

**Chainmail Co-catalyst of NiO shell-encapsulated Ni for Improving Photocatalytic
CO₂ Reduction over g-C₃N₄**

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Experimental Section

Materials

Thiourea (ACS, $\geq 99.0\%$) and nickel nitrate hexahydrate (AR, 98%) were purchased from Aladdin and used without further purification. NaHCO_3 and triethanolamine were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis

g-C₃N₄: Thiourea (20 g) was heated to 500 °C for 3 h in air, applying a heating rate of 5 °C min⁻¹. The resultant yellow bulk was milled into g-C₃N₄ powder.

Ni/NiO/g-C₃N₄: This system was prepared from a solution containing g-C₃N₄ powder (180 mg), nickel nitrate hexahydrate solution (3 g L⁻¹), triethanolamine (10 mL), and distilled water with a total volume of 100 mL. Then, this system was vacuumed by irradiation using a xenon lamp (PLS SXE300, Beijing Perfect Light Technology Co., Ltd., Beijing, China) for 3 h. The Ni core was synthesized by photocatalytic reduction of Ni²⁺. Then, the suspension in the system was centrifuged, washed three times with absolute ethanol to obtain NiO shell by atmospheric oxidation, and dried under vacuum at 60 °C. The dried Ni/NiO/g-C₃N₄ powder was stored under an argon atmosphere.

Characterization

The crystalline phase of the samples was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer at room temperature with Cu-K α radiation. Diffraction patterns were recorded in the range of 5–80°. X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo ESCALAB 250XI X-ray photoelectron spectrometer (Al K α , 150 W, C1 s 284.8 eV). UV–Vis diffuse reflectance spectroscopy (DRS) was performed using a UV–Vis spectrometer (Perkin Elmer, Lambda 850, BaSO₄ reference) in a wavelength range of 190–800 nm. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were recorded on a JEOL JEM–2100F (URH) Field Emission Electron Microscope. Time-resolved photoluminescence (PL) spectroscopy (excitation wavelength, 310 nm) was recorded on a FLS980 Multifunction Steady-State and Transient-State Fluorescence Spectrometer (Edinburgh Instruments) at room

temperature. Brunauer–Emmett–Teller (BET) surface areas were measured using a Quantachrome Autosorb-iQ automated gas sorption system at 77 °K. Transient surface photovoltage data were recorded on a 500 MHz digital oscilloscope (TDS 3054C, Tektronix; Beaverton, OR, USA). The powder samples were placed on an indium-tin-oxide (ITO) electrode, and another ITO electrode was used to press the sample into a thin film. A laser pulse ($\lambda = 355$ nm; pulse width: 4 ns) using the third-harmonic generation of a Nd:YAG laser (Quantel Brilliant Eazy: BRILEZ/IR-10) was employed as the light source. Steady-state surface photovoltage and transient photovoltage were measured by self-assembled surface photovoltaic testing equipment (SPV) based on lock-in amplifier including xenon lamp light source (CHF-XM500 W), phase-locked amplifier (SR830-DSP), monochromator (Omni-5007), modulation fan (SR540), sample cell and computer.

Photocatalytic reduction of CO₂

Ni/NiO/g-C₃N₄ or g-C₃N₄ photocatalyst (0.05 g) were uniformly dispersed on a glass plate with an area of 26 cm². Then, the glass plate was transferred into a quartz reactor with a volume of 350 mL with 5 mL water and 1atm Ar gas. 1 mL high-purity CO₂ gas (99.99%) was injected into the quartz reactor. Subsequently, the reactor was irradiated using a xenon lamp (PLS SXE300, Beijing Perfect Light Technology Co., Ltd., Beijing, China). At regular time intervals, 1 mL of gas was extracted from the reactor with a syringe, and the gas composition was analyzed by gas chromatography (GC 9790II, Zhejiang Fuli Analytical Instrument Co., Ltd., China) with a flame ionization detector (FID, TDX-01 columns) and a thermal conductivity detector (TCD, 5A columns). Selectivity = CO/(CO + CH₄). The production yield was quantified using a calibration curve. The outlet gases were determined to be mainly CO, CH₄, and small quantities of O₂ and H₂. ¹³CO was detected by Hiden HPR20 on-line gas mass spectra analysis system.

Photoelectrochemical measurements

Photoelectrochemical measurements of the catalysts were measured on an electrochemical workstation (CHI 660e) in a three-electrode (counterpart electrode: Pt, reference electrode: Ag/AgCl) quartz reactor. 0.5 M Na₂SO₄ solution, a mixed

solution of 0.1 M $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]\cdot 3H_2O$ are used as the electrolyte solutions for photocurrent and LSV, and electrochemical impedance, respectively. Working electrodes for $g-C_3N_4$ and $Ni/NiO/g-C_3N_4$ were prepared applying the doctor-blading method. Then, 0.01 g ethyl cellulose was dissolved in about 15 mL ethanol with 0.1 g catalyst. Subsequently, a glass stick was applied to FTO with a layer of high-temperature adhesive tape on the edge, followed by drying in air and activation at 120 °C for 2 h.

In-situ Fourier transform infrared spectrometer (FT-IR) analysis

In-situ Fourier transform infrared spectrometry was performed on a Nicolet IS-50 instrument. The sample was filled into an in-situ IR cell, and CO_2 and H_2O vapors were introduced into the cell and fiber source (FX300, Beijing Perfect Light Technology Co., Ltd., Beijing, China) through the CaF_2 window of the cell. Before the measurement, the samples were degassed at 423 °K for 4 h. The baseline was obtained before the sample reached CO_2 adsorption equilibrium within 1 h.

Computational details

DFT calculation

DFT calculations were performed using DMol³ code based on Materials Studio software. The electron exchange and correlation were approximated by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. Dispersion corrected DFT (DFT-D) by Grimme was used to describe the van der Waals interaction between the gas molecules and the $g-C_3N_4$ surface (001), which has been successfully applied to simulate the surface and reaction properties for various catalysts. The valence electron configurations were $1s^1$ for H, $2s^22p^2$ for C, $2s^22p^3$ for N, $2s^22p^4$ for O and $3d^84s^2$ for Ni, respectively. The Monkhorst-Pack grid of $2\times 2\times 1$ k-point was used for Brillouin-zone. For convergence threshold, the total energy of the system, maxforce, and displacement tolerances were set to be 1×10^{-5} Ha, 0.002 Ha/Å and 0.005 Å, respectively. In order to avoid interaction of two slab a vacuum space of 20 Å was built. All electrons core treatment was included in calculations and all the precision was setting as fine.

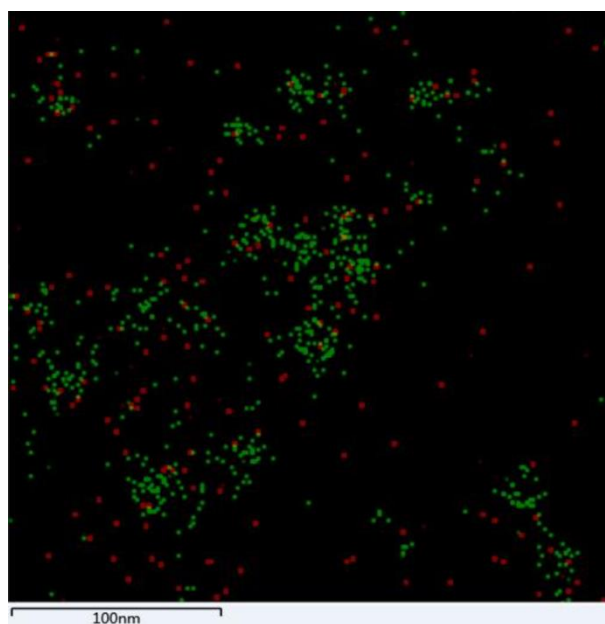


Figure S1. Elemental mapping of Ni (green) and O (red).

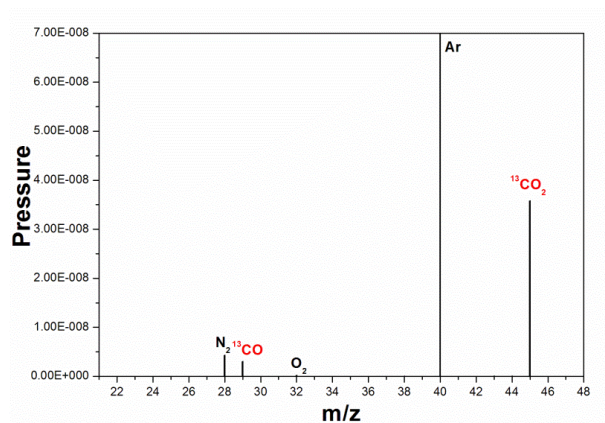


Figure S2. ¹³CO was detected by Hiden HPR20 on-line gas mass spectra analysis system.

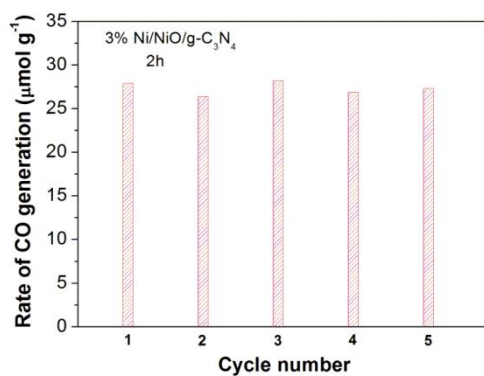


Figure S3. Photocatalytic stability experiments of Ni/NiO/g-C₃N₄ for photocatalytic CO₂ reduction.

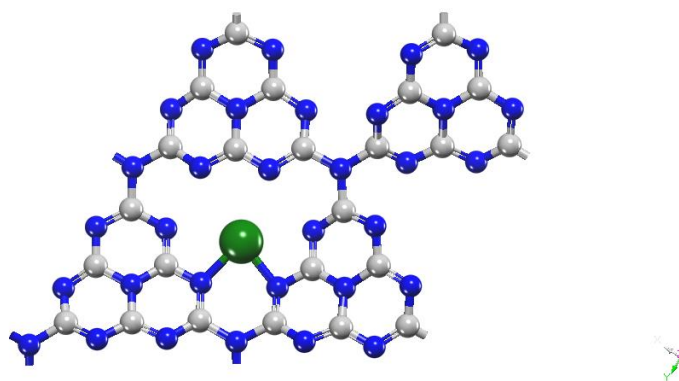


Figure S4. Model of Ni-g-C₃N₄ for DFT calculation.

Table S1 Comparison of g-C₃N₄-based photocatalysts for CO₂ conversion.

Photocatalysts	light source	CO generation	Ref.
		rate $\mu\text{mol g}^{-1} \text{h}^{-1}$	
g-C ₃ N ₄ /NiAl-LDH	300 W xenon lamp, $\lambda > 420 \text{ nm}$	2.84	S1
Mg/g-C ₃ N ₄	300 W xenon lamp	2.85	S2
Cu/g-C ₃ N ₄	350 W xenon lamp	9.89	S3
(-CN)/g-C ₃ N ₄	300 W xenon lamp, $\lambda > 420 \text{ nm}$	0.39	S4
c-Cu ₂ O_gC ₃ N ₄	LED lamp (8 W)	0.002	S5
Au/g-C ₃ N ₄	300 W xenon lamp	6.59	S6
NiO/g-C ₃ N ₄	300 W xenon lamp	4.17	S7
g-C ₃ N ₄		1.52	This
Ni/NiO/g-C ₃ N ₄	300 W xenon lamp	13.96	work

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