

## Electronic Supplementary Material

# **Engineering Surface Defects on Two-Dimensional Ultrathin Mesoporous Anatase TiO<sub>2</sub> Nanosheets for Efficient Charge Separation and Exceptional Solar-Driven Photocatalytic Hydrogen Evolution**

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### **1. Characterization**

Two-dimensional ultrathin mesoporous anatase TiO<sub>2</sub> nanosheets with engineered surface defects were measured by X-ray diffraction over the diffraction angle range ( $2\theta$ ) 20-60° with a Bruker-Norius D8 advanced diffractometer, using a Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation source operated at 40 kV and 40 mA. The pictures from scanning electron microscopy (SEM) were obtained with a Hitachi S-4800 instrument working at 15 kV. The images of transmission electron microscopy (TEM) were obtained with a JOEL JEM 2100F instrument operated at 200 kV. Diffuse reflectance spectroscopy (DRS) was measured by a UV/vis spectrophotometer (Shimadzu UV-2550) in the

range of 200-800 nm. Nitrogen adsorption-desorption isotherms at 77 K were collected on an AUTOSORB-1 (Quantachrome Instruments) nitrogen adsorption apparatus. All samples were degassed under vacuum at 150 °C for at least 8 h prior to the measurement. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area. Pore size distributions were obtained using the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the isotherms. The photoluminescence (PL) spectra were studied by a PE LS 55 spectrofluorophotometer with an excitation wavelength of 325 nm. Surface photovoltage spectroscopy (SPS) tests were carried out with a home-built apparatus equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). A scanning Kelvin probe (SKP) test (SKP5050 system, Scotland) was executed to evaluate the work function.

## **2. Photocatalytic activity**

The photocatalytic hydrogen production tests were carried out in an on-line photochemical reaction system at room temperature (AuLight, Beijing, CEL-SPH2N). Classically, the photocatalysts (20 mg) were loaded with Pt (0.5 wt %) evenly dispersed in 90 mL of deionized water and 10 mL of methanol. The suspension of photocatalysts was sealed in the closed-gas circulation reaction cell. Prior to reaction, the reactor and the entire photocatalytic gas circulation system were degassed by a vacuum pump for about 30 min. Hydrogen evolution was studied under AM 1.5G irradiation with a power density of 100 mW cm<sup>-2</sup> from a 300 W Xe lamp and was measured by an online gas chromatograph (SP7800, TCD, 5 Å molecular sieve, N<sub>2</sub>

carrier, Beijing Keruida Limited). To confirm the stability of the photocatalysts, a stability test was carried out by recycling the catalysts, which were subsequently washed with ethanol and deionized water to reactivate the performance.

### **3. Photoelectrochemical measurement**

Photoelectrochemical properties were investigated using a Princeton Versa STAT 3 in a standard three electrode configurations with SDUATNs and UATNs materials used as photoanodes, with Pt plate as counter electrode and Ag/AgCl as reference and containing 1 M KOH solution. The 1 M KOH solution was purged with N<sub>2</sub> at least 30 min and used as the electrolyte. The transparent conducting glass (TCO, fluorine doped SnO<sub>2</sub> layer, sheet resistance 20 Ω/square) substrates were washed with detergent solution and ethanol by ultrasonic 1 h in order to remove the residue. The photoanodes were prepared by using spray pyrolysis technology to anchor the mixture onto the TCO substrates, using a glass-rod to roll a paste containing 50 mg of powders and 3 mL of EtOH on a transparent FTO glass-substrate with an effective diaphragm area 1 cm<sup>2</sup>, followed by calcining 120 min at 400 °C in constant N<sub>2</sub> flow with a constant heating rate of 7 °C min<sup>-1</sup>. An AM 1.5G power system (Autolight CEL-HXF300) was used as the light irradiation source. Linear sweeps voltammograms are analyzed at voltage from -1.2 V to 1.2 V, the chronoamperometry responses are tested at a bias voltage (0.5 V), electrochemical impedance spectroscopy was measured with amplitude of 5 mV and frequencies varying from 0.05 to 10000 Hz. Mott-Schottky plots were performed using a frequency of 1 kHz in the dark.

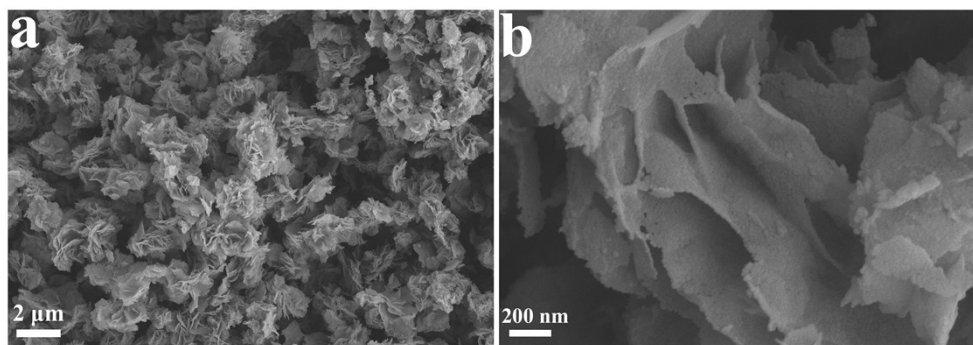


Fig. S1 SEM images (a, b) of UATNs.

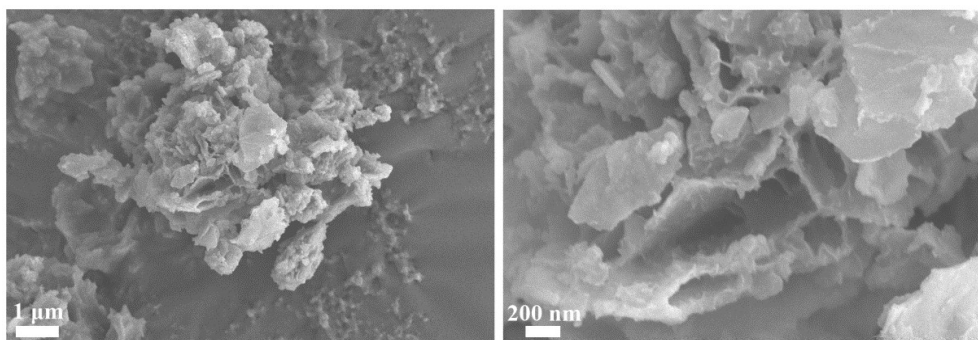


Fig. S2 SEM images of SDUATNs without the treatment of ethylenediamine.

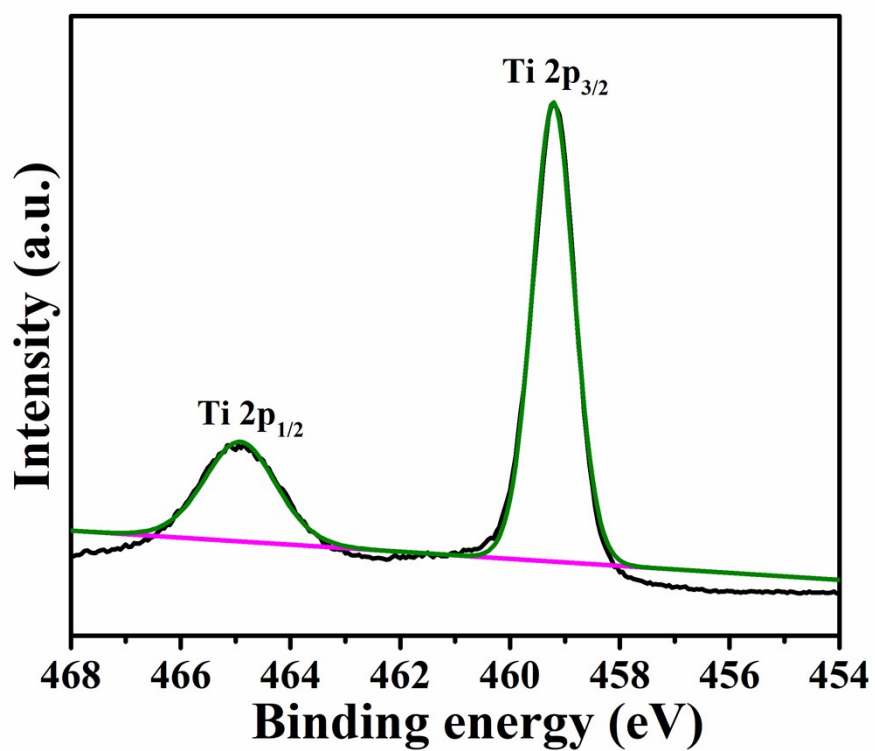
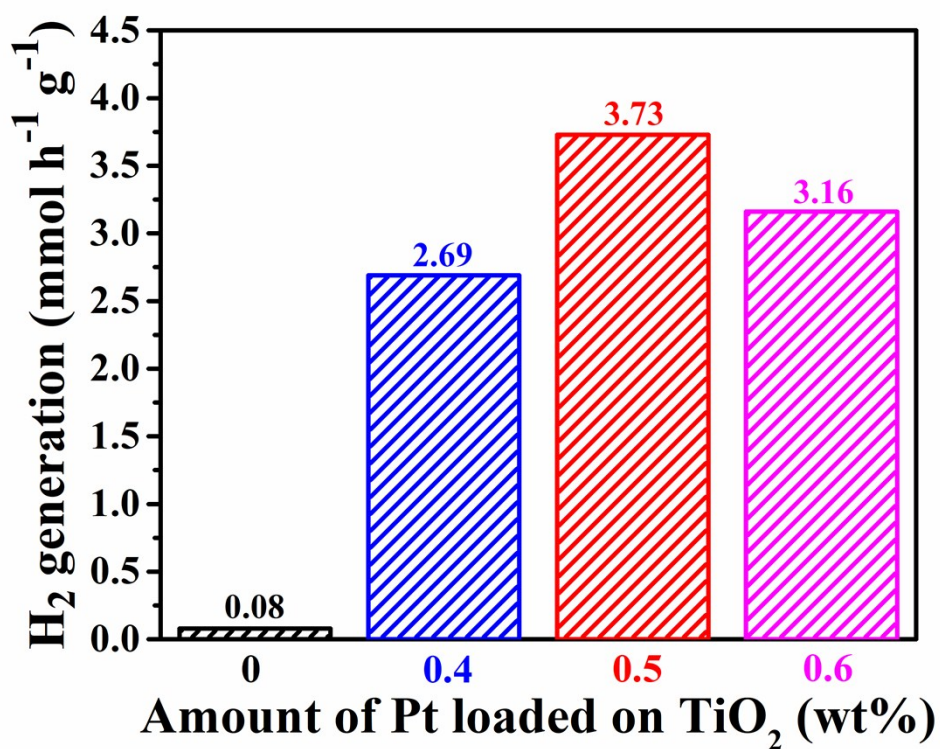


Fig. S3 The XPS spectrum Ti 2p of UATNs.



**Fig. S4** Photocatalytic H<sub>2</sub> production using different Pt loading amounts under AM 1.5G of SDUATNs.

**Table S1** Lattice parameters of SDUATNs and UATNs.

Samples	a	b	c
UATNs	3.7794 Å	3.7794 Å	9.4968 Å
SDUATNs	3.7836 Å	3.7836 Å	9.5106 Å

**Table S2** Comparison of the photocatalytic hydrogen evolution efficiency for the anatase TiO<sub>2</sub> photocatalysts.

Photocatalyst	Light source	Sacrificial agent	H <sub>2</sub>	Ref.
anatase TiO <sub>2</sub>	AM 1.5	methanol	3.73 mmol h <sup>-1</sup> g <sup>-1</sup>	this work
anatase TiO <sub>2</sub>	AM 1.5	methanol	2033.6 μmol h <sup>-1</sup> g <sup>-1</sup>	1
anatase TiO <sub>2</sub>	AM 1.5	methanol	1320 μmol h <sup>-1</sup> g <sup>-1</sup>	2
anatase TiO <sub>2</sub>	UV	methanol	8.66 mmol h <sup>-1</sup> g <sup>-1</sup>	3
anatase TiO <sub>2</sub>	AM 1.5	methanol	3.3 mmol h <sup>-1</sup> g <sup>-1</sup>	4
anatase TiO <sub>2</sub>	AM 1.5	methanol	1272.66 μmol h <sup>-1</sup> g <sup>-1</sup>	5

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