Supporting Information

In-situ morphology transformation of bismuth-based catalysts for effective electroreduction of carbon dioxide

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Physicochemical Characterizations

The morphology and microstructure of the obtained electrocatalysts were observed by a scanning electron microscope (SEM, Hitachi SU8010) equipped with a Horiba Scientific energy dispersive spectrometer (EDS) analyzer, and the nanostructure was analyzed with a JEM-2100F transmission electron microscope (TEM, JEOL, Japan). The crystalline structures of the electrocatalysts were determined by X-ray diffraction (XRD, RigakuSmartLab X-Ray Diffractometer) using a Cu-Kα (λ=1.5405 Å) radiation source. The surface compositions and their valence states on the catalyst were characterized by using a X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250XI).

Electrochemical Characterizations

Linear sweep voltammetry (LSV) was carried out in a potential range of -0.8 to -2 V at a scan rate of 10 mV s\(^{-1}\) in either N\(_2\) or CO\(_2\)-saturated 0.1 M KHCO\(_3\) solutions. Electric double layer capacitance was determined by cyclic voltammetry (CV) measurements at various scan rates (40, 80, 120, 160, 200 mV s\(^{-1}\)) in N\(_2\)-saturated 0.1 M KHCO\(_3\) solution. The double layer capacitance of each electrode was calculated using Equation (1):

\[
J = C \times \frac{dV}{dt}
\]  (1)
where \( J \) is the current density, \( C \) the capacitance, and \( dV/dt \) the scan rate.

Electrochemical impedance spectroscopy (EIS) was performed within a frequency range of 0.01 Hz - 0.1 MHz in a CO\(_2\)-saturated 0.1 M KHCO\(_3\) solution at -1.2 V.

**Calculation of the Overpotential**

The overpotential in Tafel curve was calculated as the difference between the cathodic potential and the standard (equilibrium) reduction potential \( (\eta = |E_{Cd} - E_{eq}|) \). The standard reduction potential for converting CO\(_2\) into HCOOH in aqueous 0.1 M KHCO\(_3\) electrolyte solution is -0.09 V vs. RHE.\(^1\) The formula used to convert potentials vs. Ag/AgCl (1M) to vs. RHE is: \( E \) vs. RHE = \( E \) (V) vs. Ag/AgCl (saturated KCl) + 0.198 (V) + 0.059 (V) × pH (6.8).

**Calculation of the electrochemically active surface area (ECSA)**

The ECSA of electrode was calculated from the double layer capacitance \( (C_{dl}) \) according to equation 2:

\[
\text{ECSA} = \frac{C_{dl}}{\alpha}
\]

where \( \alpha \) is the specific capacitance of the sample or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions.

**Product Analysis**
Gas products were analyzed with a gas chromatography (GC, Agilent 7890A GC system, USA), by which CO and H\textsubscript{2} were detected with two thermal conductivity detectors (TCD), respectively. Liquid products were analyzed using a Shimadzu high performance liquid chromatography (HPLC) equipped with SPD-20AV and RID-10A detectors. Supelcogel C610-H (30 cm×7.8 mm, Sigma) and H\textsubscript{3}PO\textsubscript{4} (0.05 \%) solution were used as the column and mobile phase, respectively. The temperature of the oven CTO-20A was set at 40 \(^\circ\)C. The faradaic efficiency of HCOOH, CO or H\textsubscript{2} was calculated as follows:

\[
\text{Faradaic efficiency} = \frac{2F \times n}{Q}
\]  

where \(F\) is the faraday constant, \(n\) the total amount of products (in moles), and \(Q\) the amount of total charge (in Coulomb).

**DFT Computational Details**

Bi and Bi\textsubscript{2}O\textsubscript{2}CO\textsubscript{3} crystal structures with the ICSD numbers of 053797 and 036245 respectively were imported. All the models were optimized by using the spin-polarized DFT computations with an all-electron method by the DMol3 module in Materials Studio software.\(^4\)-\(^5\) The electron exchange-correlation functions of generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE), and basis set of double numerical plus polarization (DNP) were used for these calculations.\(^2\) Specifically, the van der Waals correction was employed by using DFT-D\textsuperscript{3} to accurately describe the long-range electrostatic interactions. The solvent effects were also
applied by using a conductor-like screening model (COSMO) with the H$_2$O dielectric constant of 78.54.

Other specific parameters selected in this study were consistent with the data reported in the literature. In detail, the convergence criterion was selected as 10$^{-6}$ a.u. with the maximum force of 0.002 a.u. Å$^{-1}$ and the maximum displacement of 0.005 Å. The k points were set as 5×5×1 by using the Monkhorst-Pack method. The real-space global orbital cutoff radius was chosen as 4.7 Å in all the computations to ensure high quality.

The free energy of electrochemical reduction of CO$_2$ was calculated based on a computational hydrogen electrode (CHE) model, in which the chemical potential of a proton/electron (H$^+$ + e$^-$) in solution is equal to the half chemical potential of a gas-phase H$_2$.

The adsorption energy of adsorbate was defined as:

$$E_{ad} = E_{surface-adsorbate} - E_{surface} - E_{adsorbate}$$

(4)

where $E_{surface-adsorbate}$, $E_{surface}$, and $E_{adsorbate}$ are the DFT total energy for the adsorbate on the surface, surface, and adsorbate itself, respectively.

The change in Gibbs free energy ($\Delta G$) was evaluated by the following equation:

$$\Delta G = \Delta E + \Delta E_{zpe} - T \Delta S - n e U$$

(5)
where the $\Delta E$, $\Delta E_{\text{zpe}}$ and $\Delta S$ are the differences of DFT energy, zero point energy and entropy between products and reactants, respectively. $T$ was set at 298.15 K in this work. $E_{\text{zpe}}$ can be obtained by the vibrational frequency analysis over all normal modes $\nu$ ($E_{\text{zpe}} = 1/2\sum \hbar \nu$). The entropies of the free molecules (CO, CO$_2$, HCOOH, H$_2$, and H$_2$O) were obtained from the NIST database. The configurational entropy in the adsorbed state was neglected by fixing the surfaces according to the way in most of the literatures.$^{9-11}$ $U$ is the applied potential vs. normal hydrogen electrode (NHE), $e$ is the elementary charge transferred and $n$ is the number of proton-electron pairs transferred.

**Investigation of morphology transformation conditions**

In order to confirm the formation mechanism of Bi$_2$O$_2$CO$_3$ nanosheets, a series of treatment processes were performed and the morphology of electrode surface was observed the by SEM. Because the *in-situ* treatment process consisted of two steps, the first was electrochemical treatment step, and the second was the dry step in the air. In order to confirm whether two steps were necessary, a set of parallel experiments were performed. Four Bi/Cu foam electrodes were treated with the following four different treatment methods and then the surface morphologies were observed.
(1) Bi/Cu foam $\xrightarrow{\text{Dry. Air, 12 h.}}$ Electrode A

(2) Electrode A $\xrightarrow{\text{Soaking. CO}_2\text{-saturated 0.1M KHCO}_3\text{ aqueous electrolyte, 2 h.}}$ $\xrightarrow{\text{Dry. Air, 60°, 12 h.}}$ Electrode B

(3) Electrode A $\xrightarrow{\text{Electrochemical treatment. CO}_2\text{-saturated 0.1M KHCO}_3\text{ aqueous electrolyte, -1.6 V, 2 h.}}$ $\xrightarrow{\text{Dry. Vacuum, 60°, 12 h.}}$ Electrode C

(4) Electrode A $\xrightarrow{\text{Electrochemical treatment. CO}_2\text{-saturated 0.1M KHCO}_3\text{ aqueous electrolyte, -1.6 V, 2 h.}}$ $\xrightarrow{\text{Dry. Air, 60°, 12 h.}}$ Electrode D

The obtained SEM images for the surfaces of four electrodes are shown as follows:
The freshly prepared Bi/Cu foam electrode was directly dried in the air as the initial electrode A for comparison. The two same electrodes of A were only soaked and electrochemically treated in the electrolyte for 2 hours using the above methods, respectively, and then the two electrodes were taken out and exposed to the air for 12 hours, which are called as electrodes B and D respectively. As shown in the Fig. S1a, b and d, significant change was observed for the electrochemically treated electrode D, and the electrodes without electrochemical treatment had only a slight surface change. Another electrode A was electrochemically treated at first and
then placed in a vacuum oven to avoid contact with air to obtain electrode C. As shown by the
SEM image, the electrode surface became rough after the electrochemical treatment.

For the electrode B, since there was no electrochemical treatment process, in this case, as
reported in the literature, Bi$_2$O$_2$CO$_3$ was slowly formed on the electrode by reaction with the
electrolyte (KHCO$_3$) remained on the surface as follows.\textsuperscript{12}

\begin{equation}
4\text{Bi} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{BiO}^+ + 4\text{OH}^-
\end{equation}

\begin{equation}
2\text{BiO}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{Bi}_2\text{O}_2\text{CO}_3
\end{equation}

As such, even without the electrochemical treatment, the electrode B still underwent a slight
morphological transformation (Fig. S1b).

For the electrode C, as reported in the literature, in the process of electrochemical reduction
of CO$_2$, some reactions like equations of 8-10 may occur on the surface of the electrode at first,
thereby accumulating a large amount of OH$^-$ on the surface, resulting in local alkalinity.\textsuperscript{13}

\begin{equation}
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{HCOO}^- + \text{OH}^-
\end{equation}

\begin{equation}
\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{CO} + 2\text{OH}^-
\end{equation}

\begin{equation}
2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-
\end{equation}

\begin{equation}
\text{Bi}^{3+} + \text{OH}^- \rightleftharpoons \text{Bi(OH)}_3
\end{equation}

\begin{equation}
2\text{Bi(OH)}_3 + \text{CO}_2 \rightleftharpoons \text{Bi}_2\text{O}_2\text{CO}_3 + 3\text{H}_2\text{O}
\end{equation}
Then, the OH$^{-}$ reacted with the Bi$^{3+}$ present on the surface of the electrode to form Bi(OH)$_3$.

Since electrode C was directly dried in a vacuum oven after electrochemical treatment, the further reaction between Bi(OH)$_3$ formed on the surface and CO$_2$ in the air was avoided. In this case, since the solubility of CO$_2$ in the aqueous solution is very low, only a small amount of Bi$_2$O$_2$CO$_3$ could be formed on the electrode surface. As a result, the formation of Bi(OH)$_3$ and a small amount of Bi$_2$O$_2$CO$_3$ species resulted in a rough electrode surface but without further morphological transformation (Fig. S1c).

However, for the electrode D, after electrochemical treatment, since the electrode was directly exposed to air, Bi(OH)$_3$ should react with CO$_2$ in the air to form Bi$_2$O$_2$CO$_3$ as indicated by the equation 12. Meanwhile, after the electrochemical treatment, the rough electrode surface could also accelerate the conversion of the metal Bi to Bi$_2$O$_2$CO$_3$ as indicated by the equations of 6-7. These caused its surface to be transformed to petal-shaped Bi$_2$O$_2$CO$_3$ nanosheets completely (Fig. S1d). In addition, it should be noted that, in order to make the morphological transformation more fully, the electrolyte remaining on the electrode surface after electrochemical treatment should not be washed away.
**Fig. S2** Calculated XRD patterns of (a) Bi and (b) Bi$_2$O$_2$CO$_3$ crystalline structures based on the models and compared with the standard PDF cards from ICDD database.

**Fig. S3** Optimized structures of different intermediates on the Bi (012) and Bi$_2$O$_2$CO$_3$ (001) facets.
Fig. S4 SEM images of Cu foam with different scales.

Fig. S5 SEM images of Bi/CP electrode (a, b) before and (c, d) after the in-situ treatment.
Fig. S6 SEM images of Bi/Cu foam-in situ treated electrode with different magnification scales.
Fig. S7 EDS analysis results of (a) Bi/Cu foam and (b) Bi/Cu foam-in-situ treated electrodes.
**Fig. S8** EDS analysis results of Bi/CP electrode for (a) bulk and (b) nanosheet structures. It can be seen that the area where the morphological transformation has taken place has a higher oxygen content.

**Fig. S9** (a) XRD patterns and (b) high-resolution Bi 4f XPS spectra of Bi/CP and Bi/CP-*in-situ* treated electrodes.
Fig. S10 (a, b and c) Determination of electrochemical double layer capacitance and (d) electrochemical impedance spectroscopy (EIS) tests for Bi/Cu foam and Bi/Cu foam-in-situ treated electrodes.
**Fig. S11** Linear sweep voltammetry (LSV) curves of the Cu foam, Bi/Cu foam and Bi/Cu foam-*in-situ* treated electrodes in either N$_2$-saturated (dashed) or CO$_2$-saturated (solid) 0.1 M KHCO$_3$ solutions at a scan rate of 10 mV s$^{-1}$.

**Fig. S12** The stability test of the Bi/Cu foam-*in-situ* treated electrode continuously operated at -1.6 V in a CO$_2$ saturated 0.1 M KHCO$_3$ solution (without refreshing) for 20 h.
**Fig. S13** (a) SEM and (b) TEM images of Bi/Cu foam-*in-situ* treated electrode after 20 h electrocatalysis.

**Fig. S14** (a) XRD patterns and (b) high-resolution Bi 4f XPS spectra of Bi/Cu foam-*in-situ* treated electrode before and after 20 h electrocatalysis.
**Fig. S15** Projected density of states (PDOS) of C of *COOH intermediate and Bi atoms on the (a) Bi(012) and (b) Bi$_2$O$_2$CO$_3$(001) facets. The Fermi level is denoted with a red dashed line.

**Fig. S16** Calculated free energy diagrams for the H$_2$ evolution on Bi(012) and Bi$_2$O$_2$CO$_3$(001) facets.
Fig. S17 Calculated free energy diagrams for the electroreductions of $^*$HCO$_3$ to HCOOH and CO on (a) Bi(012) and (b) Bi$_2$O$_2$CO$_3$(001)$_{ Bi_2O_2}$ terminal and (c) Bi$_2$O$_2$CO$_3$(001)$_{ CO_3}$ terminal facets. For Bi$_2$O$_2$CO$_3$, its (001) crystal plane has two terminals, the Bi$_2$O$_2$CO$_3$(001)$_{ CO_3}$ terminal can be combined with a $^*$H to form $^*$CO$_3$H and then further reduced.
### Table S1
The quantitative results of XPS spectra for the Bi/Cu foam electrode before and after *in-situ* treatment.

<table>
<thead>
<tr>
<th>Species</th>
<th>Bi/Cu foam</th>
<th>Bi/Cu foam-in-situ treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>43.36</td>
<td>28.41</td>
</tr>
<tr>
<td>O</td>
<td>52.91</td>
<td>69.32</td>
</tr>
<tr>
<td>Cu</td>
<td>3.73</td>
<td>2.27</td>
</tr>
</tbody>
</table>

### Table S2
The lattice spacings of Bi and Bi$_2$O$_2$CO$_3$.

<table>
<thead>
<tr>
<th>Facet</th>
<th>Bi</th>
<th>Bi$_2$O$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lattice spacing d (Å)</td>
<td>Lattice spacing d (Å)</td>
</tr>
<tr>
<td>003</td>
<td>3.954</td>
<td>6.841</td>
</tr>
<tr>
<td>101</td>
<td>3.737</td>
<td>3.720</td>
</tr>
<tr>
<td>012</td>
<td>3.280</td>
<td>3.420</td>
</tr>
<tr>
<td>104</td>
<td>2.369</td>
<td>2.952</td>
</tr>
<tr>
<td>110</td>
<td>2.273</td>
<td>2.734</td>
</tr>
<tr>
<td>015</td>
<td>2.032</td>
<td>1.933</td>
</tr>
</tbody>
</table>

### Table S3
$j_{\text{HCOOH}}$ at -1.2 V (vs. Ag/AgCl, -0.6 V vs. RHE), measured double layer capacitance, and $j_{\text{HCOOH}}$ per ECSA of the Bi/Cu foam and Bi/Cu foam-*in-situ* treated electrodes.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$j_{\text{HCOOH}}$ (mA cm$^{-2}$)</th>
<th>$C_{\text{dl}}$ (mF cm$^{-2}$)</th>
<th>$j_{\text{HCOOH}}$ per ECSA (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/Cu foam</td>
<td>0.08</td>
<td>1.12</td>
<td>0.07*α</td>
</tr>
<tr>
<td>Bi/Cu foam-<em>in-situ</em> treated</td>
<td>0.45</td>
<td>4.02</td>
<td>0.11*α</td>
</tr>
</tbody>
</table>

The α (mF cm$^{-2}$) represents the specific capacitance of bismuth.
Table S4 The calculated binding energies ($E_{ads}$, eV) of various CO$_2$RR species on Bi(012) and Bi$_2$O$_2$CO$_3$(001) facets.

<table>
<thead>
<tr>
<th>Species</th>
<th>*COOH</th>
<th>*OOCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi (012)</td>
<td>-1.41</td>
<td>-2.33</td>
</tr>
<tr>
<td>Bi$_2$O$_2$CO$_3$ (001)</td>
<td>-1.77</td>
<td>-3.41</td>
</tr>
</tbody>
</table>
**Table S5** Comparison of electrochemical reduction of CO\(_2\) performance for Bi-based catalysts.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Electrolyte</th>
<th>Applied potential (V)</th>
<th>Faradaic efficiency (%)</th>
<th>Current density (mA cm(^{-2}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/Cu foam</td>
<td>0.1 M KHCO(_3)</td>
<td>-1.7 V vs. Ag/AgCl (-1.1 V vs. RHE)</td>
<td>92.3</td>
<td>10.29</td>
<td>This work</td>
</tr>
<tr>
<td>Bi nanoflakes</td>
<td>0.1 M KHCO(_3)</td>
<td>-0.4 V vs. RHE</td>
<td>79.5</td>
<td>-</td>
<td>Nano Energy, 2017, 39, 44-52.</td>
</tr>
<tr>
<td>Bi/BiOCl</td>
<td>0.5 M KHCO(_3)</td>
<td>-1.50 V vs. SCE</td>
<td>92</td>
<td>3.7 mA mg(^{-2})</td>
<td>Electrochemistry Communications, 2014, 46, 63-66.</td>
</tr>
<tr>
<td>Size tunable nano-Bi</td>
<td>0.5 M KHCO(_3)</td>
<td>-1.60 V vs. SCE</td>
<td>98.4</td>
<td>9.7</td>
<td>Journal of CO(_2) Utilization, 2017, 20, 328-335.</td>
</tr>
<tr>
<td>Oxide-derived Bi films</td>
<td>0.5 M KHCO(_3)</td>
<td>-0.92 V vs. RHE</td>
<td>82</td>
<td>(\dot{J}_{\text{HCOOH}}) = 8.3 mA cm(^{-2})</td>
<td>Journal of CO(_2) Utilization, 2017, 19, 276-283.</td>
</tr>
<tr>
<td>Ultrathin Bismuth nanosheets</td>
<td>0.5 M NaHCO(_3)</td>
<td>-1.0 V vs. RHE</td>
<td>Over 90%</td>
<td>12.5</td>
<td>ChemSusChem, 2018, 11, 848-853.</td>
</tr>
<tr>
<td>Nano-sized Bi</td>
<td>0.1 M KHCO(_3)</td>
<td>-1.70 V vs. Ag/AgCl</td>
<td>91.3</td>
<td>6</td>
<td>Applied Surface Science, 2017, 393, 191-196</td>
</tr>
<tr>
<td>Bi(_{45})/GDE</td>
<td>0.5 M KHCO(_3)</td>
<td>-1.45 V vs. SCE</td>
<td>90</td>
<td>4</td>
<td>Applied Catalysis B: Environmental, 2017, 218, 46-50.</td>
</tr>
<tr>
<td>P-orbital delocalization (POD)-Bi</td>
<td>0.5 M KHCO(_3)</td>
<td>-1.16V vs. RHE</td>
<td>95</td>
<td>55</td>
<td>Angewandte Chemie International Edition, 2018, 57, 16114-16119.</td>
</tr>
<tr>
<td>Bi Dendrite</td>
<td>0.5 M KHCO(_3)</td>
<td>-0.74 V vs. SCE</td>
<td>89</td>
<td>2.6</td>
<td>ACS Catalysis, 2017, 7, 5071-5077.</td>
</tr>
<tr>
<td>Lattice-dislocated Bismuth Nanowires/Cu foam</td>
<td>0.5 M NaHCO(_3)</td>
<td>-0.69 V vs. RHE</td>
<td>95</td>
<td>15</td>
<td>Energy &amp; Environmental Science, 2019,12, 1334-1340.</td>
</tr>
<tr>
<td>Bi(_2)S(_3)-derived Bi</td>
<td>0.5 M NaHCO(_3)</td>
<td>-0.75 V vs. RHE</td>
<td>84</td>
<td>5</td>
<td>Journal of Materials Chemistry A, 2018,6, 4714-4720.</td>
</tr>
</tbody>
</table>
References