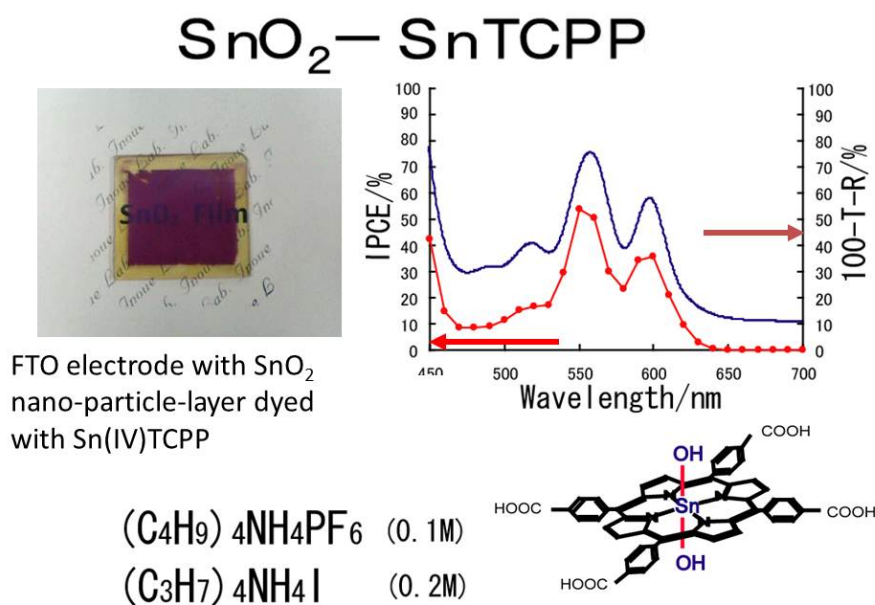


## Hydrogen Evolution Coupled with the Photochemical Oxygenation of Cyclohexene with Water Sensitized by Tin(IV) porphyrins by Visible Light

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### Electronic Supporting Information – 1

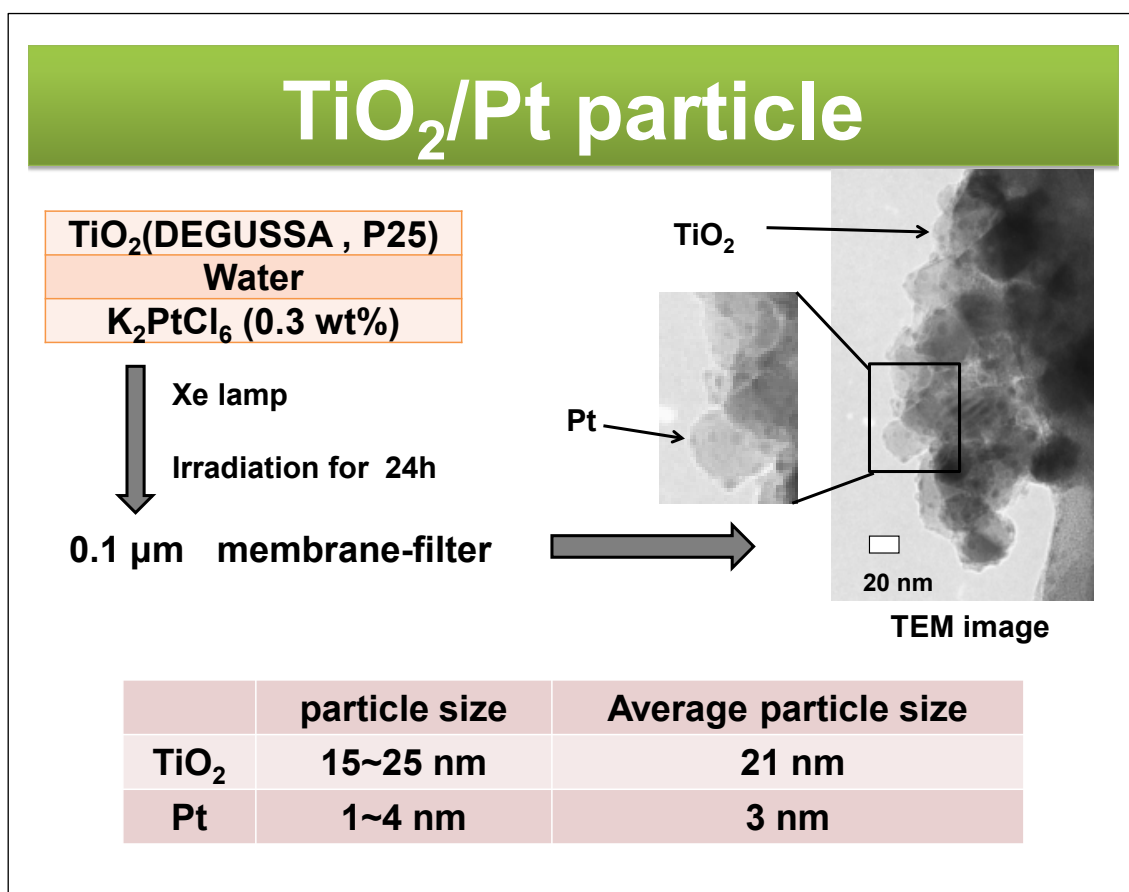
IPCE (Incident photon to current conversion efficiency) data of SnTCPP on SnO<sub>2</sub>.



The IPCE measurements were carried out by a photoelectrochemical setup described in the Experimental of Electronic Supporting Information (ESI-4). Tetrabutyl ammonium hexafluorophosphate (0.1M) as a supporting electrolyte and tetrapropylammonium iodide (0.2 M) was an electron mediator were used in acetonitrile. The above figure (right) shows IPCE values (red colored) and absorption character of Sn TCPP/SnO<sub>2</sub>/FTO electrode (blue colored).

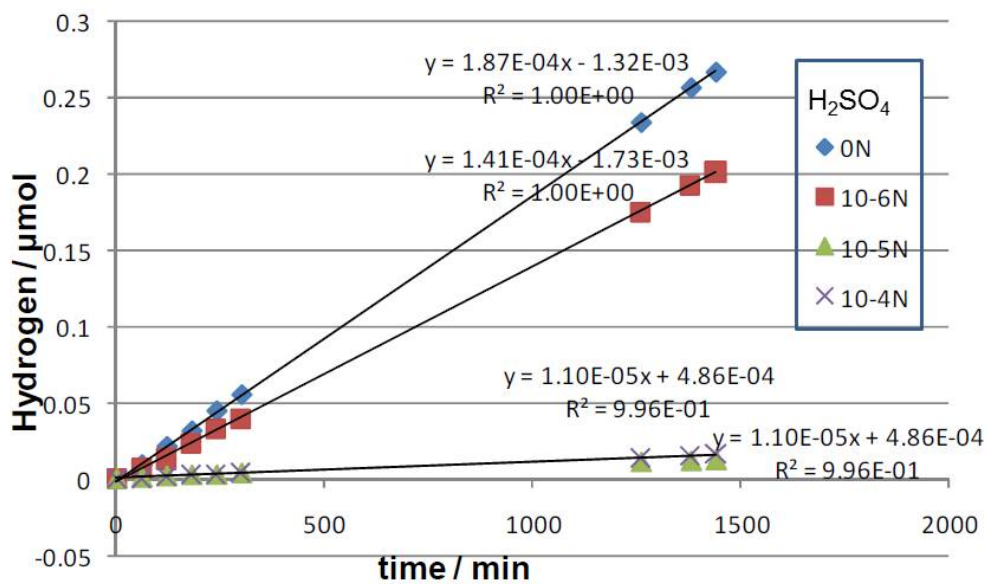
Electronic Supporting Information – 2

TEM image of the Pt loaded  $\text{TiO}_2$

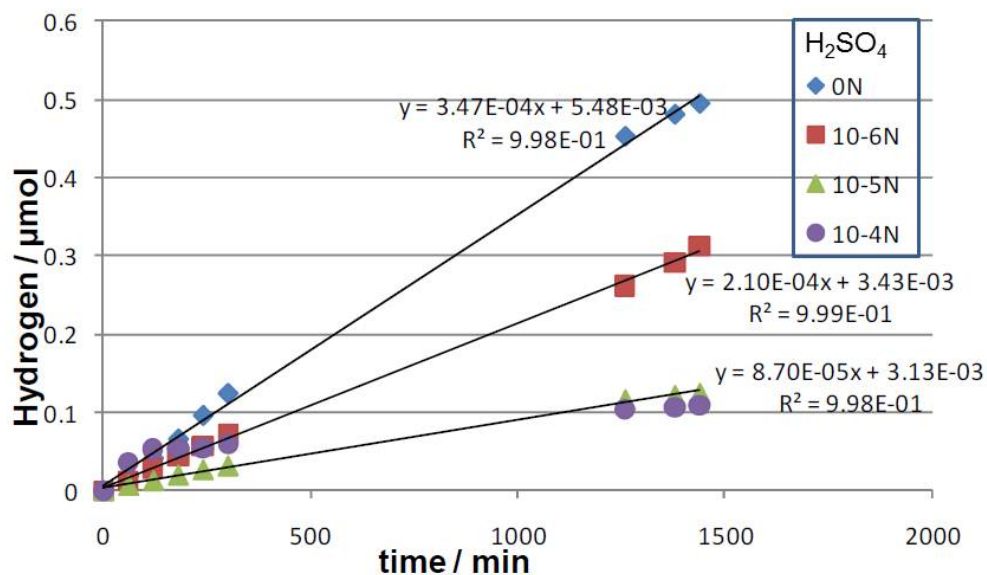


The detail of the preparation is described in the Experimental of the Electronic Supporting Information (ESI-4).

Electronic Supporting Information – 3



ESI-3 (a) Hydrogen evolution upon visible light ( $\lambda = 430\text{nm}$ , 8.3 mW) irradiation of SnTCPP/Pt/TiO<sub>2</sub> system (0.28 mmol of Sn(IV)TCPP/ 1g of Pt/TiO<sub>2</sub> (DEGUSSA P-25)) in CH<sub>3</sub>CN/H<sub>2</sub>O (9/1) with various concentration of H<sub>2</sub>SO<sub>4</sub> (0-10<sup>-4</sup> M) (5 ml) in the presence of cyclohexene (0.1 M) under Ar atmosphere.



ESI-3 (b) Hydrogen evolution upon visible light ( $\lambda > 480\text{nm}$ ) irradiation of SnTCPP/Pt/TiO<sub>2</sub> system (0.28 mmol of Sn(IV)TCPP/ 1g of Pt/TiO<sub>2</sub> (DEGUSSA P-25)) in CH<sub>3</sub>CN/H<sub>2</sub>O (9/1) with various concentration of H<sub>2</sub>SO<sub>4</sub> (0-10<sup>-4</sup> M) (5 ml) in the presence of cyclohexene (0.1 M) under Ar atmosphere.

## Electronic Supporting Information-4

### Experimental

#### Materials

##### *Tetra(4-carboxy)phenylporphyrinatotin(IV) (Sn(IV)TCPP(OH)<sub>2</sub>)*

Free base of tetra(carboxy)phenylporphyrine (H<sub>2</sub>TCPP, 0.957 g, 1.21 mmol: Frontier Science Inc.) in methanol (500 ml) was treated with concentrated H<sub>2</sub>SO<sub>4</sub> (2.5 ml) under refluxed condition for 2 days. The reaction mixture was neutralized by adding 1M NaOH aqueous solution to precipitate purple crystal, methyl ester of H<sub>2</sub>TCPP (H<sub>2</sub>TCPP-Meester). The precipitate was filtered, once solubilized in CH<sub>2</sub>Cl<sub>2</sub>, washed well with pure water, and the resultant CH<sub>2</sub>Cl<sub>2</sub> solution was evaporated. The yield of H<sub>2</sub>TCPP-Meester was 0.986 g, 96.2 %. <sup>1</sup>H-NMR (270 MHz, CD<sub>3</sub>Cl, TMS): δ 2.80 (s, 2H, NH), δ 4.12 (s, 12H, Me), δ 8.29 (d, *J* = 8.2 Hz, 8H, m-phenyl), δ 8.45 (d, 2H, *J* = 8.2 Hz, 8H, o-phenyl), δ 8.82 (s, 8H, pyrrole). FAB-MS (*m*-nitrobenzylalcohol): *m/z* 847, (M+H). The obtained H<sub>2</sub>TCPP-Meester was used without further purification.

Insertion of Sn was carried out by the following procedures. H<sub>2</sub>TCPP-Meester (0.238 g, 0.284 mmol) and SnCl<sub>2</sub> (0.995 g, 5.25 mmol: Wako Chemicals) in dry pyridine (15ml) were refluxed for 35 min. The reaction mixture was cooled down to ambient temperature, poured into 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. The resultant mixture was washed well with 3N HCl aqueous solution, further with neutral water, and was dried by adding Na<sub>2</sub>SO<sub>4</sub>. The crude crystal obtained by an evaporation was purified by gradual crystallization from CH<sub>2</sub>Cl<sub>2</sub> (80 ml) covered with methanol over the CH<sub>2</sub>Cl<sub>2</sub> solution. After one week, needle crystal was obtained. The yield was 0.169 g, 58% as SnTCPP-meester(Cl)<sub>2</sub>. <sup>1</sup>H-NMR (270 MHz, CD<sub>3</sub>Cl, TMS): δ 4.14 (s, 12H, Me), δ 8.41 (d, *J* = 8.2 Hz, 8H, m-phenyl), δ 8.52 (d, *J* = 8.2 Hz, 8H, o-phenyl), δ 9.19 (s, 8H, pyrrole).

The obtained SnTCPP-Meester(Cl)<sub>2</sub> was hydrolyzed by NaOH. SnTCPP-Meester(Cl)<sub>2</sub> (0.169g, 0.187mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (200 ml) and was treated with 3M NaOH aqueous solution (200 ml) at ambient temperature for one day. The aqueous layer was separated and excess amount of 3N HCl aqueous solution was added to precipitate purple crystal. The crystal was washed well with water and dried. The yield was 0.116 g, 75 % as SnTCPP(OH)<sub>2</sub>. <sup>1</sup>H-NMR (270 MHz, D<sub>2</sub>O+NaOH, DSS): δ 8.35 (d, *J*=8.0 Hz, 8H, m-phenyl), δ 8.45 (d, *J*=8.0 Hz, 8H, o-phenyl), δ 9.36 (t, *J*=11.7 Hz(Sn-H), 8H, pyrrole). UV-vis: UV-vis: λ<sub>max</sub> = 420.5 nm, ε = 6.4 x 10<sup>5</sup> M<sup>-1</sup>cm<sup>-1</sup> in 10<sup>-3</sup>M NaOH aqueous solution.

***Semiconductor nano particles:***

TiO<sub>2</sub> (P25; Degussa) and SnO<sub>2</sub> nano particle ( $\phi$ ; 20~30 nm; CI Chemicals) were used as received.

***Platinum loading on TiO<sub>2</sub>:***

TiO<sub>2</sub> (1g) and K<sub>2</sub>PtCl<sub>6</sub> (7.37mg, 0.154 mmol) were dispersed in ion-exchanged water (200 ml) and sonicated for 2 hours. The mixture was light-irradiated with 500 W Xe lamp (Ushio-500DXO) through IR cut filter for 24 hours under vigorous stirring. The mixture was filtered through a hydrophilic membrane filter (pore size; 0.1  $\mu$ m) and the particles were washed well with water and vacuum dried. The yield was 0.891 g. The platinum loaded TiO<sub>2</sub> (TiO<sub>2</sub>/Pt) was observed by Transmitting Electron Micrography (TEM, JEOL, JEM-200FX, 200kV). The TEM image is shown in ESI-2.

***Preparation of semiconductor electrode on FTO:***

Transparent fluorine doped tin oxide electrode (FTO; TOUKI Co. Ltd.) was washed well with ion-exchanged water and was allowed to a surface cleaning by UV/Ozone method (UV/Ozone Cleaner, UV253E, Filgen) for 2 hours before the preparation of semiconductor electrode on FTO.

***SnO<sub>2</sub> loaded FTO electrode:*** SnO<sub>2</sub> particle (4g), ethanol (10ml), acetylacetone (0.4 g), Triton X (0.2 g), and 5 drops of HNO<sub>3</sub> were vigorously stirred for 30 min. The resultant paste was spread over FTO by a squeeze-method and was dried overnight. The SnO<sub>2</sub> loaded FTO electrode (SnO<sub>2</sub>/FTO) was heat-treated at 400 °C for 1 hour.

***TiO<sub>2</sub> loaded FTO electrode:*** The TiO<sub>2</sub>/FTO electrode was prepared with almost the same procedures with that for SnO<sub>2</sub>/FTO except the heat treatment at 450°C.

***Dye adsorption to the semiconductor electrode on FTO:*** SnO<sub>2</sub>/FTO and TiO<sub>2</sub>/FTO electrodes were each immersed in a saturated ethanol solution of SnTCPP(OH)<sub>2</sub> (~0.5 mg of SnTCPP(OH)<sub>2</sub> in 20 ml of ethanol) for 3 days with mild stirring. The dyed electrodes were washed well with ethanol and dried under vacuum. These electrodes were used for the photoelectrochemical measurements.

***Dye adsorption to TiO<sub>2</sub>/Pt particles (SnTCPP(OH)<sub>2</sub>/SnO<sub>2</sub>/Pt):*** SnTCPP(OH)<sub>2</sub> (0.5 mg), ethanol (50 ml), and H<sub>2</sub>SO<sub>4</sub> (10<sup>-5</sup> N) were heated to 70°C with stirring and the mixture was filtered through membrane filter (0.2  $\mu$ m). TiO<sub>2</sub>/Pt particles (5 mg) were added to the filtrate solution. The mixture was sonicated for one day, filtered by membrane filter (0.2  $\mu$ m), washed with water, and dried under vacuum.

***Photoelectrochemical experiment for the semiconductor loaded FTO electrode dyed with***

### ***SnTCPP(OH)<sub>2</sub>***

A specially designed four-necked cylinder type cell with flat windows was used for the photoelectrochemical experiment. The working TiO<sub>2</sub>/FTO or SnO<sub>2</sub>/FTO electrode was placed in tight contact with the flat window. Through three of the necks, lead wires were inserted and connected with working, reference, and counter electrodes. A Hokuto Denko HA1010mM1A electrochemical system was used for measuring the photocurrent. The dissolved oxygen was purged out by Ar gas bubbling for 1 hour and the photoelectrochemical cell was irradiated by visible light ( $\lambda = 420, 550$  nm) through each couple of interference filter (KL-43, Toshiba) with cut-off filter (VY-41, Toshiba) for  $\lambda = 420$  nm, and KL-55 with VY-53 for  $\lambda = 550$  nm from a 500-W Xe lamp (USHIO 500-DKO). The incident light intensity was determined using a power meter (ADVANTEST Optical Power Meter TQ8210). The reaction mixture after the photoreaction was vacuum-distilled and the products were analyzed by GC-MS spectroscopy. Gas chromatographic analyses were performed on a Shimadzu GC-17A equipped with a TC-17 column (GL Sciences Inc. 30m, 60-250C), and a mass spectrograph (Shimadzu QP-5000) as a detector. The practical detection limit of the GC-MS was ca. 10<sup>-7</sup> M. Quantitative analysis was carried out in the selected ion monitoring (SIM) detection mode.

### ***Photochemical evolution of hydrogen in SnTCPP(OH)<sub>2</sub>/TiO<sub>2</sub> dispersion system:***

The SnTCPP(OH)<sub>2</sub>/TiO<sub>2</sub>/Pt particles (0.5 mg), cyclohexene (0.1 M) in 9:1 CH<sub>3</sub>CN·H<sub>2</sub>O in the presence of H<sub>2</sub>SO<sub>4</sub> (0, 10<sup>-6</sup>, 10<sup>-5</sup>, or 10<sup>-4</sup> M) was placed in a quartz cell (1 x 1 x 4 cm) connected with a round glass tube sealed by a septum through which purging of the dissolved oxygen by Ar bubbling and the sealing-off were carried out. Gas samples were taken with a gas-tight syringe through the septum. The gaseous reaction products, H<sub>2</sub>, in the gas phase over the reaction mixture were detected by GC-TCD. The oxygenated products of cyclohexene were analyzed as described above.

### ***General Procedures:***

UV-visible spectra and diffuse reflectance spectrum were measured on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer. Oxidation potential of SnTCPP(OH)<sub>2</sub> was measured by cyclic voltammetry with a Hokuto Denko HA1010mM1A electrochemical system, with a boron doped diamond as a working electrode, Ag/AgCl a reference one, and Pt wire as a counter one in 2 x 10<sup>-4</sup>M NaOH aqueous solution containing 0.1 M supporting electrolyte, Na<sub>2</sub>SO<sub>4</sub>. An Nd<sup>3+</sup>YAG laser-pumped OPG (EKSPLA, PL2143B + PG401; FWHM 25 ps, 5 Hz) as the excitation source for measuring the fluorescence lifetime of

SnTCPP(OH)<sub>2</sub>. The fluorescence was monitored by a streak camera (Hamamatsu, C4334) equipped with a polychromator (CHROMEX, 250IS). All spectral measurements were carried out at room temperature (294 K). Gas chromatographic analyses were performed on a Shimadzu GC-9A equipped with a 13X column. Fast atom bombardment (FAB) mass spectra were measured on a JEOL JMS-LX1000 instrument with the use of *m*-nitrobenzyl alcohol matrix. <sup>1</sup>H-NMR spectra were measured on JEOL JNM-EX270 and JNM-AL400 spectrometers. Liquid chromatography was carried out with an electrospray ionization-mass spectroscopic (ESI-MS) detector (Shimadzu LCMS-2010).