Supporting Information

Atomically Dispersed Copper Catalysts for Highly Selective CO$_2$ 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 ($CuCl_2 \cdot 2H_2O$, 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-NH₂-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 $CuCl_2 \cdot 2H_2O$ 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 CuN₃/NC/T-ZrO₂. The powder of UIO-66-NH₂-Cu was placed in a tube furnace. Then the sample was heat-treated in Ar atmosphere at 900 °C for 3 h with a heating rate of 5 °C/min and then naturally cooled to room temperature. Furtherly, the powder was washed 3 times with deionized water and dried in vacuum at 70 °C for overnight.

Synthesis of CuN₃/NC/M-ZrO₂. The powder of UIO-66-NH₂-Cu was placed in a tube furnace. Then the sample was heat-treated in Ar atmosphere at 700 °C for 3 h with a heating rate of 5 °C/min and then naturally cooled to room temperature. Furtherly, the powder was washed 3 times with deionized water and dried in vacuum

at 70 °C for overnight.

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 (λ=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 maxium 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)

sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3}Å^2)$	ΔE_0(eV)	R factor
CuN$_3$/NC/T-ZrO$_2$	Cu-N/C	2.87	1.95	6.35	4.14	0.0131
Cu foil	Cu-Cu	12*	2.54	8.56	4.3	0.0035

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 Perdewe-Burkee-Ernzerhof (PBE) functional.[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 [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_2RR 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:

$FE = Q_{CO}/Q_{total} = (n × Z × F)/Q_{total}$

Q_{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 C/mol.

References:

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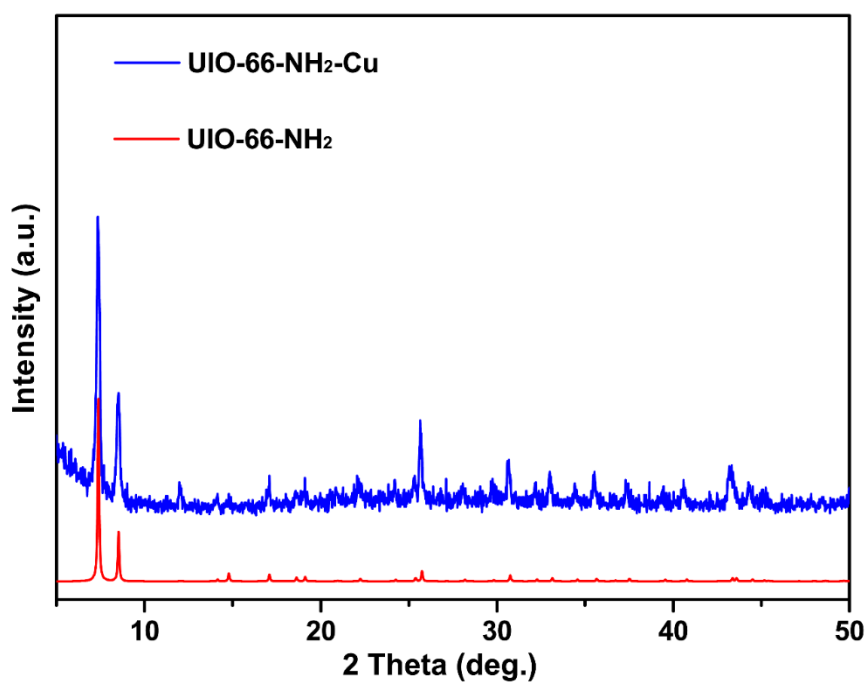
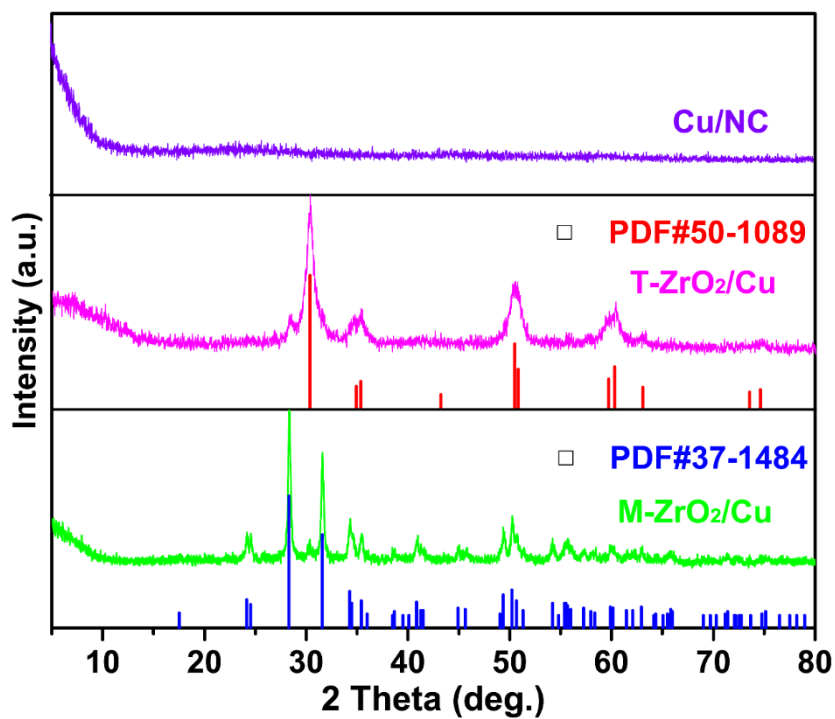Fig. S1. The PXRD of UIO-66-NH$_2$-Cu and the simulation data of UIO-66-NH$_2$.

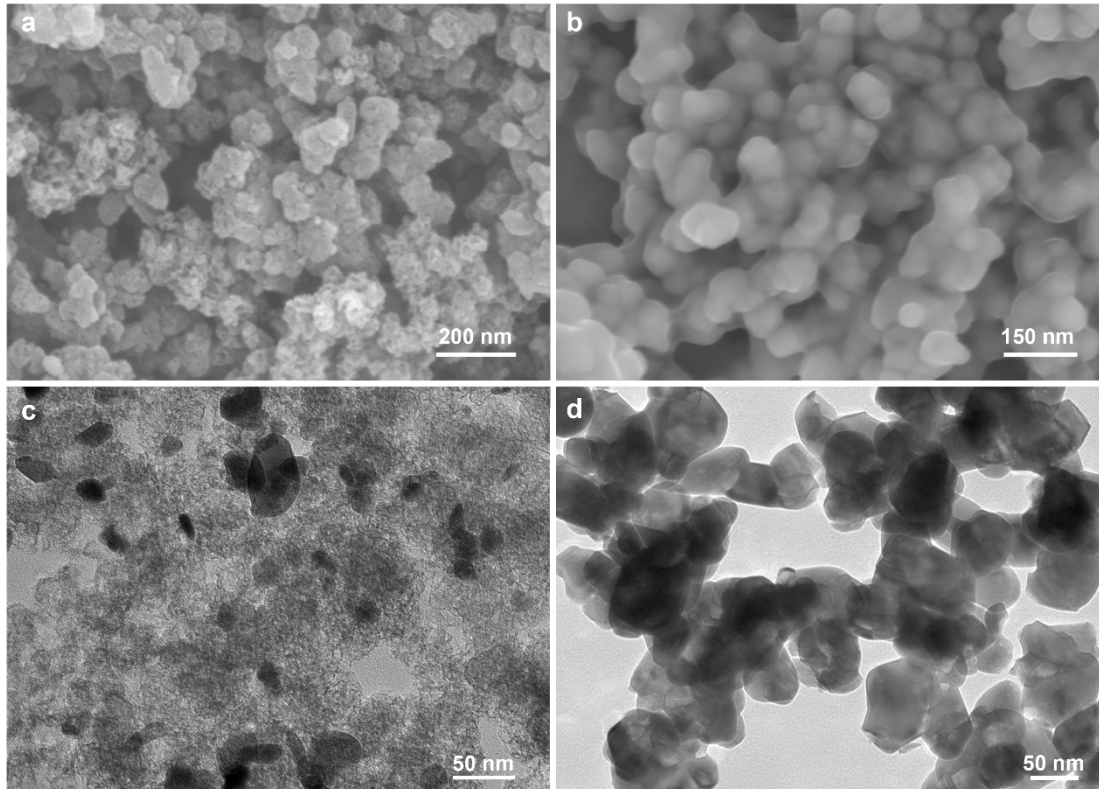Figure S2. The powder X-ray diffraction patterns of the catalysts.

Figure S3. (a) and (b) the SEM images of CuN$_3$/NC and CuN$_3$/NC/M-ZrO$_2$; (c) and (d) the TEM
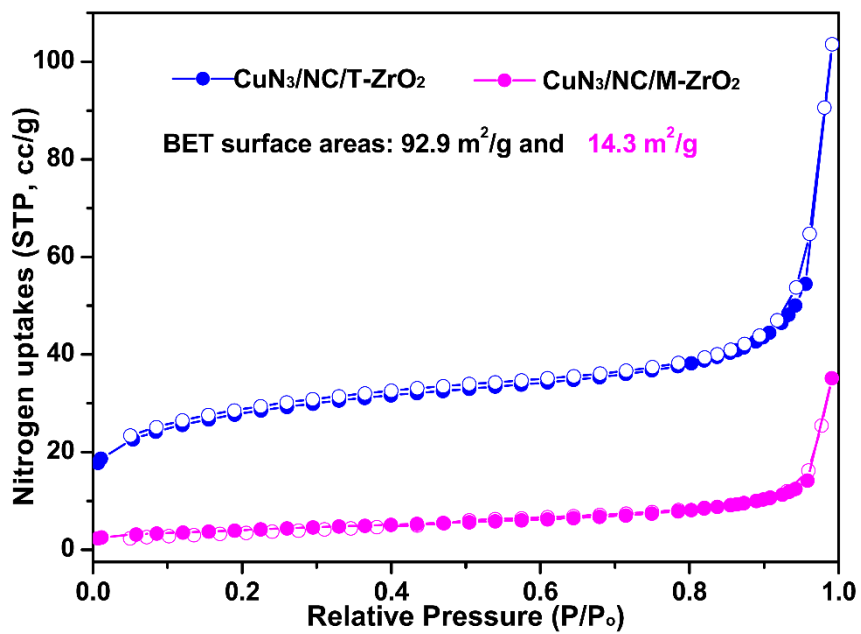
images of CuN$_3$/NC and CuN$_3$/NC/M-ZrO$_2$.

Fig. S4. The nitrogen uptakes of the catalysts.
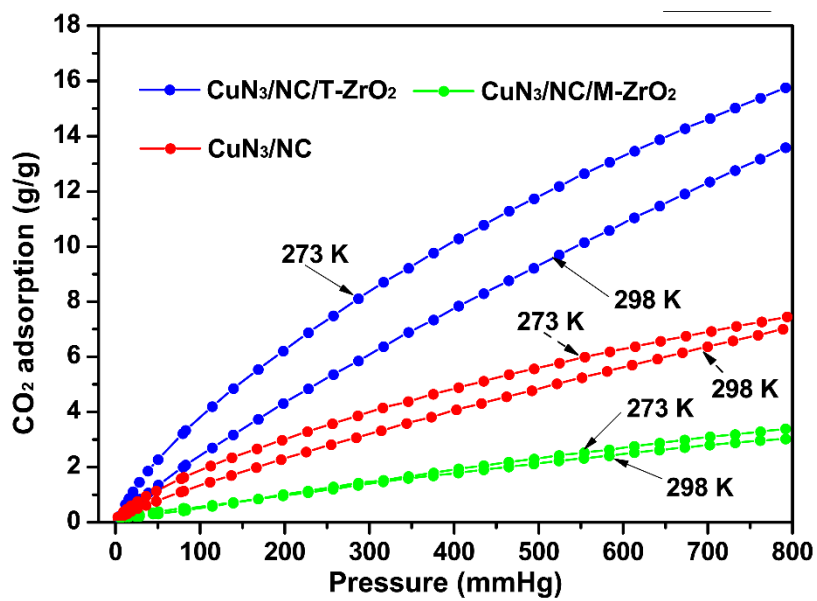
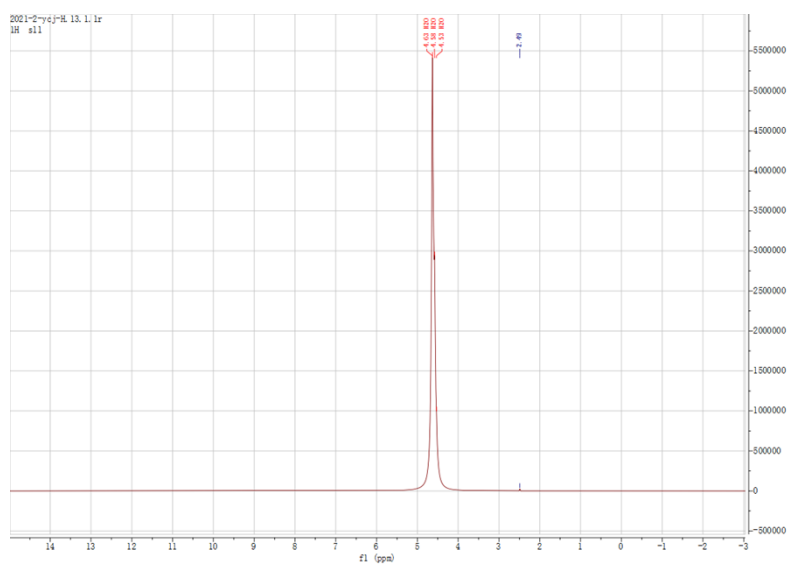Figure S5. The CO$_2$ adsorption isotherms of CuN$_3$/NC/T-ZrO$_2$, CuN$_3$/NC/M-ZrO$_2$, and CuN$_3$/NC.

Figure. S6. ^{1}H NMR spectroscopy of the liquid product after 2 h CO$_2$RR process catalyzed by
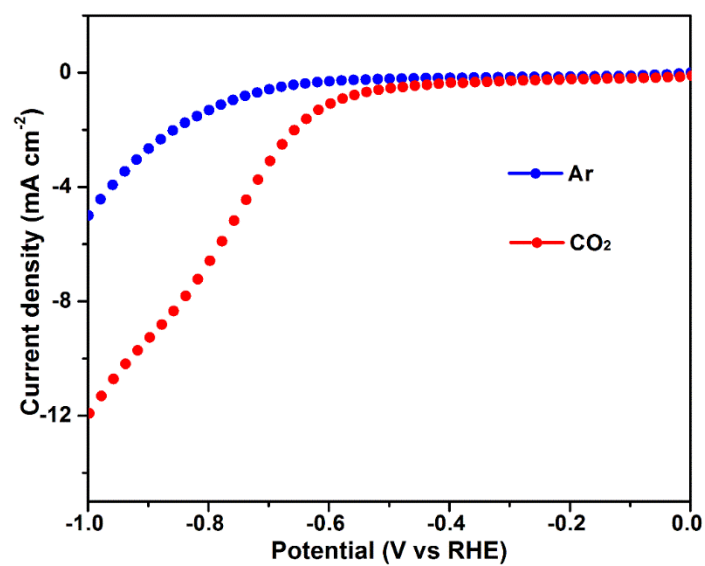
CuN$_3$/NC/T-ZrO$_2$.

Figure. S7. linear sweep voltammetric curves of $CuN_3/NC/T-ZrO_2$ in Ar-saturated and CO_2-
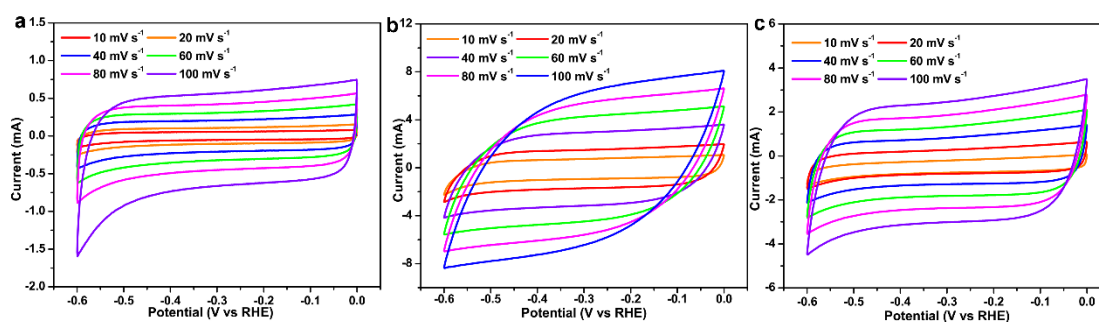
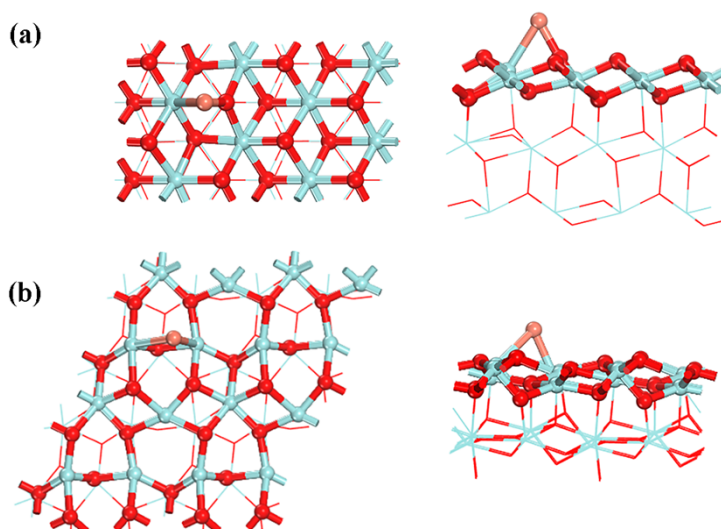saturated 0.5 m $KHCO_3$ aqueous solution.

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.

Table S1. ICP-AES and element analysis results for the contents of Cu and Zr in catalyst.

Sample	The content of Zr (%)	The content of Cu (%)
$CuN_3/NC/T-ZrO_2$	11.51	2.10
$CuN_3/NC/M-ZrO_2$	11.02	2.27
CuN_3/NC	0	2.40

Table S2. CO faradaic efficiency results from CO_2 electrochemical reduction at Cu-based catalysts.

Sample	FE_{CO}
$CuN_3/NC/T-ZrO_2$	94
$CuN_3/NC/M-ZrO_2$	<5
Cu-Au HF[1]	64.7
Cu-Ni HF[1]	76.3
Cu-Fe-N_6-C[2]	98

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