Supporting Information

Atomically Dispersed Copper Catalysts for Highly Selective CO₂ Reduction

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Experimental Details

Reagents and Chemicals. All of the chemicals in this experiment were purchased from commercial sources and used without further purification. Copper(II) chloride nonahydrate (CuCl$_2$$\cdot$2H$_2$O, Sinopharm Chemical), Zirconium chloride (ZrCl$_4$, Sinopharm Chemical), 2-amino-terephthalic acid (Aladdin), DMF (Sinopharm Chemical), Nafion solution (5.0 wt%, Alfa Aesar), Deionized water (18.2 MΩ cm) was obtained from a Millipore system.

Synthesis of UIO-66-NH$_2$-Cu. 1.64 g ZrCl$_4$ was dissolved in 80 ml N’ N-Dimethyl Formamide under ultrasound for 5 min, which was subsequently added into 1.27 g 2-amino terephthalic acid and CuCl$_2$$\cdot$2H$_2$O under vigorous stirring. The obtained solution was put into the Steel kettle for heating 24 h under 120 ºC. The precipitate was collected by centrifugation and washed with methanol several times and dried in vacuum at 70 ºC for overnight.

Synthesis of CuN$_3$/NC/T-ZrO$_2$. The powder of UIO-66-NH$_2$-Cu was placed in a tube furnace. Then the sample was heat-treated in Ar atmosphere at 900 ºC for 3 h with a heating rate of 5 ºC/min and then naturally cooled to room temperature. Furtherly, the powder was washed 3 times with deionized water and dried in vacuum at 70 ºC for overnight.

Synthesis of CuN$_3$/NC/M-ZrO$_2$. The powder of UIO-66-NH$_2$-Cu was placed in a tube furnace. Then the sample was heat-treated in Ar atmosphere at 700 ºC for 3 h with a heating rate of 5 ºC/min and then naturally cooled to room temperature. Furtherly, the powder was washed 3 times with deionized water and dried in vacuum
Synthesis of CuN$_3$/NC. The powder of CuN$_3$/NC/T-ZrO$_2$ was added into 15 mL water and 0.1 mol HF solution, and then the mixture solution was put static in 2 hours. After that, the powder was washed 3 times with deionized water and dried in vacuum at 70 °C for overnight.

Characterization. The Powder X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda=1.54$ Å). Transmission electron microscopy (TEM) images were obtained by Hitachi HT7700 (accelerating voltage of 100 kV). Scanning electron microscopy (SEM) was carried out by a Hitachi 8100 (scanning electron microscope at an acceleration voltage of 5 kV). High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) measurements were taken on a JEM-ARM200F. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on ESCALAB 250. Elemental analysis of Fe in the solid samples was quantified by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). Nitrogen and CO$_2$ sorption measurements were conducted using a Micromeritics ASAP 2460 system.

XAFS measurements

The X-ray absorption fine structure (XAFS) spectra data (Co K-edge) were recorded at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF, electron storage ring operated at 2.5 GeV with a maximum current of 250 mA). The data were collected in fluorescence excitation mode using a Lytle detector. All solid samples were
pelletized as disks of 13 mm diameter with 1 mm thickness using graphite powder as
a binder and measured at room temperature.

**Table S1.** Structural parameters extracted from the Cu K-edge EXAFS fitting. (S$_0^2$=0.86)

<table>
<thead>
<tr>
<th>sample</th>
<th>Scattering pair</th>
<th>CN</th>
<th>R(Å)</th>
<th>σ$^2$(10$^{-3}$Å$^2$)</th>
<th>ΔE$_0$(eV)</th>
<th>R factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuN$_3$/NC/T-ZrO$_2$</td>
<td>Cu-N/C</td>
<td>2.87</td>
<td>1.95</td>
<td>6.35</td>
<td>4.14</td>
<td>0.0131</td>
</tr>
<tr>
<td>Cu foil</td>
<td>Cu-Cu</td>
<td>12*</td>
<td>2.54</td>
<td>8.56</td>
<td>4.3</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

1S$_0^2$ is the amplitude reduction factor; CN is the coordination number; R is
interatomic distance (the bond length between central atoms and surrounding
coordination atoms); σ$^2$ is Debye-Waller factor (a measure of thermal and static
disorder in absorber-scatterer distances); ΔE$_0$ is edge-energy shift (the difference
between the zero kinetic energy value of the sample and that of the theoretical model).
R factor is used to value the goodness of the fitting.

* This value was fixed during EXAFS fitting, based on the known structure.

Error bounds that characterize the structural parameters obtained by EXAFS
spectroscopy were estimated as N ± 10%; R ± 1%; σ$^2$ ± 15%; ΔE$_0$ ± 20%.

Cu-475 (FT range: 2.0-10.0 Å$^{-1}$; fitting range: 1.12-2.5 Å)
Cu foil (FT range: 3.0-12.0 Å$^{-1}$; fitting range: 1.0-3 Å)

**Computational methods**

Generalized gradient approximation (GGA) with the projector-augmented wave
(PAW) method were used to describe the core electrons using the Perdew-Burke-
Ernzerhof (PBE) functional.\textsuperscript{1-3} A cutoff energy of 400 eV was set. The convergence
criterion for an electronic self-consistent iteration was set at 10$^{-5}$ eV, and the forces on
all atoms were smaller than 0.02 eV/Å. The Brillouin zone was sampled with a 2×3×1
Monkhorst-Pack\textsuperscript{4} scheme for the tetragonal (101) surface and a 2×2×1 Monkhorst-
Pack mesh for the monoclinic (-111) surface. All DFT calculations were implemented
in the Vienna Ab initio Simulation Program (VASP). 5

We employ the most stable surface (101) of tetragonal ZrO$_2$ and (-111) of monoclinic ZrO$_2$ 6 to calculate the mechanism of the catalytic conversion. The T-ZrO$_2$ (101) surface (see Figure S9a) and the CuN$_3$/NC/M-ZrO$_2$(-111) surface (see Figure S1b) are modeled using a (2 × 2) supercell. For the CuN$_3$/NC/T-ZrO$_2$(101) surface, the top six layers together with the adsorbed Cu atom is allowed to relax and the rest are frozen in the bulk positions. With regard to the CuN$_3$/NC/M-ZrO$_2$(-111) surface, the top layer together with the adsorbed Cu atom is allowed to relax and the rest are frozen in the bulk positions.

The adsorption energy of adsorbates was defined by the definition:

$$E_{ads} = E_{adsorbate/adsorbent} - E_{adsorbate} - E_{adsorbent}$$

where $E_{adsorbate/adsorbent}$ is the total energy of the surface with adsorbate, $E_{adsorbate}$ represents the energy of the free adsorbate species, and $E_{adsorbent}$ is the energy of the optimized surface.
Electro-catalysis experiments

All electrochemical experiments were carried out in a standard three-electrode system using the electrochemical workstation (CHI660E). Carbon rod and Ag/AgCl were used as counter electrode and reference electrode, respectively, and modified carbon paper was used as work electrode. The electrochemical CO$_2$RR performance was carried out in an airtight electrochemical H-type cell containing 0.5 M KHCO$_3$ solution, in which, the anode and cathode of electrolytic cell were separated by a Nafion®117 proton exchange membrane. The catalyst-modified carbon paper electrode (denoted as CPE, 1 cm × 2 cm) was prepared as follows. 5 mg catalyst and 1 mg acetylene black (AB) were grounded together to form the uniform black powder. This black powder was dispersed into 0.1 mL 1% Nafion solution with 0.4 mL deionized water and sonication for 30 min to form uniform catalyst ink. Then, the ink was dropped directly onto the surface of carbon paper (1 cm × 1 cm) with a catalyst loading density of ~1 mg cm$^{-2}$ and dried at ambient temperature. The polarization curves were performed by linear sweep voltammetry (LSV) mode at a scan rate of 10 mV s$^{-1}$. In this experiment, polarization curves were recorded successively in Ar-saturated and CO$_2$-saturated KHCO$_3$ solution.

Faradaic efficiency was calculated as following:

$$\text{FE} = \frac{Q_{CO}}{Q_{\text{total}}} = \frac{(n \times Z \times F)}{Q_{\text{total}}}$$

$Q_{\text{total}}$: the charge passed, C;

$Q_{CO}$: the charge used for the reduction of CO, C;

$n$: the number of moles for CO (measured by GC), mol;
Z: the number of electrons transferred, which is 2 for CO;

F: Faradaic constant: $96485 \text{ C/mol.}$

References:


Characterization Section

Fig. S1. The PXRD of UIO-66-NH$_2$-Cu and the simulation data of UIO-66-NH$_2$.

Figure S2. The powder X-ray diffraction patterns of the catalysts.
Figure S3. (a) and (b) the SEM images of CuN\textsubscript{3}/NC and CuN\textsubscript{3}/NC/M-ZrO\textsubscript{2}; (c) and (d) the TEM images of CuN\textsubscript{3}/NC and CuN\textsubscript{3}/NC/M-ZrO\textsubscript{2}.

Fig. S4. The nitrogen uptakes of the catalysts.
Figure S5. The CO₂ adsorption isotherms of CuN₃/NC/T-ZrO₂, CuN₃/NC/M-ZrO₂, and CuN₃/NC.

Figure S6. ¹H NMR spectroscopy of the liquid product after 2 h CO₂RR process catalyzed by CuN₃/NC/T-ZrO₂.
Figure S7. Linear sweep voltammetric curves of CuN$_3$/NC/T-ZrO$_2$ in Ar-saturated and CO$_2$-saturated 0.5 m KHCO$_3$ aqueous solution.

Figure S8. CV curves of the catalysts.

Figure S9. Top and side views of the ZrO$_2$ surface for the (a) tetragonal (101) and (b) monoclinic (-111). Red and white-blue balls stand for O and Zr atoms, respectively.

Figure S9. Top and side views of the ZrO$_2$ surface for the (a) tetragonal (101) and (b) monoclinic (-111). Red and white-blue balls stand for O and Zr atoms, respectively.
Table S1. ICP-AES and element analysis results for the contents of Cu and Zr in catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>The content of Zr (%)</th>
<th>The content of Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuN₃/NC/T-ZrO₂</td>
<td>11.51</td>
<td>2.10</td>
</tr>
<tr>
<td>CuN₃/NC/M-ZrO₂</td>
<td>11.02</td>
<td>2.27</td>
</tr>
<tr>
<td>CuN₃/NC</td>
<td>0</td>
<td>2.40</td>
</tr>
</tbody>
</table>

Table S2. CO faradaic efficiency results from CO₂ electrochemical reduction at Cu-based catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FE₇₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuN₃/NC/T-ZrO₂</td>
<td>94</td>
</tr>
<tr>
<td>CuN₃/NC/M-ZrO₂</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Cu-Au HF₁</td>
<td>64.7</td>
</tr>
<tr>
<td>Cu-Ni HF₁</td>
<td>76.3</td>
</tr>
<tr>
<td>Cu-Fe-N₄-C²</td>
<td>98</td>
</tr>
</tbody>
</table>
