Supporting Information

Ce-doped Bi based catalysts for highly efficient electroreduction of CO$_2$ to formate

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**S1. Materials**

Bismuth nitrate pentahydrate (AR), Cerium nitrate hexahydrate (AR) 1,4-Naphthalenedicarboxylic acid (Aladdin, AR, 99%), imidazole (TCI, AR, 98%), potassium bicarbonate (MACKLIN, 99.99%), Nafion (Alfa Aesar, 5wt%), dimethyl sulfoxide (GENERAL-REAGENT, AR, 99%), and deuterium oxide (CIVI-CHEM, 99.9%) were used as received without further purification. N’N-dimethylformamide (AR) and absolute ethyl alcohol (AR) were purchased from Sinopharm Chemical Reagent Co, Ltd. Carbon paper (TGP-H-060, Toray) was used to prepare working electrode. Cationic ion exchange membrane Nafion 117 was purchased from DuPont (Wilmington, DE, USA). CO₂ (99.999%), Ar (99.99%) and gas mixture of H₂/Ar (90:10 vol%) were purchased from the Yuanhua gas company. All aqueous solutions were prepared with Milli Q ultrapure water (18.2 MΩ cm).

**S2. Experimental Details**

**S2.1 Synthesis of Bi-MOFs and Cerium-doped Bi-MOFs**

The Bi based metal-organic framework used as precursor (denoted as Bi-P1) for Bi@BiOₓ/C was synthesized via a solvothermal method. Typically, 0.6 mmol Bi(NO₃)₃·5H₂O, 4 mmol 1,4-Naphthalenedicarboxylic acid and 0.6 mmol imidazole were dispersed in 16 mL DMF under continuous magnetic stirring (600 rpm) at room temperature. The mixture was then heated up to 90 °C and maintained for 72 h. The final product was collected by centrifugation and washed several times with DMF and absolute ethyl alcohol. Finally, the Bi-P1 white powder was dried in vacuum at 60 °C for 8 h. The dry white sample was collected for further use. The synthetic procedure of Cerium-doped Bi based metal-organic framework precursor (denoted as Ce-Bi-P1) for Ce-Bi@CeBiOₓ/C was similar to that of Bi-P1 except that the 0.6 mmol Bi(NO₃)₃·5H₂O was replaced by 0.54 mmol Bi(NO₃)₃·5H₂O and 0.06 mmol Ce(NO₃)₃·6H₂O.

**S2.2 Synthesis of Bi@BiOₓ/C and Ce-Bi@CeBiOₓ/C**

The as synthesized Bi-P1 and Ce-Bi-P1 precursors were firstly annealed at 200°C for 2 h and then the temperature was increased and kept at 500 for another 2 h. The heating
rate was controlled at 3 °C/min and the whole process was carried out under a reduction atmosphere of H₂/Ar (90:10 vol%, 30 mL/min). Then, as the as-prepared black samples were ground and collected for further use.

S2.3 Preparation of electrodes
To prepare the working electrode, the substrate of carbon paper was dipped in absolute ethyl alcohol for 60 minutes to remove impurities before using. 20 mg of catalyst was dispersed in a mixed solution of 275 μL of deionized water, 275 μL absolute ethyl alcohol and 55 μL of Nafion solution (5% wt) by sonicating for 0.5 h to form a homogeneous ink. The mixture was then dropped onto a carbon paper of 1 cm² to make sure the catalyst loading was 4 mg cm².

S2.4 Physicochemical characterization
Scanning electron microscopy (SEM) images were obtained from a JSM6700-F microscope integrated with energy dispersive spectroscopy (EDS) operating at 15 kV. Transmission electron microscopy (TEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) characterizations were performed in a Talos-F200X field emission transmission electron microscope operating at an acceleration voltage of 200 kV. The phase structures were examined by X-ray diffraction (XRD), which were obtained with a MiniFlex600 diffractometer (Rigaku) fitted with Cu Kα (λ = 1.5406 Å) radiation in reflection mode from 5° to 80°. X-ray photoelectron spectroscopy (XPS) was performed on an Escalab 250 spectrometer (VG Systems) equipped with an Al-Kα (1486.7 eV) anode as an X-ray source. The standard C1s value of 284.8 eV was used to correct all reported XPS spectra. Electron spin resonance (EPR) spectra were recorded on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in the X band at room temperature. The content of Bi in different catalysts was determined by an inductively coupled plasma spectrometer (ICP, Ultima2).

S2.5 Electrochemical measurements and product analysis
Except the electrochemical impedance spectroscopy (EIS) measure, all the electrochemical measurements of the catalysts were conducted with Bio-Logic VMP3 at room temperature. EIS measurements (performed at open circuit potential with a frequency from 1000000 Hz to 0.01 Hz) were completed in a conventional three-electrode glass cell in 0.5 M KHCO$_3$ aqueous solution with CHI920D. All the other electrochemical experiments were performed in the H-type gas tight cell with two compartments separated by a cation exchange membrane (Nafion 117, Dupont). The prepared Bi-based electrodes and platinum plate were served as working and counter electrodes, respectively.

The electrolyte was bubbled with CO$_2$ before the electrochemical tests for at least 30 minutes and then the flow rate of CO$_2$ was changed to 10 sccm during the whole test process (pH =7.4). Linear sweep voltammetry (LSV) was carried out at a scan rate of 50 mV/s. During chronoamperometric test, the gas products from the cell was introduced directly to the gas sample loop of gas chromatograph (GC), which equipped with 2 of Porapak-N, C13 and SE30 columns for quantifications. The gas-phase product was analyzed by GC every 5 minutes. CO in the gas products was analyzed by flame ionization detector (FID) after conversion by methane reformer while H$_2$ in the gas products was analyzed by thermal conductivity detector (TCD). The liquid products were characterized by $^1$H nuclear magnetic resonance (H-NMR) spectra. Typically, 0.49 mL electrolyte after electrolysis was mixed with 0.1 mL D$_2$O, and 0.01 mL dimethyl sulfoxide (DMSO) water solution (1%, v%) was added as an internal standard. The one-dimensional $^1$H spectrum was measured with water suppression using a solvent pre-saturation technique.

The stability test was carried out at the potential of –1.6 V vs. SCE for 10 h. CO$_2$-saturated 0.5 M KHCO$_3$ aqueous solution was replaced by Ar-saturated 0.5 M KHCO$_3$ aqueous solution for checking that the formate was produced from the reduction of CO$_2$ rather than the decomposition of HCO$_3^-$.

Tafel slopes for formate production were calculated from the corresponding geometric current densities and the formate Faradaic efficiency.

The electrochemical surface area (ECSA) was obtained by the double-layer capacitance
method using the follow equation:

$$ECSA = \frac{C_{dl}}{C_s}$$

where $C_{dl}$ is the double-layer capacitance measured by cyclic voltammetry (CV) method with different scan rates at the potential from -0.93 to 0.66 V. $C_{dl}$ was determined from the plot slope of the double-layer charging current versus the scan rate. $C_s$ is the specific capacitance which value is 40 $\mu$F cm$^{-2}$ used in this work.

### S2.7 Calculation of Faradaic Efficiency

#### S2.7.1 Liquid products

$$FE_{\text{liquid}} = V \times c \times \frac{nF}{Q}$$

- $V$: the volume of the electrolyte in the working cell;
- $c$: the concentration of liquid product after electrolysis, determined by $^1$H NMR;
- $n$: number of transferred electrons for certain product;
- $F$: 96485 C mol$^{-1}$;
- $Q$: total charge consumed in the electrolysis.

#### S2.7.1 Gaseous products

$$FE_{\text{gas}} = V_t \times n \times \frac{nFp^0}{RT^0I_t}$$

- $V_t$: the volume concentration of H$_2$ or CO based on a calibration of the GC;
- $n$: number of transferred electrons for certain product;
- $F$: 96485 C mol$^{-1}$;
- $p^0$: 101.3 kPa;
- $R$: Gas constant in J K$^{-1}$mol$^{-1}$;
- $T^0$: the temperature for testing;
- $I_t$: the steady-state current measured during a constant-potential electrolysis.

### S2.8 Randles–Sevcik equation

$$i_p = 0.4463nFAC\left(\frac{nFvD}{RT}\right)^{\frac{1}{2}}$$

If part of the parameters are controlled, the equation could be simplified as follow

$$i_p = kD^{\frac{1}{2}} \times v^{\frac{1}{2}}$$
$i_p$: current maximum in amps

$n$: number of electrons transferred in redox event

$A$: electrode area in cm$^2$

$F$: 96485 C mol$^{-1}$;

$D$: diffusion coefficient in cm$^2$/s

$C$: concentration in mol/cm$^3$

$v$: scan rate in V/s

$R$: Gas constant in JK$^{-1}$mol$^{-1}$

$T$: temperature in K

**Supplementary figures**

Fig. S1. SEM images with different magnifications of Bi-P1 precursor (a, c), and Ce-Bi-P1 precursor (b, d).
Fig. S2. XRD patterns of Bi-P1 and Ce-Bi-P1 precursors.

Fig. S3. TEM images of a) Ce-Bi@CeBiOₓ/C and b) Bi@BiOₓ/C
Fig. S4. SEM images of Bi@BiO<sub>x</sub>/C and Ce-Bi@CeBiO<sub>x</sub>/C

Fig. S5. Raman spectra of Bi@BiO<sub>x</sub>/C and Ce-Bi@CeBiO<sub>x</sub>/C
Fig. S6. Element mapping for all elements of Ce-Bi@CeBiO\textsubscript{x}/C.

Fig. S7. a) HRTEM images of Bi@BiO\textsubscript{x}/C; b) and c) is a magnification of the white squares in a) and b) respectively; d) EDS elemental mappings of Bi@BiO\textsubscript{x}/C.
Fig. S8. a,d) HRTEM images of Ce-Bi@CeBiO\textsubscript{x}/C; b) and e) is a magnification of the white squares in a) and d) respectively; c,f) the corresponding FFT images of b) and e).

Fig. S9. a,d) HRTEM images of Bi@BiO\textsubscript{x}/C; b) and e) is a magnification of the white squares in a) and d) respectively; c,f) the corresponding FFT images of b) and e).
Fig. S10. EDS line scan Ce-Bi@CeBiOₓ/C and b) Bi@BiOₓ/C

Fig. S11. XPS survey spectra of Bi@BiOₓ/C and Ce-Bi@CeBiOₓ/C (the inset shows the Ce 3d spectrum of Ce-Bi@CeBiOₓ/C)
Fig. S12. Ce 3d spectrum of Ce-Bi@CeBiO$_x$/C

Fig. S13. Chronoamperometry curves of Bi@BiO$_x$/C (a) and Ce-Bi@CeBiO$_x$/C (b) at different applied potentials in CO$_2$-saturated 0.5 M KHCO$_3$ solution.
Fig. S14. FE of H$_2$ (a) and CO (b) for Bi@BiO$_x$/C and Ce-Bi@CeBiO$_x$/C.

Fig. S15 CVs of a) Bi@BiO$_x$/C and b) Ce-Bi@CeBiO$_x$/C recorded at different scan rates in 0.5 M KHCO$_3$ electrolyte with a potential range from -0.93 V to -0.66 V.; c) The fitting plots of current densities versus scan rates for Bi@BiO$_x$/C and Ce-Bi@CeBiO$_x$/C, the current densities were obtained from the double layer charge/discharge curves at -0.80 V; d) Partial current densities of formate normalized by ECSA for Bi@BiO$_x$/C and Ce-Bi@CeBiO$_x$/C.
Fig. S16. H NMR spectra of the electrolyte after electrolysis at -1.6 V vs. SCE for Ce-Bi@CeBiO$_x$/C in CO$_2$-saturated and Ar-saturated 0.5M KHCO$_3$ aqueous solution, respectively.
Fig. S17 Reduction current density at -1.8 V plotted against the square root of scan rate for Bi@BiO$_x$/C and Ce-Bi@CeBiO$_x$/C

Table S1. The ICP analysis of Bi, Ce in Bi@BiO$_x$/C and Ce-Bi@CeBiO$_x$/C

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ce (wt%)</th>
<th>Bi (wt%)</th>
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<tbody>
<tr>
<td>Bi@BiO$_x$/C</td>
<td>-</td>
<td>61.48</td>
</tr>
<tr>
<td>Ce-Bi@CeBiO$_x$/C</td>
<td>1.30</td>
<td>63.41</td>
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Table S2. Comparison of the performances for electrochemical reduction of CO$_2$ to formate on Ce-Bi@CeBiO$_x$ and those Bi-based catalysts reported in literatures.

<table>
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<tr>
<th>Catalyst</th>
<th>$E$ (vs. RHE)</th>
<th>$F_{\text{Formate}}$ (%)</th>
<th>$j_{\text{Formate}}$ (mA cm$^{-2}$)</th>
<th>Ref</th>
</tr>
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<tbody>
<tr>
<td>Ce-Bi@CeBiO$_x$</td>
<td>-1.0 V</td>
<td>96</td>
<td>11.8 mA cm$^{-2}$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>-1.1 V</td>
<td>88</td>
<td>15.2 mA cm$^{-2}$</td>
<td>This work</td>
</tr>
<tr>
<td>Bi$_2$O$_3$NSs@MCCM</td>
<td>-1.256 V</td>
<td>93.8</td>
<td>14 mA cm$^{-2}$</td>
<td>1</td>
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<td>BiOC nanosheets</td>
<td>-0.7 V</td>
<td>85</td>
<td>10.5 mA cm$^{-2}$</td>
<td>2</td>
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<tr>
<td>defect-rich Bi</td>
<td>-0.75 V</td>
<td>84</td>
<td>5 mA cm$^{-2}$</td>
<td>3</td>
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<tr>
<td>Bi/Cu</td>
<td>-1.07 V</td>
<td>95</td>
<td>6 mA cm$^{-2}$</td>
<td>4</td>
</tr>
<tr>
<td>Bi nanosheets</td>
<td>-1.1 V</td>
<td>86</td>
<td>14.2 mA cm$^{-2}$</td>
<td>5</td>
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<tr>
<td>Bi nanoparticle</td>
<td>-0.88 V</td>
<td>90</td>
<td>6.5 mA cm$^{-2}$</td>
<td>6</td>
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<tr>
<td>BiOCl$<em>{0.5}$Br$</em>{0.5}$</td>
<td>-0.93 V</td>
<td>98</td>
<td>9.47 mA cm$^{-2}$</td>
<td>7</td>
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<tr>
<td>oxide-derived Bi films</td>
<td>-0.92 V</td>
<td>75</td>
<td>8.3 mA cm$^{-2}$</td>
<td>8</td>
</tr>
<tr>
<td>BiOCl nanosheets</td>
<td>-0.83 V</td>
<td>92</td>
<td>3.4 mA cm$^{-2}$</td>
<td>9</td>
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<tr>
<td>Bi$_{45}$/GDE</td>
<td>-0.80 V</td>
<td>90</td>
<td>1.3 mA cm$^{-2}$</td>
<td>10</td>
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<td>Bi dendrite</td>
<td>-0.74 V</td>
<td>89</td>
<td>2.3 mA cm$^{-2}$</td>
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<tr>
<td>5 nm SnO$_2$ nanoparticles</td>
<td>-1.189 V</td>
<td>93</td>
<td>10.8 mA cm$^{-2}$</td>
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<tr>
<td>nanoporous Sn/SnO$_2$ composites</td>
<td>-1.1 V</td>
<td>80</td>
<td>12.8 mA cm$^{-2}$</td>
<td>13</td>
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References:
2017, 393, 191–196.