Chainmail Co-catalyst of NiO shell-encapsulated Ni for Improving Photocatalytic CO\textsubscript{2} Reduction over g-C\textsubscript{3}N\textsubscript{4}

Chunqiu Han,\textsuperscript{a} Rumeng Zhang,\textsuperscript{a} Yinghao Ye,\textsuperscript{c} Li Wang,\textsuperscript{a} Zhaoyu Ma,\textsuperscript{a} Fengyun Su,\textsuperscript{a} Haiquan Xie,\textsuperscript{a} Ying Zhou,\textsuperscript{c} Po Keung Wong,\textsuperscript{d} Liqun Ye,\textsuperscript{ab*}

a. Engineering Technology Research Center of Henan Province for Solar Catalysis, College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, P. R. China.
b. College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, P. R. China.
c. State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, School of Materials Science and Engineering, Southwest Petroleum University, Chengdu, 610500, P. R. China.
d. School of Life Sciences, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR, P. R. China.

**Corresponding Author**

* Prof. Liqun Ye

E-mail: yeliqun@163.com
Experimental Section

Materials
Thiourea (ACS, ≥ 99.0%) and nickel nitrate hexahydrate (AR, 98%) were purchased from Aladdin and used without further purification. NaHCO₃ and triethanolamine were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis

\textbf{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.

\textbf{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–Kα 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 Kα, 150 W, C1s 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 (λ = 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 1 atm 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$_3$N$_4$ and Ni/NiO/g-C$_3$N$_4$ 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$_2$O 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 DMol$^3$ 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$_3$N$_4$ 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$^2$2p$^2$ for C, 2s$^2$2p$^3$ for N, 2s$^2$2p$^4$ for O and 3d$^8$4s$^2$ for Ni, respectively. The Monkhorst-Pack grid of 2×2×1 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. $^{13}$CO was detected by Hiden HPR20 on-line gas mass spectra analysis system.

Figure S3. Photocatalytic stability experiments of Ni/NiO@g-C$_3$N$_4$ for photocatalytic CO$_2$ reduction.
Figure S4. Model of Ni-g-C$_3$N$_4$ for DFT calculation.
<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>light source</th>
<th>CO generation rate $\mu$mol g$^{-1}$ h$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C$_3$N$_4$/NiAl-LDH</td>
<td>300 W xenon lamp, $\lambda &gt; 420$ nm</td>
<td>2.84</td>
<td>S1</td>
</tr>
<tr>
<td>Mg/g-C$_3$N$_4$</td>
<td>300 W xenon lamp</td>
<td>2.85</td>
<td>S2</td>
</tr>
<tr>
<td>Cu/g-C$_3$N$_4$</td>
<td>350 W xenon lamp</td>
<td>9.89</td>
<td>S3</td>
</tr>
<tr>
<td>(-CN)/g-C$_3$N$_4$</td>
<td>300 W xenon lamp, $\lambda &gt; 420$ nm</td>
<td>0.39</td>
<td>S4</td>
</tr>
<tr>
<td>c-Cu$_2$O$_x$gC$_3$N$_4$</td>
<td>LED lamp (8 W)</td>
<td>0.002</td>
<td>S5</td>
</tr>
<tr>
<td>Au/g-C$_3$N$_4$</td>
<td>300 W xenon lamp</td>
<td>6.59</td>
<td>S6</td>
</tr>
<tr>
<td>NiO/g-C$_3$N$_4$</td>
<td>300 W xenon lamp</td>
<td>4.17</td>
<td>S7</td>
</tr>
<tr>
<td>g-C$_3$N$_4$</td>
<td></td>
<td>1.52</td>
<td>This</td>
</tr>
<tr>
<td>Ni/NiO/g-C$_3$N$_4$</td>
<td>300 W xenon lamp</td>
<td>13.96</td>
<td>work</td>
</tr>
</tbody>
</table>


