Supporting Information

Selective Electroreduction of CO₂ to Ethanol over Highly Stabile Catalyst Derived from Polyaniline/CuBi₂O₄

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1. Experimental Section

1.1 Materials and methods

1.1.1 Chemical Materials: Copper acetate monohydrate (C₄H₆CuO₄·H₂O, AR), Potassium hydroxide (KOH, AR), Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, AR), Potassium bicarbonate (KHCO₃, AR), Ammonium persulfate ((NH₄)₂S₂O₈ or APS, AR), polyvinyl pyrrolidone K30 (PVP, AR) was purchased from Chron-Chemicals (Chengdu, China) and used as received; aniline (C₆H₇N, AR) was purchased from Sigma-Aldrich and used after decompress distillation.

1.1.2 Synthesis of Cu₂O

Cu₂O was synthesized by a method reported in literature¹, for typical procedure: 5.0 mL NaOH aqueous solution (2.0 M) carefully dropped into 50 mL CuCl₂ aqueous solution (0.01 M) at 55°C. After adequately stirring for 0.5 h, 5.0 ml ascorbic acid aqueous solution (0.6 M) slowly drop into the solution. The mixed solution was continuously stirred at 55°C for 3 h. The product was collected by centrifugation and decanting, then cleaned with distilled water, and finally dried in vacuum at 80°C for 12 h.

1.1.3 Synthesis of CuBi₂O₄

CuBi₂O₄ was synthesized by improved hydrothermal method². As a typical procedure, 181.9 mg Bi(NO₃)₃·5H₂O completely dissolved in 20 mL HNO₃ aqueous solutions (2.0 vol.%), then...
PVP (0.75 g) was added into the solution under continuously ultrasound to form solution A. 37.5 mg Cu(CH$_3$COO)$_2$·H$_2$O fully dissolved in 20 mL deionized, and dropped into solution A. Then, 20 mL KOH (2.0 M) was added dropwise into the mixture and kept continuously stirring for 0.5 h at room temperature. The solution mixture turned into a 100 mL Teflon-lined stainless-steel autoclave and sealed at 150 °C under autogenous pressure for 12 h. The mixture washed with deionized water multiple times after cooling to room temperature, finally vacuum dry at 80°C for 12 h.

1.1.4 Synthesis of PANi/CuBi$_2$O$_4$

PANi/CuBi$_2$O$_4$ was synthesized by in-situ polymerized growth method. Typically, 12.0 mg fresh aniline which had done the decompress distillation at 150°C, dissolved completely 20 mL aqueous ethanol solution (25 vol.%). Then, 80 mg CuBi$_2$O$_4$ were dispersed in the solution and kept adequately stirring for 5 h to form the high-spread mixture, meanwhile 23.45 mg APS dissolved in 20 mL hydrochloric acid (0.2 vol.%) and was added dropwise into the mixture carefully. Specifically, the polyreaction need react at room temperature for 30 min and quickly transfer to ice bath (0~5°C) for 24 h. Subsequently, the product washed at least 5 times with ultrapure water, and vacuum dry at 80°C for 24 h.

1.1.5 Synthesis of CuBi$_2$O$_4$-CR

CuBi$_2$O$_4$-CR was synthesized by H$_2$ reduction method. 0.1 g CuBi$_2$O$_4$ which synthesized in aforementioned work, was pretreat at N$_2$ (30 mL/min,99.99%) at 200°C for 2 h, then, reduced in the H$_2$ atmosphere (10 mL/min,99.999%) at 500°C for 3 h. Subsequently, cooled to the room temperature and obtained the material.

1.1.6 Synthesis of Bi$_2$O$_3$

Bi$_2$O$_3$ was synthesized by hydrothermal method. Typically, 2.0 mmol Bi(NO$_3$)$_3$·5H$_2$O and 3.0 mmol structural inducers dissolved on 40 mL deionized water, and kept adequately stirring for 45 min. Then, 40 mL alkali liquor (0.45 mM) added to the above solution, and kept continuous stirring for 2 h. Subsequently, the solution mixture turned into a 100 mL Teflon-lined stainless-steel autoclave and sealed at 150 °C under autogenous pressure for 12 h. The mixture washed deionized water multiple times after cooling to room temperature, finally vacuum dry at 80°C for 12 h. The formulations of different lye and structural inducers are shown in the Table-S 1.

Table S1. Three Bi$_2$O$_3$ was synthesized by different structure inducers and lye environments
<table>
<thead>
<tr>
<th>Designation</th>
<th>Alkaline</th>
<th>Structural inducers</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NaOH</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>B</td>
<td>Urea</td>
<td>Ethane diamine</td>
</tr>
<tr>
<td>C</td>
<td>Urea</td>
<td>Glycol</td>
</tr>
</tbody>
</table>

1.2 Materials characterizations.

The crystal structures were investigated by XRD apparatus using a Rigaku D/max-3C, equipped with a graphite monochromator for Cu Kα (40 kV, 40 mA, λ=1.542 Å) radiation. The SEM and TEM characterizations were carried out using an JSM-7800F and FEI Talos F200s G2, equipped with energy dispersive X-ray spectroscopy (EDX). X-ray photoelectron spectroscopy (XPS) study was performed on the Kratos AXIS Ultra DLD instrument with monochromatic Al Kα X-ray source (1486.6 eV) at power of 450 W (30 mA, 15kV). The TGA was performed using a TGA-DSC1 1600LF, and the analysis was carried out in N₂ with the heating rate was 5°C min⁻¹.

**CO₂-TPD and CO-TPD:** TPD was carried out on TP-5080. For CO₂-TPD, the sample was reduced under H₂ at 100°C first and then cooled down to room temperature in Ar.³ The sample immersion CO₂-flowing (99.99%) atmosphere (10 mL/min) for 1h at 200°C to achieved highest adsorption. Then, 35 mL/min He gas (99.99%) was passed through to remove the physical adsorptive CO₂ on 300°C for 30 min. The test process was carried out temperature program of desorption with heat rate of 5°C/min from 100°C~600°C. For CO-TPD, the samples pretreated at 100°C. CO (99.99%) passed through the sample with flow-rate 10 mL/min at 50°C for 1 h. 35 mL/min He gas (99.99%) was passed through to remove the physical adsorptive CO on 100°C for 30 min. The test was run at a heat rate of 5°C/min.

2. Electrochemical Measurement

2.1 Preparation of electrodes

To make the work electrode, 4.2 mg catalyst dispersed in a mixture contained 395 μL isopropanol and 5 μL Nafion ionomer solution (5 wt% in H₂O) by continuously sonicate for 15 min. Then, 5 μL of the catalyst slurry (contained 0.05 mg) uniformly coated on glassy carbon electrode (0.07 cm²). Pt (99.99%) worked as the counter electrode, while the saturated calomel electrode (SCE) as the reference electrode.

2.2 The electro-chemical activation process
The Cyclic-Voltammetry process was used as the method of electrochemical activation for the electrode material which coated on the glassy carbon on CO₂ atmosphere. During the process of activation, the CV program was carried out until the curves no more change.

2.3 Electrochemical research

All electrochemical studies were carried out in a gastight H-cell which separated by Nafion-117 membrane. All the electrochemical experiments tested by electrochemical workstation and (CHI 760E, Shanghai CH Instruments Co., China) a typical three-electrode system. Before each test, a continuous ventilation had been done by high-purity N₂ (99.99%) to exclude any dissolved gases. Then the pure CO₂ (99.99%, 6 mL/min) bubbled into electrolyte for at least 30 min to saturate the 0.1 M KHCO₃ (298 K).

2.4 EIS test

The EIS measurement was carried out in 0.1 M KHCO₃ solution at -1.0 V with amplitude of 5 mV of 1 to 10⁵ Hz in different atmosphere.

2.5 Double-layer capacitance (C_{dl}) tests

The electrochemically active area is positive relevant to with C_{dl} value, which could determine by measuring the capacitance current related to double-layer charging and determining its dependence on the scan rate of the cyclic voltammogram (CV). The test carried out range from 0 V~0.1 V vs.RHE. The Δj was calculated by Δj = jₐ - jₖ (jₐ: anodic current density; jₖ: cathodic current density) at -0.05 V vs.RHE. The scan rates were 20, 30, 50, 80, 100 and 120 mV s⁻¹. For better to compare with literature, all potential in this paper was rescaled to RHE reference:

\[ E (\text{vs. RHE}) = E (\text{vs. SCE}) + 0.0591 \times \text{pH} + 0.24 \text{ V} \]

CO₂RR was conducted in CO₂-saturated 0.1 M KHCO₃ (298 K, pH=6.8) at room temperature and atmospheric pressure.

3. Product analysis.

3.1 Gas products analysis

The gaseous products produced in the electrocatalytic reduction process were collected by the gas bags and analyzed by gas chromatography (GC-1100), which was equipped with TCD detectors using N₂ as the carrier gas for H₂ and CO detection, meanwhile, it equipped with FID detectors using N₂ as the carrier gas for hydrocarbon gas detection. Due to the small difference in thermal conductivity between N₂ (5.8 cal/(cm²·C·s)) and CO (5.6 cal/(cm²·C·s)), therefore, the use of TCD
detection will bring greater error. Hence, we used CO gas analyzer (Sensonic 4000) for more precise measurement.

The calculations of Faradaic efficiencies (FE) of gaseous products by followed equation:

\[ FE = \frac{n_{\text{gas}}}{Q/zF} \times 100\% \]

\( n_{\text{gas}} \): moles of gas product (mol);
\( Q \): electric quantity (C);
\( F \): Faradaic constant (96485 C/mol)
\( z \): the number of electrons for generate the gas product

### 3.2 Liquid products analysis

The liquid product was analyzed by \(^1\)H NMR (Agilent DD2, 600M MHz) in deuteroxide. Typically, add 0.8 μL of DMSO (as the internal standard substance) into 20 mL of electrolyzed electrolyte, and ultrasound for 0.5 h to mix well. Subsequently, 400 μL of the mixed solution and 110 μL of D₂O (as a deuterated reagent) were added to the NMR tube, let it stand overnight to deuterate completely. Then 600 M \(^1\)H NMR was used for analysis, and the excitation sculpting was used to effectively suppress the water peak. (Figure S10)

The FE of liquid products is:

\[ FE = \frac{n_{\text{liquid}}}{Q/zF} \times 100\% \]

\( n_{\text{liquid}} \): moles of liquid product (mol);
\( Q \): electric quantity (C);
\( F \): Faradaic constant (96485 C/mol)
\( z \): the number of electrons for generate the gas product

### 4. Computational Method

All calculations were performed by using the DMol³ package.\(^5\), \(^6\) The DFT semi-core pseudopotential (DSSP) method was employed to treat core electrons, which introduced some degree of relativistic correction into the core. The gradient-corrected functionals (GGA) with the Perdew, Burke, and Ernzerhof (PBE) functional were adopted to describe the exchange and correlation potential,\(^7\) meanwhile, Grimme’s scheme\(^8\) was used to deal with the dispersion correction for DFT. The double numerical plus polarization (DNP) was chosen as the atomic orbital basis set. The surface of catalyst was described by a simplified model system. For the
surface of Cu, a periodic (6×5) Cu (100) with five-layer slabs, while for the surface of Cu-Bi, doped Bi atoms on the above surface of Cu, separated perpendicularly by 20 Å vacuum in the z-direction. To ensure high-quality computational results, the convergence tolerances of energy, maximum force, and displacement were set to 1.0×10⁻⁵ Ha, 0.002 Ha·Å⁻¹, 0.005 Å, respectively, and the global orbital cut-off was set with fine quality scheme. The reciprocal space was sampled using a 5 × 5 × 1 k-point grid for the geometry optimizations with the atoms on the two top layers relaxation, while a 10×10×1 grid was used for the electronic structure computations. The charge transfer and the magnetic moment were determined according to the Hirshfeld method. The most favorable adsorption structure was explored for all of the intermediate species.

The adsorption energies \( E_{\text{ads}} \) were calculated according to the following equation:

\[
E_{\text{ads}} = E_{\text{adsorbate/substrate}} - E_{\text{adsorbate}} - E_{\text{substrate}}
\]

\( E_{\text{adsorbate/substrate}} \): the total energy of the adsorbate-substrate system in the equilibrium state.
\( E_{\text{adsorbate}} \) and \( E_{\text{substrate}} \): the total energy of the free adsorbate and substrate, including hydrocarbon, metal-oxide cluster and H atom, respectively.

The computational hydrogen electrode (CHE) model was used to calculate the free energies of CO₂ reduction intermediates via the following equation:

\[
\Delta G = \Delta E + \Delta ZPE - T\Delta S + \int c_p dT
\]

where \( \Delta E \) is the electronic adsorption energy, \( \Delta ZPE \) is the variation in zero-point energy (ZPE) and \( \Delta S \) is the change in entropy before and after the reaction. T is the temperature (298 K). The standard entropy values were cited from the literature. Furthermore, the free energy calculated via DFT can be extrapolated to other potentials by following equation:

\[
\Delta G_{\text{act}} = \Delta G^{0}(U^{0} = 0) + n\beta(U - U^{0})
\]

where \( \beta \) is the reaction effective symmetry factor and was approximated to be 0.5 for all steps; while the \( n \) was the amount of electron transferred and single electron transmission for all steps.
Figure S1. The SEM of catalyst: a) Bi$_2$O$_3$; b) Bi$_2$O$_3$@PANI; c) Bi$_2$O$_3$@PANI after activation; d) Bi$_2$O$_3$@PANI before and after CV activation.
Figure S2. a) XRD and b) SEM of Cu₂O
Table S2. The contents of the series of CuO-CuBi₂O₄-x

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inventory Rating (mg)</th>
<th>Quantitative analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(NO₃)₃ • 5H₂</td>
<td>Cu (Ac)₂</td>
<td>CuBi₂O₄</td>
</tr>
<tr>
<td>CuO-CuBi₂O₄-A</td>
<td>181.9</td>
<td>18.8</td>
</tr>
<tr>
<td>CuO-CuBi₂O₄-B</td>
<td>181.9</td>
<td>37.5</td>
</tr>
<tr>
<td>CuO-CuBi₂O₄-C</td>
<td>181.9</td>
<td>56.3</td>
</tr>
<tr>
<td>CuO-CuBi₂O₄-D</td>
<td>181.9</td>
<td>75.0</td>
</tr>
<tr>
<td>CuO-CuBi₂O₄-E</td>
<td>181.9</td>
<td>112.5</td>
</tr>
<tr>
<td>CuO-CuBi₂O₄-F</td>
<td>181.9</td>
<td>150.0</td>
</tr>
</tbody>
</table>

“~” : the content belowed detection limit of XRD and no relevant peak signal was detected

Figure S3. XRD patterns for the series of CuO-CuBi₂O₄-x
Figure S4. The optimization for the concentration of structure inducer PVP

As above figure shows, when the PVP concentration is 16 mg/mL, CuBi$_2$O$_4$ has the best CuBi$_2$O$_4$ crystallinity.
By comparing the current density difference between N$_2$ atmosphere and CO$_2$ atmosphere, the synthesized catalyst has the highest CO$_2$ activity when the aniline concentration is 0.3 mg/mL.

Figure S5. LSV curves of PANi/CuBi$_2$O$_4$ synthesized in different aniline concentration.
Figure S6. The images of b) STEM and mappings for the surface laminated structure of PANi/CuBi$_2$O$_4$; a) N; c) Bi; d) C; e) C-Cu overlap; f) Cu.
Figure S7. The SEM images of CuBi$_2$O$_4$: a-1~3) before acid etching; b-1~3) etching by 0.1 vol.% hydrochloric acid, c-1~3) etching by 0.2 vol.% hydrochloric acid, d-1~3) etching by 0.3 vol.% hydrochloric acid
Figure S8. The EIS of three catalysts on the atmosphere of N₂ (Hollow tag) and CO₂ (Solid tag) at -0.96V vs RHE.
Figure S9. $^1$H-NMR spectra of the liquid products of PANi/CuBi$_2$O$_4$ for CO$_2$RR at -0.96V vs RHE
Figure S10. GC analysis of the C$_2$H$_4$ gas products by FID detector over different catalysts at -0.96V vs RHE
Figure S11. The $\Delta E_{\text{ads}}$ of CO$_2$ on lattice plane of Bi(012), (104), (110);
Figure S12. a) The CO₂RR products distribution over PANi/CuBi₂O₄ at different reaction potential; b) the FE analysis for different consistence of CuO and CuBi₂O₄ at -0.96 V vs. RHE.; The tendency of FE for catalysts: c) CuBi₂O₄, d) Cu₂O.
Figure S13. a) The LSV tests of catalysts in different atmosphere; b) XRD of the catalysts after reduction: CuBi$_2$O$_4$-ER (red line), CuBi$_2$O$_4$-CR (dark line); c-1~3) The SEM of CuBi$_2$O$_4$ after H$_2$ treatment in high temperature at different resolutions.
Figure S14. The XRD patterns of CuBi$_2$O$_4$ before and after CV activation.
Figure S15. The XPS spectrum of CuBi₂O₄ after electrochemical activation: (a) survey XPS spectrum, (b) high-resolution Cu 2p XPS spectrum
Figure S16. a) TG plots of catalysts; b) DSC plots of catalysts.
Figure S17. The XPS spectrum of PANi/CuBi$_2$O$_4$ before electrochemical activation: (a) survey XPS spectrum, (b) high-resolution Cu 2p XPS spectrum, (c) high-resolution Bi 4f spectrum, (d) high-resolution N 1s spectrum
Figure S18. The XPS spectrum of PANi/CuBi$_2$O$_4$ after electrochemical activation: (a) survey XPS spectrum, (b) high-resolution Cu 2p XPS spectrum, (c) high-resolution Bi 4f spectrum, (d) high-resolution N 1s spectrum"
Table S3. The surface content of Cu and Bi before and after the electrochemical activation

<table>
<thead>
<tr>
<th></th>
<th>Cu 2p (%)</th>
<th>Bi 4f (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu(^{2+})/ (Cu(^{0+}) + Cu(^{2+}))</td>
<td>Cu(^{0+})/ (Cu(^{0+}) + Cu(^{2+}))</td>
</tr>
<tr>
<td><strong>Before activation</strong></td>
<td>100</td>
<td>~</td>
</tr>
<tr>
<td><strong>After activation</strong></td>
<td>26.05</td>
<td>73.95</td>
</tr>
</tbody>
</table>

According to the XPS test results, after activation, the ratio of the sum of Cu atoms on the surface to the sum of Bi atoms was still 1:2. So the ratios of Cu\(^{0+}\) to Bi\(^{3+}\) was 5.6 to 1.
Figure S19. The long period stability test of PANi/CuBi$_2$O$_4$ with 110 h on -0.96 V vs RHE.
Figure S20. CV curves had been studied under different switching sequences of N₂ and CO₂ atmospheres for three Bi₂O₃.
Figure S21. Proposed detail reaction steps for C$_2$H$_3$O* to C$_2$H$_5$OH: a) on the surface of Cu(100); and b) on the surface of Bi doped Cu(100). The atoms in yellow, violet, red, gray and white represent Cu, Bi, O, C and H, respectively.

The proposed reaction mechanism about C$_2$H$_3$O* to C$_2$H$_5$OH$^4$

\[
\begin{align*}
\text{C}_2\text{H}_3\text{O}^* \ + \ (\text{H}^+ \ + \ e^-) & \rightarrow \text{C}_2\text{H}_4\text{O}^* \\
\text{C}_2\text{H}_4\text{O}^* \ + \ (\text{H}^+ \ + \ e^-) & \rightarrow \text{C}_2\text{H}_5\text{O}^* \\
\text{C}_2\text{H}_5\text{O}^* \ + \ (\text{H}^+ \ + \ e^-) & \rightarrow \text{C}_2\text{H}_5\text{OH}
\end{align*}
\]
Figure S22. Proposed detail reaction steps for C$_2$H$_3$O$^*$ to C$_2$H$_4$: a) on the surface of Cu(100); and b) on the surface of Bi doped Cu(100). The atoms in yellow, violet, red, gray and white represent Cu, Bi, O, C and H, respectively.

The proposed reaction mechanism about C$_2$H$_3$O$^*$ to C$_2$H$_4$

\[
C_2H_3O^* + (H^+ + e^-) \rightarrow C_2H_4 + O^*
\]
\[
O^* + (H^+ + e^-) \rightarrow OH^*
\]
\[
OH^* + (H^+ + e^-) \rightarrow H_2O + ^*
\]
| Table S4. Comparison of alcohols in CO$_2$RR on various Cu-based catalysts. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Catalyst        | electrolyte     | Reaction potential | FE$_{\text{C}_2\text{+}}$ | FE$_{\text{C}_2\text{H}_5\text{OH}}$ | FE$_{\text{C}_2\text{H}_5\text{O}}$ | Partial current density of ethanol (mA/cm$^2$) | Reference |
| (1) PANi/CuBi$_2$O$_4$ | 0.1 M KHCO$_3$ | -0.96 V vs RHE | 73.64% | 64.15% | 87.05% | 6.27 | In H-Cell |
| (2) N-doped graphene | 0.1 M KHCO$_3$ | -1.11 V vs RHE | 78.00% | 16.00% | 20.51% | ~31.2 | In H-Cell |
| (3) N-doped graphene quantum dots (NGQ) on CuO-derived Cu nanorods (NGQ/Cu-nr) | 1.0 M KOH | -0.9 V vs. RHE | 80.40% | 52.40% | 65.17% | 147.8 | In electrochemical flow cell |
| (4) Planar Copper Nitride-Derived Mesoporous Copper (Cu$_3$N) | 0.1 M CsHCO$_3$ | -1.00 V vs RHE | 68.00% | 20.00% | 29.41% | ~3.56 | gas-tight electrochemical cell |
| (5) Cu GNC-VL | 0.5 M KHCO$_3$ | -0.87 V vs RHE | 70.52% | 70.52% | 100% | 8.69 | In H-Cell |
| (6) Ag-Cu$_3$O$_{PB}$ | 0.1 M KHCO$_3$ | -1.2 V vs RHE | 43.65% | 34.15% | 78.2% | ~1.02 | In H-Cell |
| (7) Cu$_4$Zn | 0.1 M KHCO$_3$ | -1.05 V vs RHE | 47.00% | 29.1% | 61.91% | ~3.14 | In H-Cell |
| (8) BND | 0.1 M NaHCO$_3$ | -1.0 V vs RHE | 93.2% | 93.2% | 100% | ~0.93 | In H-Cell |
| (9) Nitrogen-Doped Mesoporous Carbon | 0.1 M KHCO$_3$ | -0.56 V vs RHE | 77% | 77% | 100% | ~0.27 | In H-Cell |
| (10) Ag-G-NCF | 0.1 M KHCO$_3$ | -0.6 V vs RHE | 85.2% | 85.2% | 100% | 0.32 | In H-Cell |
| (11) Cu NPs | 0.1 M KHCO$_3$ | -0.5 V vs. RHE | 76% | 50% | 65.79% | 6.6 | In H-Cell |
| (12) Ag$_{0.14}$/Cu$_{0.86}$ | 1 M KHCO$_3$ | -0.67 V vs RHE | 84% | 41% | 48.80% | 250 | In GDE |
References: