## **Supporting Information**

# Efficient Hydrogen Peroxide Synthesis by Metal-free Polyterthiophene via Photoelectrocatalytic Dioxygen Reduction

Wenjun Fan,<sup>ab</sup> Bingqing Zhang,<sup>ab</sup> Xiaoyu Wang,<sup>c</sup> Weiguang Ma,<sup>a</sup> Deng Li,<sup>a</sup> Zhiliang Wang,<sup>a</sup> Michel Dupuis,<sup>c</sup> Jingying Shi,\*<sup>a</sup> Shijun Liao,\*<sup>b</sup> and Can Li\*<sup>a</sup>

<sup>a</sup> State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China.

<sup>b</sup> The Key Laboratory of Fuel Cell Technology of Guangdong Province & The Key Laboratory of New Energy Technology of Guangdong University, School of Chemistry and Chemical Engineering, South China University of TecFhnology, Guangzhou 510641, Guangdong, China.

<sup>c.</sup> Department of Chemical and Biological Engineering, University at Buffalo, State University of New York Buffalo, NY 14260, USA

Corresponding authors:

E-mail: jingyingshi@dicp.ac.cn (Jingying Shi), chsjliao@scut.edu.cn (Shijun Liao), canli@dicp.ac.cn (Can Li)

#### 1. Materials

All chemicals were used without further purification unless otherwise stated.

A CHI 760E potentiostat was used for the photoelectrochemical and electrochemical experiments. A rotating disk electrode/rotating ring-disk electrode (RDE/RRDE) with a disk area of 0.247 cm<sup>2</sup> was used for the photoelectrochemical and electrochemical ORR test. Carbon paper (CP) was cleaned with acetone, then with ethanol at 80 °C and washed with distilled water. For the pH dependent experiments, electrolytes with different pH values were prepared by selecting the appropriate buffer solution that would provide buffering capacity for the required pH range. The ion strength was kept constant at 0.1 M. At pH 4.0-9.4, phosphate buffer could be obtained by mixing sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>) with sodium phosphate dibasic (Na<sub>2</sub>HPO<sub>4</sub>); while at pH<4.0, solutions were prepared with 5M H<sub>2</sub>SO<sub>4</sub> adding into 0.1 M NaH<sub>2</sub>PO<sub>4</sub> solution. For electrolytes of pH>9.4, 5M KOH was added to 0.1 M Na<sub>2</sub>HPO<sub>4</sub> solution to tune the pH.

# 2. Methods

#### **Preparation of pTTh electrodes**

pTTh electrode was prepared using TTh as the monomer by electropolymerization method. The electropolymerization method has been proven to be an especially useful approach for the preparation of electroactive and conducting polymer films. Generally, the precursors are oxidized electrochemically and the coupling reaction between the precursors occurs at the electrode surface with deposition of the polymer film onto the electrode. In this work, polymerization of TTh on disk electrode was conducted in a three-electrode cell with a saturated calomel electrode (SCE) reference electrode and a Pt foil counter electrode. Before polymerization, the GC electrode was polished using

aqueous alumina suspension on felt polishing pads and then washed with copious of water, blow with compressed air. The polymerization was proceeded in the acetonitrile solution containing 30 mmol L<sup>-1</sup> TTh monomer and 0.1 M LiClO<sub>4</sub>. Prior to polymerization, the solution was purged with argon gas for 1h, and subsequently performed cyclic voltammetry between 0 and 1.2 V at a scan rate of 50 mV s<sup>-1</sup> for 30 cycles. The pTTh electrode was then rinsed with acetonitrile solution and water, followed by drying in air. Polymerization of TTh on CP was the same as that on disk electrode. Except that a larger Pt foil counter electrode was used to enable the uniform electropolymerization on the working electrode. For comparison, graphite rod counter electrode was also used for the electropolymerization of pTTh to rule out the influence of Pt. The Inductively Coupled Plasma (ICP) of the resulting pTTh shows only 0.02 ppm of Pt, which is nearly neglectable. In addition, during the electropolymerization and the growth of pTTh, the reaction on the Pt counter electrode is a reduction reaction, which means that Pt is hardly been oxidized and redeposited on the pTTh surface. The photoelectrochemcial performance of pTTh electropolymerized from graphite rod counter electrode exhibited a similar selectivity and activity (Figure S25), elucidating the use of Pt does not influence the conclusion of our work.

## **Preparation of BiVO<sub>4</sub> electrodes**

The BiVO<sub>4</sub> electrodes were fabricated according to the methods reported elsewhere<sup>1, 2</sup> with a few modifications. The FTO substrate was rigorously washed with acetone, isopropyl ethanol, ethanol and distilled water, respectively. Then, the FTO substrate was purged with compressed gas. The BiOI precursor for BiVO<sub>4</sub> electrode was electrodeposited on the FTO substrate in a three-electrode cell with a saturated SCE reference electrode and a Pt counter electrode. The deposition solution was prepared by mixing 50 mL of pH 1.2 HNO<sub>3</sub> aqueous solution containing 0.03 M Bi(NO<sub>3</sub>)<sub>3</sub> and 0.4 M NaI, with 20 mL of 0.3 M p-benzoquinone in ethanol, and was vigorously stirred for a few minutes. To ensure even deposition, an initial 10 s cathodic deposition was performed potentiostatically at -0.35 V vs SCE without stirring, with the reference electrode being placed right behind the glass side of FTO working electrode at a distance of ca. 2 cm. Subsequently, the electrode was conducted at -0.15 V vs SCE at a total charge of 0.3 C cm<sup>-2</sup> to complete the deposition, and then rinsed with Milli-Q water and dried in air.

 $0.05 \text{ mL cm}^2$  of a dimethyl sulfoxide (DMSO) solution containing 0.4 M vanadyl acetylacetonate (VO(acac)<sub>2</sub>) was placed on the BiOI electrode with drop-casting and was transferred into a muffle furnace preheated to 120 °C. The annealing temperature was first raised to 280 °C with a ramping rate of 1 °C min<sup>-1</sup>, further to 450 °C with a ramping rate of 2 °C min<sup>-1</sup>, and was held at 450 °C for 2 h. Excess V<sub>2</sub>O<sub>5</sub> present in the BiVO<sub>4</sub> was removed by soaking them in 0.1 M NaOH solution for 10 min with gentle stirring. The resulting pure BiVO<sub>4</sub> electrodes were rinsed with Milli-Q water and dried in air.

## Photo-assisted electrodeposition of cocatalyst on BiVO<sub>4</sub> electrodes

NiFeO<sub>x</sub>-B<sub>i</sub> was deposited in a three-electrode cell containing a solution of 0.8 mmol L<sup>-1</sup> iron (II) acetate and 0.8 mmol L<sup>-1</sup> nickel (II) acetate in 0.125 mol L<sup>-1</sup> potassium borate buffer. Prior to the photodeposition, the solution was purged with argon gas for 1 h. A three-electrode cell was used for deposition which was composed of a BiVO<sub>4</sub> working electrode, a Pt counter electrode, and a saturated

SCE reference electrode. The BiVO<sub>4</sub> electrode was activated by performing cyclic voltammetry between 0 and 1 V vs RHE at a scan rate of 100 mV s<sup>-1</sup> for 10 cycles in the dark. At a bias of -0.35 V vs SCE under AM 1.5 1 sun irradiation (back illumination), NiFeO<sub>x</sub>-B<sub>i</sub> cocatalyst was deposited on BiVO<sub>4</sub> electrode passing a total charge of 25 mC cm<sup>-2</sup>. The BiVO<sub>4</sub> electrode was then rinsed with Milli-Q water and dried in air.

## 3. Characterization

## Materials Characterization

The UV-visible (UV-vis) diffuse reflectance spectra were recorded on a UV-vis spectrophotometer (JASCO V-550) equipped with an integrating sphere. X-ray powder diffraction (XRD) was characterized on a Rigaku D/Max-2500/PC power diffractometer using Cu K $\alpha$  radiation (operating voltage: 40 kV, operating current: 200 mA, scan rate: 5° min<sup>-1</sup>). The morphologies of the electrodes were performed by a Quanta 200 FEG scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (accelerating voltage of 20 kV). TEM micrographs were taken on a FEI Tecnai G<sup>2</sup> F30 transmission electron microscope. The zeta-potential was detected by Zetasizer Nano ZS 90 (Marvern Instruments Corporate).

## Mott-Schottky analysis

Electrochemical impedance spectroscopy (EIS) was conducted on the film electrodes on glassy carbon (GC) substrate using a Princeton PARSTAT<sup>TM</sup> MC to obtain Mott-Schottky plots. The EIS measurements were conducted in a 0.1 M KOH solution with AC amplitude of 10 mV at each applied potential with frequency 500 Hz. Using the Boltzmann distribution to describe the distribution of electrons in the space charge region and Gauss' law relating the electric field through the interface to the charge contained within that region, Poisson's equation can be solved to give the Mott-Schottky equation (1):

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} \left( V - V_{fb} - \frac{k_B T}{e} \right) \tag{1}$$

Here *C* and *A* are the interfacial capacitance and area, respectively,  $N_D$  the number of donors, *V* the applied voltage,  $k_B$  is Boltzmann's constant, *T* the absolute temperature, and *e* is the electronic charge. Therefore, a plot of  $1/C^2$  against V should yield a straight line from which  $V_{fb}$  can be determined from the intercept on the *V* axis. The value of  $N_D$  can also be conveniently found from the slope knowing  $\varepsilon$  and A.

# HOMO-LUMO test

The electrochemical properties were measured by cyclic voltammetry experiment to determine the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energy level of pTTh. The voltammogram experiments were carried out in acetonitrile solution

containing 0.1 M of Tetrabutylammonium Perchlorate as the supporting electrolyte. The energy level of pTTh were estimated by using the ferrocene/ferrocenium ion  $(Fc/Fc^+)$  as the internal standard.

#### Electrochemically active surface area (ECSA) measurements

The electrochemical double layer capacitance ( $C_{dl}$ ) of the resulting catalysts was determined to estimate the ECSA of the catalysts within a potential window without faradaic response. Typically, a series of CV curves were obtained at various scan rates (5, 10, 20, 50, 100 mV s<sup>-1</sup>) within the potential range of 0.05-0.15 V (*versus* SCE). The working electrode was held at each potential vertex for 10 s before beginning the next step. The double layer charging current is equal to the product of the scan rate, *v*, and the electrochemical double layer capacitance,  $C_{DL}$ , as given by equation (2):

 $i_c = v C_{DL}$  (2)

The ECSA of the material is calculated from the double-layer capacitance:

 $ECSA = C_{DL}/C_s \qquad (3)$ 

where  $C_s$  is the specific capacitance of the sample of the material. Given that the pTTh material belongs to the doped carbon material, we used the specific capacitance of 22  $\mu$ F cm<sup>-2</sup> based on the typical reported value for carbon in alkaline solutions.<sup>3, 4</sup> It is noted that even though the chosen specific capacitance values may vary, they are still within the +/- order of magnitude.

#### Photoelectrochemical test

All of the photoelectrochemical performance were measured in a three-electrode system with a potentiostat (Iviumstat, Ivium Technologies). The PEC performance of pTTh electrode was evaluated using the custom-made rotating disk electrode/rotating ring-disk electrode (RDE/RRDE) system where the irradiation from Xenon lamp at the electrode surface was 100 mW cm<sup>-2</sup> by the Newport light intensity meter. For the BiVO<sub>4</sub> electrodes, the PEC performance was evaluated under simulated AM 1.5G light irradiation (100 mW cm<sup>-2</sup>, Newport Sol 3A, Class AAA Solar simulator). The fabricated electrode, a platinum electrode, and SCE were used as working, counter and reference electrodes, respectively. All measured potentials were converted to V *vs*. RHE ( $E_{RHE}=E_{SCE}+0.059$  V × pH + 0.24 V).

# Rotating disk electrode (RDE) test

For the RDE measurements, pTTh polymerized on disk electrode was prepared by the method as described before. The RDE measurements were carried out using an RDE system (Pine research Instrumentation, USA) coupled with an electrochemical workstation (Ivium, Netherlands). The ORR performance of pTTh was studied using linear sweep voltammetry (LSV) at a scan rate of 10 mV s<sup>-1</sup> and at different disk rotation rates. All current densities were normalized to the geometric area of the RDE. The electron transfer number per oxygen molecule involved was calculated based on the Koutecky-Levich (K-L) equation (Equation (4)), where *J* is the measured current,  $J_k$  is the kinetic-limiting current, and  $\omega$  is the electrode rotation rate. By changing the electrode rotation rate, we

obtained a series of current values (*J*). A linear plot could then be obtained by plotting *J* versus  $\omega$ . The electron transfer number (*n*) per oxygen molecule involved could be calculated from the slope (*B*) of the linear plot (Equation (5)), where *n* is the overall number of transferred electrons in the ORR process, *F* is the Faradaic constant (96485 C mol<sup>-1</sup>),  ${}^{C_{O_2}}$  is the oxygen concentration (solubility) in 0.1 M KOH (1.2 × 10<sup>-6</sup> mol cm<sup>-3</sup>),  ${}^{D_{O_2}}$  is the oxygen diffusion coefficient in 0.1 M KOH (1.90 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>) and *v* is the kinematic viscosity of 0.1 M KOH (0.01 cm<sup>2</sup> s<sup>-1</sup>).

$$J^{-1} = J_{L}^{-1} + J_{K}^{-1} = B^{-1}\omega^{-1/2} + J_{K}^{-1}$$
(4)

$$B = 0.62 n F C_{O_2} D_{O_2}^{2/3} v^{-1/6}$$
(5)

For an ideal catalyst, the expected shape of the voltammetric profile would have a sigmoidal shape, reaching a maximum value, which is called limiting diffusion current. This current value is obtained when the electrode kinetics is very fast and the reaction rate is controlled by the diffusion of the reactants to the surface of the electrode. This diffusion-limited current can be easily calculated using the Levich equation:

$$i_{\rm lim} = -0.62 n \rm{AFD}^{2/3} v^{-1/6} c_{\rm b} \omega^{1/2}$$
 (6)

where n is the number of electrons exchanged in the process, A is the geometrical area of the electrode, D is the diffusion coefficient, v is the kinematic viscosity,  $c_b$  is the bulk concentration of oxygen, and  $\omega$  is the rotation rate. Using the reported values D and  $c_b$  for oxygen and v, and the geometrical area of the electrode (0.197 cm<sup>2</sup>), a current value of 0.430 mA is obtained when hydrogen peroxide is formed (n =2) or 0.865 mA for water (n = 4) for 1600 rpm. These values are equivalent to current density values per geometrical area of 2.19 and 4.39 mA cm<sup>-2</sup>, respectively.

## Rotating ring disk electrode (RRDE) test

For the RRDE measurements, the collection efficiency was determined with  $K_3Fe[CN]_6/K_2Fe[CN]_6$ as the redox couple (Figure S26). The plots of collection efficiency were collected at -0.2 V and -0.4V at different rotation rates. pTTh polymerized on disk electrode was prepared by the method as described by our previous work. The disk electrode was scanned cathodically at a rate of 10 mV s<sup>-1</sup> and the ring potential was constant at 1.5 V *vs* RHE. The HO<sub>2</sub>-% and the electron transfer number (n) were determined by the following Equations (7) and (8):

$$\% HO_{2}^{-} = 200 \times \frac{I_{r}/N}{I_{d} + I_{r}/N}$$
(7)

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \tag{8}$$

Where  $I_d$  is disk current,  $I_r$  is ring current and N is the current collection efficiency (N) of the Pt ring. N was determined to be 0.38 from the reaction of reduction of  $K_3Fe[CN]_6/K_2Fe[CN]_6$ .

#### **PEC** $H_2O_2$ production from the pTTh photocathode

The production and accumulation of  $H_2O_2$  were performed in a quartz two-compartment cell equipped with a Nafion membrane (F117, thickness 183 micrometers) between the working electrode (WE) and counter electrode (CE) to prevent reoxidation of  $H_2O_2$  back to  $O_2$ . The SCE reference electrode was fixed in the WE chamber. The WE was saturated by continuous bubbling with oxygen for 30 min before the photoelectrochemical reaction and the bubbling was continued during the reaction. The WE chamber was illuminated under 300 W Xe arc lamp adjusted to 100 mW cm<sup>-2</sup> with an ultra-violet filter and a water filter from the front side of CP. The amount of produced  $H_2O_2$  was recorded using spectroscopic titration as the following stated.

#### Unbiased $H_2O_2$ production by coupling with photoanode

Photoelectrochemical production of  $H_2O_2$  was performed using a two-compartment quartz cell in which photoanode and photocathode were separated by a Nafion membrane (F117). The photoanode cell consists of the BiVO<sub>4</sub> electrode for water oxidation in an Ar-saturated aqueous solution (40 ml) containing 1M potassium borate buffer, which was prepared by adjusting the pH of a 1M H<sub>3</sub>BO<sub>3</sub> solution to 9.5 with KOH. The photocathode chamber consists of the as-prepared pTTh/CP electrode for O<sub>2</sub> reduction in an O<sub>2</sub>-saturated solution (20 ml) containing 0.1 M KOH. The two electrodes were connected with each other without bias and the passed charge was recorded. The photoanode and photocathode were illuminated under 300 W Xe arc lamp adjusted to 100 mW cm<sup>-2</sup> with an ultra-violet filter and a water filter from FTO contact (back-side illumination) and the front side of CP, respectively. The amount of produced H<sub>2</sub>O<sub>2</sub> was recorded using spectroscopic titration. Although there is a mismatch of pH between the photoanode and the photocathode, the potassium ion would transfer from the photocathode through the Nafion membrane. We are working on developing the bipolar membrane to fabricate more efficient H<sub>2</sub>O<sub>2</sub> production.

**Reaction equations for the H\_2O\_2 production** One could use an electrolyzer with water oxidation at the anodic side and oxygen reduction to  $H_2O_2$  at the cathodic side. The  $H_2O_2$  production proceeds via the reduction of  $O_2$  in two different ways:

At pH < 11.6

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad U_0 = 0.70 \text{ V vs RHE}$$
 (9)

At pH > 11.6, the product of the  $2^{e^-}$  pathway changes from  $H_2O_2$  to  $\frac{HO_2}{2}$ , then it yields

$$O_2 + H_2O + 2e^- \rightarrow \frac{HO_2}{2} + OH^- U_0 = 0.74 \text{ V vs RHE}$$
 (10)

*Hydrogen peroxide detection by spectroscopic titration* The concentration of accumulated  $H_2O_2$  was determined by spectroscopic titration with a hydrochloric acid solution containing TiO(tpypH<sub>4</sub>)<sup>4+</sup> (the

Ti-TPyP reagent)<sup>5</sup>. The Ti-TPyP reagent was prepared by dissolving 8.5 mg of the TiO(tpyp) complex in 250 mL of 50 mmol L<sup>-1</sup> HCl solution. A solution of concentrated H<sub>2</sub>O<sub>2</sub> (ca. 0.1 M) was standardized by titration with potassium permanganate and then a series of standard H<sub>2</sub>O<sub>2</sub> solution (1  $\mu$ M - 30  $\mu$ M) was prepared by diluting concentrated H<sub>2</sub>O<sub>2</sub> with water. The diluted H<sub>2</sub>O<sub>2</sub> (0.25 ml) was added into an equivalent volume of HClO<sub>4</sub> and Ti-TPyP reagent, then the mixed solution was allowed to stand for 5 min. Subsequently, the solution was diluted to 2.5 ml with water and used for spectroscopic characterization. The absorbance at 433 nm was measured (A<sub>s</sub>) on a spectrophotometer (Jasco V-650, Japan). A blank solution was prepared in a similar manner, using water instead of the standard H<sub>2</sub>O<sub>2</sub> solution with its absorbance designated as A<sub>B</sub>. The difference in absorbance was determined as follows:  $\Delta A_{433}$ = A<sub>B</sub>-A<sub>s</sub>. Based on the above results, the amount of H<sub>2</sub>O<sub>2</sub> was determined (Supplementary Figure S27).

**Solar-to-H**<sub>2</sub>**O**<sub>2</sub> *efficiency* During the operation of the three-electrode system and two-compartment cell, the accumulation of H<sub>2</sub>O<sub>2</sub> was recorded. The solar-to-H<sub>2</sub>O<sub>2</sub> efficiency could be defined as the ratio of the chemical energy stored in H<sub>2</sub>O<sub>2</sub> to the solar energy input. The mathematical expression is given by Equation (11):

Solar-to-H<sub>2</sub>O<sub>2</sub> efficiency (%)=  $\frac{\text{Gibbs free energy change of equation} \times \text{ rate of H}_2\text{O}_2 \text{ production}}{\text{density of incident solar light} \times \text{ irradiation area}} \times 100$ (11)

The chemical energy, the numerator in Equation (5), is calculated by multiplying the rate of  $H_2O_2$  production by the change in the Gibbs free energy per mole of  $H_2O_2$ . The solar energy input, the denominator in Equation (8), is calculated by multiplying the power density of the incident light by the illuminated electrode area.

*Faradaic efficiency* For both cases of the three-electrode system and two-compartment cell, the ratio between the charge used for the production of  $H_2O_2$ ,  $N_F$  and the overall charge flow through the external circuit,  $N_T$  (as shown in Equation (12)), which reflects the percentage of charges generated used for  $H_2O_2$  production. To calculate the total number of electrons flowing through the external circuit ( $N_T$ ), the photocurrent (J) profile as a function of time (t) is measured. The integration of the

er time, 
$$\int_{0}^{\Delta t} J(t)dt$$
, represents the total charge flowing through the external  $\int_{0}^{\Delta t} J(t)dt$ 

measured photocurrent ov

circuit. Then, N<sub>T</sub> can be calculated by  $0^{-}$  /e, in which e is the electrical charge of one electron. To calculate the number of electrons used for H<sub>2</sub>O<sub>2</sub> generation (N<sub>F</sub>), the amount of H<sub>2</sub>O<sub>2</sub> generated is measured by spectroscopic titration. Then, N<sub>F</sub> can be expressed as n<sub>H2O2</sub> × 2N<sub>A</sub>, in which N<sub>A</sub> is the Avogadro constant (6.02 × 10<sup>23</sup>).

$$\eta_F = N_F / N_T \times 100\%$$
 (12)



Figure S1 The Tauc plot (blue) calculated based on the absorption spectrum (green) of pTTh/CP electrode.

The Tauc plot was used to evaluate the bandgap of semiconductors based on the equation:  $\alpha hv = A$ ( $hv - E_g$ )<sup>n</sup>, in which  $\alpha$  is the absorption coefficient of the materials, hv is the energy of photons, A and n are both the constant and  $E_g$  is the bandgap of the evaluated material. The  $E_g$  could be estimated by plotting the ( $\alpha hv$ )<sup>1/n</sup> against hv and get the value by the intercept with X axis.



**Figure S2** (a) The cyclic voltammograms obtained in acetonitrile and 0.1M Tetrabutylammonium Perchlorate. Ferrocenium/ferrocene (Fc/Fc<sup>+</sup>) redox potential has been measured at the end of each experiment in order to calibrate the pseudo reference electrode (0.0565V vs. Ag in the present study). (b) Zoom of the voltammograms as shown in (a). The energetic levels of pTTh is determined as follows:  $E_{HOMO}$  (eV) ~ ionization potential = -4.8 - e ( $E_{ox\_onset}$ -0.0565) and  $E_{LUMO}$  (eV) ~ electronic affinity = -4.8 - e ( $E_{red\_onset}$ -0.0565). (c) Mott-Schottky plots from an electropolymerized pTTh film on GC substrate in aqueous electrolyte at pH 12.9. The flat band potential locates at ca. 0.48 V vs NHE at pH 13. Assuming valence band is 0.1 V positive than the flat band, then the valence band is 0.58 V. (d) Energy band diagram of pTTh under flat-band condition at pH 12.9. Accordingly, the bare GC electrode exhibited a featureless curve (data not shown), obviously distinct from that of the pTTh/GC electrode.

For pTTh material, we found that the main p-doping (oxidation) and n-doping (reduction) process are irreversible, and the values of the peak potential versus standard hydrogen electrode (SHE) are -2.1 V (reduction) and 1.25 V (oxidation), yielding an energy gap of ~3.35 eV. This numerical value is surprising given that pTTh absorbs visible light. Indeed, a careful analysis of the CV (zoom at lower current, Figure S2b) reveals oxidation and reduction processes occurring at lower potentials (0.39 V for oxidative potential). The corresponding HOMO energy level was -5.13 eV by the formula (*vide supra*). The LUMO energy was -3.13 eV by adding the optical bandgap (E<sub>g</sub>) to the calculated HOMO energy level.



Figure S3 (a) Schematic diagram of experimental setup. (b) Working principle of the RDE or RRDE electrode.

The characterization of photoelectrochemical ORR could not be achieved through the conventional RDE/RRDE station. Thus, a custom-made RDE/RRDE station was needed and designed by integrating with a Xe-lamp, in which the Xe-lamp serves as the light source to excite the photocathode. An optical cable was connected with the Xe-lamp and used to transmit light to the electrode surface. During the reaction, light source from the Xe-lamp vertically illuminated at the rotating electrode, where the photoelectrochemical kinetic information and the formation of peroxide could be obtained.



**Figure S4** J-V curve of pTTh/RDE electrode measured using RDE in O<sub>2</sub>-saturated and Ar-saturated 0.1 M KOH under Xe lamp, 100 mW cm<sup>-2</sup> illumination; Rotating rate: 1600 rpm.



**Figure S5** Double-layer capacitance measurements for determining electrochemically active surface area for the pTTh from voltammetry in 0.1 M KOH. (a) Cyclic voltammograms were measured in a non-Faradaic region of the voltammogram at the following scan rate: decrease in the order 0.1, 0.05, 0.02, 0.01, 0.005 V/s. The working electrode was held at each potential vertex for 10 s before the beginning the next sweep. All current is assumed to be due to capacitive charging. (b) The cathodic and anodic charging currents measured at 0.1 V vs SCE plotted as a function of scan rate. (c) Current density normalized by ECSA in O<sub>2</sub> saturated solution at pH 12.9 under 1 sun illumination, rotation speed 1600 rpm. The ECSA of pTTh was calculated based on the C<sub>DL</sub> by CVs and the C<sub>s</sub> of carbon materials in alkaline solution (equation 3), which are 0.011 mF and 22  $\mu$ F cm<sup>-2</sup>, respectively. Thus, the ECSA is calculated to be 0.5 cm<sup>2</sup>.



**Figure S6** (a) J-V curve of pTTh/RDE electrode measured in O<sub>2</sub>-saturated with different rotating rates; (b) K-L plots at different potentials calculated from the LSVs with different rotating rates.



**Figure S7** (a) Effect of temperature on  $H_2O_2$  degradation in 0.1 M KOH, heating time: 24h; (b) Time course for  $H_2O_2$  degradation under 100 mW cm<sup>-2</sup> irradiation in 0.1 M KOH.

 $H_2O_2$  is sensitive to the temperature and light wavelength. As can be seen from Figure S6,  $H_2O_2$  decomposition becomes appreciable when temperature is higher than 40 °C or when the  $H_2O_2$  solution is irradiated with light source that contains ultraviolet (UV) region. In addition, the decomposition rate increases rapidly as temperature rises. In order to avoid the effect bought by temperature and UV light, we kept the temperature constant at 20 °C and irradiated using an UV filter at  $\lambda > 420$  nm.

Entry	Catalyst	Sacrificial reagent	$\begin{array}{c} Maximu\\ m \ H_2 O_2\\ formed\\ (mmol\\ L^{-1}) \end{array}$	Selectivity (%)	Solar-to- $H_2O_2$ efficiency (%)	Refs.
1	CdS	alcohol	0.1			6
2	TiO <sub>2</sub>	alcohol	< 0.1	< 0.2		7
3	Au-TiO <sub>2</sub>	formic acid	1		—	8
4	ZnO	formate	2	_	_	9
5	g-C <sub>3</sub> N <sub>4</sub>	alcohol	6	90	_	7
6	g-C <sub>3</sub> N <sub>4</sub> /PDI/rGO		2	90	0.2	10
7	g-C <sub>3</sub> N <sub>4</sub> /BDI		0.4	90	0.13	11
8	O-enriched g-C <sub>3</sub> N <sub>4</sub>	isopropyl alcohol	9	73	—	12
9	EPI	—	3	96		13
10	BiVO <sub>4</sub> /WO <sub>3</sub>	hydrogen carbonate	2	30		14
11	cobalt chlorin complex	sea water	48	70	0.55	15
12	pTTh	—	110	~98	_	This work

Table S1. Comparison of semiconductor photocatalysts for oxygen reduction to hydrogen peroxide.

Notes: The Solar-to-H<sub>2</sub>O<sub>2</sub> efficiency in the unbiased dual-photoelectrode is 0.3% and peaks at 0.7% at the initial 2h.

# Kinetic analysis for H<sub>2</sub>O<sub>2</sub> decomposition using K<sub>f</sub> and K<sub>d</sub>

The formation rate constant ( $K_f$ , mmol  $L^{-1} h^{-1}$ ) and decomposition rate constant ( $K_d$ ,  $h^{-1}$ ) follow the zero-order and first-order kinetics toward [ $H_2O_2$ ], respectively. Therefore, the formation rate could be expressed as  $r_f = k_f$ , and decomposition rate could be expressed as  $r_d = k_d [H_2O_2]$ . The concentration

of H<sub>2</sub>O<sub>2</sub> can be obtained as a function of r<sub>f</sub> and r<sub>d</sub>; [H<sub>2</sub>O<sub>2</sub>] =  ${}^{0}$   ${}^{0}$ . Finally, the equation can be expressed: [H<sub>2</sub>O<sub>2</sub>] = (k<sub>f</sub>/ k<sub>d</sub>)[1-exp(-k<sub>d</sub>t)]. The expected maximum concentration is calculated to be 165 mmol L<sup>-1</sup>, according to the equilibrium between the formation rate and the decomposition rate, i.e., K<sub>f</sub> = k<sub>d</sub> [H<sub>2</sub>O<sub>2</sub>].



Figure S8 Current changes upon addition of  $H_2O_2$  in Ar-saturated 0.1M KOH (a) in the dark; (b) under illumination; (c) comparison with that in  $O_2$  under illumination. Light intensity: 100 mW cm<sup>-2</sup>.



Figure S9 (a) Zeta-potential of pTTh dispersed in water of different values; (b) Scheme for pTTh catalyzed  $H_2O_2$  formation.



**Figure S10** (a) The Tauc plot (blue) calculated based on the absorption spectrum (green) of NiFeO<sub>x</sub>/BiVO<sub>4</sub> electrode. (b) Mott-Schottky plots of the NiFeO<sub>x</sub>/BiVO<sub>4</sub> electrode in aqueous borate buffer, pH 9.5.

We carried out the energy levels of BiVO<sub>4</sub> based on the UV-vis and the Mott-Schottky results. The light absorption edge of BiVO<sub>4</sub> is ca.520 nm, with an indirect bandgap of 2.4 eV, as indicated by the Tauc plot in Figure S10. The Flat band ( $E_{FB}$ ) is estimated to be ca. 0.21 eV, according to the Mott-Schottky analysis. Assuming that the  $E_{FB}$  is 0.1 negative that the conduction band edge at ca. 0.11 eV, then the valence band edge is calculated to be 2.51 eV.



Figure S11 The schematic energy diagram and the photogenerated carriers transfer process.



**Figure S12** (a) TEM, (b) HRTEM, (c) HAADF-STEM images of NiFeO<sub>x</sub>/BiVO<sub>4</sub> partilces and (d) the Ni, Fe, Bi and B elemental profiles along the red line across the NiFeO<sub>x</sub>/BiVO<sub>4</sub> partilces in c.



**Figure S13** J-V curve of BiVO<sub>4</sub> (green) and NiFeO<sub>x</sub>/BiVO<sub>4</sub> (red) photoanode for water oxidation measured in a 1 M borate buffer (pH 9.5) under 100 mW cm<sup>-2</sup> illumination. Dark current is shown as a black line.



Figure S14 Digital photos of the as-prepared  $NiFeO_x/BiVO_4$  and pTTh electrodes.



**Figure S15** Stability of NiFeO<sub>x</sub>/BiVO<sub>4</sub> photoanode for water oxidation measured in a 1 M borate buffer under 100 mW cm<sup>-2</sup> illumination at 0.7 V vs RHE. Counter electrode: Pt; reference electrode: SCE.



Figure S16 XRD patterns of BiVO<sub>4</sub>/NiFeO<sub>x</sub> electrode before and after cycles and the corresponding SEM images.



Figure S17 SEM images of PTTh on CFP (a) before cycles and (b) after cycles.



**Figure S18** I-V (red) and I-P (green) curves of the one-compartment  $H_2O_2$  fuel cell with Ni mesh anode and Prussian blue/carbon paper cathode in the reaction solution containing 100 mmol L<sup>-1</sup>  $H_2O_2$  produced by the unbiased reaction in 1 M KCl, pH was tuned with  $H_2SO_4$  to 1.



**Figure S19** (a) RRDE voltammograms at 1600 rpm with ring potential constant at 1.5 V vs RHE. (b) Percentage of peroxide and the corresponding electron transfer number (n) at various potentials, based on the RRDE data. The results were acquired in the dark.



**Figure S20** J-V curve of pTTh electrode measured using RDE in O<sub>2</sub>-saturated 0.1 M KOH with rotating rate 1600 rpm with illumination.



**Figure S21** (a) LSVs of pTTh electrode measured in  $O_2$ -saturated electrolytes with different pH values. Rotation rate: 1600 rpm. (b) Correlation between current densities of ORR at -0.1 and 0 V versus RHE and the pH values. (c) Correlation between onset potentials at 0.01 mA cm<sup>-2</sup> and the pH values.

The ORR activities differ dramatically with the pH of the electrolytes and increase with the increasing pH values (Figure S16a). The current densities at a specific potential for each ORR are extracted and plotted versus the corresponding pH. Figure S16b exhibits gradually enhanced photocurrent and onset potential also increases with the increasing pH at all chosen potentials (-0.1 and 0 V), indicating that the ORR activity in the dark exhibit the same ORR behavior as that under illumination.



Figure S22 Comparison of the pH dependent hydrogen peroxide selectivity under illumination and in the dark.

# 4. Calculation Details

**Computational Method** We carried out density functional theory (DFT) calculations with the CAM-B3LYP hybrid functional and correlation-consistent basis sets of contracted Gaussian functions denoted "aug-cc-pVTZ"<sup>16</sup>for all elements. We used the program ORCA.<sup>17</sup> Geometries of all species were fully optimized until forces on all atoms were smaller than 10<sup>-4</sup> a.u./bohr. We used the implicit SMD solvation model to calculate the solvation effect corrections when modeling the reactions in aqueous phase. The solvation correction  $E_{SOL}$  was taken as  $E_{SOL} = E(SMD) - E(gas)$  where E(gas) is the CAM-B3LYP energy of the molecule in the gas phase, and E(SMD) is the CAM-B3LYP energy in the aqueous phase. The smaller basis set 'cc-pVDZ'<sup>16</sup> was used to perform the vibrational frequency analysis by the finite difference method to calculate the zero-point energy and entropy. We applied a scaling factor  $\gamma$  of 0.962 <sup>18</sup> to the vibrational frequencies to match the zero-point energy to the experiment. The enthalpy energies were given by  $H = E + \gamma ZPE$ , in which E is the single point energy of the optimized geometry and ZPE is the zero-point energy. Then the Gibbs free energies were calculated with the equation G = H - TS, where S is the entropy term.

We calculated the reaction free energy for the following electrode reaction to assess the accuracy of the method:

 $H_2O_2(aq) + 2 H^+(aq) + 2 e^-(g) \rightleftharpoons 2 H_2O(l) (1)$ 

We assumed that the reactions occur under pH = 0 and at a pressure of 1 atm, thus the energy of [  $H^+(aq) + e^-(g)$  ] can be replaced with 1/2 the energy of  $H_2(g)$ . A solvation energy correction of -2.05 kcal/mol or -0.089 eV<sup>19</sup> was applied to the energy of a water molecule in the gas phase to get the energy of a water molecule in the aqueous phase. We took also the solvation energy of the proton in aqueous solution to be = 11.53 eV<sup>19</sup>. With these data we found (see Table S4) that the energy of reaction (1) is in excellent accord with experiment, within 0.1 kcal/mol.

	E, a.u.	ZPE, kcal/mol	TS, kcal/mol	E <sub>SOL</sub> , eV
H <sub>2</sub> O	-76.43805	13.54	13.44	
HOO-	-150.96123	8.05	15.69	-3.784
OH-	-75.80919	5.33	11.86	-4.016
OH•	-75.74251	5.39	12.28	-0.225
pTTh	-1656.61719	102.89	30.48	-0.093
pTTh <sup>-</sup>	-1656.64122	100.14	31.71	-1.711
pTTh-OO	-1806.91693	106.31	34.48	-0.279
pTTh-OO <sup>-</sup>	-1806.98612	105.20	34.58	-2.749
pTTh-OOH	-1807.55793	113.62	34.07	-0.391
pTTh-OOH <sup>-</sup>	-1807.62164	112.83	34.44	-1.876
pTTh=O	-1731.79948	105.80	31.31	-0.257
pTTh-OH	-1732.42343	111.78	33.24	-0.280
pTTh-H-OOH	-1808.18531	121.93	34.15	-0.398

**Table S2.** Energy, zero-point energy, entropy contribution, and the solvation correction for all species involved in this work. The ZPEs are unscaled in the list, and the solvation energy were taken from E(cam-b3lyp + SMD @ cam-b3lyp geometry) - E(cam-b3lyp @ cam-b3lyp geometry). Data are for the most stable structures of the species.

# Adsorption energies EABS of O2 on pTTh or pTTh-



Figure S23 Site definition of the TTh model.

**Table S3**. A comparison of adsorption energies  $E_{ABS}$  on different reaction sites. Site definition is shown in Figure S3. Adsorption energies are in eV, and bond lengths are given in Å.

Adaption Site (*)	O <sub>2</sub> a	dsorption to	pTTh	(	$D_2$ adsorption to p'	TTh-
	C1	C2	C3	C1	C2	C3
E <sub>ABS</sub> , g	1.33	1.88	1.54	0.22		0.71
E <sub>ABS</sub> , aq	1.14	1.73	1.38	-0.82		-0.26
C-O bond length	1.48	1.53	1.51	1.32	No bond	1.39
O-O bond length	1.30	1.30	1.30	1.45		1.44

**Table S4.** A comparison between the experimental data and DFT result. Numbers are shown in kcal mol<sup>-1</sup> (for energy) or V (for potential).

$H_2O_2(aq) + H_2(g) \rightleftharpoons 2 H_2O(l)$	E(V)	delta G (kcal/mol)
Experiment	-1.774	-82.4
cam-b3lyp/aug-cc-pVTZ/SMD	-1.776	-82.3

As a further assessment of the accuracy of our DFT calculations, we calculated the reaction energy for  $2 \text{ H}_2\text{O}(l) \rightleftharpoons \text{O}_2(g) + 2 \text{ H}_2(g)$  (2)

In this way the energy of a ground state oxygen molecule can be related to the energy of a water molecule in the aqueous phase and a hydrogen molecule in the gas phase. This approach provides a means to overcome the larger error in the direct calculation of the free energy of O<sub>2</sub> compared to H<sub>2</sub>O and H<sub>2</sub>. Accordingly,  $G(O_2, g) = 4.92 \text{ eV} - 2 G(H_2, g) + 2 G(H_2O, aq)$ , where 4.92 eV is the experimental dissociation free energy of reaction (2). Lastly, the absolute redox energy of the hydrogen electrode reaction  $\frac{1}{2}$  H<sub>2</sub>  $\rightleftharpoons$  H<sup>+</sup> + e<sup>-</sup> obtained from CAM-B3LYP calculations is found to be +4.48 eV compared to the experimental value of 4.28 eV, using the DFT energy of H<sub>2</sub> and H.



Figure S24 Overall reaction energy profile for ORR on pTTh.



**Figure S25** Photoelectrochemical ORR performance of pTTh using graphite rod in the electropolymerization. (a) J-V curve of pTTh/RDE electrode measured using RDE in  $O_2$ -saturated and Ar-saturated 0.1 M KOH under Xe lamp, 100 mW cm<sup>-2</sup> illumination; Rotating rate: 1600 rpm. (b) RRDE voltammograms of pTTh in  $O_2$  saturated solution at pH 12.9 under 1 sun illumination with the disc current, ring current. The disk potential was scanned at 10 mV s<sup>-1</sup> and the ring potential was constant at 1.5 V vs RHE. (c) Percentage of peroxide and the electron transfer number (n) of pTTh at various potentials, calculated from RRDE data.



**Figure S26** Determination of correction efficiency of RRDE with  $K_3Fe[CN]_6$ . LSVs of a Ar-saturated aqueous solution of  $K_3Fe[CN]_6$  (10 mmol L<sup>-1</sup>) in the presence of KNO<sub>3</sub> (0.1 M) recorded at a rorating-ring (Pt) and disk (GC) electrode. (a) RRDE voltammograms. The disk potential was scanned at 10 mV/s and the ring potential was constant at 0.9 V vs SCE. (b) Plots of collection efficiency at -0.2 V and -0.4V vs rotation rates.



**Figure S27** (a) Absorption spectra changes of the Ti-TPyP reagent in the reaction of Ti-TPyP (50  $\mu$ M) with H<sub>2</sub>O<sub>2</sub> (0  $\mu$ M – 30 $\mu$ M) in an aqueous solution containing HClO<sub>4</sub> (0.5 M). (b) Plot of the absorbance change at  $\lambda$ =433 nm as a function of the concentration of H<sub>2</sub>O<sub>2</sub>.

A. XYZ Coordinates for Optimized Geometries (CAM-B3LYP/aug-cc-pVTZ)  $H_2O_2$ 0 0.02453212121097 -0.00385446835433 -0.02766551245586 Ο -0.51986781978491 -0.18175888776266 1.32242416386958 Η 1.80134628195347 0.24362503459659 -0.49621199748032 Η -0.08003167703402-0.01432199645735 0.92111498769884  $H_2O$ 0 -0.000007843194710.11535395473805 0.000000000000000 Η 0.0000000000000000 -0.75580615608288 -0.46122364292789 Η 0.75576123257759 -0.46126196181015  $H_2$ Н -0.36985871678117 Η 0.36985871678117 0.000000000000000 0.000000000000000 HOO-0 -0.76617771047601 0.08612036555583 0.000000000000000 0 0.73169314393422 -0.07381364124897 0.000000000000000 Н -0.99899537795821 -0.85075942980686 0.0000000000000000 OH-0 -0.00232252558333 0.13230503292508 0.000000000000000 Η -0.75433750681667 -0.468773919225080.00000000000000 OH Ο 0.00195299081540 0.13572241553179 0.000000000000000 Η -0.75861302321540 -0.47219130183179 PTTh С -0.14910516024786 -5.12769405658470 -0.00000118179383 С -4.60338628877458 -1.39903051510391 -0.00000024468500 С -3.18726043459544 -1.39695994500819 0.00000054948614 С -2.64699611537006 -0.14375645709308 0.00000011989943 S -3.90129793944914 1.04947590727815 -0.00000136913727 С -1.25033196985176 0.23830275062109 0.0000065221688 С -0.70591889161389 1.48815397397299 0.00000070575561 С 0.70591927019965 1.48815333034789 0.00000077533696 С 0.00000078992156 1.25033138838152 0.23830165279757 С 2.64699555115053 -0.14375766426210 0.00000042102257 С 3.18726068978471 -1.39696079608651 0.00000025756841 С 4.60338661703544 -1.39903041099317 -0.00000054686529 С 5.12769342485136 -0.14910470865455 -0.00000095147916S 3.90129655345695 1.04947553550456 0.00000045888654

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