

Supporting materials:

**Preparing of diazanyl and SnO₂ bi-activated g-C₃N₄ for
enhanced photocatalytic CO₂ reduction**

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Experimental Section

Chemicals

Urea (H_2NCONH_2 , AR, $\geq 99.0\%$), stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, AR, $\geq 98.0\%$) and silver nitrate (AgNO_3 , AR, $\geq 98.0\%$) were purchased from Tianjin kemio chemical reagent co., Ltd. Sodium nitrite (NaNO_2 , AR, $\geq 99.0\%$), concentrated hydrochloric acid (HCl , 36.0-38.0%), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25-28%) and hydrogen peroxide (H_2O_2 , 30%) were obtained from Tianjin Yongda Chemical Reagent co., Ltd. All the reagents were used without further purification. All the water used in the experiment was deionized water.

Catalyst preparation

UCN: Pure g- C_3N_4 named as UCN was prepared by thermal polycondensation of urea in a muffle furnace according to our previous report [S1].

$\text{SnO}_2/\text{HyUCN}$: The preparation of diazanyl and SnO_2 bi-activated g- C_3N_4 ($\text{SnO}_2/\text{HyUCN}$) was showed in Figure 1. Typically, 0.2 g UCN sample was dispersed in 50 mL 18% HCl aqueous solution in the ice bath. Then, 50 mL NaNO_2 (1 mol/L) aqueous solution was added dropwise. After being stirred for 1 h, 30 mL concentrated HCl solution with 0.1 mol SnCl_2 solute was added to the above reaction mixture in the ice bath, which was then stirred for 2 h at normal temperature. Subsequently, it was filtered and washed thoroughly by deionized water nearly neutrally. Then the obtained sediment was dispersed in 50 mL water and concentrated ammonia water was added dropwise until the $\text{pH} = 9$. The suspension was filtered, washed with water nearly neutrally, and dried at $60\text{ }^\circ\text{C}$ in vacuum.

SnO₂/UCN: In order to reveal the attribution of diazanyl and SnO₂ to the enhancement of photocatalytic performance, diazanyl was removed by H₂O₂. Typically, 0.2 g as prepared SnO₂/HyUCN sample was dispersed in 30 mL deionized water, then 20 mL H₂O₂ was added dropwise and the reaction mixture was continued stirring for 1 h. Then it was filtered, washed with deionized water more than three times, and finally dried at 60 °C in vacuum. The surface diazanyl of SnO₂/UCN has been proved to be removed completely according to the XPS spectrum of Ag/SnO₂/UCN (see supporting materials, Figure S4).

Catalyst characterization

A Smart Lab X-ray diffractometer (Rigaku, Tokyo, Japan) was used to record X-ray diffraction (XRD) patterns, which was operated at 40 kV and 40 mA using Cu Ka radiation. The infrared spectra were obtained on a Fourier transform infrared (FT-IR) spectrometer (Nicolet Magna-IR 55), for which KBr was used as the reference. Morphology of the photocatalysts was imaged using a scanning electron microscope (SEM, ZEISS Sigma 500) and a transmission electron microscopy (TEM, JEOL JEM-2100F (RH)). X-ray photoelectron spectra (XPS) were obtained by an X-ray photoelectron spectrometer (Thermo ESCALAB 250XI). N₂ and CO₂ adsorption-desorption tests were carried out on a Quantachrome Autosorb-IQ automated gas sorption system (TriStar II 3020) at 77 and 303.15 K, respectively. UV-vis diffuse reflectance spectra (DRS) were obtained using a UV-vis spectrometer with BaSO₄ as a reference (Perkin Elmer, Lambda 650 s). Time-resolved photoluminescence (PL) spectroscopy (excitation wavelength = 350 nm) was recorded on a FLS980

Multifunction Steady-State and Transient-State Fluorescence Spectrometer (Edinburgh Instruments). Steady-state surface photovoltage (SPV) was obtained by self-assembled surface photovoltaic testing equipment based on lock-in amplifier including a CHF-XM xenon lamp light source (500W), an SR830-DSP phase-locked amplifier, an Omni-5007 monochromator, an SR540 modulation fan, a sample cell and a computer. A Nicolet IS-50 instrument was used to perform In-situ Fourier transform infrared spectroscopy [23].

DFT Computation

DFT calculations were conducted on Materials Studio software using DMol3 code [S2-S5]. The adsorption energy (E_{ads}) was calculated as follows:

$$E_{ads} = E_{adsorbates + surface} - E_{surface} - E_{adsorbates}$$

Where $E_{adsorbates + surface}$ was the total energy of g-C₃N₄ surface with adsorbates, $E_{surface}$ is the total energy of the clean surface, and $E_{adsorbates}$ was the total energy of adsorbates.

Photoelectrochemical measurement

Transient photocurrent response of the samples were measured in a three-electrode system on a CHI660E electrochemical workstation (CHI Instruments, Shanghai, China) using a 0.5 M Na₂SO₄ aqueous solution as electrolyte. A certain amount photocatalyst samples located on a fluorinated-tin-oxide (FTO) conducting glass was used as the working electrode, which was obtained by a blade method using ethyl cellulose as the filmogen [S6]. Ag/AgCl and Pt were used as the reference and counter electrodes, respectively. The photocurrent response was recorded at their open circuit potential (0.268 V vs Ag/AgCl).

Photocatalytic reduction of CO₂

The experiments of photocatalytic reduction CO₂ were conducted on a Labsolar-III AG closed system (Pyrex glass, Beijing Perfect Light Technology Co. Ltd., China) with a volume of 350 mL. After adding 5 ml of deionized water (provides the water vapor required for carbon dioxide reduction) to the reactor, 50 mg photocatalyst was uniformly dispersed onto a glass sheet (26 cm²) in the glass reactor. Before light irradiation, the air in the system was removed by vacuum degassing for 5 min and then poured in Ar gas. Then 1 mL CO₂ gas was inject in the system. Subsequently, the reactor was irradiated by a 300 W xenon lamp (PLS-SXE300, Beijing Perfect light Technology Co., Ltd China) from the top. At each time interval, 1 mL gas was taken from the reactor and qualitatively analyzed by a gas chromatography (GC9790II, Zhejiang FuLi Analytical Instrument Co., Ltd China).

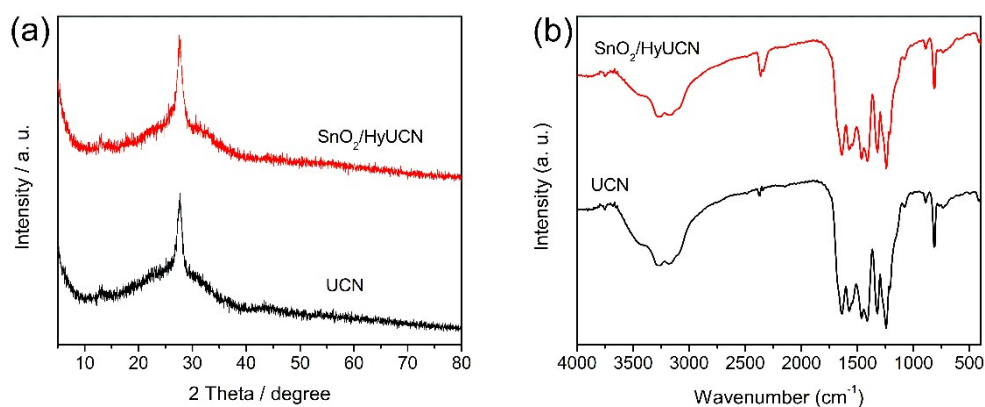


Fig. S1 XRD patterns (a) and FT-IR spectra (b) of UCN and SnO₂/HyUCN.

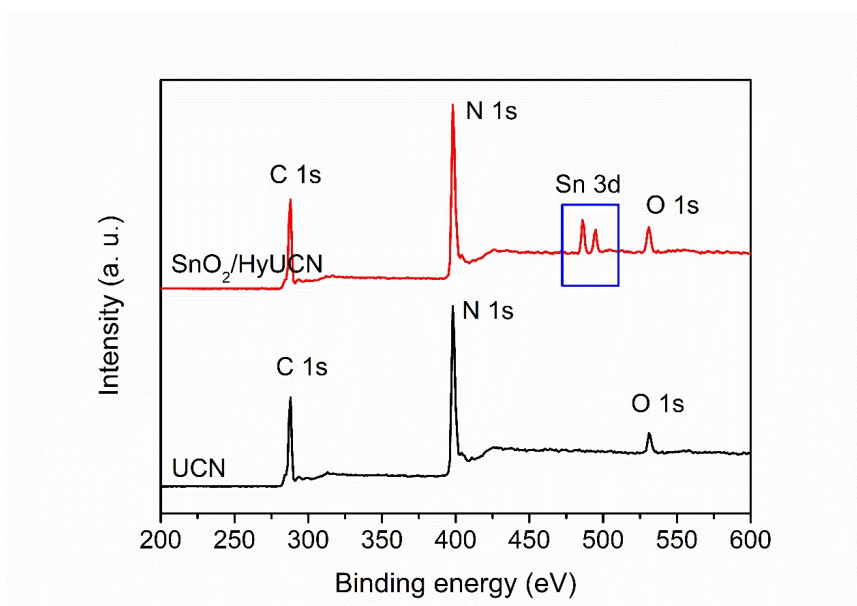


Fig. S2 Survey XPS spectra of UCN and SnO₂/HyUCN.

Preparing of Ag@UCN/SnO₂

Ag⁺ oxidation method: 0.1 g SnO₂/HyUCN was dispersed in 50 mL deionized water, then 10 mL 0.05 M AgNO₃ aqueous solution was added dropwise and the reaction mixture was stirred for 2 h subsequently. During the stirring process, the dispersion changed from light yellow color to light brown, and finally a brown product after drying was obtained, which was named as Ag@UCN/SnO₂.

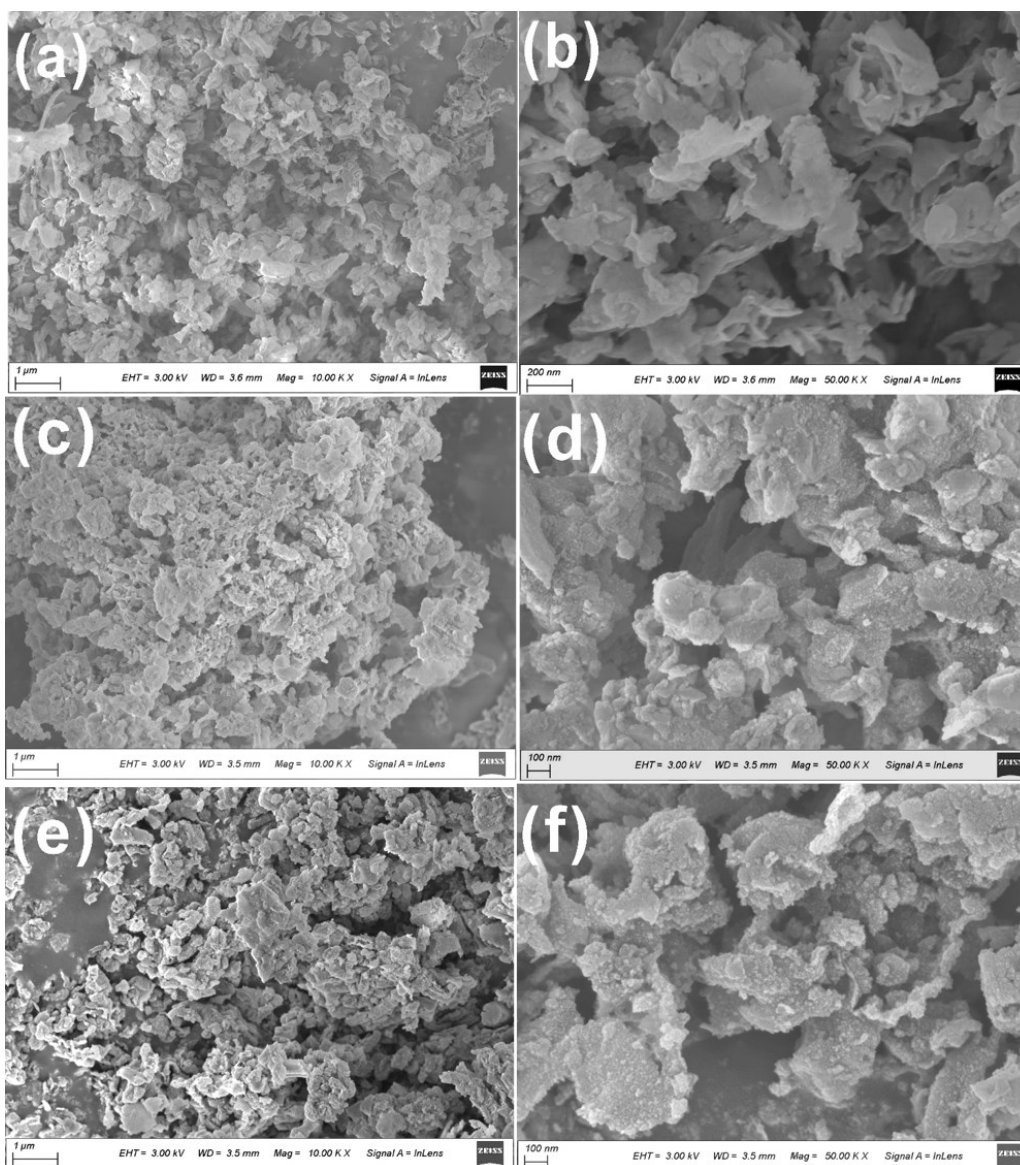


Fig. S3 SEM images of UCN (a, b), SnO₂/HyUCN (c, d) and Ag@UCN/SnO₂ (e, f)

Preparing of Ag/SnO₂/UCN:

Ag⁺ oxidation method was also used to determine whether the diazanyl groups of SnO₂/UCN were removed completely by H₂O₂. Typically, 0.1 g SnO₂/UCN was dispersed in 50 mL deionized water, then 10 mL 0.05 M AgNO₃ aqueous solution was added dropwise and the reaction mixture was stirred for 2 h subsequently. During the stirring process, the color of the dispersion did not change. After washing thoroughly with water and drying in an electronic oven, a sample was obtained and named

Ag/SnO₂/UCN. Fig. S4 was its XPS spectra, from which Ag element could not be found. Therefore, the diazanyl groups of SnO₂/UCN were proved to be removed completely by H₂O₂.

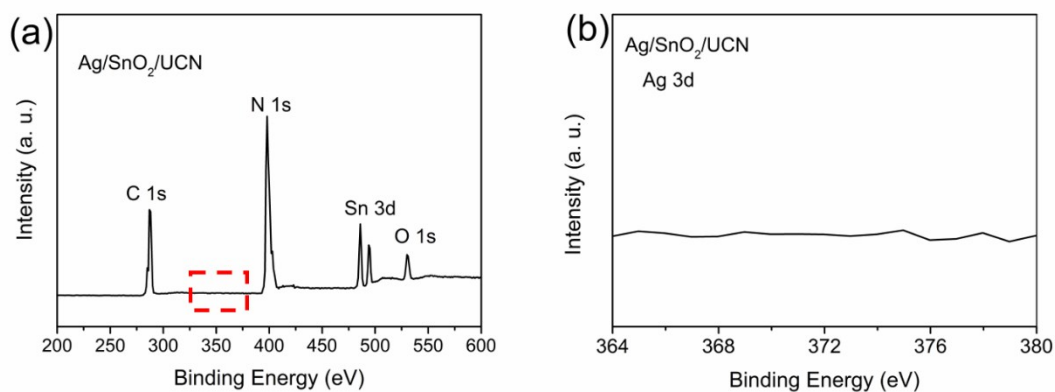


Fig. S4 Survey XPS (a) and high-magnified spectrum of Ag 3d (b) of Ag/SnO₂/UCN.

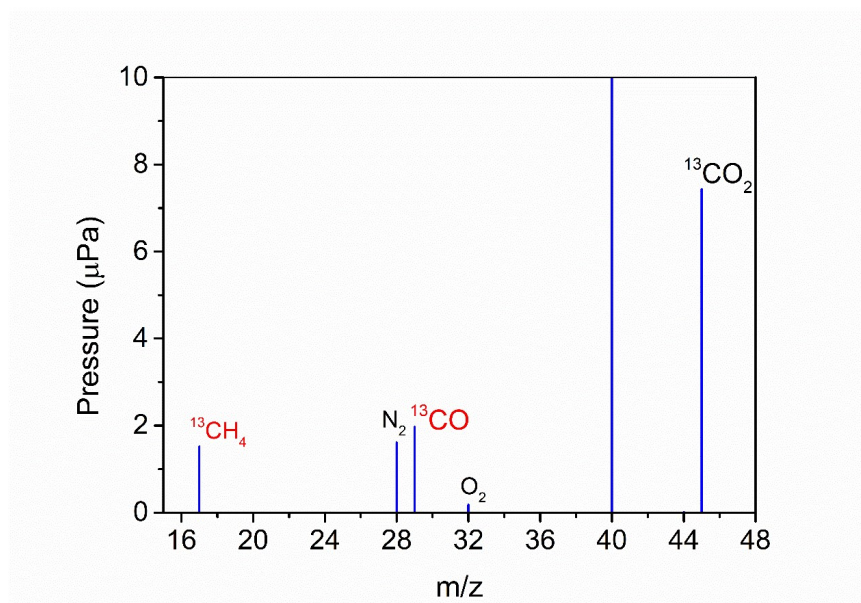


Figure S5. ¹³CO and ¹³CH₄ was detected by Hiden HPR20 on-line gas mass spectra analysis system.

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