# **Supporting Information**

## Sub-10 nm anatase TiO<sub>2</sub> nanoparticles for rapid photocatalytic

## H<sub>2</sub> production from lignocellulosic biomass

Ze-Xin Huang,a Chi Ma,a Fu-Guang Zhang,a Quan Cheng,a Qing-Yu Liu,a Yong-Jun Yuan\*a and Xuefeng Zhanga

<sup>a</sup>College of Materials and Environmental Engineering, Hangzhou Dianzi University, Hangzhou, 310018, People's Republic of China.

E-mail: yjyuan@hdu.edu.cn

#### Methods

The Sub-10 nm TiO<sub>2</sub> nanoparticles were prepared by a hydrothermal method in an ethanol/water solution by using the Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> as titanium source. Firstly, 6.8 mL of Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> was dissolved in 35ml ethanol, then the mixture was added dropwise to120 ml of H<sub>2</sub>O or 1:6, 1:2, 1:1, 2:1, 5:1 ethanol/H<sub>2</sub>O solution. After stirring for 120 minutes, the milk-white suspension was transferred into five 50 mL stainless steel autoclave with a Teflon liner, and these autoclaves were kept at 180 °C for 10 h in an oven. After cooling to room temperature, the white precipitate was collected via centrifugation at 10000 rpm. After the product was washed thoroughly with distilled water and ethanol, the solid was dried in a vacuum drying oven at room temperature. The product synthesized in 120 ml of H<sub>2</sub>O or 1:6, 1:2, 1:1, 2:1, 5:1 ethanol/H<sub>2</sub>O solution was named as TiO<sub>2</sub>-1, TiO<sub>2</sub>-2,TiO<sub>2</sub>-3,TiO<sub>2</sub>-4,TiO<sub>2</sub>-5 and TiO<sub>2</sub>-6, respectively.

### Synthesis of Pt NCs/TiO<sub>2</sub> photocatalyst.

Typically, 300 mg of as-synthesized sub-10 nm TiO<sub>2</sub> nanoparticles was added in 100 mL deionized water with sonication for 20 minutes, and then the mixed solution was placed in an ice-bath to lower the temperature to 0 °C. A certain quantity of 5 mg·mL<sup>-1</sup> K<sub>2</sub>PtCl<sub>6</sub>aqueous solution was added into the above mixed solution, which was placed at dark environment at 0 °C with magnetic stirring for 4h. After the product was separated from solution by centrifugation at 10000rpm, the solid was washed with deionized water and ethanol for three times. Finally, the precipitate was dried at room temperature in vacuum drying oven to obtain different Pt NCs/TiO<sub>2</sub> photocatalysts. The amount of Pt NCs in Pt NCs/TiO<sub>2</sub>was adjusted by using different quantity of 5 mg·mL<sup>-1</sup> K<sub>2</sub>PtCl<sub>6</sub> during preparation process.

#### Photocatalytic lignocellulosic biomass-to-H<sub>2</sub> conversion experiments.

The photocatalytic H<sub>2</sub> production experiments were carried out in a 350 ml Pyrex photoreactor with a top window which connected to a closed gas-circulating vacuum system, and a 300 W Xe lamp was used as light source. Typically, 100 mg Pt NCs/TiO<sub>2</sub> photocatalyst and 1g substance were added in a 250 ml of aqueous solution with sonication for 10 minutes in the photoreactor. The lignocellulosic biomass including rice straw, wheat straw, polar wood chip, bamboo, rice hull and corncob was sieved on 80 mesh (180  $\mu$ m) sifter, and the lignocellulosic biomass with size less than 180  $\mu$ m were used as substance for photocatalytic reaction. The photocatalytic H<sub>2</sub> production reaction was performed under a vacuum environment with magnetic stirring. The temperature of photoreactor was kept at room temperature controlled by a flow of cooling water. An on-line GC1690 gas chromatography with a TCD detector (Jiedao, 5 Å molecular sieves column, Ar as the carrier gas) was used to analyze evolved H<sub>2</sub>. For outdoor photocatalytic H<sub>2</sub> production experiments, the reaction solution was transferred into a sealed glass reactor, and the outdoor sunlight was used as light source. Before irradiation, the air in the glass reactor was evacuated, and the solution was illuminated by outdoor sunlight with magnetic stirring. The generated gas (1.0 ml) extracted from the headspace of reaction system was injected into the gas chromatography to analyze the amount of H<sub>2</sub>. The apparent quantum efficiency (AQY) of photocatalytic H<sub>2</sub> production system was conducted by the same process as above expect using monochromatic light filter, and the AQY was calculated according to the following equations:

$$n_{\text{photons}} = \frac{P\lambda}{hc} \times t$$
(1)  

$$AQY[\%] = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$
  

$$= \frac{2 \times \text{number of evolved H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100$$
(2)

where *P*,  $\lambda$ , *h*, *c* and *t* is the input optical power, wavelength of the light, Planck's constant, speed of light and the illumination time, respectively.

#### Characterization

The morphologies of photocatalysts were performed on a JEOL JEM 2010 transmission electron microscope at an accelerating voltage of 200 kV. The crystalline structures were measured on a Rigaku-miniflex 6 X-ray diffractometer (Japan) equipped with Cu  $K\alpha$  ( $\lambda$  = 0.15406 nm) radiation. The Raman spectra was examined by a J-Y T64000 Raman spectrometer equipped with 532 nm wavelength incident laser light. The optical properties of photocatalysts were assessed by using Varian cary 500 UV-vis spectrophotometer by using  $BaSO_4$  as the background. The chemical states of photocatalysts were analyzed on a Thermo ESCALAB 250XI XPS system with Al Ka X-ray source. Apherical aberration-corrected HAADF-STEM and EDX elemental mapping images of Pt NCs/TiO<sub>2</sub> were performed by a JEM-ARM200F electron microscope. The specific surface area of photocatalysts was measured from nitrogen adsorption-desorption isotherms measured at 77 K using a micromeritics ASAP 2460 apparatus, the BET surface area was calculated from the adsorption data, and the pore size was obtained by the Barret-Joyner-Halenda method. The transient photocurrent response of various TiO<sub>2</sub> electrodes was performed in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution with a standard three-electrode system in which a saturated

Ag/AgCl electrode, Pt wire and sample-coated ITO glass were used as the reference electrode, counter electrode and working electrode, respectively. The threeelectrode system was equipped on an CHI660E electrochemical workstation (Shanghai Chenhua Limited, China) with an external voltage of 0.5 V vs. RHE, and scan rate was 100 mV·S<sup>-1</sup>. To prepare sample-coated ITO glass working electrode, a suspension solution of photocatalyst (1 mg·ml<sup>-1</sup>) was coated on the ITO glass and dried at room temperature. The LSV plots were measured in standard threeelectrode system as described above expect by using sample-coated platinum carbon electrode as the working electrode, and a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. To prepare sample-coated platinum carbon working electrode, 5 mg sample was added to 2 ml of 2 Vol % Nafion ethanol solution, which becomes a relatively uniform mixture after ultrasonic treatment for 1 h. And then, 20 µL of the dispersion was coated on a glassy carbon electrode and dried at temperature to obtain the working electrode. For the CO<sub>2</sub> detection, 1ml gas extracted from the photocatalytic reaction system was detected by a carbon dioxide analyzer (AR8200, Smart Seneor, China). The high performance liquid chromatography (HPLC) spectra were conducted on an Agilent HPLC 1260 chromatographic instrument. The total organic carbon (TOC) in reaction solution was determined with a total organic carbon (TOC) analyzer (Vario TOC, Elementar, Germany).

S5



Figure S1. UV-Vis DRS spectra of various Pt NCs/TiO<sub>2</sub>-3 photocatalysts.



**Figure S2**. XRD of  $TiO_2$ -3 modified with various amount of Pt NCs.



**Figure S3**. (a) Raman spectra of various  $TiO_2$  samples; (b) Raman spectra of  $TiO_2$ -3 modified with various amount of Pt NCs.



Figure S4. TEM and HR-TEM images of TiO<sub>2</sub>-1 sample.



Figure S5. TEM and HR-TEM images of  $TiO_2$ -2 sample.



Figure S6. TEM and HR-TEM images of  $TiO_2$ -3 sample.



**Figure S7**. TEM and HR-TEM images of TiO<sub>2</sub>-4 sample.



Figure S8. TEM and HR-TEM images of  $TiO_2$ -5 sample.



Figure S9. TEM and HR-TEM images of  $TiO_2$ -6 sample.



**Figure S10.** Size distribution of various  $TiO_2$  nanoparticles,  $TiO_2$ -1,  $TiO_2$ -2,  $TiO_2$ -3,  $TiO_2$ -4,  $TiO_2$ -5 and  $TiO_2$ -6.



Figure S11. N<sub>2</sub> adsorption-desorption isotherms of P25.



Figure S12. SEM image of Pt NCs/TiO<sub>2</sub>-3 photocatalyst .



**Figure S13**. The size distribution of Pt NCs in 0.5% Pt NCs/TiO<sub>2</sub>-3 sample.



Figure 14. Survey XPS spectra of TiO<sub>2</sub>, 0.5% and 1.0% Pt NCs/TiO<sub>2</sub>.



**Figure S15**. Liquid chromatogram analysis for decomposition products of lignocelluloses after 24 h of irradiation.



Figure S16. Chemical structure of decomposition products of lignocelluloses.



**Figure S17**. Possible reaction mechanism for the decomposition of  $\alpha$ -cellulose. The highly reactive 'OH radical could promote the cleavage of  $\beta$ -1,4-glycosidic bonds of  $\alpha$ -cellulose during the oxidation of  $\alpha$ -cellulose, resulting in the hydrolysis of  $\alpha$ -cellulose and the formation of glucopyranose. And then the glucopyranose could convert to the open-chain glucose or fucose. These monoses would be successively oxidized by the 'OH radical or photogenerated hole to form galacturonic acid, lactic acid and CO<sub>2</sub> during the photoreforming processes.



**Figure S18**. SEM images of fresh  $\alpha$ -cellulose (a) and solid residue from photocatalytic H<sub>2</sub> production system after 8 h of irradiation and (b)



**Figure S19**. FT-IR spectra of solid residue from photocatalytic H<sub>2</sub> production system after 8 h of irradiation, as compared to that of fresh  $\alpha$ -cellulose. After photocatalytic reaction, the solid residue separated from photocatalytic H<sub>2</sub> production shows much more surface groups, including  $\delta$ -C-OH (668 cm<sup>-1</sup>),  $\gamma$ -CO (1030 cm<sup>-1</sup>),  $\gamma$ -ring (1105 cm<sup>-1</sup>),  $\gamma$ -C-O-C (1162 cm<sup>-1</sup>),  $\delta$ -CH (1370 cm<sup>-1</sup>),  $\delta$ -CH<sub>2</sub> (1429 cm<sup>-1</sup>),  $\gamma$ -CH(sp<sub>3</sub>, 2899 cm<sup>-1</sup>),  $\gamma$ -OH(3340 cm<sup>-1</sup>).<sup>[1]</sup> As compared to  $\alpha$ -cellulose, these increased surface groups in the solid residue of  $\alpha$ -cellulose indicate that the surface of  $\alpha$ -cellulose was constantly oxidizing during the photocatalytic reaction.



**Figure S20.** The light power density of outdoor sun for photocatalytic  $H_2$  production from cellulose, hemicelluloses (Xylan from corncob) and lignin (Figure 5b).



Figure S21, Photocatalytic H<sub>2</sub> production form  $\alpha$ -cellulose (1g), methanol (1g), mixture of  $\alpha$ -cellulose (1g) and methanol (1g) over 0.5% Pt NCs/TiO<sub>2</sub>-3 photocatalyst. The addition of methanol into the  $\alpha$ -cellulose solution results in an improved photocatalytic H<sub>2</sub> production activity, which can be assigned to the role of methanol acted as a hydroxy scavenger. Photocatalytic reaction conditions: 100 mg photocatalyst, 300 W Xe lamp, 250 ml H<sub>2</sub>O.



Figure S22. SEM images of fresh  $\alpha$ -cellulose (a) and solid residue from photocatalytic H<sub>2</sub> production system in the presence of CH<sub>3</sub>OH as a •OH scavenger (b).



Figure S23. Mot-Shottky plots of TiO<sub>2</sub>-3 electrode in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.



**Figure S24.** Calculated band gaps of TiO<sub>2</sub>-3 by a related curve of  $(\alpha hv)^2$  versus photon energy.

**Table S1**. Comparison of photocatalytic performance for  $H_2$  production between the current work and other reported studies.

Enery	Photocatalyst	Sacrificial reagent.	Light	$H_2$ evolution rate	AQY(%)	ref
			source	(umol·h <sup>-1</sup> ·g <sup>-1</sup> )		
1	$RuO_2/Pt/TiO_2$	cellulose	Xe lamp	41		2
2	Pt/P25	cellulosic	AM 1.5	129	-	3
3	Pt/P25	rice husk suspension	AM 1.5	62.5	-	3
4	Pt/TiO <sub>2</sub>	Cherry wood	Xe lamp	49	1.1	4
5	Pt/P25	celluloses	Xe lamp	~230	-	5
6	MoS <sub>2</sub> /TiO <sub>2</sub>	cellulose	Xe lamp	201	1.45(380 nm)	6
7	Pt/TiO <sub>2</sub>	cellulose	UV-lamp	133		7
8	Pt/TIO <sub>2</sub> NSs	cellulose	Xe lamp	275	1.47 (380 nm)	8
9	Pt/Cu-TiO <sub>2</sub>	cellulose	Hg lamp	510		9
10	NiO <sub>x</sub> //TiO <sub>2</sub>	cellulose	Hg lamp	270		10
8	Pt NCs/TIO <sub>2</sub>	cellulose	Xe lamp	540	4.1 (380 nm)	This
						work

- 1. S. Cichosz, A. Masek, K. Dems-Rudnicka, Sci. Rep. 2022, 12, 19739.
- 2. T. Kawai, T. Sakata, Nature 1980, 286, 474-476
- 3. A. Speltini, M. Sturini, D. Dondi, E. Annovazzi, F. Maraschi, V. Caratto, A. Profumo, A. Buttafav. *Photochem. Photobiol. Sci.*, **2014**, *13*, 1410-1419.
- 4. M. R. St. John, A. J. Furgala, A. F. Sammells. J. Phys. Chem., 1983, 87, 801-805.
- A. Caravaca, W. Jones, C. Hardacre, M. Bowker. Proc. R. Soc. A 2016, 472: 20160054.
- P. Wang, Y. J. Yuan, Q. Y. Liu, Q. Cheng, Z. K. Shen, Z. T. Yu, Z. Zou. ChemSusChem 2021, 14, 2860-2865.
- L. Lan, Y. Shao, Y. Jiao, R. X. Zhang, C. Hardacre, X. Fan. Chin. J. Chem. Eng. 2020, 28, 2084-2091.
- Q. Cheng, Y. J. Yuan, R. Tang, Q. Y. Liu, L. Bao, P. Wang, J. S. Zhong, Z. Y. Zhao,
   Z. T. Yu, Z. G. Zou, ACS Catal. 2022, 12, 2118–2125.
- S. Belda-Marco, M. A. Lillo-Rodenas, M. C. Roman-Martínez, *Catal. Today*, 2022, Doi: 10.1016/j.cattod.2022.11.006.
- L. Zhang, W. Wang, S. Zeng, Y. Su, H. Hao, *Green Chem.*, **2018**, *20*, 3008-3013.