**Supplementary Figure 1.** HER activity of CoNₓ/C catalysts prepared with different precursors as a function of pyrolysis temperature. Three precursors have been used in this work, including metal-N₄ macrocycles (CoTMPP), biomolecules (VB12), and a mixture of cobalt salts and nitrogen-containing aromatic molecules (Co-oPD). The pyrolysis temperature was separately optimized from 600 to 900 °C for each precursor. The best pyrolysis temperature was found to be 800, 750, and 900 °C for CoTMPP, VB12, and Co-oPD, respectively. The VB12-derived carbon catalyst exhibited a slightly lower HER activity than the Co-oPD-derived catalyst but a significantly higher HER activity than the CoTPMM-derived catalyst.

**Supplementary Figure 2.** Comparison of the HER activity of CoNₓ/C catalysts prepared with different precursors. Each catalyst has been optimized as function of pyrolysis temperature, as shown in Figure S1. The VB12-derived carbon catalyst exhibited a slightly lower HER activity than the Co-oPD-derived catalyst but a significantly higher HER activity than the CoTPMM-derived catalyst.
**Supplementary Figure 3.** HER polarization curve of non-doped porous carbon prepared with sucrose as precursor and silica colloid as template.

**Supplementary Figure 4.** Ohmic and capacitive corrections of the as-measured HER activity of the CoNₓ/C catalyst. The as-measured HER activity of the CoNₓ/C catalyst (“raw”, dashed black line) is capacity-corrected by taking an average of forward and backward (positive and negative-going) scans. The capacity-corrected HER current (solid blue line) is then ohmically corrected with the measured ionic resistance (≈ 7 Ω) to yield the final electrode HER activity (solid magenta line).
**Supplementary Figure 5.** Electrochemical impedance spectroscopy (EIS) analyses of the catalysts. EIS measurements were recorded on RDE in Ar-saturated 0.5 M H$_2$SO$_4$ at –0.1 V vs. RHE with 5 mV AC potential from 10 kHz to 0.01 Hz. Electrode rotation speed: 1600 rpm. The measured impedance can be presented in the form of imaginary (Im) vs. real (Re) parts at various frequencies. It has been recognized that the high frequency interception of the Re-axis represents the resistance of the electrodes and that the width of the semicircle on the Re-axis corresponds to the charge-transfer resistances and indicates the overall kinetic effects. Clearly, all three catalysts exhibited almost the same intrinsic resistance, while the charge-transfer resistance of CoN$_x$/C was much lower than that of N/C and Co/C, suggesting a faster HER kinetic process on CoN$_x$/C, which is in good agreement with the RDE analysis.
**Supplementary Figure 6.** Comparison of the HER activity of the N/C and CoNₓ/C catalysts prepared with increasing Co/oPD ratios from 5.0 to 20 wt%. The strong positive shift of the HER polarization curves indicated that the incorporation of only 5 wt% Co could dramatically improve the HER performance compared that of the metal-free N/C catalyst. The optimal Co/oPD ratio was found to be 10 wt%. Further increasing the ratio from 10 to 20 wt% resulted in a much lower HER activity due to the greatly reduced specific surface area (S_{BET} = 1070 m^2 g^{-1} for 10 wt% vs. 410 m^2 g^{-1} for 20 wt%).

**Supplementary Figure 7.** HER activity of the catalysts in a neutral medium. HER polarization curves of CoNₓ/C and reference materials in 1.0 M PBS, indicating that the CoNₓ/C catalyst can also work very well in neutral media, with an overpotential of 247 mV at a current density of 10 mA cm^{-2}.
Supplementary Figure 8. HER polarization of CoNx/C initially and after 5000 cyclic voltammograms cycles between 0.20 V and −0.25 V vs. RHE (not iR-corrected) in 1.0 M KOH (a) and 1.0 M PBS (b).

Supplementary Figure 9. XRD patterns of CoNPs/CoNx/C and CoNx/C, further conforming the absence of any other inorganic crystalline phase in leached sample.
Supplementary Figure 10. Additional TEM image of the CoN\textsubscript{x}/C catalyst. Scale bar: 100 nm. All cobalt-containing nanoparticles were leached out by acid.

Supplementary Figure 11. Room-temperature magnetic hysteresis loops at 300 K of (a) CoNPs/CoN\textsubscript{x}/C and (b) CoN\textsubscript{x}/C catalysts. While the CoNPs/CoN\textsubscript{x}/C exhibited a strong metallic ferromagnetic behavior, the CoN\textsubscript{x}/C catalyst showed diamagnetic state, which is the typical magnetic property of carbons. The magnetic data further confirmed that all metallic cobalt nanoparticles have been leached out by acid treatment.
**Supplementary Figure 12.** $\text{N}_2$ adsorption/desorption isotherms of CoNPs/CoN$_x$/C and CoN$_x$/C, showing an increasing BET surface area after the leaching out of cobalt nanoparticles.

**Supplementary Figure 13.** Pore size distribution of CoNPs/CoN$_x$/C and CoN$_x$/C catalysts based on calculation with the NLDFT method.
Supplementary Figure 14. Tafel plots obtained from the HER polarization curves in Figure 4b, indicating that the activity of CoN\textsubscript{x}/C catalyst at the overpotential of 150 mV decreased 61.7% upon introducing SCN\textsuperscript{−} into the electrolyte.

Supplementary Figure 15. KSCN poisoning of the N/C and Co/C catalysts. HER polarization curves of N/C and Co/C catalysts with and without 10 mM KSCN in Ar-saturated 0.5 M H\textsubscript{2}SO\textsubscript{4}. Similarly to the CoN\textsubscript{x}/C catalyst, the polarization curve of the Co/C catalyst is greatly negatively shifted upon addition of 10 mM KSCN into the acidic electrolyte, indicating a direct contribution of Co to the HER. In contrast, we did not observe any obvious effect of the SCN\textsuperscript{−} ions on the HER performance of metal-free N/C catalysts.
**Supplementary Figure 16.** Comparison of the HER activity of MeNₙ/C catalysts with different metal centers in 0.5 M H₂SO₄. The order of HER activity is Co > Ni >> Mn > Fe >> metal-free.
### Supplementary Table 1. Summary of recently reported HER performance of molecular as well as solid-state catalysts in acidic aqueous solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst loading (mg cm(^{-2}))</th>
<th>Onset overpotential (mV)</th>
<th>Overpotential at10 mA cm(^{-2}) (mV)</th>
<th>TOF (H(_2) s(^{-1}))</th>
<th>Tafel slope (mV/decade)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-bisdiphosphine/CNTs</td>
<td>0.06</td>
<td>20</td>
<td>&gt;300</td>
<td>2.78 at 300 mV overpotential</td>
<td>unknown</td>
<td>1</td>
</tr>
<tr>
<td>Cobalt diimine-dioxime complexes</td>
<td>unknown</td>
<td>350</td>
<td>&gt;590</td>
<td>2.2 at 590 mV overpotential</td>
<td>160</td>
<td>2</td>
</tr>
<tr>
<td>Electrodeposited H(_2)-CoCat</td>
<td>0.059 (only Co)</td>
<td>50</td>
<td>&gt;385</td>
<td>0.02 at 380 mV overpotential</td>
<td>140</td>
<td>3</td>
</tr>
<tr>
<td>UHV MoS(_2)Au (111)</td>
<td>&lt;monolayer</td>
<td>~100</td>
<td>unknown</td>
<td>2.4 at 150 mV overpotential</td>
<td>55-60</td>
<td>4</td>
</tr>
<tr>
<td>[Mo(<em>3)S(</em>{13})](^2)-GP</td>
<td>0.1</td>
<td>100</td>
<td>180</td>
<td>0.59 at 200 mV overpotential</td>
<td>38-40</td>
<td>5</td>
</tr>
<tr>
<td>Amorphous molybdenum sulfide</td>
<td>unknown</td>
<td>~150</td>
<td>&gt;200</td>
<td>0.8 at 220 mV overpotential</td>
<td>40</td>
<td>6</td>
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<tr>
<td>Double-gyroid MoS(_2)</td>
<td>unknown</td>
<td>150</td>
<td>240</td>
<td>0.78 at 200 mV overpotential</td>
<td>50</td>
<td>7</td>
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<tr>
<td>MoS(_2) Nano-sheets</td>
<td>unknown</td>
<td>~150</td>
<td>187</td>
<td>unknown</td>
<td>43</td>
<td>8</td>
</tr>
<tr>
<td>Ni(_2)P nanoparticles</td>
<td>1.0</td>
<td>~50</td>
<td>187</td>
<td>0.015 at 100 mV overpotential</td>
<td>46</td>
<td>9</td>
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<tr>
<td>CoP nanoparticles</td>
<td>2.0</td>
<td>~0</td>
<td>75</td>
<td>0.014 at 80 mV overpotential</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>NiMoN(_x) nanosheets/C</td>
<td>0.25</td>
<td>78</td>
<td>&gt;200</td>
<td>unknown</td>
<td>35.9</td>
<td>11</td>
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<tr>
<td>Mo(_3)C/CNTs</td>
<td>2.0</td>
<td>~0</td>
<td>152</td>
<td>unknown</td>
<td>55</td>
<td>12</td>
</tr>
<tr>
<td>Tungsten Carbonitride</td>
<td>0.4</td>
<td>100</td>
<td>220</td>
<td>unknown</td>
<td>47</td>
<td>13</td>
</tr>
<tr>
<td>C(_3)N(_4)@NG</td>
<td>0.1</td>
<td>~150</td>
<td>240</td>
<td>unknown</td>
<td>51.5</td>
<td>14</td>
</tr>
<tr>
<td>Porous C(_3)N(_4)@N-G films</td>
<td>unknown</td>
<td>8</td>
<td>80</td>
<td>unknown</td>
<td>49.1</td>
<td>15</td>
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<tr>
<td>Co NPs@N-CNTs</td>
<td>0.28</td>
<td>50</td>
<td>260</td>
<td>unknown</td>
<td>69</td>
<td>16</td>
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<tr>
<td>FeCo NPs@N-CNTs</td>
<td>0.32</td>
<td>70</td>
<td>280</td>
<td>unknown</td>
<td>74</td>
<td>16</td>
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<tr>
<td>Fe NPs@single shell carbon</td>
<td>0.18</td>
<td>0</td>
<td>77</td>
<td>unknown</td>
<td>40</td>
<td>17</td>
</tr>
<tr>
<td>CoN(_x)/C</td>
<td>2.0</td>
<td>20</td>
<td>133</td>
<td>0.39/6.5 at 100/200 mV overpotential</td>
<td>57</td>
<td>This work</td>
</tr>
</tbody>
</table>

This work
**Supplementary Table 2.** Summary of HER performance of reported catalysts in alkaline and neutral aqueous solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Catalyst loading (mg cm(^{-2}))</th>
<th>Onset overpotential (mV)</th>
<th>Overpotential at 10 mA cm(^{-2}) (mV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(_2)C</td>
<td>1.0 M KOH</td>
<td>0.8</td>
<td>110</td>
<td>190</td>
<td>18</td>
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<tr>
<td>Ni-Mo nanopowders</td>
<td>1.0 M NaOH</td>
<td>1.0</td>
<td>~0</td>
<td>80</td>
<td>19</td>
</tr>
<tr>
<td>Tungsten Carbonitride</td>
<td>unknown (pH = 13)</td>
<td>0.4</td>
<td>120</td>
<td>250</td>
<td>13</td>
</tr>
<tr>
<td>Co NPs@N-CNTs</td>
<td>1.0 M KOH</td>
<td>0.28</td>
<td>~100</td>
<td>370</td>
<td>16</td>
</tr>
<tr>
<td>Co NPs@N-CNTs</td>
<td>1.0 M PBS (pH = 7)</td>
<td>0.28</td>
<td>~250</td>
<td>540</td>
<td>16</td>
</tr>
<tr>
<td>NiO/Ni-CNT</td>
<td>1.0 M KOH</td>
<td>0.28</td>
<td>~0</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Cu(_2)MoS(_4)</td>
<td>0.1 M PBS (pH = 7)</td>
<td>0.04</td>
<td>~550</td>
<td>~750</td>
<td>21</td>
</tr>
<tr>
<td>Co NPs@N-C</td>
<td>1.0 M KOH</td>
<td>unknown</td>
<td>~50</td>
<td>210</td>
<td>22</td>
</tr>
<tr>
<td>Co(_{N_x})/C</td>
<td>1.0 M KOH</td>
<td>2.0</td>
<td>30</td>
<td>170</td>
<td>This work</td>
</tr>
<tr>
<td>Co(_{N_x})/C</td>
<td>1.0 M PBS (pH = 7)</td>
<td>2.0</td>
<td>30</td>
<td>247</td>
<td>This work</td>
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</tbody>
</table>

**Supplementary Table 3.** Elemental composition measured by XPS and ICP-AES and specific surface area of the CoNPs/Co\(_{N_x}\)/C and Co\(_{N_x}\)/C catalysts.

<table>
<thead>
<tr>
<th>sample</th>
<th>Co-XPS (at%)</th>
<th>Co-ICP (wt%)</th>
<th>N-XPS (at%)</th>
<th>O-XPS (at%)</th>
<th>C-XPS (at%)</th>
<th>S(_{\text{BET}}) (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoNPs/Co(_{N_x})/C</td>
<td>1.16</td>
<td>7.7</td>
<td>2.96</td>
<td>6.7</td>
<td>89.18</td>
<td>745</td>
</tr>
<tr>
<td>Co(_{N_x})/C</td>
<td>ND</td>
<td>0.14</td>
<td>3.86</td>
<td>4.52</td>
<td>91.18</td>
<td>1070</td>
</tr>
</tbody>
</table>

ND, no Co was detected by XPS.
Supplementary Note 1. TOF calculation of the CoNₓ/C catalyst.

To calculate the turnover frequency (TOF) per cobalt site in the CoNₓ/C catalyst, we used the following formula:

\[
\text{TOF} = \frac{\text{# total hydrogen turnover / cm}^2 \text{ geometric area}}{\text{# active sites / cm}^2 \text{ geometric area}} \tag{1}
\]

The total number of hydrogen turn overs was calculated from the current density according to \(^5\,^2^3^1\):

\[
\text{# } \text{H}_2 = \left( \frac{\text{j mA cm}^{-2}}{1000 \text{mA cm}^{-2}} \right) \left( \frac{1 \text{C/s}}{96485.3 \text{C}} \right) \left( \frac{1 \text{mol e}^-}{2 \text{mol e}^-} \right) \left( 6.02 \times 10^{23} \text{ molecules H}_2 \right) = 3.12 \times 10^{15} \frac{\text{H}_2/\text{s}}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2} \tag{2}
\]

The upper limit of the number of active sites was calculated based on the hypothesis that all cobalt atoms in the CoNₓ/C catalyst formed active CoNₓ centers and all of them were accessible to the electrolyte. The real number of active and accessible cobalt sites should be considerably lower than the calculated value. The bulk cobalt content of CoNₓ/C revealed by the ICP-AES measurement was 0.14 wt%. Accordingly, the upper limit of active site density is

\[
\frac{0.14 \text{ mg}}{100 \text{ mg}} \times 2.0 \frac{\text{mg}}{\text{cm}^2} \times \frac{1 \text{ mmol}}{58.93 \text{ mg}} \times 6.022 \times 10^{20} \text{ sites mmol}^{-1} = 2.85 \times 10^{16} \text{ sites cm}^{-2} \tag{3}
\]

Particularly, at an overpotential of 100 mV, the HER current density is 3.57 mA per cm\(^2\), and the TOF value of CoNₓ/C was calculated to be

\[
\text{TOF} = \frac{3.12 \times 10^{15} \frac{\text{H}_2/\text{s}}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2} \times 3.57 \frac{\text{mA}}{\text{cm}^2}}{2.85 \times 10^{16} \text{ sites per cm}^2} = 0.39 \text{ s}^{-1} \tag{4}
\]

Similarly, the TOF value of CoNₓ/C at an overpotential of 200 mV was calculated to be

\[
\text{TOF} = \frac{3.12 \times 10^{15} \frac{\text{H}_2/\text{s}}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2} \times 59.3 \frac{\text{mA}}{\text{cm}^2}}{2.85 \times 10^{16} \text{ sites per cm}^2} = 6.5 \text{ s}^{-1} \tag{5}
\]
Supplementary References


