## Electronic Supplementary Information (ESI) Facile synthesis of defect-mediated TiO<sub>2-x</sub> with enhanced

### visible light photocatalytic activity

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#### **Experimental section**

#### Synthesis

Synthesis of defect-mediated  $TiO_{2-x}$ : the reduced  $TiO_{2-x}$  was synthesized by a facile hydrothermal method. In a typical procedure, 400 mg titanium monoxide (TiO) was placed in dried Teflon autoclave with capacity of 50 mL, followed by addition of 20 mL 3M HCl solution. The mixture was sonicated for 15 min and being stirred for 1 h at room temperature. Then, the autoclave was transfer to oven and kept at 160 °C for 24 h. After being cooled to room temperature, the precipitate was collected, washed by deionized water for several times until the ionic strength was less than 10, and then dried in vacuum at 60 °C for 12 h.

*Synthesis of N-doped TiO*<sub>2</sub>: the nitrogen doped TiO<sub>2</sub> was prepared according to a reported method<sup>1</sup>. Typically, a certain amount of anatase was nitrogenized under NH<sub>3</sub> flow at 500 °C for 10 h. After cooling to room temperature, light-yellow powder was obtained and marked as N-T.

*Co-catalyst loading:* Pt species loading was achieved by photodeposition of  $H_2PtCl_6$  under UV light irradiation. 150 mg TiO<sub>2-x</sub> was dispersed into 30 mL H<sub>2</sub>O, then certain amount of  $H_2PtCl_6$  was added to ensure the nominal weight ration of Pt to TiO<sub>2-x</sub> being 1 wt%. After irradiation for 30 min, the precipitates were collected and dried in vacuum at 60 °C.

#### Characterization

Crystal structure identification was performed using Bruker D8 X-ray diffractometer (XRD) with Cu K<sub>a</sub> radiation ( $\lambda = 0.15418$  nm) operating at 40 kV and 40 mA. The data were recorded in the 2 $\theta$  range of 20-80° with a step width of 0.02°. Raman scattering measurements were performed with a multichannel modular triple Raman system (Renishaw Co.) with confocal microscopy at room temperature using the 532 nm laser. A 50× microscope objective lens was used for focusing the laser beam and collection of the scattered light. For both XRD and Raman measurements, the samples were casted onto a glass slides with groove. Scanning electron microscope (SEM) images was obtained with an FEI Nova NanoSEM 230 field-emission scanning electron microscope. The

powders were grinded into 200 mesh and pasted onto conductive adhesives connecting to the sample stage. Microstructures and morphologies were investigated using TecnaiG2 F20 S-TWIN (FEI company) Transmission electron microscopy (TEM) with a field emission gun at 200 kV. Samples were prepared by drop-casting a dispersion of powders in ethanol on a 300 mesh carbon-coated copper TEM grid followed by drying at 60 °C for several minutes. Diffuse reflection spectra (DRS) of the samples were recorded on a Varian Cary-500 spectrophotometer in the range from 250 to 700 nm, and BaSO<sub>4</sub> was used as a reference. X-ray photoelectron spectroscopy (XPS) analysis was conducted on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scienctific) at  $1.2 \times 10^{-9}$  mbar using Al K<sub>a</sub> X-ray beam (1486.6 eV). The XPS spectra are charge corrected to the adventitious C 1s peak at 284.6 eV. The TiO<sub>2-x</sub> powders were squeezed into tablet and etched for 5 seconds with an argon ion gun (1 kV, 0.5  $\mu$ A) before XPS measurement. A Bruker model A300 spectrometer was used for detection of the electron-spin resonance (ESR) signals of samples at 77 K. The settings were center field, 3512.48 G; microwave frequency, 9.86 GHz; and power, 6.35mW. The photoluminescence (PL) spectra were obtained using a Varian Cary-Eclipse 500 with an excitation wavelength at 300 nm. Photoelectrochemical tests were conducted on a ZENNIUM electrochemical workstation (Zahner, Germany) with a typical three-electrode system. The FTO/TiO<sub>2-x</sub> film electrodes served as the working electrode. The counter and reference electrodes were Pt plate and Ag/AgCl electrode, respectively. 0.2 M Na<sub>2</sub>SO<sub>4</sub> (pH=6.8) served as electrolyte. The nitrogen adsorption and desorption isotherms were characterized using a Micrometrics ASAP 2020 analyzer. The degassing process was conducted at 120°C for 5 h. Nitrogen adsorption measurements were recorded at 77K and the relative pressure ranges used for calculating the BET specific surface area was 0.06-0.3.

#### **Photocatalytic Measurement**

Photocatalytic  $H_2$  production experiments were conducted in a side-irradiation vessel connected to a glass-enclosed gas circulation system. In a typical run, 0.1g of sample loaded with Pt was suspended in 100 mL 20% methanol aqueous solution under magnetic stirring. After degassing the system for half an hour, a 300 W Xe lamp with a 400 nm cut-on filter (PerfectLight Corp.) was applied to execute the photocatalytic reaction. The products were analyzed by gas chromatography (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD). For cycling test, all the  $H_2$  was evacuated off and then another test proceeded.



Fig. S1 O 1s XPS spectrum of TiO<sub>2-x</sub>



Fig. S2 Digital pictures of  $TiO_{2-x}$  and two control samples



Fig. S3  $N_2$  adsorption-desorption isotherms of TiO<sub>2-x</sub> and N-T at 77k

#### Reference

1 K. Nukumizu, J. Nunoshige, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *Chem. Lett.* 2003, **32**, 196.