lightweight materials and built-in mechanical flexibility, etc. (16, 17). Recent advances in this area have led to improvements in power-conversion efficiencies of up to 16.5% for single junction and 17.3% for tandem devices (18–24).

Here we exploit the second configuration with a PEC/PV tandem cell that utilizes an n-type, dye-sensitized photoanode in the dye-sensitized photoelectrosynthesis cell (DSPEC) and organic light absorbers in the PV component cell. The combined tandem, dye-sensitized PEC cell uses electrodes for the conversion of water into O_2 and H_2 with light as the only energy input. It consists of a DSPEC that includes a photoanode and dark cathode, wired in series with an organic solar cell. In this configuration, the photoanode of the DSPEC is connected to the cathode of the OSC and the anode of the OSC is connected to the cathode of the DSPEC.

The results described here offer a major improvement for solar-to- H_2 conversion efficiency for a single visible light-absorbing electrode and a benchmark for molecularly based solar fuel conversion efficiencies (15, 25–29). The STH% obtained by combining a DSPEC photoanode with an OSC for water splitting was 1.5%, compared to $\sim 1\%$ for natural photosynthesis (30).

Results and Discussion

The water-splitting photoelectrochemical tandem cell is illustrated in Fig. 1. Overall, the cell operates by absorbing light over a wide spectral range and utilizes the resulting excitation to oxidize water at a photoanode, electrode 1#(FTO| SnO_2 | TiO_2 |-Chrom-Catalyst) in Fig. 1, reducing H^+ to hydrogen gas at a separate cathode, electrode 4#. Under illumination, the PV cell (electrodes 2#[ITO|ZnO-organic semiconductors] and 3#[MoO_3 |Al]), connected in series, provide the needed bias to drive the production of H_2 at electrode 4#(Pt electrode). Light first passes through the DSPEC electrode and then to the ZnO/ITO side of the OSC to the less-transparent MoO_3 -Al contact for the OSC cell.

The system design shown in Fig. 1 represents an artificial, photosynthetic Z-scheme. Although sharing design elements with natural photosynthesis, the ability to vary and tune the spectral and molecular levels through a selection of semiconductor materials and

light absorbers can result in efficiencies much higher than those observed in nature. The design shown here integrates a tandem DSPEC electrode with an organic solar cell, providing two distinct light absorbers with complementary spectral and redox properties. The light-absorbing dye for water oxidation was a Ru(II)polypyridyl dye. It was integrated with a water oxidation catalyst (Fig. 2A) at external electrode 1#. Chromophore and catalyst were chemically attached to the surfaces of fluorine-doped tin oxide (FTO)| SnO_2 | TiO_2 core/shell electrode. The inner electrode in Fig. 1, Right was the organic film of the polymer donor, BnDT-FTAZ (31), and the nonfullerene acceptor ITIC (32) as the components of the internal organic solar cell (Fig. 2B). The organic solar cell exploits the highly complementary light absorption (33), favorable morphology (33), and high mobility for the BnDT-FTAZ pair (on the order of $10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) (34) with its capability for large-area device fabrication (35). More importantly, as shown in Fig. 2C, the overall light absorption by the Ru(II)polypyridyl dye and the organic cell are highly complementary, enabling a high utilization of the solar input.

Cell Design. In designing the tandem photoanode–PV device, the optical density of the initial layer was chosen to allow sufficient transmission of light to the inner absorber. The DSPEC photoanode thin films were deposited on optically transparent electrodes on FTO. In detail, 4- μm -thick, 20-nm-diameter-size SnO_2 films were prepared by sol-gel synthesis with doctor blading and sintering. They were coated with 4.5 nm TiO_2 , added by atomic layer deposition (ALD). The SnO_2 / TiO_2 core/shell structures were used to maximize electrode performance by decreasing local back-electron transfer to TiO_2 following injection and electron transfer to SnO_2 (36–38).

The relative configurations for the PA and the OSC are shown in *SI Appendix, Fig. S1*. The digital basis for assembling the tandem cell is also shown in *SI Appendix, Fig. S1*. In the photoanode, the Ru(II)-polypyridyl dye, RuP^{2+} , [$Ru^{II}(4,4'-(PO_3H_2)-2,2'$ -bipyridine) ($2,2'$ -bipyridine) $_2$] $^{2+}$ Fig. 2A, has a molar extinction coefficient of $\epsilon = 13,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 450 nm with a known, near-unity injection efficiency and high aqueous stability (39). Surface analysis of the electrodes was based on absorption measurements, with $\Gamma(\text{mol}/\text{cm}^2) = A_\lambda/(\epsilon_\lambda 1,000)$, and Γ the surface loading in moles per square centimeter. Analysis was based on absorption measurements at a wavelength λ with molar extinction coefficients ϵ_λ . Analysis of data at 450 nm, shown in *SI Appendix, Fig. S2*, gave a surface loading of $\Gamma = 6 \times 10^{-8} \text{ mol}/\text{cm}^2$ for the films. As discussed previously, the water oxidation catalyst, $Ru(bda)(4,4'$ -bpy) $_2(4,4'$ -bpy) $^{2+}$ (WOC in Fig. 2A with

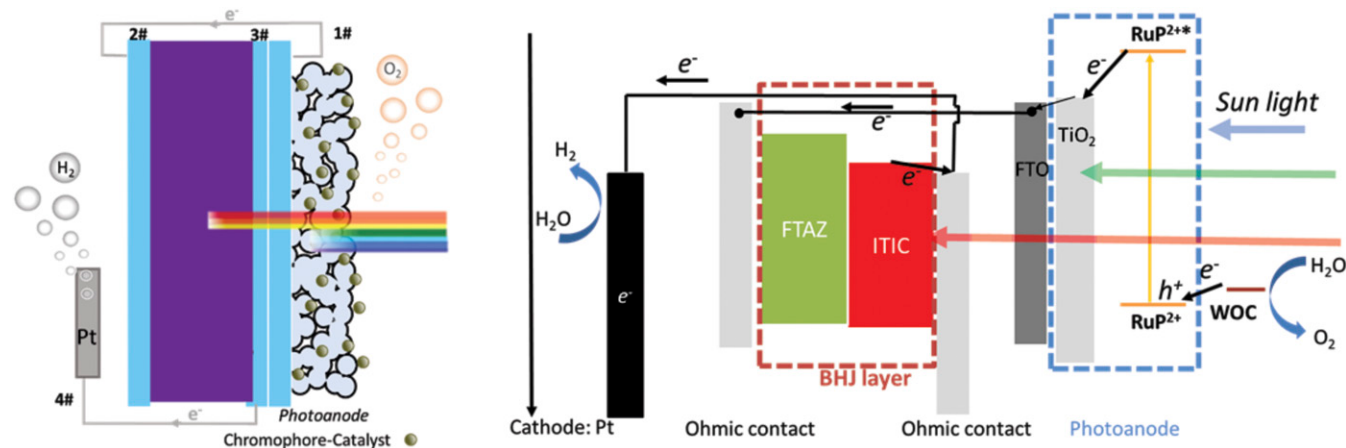


Fig. 1. (Left) Diagram of the tandem device with an OSC connected externally to a DSPEC PA with an external Pt cathode. (Right) Energy-level diagram illustrating the direction of electron flow in the tandem cell for water splitting.

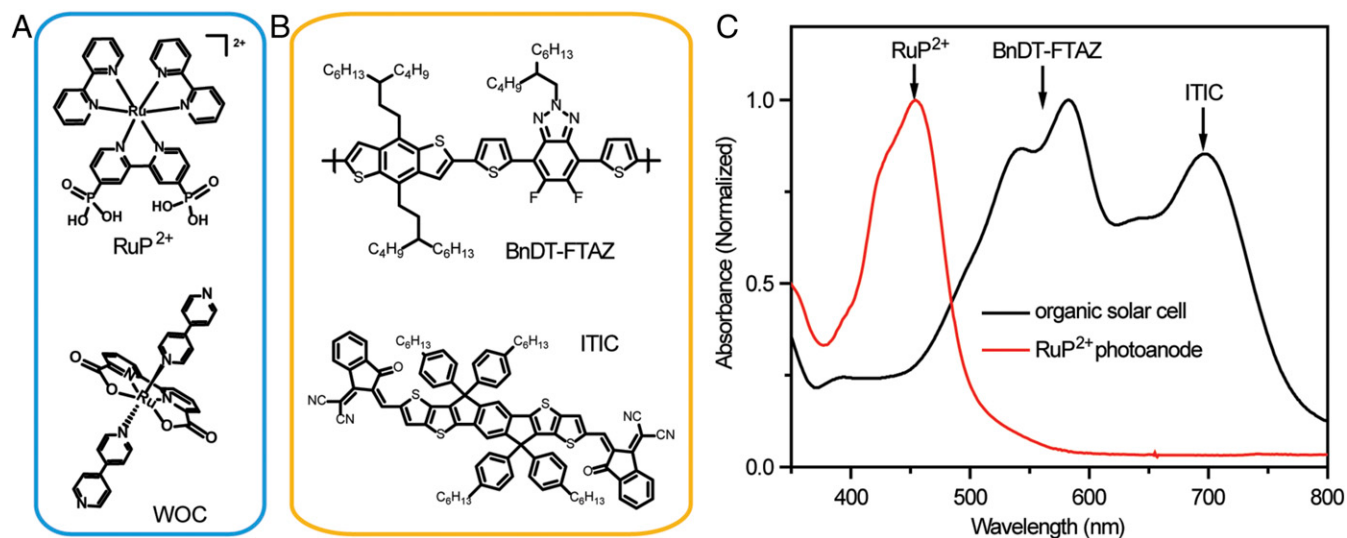


Fig. 2. Molecular structures of the molecular components in the DSPEC (A) and the OSC (B) and their combined absorption spectra (C).

4,4'-bipyridine and bda = 2,2-bipyridine-6,6-dicarboxylate), was added as a second layer on the $\text{SnO}_2/\text{TiO}_2$ electrode at a chromophore:catalyst ratio of 5:1, in a subsequent step. The ratio of the two was established by spectrophotometric measurements on the final photoanodes (PA) (40). The absorbance of the OSC is shown in *SI Appendix, Fig. S3*.

Fig. 3 illustrates the optical transmittance spectrum of the photoanode, PA. Based on transmittance measurements, the percentage of visible absorption in the orange-colored PA was >90% at its maximum in $(1-T)$ at 450 nm. The absorption characteristics of the electrode determine the maximum photocurrent level that can be generated by the DSPEC PA. Transmitted light controls the fraction of incident light that reaches the underlying OSC. The procedure for preparing the organic solar cell is described in *SI Appendix*. With a transmittance of nearly 50%, at wavelengths in excess of 600 nm, the PA film displays considerable light scattering from the external $\text{FTO}|\text{SnO}_2/\text{TiO}_2$ film.

Electrodes. Light-driven water oxidation was investigated in a standard, three-electrode PEC cell under 1-sun illumination ($100 \text{ mW}/\text{cm}^2$ by using a 400-nm long-pass filter). A platinum mesh electrode was used as the counter electrode with a Ag/AgCl (3 M KCl) reference electrode.

In characterizing the electrode, J_{PEC} was the measured photocurrent density (in mA/cm^2) and P_{IN} was the power density of the incident photon flux ($100 \text{ mW}/\text{cm}^2$ at standard AM 1.5G conditions). λ is the wavelength of the incident photon flux. A characteristic $J-V$ curve is shown in *SI Appendix, Fig. S4*. Under AM 1.5G illumination, the OSC exhibited a power conversion efficiency of 9.15% with an active area of 1.40 cm^2 . There was no obvious loss of short-circuit current density nor open-circuit voltage when the OSC area was increased from 0.13 to 1.40 cm^2 .

$$\text{IPCE} = 1,240 \times I_{\text{ph}} / (\lambda \times J_{\text{light}}). \quad [4]$$

Incident photon conversion efficiency (IPCE) values were calculated by using Eq. 4, with I_{ph} the photocurrent in milliamperes, J_{light} the incident light intensity in milliwatts, and λ the incident wavelength in nanometers (40). An IPCE value of 20.2% was obtained for the PA at a bias of 0.8 V vs. reversible hydrogen electrode (RHE), in 0.1 M acetate buffer at pH 4.65, 0.4 M in NaClO_4 . The potential was converted into E_{RHE} by the

Nernst equation, $E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + E_{\text{applied}} + 0.059\text{pH}$. The IPCE profiles demonstrate that the current response overlaps with the visible absorption spectrum of RuP^{2+} . The IPCE value for the OSC is consistent with the absorbance of the cell as shown Fig. 2 and *SI Appendix, Fig. S3*. The integrated photocurrent obtained from the IPCE (*SI Appendix, Fig. S6*, $15.2 \text{ mA}/\text{cm}^2$) correlates well with the measured short-circuit current density (J_{SC}) of $15.5 \text{ mA}/\text{cm}^2$ (*SI Appendix, Fig. S5*). The measured OSC open-circuit voltage (V_{OC}) of 0.92 V pointed to an absence of V_{OC} loss after placing the PA in front of the OSC. The high voltage from this single-junction device, in combination with the large fill factor (0.61), show that its properties are favorable for operating as the OSC as an integrated PA.

To simulate the tandem configuration, the same solar cell was also examined with the PA thin film in front of the light source. In this configuration, the PA window acts as a long-pass filter blocking the majority of light below $\sim 600 \text{ nm}$. The switch in electrode positions resulted in a nearly 50% reduction in power density compared to 1-sun conditions.

The $J-V$ curve in Fig. 4 demonstrates the exceptional performance of the OSC under these conditions. Without high-energy

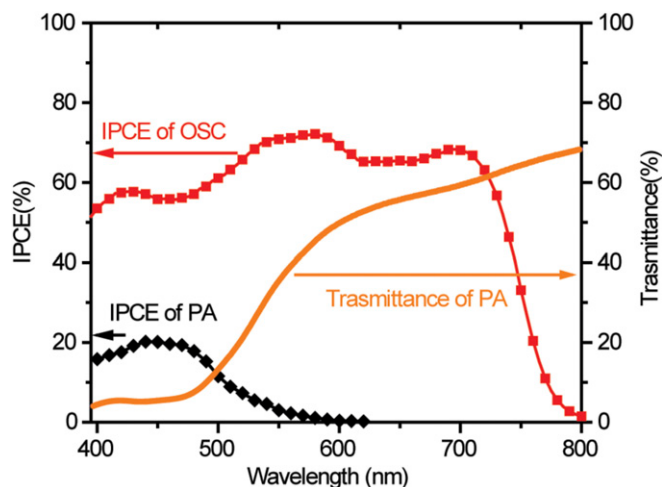


Fig. 3. IPCE spectra for the DSPEC at 0.8 V versus RHE, and OSC under short-circuit conditions in the absence of the DSPEC.

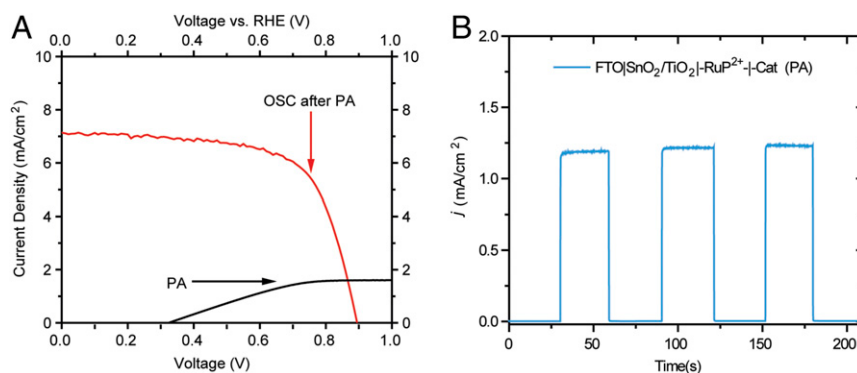


Fig. 4. (A) Overlay of J - V plots for PA and OSC in 0.1-M acetate buffer solutions (pH 4.65). The PV parameters were recorded in the OSC after the PA film. The crossing point of the two curves designates the anticipated photocurrent output of the series-connected, tandem assembly. (B) Current vs. time plots of the DSPEC with no applied bias over 30-s dark/light cycles.

excitation, J_{SC} remained at 7.14 mA/cm^2 which is nearly half of the value under 1-sun irradiation (15.5 mA/cm^2). In these experiments, a slight decrease in open-circuit potential ($V_{OC} = 0.90$) was observed with an increased fill factor of 0.68 that gave a power conversion efficiency of 4.24%. Given that the voltage and fill factor in the underlying solar cell in the PAOSC system have a profound impact on overall device performance, the constancy of the parameters in the presence of the PA was essential for efficient tandem solar fuel generation. The J - V and IPCE value at the OSC with and without the added PA film in a glove box was also measured. Results are shown in *SI Appendix*, Figs. S5 and S6. In analyzing the data, the near constancy in the shape of the IPCE curve is consistent with absorption by the organic semiconductors. Integration of the IPCE curves further confirmed that OSC loss is by PA electrode scattering.

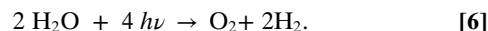
In assembling the PA-OSC device, the light-harvesting modules were arranged in a layered fashion and connected in series (27, 29). A scheme depicting the overall PA-OSC architecture is also shown in Fig. 1. It illustrates transmission at wavelengths $> 600 \text{ nm}$ through the PA electrode. In this configuration, complementary spectral sensitization of the components in the tandem assembly facilitates selective harvesting of photons during single-pass excitations.

Water Splitting. A series of experiments were performed in 0.1 M acetate buffered aqueous solutions (pH 4.65) to test the ability of the tandem device to mediate water splitting. The photocurrents generated with illumination resulted in an STH efficiency of 1.5% for the PA-OSC tandem device (Fig. 4B). Fig. 4A shows the anticipated operating point for the PA-OSC water-splitting

device which was dictated by the intersection between the J - V curves for the component electrodes. The latter predicts a photocurrent output of 1.61 mA/cm^2 . The performance of the tandem device in 0.1 M acetate buffer solutions (pH 4.65) is shown in Fig. 5B. The photocurrent response verifies that the combined cell, PA-OSC, does produce sufficient energy for water splitting. Taking the η_F as unity, and given the thermodynamic potential for water splitting of 1.23 V, the unassisted STH efficiency (η_{STH}) can be calculated from Eq. 5 (29). In Eq. 5, J_{OP} is the operating current density (mA/cm^2), the η_F is assumed to be 100%, and P_{solar} is the irradiance intensity of 100 mW cm^{-2} which gave $STH = 1.5\%$ for the combined PA-OSC tandem cell.

$$STH = (J_{OP} \times 1.23 \times \eta_F) / (P_{solar}). \quad [5]$$

The output of the cell was consistent with water splitting driven at the $\text{Ru}(\text{bda})\text{L}_2$ catalyst. In order to verify that the measured photocurrents were due to water splitting, evolved gases were monitored at the electrodes by probe electrodes over a period of 60 min. As shown by the data in Fig. 5, the results were consistent with water splitting, Eq. 6, with η_F of 95% or above.



Water splitting was observed for more than 1 h with the current falling by 30% (Fig. 5A). After an hour, analysis of the electrodes showed that degradation in overall performance was due to loss of activity by the DSPEC electrode with a potential for significantly enhanced performance by improvements in its the stability (*SI Appendix*, Fig. S7).

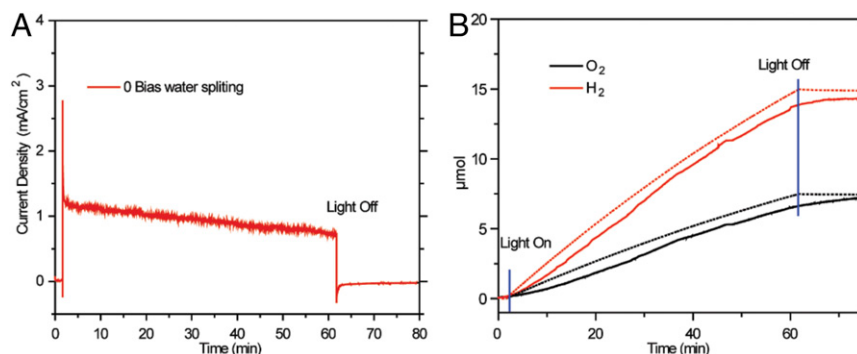


Fig. 5. (A) Photocurrents during gas evolution. (B) Quantification of H_2 and O_2 produced during water splitting. Red and black lines correspond to H_2 and O_2 measured externally. The black and red dotted lines correspond to integrated photocurrents over time with the theoretical value of gas produced from current curves shown.

Conclusion

We demonstrate here that an efficient, stable, water-splitting, tandem PEC–PV PA can be prepared for solar water splitting with a solar-to-hydrogen efficiency of 1.5%. The key in designing the cell was the alignment of an appropriate DSPEC and an organic solar cell in series at the PA. Analysis of the tandem cell for water splitting, with a Pt cathode, based on photovoltage and internal OSC power measurements, was undertaken to give conversion efficiencies with and without light, and by linear scan voltammetry. The high open-circuit voltage in the water-splitting cell, > 0.9 V, arises from the driving force from the organic solar cell which is sufficient to drive water oxidation at the PA. The two in parallel provide the potential required for unassisted, light-induced water splitting. The performance of the tandem electrode was limited by low photocurrents for O₂ generation at the PA, as shown by comparisons with photocurrent densities for the

stand-alone OSC, and by the long-term instability of the oxygen electrode.

Data Availability. All data analyzed in this study are included in the main text and *SI Appendix*.

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