

## Supporting Information

### Hierarchical TiO<sub>2</sub>/Ni(OH)<sub>2</sub> Composite Fiber with Enhanced Photocatalytic CO<sub>2</sub> Reduction Performance

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#### 1. Experimental

**Synthesis of TiO<sub>2</sub> nanofibers.** TiO<sub>2</sub> nanofibers were prepared by electrospinning method. In a typical procedure, the precursor solution consisting of 0.9 g polyvinyl pyrrolidone (PVP), 10 mL ethanol, 2 mL glacial acetic acid (CH<sub>3</sub>COOH) and 3 mL tetrabutyl titanate (TBOT) was continuously stirred for 12 h to obtain a homogeneous solution. Then the solution was added into 20 mL plastic syringe connecting with a stainless steel needle (diameter of 0.4 mm) at the tip. Electrospinning was conducted at an applied potential of 20 kV with a feeding rate of 3 mL/h and a distance of ~13 cm from the tip to the round collector. The temperature and relative humidity of the chamber was 25 °C and 30 %, respectively. Finally, the as-obtained mats of nanofibers were annealed at 500 °C for 1 h with a heating rate of 2 °C/min to eliminate PVP and denote as T.

**Synthesis of hierarchical TiO<sub>2</sub>/Ni(OH)<sub>2</sub> composite nanofibers.** TiO<sub>2</sub> nanofibers inserted grown with Ni(OH)<sub>2</sub> were fabricated by a facile precipitation method. 150 mg of TiO<sub>2</sub> nanofibers was well dispersed into 40 mL of distilled water by sonication. Then 0.112 g of hexamethylenetetramine, 0.023 g of citric acid trisodium salt dehydrate and a certain amount of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were added

into the above dispersion to form a light green solution. The as-obtained dispersion was heated at 90 °C in an oil bath for 6 h with continuously stirring. After cooling down naturally, the light green precipitate was separated by centrifugation and washed with distilled water for several times, dried at 80 °C overnight. The as-obtained TiO<sub>2</sub>/Ni(OH)<sub>2</sub> nanofibers sample was denoted as TN<sub>x</sub>, the x means the weight ratio of Ni(OH)<sub>2</sub> to TiO<sub>2</sub>, amongst, TN15 was chose for further characterization due to its large ration of Ni(OH)<sub>2</sub> and remarkable selective alcohol production from photocatalytic CO<sub>2</sub> reduction. The Ni(OH)<sub>2</sub> nanosheets were prepared via a similar process without adding TiO<sub>2</sub> nanofibers as support and denoted as N.

## 2. Characterization

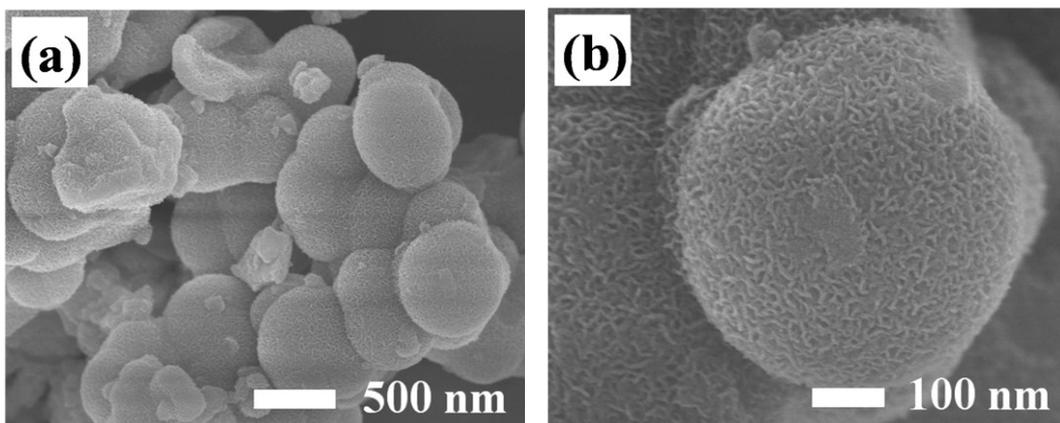
The X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer with Cu K $\alpha$  irradiation source ( $\lambda=0.15418$  nm) at a scan rate( $2\theta$ ) of 0.05°s<sup>-1</sup>. The accelerating voltage was 40 kV. The morphology observation was conducted on a JSM-7500 field emission scanning electron microscope (FESEM, JEOL, Japan) at an accelerating voltage of 5 kV, equipped with an X-Max 50 energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, Britain). Transmission electron microscopy (TEM) images were collected using a Titan G260-300 microscope at an accelerating voltage of 300 kV. The nitrogen adsorption and desorption isotherms of the samples were measured using an ASAP 2020 nitrogen adsorption apparatus (Micromeritics Instruments, USA). The samples were subjected to be degassed at 150 °C. The BET surface area was determined by a multi-point BET method using the adsorption data in the relative pressure ( $P/P_0$ ) range of 0.05–0.3. The pore size distribution of the samples was determined by Barret–Joyner–Halender (BJH) method. The UV–vis diffuse reflectance spectra (DRS) were obtained with a UV-vis spectrophotometer (UV2550, Shimadzu, Japan) with BaSO<sub>4</sub> as a reflectance standard. X-ray

photoelectron spectroscopy (XPS) was performed with ultrahigh vacuum VG EXCALAB 210 electron spectrometer with Mg K $\alpha$  (1253.6 eV) as radiation source. Fourier transform infrared (FTIR) spectra were obtained on a Shimadzu IR Affinity-1 FTIR spectrometer. The CO<sub>2</sub> adsorption was measured using a Micromeritics ASAP 3020 carbon dioxide adsorption apparatus (USA). *In situ* DRIFTS were recorded on Nicolet iS50 spectrometer (Thermo Scientific, USA) equipped with a HgCdTe (MCT/A) detector. Before testing, the sample was firstly degassed at 150 °C for 4 h to clean the surface. During the measurement, the sample was uniformly dispersed into the DRIFTS cell, then CO<sub>2</sub> gas and H<sub>2</sub>O vapor was introduced into the reaction cell and maintained for 60 min under irradiation of a LED light (3 W, 365 nm, Shenzhen Lamplic Technology Co. Ltd) to obtain the adsorption curves. The light spectrum of Xenon lamp was measured using a typical microreflectivity/microtransmission fiber spectrometer (Ocean Optics USB2000+ fiber spectrometer). The photoelectrochemical measurement was performed in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution by a CHI660C electrochemical analyzer using a standard three-electrode system. The sample was coated onto a 2 × 1.5 cm FTO glass electrode, which was used as working electrode. Pt wire and Ag/AgCl (saturated KCl) were served as counter-electrode and reference electrode, respectively. A 3 W UV-LED (365 nm) was used as the light source.

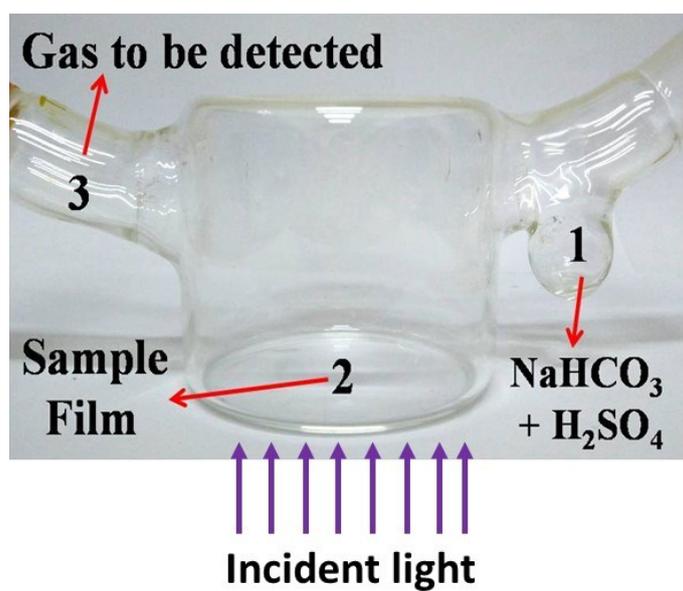
### **3. Photocatalytic reduction of CO<sub>2</sub>**

The photocatalytic reduction of CO<sub>2</sub> was performed in a 200 mL homemade Pyrex reactor (Figure S2). During the photocatalytic reaction, a 350 W Xe arc lamp was used as the simulated sunlight source and positioned 10 cm above the photocatalytic reactor, the spectrum of the Xe light is shown in Figure S3. The light intensity was measured to be 40 mW cm<sup>-2</sup> by an UV radiometer.

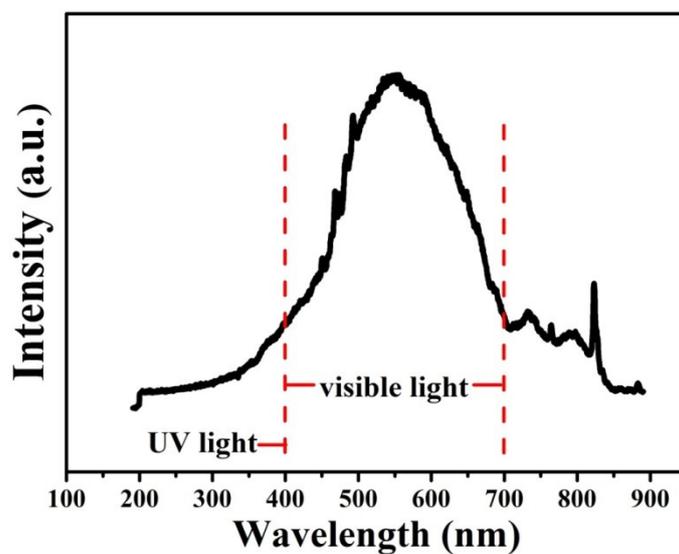
Typically, 50 mg of the sample was uniformly dispersed into 10 mL deionized water, followed by depositing on the bottom of the reactor after drying at 80 °C. CO<sub>2</sub> and H<sub>2</sub>O vapor were *in situ* generated by the reaction of NaHCO<sub>3</sub> (0.084 g, added into the reactor before seal) and H<sub>2</sub>SO<sub>4</sub> aqueous solution (0.3 mL, 2 M) which was introduced into the reaction cell using a syringe. Before irradiation, the reactor was blown with nitrogen for 30 min to remove air and assure that the reaction system was under anaerobic conditions. 1 mL of gas was pumped from the reactor and analyzed by a gas chromatograph (PGC-80, PANNA instrument, Changzhou, China) equipped with a flame ionized detector (FID) and methanator. Blank experiments were carried out in the absence of light irradiation or CO<sub>2</sub> to confirm that light and CO<sub>2</sub> were two key influencing elements for photocatalytic CO<sub>2</sub> reduction. <sup>13</sup>CO<sub>2</sub> isotope tracer experiment was conducted to verify the carbon resource. Similar photocatalytic reaction process was performed except that CO<sub>2</sub> and H<sub>2</sub>O were generated using isotope-labelled sodium bicarbonate (NaH<sup>13</sup>CO<sub>3</sub>, Cambridge Isotope Laboratories Inc., USA) and H<sub>2</sub>SO<sub>4</sub> aqueous solution. After 1 h of photocatalytic reaction, 250 μL of mixed gas was taken out from the reactor and examined by a gas chromatography-mass spectrometer (6980N network GC system–5975 inert mass selective detector, Agilent technologies, USA) to analyze the products.



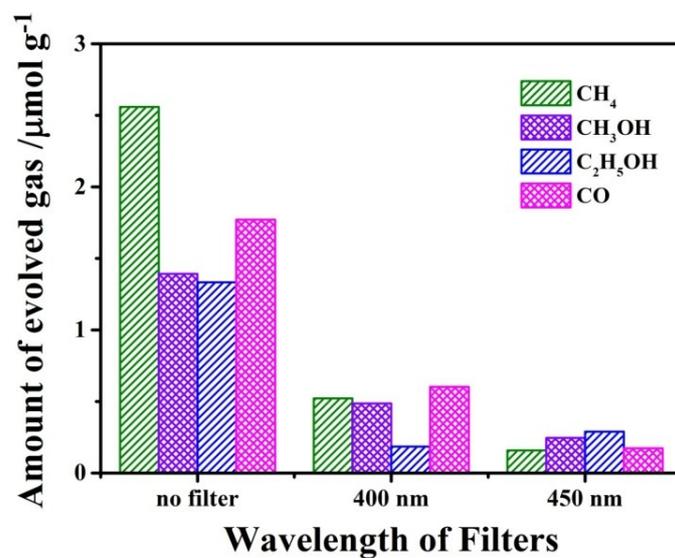
**Fig. S1** FESEM images of  $\text{Ni}(\text{OH})_2$  synthesized without the  $\text{TiO}_2$  nanofiber support.



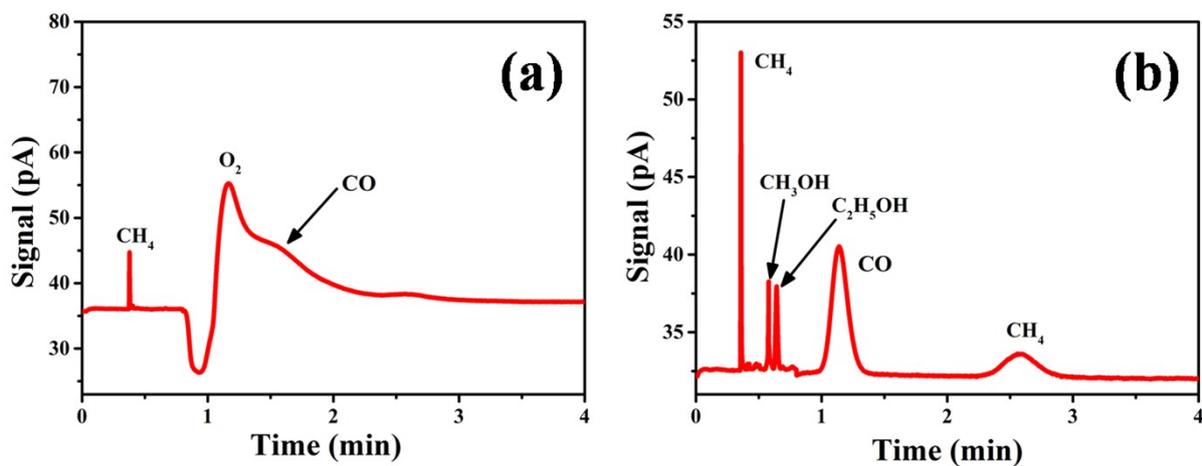
**Fig. S2** Homemade Pyrex reactor for photocatalytic  $\text{CO}_2$  conversion.



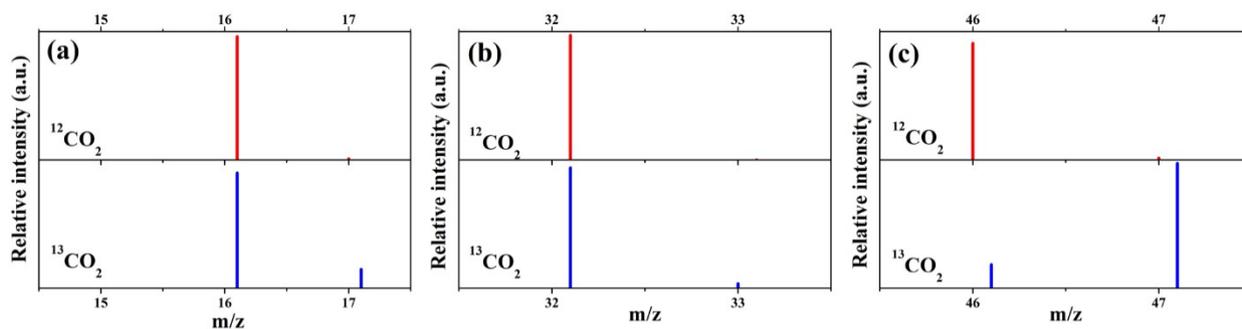
**Fig. S3** The spectrum of the 350 W Xenon lamp.



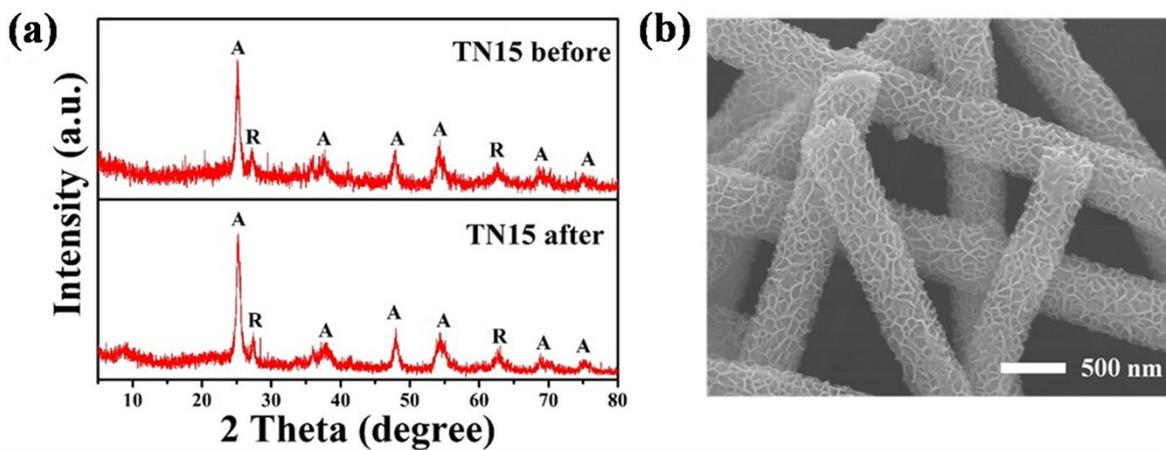
**Fig. S4** The photocatalytic  $\text{CO}_2$  conversion over sample TN15 for 3 h in the presence of 400 and 450 nm filter, respectively.



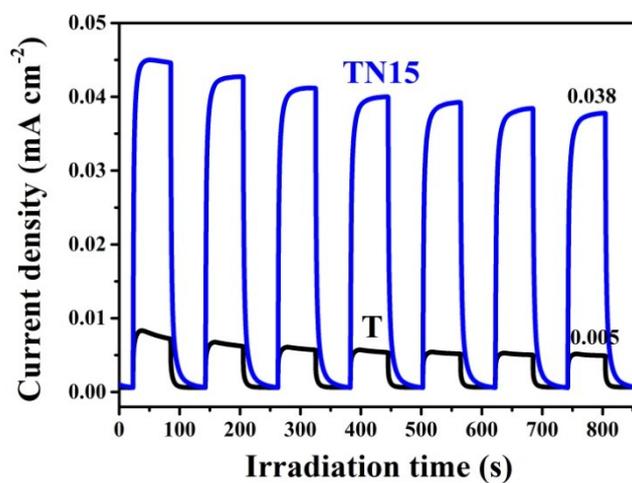
**Fig. S5** Gas chromatogram result after 4 h of irradiation for photocatalytic CO<sub>2</sub> reduction over sample T (a) and TN15 (b).



**Fig. S6** The GC-MS patterns of the produced CH<sub>4</sub> (a), CH<sub>3</sub>OH (b) and C<sub>2</sub>H<sub>5</sub>OH (c) over sample TN15 using <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> as the carbon source, respectively.



**Fig. S7.** (a) XRD patterns of sample TN15 before and after photocatalytic CO<sub>2</sub> reduction. (b) SEM image of TN15 after photoreaction.



**Fig. S8** Transient photocurrent responses of the electrodes deposited using sample T and TN15 under the illumination of 365 nm LED illumination.

**Table S1.** Specific surface areas, pore volumes, average pore sizes of the samples.

Sample	Ni(OH) <sub>2</sub> (wt %)	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	APS (nm)
T	0	49	0.10	7.78
TN15	15	42	0.08	7.03
N	100	80	0.11	5.68

Notes: S<sub>BET</sub>: the specific surface area; V<sub>p</sub>: pore volume; APS: average pore size.