Optimizing Bi Active Sites by Ce Doping for Boosting Formate-Production in A Wide Potential Window

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Figure S1. XRD patterns of Bi-MOF and Ce$_{0.05}$Bi$_{0.95}$-MOF precursor.
Figure S2. SEM patterns of (a,b) Bi-MOF NRs and (c,d) Ce$_{0.05}$Bi$_{0.95}$-MOF NRs.
Figure S3. (a) XRD and (b) SEM patterns of Ce-MOF with broom-like structure.
Figure S4. (a) SEM and (b,c) TEM patterns of Bi@C NRs.
Figure S5. Elemental mapping of Ce$_{0.05}$Bi$_{0.95}$@C NRs.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass%</th>
<th>Atom%</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>20.88</td>
<td>81.82</td>
</tr>
<tr>
<td>Ce</td>
<td>3.28</td>
<td>1.10</td>
</tr>
<tr>
<td>Bi</td>
<td>75.84</td>
<td>17.08</td>
</tr>
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</table>
Figure S6. The full range XPS spectrum of Bi@C and Ce$_{0.05}$Bi$_{0.95}$@C NRs.

For the High-resolution XPS spectrum of Ce 3d of Ce$_{0.05}$Bi$_{0.95}$@C NRs, these peaks could be fitted into eight peaks that these four characteristic peaks (882.69 eV, 884.00 eV, 889.11 eV, and 898.73 eV) are ascribed to the Ce 3d$_{5/2}$ and those two characteristic peaks (901.19 eV, 902.12 eV, 907.43 eV, and 917.14 eV) are assigned to the Ce 3d$_{3/2}$. Specifically, the pair of peaks at 884.00 eV and 902.12 eV corresponds to Ce$^{3+}$, while the other peaks belong to Ce$^{4+}$. Therefore, the hybrid of Ce$^{3+}$ and Ce$^{4+}$ were introduced on the surface of 5% Ce-doped Bi@C NRs.
Figure S7. Raman spectra of (a) Bi@C NRs; (b) Ce$_{0.01}$Bi$_{0.99}$@C NRs; (c) Ce$_{0.05}$Bi$_{0.95}$@C NRs; (d) Ce$_{0.1}$Bi$_{0.9}$@C NRs.
Figure S8. FEs of product distributions at different applied potentials on Bi@C.
Figure S9. LSV curves of Bi@C NRs with different amounts of Ce doping in CO$_2$-saturated 0.1 M KHCO$_3$. 
Figure S10. $F_{\text{H}_2}$ of Bi@C NRs with different amounts of Ce doping at different applied potentials.
Figure S11. SEM image of Ce$_{0.05}$Bi$_{0.95}$@C NRs after stability test.
Figure S12. XRD pattern Ce$_{0.05}$Bi$_{0.95}$@C NRs after stability test.
Figure S13. CV curves of Bi@C NRs with different amounts of Ce doping.

Electrochemical active surface area (ECSA)

The ECSA of a material with similar composition is proportional to its electrochemical double-layer capacitance ($C_{dl}$), which is measured by CV in a non-Faradaic region at different scan rates ($V_s$) of 20, 40, 60, 80, 100, 120 mV s$^{-1}$. Then the double-layer capacitance ($C_{dl}$) was determined by plotting the $\Delta j = (j_a - j_c)$ at -0.5 V vs. SCE as a function of the scan rate. It can be calculated through the following equation:

$$C_{dl} = \frac{d(\Delta j)}{2dV_s}$$

The ECSA can be calculated from the $C_{dl}$ according to:

$$ECSA = \frac{C_{dl}}{C_s}$$
Where $C_s$ is the specific capacitance of a flat surface with 1 cm$^2$ of real surface area. Here, the average double-layer capacitance of a smooth metal surface is assumed to be 20 μF cm$^{-2}$ [1]. The calculated value of ECSA for Bi@C NRs was about 10.19 cm$^2$, while the value for 1%, 5%, and 10% Ce-doped Bi@C NRs were 11.49 cm$^2$, 23.68 cm$^2$, and 26.75 cm$^2$, respectively. ECSA-corrected Tafel slopes for formate formation were calculated based on the corresponding ECSA-corrected formate partial current densities and overpotentials.
Figure S14. $\text{CO}_2$ adsorption isotherms of Bi@C NRs and Ce$_{0.05}$Bi$_{0.95}$@C NRs.
Figure S15. (a) XAS spectra of Bi@C and Ce-doped Bi@C NRs; (b) Fourier transforms of $k^2$-weighted EXAFS spectra to the $R$ space of Bi@C and Ce-doped Bi@C NRs.
Figure S16. Representative fitting of the EXAFS spectra to the R-space of (a) $\text{Ce}_{0.01}\text{Bi}_{0.99}@\text{C}$ NRs; (b) $\text{Ce}_{0.1}\text{Bi}_{0.9}@\text{C}$ NRs.
Figure S17. Morlet wavelet transform of EXAFS spectra in both \( R \)-space and \( k \)-space of (a) Bi@C NRs and (b) Ce\(_{0.05}\)Bi\(_{0.95}\)@C NRs, respectively; (c) Fitting results of EXAFS spectra to \( k \)-space.
Figure S18. Thermogravimetric analysis of Ce$_{0.05}$Bi$_{0.95}$@C NRs.
Figure S19. Elemental mapping of Ce$_{0.05}$Bi$_{0.95}$@C NRs after stability test.
**Table S1.** Peak fitting results of Raman spectrum of (a) Bi@C NRs; (b) Ce$_{0.01}$Bi$_{0.99}$@C NRs; (c) Ce$_{0.05}$Bi$_{0.95}$@C NRs; (d) Ce$_{0.1}$Bi$_{0.9}$@C NRs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$I_D/I_G$</th>
</tr>
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<tbody>
<tr>
<td>Bi@C</td>
<td>2.237</td>
</tr>
<tr>
<td>Ce$<em>{0.01}$Bi$</em>{0.99}$@C</td>
<td>2.446</td>
</tr>
<tr>
<td>Ce$<em>{0.05}$Bi$</em>{0.95}$@C</td>
<td>2.670</td>
</tr>
<tr>
<td>Ce$<em>{0.1}$Bi$</em>{0.9}$@C</td>
<td>2.144</td>
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Table S2-1. Summary of Bi-based catalysts for formate production in CO$_2$RR (CO$_2$-saturated 0.1 M KHCO$_3$).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>FE$_{\text{formate}}$</th>
<th>j$_{\text{formate}}$</th>
<th>Potential</th>
<th>Stability</th>
<th>Potential window</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/Sn [2]</td>
<td>94.8%</td>
<td>32 mA/cm$^2$</td>
<td>$-1.0$ V vs. RHE</td>
<td>20 hrs</td>
<td>200 mV</td>
</tr>
<tr>
<td>Bi$_2$O$_3$@MCCM [3]</td>
<td>90%</td>
<td>17.7 mA/cm$^2$</td>
<td>$-1.36$ V vs. RHE</td>
<td>12 hrs</td>
<td>300 mV</td>
</tr>
<tr>
<td>BiOx/C [4]</td>
<td>96%</td>
<td>12.5 mA/cm$^2$</td>
<td>$-1.37$ V vs. RHE</td>
<td>0.5 hrs</td>
<td>350 mV</td>
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<tr>
<td>BiOBr [5]</td>
<td>95%</td>
<td>60 mA/cm$^2$</td>
<td>$-0.9$ V vs. RHE</td>
<td>65 hrs</td>
<td>50 mV</td>
</tr>
<tr>
<td>Bi-Sn aero gel 6]</td>
<td>93.9%</td>
<td>9.3 mA/cm$^2$</td>
<td>$-1.1$ V vs. RHE</td>
<td>10 hrs</td>
<td>200 mV</td>
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<tr>
<td>Bi NSs [7]</td>
<td>98%</td>
<td>16 mA/cm$^2$</td>
<td>$-0.9$ V vs. RHE</td>
<td>100 hrs</td>
<td>400 mV</td>
</tr>
<tr>
<td>Bi/Cu [8]</td>
<td>100%</td>
<td>4 mA/cm$^2$</td>
<td>$-1.5$ V vs. RHE</td>
<td>24 hrs</td>
<td>520 mV</td>
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<tr>
<td>Bi MSs [9]</td>
<td>96.2%</td>
<td>15 mA/cm$^2$</td>
<td>$-1.0$ V vs. RHE</td>
<td>50 hrs</td>
<td>500 mV</td>
</tr>
<tr>
<td>BOC [10]</td>
<td>92.6%</td>
<td>35 mA/cm$^2$</td>
<td>$-1.5$ V vs. RHE</td>
<td>8 hrs</td>
<td>300 mV</td>
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<tr>
<td>Bi NPs [11]</td>
<td>98%</td>
<td>21.6 mA/cm$^2$</td>
<td>$-1.5$ V vs. RHE</td>
<td>20 hrs</td>
<td>500 mV</td>
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<tr>
<td>Bi-Cu [12]</td>
<td>94.1%</td>
<td>24.4 mA/cm$^2$</td>
<td>$-1.0$ V vs. RHE</td>
<td>20 hrs</td>
<td>500 mV</td>
</tr>
<tr>
<td>Bi NTs [13]</td>
<td>97%</td>
<td>39.4 mA/cm$^2$</td>
<td>$-1.1$ V vs. RHE</td>
<td>10 hrs</td>
<td>400 mV</td>
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<tr>
<td>5% Ce-doped B@C</td>
<td>96.1%</td>
<td>30.3 mA/cm$^2$</td>
<td>$-1.5$ V vs. RHE</td>
<td>40 hrs</td>
<td>1000 mV</td>
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Table S2-2. Comparison of Highest FE$_{\text{formate}}$ with catalysts working in different conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Highest FE$_{\text{formate}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Ce-doped B@C</td>
<td>0.1 M KHCO$_3$</td>
<td>96.1%</td>
</tr>
<tr>
<td>Bi$_2$O$_3$@GO [14]</td>
<td>0.5 M KHCO$_3$</td>
<td>87.17%</td>
</tr>
<tr>
<td>MnO$_2$/g-C$_3$N$_4$ [15]</td>
<td>0.5 M KHCO$_3$</td>
<td>68.65%</td>
</tr>
<tr>
<td>ZnO/g-C$_3$N$_4$ [16]</td>
<td>0.5 M KHCO$_3$</td>
<td>87.17%</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$@rGO [17]</td>
<td>0.5 M KHCO$_3$</td>
<td>91.20%</td>
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References