

## Electronic Supplementary Information

### Sustained production of H<sub>2</sub>O<sub>2</sub> in alkaline water solution by using borate and phosphate modified Au/TiO<sub>2</sub> photocatalysts

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**Materials.** Anatase TiO<sub>2</sub>, chloroauric acid, horseradish peroxide (POD) and N,N–diethyl-p-phenylenediamine (DPD) purchased from Sigma–Aldrich. Others in analytical grade were from Sinopharm Chemical Reagent Co., Ltd., including HClO<sub>4</sub>, NaOH, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O, Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O, phenol, H<sub>2</sub>O<sub>2</sub> polyvinyl alcohol (PVA) and CH<sub>3</sub>OH. Milli-Q ultrapure water was used in this study. The solution pH was adjusted with a dilute solution of HClO<sub>4</sub> or NaOH.

**Synthesis of Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub>.** Au-loaded TiO<sub>2</sub> was prepared by a deposition-precipitation method. An aqueous suspension (50 ml) containing 1.0 ml of 10 g/L of HAuCl<sub>4</sub> was adjusted to pH 6.0 with 1 M NaOH. To this solution, 1.0 g of TiO<sub>2</sub> particles, calcined at 650 °C for pre-treatment, were added and magnetically stirred at 70 °C for 1 h. The solid was filtered, washed thoroughly with distilled water, and dried overnight in an oven at 60 °C. The amount of HAuCl<sub>4</sub> remaining in the filtrate was measured by an inductively coupled plasma mass spectroscopy, from which the amount of Au in Au/TiO<sub>2</sub> was calculated to be 0.61 wt%.

Pt-loaded TiO<sub>2</sub> was prepared by a photochemical deposition method. An aqueous suspension (50 ml) containing 0.9 g of TiO<sub>2</sub>, 4 mL of CH<sub>3</sub>OH and 120 μL of H<sub>2</sub>PtCl<sub>6</sub> stock solution was stirred

in the dark for 30 min, followed by irradiation with a 300 W mercury lamp for 3 h. The solid was filtered, washed thoroughly with distilled water, and dried overnight in an oven at 80 °C. The amount of  $\text{H}_2\text{PtCl}_6$  remaining in the filtrate was measured by an inductively coupled plasma mass spectroscopy, from which the amount of Pt in  $\text{Pt}/\text{TiO}_2$  was calculated to be 0.52 wt%.

**Characterization.** X-ray diffraction (XRD) pattern was recorded on a D/max-2550/PC diffractometer (Rigaku), using a  $\text{Cu K}\alpha$  as the X-ray irradiation source. Adsorption-desorption isotherm of  $\text{N}_2$  on solid was measured at 77 K on a Micromeritics ASAP2020 apparatus. Diffuse reflectance spectrum (DRS) was recorded on a Shimadzu UV-2550 with  $\text{BaSO}_4$  as a reference. X-ray photoelectron spectroscopy (XPS) was made on a Kratos AXIS Ultra DLD spectrometer. The binding energies were calibrated with C 1s at 284.8 eV. Scanning electron microscope (SEM) measurement was performed on a SU-8010, attached with energy-dispersive X-ray spectroscopy (EDS). The HRTEM image was obtained with a JEM-2100F.

**Electrochemical measurement.**  $\text{Au}/\text{TiO}_2$  film electrode was prepared by doctor blade method. A gel containing 0.8 wt%  $\text{Au}/\text{TiO}_2$  and 2.9 wt% PVA was coated on FTO substrate, and then sintered at 500 °C for 2 h. The FTO substrate was cut into pieces. Each piece had an exposed area of  $1 \times 1 \text{ cm}^2$ , and other part was sealed by an epoxy resin. These glass were used as working electrodes. Measurement was carried out on a CHI660E Electrochemical Station (Chenghua, Shanghai), using a  $\text{Ag}/\text{AgCl}$  as the reference electrode, a platinum gauze as the counter electrode. The supporting electrolyte was 0.5 M  $\text{NaClO}_4$ . The working electrode was illuminated through a quartz window with a 500 W Xe lamp from the electrode/electrolyte side.

**Photocatalysis and  $\text{H}_2\text{O}_2$  measurement.**  $\text{Au}/\text{TiO}_2$ -photocatalyzed  $\text{H}_2\text{O}_2$  production was carried out as follows:  $\text{Au}/\text{TiO}_2$  (0.05 g) was added to water solution (50 mL) containing 4 vol%  $\text{CH}_3\text{OH}$  or 0.86 mM phenol as electron donor, and the temperature of the suspension was controlled by thermostat at 20 °C. The suspension was firstly stirred in the dark for 30 min to reach the

adsorption-desorption equilibrium, and then irradiated by a high pressure mercury lamp ( $\lambda > 320$  nm, light intensity:  $4.5 \text{ mW cm}^{-2}$ ) in air-saturated condition. The  $\text{H}_2\text{O}_2$  concentration in the filtrate was measured on an Agilent 8453 UV-visible spectrophotometer at 553 nm through the POD-catalyzed oxidation of DPD.<sup>1</sup> The phenol concentration was analyzed by HPLC (high performance liquid chromatography) on a Dionex P680 (Apollo C18 reverse column). The eluent was a mixture of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  at a volume ratio of 5:5 in the presence of 0.1% acetic acid.

**Derivation process of  $\text{H}_2\text{O}_2$  concentration in the catalyst suspension solution.**

$$r = r_f - r_d \quad (1)$$

In equation (1),  $r$  is the real reaction rate, and  $r_f$  and  $r_d$  are the formation and decomposition rates of  $\text{H}_2\text{O}_2$ , respectively. Assume that  $\text{H}_2\text{O}_2$  formation is zero-order, and  $\text{H}_2\text{O}_2$  decomposition is first-order. Then, equation (2) is obtained, where  $[\text{H}_2\text{O}_2]$  is  $\text{H}_2\text{O}_2$  concentration,  $k_f$  and  $k_d$  are the rate constants for  $\text{H}_2\text{O}_2$  formation and decomposition, respectively.

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_f - k_d[\text{H}_2\text{O}_2] \quad (2)$$

Define  $x = t$ , and  $y = [\text{H}_2\text{O}_2]$ . Then, equation (2) is transferred as  $y'(x) = k_f - k_d y(x)$

In standard form for a linear equation,  $y'(x) + k_d y(x) = k_f$

Integrating factor,  $\mu(x) = e^{\int k_d dx} = e^{k_d x}$

Use formula where C is a constant value,

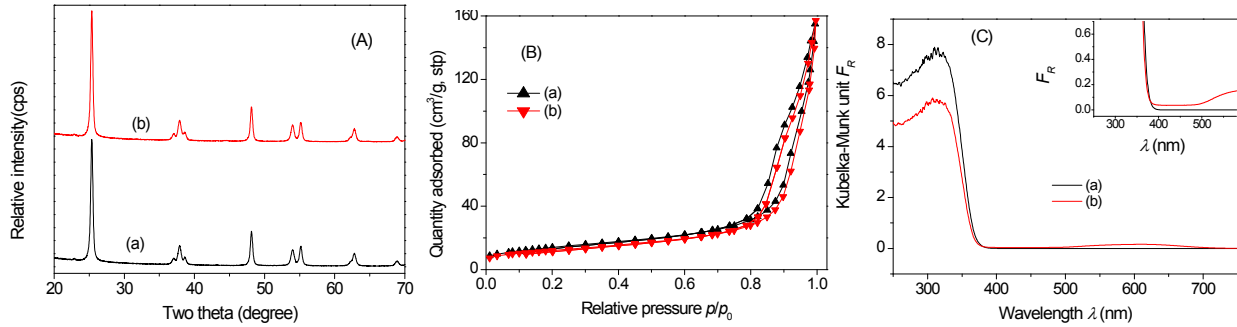
$$y(x) = \frac{1}{\mu(x)} \left[ \int \mu(x) k_f dx + C \right] = \frac{k_f}{k_d} + C e^{-k_d x} \quad (3)$$

By using Initial condition,  $y(0) = 0$  and equation (3), it follows that  $C = -\frac{k_f}{k_d}$

Specific solution: 
$$y(x) = \frac{k_f}{k_d} (1 - e^{-k_d x})$$

Finally,  $H_2O_2$  concentration is obtained as follows

$$[H_2O_2] = \frac{k_f}{k_d} [1 - \exp(-k_d t)]$$

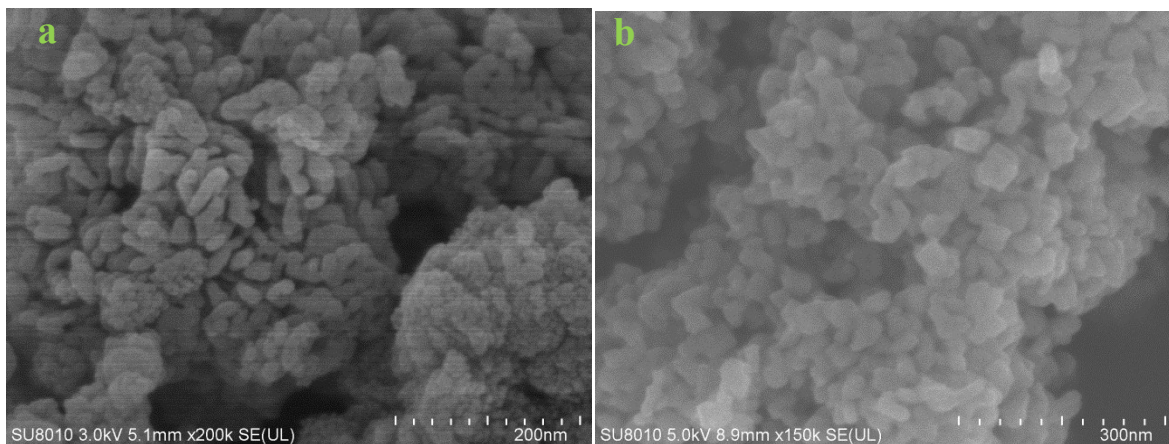


**Fig. S1** (A) XRD pattern, (B)  $N_2$  adsorption–desorption isotherms, (C) UV-vis diffuse reflectance spectra for (a)  $TiO_2$ , (b)  $Au/TiO_2$ . The Kubelka–Munk (K–M) absorbance ( $F_R$ ) is calculated by using the equation,  $F_R = (1 - R)^2/2R$ , where  $R$  is the solid reflectance.

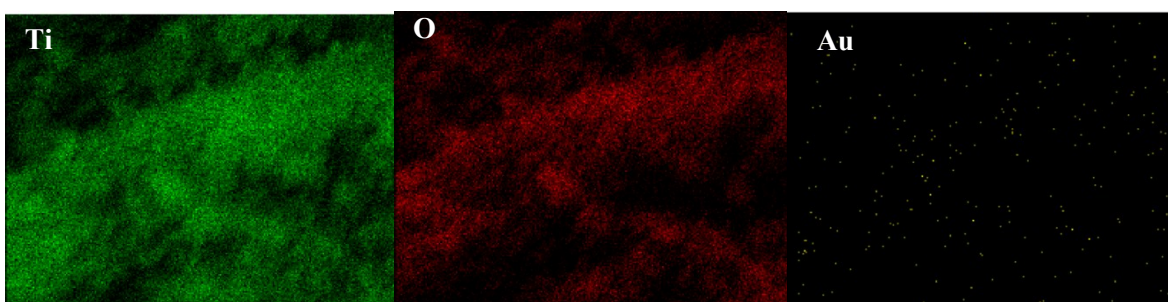
**Table S1.** Physical Parameters of the Catalysts<sup>a</sup>

Samples	$E_g$ (eV)	$d_s$ (nm)	$A_{sp}$ (m <sup>2</sup> /g)	$d_p$ (nm)	$V_p$ (cm <sup>3</sup> /g)	$V_m$ (cm <sup>3</sup> /g)
$TiO_2$	3.20	23.5	49.5	16.39	0.3238	0.0044
$Au/TiO_2$	3.20	24.3	42.7	19.38	0.3524	0.0014

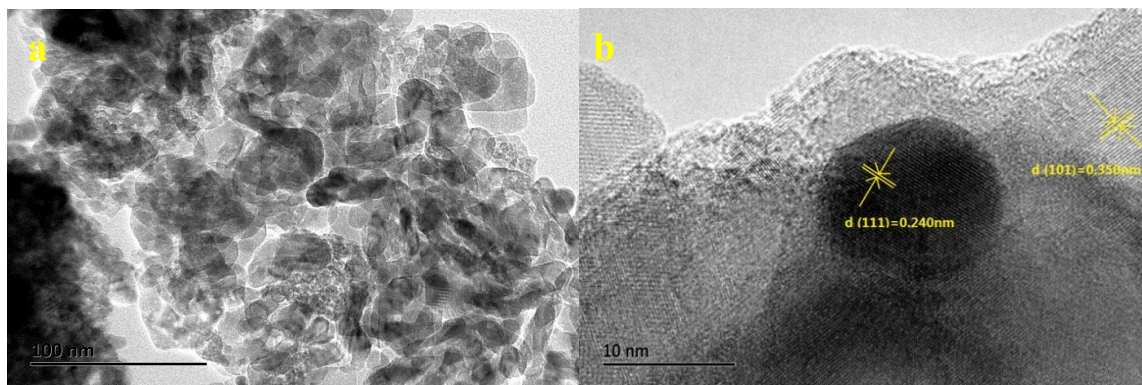
<sup>a</sup> $E_g$ , band gap energy;  $d_s$ , crystallite size estimated by XRD from the (101) facet;  $A_{sp}$ , Brunauer–Emmett–Teller (BET) surface area measured by  $N_2$  adsorption;  $d_p$ , average pore size;  $V_p$ , total pore volume;  $V_m$ , micropore volume. All the data were obtained from Fig. S1.



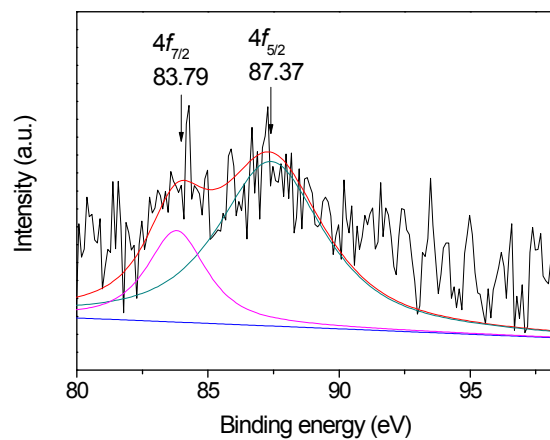
**Fig. S2** Scanning Electron Microscope (SEM) images of (a)  $\text{TiO}_2$  and (b)  $\text{Au/TiO}_2$ .



**Fig. S3** Element distribution of Ti, O and Au in  $\text{Au/TiO}_2$ , recorded by EDS spectra.



**Fig. S4** High-resolution TEM images of the samples: (a)  $\text{TiO}_2$ , (b)  $\text{Au/TiO}_2$ .



**Fig. S5** X-ray photoelectron spectroscopy (XPS) of Au 4f, obtained with Au/TiO<sub>2</sub> sample.

## Reference

- 1 H. Bader, V. Sturzenegger and J. Hoigne, *Water Res.*, 1988, **22**, 1109-1115.