Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information of the manuscript entitled

Hydrogenated nanotubes/nanowires assembled from TiO_2 nanoflakes exposing {111} facets: excellent photocatalytic CO_2 reduction activity and charge separation mechanism between polar (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces

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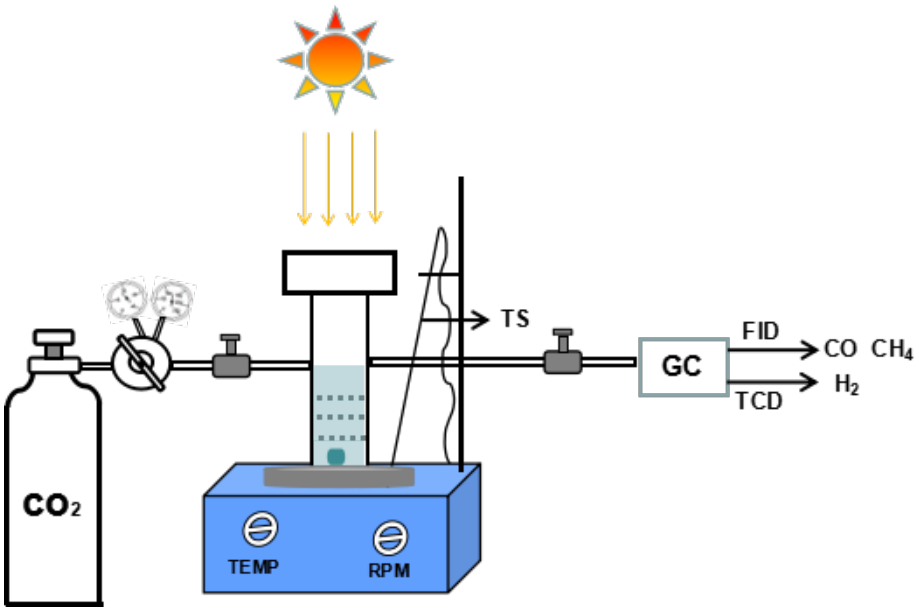

TS: Temperature sensor TEMP: Temperature RPM: Revolutions Per Minute

GC: Gas chromatography FID: Flame Ionization Detector

TCD:Thermal Conductivity Detector

Figure S1 The reactor and detector used for photocatalytic reduction of CO_2 with H_2O

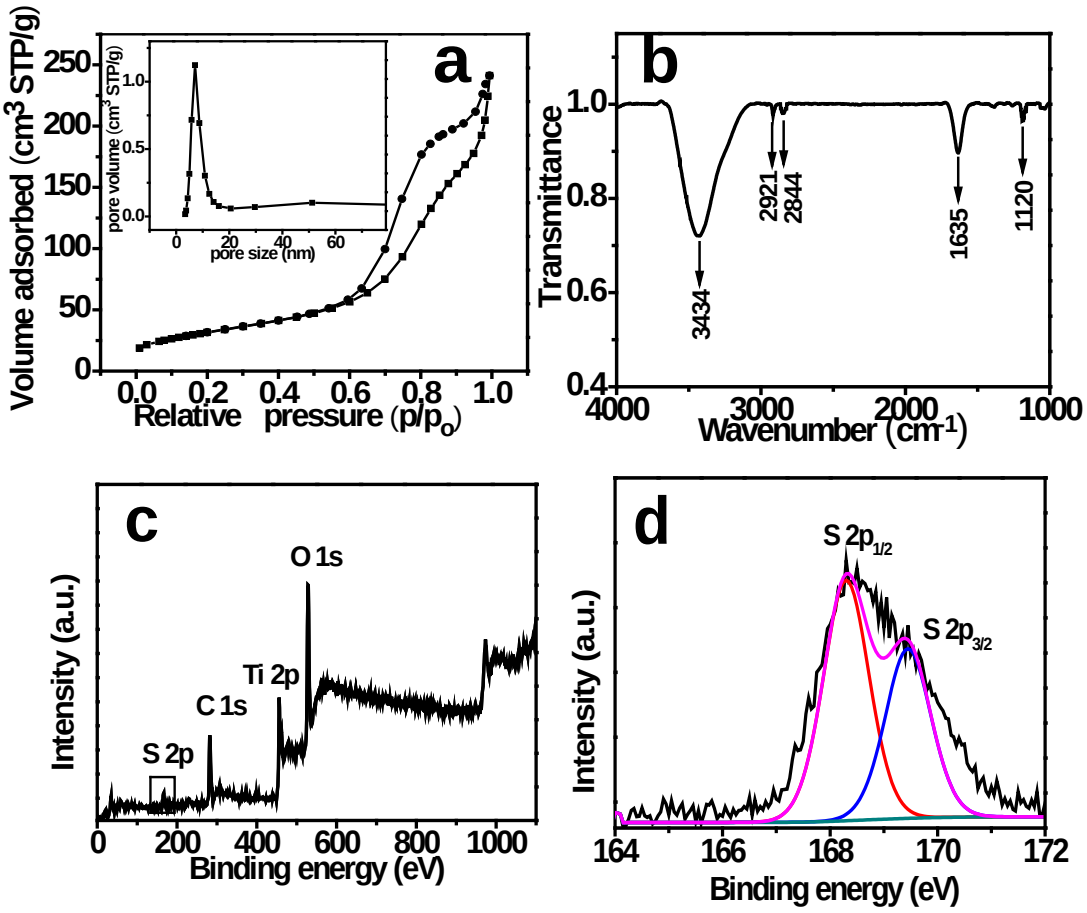

Figure S2 (a) N_2 adsorption-desorption isotherm and (inset) corresponding Barrett–Joyner–Halenda (BJH) pore size distribution, (b) IR spectrum, (c) Survey XPS and (d) S 2p XPS spectra of the as-synthesized TiO_2 nanotubes/nanowires.

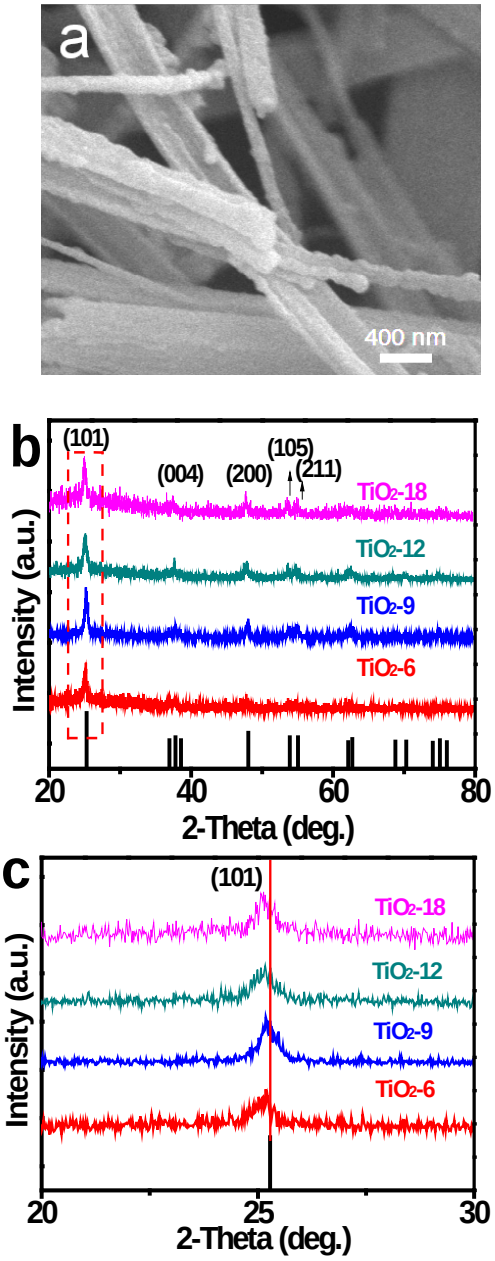

Figure S3 (a) SEM image of TiO_2-18 hydrogenated TiO_2 samples, (b) XRD patterns of the TiO_2-6, TiO_2-9, TiO_2-12 and TiO_2-18 hydrogenated TiO_2 samples and (c) enlargement of (101) peaks in (b).

The apparent quantum yield measurement

According to the literature [1], the apparent quantum yields for H_2, CO and CH_4 were measured with monochromatic light obtained by using band pass filter of 365 nm with the intensity of 40 mW cm^{-2}. The irradiation area was controlled as 12.56 cm^2, and the apparent quantum yield was calculated as below:

$$\eta_{AQY} = \frac{Ne}{Np} \times 100\% = \frac{n \times M \times N_A}{\frac{E_{total}}{E_{photo}}} \times 100\% = \frac{n \times M \times N_A}{\frac{S \times P \times t}{h \times \frac{c}{\lambda}}}$$

$$= \frac{n \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where n is 2, 2 and 8, for H_2, CO and CH_4, respectively. M is the amount of production (mol), N_A is Avogadro constant (6.022×10^{23} /mol), h is the Planck constant (6.626×10^{-34} J·s), c is the speed of light (3×10^8 m/s), S is the irradiation area (cm^2), P is the intensity of irradiation light (W/cm^2), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m).

Preparation of TiO_2 photocatalyst film on indium-tin oxide (ITO) conductor glass

TiO_2 photocatalyst film was prepared on ITO) conductor glass. Typically, an ITO conductor glass with the size of 2.0 cm × 2.0 cm was cleaned ultrasonically with ethanol,

acetone and isopropanol for 10 min., respectively, and then dried by nitrogen to obtain a clean ITO glass. The cleaned ITO glass is irradiated by a 30 W UV lamp for 6 min. 0.020 g of photocatalyst was added into 4 mL ethanol. The mixture was treated under ultrasonic irradiation for 3.0 h, forming a turbid liquid. 150 μL of turbid liquid was added into the ITO glass substrate, which were rotated at 500 revolutions per minute (rpm) for 10 s, and subsequently rotated at 2000 rpm for 30 s. The film was heated at 50 ^{o}C for 10 min in air. The procedure was repeated eight times to obtain TiO_2 photocatalyst film.

The current-voltage (I-V) property measurement.

I-V property of the as-prepared TiO_2 photocatalyst film was measured in dark. Schematic diagram of the current sensing measurement is shown in Figure. S4. The electrical property was recorded by a Keithley 2601 source measurement unit at room temperature.

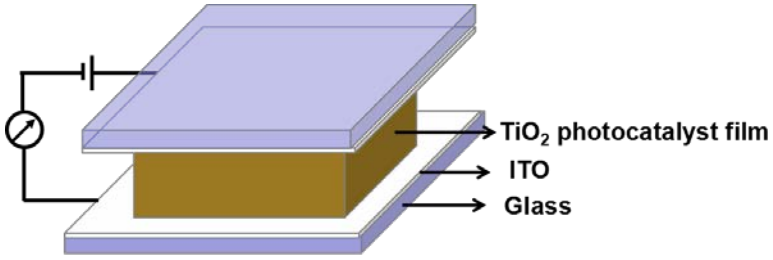

Figure S4. Schematic diagram of the current-voltage measurement.

The Photocurrent measurement

The photocurrent measurement of the as-prepared TiO_2 photocatalyst film was performed on a CHI 660E electrochemical station (Shanghai Chenhua) with a three-electrode system, in which Pt foil and saturated Ag/AgCl (E_0 = 0.2046 V) were used as the counter electrode and reference electrode, respectively. The electrolyte was 0.5 M Na_2SO_4 solution (PH = 7). A 3 W light emitting diode (LED) lamp (λ= 365 nm) was used as the UV irradiation source. Distance between the LED lamp and work electrode is 10.0 cm. The schematic illustration for set up of photocurrent measurement is shown in Figure. S5.

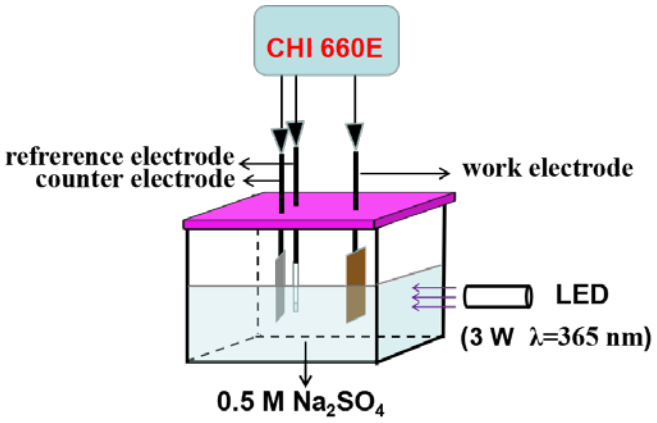

Figure S5. Schematic illustration for set up of photocurrent measurement

Reference

[1] Z. J. Wang, X. Y. Yang, T. J. Yang, Y. B. Zhao, F. Wang, Y. Chen, J. H. Zeng, C. Yan, F. Huang, J. X. Jiang, *ACS Catal.*, 2018, **8**, 8590–8596.