Electronic Supplementary Material (ESI) for Chemical Communications. This journal is © The Royal Society of Chemistry 2017

## **Electronic Supplementary Information (ESI):**

# Accelerated room-temperature crystallization of ultrahigh-surface-area

## porous anatase titania by storing photogenerated electrons

Juan Su,<sup>a</sup> Xiaoxin Zou,<sup>c</sup> Binghan Li,<sup>a</sup> Hui Chen,<sup>c</sup> Xinhao Li,<sup>b</sup> Qiuying Yu,<sup>b</sup> Qixi Mi,\*<sup>a</sup> Jie-Sheng Chen\*<sup>b</sup>

<sup>*a.*</sup> School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China.

<sup>b.</sup> School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240,

China.

<sup>c.</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun

130012, China.

\* To whom correspondence should be addressed (*miqx@shanghaitech.edu.cn; chemcj@sjtu.edu.cn*)

#### **Experimental Section**

**Materials:** Titanium (IV) n-butoxide was purchased from Titan. Ethylene glycol was purchased from Macklin. Titania P25 with a BET surface area of about 50  $m^2/g$  was purchased from Beijing Entrepreneur Science & Trading Co. Ltd. Absolute ethanol, absolute methanol and (hydro)chloroplatinic acid was purchased from Sinopharm Chemical Reagent Co. Ltd. All the above chemicals were used without further purification and deionized water was used in all experiments.

**Preparation of porous amorphous TiO<sub>2</sub> (Am-TiO<sub>2</sub>)**: According to the previous report, Am-TiO<sub>2</sub> was synthesized by photochemical synthesis technique. <sup>[S1,S2]</sup> Typically, Titanium n-butoxide (20 mL) was dropped into ethylene glycol (200 mL) under vigorous stirring, and subsequently refluxed at 160 °C for 3 h. After cooling down to room temperature, the white crystalline titanium glycolate (TG) solid was separated from the mixture and dispersed in deionized water (40 g/L). After UV-light irradiation for 2 h (125 W high pressure mercury lamp), the as-obtained porous Am-TiO<sub>2</sub> was separated and washed twice by deionized water. The stored photogenerated electrons were removed during washing due to the oxidation of O<sub>2</sub> in air.

**Preparation of porous anatase titania by accelerated room-temperature crystallization**: Am-TiO<sub>2</sub> was dispersed in 50 vol% methanol aqueous (40 g/L). After UV-light irradiation for 30 min, TiO<sub>2</sub>(e<sup>-</sup>) was obtained as the color of mixture transformed from white to dark gray (Movie 1). Subsequently, the mixture system was preserved in sealed beaker for 2, 5, and 40 days, and the responding solid products were separated and washed twice by deionized water. After dried in air, the samples were denoted as TiO<sub>2</sub>(e<sup>-</sup>)-2d, TiO<sub>2</sub>(e<sup>-</sup>)-5d and TiO<sub>2</sub>(e<sup>-</sup>)-40d, respectively. The surface Ti<sup>3+</sup>/e<sup>-</sup> were oxidized by O<sub>2</sub> in air during washing and drying process.

General Characterization: The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D2 PHASER X-ray diffractometer using Cu<sub>Ka</sub> radiation ( $\lambda = 1.5418$  Å) operated at 200 mA and 50 kV. The high-resolution TEM (HR-TEM) image and the selected area electron diffraction (SAED) patterns were obtained on a Philips-FEI Tecnai G2S-Twin with a field emission gun operating at 200 kV. The nitrogen adsorption and desorption isotherms were measured by using a Micromeritics ASAP 2020M system. Prior to each measurement, the sample was evacuated at 300 K for 12 h to remove the adsorbed guest species such as water. The surface area data were calculated on the basis of the Brunauer-Emmett-Teller (BET) model. The thermal gravimetric analysis curve was recorded on a NETZSCH STA 449C TG thermal analyzer from 25 to 800 °C at a heating rate of 10 °C min<sup>-1</sup> in air. The Infrared spectra were acquired on a Bruker IFS 66v/S FT-IR spectrometer, and all the samples applied for measurement are in the same mass. The carbon and hydrogen content of the samples were determined through elemental analysis on a Perkin-Elmer 2400 elemental analyzer. The electron paramagnetic resonance spectra were obtained on a JES-FA 200 EPR spectrometer. The details of the instrumental parameters were as follows: microwave frequency: 9.10 GHz (77 K), 9.45 GHz (room-temperature); central field: 3360 G; scanning width: 8000 G; scanning power: 0.998 mW; scanning temperature: 77 K and room-temperature. For EPR measurement, the sample was first dried by evacuation at 100 °C for 1h, and then the dry solid sample was sealed in guartz tubes for measurements. UV-visible diffuse reflectance spectra were recorded on a Cary Series UV-Vis-NIR Spectrophotometer. The surface photovoltage spectroscopy (SPS) measurement was performed on home-made surface photovoltage equipments. The SPS measurement system consisted of a source of monochromatic light, a lock-in amplifier with a light chopper, a photovoltaic cell, and a computer. A 500 W xenon lamp and a grating monochromator were combined to provide the monochromatic light. A low chopping frequency

of  $\sim 23~\text{Hz}$  was used. The photovoltaic cell was a sandwich-like structure consisting of ITO-sample-ITO.

**Evaluation of photocatalytic activity:** The photocatalytic activities of the samples were evaluated by photocatalytic  $H_2$  evolution under Xe lamp irradiation. The photocatalytic reaction was performed in a 250 mL quartz cell, which was placed into a temperature-controlled block at 25 °C and degassed to remove the air and irradiated from top of the reactor using a 300 W Xe-lamp with 15 A working current.

A photocatalyst (50 mg) was added into aqueous methanol solution (50 vol %, 100 mL) in the cell and the aqueous system was magnetically stirred during the whole photocatalytic testing. Pt cocatalyst (1 wt. %) was loaded onto the surface of photocatalysts by an in situ photo-deposition method (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was used as precursor).<sup>[S3]</sup> Before light irradiation, the system was evacuated to eliminate air and the temperature of the system during photocatalytic reaction was kept around 25 °C by a continuous flow of water. The evolved gases were detected *in situ* using an online gas chromatograph (TCD, Molecular sieve 5 Å, Nitrogen gas), which was connected to the system and was equipped with a thermal conductivity detector. Control experiments in absence of photocatalyst or light were also performed.



**Fig. S1.** A picture of self-made reactor applied for storing photogenerated electrons in titania. A quartz reactor: a cylindrical reagent container is fixed in the center and circled with tubular high pressure mercury lamp (up to six) and circulating water. The whole reactor is placed in an aluminum black box with front and upper door. An electric stirrer with variable speed is used for continuous stirring. This reactor with volume of 3.5 L is able to be applied for synthesis in scale.



**Fig. S2.** The electron paramagnetic resonance (EPR) spectra of  $TiO_2(e^{-})$  preserved for 2 d (A) and  $TiO_2(e^{-})$ -2d (B) at 77 K; The  $e^{-}/Ti^{3+}$  were on the surface of titania, and thus apt to be oxidized by  $O_2$  in air during washing and drying process. Therefore, there is no characteristic signal of  $Ti^{3+}$  in  $TiO_2(e^{-})$ -2d sample.



**Fig. S3.** High-resolution TEM (HR-TEM) image of  $TiO_2(e^2)$ -2d. The observed lattice spacing 0.35 nm, 0.24 nm, and 0.19 nm in HR-TEM image correspond to the distance between the (101), (004) and (200) crystal planes of anatase titania, respectively.



Fig. S4. Selected area electron diffraction (SAED) patterns of TiO<sub>2</sub>(e<sup>-</sup>)-2d.



Fig. S5. (a)  $N_2$  adsorption-desorption isotherms and (b) pore size distribution of TiO<sub>2</sub>(e<sup>-</sup>)-5d.



Fig. S6 The powder X-ray diffraction (XRD) patterns of Am-TiO<sub>2</sub>, TiO<sub>2</sub>( $e^{-}$ )-2d, TiO<sub>2</sub>( $e^{-}$ )-5d and TiO<sub>2</sub>( $e^{-}$ )-40d.



Fig. S7. The powder X-ray diffraction (XRD) patterns of Am-TiO<sub>2</sub>, TiO<sub>2</sub>-80d and TiO<sub>2</sub>-300d.



Fig. S8. Schematic representation for the transformation from TG to Am-TiO<sub>2</sub>, and to anatase titania. TG as the precursor of Am-TiO<sub>2</sub> is constructed by infinite chains, which are consist of edge-sharing TiO<sub>6</sub> octahedra and organic ligands.<sup>[S4,S5]</sup> After removing the organic ligands by UV irradiation, TG was transformed to Am-TiO<sub>2</sub> consisting of randomly arranged TiO<sub>6</sub> octahedra or their edge-shared fragments with some residual ethylene glycol group. An orderly rearrangement and connection of octahedral TiO<sub>6</sub> units (edge/corner-sharing) would produce anatase titania. Typically, the reaction time of the room-temperature crystallization from Am-TiO<sub>2</sub> to anatase titania is dramatically reduced from 80 d to 2 d through storing e<sup>-</sup> under UV-light irradiation in the presence of methanol (intermediate is  $TiO_2(e^{-})$ ). Methanol as sacrificial agent of photogenerated holes improves the accumulation of  $e^{-}$  on Am-TiO<sub>2</sub>. The storage of  $e^{-}$  may accelerate the room-temperature crystallization through the following two ways: I. The residual ethylene glycol remaining from TG may hinder the rearrangement and interconnection of  $TiO_6$  octahedra in Am-TiO<sub>2</sub>. We propose that the storage of  $e^-$  facilitates the removal of residual ethylene glycol from TiO<sub>6</sub> octahedra and thus accelerates the room-temperature crystallization of porous titania. **II.** A proton was proved to be attached to the surface oxygen in combination with an  $e^{-}$  stored on the Ti<sup>3+</sup> in the vicinity.<sup>[S2]</sup> These protonated surfaces would be easily combined with the hydroxyl group of other TiO<sub>6</sub> octahedral.<sup>[S6]</sup> Thus, oxygen bridge bond (Ti-O-Ti) is formed between two neighbouring TiO<sub>6</sub> octahedral after eliminating a H<sub>2</sub>O molecule, which favors the connection of TiO<sub>6</sub> octahedra to form anatase.



**Fig. S9.** The powder X-ray diffraction (XRD) patterns (a) and infrared spectra (b) of precursor TG and Am-TiO<sub>2</sub>. After UV-light irradiation of TG for 2 h, the crystal structure of TG was completely disintegrated, and the highly crystalline TG was transformed to amorphous Am-TiO<sub>2</sub>. During this transformation, the organic components in TG are mostly removed due to the decomposition by photocatalytic oxidation.



**Fig. S10.** Infrared spectra of Am-TiO<sub>2</sub>, TiO<sub>2</sub>(e<sup>-</sup>)-2d, and TiO<sub>2</sub>(e<sup>-</sup>)-5d in the range of 800 ~ 3800 cm<sup>-1</sup> (a) and 1000 ~ 1500 cm<sup>-1</sup> (b). Characteristic adsorption band of ethylene glycol were observed in the samples.



**Fig. S11.** Thermogravimetric analysis of Am-TiO<sub>2</sub>, TiO<sub>2</sub>( $e^{-}$ )-2d, and TiO<sub>2</sub>( $e^{-}$ )-5d. Their contents of ethylene glycol were about 7.3%, 5.6% and 3.8%, respectively. The residual ethylene glycol in titania are gradually reduced as increasing the storage time of  $e^{-}$ .



**Fig. S12.** Surface photovoltage (SPV) spectra of TiO<sub>2</sub>-80d, TiO<sub>2</sub>(e<sup>-</sup>)-2d, and TiO<sub>2</sub>(e<sup>-</sup>)-5d. The signal of SPV is attributed to the change of surface potential barriers before and after light illumination. The SPV amplitude reveals the photogenerated charge separation efficiency of the samples (TiO<sub>2</sub>(e<sup>-</sup>)-5d > TiO<sub>2</sub>(e<sup>-</sup>)-2d > TiO<sub>2</sub>-80d).



**Fig. S13.** UV-visible diffuse reflectance spectra of  $TiO_2$ -80d,  $TiO_2(e^-)$ -2d, and  $TiO_2(e^-)$ -5d. There are no obvious differences of absorption onset or band gap among the above three samples.



**Fig. S14.** The photocatalytic  $H_2$  evolution over  $TiO_2(e^-)$ -2d was continued for 30 h with evacuation every 3 h (dashed line). Reaction conditions: 50 mg catalyst, 1 wt. % Pt loading; aqueous methanol solution (50 vol%, 100 mL); 300 W Xe lamp as light source.



**Fig. S15.** The powder X-ray diffraction (XRD) patterns of  $TiO_2(e^-)$ -2d before and after photocatalytic H<sub>2</sub> evolution for 30 h.

**Table S1.** Comparison with some recently-reported porous anatase titania with large surface area (> 200  $m^2 \cdot g^{-1}$ , with the order from large to small).

BET surface area (m <sup>2</sup> ·g <sup>-1</sup> )	Crystallization methods	Crystallization temper (°C)	rature References
736	Storage of e <sup>-</sup>	<b>Room temperature</b>	This work
580	Calcination	400	<u>Chem. Commun., 2003, 2078.</u>
554	Hydrothermal treatment	80 <u>J. Am. Chem. Soc.</u> , 2003, <b>125</b> , 149	
$479\pm39$	Calcination	400	Microporous Mesoporous Mater., 2014, 184, 7.
500	Solvothermal treatment	200	Energy Environ. Sci., 2014, 7, 2592.
486	Solvothermal treatment	107	<u>RSC Adv., 2016, 6, 48985.</u>
400	Spontaneous crystallization	Room temperature	Chem. Commun., 2013, 49, 8217.
350 ~ 400	Calcination	450	J. Am. Chem. Soc., 2009, 131, 1802.
347	Calcination	500	<u>RSC Adv., 2015, 5, 8210.</u>
332	Microwave treatment	Room temperature	J. Mater. Chem. A, 2015, 3, 9714.
314	Solution plasma processing	Room temperature	J. Mater. Chem. A, 2014, 2, 1721.
314	Solvothermal treatment	400	J. Phys. Chem. B 2004, 108, 2868.
310	Ionic liquid assistance	60	<u>Dig. J. Nanomater.Bios., 2014, 9, 1451.</u>

304	Calcination	470	ACS Appl. Mater. Interfaces 2016, 8, 22201.
300	Microwave treatment	50	J. Am. Chem. Soc., 2010, 132, 12605.
284	Hydrolysis	Room temperature	Mater. Design, 2016, 108, 269.
284	Calcination	500	J. Colloid Interface Sci., 2010, 341, 359.
250	Solvothermal treatment	140	J. Colloid Interface Sci., 2006, 302,530.
250	Calcination	450	J. Alloys Compd., 2014, 594, 114.
250	Aging	Room temperature	Mater. Chem. Phys., 2006, 97, 207.
245	Calcination	400	J. Mater. Chem., 2012, 22, 22082.
245	Hydrolysis	100	<u>Chem. Commun., 2008, 1184</u> .
242	Solvothermal treatment	120	<u>Crystal Growth &amp; Design, 2009, 9, 1511.</u>
239	Hydrothermal treatment	90	<u>Bull. Korean Chem. Soc. 2015, <b>36</b>, 1694</u> .
227	Solvothermal treatment	140	J. Am. Chem. Soc., 2011, <b>133</b> , 17652.
223	Annealing	250	J. Mater. Chem., 2005, 15, 1263.
223	Water bath heating	70	<u>Appl. Surf. Sci., 2015, 351, 416.</u>
220	Calcination	380	<u>J. Mater. Chem. A, 2014, 2, 12571</u> .
219	Calcination	200	Powder Technol., 2009, 194, 149.
217	Hydrothermal treatment	150	J. Mater. Chem. A, 2015, 3, 3710.
207	Calcination	750	J. Mater. Chem., 2010, <b>20</b> , 2206.
201	Hydrolysis	Room temperature	Appl. Phys. A, 2015, 120, 341.
201	Calcination	350	<u>Chem. Commun. 2000, 1755.</u>

Table S2. BET surface area and average pore size of Am-TiO<sub>2</sub>, TiO<sub>2</sub>-80d, TiO<sub>2</sub>(e<sup>-</sup>)-2d, and TiO<sub>2</sub>(e<sup>-</sup>)-5d.

Samples	Am-TiO <sub>2</sub>	TiO <sub>2</sub> -80d	$TiO_2(e^-)-2d$	$TiO_2(e^-)-5d$
BET surface area $(m^2/g)$	630	400	736	689
Average pore size ( Å )	11.7	17.6	12.8	13.5

Samples	Am-TiO <sub>2</sub>	$TiO_2(e^{-})-2d$	$TiO_2(e^-)-5d$	
Carbon content (%)	2.8	2.5	2.2	
Hydrogenation content (%)	1.8	1.5	1.4	

Table S3. Carbon and Hydrogenation content of Am-TiO<sub>2</sub>, TiO<sub>2</sub>(e<sup>-</sup>)-2d, and TiO<sub>2</sub>(e<sup>-</sup>)-5d.

**Movie 1**. The color of reaction system is gradually turning from white to dark gray as  $e^{-}$  storing on the surface of titania through UV irradiation. Light source: 125 W high pressure mercury lamp; the actual irradiation time is 30 min; the play of movie is accelerated 90 times (20 s).

#### **ESI References:**

- [S1] X. X. Zou, G. D. Li, K. X. Wang, Lu. Li, J. Su and J. S. Chen, Chem. Commun., 2010, 46, 2112;
- [S2] J. Su, X.-X. Zou, G.-D. Li, L. Li, J. Zhao and J.-S. Chen, Chem. Commun., 2012, 48, 9032.
- [S3] F. Zuo, K. Bozhilov, R. J. Dillon, L. Wang, P. Smith, X. Zhao, C. Bardeen, and P. Feng, Angew. Chem. Int. Ed. 2012, 51, 6223.
- [S4] X.-X. Zou, G.-D. Li, M.-Y. Guo, X.-H. Li, D.-P. Liu, J. Su, J.-S. Chen, *Chem. Eur. J.* 2008, **14**, 11123.
- [S5] D. Wang, R. Yu, N. Kumada, N. Kinomura, Chem. Mater., 1999, 11, 2008.
- [S6] H. Yin, Y. Wada, T. Kitamura, S. Kambe, S. Murasawa, H. Mori, T. Sakatac and S. Yanagida, J. Mater. Chem., 2001, 11, 1694.