

Supplementary Information

Visible light driven water splitting in a molecular device with unprecedentedly high photocurrent density

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S1 Experimental Procedures

FTO glass was purchased from Wuhan Geao science and education instrument company (thickness ~ 2.2 mm, transmittance $> 90\%$, resistance $\sim 15 \text{ m}\Omega/\text{cm}^2$). All reagents were purchased from Aladdin chemical company. Solvents were dried and distilled according to the standard methods. Synthetic reactions were carried out under N_2 atmosphere with standard Schlenk techniques.

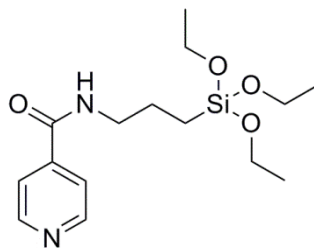
S1.1 Sample preparation and characterization

$\text{Ru}(\text{DMSO})_4\text{Cl}_2$ and 2,2'-bipyridine-6,6'-dicarboxylic acid (H_2bda) were prepared according to the literature methods.¹ Iso-nicotinoyl chloride was synthesized as reported.² ^1H NMR Spectra were collected at 298 K using a Bruker DRX-400 instrument. Electrospray ionization mass spectra were recorded on a Q-ToF Micromass spectrometer (Manchester, England). EI-MS analyses were carried out on a gas chromatograph fitted with a mass spectrometer (GC-MS 6890/5973, Agilent, USA). UV-Vis absorption measurements were carried out on a HP 8450 spectrophotometer. The light intensity was measured by Nova-II laser power monitor.

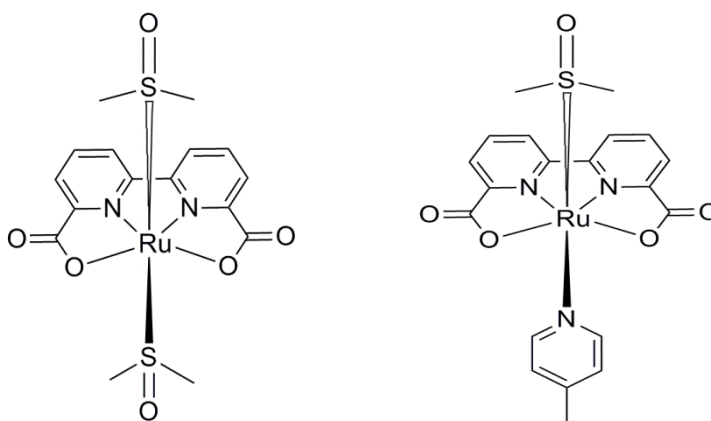
S1.2 Electrochemistry

The electrochemical measurements were recorded on a BAS-100W electrochemical potentiostat in a three-electrode cell under argon atmosphere. The working electrode was a TiO_2 -sintered FTO electrode absorbing with catalyst or photosensitizer. The counter electrode was a platinum wire. The reference electrode was an aqueous Ag/AgCl electrode. The surface loading of catalyst was measured according to CV by a known method reported by Meyer et al.^{3,4} The turnover number (TON) were calculated according to the formula of $\text{TON} = n_{\text{O}_2}/n_{\text{cat}} = (Q/4F)/n_{\text{cat}}$ (Faraday constant $F = 9.6 \times 10^4 \text{ C/mol}$) by converting the measured charges, and turnover frequency (TOF) were calculated according to the formula of $\text{TOF} = \text{TON}/t$.⁵

S2.1 Synthesis and characterization



N-(3-(triethoxysilyl)propyl)isonicotinamide: Iso-nicotinoyl chloride (141 mg, 1.0 mmol), (3-Aminopropyl)triethoxysilane (0.195 mL, 1.1 mmol) and NEt₃ (0.12 mL) in dichloromethane (10 mL) was stirred under 0 °C for 2 hours. The solvent was removed under vacuum and washed with anhydrous Et₂O to obtain viscous product. ¹H NMR (400 MHz, CD₃OD) δ ppm 8.7 (d, 2H), 7.8 (d, 2H), 3.0 (t, 1H), 3.38 (m, 2H), 1.7 (m, 2H), 3.5 (m, 6H), 1.3 (t, 9H).



Ru(bda)(DMSO)₂: A mixture of 2,2'-bipyridine-6,6'-dicarboxylic acid (H₂bda) (244 mg, 1.0 mmol), Ru(DMSO)₄Cl₂ (484 mg, 1.0 mmol) and NEt₃ (0.8 mL) in methanol (20 mL) was degassed with N₂ and refluxed over 4 hours. A brown powder was obtained after filtration, 200 mg (yield: 40%). ¹H NMR (400 MHz, DMSO-d₆) δ ppm 8.6 (d, 2H), 8.1 (t, 2H), 8.0 (d, 2H), 2.5(s, 6H) MS (ESI): m/z⁺ 522.9555 [M+Na]⁺. Calcd: 522.9542.

Ru(bda)(DMSO)(4-picoline): A mixture of 4-picoline (93 mg, 1.0 mmol) and Ru(bda)(DMSO)₂ (500 mg, 1.0 mmol) in methanol (40 mL) was degassed with N₂ and refluxed over 1 hours. After purification by column chromatography on silica gel using dichloromethane-methanol (1:1, v:v) as eluents, a brown solid production was obtained, 130 mg (yield: 24%). ¹H NMR (400 MHz, CD₃OD) δ ppm 8.5 (m, 2H), 8.1 (t, 4H), 7.7 (d, 2H), 7.1 (d, 2H), 2.9 (s, 6H), 2.3 (s, 3H). MS (ESI): m/z⁺ 537.9979 [M+Na]⁺. Calcd: 537.9981.

[Ru(bpy)₂(4,4-(PO₃H₂)₂bpy)]Br₂: This Ru complex was synthesized as reported previously.⁶

S2.2 Self-assembly and co-adsorption of catalyst and dye on working electrodes

A mixture of Ru(bda)(DMSO)(4-picoline) (538 mg, 1.0 mmol) and N-(3-(triethoxysilyl)propyl)-isonicotinamide (326 mg, 1.0 mmol) in methanol (40 mL) was degassed with N₂ and refluxed over 8 hours. A brown solid mixture of catalyst **2** was obtained after removing solvent under vacuum. It was difficult to purify catalyst **2** due to the fact that the silicon group has a strong adsorption on silica gel when running column chromatography. In addition, the silicon group could polymerize in the solution, therefore, crude product of catalysts **2** has been used directly to the immobilization reaction.

TiO₂-sintered FTO electrode with a 12 μ m thickness nano TiO₂ film was made by screen-printing method with 18 nm TiO₂ paste. This electrode was sensitized with 60 mg of the crude catalyst **2** and/or 6 mg photosensitizer **1** by soaking in a solution of 20 mL ethanol for 2 hours. It was then washed with ethanol and water for several times and dried in dark at room temperature to obtain working electrodes. The same sensitized films were also used in the electrochemistry studies.

S3 Optical and electrochemical data

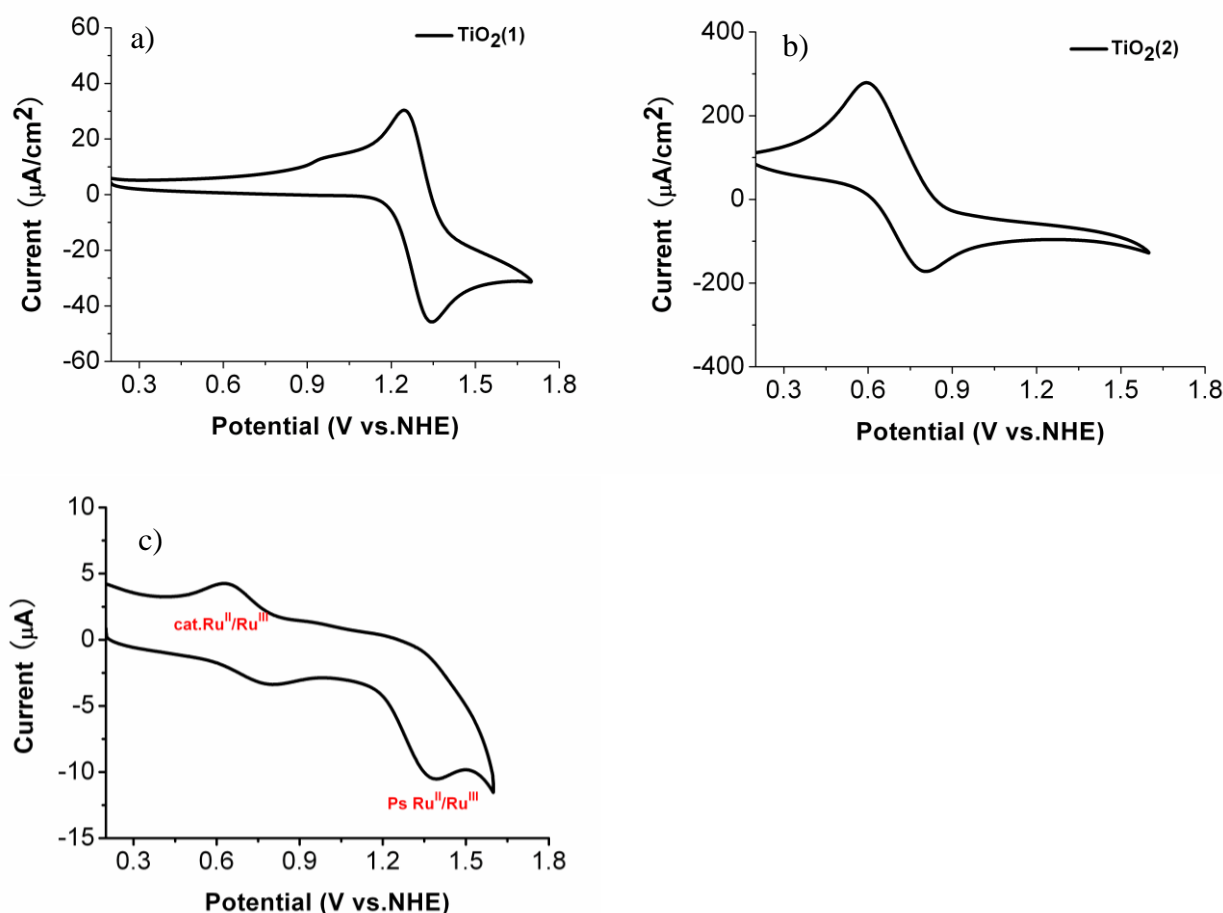


Figure S1. Cyclic voltammograms of the working electrodes TiO₂(1) (a) and TiO₂(2) (b) in

phosphate buffer solution (pH 6.8); (c) CV of the working electrode $\text{TiO}_2(1+2)$ in CH_3CN .

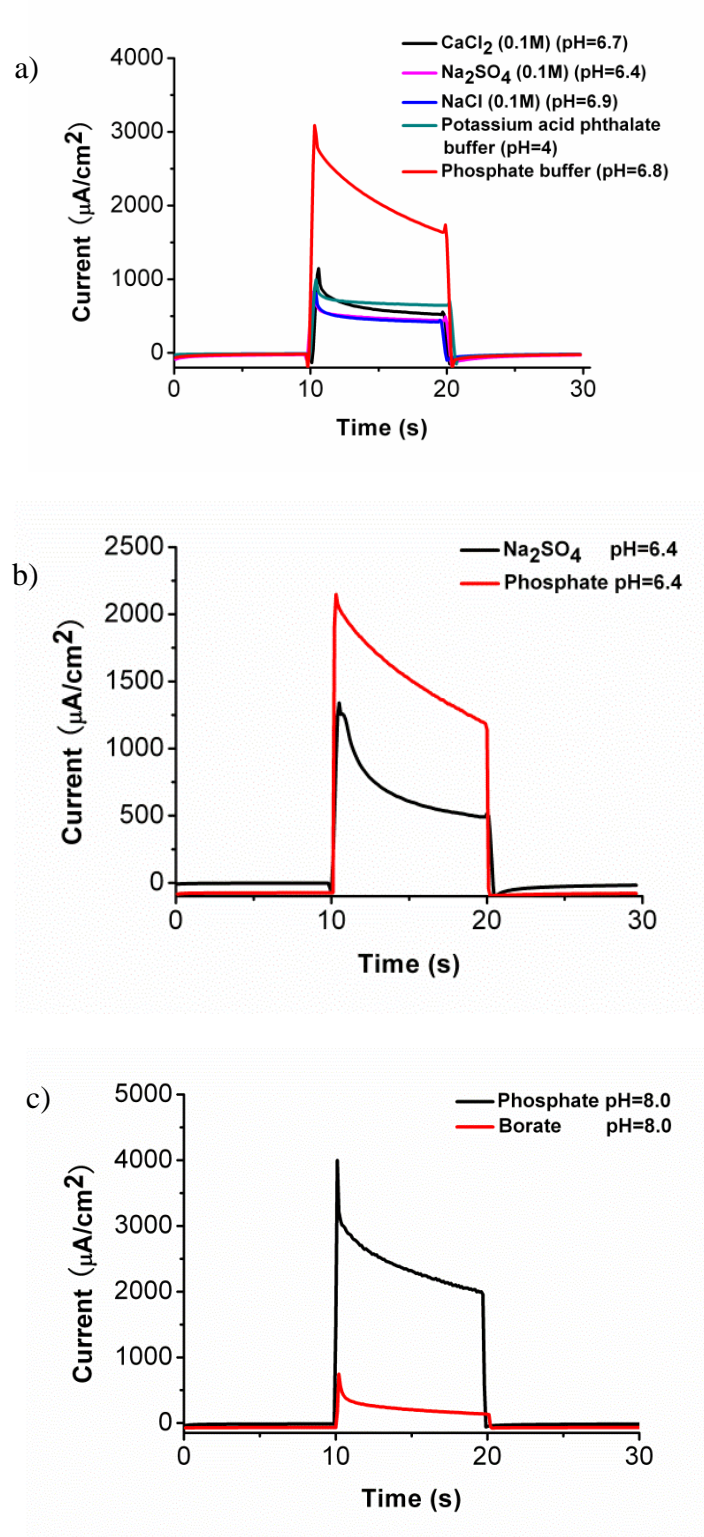


Figure S2. Three-electrode light control photocurrent measurements with a 0.2 V vs. NHE external bias for working electrode $\text{TiO}_2(1+2)$ (0.8 cm^2) in different electrolytical solutions upon illumination with a 500 W xenon lamp white-light source coupled to a 400 nm long-pass filter (300

mW/cm²). a) In different electrolytical solutions; b) In 0.1 M Na₂SO₄ aqueous and phosphate buffer at pH 6.4; c) In borate buffer and phosphate buffer at pH 8.0.

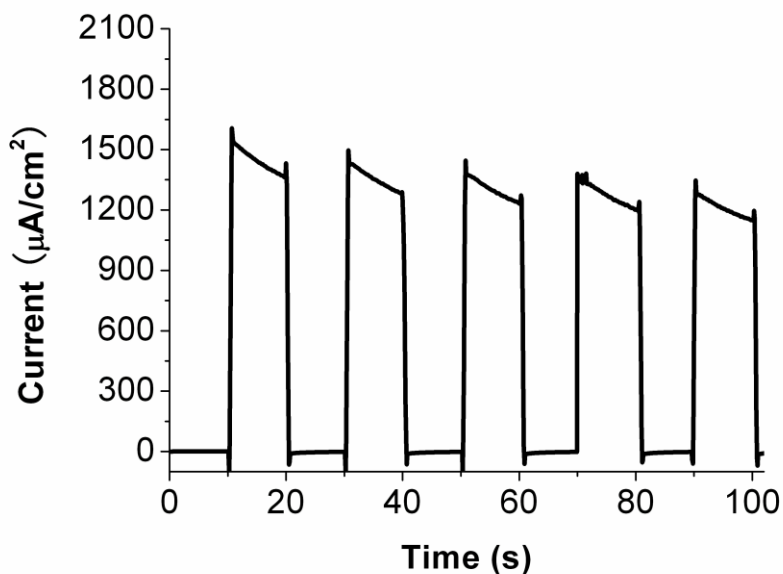
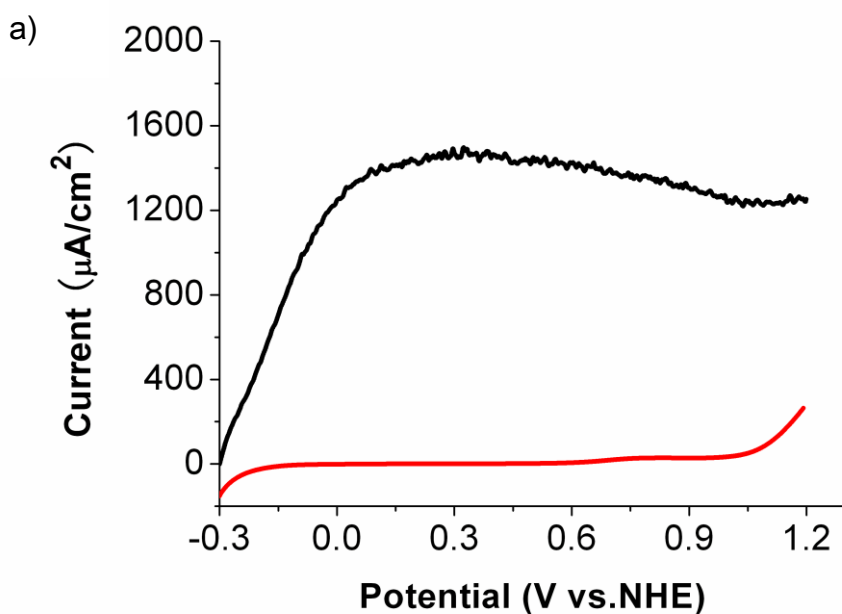


Figure S3. Three-electrode light control photocurrent measurements with a 0.2 V vs. NHE external bias for working electrodes (0.8 cm²) in pH = 6.8 phosphate buffer solution upon illumination with a 500 W xenon lamp white-light source coupled to a 400 nm long-pass filter (300 mW/cm²).



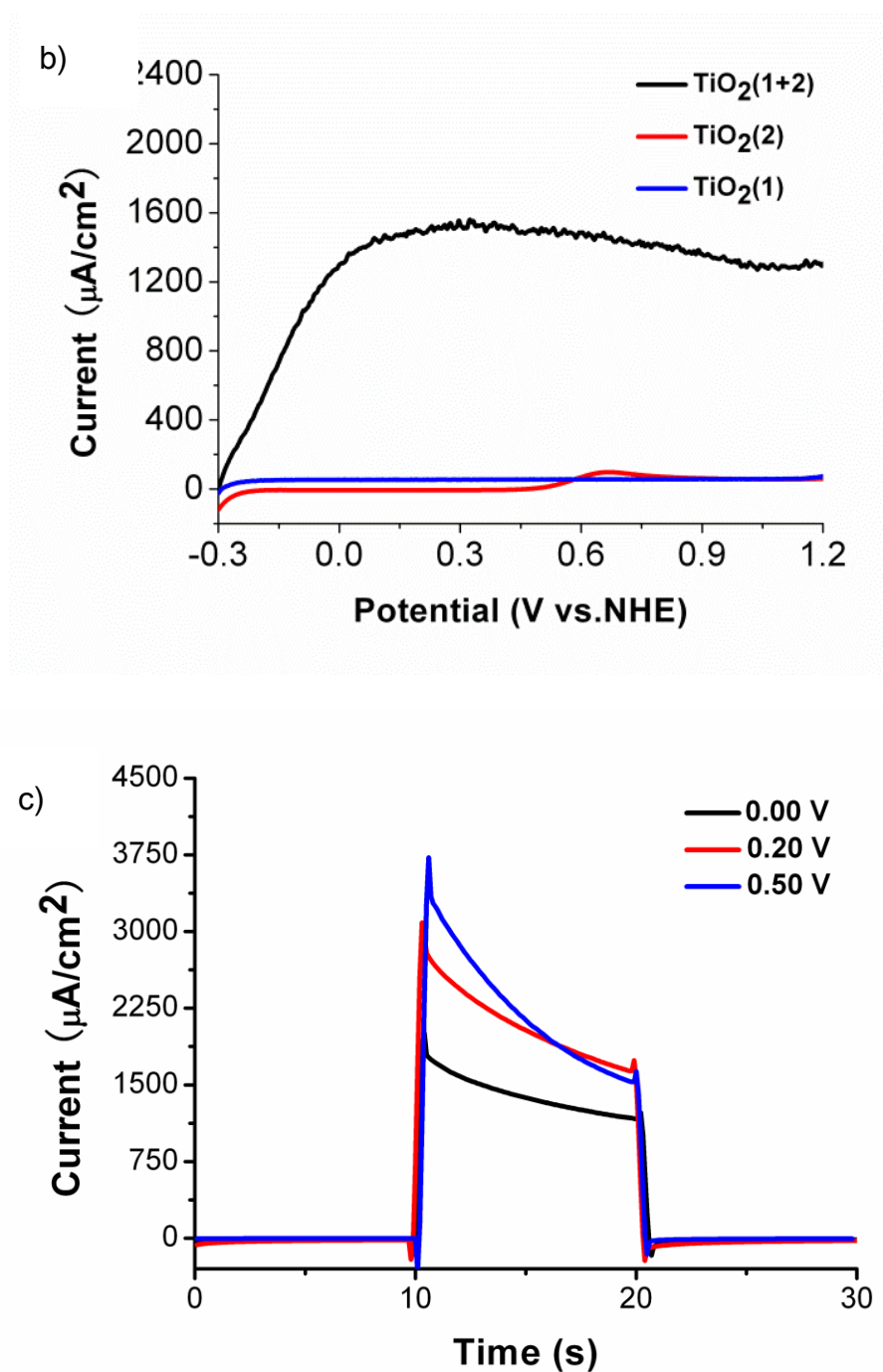


Figure S4. Cyclic voltammograms of the working electrodes in phosphate buffer solution, Ag/AgCl as reference electrode and Pt wire as counter electrode with a scan rate of 50 mV/s. (a) Working electrode TiO₂(1+2), in the dark (red line) and under the light illumination (black line); (b) Working electrodes under the light, TiO₂(1+2) (black line), TiO₂(1) (blue line) and TiO₂(2) (red line). (c) Working electrode TiO₂(1+2), with applied external bias of 0 V (black line), 0.2 V (red line), 0.5 V (blue line) (vs. NHE).

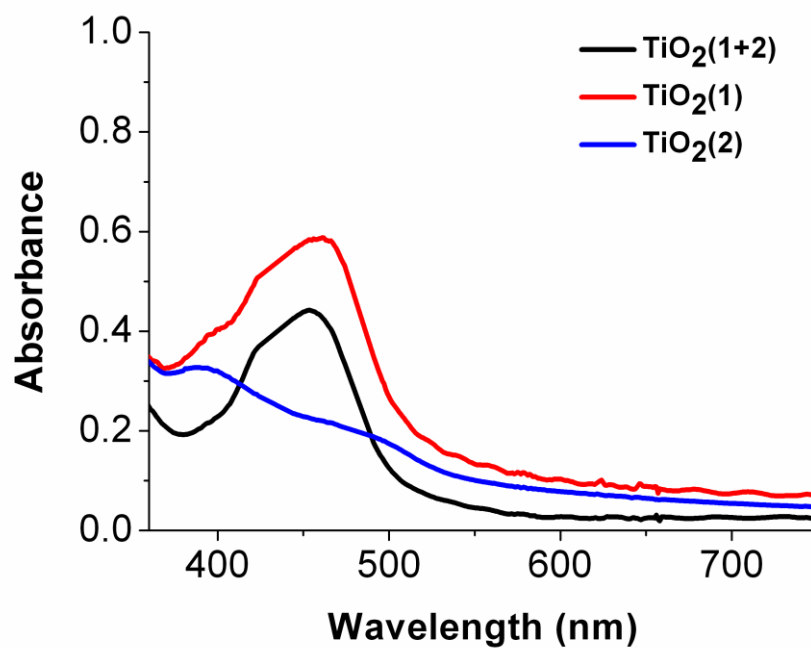


Figure S5. UV-Vis absorption spectra of TiO₂(2) (blue line), TiO₂(1) (red line), TiO₂(1+2) (black line) films.

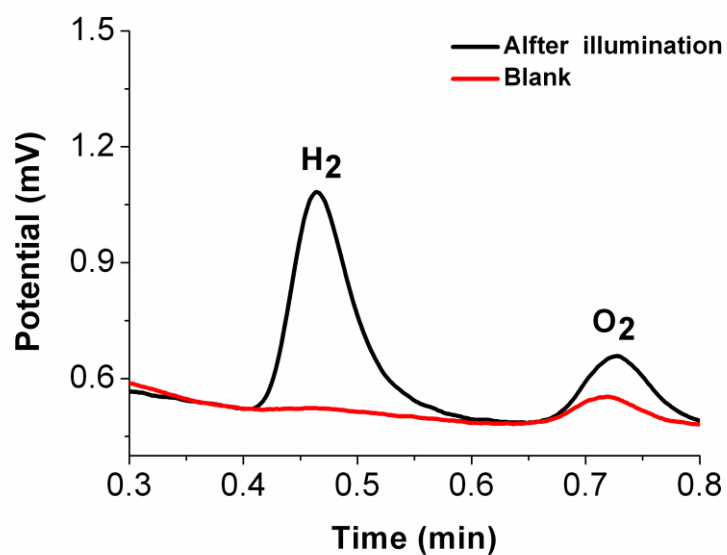


Figure S6. GC data for the PEC cell after light illumination, the first peak was ascribed to hydrogen and the second for oxygen.

References

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