

Supporting information for:

## Direct Light-Driven Water Oxidation by a Ladder-Type Conjugated Polymer Photoanode.

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### EXPERIMENTAL METHODS

**Materials:** The following materials were used as received: Methanesulfonic acid (MSA) (Sigma-Aldrich,  $\geq 99.5\%$ ), Igepal co-520 (Sigma-Aldrich, average  $M_n$  441),  $\text{HNO}_3$  (VWR International, Normapur 65%),  $\text{Na}_2\text{SO}_3$  (Sigma-Aldrich,  $\geq 98\%$ ),  $\text{Na}_2\text{SO}_4$  (Sigma-Aldrich, 99+%, ACS reagent),  $\text{KH}_2\text{PO}_4$  (Acros Organics, monobasic, 99+%, ACS reagent),  $\text{K}_2\text{HPO}_4$  (Sigma-Aldrich, reagent plus TM  $\geq 99.0\%$ ),  $\text{NaOH}$  (Reactolab SA, pur pastilles),  $\text{H}_2\text{SO}_4$  (Reactolab SA, 96%, tech.). Fluorine-doped tin oxide coated float glass substrates (FTO, Solaronix) were washed by acetone, ethanol and treated with a nitrogen plasma in a Harrick plasma cleaner before use. The poly(benzimidazobenzophenanthroline) (BBL) used for this work was supplied by Sigma-Aldrich, and was reported to have an intrinsic viscosity,  $[\eta] = 0.58 \pm 0.04 \text{ dL g}^{-1}$  (using the Huggins relation), in concentrated sulfuric acid at  $25^\circ\text{C}$ .

**Photoelectrode fabrication:** Briefly, for dip-coated films, fluorine-doped tin oxide (FTO) coated glass substrates were withdrawn from a BBL solution, dipped into water and EtOH to fix and wash the film, and subsequently dried in air. While the thickness of the resulting film can be controlled by varying the concentration and the withdrawal rate, the relatively low solubility of BBL in MSA (ca.  $1 \text{ mg mL}^{-1}$ ) limits the range of accessible film thickness. For spray-coated films, a wet-spinning method in water with the non-ionic surfactant Igepal® followed by ultrasonication afforded a dispersion of nanometer-sized BBL fibers that was sprayed on FTO and subsequently washed to remove the surfactant before drying. In this case the film thickness can be optimized by varying the quantity of the BBL dispersion sprayed. For the dip coating method, films were prepared as outline in Figure S1a (below). A saturated solution was obtained by dissolution of BBL in hot MSA ( $210^\circ\text{C}$ ). After cooling to  $20^\circ\text{C}$ , FTO was dipped into this solution and withdrawn at a  $20 \text{ mm min}^{-1}$  rate. The “wet” BBL film is then precipitated by dipping into pure water and further fixed by heat treatment at  $150^\circ\text{C}$  in air. The films were then washed by soaking in ethanol for 1 hour and annealed again for 1 hour at  $250^\circ\text{C}$  in air. The final film morphology is shown in Figure 1a (main text) and the edge of the BBL film and the underlying FTO substrate morphology are shown in Figure S1b (below). For the sprayed films, the procedure used is shown schematically in Figure S1c (below). Here a dispersion of BBL was first prepared by adapting the work of Janietz et al.<sup>S1</sup> A solution of BBL in MSA is injected (through a ca.  $100 \mu\text{m}$  diameter pipette orifice) into a 1 wt% solution of IGEPAL co-520 in water. This “wet spinning” method gives fibers of BBL of diameter of ca.  $10 \mu\text{m}$  (as shown in Figure S1d). The precipitate was broken by bath sonication for 1 hour giving an acidic solution of BBL particles. BBL precipitate was washed several times with water by a centrifugation/dispersion in fresh water cycle until the supernatant was no longer acidic. The precipitate was finally dispersed in a 0.15 wt% solution of IGEPAL in water, homogenized by sonication for 1 hour at maximum power and filtered with a  $5 \mu\text{m}$  pore diameter syringe filter. The dispersion consists of ca.  $500 \text{ nm}$  long fibers with ca.  $20 \text{ nm}$  diameter (TEM image shown in Figure S1e) and reaches a final concentration of  $2 \text{ mg mL}^{-1}$  (0.15 wt% IGEPAL and 0.03 wt% BBL). It is stable for several months at room temperature. For film deposition, an FTO substrate was placed onto

a hot plate at 200°C under a homemade external-mix two-fluid spray head. One layer of BBL was prepared by spraying 0.5 ml of the prepared BBL dispersion over 30 sec. After spraying, the film was immersed in a nitric acid bath (0.5M) and left under stirring for 1 hour to remove the IGEPAL. The extent of the removal of the IGEPAL was difficult to quantify given the relatively small amount present in the film, and the large amount of washing solution employed. However, MALDI-TOF MS confirms that the IGEPAL is removed by the washing step see (Figure S13). Importantly, the effect on the performance of the photoelectrode before and after the washing step is also evidence of its removal (also shown in Figure S13), however, we cannot discount that some of the IGEPAL remains in the film after the washing step. Nonetheless, after washing the film was then annealed at 250°C in air for 1 hour. This spray-wash-anneal procedure can be repeated to make thicker films, and thinner films can be prepared by spraying less dispersion. On selected films, a TiO<sub>2</sub> overlayer (1 nm) was deposited by using a previously published procedure.<sup>S2</sup> A Ni-Co catalyst was deposited by spin-coating a solution of 0.5 M NiSO<sub>4</sub>·6H<sub>2</sub>O and 0.5M Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and drying at 250°C for 10 minutes.

*Basic electrode characterization:* Total reflectance and transmittance spectrum of films were measured illumination from the substrate side with a Shimadzu UV-3600 UV-vis-NIR spectrophotometer (Shimadzu Co.) using an integrating sphere. Absorbance spectra (Figure S2) were then calculated through the relation ( $A = 1 - T - R$  with A the %absorbance, T the total %transmittance, and R the total %reflectance). A Tauc plot (Figure S2 inset) was constructed for a direct optical transition. The morphology of the films were examined by scanning electron microscopy with a XLF-30 microscope.

*Electrochemical characterization:* Current density-voltage measurement were recorded in a “cappuccino cell” in a three electrode configuration consisting of a BBL photoanode, an Ag/AgCl (KCl sat.) reference electrode and a platinum wire as counter electrode. Electrolytes used were either 0.5 M Na<sub>2</sub>SO<sub>3</sub> (hole scavenger) or 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.09 M KH<sub>2</sub>PO<sub>4</sub> + 0.01 M K<sub>2</sub>HPO<sub>4</sub> in water. Electrolyte pH was buffered either with 1 M NaOH or 1M H<sub>2</sub>SO<sub>4</sub>. All potentials reported in the results were converted to the RHE reference scale using  $E_{\text{RHE}} = E_{\text{Ag/AgCl KCl sat.}} + 0.197 + 0.059 \cdot \text{pH}$ . Except for the Mott-Schottky plot where potentials were reported to the NHE reference scale using  $E_{\text{NHE}} = E_{\text{Ag/AgCl KCl sat.}} + 0.197$ . Illumination was performed under simulated solar illumination (1 sun 100 mW cm<sup>-2</sup>) produced by a 450W Muller Elektronik Xenon-arc lamp (Müller-Electronik) using appropriate filters and calibrated using a Si photodiode. The illuminated area was 0.283 cm<sup>2</sup>. A potential scan rate of 10 mV s<sup>-1</sup> controlled by a SP-200 potentiostat/galvanostat (Biologic Technologies) was used for the potentiostatic current-potential measurement. Electrochemical Impedance Spectroscopy was performed in the dark using a 10 mV amplitude perturbation between 100 mHz and 200 kHz in the same configuration. A simple Randle’s circuit with a constant phase element (CPE) was used to fit data (Figure S4) and extract the space-charge layer capacitance used in the constructed Mott-Schottky plot. For incident-photon-to-current (IPCE) measurements (Figure S8), a monochromatic illumination was provided by a 75 W Xe Tunable PowerArc Illuminator (Optical Building Blocks) and the number of photons at each wavelength was measured with a photodiode power sensor (S120VC, Thorlabs). For some IPCE measurements a white light bias (a constant illumination of the sample with broad spectrum visible light) with an intensity of about 0.1 sun was applied using a 450W Xenon-arc lamp filtered by KG-1 glass. This while light was illuminating the sample during the sweep of the monochromatic illumination to increase the number of photogenerated carrier production (as the illumination intensity of the monochromatic illumination is typically quite low) and achieve conditions closer to solar operating conditions.

*Fluorescence probe experiment:* a stock solution of electrolyte with coumarin 2 mM was prepared and finally diluted to 0.1 mM of coumarin with buffered electrolyte. Amperometry measurements was performed in the three electrode cell configuration by applying 1.23 V vs. RHE under simulated solar illumination for 1 and 2 hours. The electrolyte was directly collected and fluorescence spectra were measured with a Perkin Elmer LS50B Luminescence spectrometer with excitation at 332 nm and

emission scan speed of 100 nm min<sup>-1</sup>. The average of 5 scans was taken for the results. We note that the direct electrochemical oxidation of the coumarin by the BBL was not observed by cyclic voltammetry measurements (see Figure S9) and is anyway unlikely to lead to umbelliferone production as the direct electrochemical oxidation of coumarin has been reported to be irreversible and result in an insoluble deposit on glassy carbon electrodes.<sup>S3</sup>

*O<sub>2</sub> gas measurement:* A gas chromatograph Clarus 480 (Perkin Elmer) was used for oxygen detection with an experimental setup and equipment that was explained elsewhere.<sup>S4</sup>

## ADDITIONAL DISCUSSION

*Stability measurements:* To eliminate the possibility that photocurrent arises from oxidation of the BBL itself, longer stability measurements were performed (Figure S6). A 43% decay of the photocurrent is observed over the first 10 min after which a steady-state photocurrent is obtained. During the measurement period, 31 mC passed through the exposed area of the photoanode, which is 12 times the charge needed to completely oxidize the BBL considering that 126 µg of polymer was estimated to be in the exposed area. Moreover, SEM of the electrode after 3 hours total testing time (Figure S6b) shows no visible degradation, and Raman spectra before and after testing show no difference (Figure S7).

*Non-linear IPCE observation:* The incident photon-to-current spectrum (IPCE, Figure S8) verifies that the photocurrent in non-sacrificial electrolyte at pH 7 arises from light absorption by the BBL. Integrating the IPCE with the standard solar spectrum (AM 1.5G) gives a  $J_{ph}$  of 167 µA cm<sup>-2</sup>. However when a white light bias is used during the IPCE measurement an integrated  $J_{ph}$  of 78 µA cm<sup>-2</sup> is found. This reduction of IPCE with the light bias is usually ascribed to increased geminate recombination in the film (see reference in main text). Indeed, the reduced electric field (band flattening) that occurs at higher illumination intensity due to charge accumulation at the SCLJ increases the probability of charge recombination. Since we actually expect an accumulation of photo-generated holes at the SCLJ (as indicated by the transient spikes) to be favorable for water oxidation due to the requirement of 4 photogenerated holes to participate to produce one molecule of O<sub>2</sub>, this observation brings into question the nature of the sustained oxidation reaction occurring on the bare electrode.

*Other possible routes for the production of •OH:* We note that in addition to the production of •OH via H<sub>2</sub>O<sub>2</sub>, other routes are possible. The direct one-electron production of the hydroxyl radical from the hydroxyl anion may also be feasible at high pH as the standard redox potential for the <sup>-</sup>OH/•OH couple is reported at +1.8 V<sub>NHE</sub> (which corresponds to +2.6 V<sub>RHE</sub>).<sup>S5</sup> In contrast, the direct one-electron oxidation of H<sub>2</sub>O to form •OH and H<sup>+</sup> is not expected to be thermodynamically feasible (E = +2.9 V<sub>RHE</sub>) given the HOMO level of BBL at any obtainable pH.

(S1) Janietz, S.; Sainova, D. *Macromol. Rapid Commun.* **2006**, 27, 943.

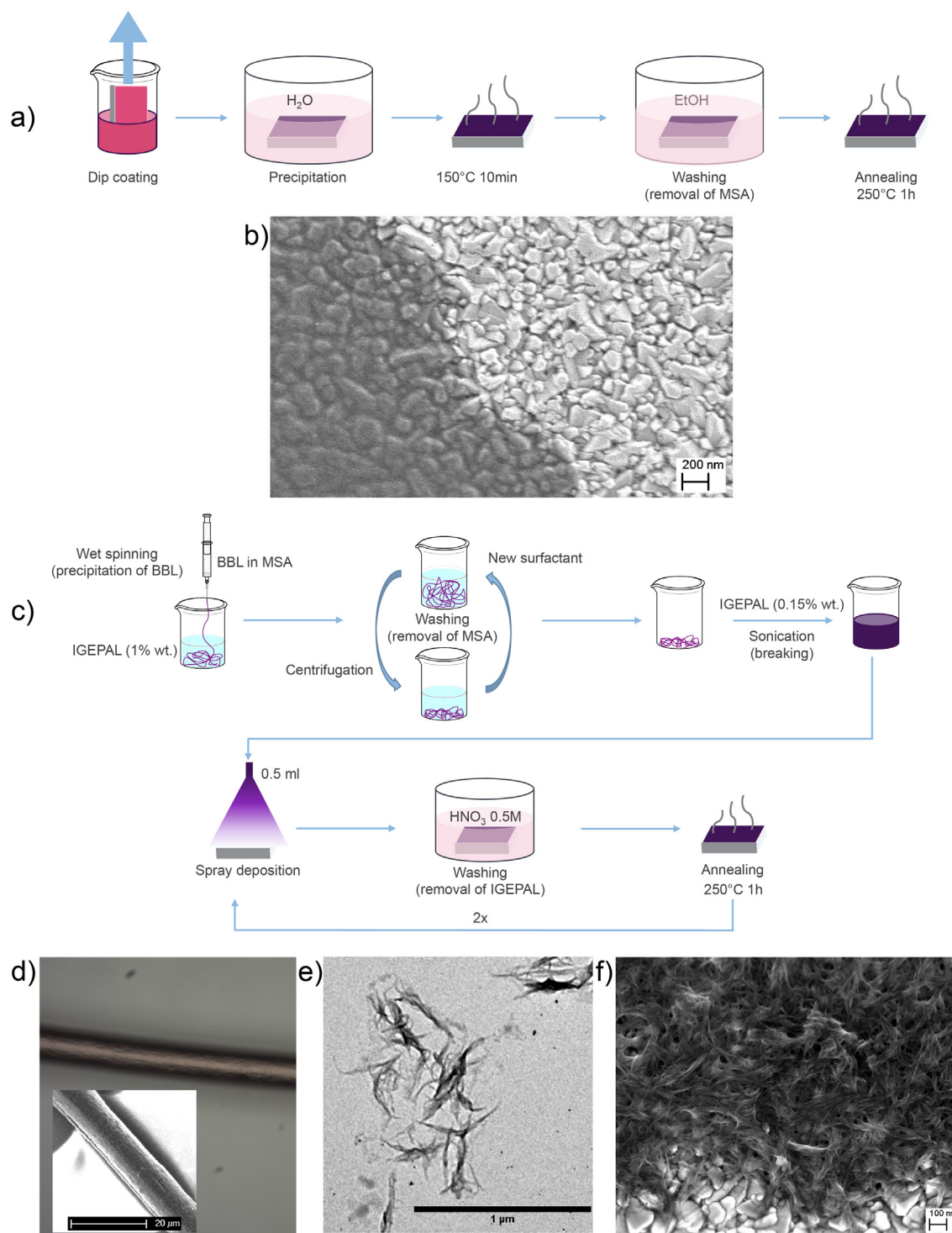
(S2) Tilley, S. D.; Schreier, M.; Azevedo, J.; Stefik, M.; Graetzel, M. *Adv. Funct. Mater.* **2014**, 24, 303.

(S3) Wu, Q.; Dewald, H. D. *Electroanalysis* **2001**, 13, 45.

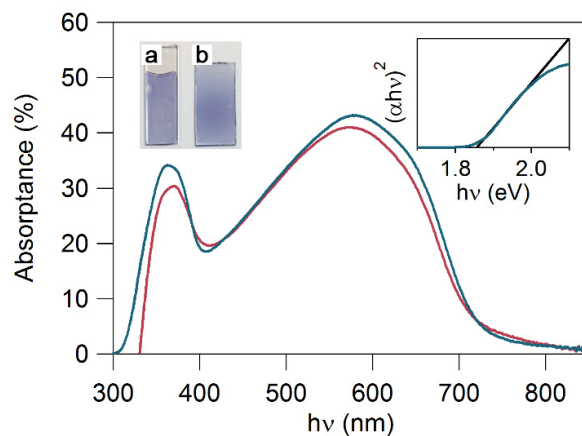
(S4) Prévot, M. S.; Guijarro, N.; Sivula, K. *ChemSusChem* **2015**, 8, 1359.

(S5) (a) Sawyer, D. T.; Roberts, J. L. *Acc. Chem. Res.* **1988**, 21, 469. (b) Koppenol, W. H.; Liebman, J. F. *J. Phys. Chem.* **1984**, 88, 99-101.

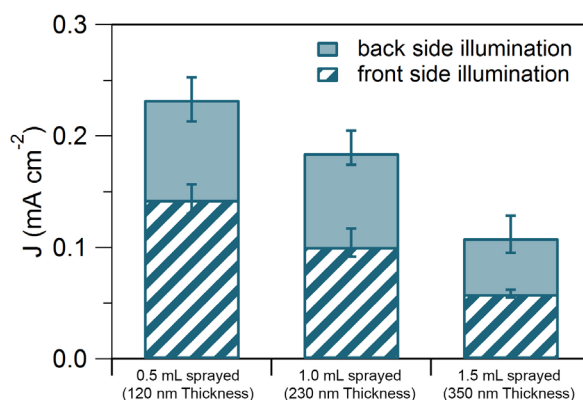
# Additional Figures:



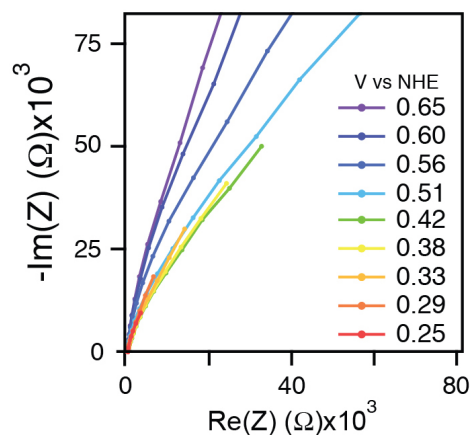
**Figure S1.** Comparison of different techniques to make thin films of BBL. a) shows the dip coated method as described in the experimental methods section, b) shows an additional SEM image of the dip-coated film at the edge revealing the underlying FTO substrate, c) shows the procedure for preparing the spray-coated films, d) shows the optical microscope and SEM (inset) morphology of the wet-spun BBL fiber, e) shows a TEM image of the final BBL dispersion, and f) shows an additional SEM image of the spray-coated BBL film at the edge revealing the FTO substrate.



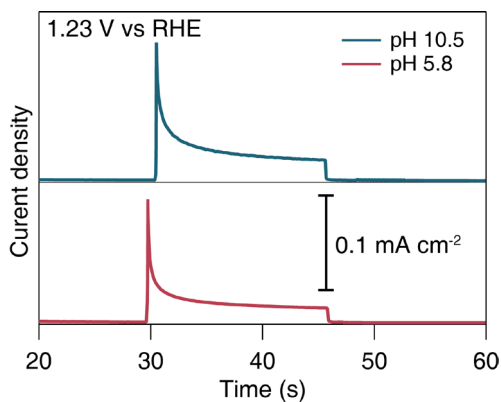
**Figure S2.** Absorbance spectra of a dip coated film (red line) and a spray-coated film (blue line) prepared at similar thickness. The optical photographs of the films (inset 1a is dip-coated and inset 1b is spray-coated) and Tauc plot (direct transition) of a 120 nm thick sprayed film (inset 2).



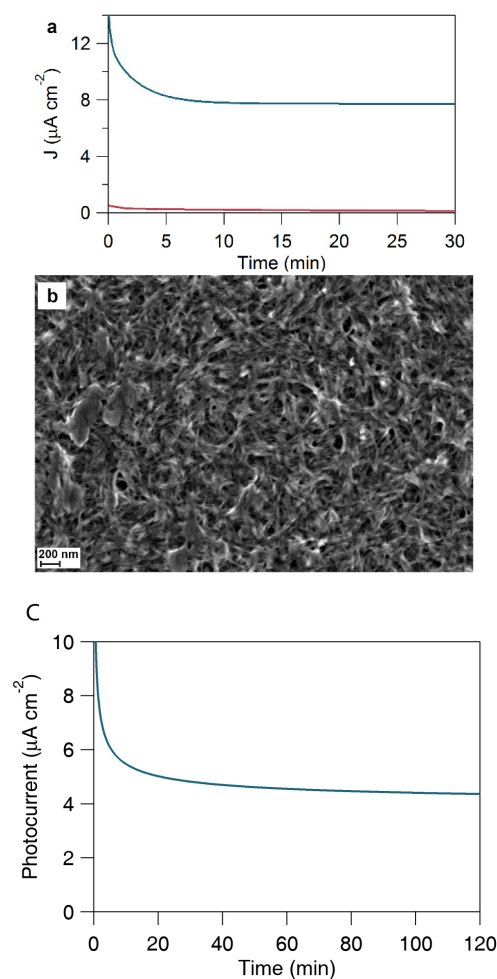
**Figure S3.** Comparison of back side (solid) and front side (striped) illumination photocurrent at 1.23 V vs. RHE of a BBL spray coated film in  $\text{Na}_2\text{SO}_3$  (pH 7) as a function of number of deposited BBL layers.



**Figure S4.** Nyquist plots (from 100 mHz to 200 kHz) of a spray-deposited BBL electrode (in dark condition) in aqueous electrolyte ( $0.5 \text{ M Na}_2\text{SO}_4 + 0.09 \text{ M KH}_2\text{PO}_4 + 0.01 \text{ M K}_2\text{HPO}_4$ , pH 7). The exposed geometric area was  $0.283 \text{ cm}^2$ .

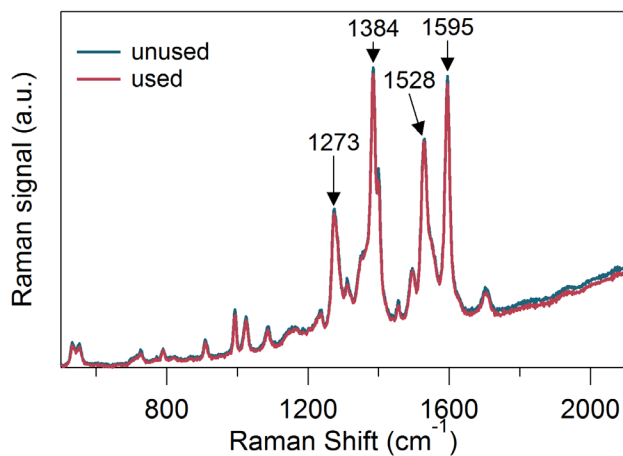


**Figure S5.** Photocurrent transient measurements of the spray-deposited BBL electrode at the indicated pH (aqueous 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.09 M KH<sub>2</sub>PO<sub>4</sub> + 0.01 M K<sub>2</sub>HPO<sub>4</sub>, pH adjusted with 1 M NaOH or 1M H<sub>2</sub>SO<sub>4</sub>) and applied potential. The steady-state photocurrent was determined as the dark current minus the photocurrent at the point where the illumination was terminated (46 sec).

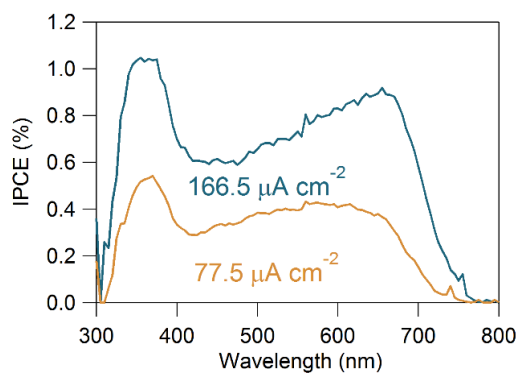


**Figure S6.** BBL stability. Panel a) shows the photocurrent (blue line) and dark current (red line) at 1.23 V vs. RHE of a BBL spray-deposited film as a function of time in aqueous electrolyte (0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.09 M KH<sub>2</sub>PO<sub>4</sub> + 0.01 M K<sub>2</sub>HPO<sub>4</sub>, pH 7). b) Shows the SEM top view of the BBL spray deposited film after electrochemical testing. Panel c) shows the photocurrent density (Current density under illumination minus the current under dark) of an duplicate BBL spray-

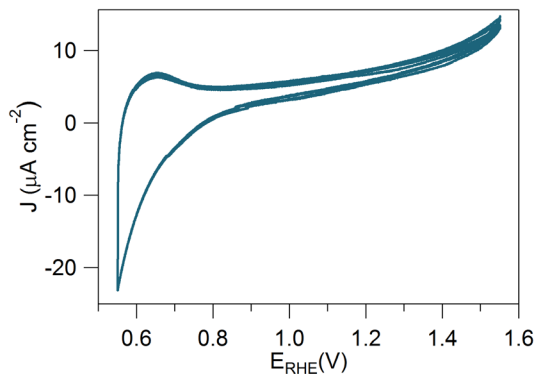
deposited film recorded for an extended stability measurement at 1.23 V vs. RHE as a function of time in aqueous electrolyte (0.5 M  $\text{Na}_2\text{SO}_4$  + 0.09 M  $\text{KH}_2\text{PO}_4$  + 0.01 M  $\text{K}_2\text{HPO}_4$ , pH 7).



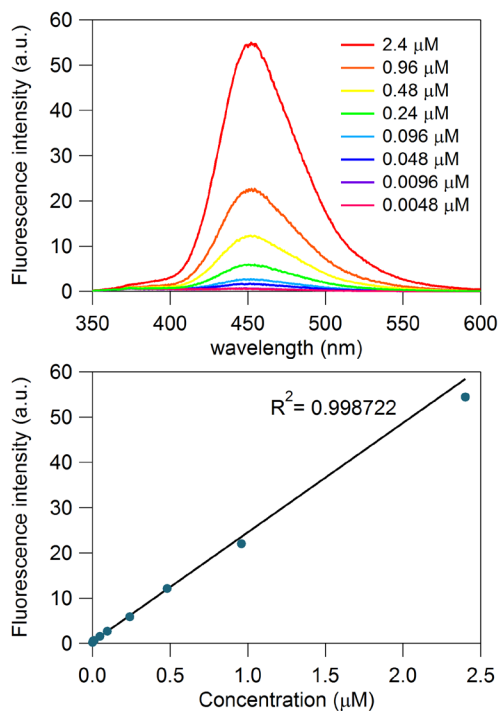
**Figure S7.** Raman spectra of a bare (without catalyst overlayers) BBL spray-deposited film before (blue) and after (red) electrochemical testing at 1.23 V vs RHE for 3 hours in aqueous electrolyte (0.5 M  $\text{Na}_2\text{SO}_4$  + 0.09 M  $\text{KH}_2\text{PO}_4$  + 0.01 M  $\text{K}_2\text{HPO}_4$ , pH 7) under 1 sun illumination.



**Figure S8.** Incident-photon-to-current efficiency of a spray-deposited BBL film at 1.23 V vs. RHE in aqueous electrolyte (0.5 M  $\text{Na}_2\text{SO}_4$  + 0.09 M  $\text{KH}_2\text{PO}_4$  + 0.01 M  $\text{K}_2\text{HPO}_4$ , pH 7) with (yellow line) and without (blue line) a white bias light of ca. 0.1 sun. Predicted values of the photocurrent density obtained by multiplying the IPCE with the standard AM 1.5G solar spectrum and integration are also shown.



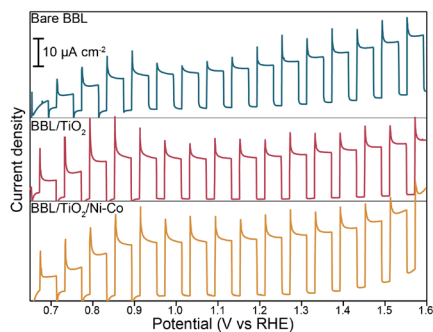
**Figure S9** Cyclic voltammogram of a spray-deposited BBL film in aqueous electrolyte (0.5 M  $\text{Na}_2\text{SO}_4$  + 0.09 M  $\text{KH}_2\text{PO}_4$  + 0.01 M  $\text{K}_2\text{HPO}_4$ , pH 7) containing 4 mM of coumarin. No oxidation wave can be detected.



**Figure S10.** (top) Fluorescence spectrum of aqueous electrolyte ( $0.5 \text{ M Na}_2\text{SO}_4 + 0.09 \text{ M KH}_2\text{PO}_4 + 0.01 \text{ M K}_2\text{HPO}_4$ , pH 7) containing different concentrations of umbelliferone. (bottom) Calibration of umbelliferone fluorescence at 450 nm as a function of its concentration.

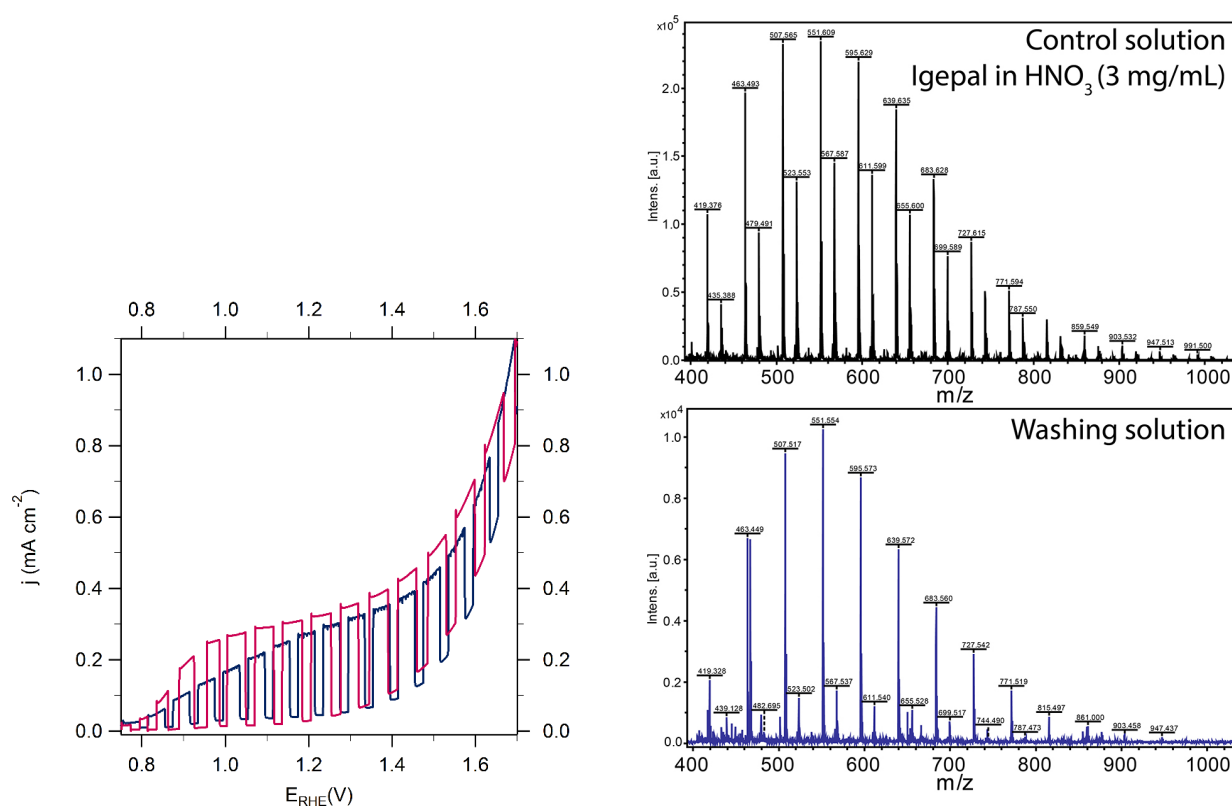
| Bare BBL film        | BBL with $\text{TiO}_2$ (1nm) |
|----------------------|-------------------------------|
|                      |                               |
| $51.5^\circ \pm 2.5$ | $25.6^\circ \pm 7$            |

**Figure S11.** Average contact angle of a sessile water drop on a bare spray-deposited BBL film and on a BBL film coated with  $\text{TiO}_2$  (ca. 1nm via ALD).



**Figure S12.** Current density, J-V (LSV), curves of a spray-deposited film of BBL (230 nm thickness) in aqueous electrolyte ( $0.5 \text{ M Na}_2\text{SO}_4 + 0.09 \text{ M KH}_2\text{PO}_4 + 0.01 \text{ M K}_2\text{HPO}_4$ , pH 7) under intermittent (simulated solar) illumination (substrate side illumination) before and after  $\text{TiO}_2$  deposition, and after the co-catalyst deposition.





**Figure S13.** The effect of the Nitric acid wash to remove the IGEAL surfactant. The left panel shows the LSV under intermittent illumination of a BBL film washed with ethanol only (blue trace) and a film washed with HNO<sub>3</sub> 0.5M in Na<sub>2</sub>SO<sub>3</sub> (pink trace). The right panel (top) shows the MALDI-TOF mass spectra analysis of a control solution of IGEAL in nitric acid. Analysis of the washing solution by MALDI-TOF MS (right bottom) shows the presence of the same peaks, confirming that IGEAL is removed from the film.