Supporting Information

Single Sb sites for efficient electrochemical CO₂ reduction

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Experimental section

Chemicals and reagents

All chemicals used in this work were of analytical grade and used without further treatments. Carbon black (Vulcan XC-72) was purchased from Fuel Cell Store. Urea and antimony trichloride were obtained from Aladdin. Ethanol, sulfuric acid, phosphoric acid, and nitric acid were obtained from Beijing Chemical Reagent Company. Nafion solution (5.0 wt%) was purchased from Sigma-Aldrich and Nafion membranes were provided by Alfa Aesar. Deionized water was used in all experiments.

Catalyst preparation

Synthesis of Sb_NC

In a typical procedure to synthesize N-doped carbon supported Sb SACs (denoted as Sb_NC), 100 mg of carbon black (Vulcan XC-72) was first activated by dispersing in 20 mL of 9 M nitric acid solution followed by refluxing at 90 °C for 3 h. After washing and drying, this activated carbon black mixed with 1000 mg of urea were added into 15 mL of antimony chloride ethanol solution (containing 5 mg of Sb³⁺). After ultrasonication for 30 min, a homogeneous dispersion was achieved, which was dried at 60 °C to evaporate the solvent. The obtained solid was then ground into powder and pyrolyzed at 800 °C for 2 h under an argon atmosphere.

The same procedure has been applied for the preparation of Sb_C without urea.
**Characterization**

XPS experiments were carried out using Thermo Scientific ESCALAB 250Xi instrument. The instrument was equipped with an electron flood and scanning ion gun. All spectra were calibrated to the C 1s binding energy at 284.8 eV. X-ray powder diffraction (XRD) was performed with a D/MAX-RC diffractometer operated at 30 kV and 100 mA with Cu Kα radiation. High-angle annular dark field scanning TEM (HAADF-STEM) was conducted using a JEOL ARM200 microscope with 200 kV accelerating voltage. STEM samples were prepared by depositing a droplet of suspension onto a Cu grid coated with a Lacey Carbon film. Nitrogen adsorption/desorption measurements at 77 K were performed on a Micromeritics ASAP2460 to obtain pore properties such as the specific surface area, total pore volume, and pore size distribution. The sample was degassed at 200 °C for 10 h. Raman spectra were collected with a Renishaw in Via Raman microscope with a He/Ne Laser excitation at 532 nm (2.33 eV).

**Cathode preparation**

Typically, 10 mg of catalyst was dispersed in 2 mL of a mixture containing isopropanol, deionized water, and 5 wt% Nafion solution with a volume ratio of 100: 100: 1 under ultrasonication for 30 min to form a homogeneous ink. 200 μL of the dispersion was then loaded onto a carbon paper electrode with an area of 1 cm × 1 cm and dried under ambient conditions. For linear sweep voltammograms in Ar- or CO₂-saturated 0.1 M KHCO₃ solution, 6 mg of a catalyst was dispersed in the mixture of 600 μL of ethanol, 600 μL of deionized water, and 600 μL of Nafion solution (1 wt%). Then the mixture was ultrasonicated for 30 min to form a homogeneous ink. 7.95 μL of the dispersion was then loaded onto glassy carbon electrode and dried under ambient conditions.

**Electrochemical measurements**

Controlled potential electrolysis of CO₂ was tested in an H-cell system (Fig. S5), which was separated by a Nafion 117 membrane. Before ECR tests, the Nafion membrane was
pre-treated subsequently by heating in 5% H$_2$O$_2$ aqueous solution and 0.5 M H$_2$SO$_4$ at 80 °C for 1 h. Then the Nafion membrane was immersed in deionized water under ambient conditions for 30 min and then washed with deionized water. Toray Carbon fiber paper with a size of 1 cm × 1 cm was used as working electrode. Pt wire and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. The potentials were controlled by an electrochemical working station (CHI 760E, Shanghai CH Instruments Co., China). All potentials in this study were measured against the Ag/AgCl reference electrode (in 3.5 M KCl solution) and converted to the RHE reference scale by

$$E_{\text{vs. RHE}} = E_{\text{vs. Ag/AgCl}} + 0.21 \text{ V} + 0.0591 \times \text{pH} \quad \text{(Eq. S1)}$$

Electrocatalytic CO$_2$ reduction was conducted in CO$_2$-saturated 0.1 M KHCO$_3$ solution at room temperature and atmospheric pressure. CO$_2$ was purged into the KHCO$_3$ solution for at least 30 min to remove residual air in the reservoir, then controlled potential electrolysis was performed at each potential for 60 min.

Gaseous products from the cell were analyzed using an Agilent 7890B GC system. Two thermal conductivity detectors and a flame ionization detector were applied to analyze and differentiate the injected samples. To characterize the gas product, 20 mL of the gas products in the dead volume of a gas bag (∼1 L) was injected into the GC under identical experimental conditions (e.g., pressure, temperature, and time) using a sample lock syringe. CO and H$_2$ peaks were detected at 11.4 and 3.7 min, respectively. The liquid product was analyzed in DMSO-d$_6$ with tetramethylsilane (TMS) as an internal standard by $^1$H nuclear magnetic resonance (NMR) (Bruker Avance III 400 HD spectrometer). No liquid products including formate were detectable by $^1$H NMR at -0.9 V (vs. RHE) in CO$_2$-saturated 0.5 M KHCO$_3$ solution (Fig. S6). This suggests that CO and H$_2$ were the main products as detected by GC.

**Faradaic efficiency (FE) measurements**

The FE values of catalysts were calculated using

$$FE = \frac{Z \times n \times F}{Q_{\text{total}}} \quad \text{(Eq. S2)}$$

where $Z$ is the number of electrons transferred ($Z = 2$ for CO and H$_2$ production), $n$ the number of
moles for a given product, $F$ Faraday’s constant (96 485 C mol$^{-1}$), $Q_{\text{total}}$ all the charge passed throughout the electrolysis process (measured by calculating the curve area of current density vs. time plot). CO and H$_2$ mole fractions of injected samples were calculated based on GC calibration curve.

**Partial current density determination**

Partial current density for CO or H$_2$ can be obtained by multiplying corresponding FE by the total current density ($J$):

$$J_{\text{CO or H}_2} = J \times \text{FE}_{\text{CO or H}_2}$$  \hspace{1cm} (Eq. S3)

**Number of active sites and turnover frequency (TOF) measurements**

The TOF for CO formation was calculated as follows:

$$\text{TOF} = \frac{J_{\text{CO}} \times S/ZF}{m_{\text{cat.}} \times \omega/M_{\text{Sb}}} \times 3600$$  \hspace{1cm} (Eq. S4)

where $J_{\text{CO}}$ is CO partial current (A cm$^{-2}$), $S$ is the geometric surface area of working electrode (cm$^2$), $Z$ is the number of electrons transferred ($Z = 2$ for CO formation), $F$ is Faraday’s constant (96 485 C mol$^{-1}$), $m_{\text{cat.}}$ is catalyst mass in the electrode (g), $\omega$ is Sb loading in the catalyst, and $M_{\text{Sb}}$ is atomic mass of Sb (121.8 g mol$^{-1}$).
**Fig. S1** Raman spectrum of Sb_NC. Major typical Raman peaks from Sb and Sb$_2$O$_3$ are added at the bottom for reference.

![Raman Spectrum of Sb_NC](image)

**Fig. S2** Wide-survey XPS spectrum of Sb_NC.

![Wide-survey XPS Spectrum](image)

**Fig. S3** (a) N$_2$ adsorption-desorption isotherms of Sb_NC. (b) Plot of pore size distribution of Sb_NC calculated from the desorption branch of the isotherms.

![N$_2$ Adsorption-Desorption Isotherms](image)
**Fig. S4** (a)-(c) HAADF-STEM images of Sb_NC over different regions.

**Fig. S5** Illustration of an H-type cell for CO$_2$ electrolysis.
**Fig. S6** $^1$H NMR plot of liquid electrolyte after 1 h of CO$_2$ electrolysis at -0.9 V vs. RHE.

**Fig. S7** Faradaic efficiencies (bar) and current densities (ball) of Sb_NC, Sb_C, NC, bulk Sb, and Sb$_2$O$_3$ at -0.9 V (vs. RHE).
Table S1. Summary for the reported single metal atom-based ECR electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potential/ V vs. RHE</th>
<th>CO partial current density/ mA cm⁻²</th>
<th>Catalyst mass/g</th>
<th>Metal content</th>
<th>Metal activity/mA mg⁻¹</th>
<th>TOF</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Sb_NC</td>
<td>-0.9</td>
<td>2.43</td>
<td>10⁻³</td>
<td>0.03 wt%</td>
<td>8100</td>
<td>11577</td>
<td>This work</td>
</tr>
<tr>
<td>Ni-N-MEGO</td>
<td>-0.7</td>
<td>26.8</td>
<td>5*10⁻⁴</td>
<td>6.7 wt%</td>
<td>800</td>
<td>875.92</td>
<td>1</td>
</tr>
<tr>
<td>Ni SAs/NCNTs</td>
<td>-1.0</td>
<td>55.38</td>
<td>8*10⁻⁴</td>
<td>6.63 wt%</td>
<td>1098</td>
<td>1176</td>
<td>2</td>
</tr>
<tr>
<td>Ni-CTF</td>
<td>-1.1</td>
<td>2.45</td>
<td>3*10⁻⁴</td>
<td>0.83 wt%</td>
<td>983</td>
<td>1077.3</td>
<td>3</td>
</tr>
<tr>
<td>Ni-N-C</td>
<td>-0.97</td>
<td>18</td>
<td>3*10⁻⁴</td>
<td>2.83 wt%</td>
<td>2120</td>
<td>2321.3</td>
<td>4</td>
</tr>
<tr>
<td>Ni-N-C</td>
<td>-0.96</td>
<td>10.5</td>
<td>5*10⁻⁴</td>
<td>0.24 wt%</td>
<td>8750</td>
<td>9580.3</td>
<td>5</td>
</tr>
<tr>
<td>Ni-N-Gr</td>
<td>-0.8</td>
<td>N/A</td>
<td>3*10⁻⁴</td>
<td>2.2 wt%</td>
<td>N/A</td>
<td>4600</td>
<td>6</td>
</tr>
</tbody>
</table>

Fig. S8 CO partial current density of Sb_NC compared with those of other reported single atom catalysts with details listed in Table S1.
<table>
<thead>
<tr>
<th>Material</th>
<th>Potential (V)</th>
<th>Scan Rate (V/s)</th>
<th>Charge (C/m²)</th>
<th>Areal Density (%)</th>
<th>Current Density (mA cm⁻²) @ 0.9 V vs. RHE</th>
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</thead>
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<tr>
<td>Ni SAs/N-C</td>
<td>-1.0</td>
<td>7.37</td>
<td>1*10⁻⁴</td>
<td>1.53</td>
<td>5070</td>
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<tr>
<td>Ni-N-C</td>
<td>-0.825</td>
<td>12.92</td>
<td>7.6*10⁻⁴</td>
<td>≈ 3.42</td>
<td>497</td>
</tr>
<tr>
<td>Co–N₃/HNP CSs</td>
<td>-0.73</td>
<td>4.5</td>
<td>3*10⁻⁴</td>
<td>3.44</td>
<td>436</td>
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<tr>
<td>Fe-N/CNF-2</td>
<td>-0.63</td>
<td>6.69</td>
<td>10⁻³</td>
<td>0.33</td>
<td>2027</td>
</tr>
<tr>
<td>C-Zn₁Ni₄/ZIF-8</td>
<td>-1.03</td>
<td>71.5</td>
<td>2*10⁻³</td>
<td>5.44</td>
<td>657.2</td>
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<tr>
<td>CoPPc/CNT</td>
<td>-0.61</td>
<td>16.8</td>
<td>10⁻³</td>
<td>2.6</td>
<td>646</td>
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<tr>
<td>A-Ni-NSG</td>
<td>-0.72</td>
<td>35</td>
<td>10⁻⁴</td>
<td>2.8</td>
<td>12500</td>
</tr>
<tr>
<td>CoPc/CNT</td>
<td>-0.63</td>
<td>15.0</td>
<td>4*10⁻⁴</td>
<td>0.26</td>
<td>14423</td>
</tr>
</tbody>
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Fig. S9 Charging current density differences plotted against scan rates.
**Fig. S10** CO FEs and partial current densities at -0.9 V (vs. RHE) of Sb_NC obtained at 700, 800, 900, and 950 ºC in Ar for 2 h.

**References**


