Supporting Information

Cobalt Single-Atoms Anchored on Porphyrinic Triazine-based Frameworks as Bifunctional Electrocatalysts for Oxygen Reduction and Hydrogen Evolution Reactions

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**Figure S1.** TGA curves of CoSAs/PTF-400, 500, 600 and Co-TPPCN.

**Figure S2.** FT-IR spectra of the Co-TPPCN and CoSAs/PTF-x ($x = 400, 500, 600 \, ^\circ\text{C}$). The characteristic peaks of the Co-N (~1002 cm$^{-1}$), the stretching vibration of C=N (~1340 cm$^{-1}$), aromatic ring (~1455 cm$^{-1}$), the triazine ring (1564 cm$^{-1}$) and carbonitrile stretching band (2227 cm$^{-1}$) are marked with dashed line.
Figure S3. PXRD patterns of CoSAs/PTF-400, 500, 600.

Figure S4. Raman spectra of CoSAs/PTF-400, 500, 600.
Figure S5. Nyquist plots of different samples over the frequency range from 100 kHz to 10 mHz by applying AC voltage with 5 mV amplitude.

Table S1 $R_{ct}$ values of CoSAs/PTF-400, 500, 600.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{ct}$ (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSAs/PTF-400</td>
<td>2101</td>
</tr>
<tr>
<td>CoSAs/PTF-500</td>
<td>1283</td>
</tr>
<tr>
<td>CoSAs/PTF-600</td>
<td>204</td>
</tr>
<tr>
<td>Pt/C</td>
<td>75</td>
</tr>
</tbody>
</table>

Table S2 Porous characteristics of CoSAs/PTF-400, 500, 600.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{Langmuir}}$ (m$^2$/g)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>Total Pore Volume (cm$^3$/g)</th>
<th>Average Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSAs/PTF-400</td>
<td>1017</td>
<td>668</td>
<td>0.58</td>
<td>3.5</td>
</tr>
<tr>
<td>CoSAs/PTF-500</td>
<td>1132</td>
<td>741</td>
<td>0.61</td>
<td>3.3</td>
</tr>
<tr>
<td>CoSAs/PTF-600</td>
<td>863</td>
<td>562</td>
<td>0.55</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Table S3. The ICP results of CoSAs/PTF-400, 500, 600.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content of Co (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer-Co</td>
<td>6.89</td>
</tr>
<tr>
<td>CoSAs/PTF-400</td>
<td>5.15</td>
</tr>
<tr>
<td>CoSAs/PTF-500</td>
<td>2.74</td>
</tr>
<tr>
<td>CoSAs/PTF-600</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Figure S6. Four representative TEM images of CoSAs/CTF-400 at different areas.
**Figure S7.** Four representative TEM images of CoSAs/CTF-500 at different areas.

**Figure S8.** HAADF-STEM images of Co SAs at different areas for the sample CoSAs/CTF-600.
**Figure S9.** XPS spectra of XPS spectra of the Co 2p region of CoSAs/PTF-400, 500, 600.

**Figure S10.** XPS spectra of the N 1s region of a) Co-TPPCN, b) CoSAs/PTF-400, c) CoSAs/PTF-500, d) CoSAs/PTF-600.
### Table S4. The content of different types of nitrogen in CoSAs/PTFs based on XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Triazine N (%)</th>
<th>Graphitic N (%)</th>
<th>Co-N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSAs/PTF-400</td>
<td>49.9</td>
<td>19.4</td>
<td>30.7</td>
</tr>
<tr>
<td>CoSAs/PTF-500</td>
<td>47.7</td>
<td>24.3</td>
<td>28.0</td>
</tr>
<tr>
<td>CoSAs/PTF-600</td>
<td>45.5</td>
<td>34.2</td>
<td>20.3</td>
</tr>
</tbody>
</table>

### Table S5 EXAFS data fitting results of Samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>CN</th>
<th>$R$(Å)</th>
<th>$\sigma^2$(10^{-3} Å²)</th>
<th>R factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co foil</td>
<td>Co-Co</td>
<td>12</td>
<td>2.49±0.01</td>
<td>6.1±0.3</td>
<td>0.0017</td>
</tr>
<tr>
<td>CoSAs/PTF-400</td>
<td>Co-N</td>
<td>4.2±0.7</td>
<td>1.90±0.01</td>
<td>8.8±2.1</td>
<td>0.0065</td>
</tr>
<tr>
<td>CoSAs/PTF-500</td>
<td>Co-N</td>
<td>3.9±0.7</td>
<td>1.90±0.02</td>
<td>7.1±2.2</td>
<td>0.0097</td>
</tr>
<tr>
<td>CoSAs/PTF-600</td>
<td>Co-N</td>
<td>3.9±0.6</td>
<td>1.89±0.01</td>
<td>6.8±1.9</td>
<td>0.0077</td>
</tr>
<tr>
<td>Co-TPPCN</td>
<td>Co-N</td>
<td>4.0±0.8</td>
<td>1.96±0.02</td>
<td>7.4±2.2</td>
<td>0.0101</td>
</tr>
</tbody>
</table>

CN, coordination number; R, distance between absorber and backscatter atoms; $\sigma^2$, Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); R factor is used to value the goodness of the fitting.
Figure S11. EXAFS fitting curves of CoSAs/PTF-400.

Figure S12. EXAFS fitting curves of CoSAs/PTF-500.
Figure S13. EXAFS fitting curves of Co-TPPCN.

Table S6 Comparison of ORR catalytic performances in alkaline solution between CoSAs/PTF-600 and other noble-metal-free electrocatalysts reported previously.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset potential (V)</th>
<th>$E_{1/2}$ (V)</th>
<th>Current density (mA/cm$^2$) at 0.2 V</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSAs/PTF-600</td>
<td>0.92</td>
<td>0.81</td>
<td>6.14</td>
<td>This work</td>
</tr>
<tr>
<td>MOFCN</td>
<td>0.92</td>
<td>0.72</td>
<td>4.10</td>
<td>S1</td>
</tr>
<tr>
<td>GPC-1000-5</td>
<td>0.87</td>
<td>0.71</td>
<td>5.40</td>
<td>S2</td>
</tr>
<tr>
<td>FeIM/ZIF-8</td>
<td>0.91</td>
<td>0.76</td>
<td>5.00</td>
<td>S3</td>
</tr>
<tr>
<td>Co@Co$_3$O$_4$@C-CM</td>
<td>0.93</td>
<td>0.81</td>
<td>4.60</td>
<td>S4</td>
</tr>
<tr>
<td>Fe–N/C-800</td>
<td>0.92</td>
<td>0.81</td>
<td>6.06</td>
<td>S5</td>
</tr>
<tr>
<td>OMC</td>
<td>0.81</td>
<td>0.69</td>
<td>3.10</td>
<td>S6</td>
</tr>
<tr>
<td>HPC-N-850</td>
<td>0.90</td>
<td>0.78</td>
<td>4.20</td>
<td>S7</td>
</tr>
<tr>
<td>Fe-N/G</td>
<td>0.87</td>
<td>0.78</td>
<td>5.21</td>
<td>S8</td>
</tr>
<tr>
<td>N:C-MgNTA</td>
<td>0.89</td>
<td>0.75</td>
<td>5.70</td>
<td>S9</td>
</tr>
</tbody>
</table>

*Note: all potentials are versus to reversible hydrogen electrode (RHE).*
**Figure S14.** PXRD patterns of CoSAs/PTF-600 and CoNPs/PTF-600.

**Figure S15.** TEM and HRTEM images of CoNPs/CTF-600.
Figure S16. (a) LSV of CoSAs/PTF-600 at different rotation speeds. (b) K-L plots.

Figure S17. The atomic structure of CoSAs/PTF. The pink, white, grey and blue spheres denotes Co, H, C and N atoms, respectively.
Figure S18 (a) The free energy variations for Co-porphyrin during the ORR process. The black, red and blue lines are for ORR under electrochemical potentials of 0, 0.38 and 1.23 V, respectively. (b) The atomic structure of Co-porphyrin. The pink, white, grey and blue spheres denotes Co, H, C and N atoms, respectively.

Figure S19. The LSV cures of rotating ring-disk electrode (RRDE) measurements of Pt/C and CoSAs/PTF-400, 500, 600.
Figure S20. Methanol-crossover effects test of CoSAs/PTF-600 and Pt/C.

Figure S21. Measuring the current collection efficiency $N$ of RRDE in N$_2$-saturated 0.1 M $K_3[Fe(CN)_6]$ solution with a constant ring potential of 0.5 V vs. Ag/AgCl. (a) LSV of RRDE with a scan rate of 10 mV/s (Id is disk current, Ir is ring current). (b) The current collection efficiency $N$ is calculated with the following equation: $N = \frac{Ir}{Id}$. 
References.


