Supporting Information

Instruments

^{1}H NMR spectra were collected at 298 K using AVANCE III 400NMR (Bruker). UV-Vis absorption measurements were performed on Lambda 750 spectrophotometer (PerkinElmer). XRD was performed with Shimadzu XRD-6000 X-ray diffraction instrument with Cu Kα radiation. X-ray photoeletron spectroscopy (XPS) was performed on ESCALAB-250 spectrometer (Thermo, America) using an Al−Kα source and a surface analysis system (PHI 5700 ESCA, America). The surface photovoltage (SPV) spectra were recorded on an instrument assembled by a monochromator (SBP300, China) equipped with xenon lamp (500 W) and the lock-in amplifier (SR830, Stanford) for signal collection. The sample was FTO/SnO_2/**1** or FTO/SnO_2/**1**+**3** electrode, in which the conductive FTO was well earthing. The monochromatic light was used to excited the sample to generate the charge separation, and metallic grid probe connected with the lock-in amplifier was employed to detect the photovoltage of the surface of the SnO_2/**1** film or SnO_2/**1**+**3** film.

Synthesis

Porphyrin **1**[1], compound **3**[2], Ru(bda)DMSO(4-picoline)[3] and ligand 3-N-(pyridin-4-ylmethylene)aminopropyltriethoxysilane[4] were prepared according to the published procedure, respectively. All of the ^{1}H NMR spectra for the above four compounds were in consistent with the reported data in the literature. Catalyst **2** was synthesized according to the procedure for similar ruthenium complex in the literature.[3] A mixture of Ru(bda)DMSO(4-picoline) (104 mg, 0.2 mmol) and the ligand 3-N-(pyridin-4-ylmethylene)-aminopropyltriethoxysilane (62 mg, 0.2 mmol) in methanol (40 mL) was refluxed for 8 hours under Ar atomsphere. As reported by the literature,[3] catalyst **2** was difficult to be purified due to the silicon group which had a strong adsorption on silica gel while running column chromatography. The reaction solution of **2** had to be used directly in the next operation.

Esterification of **3** (100 mg, 0.27 mmol) with CH_3OH (15 mL) in the presence of concetrated H_2SO_4 (0.2 mL) was carried out under reflux for 12 h. The reaction solution was cooled to room temperature and then neutralized with NaOH. The crude product was extracted with ethyl acetate and purified by chromatography column on silica gel using ethyl acetate as eluent. The ^{1}H NMR spectrum of the esterified product **3**-$COOCH_3$ was in consistent with the data for the same compound published in the literature.[5]

Praparation of SnO_2 powder

$SnCl_2 \cdot 4H_2O$ (3 g) was suspended in DI water (10 mL) under stirring. The color of the suspension was changed to pale yellow after 20 mL of HNO_3 was added dropwise. The reaction mixture was then neutralized with aqueous ammonia to form the white gel. DI water (50 mL) was added to the above gel that was mixed by sonication. The water was decanted after centrifugation. This sonication-centrifugation process was repeated for three times to remove the Cl^- ion. Finally, about 70 mL of the water-gel mixture was transferred into autoclave, which was heated at 200 ℃ for 24 h. The white solid was collected by centrifugation and dried under vacuum at 60 ℃ for 8 hours, which was then calcined at

400 ℃ for another 2 hours in the air atmosphere to get the white powder.

Photoanode fabrication

SnO_2 film with thickness of 10 μm was deposited onto FTO substrate by screen-printing with active area of 1×1 cm^2. The SnO_2 electrode was first immersed in a solution of **1** in CH_3OH (0.2 mM) in the dark for 12 hours and rinsed with CH_3OH. It was then immersed in CH_3OH solution of **2** (ca. 5 mM) in the dark for 4 hours and rinsed with CH_3OH to give FTO/SnO_2/**1**+**2** electrode. For the electron mediator **3** incorporation, it was further immersed in a 3:2 (v/v) EtOH/H_2O solution of $ZrOCl_2$ (5 mM) for 2 hours and washed with EtOH/H_2O mixture. Connection of **3** via Zr^{4+} ion linkage was accomplished by soaking the above electrode in a solution of **3** (5 mM) in EtOH for another 2 hours and rinsed with EtOH.

Electrochemistry

CV experiments in KPi buffer solution were performed with FTO/SnO_2/**1** or FTO/SnO_2/**1+2** as working electrode, Ag|AgCl ($KCl_{sat.}$) as reference electrode, Pt wire as counter electrode. The electrolyte solution was degassed by bubbling with dry argon for 10 min before measurement.

CV measurement with **3**-$COOCH_3$ in CH_3CN was carried out in a three-electrode cell under argon. The working electrode was a glassy carbon disk (diameter 3 mm) and the auxiliary electrode was a platinum wire. The reference electrode was an Ag/Ag^+ electrode (0.01 M $AgNO_3$ in CH_3CN). A solution of 0.05 M *n*-Bu_4NPF_6 in CH_3CN was used as electrolyte.

Impedance spectra were obtained on CH Instrument 660E electrochemical potentiostat under under simulated sunlight illumination dark at a bias potential of 0.4 V (vs. Ag|AgCl) with frequency range of 100 mHz to 100 kHz and amplitude of 10 mV.

Photoelectrochemical measurements

The photoanode was placed in an H-configuration cell with Ag|AgCl (KClsat.) as reference electrode, Pt foil as counter electrode, and potassium phosphate-buffered (KPi) aqueous solution (pH = 6.86) as electrolyte that was degassed by bubbling with Ar for 30min before photolysis. The headspace of the cell was still protected by Ar during photolysis. A 500 W Xe lamp was used as the light source equipped with AM 1.5G filter (100 mW/cm^2). The I-T curves were recorded on a CH Instrument 660E electrochemical potentiostat. The formation of oxygen was confirmed qualitatively by a Clark-type oxygen electrode (Hansatech Instruments, Oxygraph OXYG1 and DW2/2 unit), to which 1 mL of KPi buffer solution was pre-added and bubbled with Ar to establish the zero calibration. The injection sample was taken from the electrolyte (0.5 mL) near the photoanode before and after photolysis, respectively.

References

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3. Y. Gao, X. Ding, J. Liu, L. Wang, Z. Lu, L. Li and L. Sun , *J. Am. Chem. Soc.*, 2013, **13**5, 4219.
4. M. H. W. Lam, D. Y. K. Lee, K. W. Man and C. S. W. Lau, *J. Mater. Chem.*, 2000, **10**, 1825.
5. Y. Zhao, J. R. Swierk, J. D. Megiatto Jr, B. Sherman, W. J. Youngblood, D. Qin, D. M. Lentz, A. L. Moore, T. A. Moore, D. Gust and T. E. Mallouk, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 39.

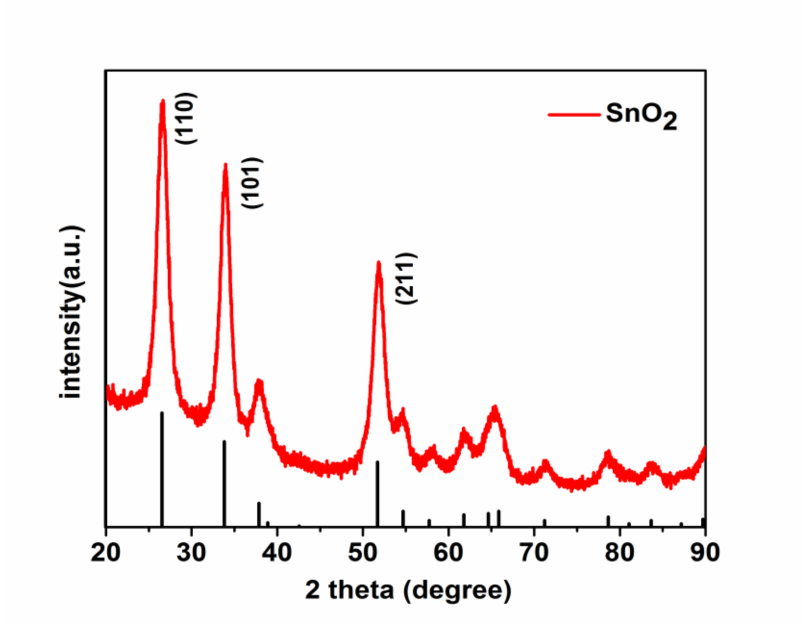

Figure S1. XRD pattern of SnO_2 powder.

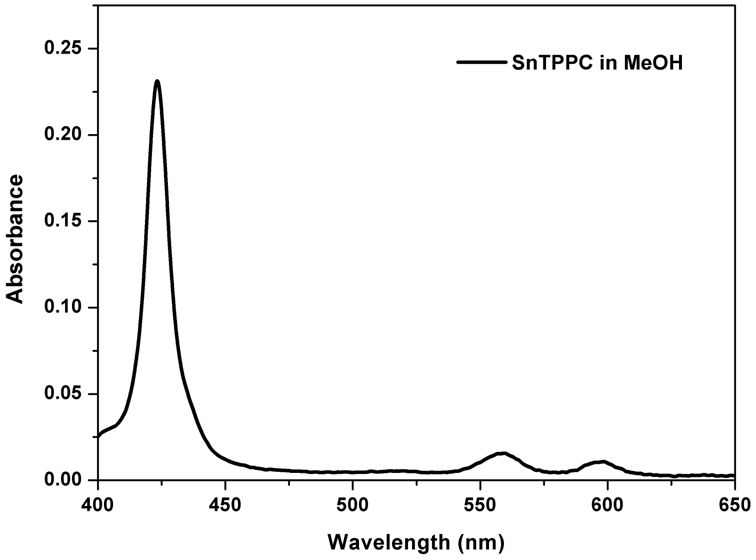

Figure S2. UV-Vis absorption spectra of **1** in MeOH solution.

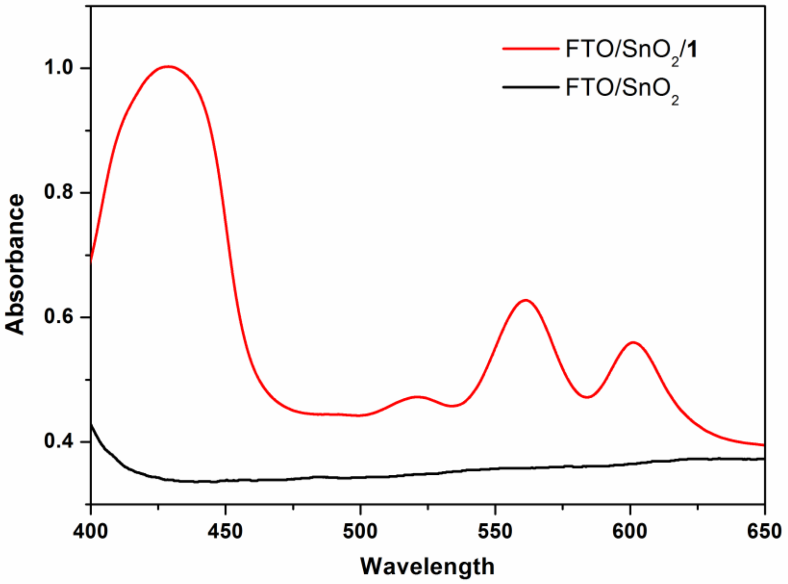

Figure S3. UV-Vis absorption spectra of FTO/SnO_2 (black) and FTO/SnO_2/**1** (red) electrodes.

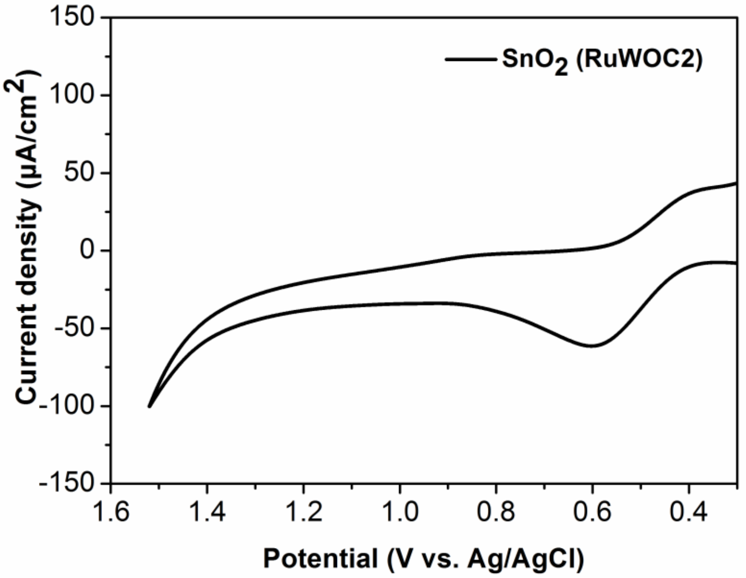

Figure S4. CV of FTO/SnO_2/**2** in KPi buffer solution (pH = 6.86).

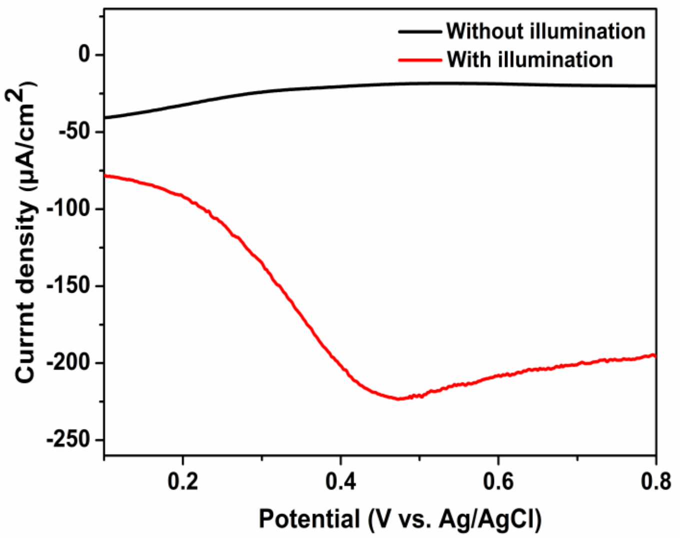

Figure S5. LSVs of FTO/SnO_2/**1**+**2** photoanode in KPi buffer solution (pH = 6.86) with light illumination (red) and under dark (black).

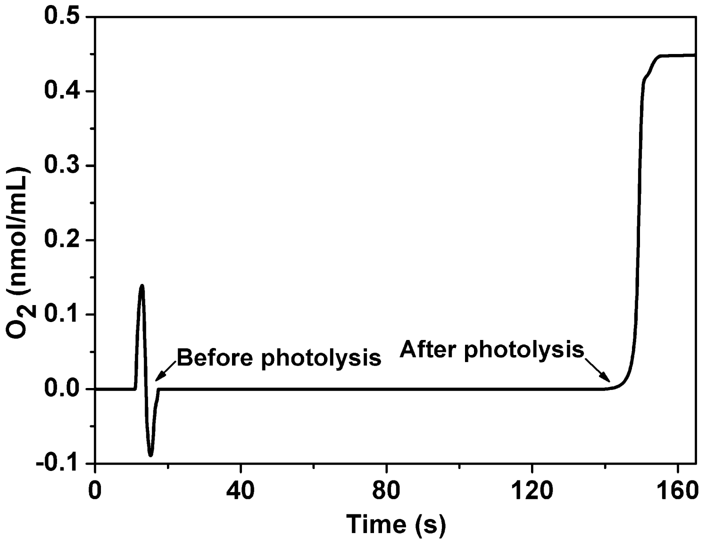

Figure S6. O_2 generation by photo-irradiation of FTO/SnO_2/**1**+**2** photoanode in KPi buffer solution (pH = 6.86) with a bias of 0.4 V (vs. Ag|AgCl).

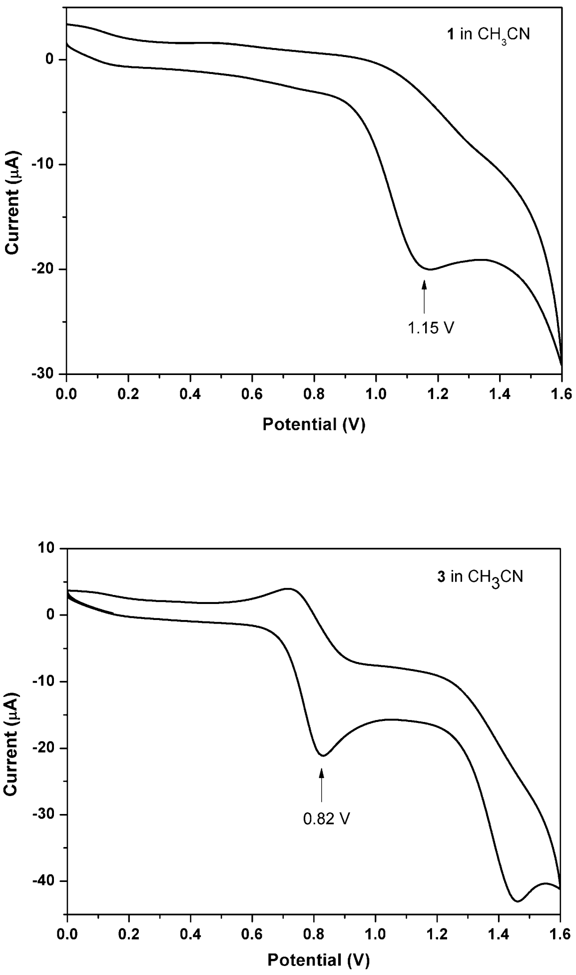

Figure S7. CV of **1** (top) and **3** (bottom) in CH_3CN. The reference electrode was an Ag/Ag^+ (0.01 M $AgNO_3$ in CH_3CN) electrode.

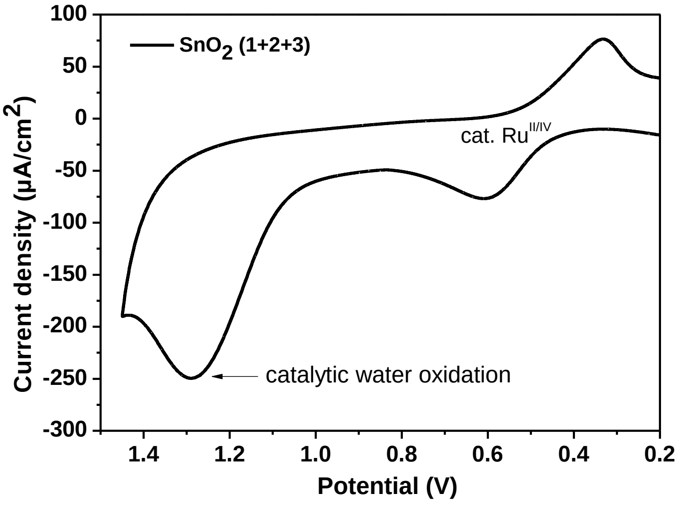

Figure S8. CV of FTO/SnO_2/**1**+**2**+**3** photoanode in KPi buffer solution (pH = 6.86) by three-electrode system in the dark.

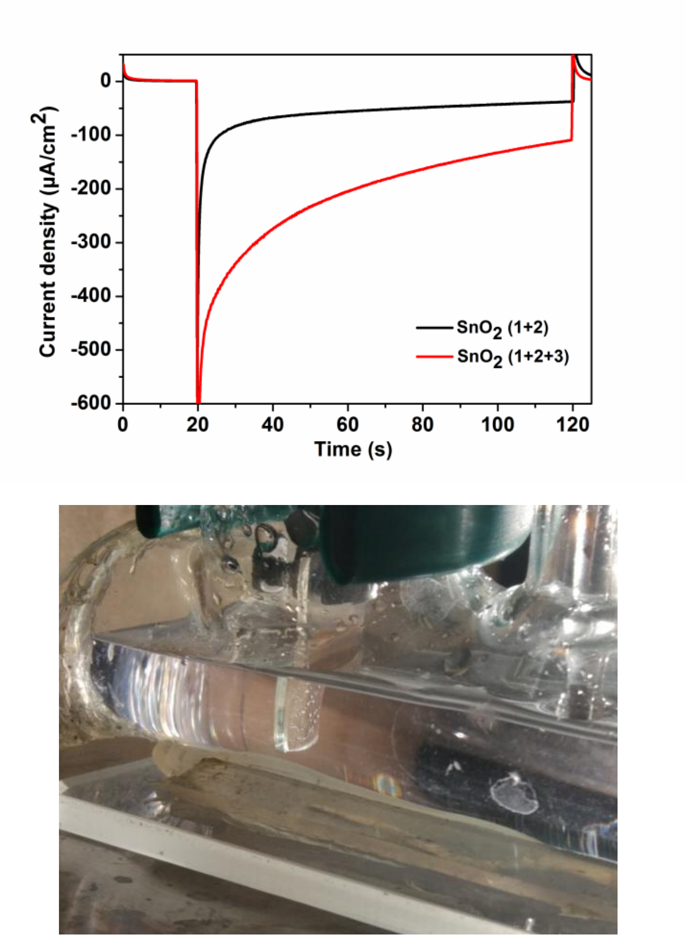

Figure S9. Top: I-T curves of FTO/SnO$_2$/**1+2** **(**black) and FTO/SnO$_2$/**1+2+3** (red) photoanode in KPi buffer solution (pH = 6.86) under light illumination with a bias of 0.4 V (vs. Ag|AgCl). Bottom: Photograph of oxygen bubbles on FTO/SnO$_2$/**1**+**2**+**3** photoanode.

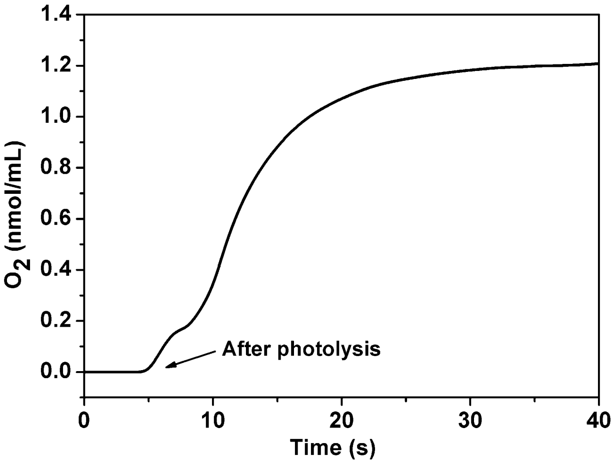

Figure S10. O$_2$ generation by photo-irradiation of FTO/SnO$_2$/**1+2+3** photoanode in KPi buffer solution (pH = 6.86) with a bias of 0.4 V (vs. Ag|AgCl). Due to the reason that the baseline would be interrupted by fast injection, the sample injection for this measurement was a little slower than that demonstrated in Figure S6.