

Supplementary Information

Efficient Nb₂O₅@g-C₃N₄ heterostructures for enhanced photocatalytic CO₂ reduction with highly selective conversion to CH₄

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S1 Experimental section

Materials. Urea (NH₂CONH₂, AR, ≥ 99.0%), Ammonium niobate oxalate hydrate (C₄H₄NNbO₉·XH₂O) and ethanol (C₂H₅OH, ≥ 99.7%) from Shanghai Titan Technology Co., Ltd. All materials were used as received and without further purification. Deionized water, with a resistivity of 18.25 MΩ cm, was used throughout the experiments.

Synthesis of g-C₃N₄. The proper amount of urea was weighed out and filled the crucible. The crucible was placed in a set muffle furnace under 550 °C for 4h to obtain g-C₃N₄ presenting light yellow powder.

Synthesis of Nb₂O₅. An appropriate amount of ammonium niobium oxalate hydrate (C₄H₄NNbO₉·XH₂O) was calcined in the crucible at 600 °C in Muffle furnace for 6h, and then took out the grinding to obtain a good crystalline Nb₂O₅ sample.

S2 Characterization

The Powder X-ray diffraction (PXRD) patterns of the samples are obtained using a X-ray diffractometer with Copper target Kα radiation (λ = 1.5418 nm), scanning range (Angle 2θ) of 10°~ 90°, scanning time of 0.5 s. The morphology of samples is investigated using scanning electron microscope (SEM) (AMRAY 1000B), the elements distribution is detected by SEM EDS mapping. And Transmission electron microscopy (TEM) images and energy dispersive spectrum (EDS) mapping were

acquired on a Thermo Scientific Talos F200X and Super-X, respectively. Elements content is evaluated by X-ray photoelectron spectroscopy (XPS) recorded by K-Alpha+ (Thermo Fisher Scientific, U.S.A.) where the source of radiation was mono Al K α . The unpaired electrons in the atoms or molecules of the sample to see whether vacancy phenomena are produced by Electron Paramagnetic Resonance (EPR) (A300, Bruker Daltonics, U.S.A.). Nitrogen (N₂) sorption–desorption measurements are applied to study the surface area and porosity of V_{O,N}-NBCN at 77K via Micromeritics Tristar apparatus. The specific surface area of the sample is equivalent to the Brunauer-Emmett-Teller (BET) theoretical model, and the gas adsorption of the prepared photocatalyst is measured by BET. The Barrett-Joyner-Halenda (BJH) model is used to obtain the pore volume and pore size distribution curves. UV–vis diffuse reflectance spectra (DRS) are obtained using a Shimadzu UV-2700 recording spectrophotometer. The electrochemical impedance spectroscopy (EIS) was performed by CHI 660D electrochemical workstation with a standard three-electrode cell at room temperature. The photo luminescence (PL) and time-resolved PL decay measurements are conducted on a fluorescence spectrometer (PF5301PC, Shimadzu, Japan) using a Xenon lamp (excitation at 330 nm) as a light source.

S3 EIS measurements

The photoelectrocatalytic performance test of the catalyst was carried out on the Chenhua electrochemical workstation of CHI600D. The 300W xenon lamp light source was used as the light source for photoelectric catalytic performance testing. The electrochemical performance test was carried out in an electrolytic cell of a three-electrode system. The ITO coated with photocatalyst sample was the working electrode, the Ag/AgCl (saturated KCl) electrode was used as the reference electrode, and the Pt sheet is the counter electrode. All test experiments are carried out at room temperature. The tested electrolyte is 0.5 M Na₂SO₄ solution. During the test, the applied bias voltage is 0 V, and the open circuit potential frequency range is 10⁶ Hz to 10⁻¹ Hz.

S4 Measurement of photocatalytic activity

The CO₂ photoreduction on the photocatalysts in the presence of H₂O was conducted in the MCP-WS1000 Photochemical workstation (Beijing Perfectlight). The photocatalytic CO₂ reduction was carried out in a 50 mL Pyrex reactor. Ultrahigh-purity CO₂ (99.99%) was fed continuously into the reactor at a rate of 0.1 L min⁻¹ for 2 h to remove oxygen in the water and saturate the solution. 15 mg of sample was

uniformly dispersed in the mixture of 20 mL of sodium bicarbonate solution, 19 mg $(\text{Ru}(\text{bpy})_2(\text{CN})_2\text{Ru}(\text{bpy}(\text{COO})_2)_{22})$ and 352 mg ascorbic acid by stirrer ($(\text{Ru}(\text{bpy})_2(\text{CN})_2\text{Ru}(\text{bpy}(\text{COO})_2)_{22})$ is photosensitizer and ascorbic acid is sacrificial agent). Photocatalytic activities were investigated using a 5 W white LED light ($400 \text{ nm} \leq \lambda \leq 800 \text{ nm}$) as the visible light source. The gas product (0.5 mL, taken from the reactor) was analyzed using a GC-9790 Plus gas chromatograph equipped with a FID and a TCD detector (ZHE JIANG FULI ANALYTICAL INSTRUMENTS INC). Only the products of CO and CH_4 were detected. The selectivity of the formed CO and CH_4 is calculated according to the following equation:

$$\text{Selectivity for CO} = \frac{2R(\text{CO})}{8R(\text{CH}_4) + 2R(\text{CO})} \times 100\%$$

$$\text{Selectivity for CH}_4 = \frac{8R(\text{CH}_4)}{8R(\text{CH}_4) + 2R(\text{CO})} \times 100\%$$

where $R(\text{CO})$ and $R(\text{CH}_4)$ are the yields of reactively-formed CO and CH_4 respectively.

To demonstrate the CH_4 and CO are derived from the photocatalytic reduction of CO_2 for NB@CN (1:5), four control experiments were conducted: (1) Experiment with NB@CN (1:5), CO_2 , water, $(\text{Ru}(\text{bpy})_2(\text{CN})_2\text{Ru}(\text{bpy}(\text{COO})_2)_{22})$ and ascorbic acid, but without light irradiation; (2) Experiment with NB@CN (1:5), CO_2 , $(\text{Ru}(\text{bpy})_2(\text{CN})_2\text{Ru}(\text{bpy}(\text{COO})_2)_{22})$, ascorbic acid and light irradiation, but without water; (3) Experiment with NB@CN (1:5), water, $(\text{Ru}(\text{bpy})_2(\text{CN})_2\text{Ru}(\text{bpy}(\text{COO})_2)_{22})$, ascorbic acid and light irradiation, but without CO_2 and the Ar is employed to replace CO_2 ; (4) Experiment with CO_2 , water, $(\text{Ru}(\text{bpy})_2(\text{CN})_2\text{Ru}(\text{bpy}(\text{COO})_2)_{22})$, ascorbic acid and light irradiation, but without NB@CN (1:5).

S5 In-situ DRIFTS measurement for CO_2 photoreduction

In-situ DRIFTS (diffuse reflectance infrared Fourier transform spectra) tests were conducted on Nicolet iS50 FT-IR spectrometer (Thermo Fisher, USA) equipped with a designed reaction chamber and a liquid water cool HgCdTe (MCT) detector. The sample along with a Cu holder was put into the reaction chamber. Then the sample was purged with N_2 (30 mL/min) for 1 h to blow out all the gases in the cell and adsorbed on the samples. Then, the mixture of CO_2 (5 mL/min) and H_2O vapor were introduced into the chamber for 30 min to make sure the sorption equilibrium before

irradiation.

S6 Supplementary figures

Table S1. Control experiments for photocatalytic of NB@CN (1:5).

photocatalyst	Reaction medium	CH ₄ yield (μmol/g)
-	No photocatalyst	0.062
NB@CN (1:5)	No light	0.108
NB@CN (1:5)	No CO ₂	0.089
NB@CN (1:5)	No H ₂ O	0.068

Table S2. Relevant products of CO₂ reduction and the corresponding reduction potentials with reference to NHE at pH=7.

Product	Reaction	<i>E</i> (V vs. NHE)
CH ₄	CO ₂ +8H ⁺ +8e ⁻ → CH ₄ +2H ₂ O	-0.24
CO	CO ₂ +2H ⁺ +2e ⁻ → CO+H ₂ O	-0.52

Table S3. The calculated E_g, E_{VB} and E_{CB} of g-C₃N₄ and Nb₂O₅ samples.

	E _{CB} /V	E _g /eV	E _{VB} /V
g-C ₃ N ₄	-0.37	2.91	2.54
Nb ₂ O ₅	-0.46	2.4	1.94

Table S4. Comparison of photocatalytic activity between NB@CN (1:5) heterojunction and reported catalysts for CO₂ reduction.

Photocatalyst	Light sources	sacrificial agent	Catalyst amount	CH ₄	CO	Ref
NB@CN (1:5)	5 W white LED light	ascorbic acid	15 mg	3.18 ($\mu\text{mol/g/h}$)	0.16 ($\mu\text{mol/g/h}$)	This work
g-C ₃ N ₄ -W ₁₈ O ₄₉	300W Xe lamp	/	50 mg	1.38 ($\mu\text{mol/g/h}$)	0.92 ($\mu\text{mol/g/h}$)	1
Nb ₂ O ₅ Nanofibers	UV Light	/	20 mg	0.09 ($\mu\text{mol/g/h}$)	1.42 ($\mu\text{mol/g/h}$)	2
g-C ₃ N ₄ @CeO ₂	300W Xe lamp	/	50 mg	1.16 ($\mu\text{mol/g/h}$)	3.36 ($\mu\text{mol/g/h}$)	3
g-C ₃ N ₄ (V _N)	300W Xe lamp	/	100 mg	1.18 ($\mu\text{mol/g/h}$)	0.63 ($\mu\text{mol/g/h}$)	4
Nb ₂ O ₅ basic bismuth nitrate	UV Light	sodium oxalate	10 mg	/	2.8 ($\mu\text{mol/g/h}$)	5
3% <i>m</i> -CeO ₂ -g-C ₃ N ₄	300W Xe lamp	/	100 mg	0.014 ($\mu\text{mol/g/h}$)	0.012 ($\mu\text{mol/g/h}$)	6
CuO-Nb ₂ O ₅	UV Light	/	300 mg	2 ($\mu\text{mol/g/h}$)	/	7
P-CeO ₂ /g-C ₃ N ₄	300W Xe lamp	/	50 mg	/	0.523 ($\mu\text{mol/g/h}$)	8

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