Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2018

## Electronic Supplementary Material (ESI) for New Journal of Chemistry

## Effective hydrothermal grafting of Eosin Y onto TiO<sub>2</sub> nanoparticles towards

# stable photocatalysts for efficient visible-light-driven photocatalytic H<sub>2</sub> evolution

Xiangyu Liu, Weiping Huang, Yonggang Lei, Yanan Li, Yuan Xue, Fang Wang, and

Shixiong Min\*

School of Chemistry and Chemical Engineering, Key Laboratory of Electrochemical Energy Conversion Technology and Application, North Minzu University, Yinchuan, 750021, Ningxia Province, People's Republic of China.

\*Corresponding author. E-mail: <u>sxmin@nun.edu.cn</u> (S. Min).

Tel: 86-951-2067917; Fax: 86-951-2067915

### 1. Experimental

## 1.1 Chemicals and reagents

All reagents were of analytical grade and used without further purification. Eosin Y (EY) dye (2',4',5',7'-tetrabromofluorescein bisodium salt) was used as the photosensitizer. TiO<sub>2</sub> nanoparticles (P25, 20% rutile and 80% anatase) were purchased from Degussa. Deionized (DI) water was produced using an YL-100B-D water-purification system (resistivity>15 M $\Omega$ ).

## 1.2 Synthesis of Eosin Y-sensitized TiO<sub>2</sub> (EY-TiO<sub>2</sub>) photocatalysts

The hydrothermally promoted grafting of Eosin Y dye onto the surface of TiO<sub>2</sub> nanoparticles was carried out as follows without the need of any coupling reagents: 12.5 mmol of TiO<sub>2</sub> powders was dispersed into 60 mL of H<sub>2</sub>O by tip ultrasonication for 3 min and stirring for 30 min to form a homogenous slurry, to which 0.3125 mmol of EY was added and stirring for 2 h in darkness to form a EY-TiO<sub>2</sub> suspension. After that, the resulted EY-TiO<sub>2</sub> suspension was transferred into a Teflon-lined autoclave (100 mL) and heat-treated at different temperatures (120, 160, and 200 °C) for 8 h. After cooled to room temperature, the product was collected by filtration through a 0.22 µm microporous membrane, copiously washed with water and ethanol for several times to remove adsorbed dye, and dried at 50 °C in air. The resulted products were denoted as EY-TiO<sub>2</sub>-HT-*x*, where the *x* represents the hydrothermal temperatures. The amount of grafted EY onto TiO<sub>2</sub> was determined by measuring the concentration of EY in the filtrate during the filtration and washing processes using UV-vis absorption spectra analysis (Table S2).

The EY dye was also adsorbed onto  $TiO_2$  surface by mixing them to obtain EY-TiO<sub>2</sub>-mix-*x* photocatalysts as follows: 12.5 mmol of TiO<sub>2</sub> powders was dispersed into 60 mL of H<sub>2</sub>O by tip ultrasonication for 3 min and stirring for 30 min to form a homogenous slurry, which was then transferred into a Teflon-lined autoclave (100 mL) and heat-treated at different temperatures (120, 160, and 200 °C) for 8 h. After cooled to room temperature, Eosin Y dye was added into the obtained suspension and the

mixture was stirred at room temperature for 8 h in darkness, and then the product was collected by removing water using vacuum rotary evaporation. The obtained samples were donated as EY-TiO<sub>2</sub>-mix-x, where the x represents the hydrothermal temperatures for the treatment of TiO<sub>2</sub> powders before mixing with EY. The added amount of EY at each x is the same as the grafted amount of EY for each EY-TiO<sub>2</sub>-HT-x sample.

#### 1.3 Titration of surface –OH density of hydrothermally treated TiO<sub>2</sub>

The surface –OH density of hydrothermally treated TiO<sub>2</sub> was titrated as following: 0.5 g of TiO<sub>2</sub> nanoparticles was added into 100 mL ethanol-H<sub>2</sub>O mixture solution consisting of 25 mL of ethanol and 75 mL of 20 wt% NaCl aqueous solution. The pH value of this solution was adjusted to be 4.0 with addition of 0.1 M HCl or 0.1M NaOH solution. Then, the pH value of the resulting suspension was titrated from 4.0 to 9.0 by carefully adding certain volume of 0.1 M NaOH solution, and the surface – OH density (µmol m<sup>-2</sup>) was calculated according to following equation (Table S1):

$$N = \frac{C_{\text{NaOH(0.1 M)}} \times V_{\text{NaOH(0.1 M)}} \times 10^{-3}}{S_{\text{TiO}_2} \times m_{\text{TiO}_2}}$$

where the  $C_{\text{NaOH}(0.1 \text{ M})}$  (mol L<sup>-1</sup>) is the concentration of NaOH solution used for titration, the  $V_{\text{NaOH}(0.1 \text{ M})}$  (mL) is the volume of NaOH solution consumed for titration, the  $S_{\text{TiO}_2}$  (m<sup>2</sup> g<sup>-1</sup>) is the BET surface area of TiO<sub>2</sub> nanoparticles, and the  $m_{\text{TiO}_2}$  (g) is the mass of TiO<sub>2</sub> nanoparticles, respectively.

### **1.4 Characterization**

Transmission electron microscopy (TEM) images were taken with a HITACHI 7700 transmission electron microscope. X-ray diffraction (XRD) patterns were investigated with a Rigaku B/Max-RB diffractometer with a nickel filtrated Cu *K*α radiation. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a K-Alpha surface analysis (Thermon Scientific) using X-ray monochromatization. The specific surface area was determined with the Brunauer-Emmett-Teller (BET) equation at 77 K by using an adsorption apparatus

(Micromeritics ASAP 2020 HD88). UV–vis diffuse reflectance spectra (UV-vis-DRS) were recorded on a Shimadzu UV-3600 UV–vis-near-IR spectrophotometer equipped with an integrating sphere and BaSO<sub>4</sub> powders were used as a reflectance standard. UV–vis absorption spectra were taken with a TU-1810 UV-vis spectrophotometer (Beijing Persee). The particle size distribution of samples was measured with a dynamic light scattering (DLS) spectrophotometer (Nanoptic 90). Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer. The fluorescence decay curves were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single photon counting mode (TCSPC) with the time resolution of 200 ps. Nano LED diode emitting pulses at 460 nm with 1 MHz repetition rate was used as an excitation source. Light-scattering Ludox solution was used to obtain the instrument response function (prompt).

#### **1.5 Photocatalytic H<sub>2</sub> evolution experiments**

The photocatalytic hydrogen evolution experiments were per-formed in a sealed reactor with a top flat quartz window for light irradiation and a silicone rubber septum was fixed on its side for sampling produced  $H_2$  in the headspace of reaction cell. A 30-W LED lamp (520 nm) was used as light source. In a typical experiment, 40.0 mg of the photocatalyst was dispersed into 100 mL of aqueous TEOA solution (10%, pH 7) by ultrasonication for 5 min. The 1 wt % Pt cocatalyst was loaded on the surface of photocatalyst by in-situ photodeposition method using  $H_2PtCl_6$ . Before irradiation, the reaction solution was thoroughly degassed by repeated evacuation- $N_2$  filling, and finally refilled with  $N_2$  to reach ambient pressure. The reaction solution was continuously stirred during the irradiation, and the amount of evolved  $H_2$  was analyzed with a precalibrated gas chromatography (Tech comp; GC-7890II) with a thermal conductivity detector, a 5 A molecular sieve column, and with  $N_2$  as carrying gas.

## **1.6 Photoelectrochemical measurements**

Photoelectrochemical measurements were carried out in a three-electrode cell made of quartz using an electrochemical work-station (CHI660E, Shanghai, China). A Pt sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. A 1.0 cm×1.0 cm of FTO glass was used as a working electrode to collect the photogenerated current form a photocatalyst suspension under light irradiation. The photocatalyst suspension was prepared by dispersing photocatalyst powders (0.4 mg mL<sup>-1</sup>) into the mixed electrolyte solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> and 10% TEOA (pH 7). Before testing, the photocatalyst suspension was degassed with N<sub>2</sub> bubbling for 20 min. A 30-W LED lamp (520 nm) was used as light source.

## 2. Additional figures and tables



Fig. S1 UV-vis absorption spectra of Eosin Y solution before and after hydrothermal treatment at different temperatures.



Fig. S2 High-resolution O 1s XPS spectra of (a) untreated  $TiO_2$  and those of  $TiO_2$  samples hydrothermally treated at (b) 120, (c) 160, and (d) 200 °C.



Fig. S3 XRD patterns of untreated  $TiO_2$  and those of  $TiO_2$  samples hydrothermally treated at 120, 160, and 180 °C.

 Table S1 Physicochemical properties of TiO2 samples treated at different temperatures for 8 h.

samples	$\begin{array}{c} S_{BET} \\ (m^2 \\ g^{-1}) \end{array}$	Average pore size (nm)	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	$W_{ m R}(\%)^a$	$W_{\rm A}(\%)^a$	$I_{\rm R}(210)/I_{\rm R}(110)$	Surface – OH density (µmol m <sup>-2</sup> )
Pure TiO <sub>2</sub>	53.6	14.7	0.196	27.2	72.8	0.12	2.05
TiO <sub>2</sub> -HT-120	50.6	27.6	0.349	13.2	86.8	2.36	2.57
TiO <sub>2</sub> -HT-160	43.9	28.8	0.316	21.1	78.9	2.48	4.10
TiO <sub>2</sub> -HT-200	53.4	20.8	0.278	15.0	85.0	4.65	4.49

<sup>*a*</sup>  $W_{\rm R}$  and  $W_{\rm A}$  are the weight ration of rutile and anatase phase for samples, which is calculated by by measuring the intensities of the (110) and (101) diffraction peaks of rutile ( $I_{\rm r}$ ) and anatase ( $I_{\rm a}$ ), respectively, according to the following equation:  $f_{\rm r}=1.26I_{\rm r}/I_{\rm a}+1.26I_{\rm r}$ .



Fig. S4 XRD patterns of pure TiO<sub>2</sub>, EY-TiO<sub>2</sub>-HT-*x*, and EY-TiO<sub>2</sub>-mix-*x* samples.

samples	$\frac{S_{BET}}{(m^2 g^{-1})}$	Average pore size (nm)	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Grafted amount of EY on TiO <sub>2</sub> $(\mu mol g^{-1})^a$	Desorption rate of EY from $TiO_2(\%)^b$
Pure TiO <sub>2</sub>	53.6	14.7	0.196	/	/
EY-TiO <sub>2</sub> -mix-120	46.3	32.4	0.375	176.6	40.8
EY-TiO <sub>2</sub> -HT-120	62.5	30.0	0.469	176.6	4.78
EY-TiO <sub>2</sub> -mix-160	38.5	30.4	0.292	235.0	46.05
EY-TiO <sub>2</sub> -HT-160	63.3	24.9	0.394	235.0	3.43
EY-TiO <sub>2</sub> -mix-200	36.7	29.5	0.270	218.4	37.4
EY-TiO <sub>2</sub> -HT-200	42.1	36.3	0.382	218.4	9.8

**Table S2** Physicochemical properties of EY-TiO<sub>2</sub>-mix-*x* and EY-TiO<sub>2</sub>-HT-*x* samples.

<sup>*a*</sup> The grafted amount of EY on  $TiO_2$  was determined by measuring the concentration of EY in the filtrate during the filtration and washing processes using UV-vis absorption spectra analysis.

<sup>b</sup> The EY-TiO<sub>2</sub>-mix-*x* and EY-TiO<sub>2</sub>-HT-*x* samples were treated with 0.2 M NaOH for 12 h in darkness and the samples were filtrated and washed several times with water. The desorption rate of EY from TiO<sub>2</sub> was calculated by measuring the concentration of EY in the filtrate during the filtration and washing processes using UV-vis absorption spectra analysis.



Fig. S5 TEM images of the (a) EY-TiO<sub>2</sub>-HT-160 and (b) EY-TiO<sub>2</sub>-mix-160 samples.

scattering measurements.								
samples	D <sub>50</sub> (nm)	samples	D <sub>50</sub> (nm)					
Pure TiO <sub>2</sub>	55.3	TiO <sub>2</sub> -HT-120	21.5					
TiO <sub>2</sub> -HT-160	14.4	TiO <sub>2</sub> -HT-200	77.7					
EY-TiO <sub>2</sub> -mix-120	146	EY-TiO <sub>2</sub> -HT-120	136					
EY-TiO <sub>2</sub> -mix-160	146	EY-TiO <sub>2</sub> -HT-160	90.5					
EY-TiO <sub>2</sub> -mix-200	164	EY-TiO <sub>2</sub> -HT-200	133					

**Table S3** The particle size distribution of samples obtained by dynamic light

 scattering measurements



Fig. S6 UV-vis-DRS spectra of pure TiO<sub>2</sub>, EY-TiO<sub>2</sub>-mix, and EY-TiO<sub>2</sub>-HT samples.



**Fig. S7** High-resolution Br 3d XPS spectra of EY-TiO<sub>2</sub>-HT-160 and EY-TiO<sub>2</sub>-mix-160 samples.



**Fig. S8** Photographs of photocatalyst suspensions taken at different irradiation times during photocatalytic H<sub>2</sub> evolution process.



Fig. S9 The comparison of PL spectra of (a) EY-TiO<sub>2</sub>-mix-120 and EY-TiO<sub>2</sub>-HT-120, (b) EY-TiO<sub>2</sub>-mix-160 and EY-TiO<sub>2</sub>-HT-160, (c) EY-TiO<sub>2</sub>-mix-200 and EY-TiO<sub>2</sub>-HT-200, and (d) normalized quenching efficiency of EY from EY-TiO<sub>2</sub>-HT-*x* with relative to their corresponding physically mixed EY-TiO<sub>2</sub>-mix-*x*.



Fig. S10 The comparison of PL decay curves of EY-TiO<sub>2</sub>-mix-x and EY-TiO<sub>2</sub>-HT-x.



**Fig. S11** Photocurrent variation of EY-TiO<sub>2</sub>-mix-*x* and EY-TiO<sub>2</sub>-HT-*x* samples over irradiation time.