Supporting Information

**Hollow cobalt phosphate microspheres for sustainable electrochemical ammonia production through rechargeable Zn-N₂ battery**

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1. Experimental Section

1.1. Preparation of electrocatalysts

In a typical synthesis, 3 mmol cobalt nitrate, 0.4 mmol bis(hexamethylene triamine penta (methylene phosphonic acid)) (BHMTMTPMA), and 6 mmol urea were dissolved into the mixture of ethanol and deionized water with the volume ratio of 1:3. Then the obtained solution was transferred into the Teflon-lined autoclave and kept at 140 °C for 24 h. The precipitates were washed with deionized water and dried at 80 °C, which was named as Co-BPA. The prepared Co-BPA was then treated at 900 °C for 2 h in flowing N₂, and the obtained material was named as CoPi/HSNPC.

For the comparison, the cobalt phosphonates with featureless structure were also prepared. Typically, 3 mmol cobalt nitrate, 0.4 mmol BHMTMTPMA were added into deionized water with stirring, and the final pH was adjusted by ammonium hydroxide to about 5. The obtained mixture was transferred into a Teflon-lined autoclave and heated at 140 °C for 24 h. The synthesized products were filtered, washed, dried, and pyrolyzed at 900 °C for 2 h in N₂ atmosphere, and the resultant material was denoted as CoPi/NPC.

To discuss the effect of carbon substrates in CoPi/HSNPC on electrochemical performance, a N,P-dual-doped carbon matrix obtained from the direct pyrolysis of BHMTMTPMA at 900 °C for 2 h in N₂ atmosphere was also fabricated, which was named as NPC.

To investigate the positive effect of phosphate groups on electrochemical reactions, the cobalt oxides were also prepared through hydrothermal treatment process. Typically, 1.2 mmol cobalt nitrate was dissolved in 6 mL ethanol, 75 mmol NaOH was dissolved in 7.5 mL ethanol. Then the former solution was slowly dropped into the latter solution under magnetic stirring, and the resulting solution and 0.3 g hexadecyl trimethyl ammonium bromide (CTAB) were together transferred into a Teflon-lined autoclave at 180 °C for 5 h. The resulting product was collected and washed with ethanol for several times and dried at 80 °C, which was labeled as CoO NPs.

1.2. Materials characterization

Scanning electron microscopy (SEM) and transition electron microscopy (TEM) were carried out on the Jeol JSM-7800F and Jeol JEM-2800 instruments, respectively. X-ray diffraction (XRD) patterns were measured on a Bruker D8 Focus diffractometer with Cu Ka radiation. Raman spectra were measured on a Thermo-Fisher Scientific DXR spectrometer. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker VECTOR 22 spectrometer with the KBr pellet technique. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCALAB 250Xi spectrometer equipped with a monochromatic Al Ka X-ray source (1486.6 eV). Thermogravimetry analysis (TGA) was performed using a TA SDT Q600 instrument. The Brunauer–Emmett–Teller (BET) specific surface area was obtained by N₂ adsorption–desorption analysis on a Quantachrome Nova 2000e sorption analyzer at liquid temperature. The UV–vis absorbance spectroscopy was measured on a UV–vis spectrophotometer (Kenfan KU-T1810). The in-situ FTIR spectroscopic data of
electrocatalytic reaction were collected on the electrochemical *in-situ* Fourier transform infrared spectrooscope (Nicolet Nexus 870). The ¹H NMR (nuclear magnetic resonance) spectra were obtained using superconducting Fourier transform nuclear magnetic resonance spectrometer (Bruker Avance-600).

1.3. Electrochemical measurements

The NRR performance tests were carried out on the CHI 760E electrochemical station using a three-electrode system with an H-type cell and Nafion 117 membrane as separator. Before NRR electrolysis, the Nafion membrane was first squeezed in ultrapure water at 80 °C for 1 h, followed by immersion in H₂O₂ (5%) solution at 80 °C for another 1 h. Then, the membrane was protonated in 0.5 M H₂SO₄ at 80 °C for 1 h and finally washed by ultrapure water for 2 h. The Ag/AgCl and Pt wire were used as the reference and counter electrodes, respectively, and the catalyst film coated carbon paper was employed as the working electrode. To prepare the working electrode, typically, 5 mg catalysts and 20 μL Nafion (5 wt%) were added into the mixture of isopropanol and deionized water (v:v = 3:1) followed by sonication. Subsequently, certain amount of the homogeneous catalyst ink was drop-coated onto the clean carbon paper, dried in air to prepare the working electrode. The measured potential (vs. Ag/AgCl) in this work was normalized to reversible hydrogen electrode (vs. RHE) according to Nernst equation.

Prior to NRR measurement, all samples were immersed into and washed with 0.1 M KOH solution three times to exclude any NH₃ or NH₄⁺ contaminant. The high-pure N₂ gas and Ar gas were purified by flowing them through 0.1 M KOH solution to remove any N contamination in the flowing gases before entering the electrolyte. Before data collection, the electrolyte was pre-saturated with high-purity N₂ for 30 min, and the working electrode were activated by steady-state potential sweeping cycles in the range of 0.15 to −0.65 V (vs. RHE) at 50 mV·s⁻¹ in an N₂-saturated 0.1 M KOH solution for 20 cycles. For NRR tests, a potentiostatic test was conducted for 2 h in an N₂-saturated 0.1 M KOH solution under atmospheric pressure and constant temperature. High-pure N₂ was continuously purged in the cathode compartment under a constant flow rate. Corresponding tests in an Ar-saturated 0.1 M KOH solution were also conducted as control experiments. Linear sweep voltammetry (LSV) was performed at 2 mV·s⁻¹ in a 0.1 M KOH solution between 0.1 and −0.5 V (vs. RHE). All polarization curves were obtained without current resistance (iR) compensation.

For OER measurement, the anodic linear sweep voltammetry (LSV) was collected in O₂-saturated 1.0 M KOH with the scan rate of 2 mV s⁻¹. All polarization curves were presented with current resistance (iR) compensation.

Zn-N₂ battery test, the rechargeable Zn-N₂ battery experiment was measured with home-made Zn-N₂ configuration with H-cell arrangement separated by the Nafion 117 membrane to avoid destroying anodic or cathodic products. The prepared samples were directly used as cathodic electrode, and the Zn plate was used as the anodic electrode. Both electrodes were immersed into 1.0 M KOH, and the catholyte was bubbled with N₂.
continuously. The cycling measurements was carried out for 4 h per cycle (2 h discharge and 2 h charge) under certain current density. After each discharging process during cycling test, the catholyte was replaced by the fresh KOH electrolyte to extract N₂ reduction products.

1.4. Detection of ammonia and hydrazine

The concentration of produced ammonia was determined by the indophenol blue method using UV-Vis spectrophotometry. Prior to detection of ammonia, several reagent were prepared. Chromogenic reagent A: 5 wt% salicylic acid and 5 wt% sodium citrate was added into 1 M NaOH. Oxidizing solution B: 0.05 M sodium hypochlorite. Catalyzing reagent C: 1 wt% sodium nitroferricyanide. In detail, 2 mL of standard solutions or sample solutions from the post-electrolysis electrolyte were mixed with 2 mL of chromogenic reagent A, 1 mL of oxidizing solution B and then with 0.2 mL of catalyzing reagent C. After shaking and standing for 2 h, the absorption spectrum of the resulting solution was measured using a UV-Vis spectrophotometer in the wavelength range 500 to 800 nm. And the absorbance at the wavelength of 656 nm was recorded. And the background was corrected with a blank solution. The standard curve was calibrated using standard NH₄Cl solution with a series of concentrations in 0.1 KOH.

The probable byproduct N₂H₄ in the cathode compartment during the NRR reaction was also estimated using the Watt and Chrisp method. The color reagent was prepared by mixing of HCl (37 wt%, 30 mL), ethanol (300 mL), and para-(dimethylamino) benzaldehyde (5.99 g). The 2 mL of above prepared color reagent was added into 2 mL aliquot of the reaction solution at room temperature. The absorbance of the resulting solution was measured at 455 nm.

1.5. Calculation of ammonia yield rate and Faradaic efficiency

The yield rate of NH₃ (υₐₙ₃) was calculated using the following equation:

\[ \nu_{\text{NH}_3} = \left( C_{\text{NH}_3} \times V \right) / \left( t \times m_{\text{cat}} \right) \]

The Faradaic efficiency (FE) for NRR was defined as the proportion of the electric charges used for synthesizing NH₃ among the total charges passing through the electrodes during NRR electrolysis. Assuming three electrons were needed to produce one NH₃ molecule, the FE could be calculated as follows:

\[ \text{FE} = \frac{3F \times C_{\text{NH}_3} \times V}{17 \times Q} \]

where \( C_{\text{NH}_3} \) is the ammonia concentration measured by the indophenol method (μg mL⁻¹); \( V \) (mL) is the volume of the reaction electrolyte after NRR; \( t \) is the electro-reduction reaction time (h); \( m_{\text{cat}} \) is the effective weight of the catalyst on the working electrode (mg). \( F \) is the Faraday constant; \( Q \) is the quantity of applied electricity.
2. Supplementary Figures

**Fig. S1** Molecule structure of BHMTPMPA.

**Fig. S2** XRD pattern of as-prepared Co-BPA.

**Fig. S3** (a, b) SEM and (c) TEM images and (d) SAED pattern of Co-BPA. (e-g) STEM image and corresponding line-scan TEM-EDS elemental distribution curves of Co-BPA. (h) EDS elemental mapping of Co-BPA.
Fig. S4 FT-IR spectrum of CoPi/HSNPC

Fig. S5 (a) XRD pattern, (b) SEM and (c, d) TEM images of CoPi/NPC.

Fig. S6 (a) XRD pattern, (b) N₂ adsorption-desorption isotherms, and (c, d) TEM images of CoO NPs sample.
Fig. S7 Raman spectrum of CoPi/HSNPC.

![Raman spectrum of CoPi/HSNPC](image)

Fig. S8 TGA curves of CoPi/HSNPC measured in flowing air.

![TGA curve](image)

Fig. S9 (a) and (b) SEM images of as-prepared NPC.

![SEM images of NPC](image)
Fig. S10 The three-electrode electrocatalytic system in this work for NRR.

Fig. S11 Polarization curves of CoPi/HSNPC in N₂- and Ar-saturated 0.1 M KOH.

Fig. S12 UV-Vis absorption spectra (a) and calibration curves (b) for NH₄⁺ in 0.1 M KOH by indophenol blue method. The standard curve was calibrated using standard NH₄Cl solution with a series of concentrations from 0 to 2.5 μg in 0.1 KOH. The fitted curves obtained a good linear relation of absorbance with NH₄⁺ concentration, \( y = 0.42082x + 0.00315 \), \( R^2 = 0.999 \).
Fig. S13 Chronoamperometry curves and the UV−vis absorption spectra of electrolyte after electrolyzation in N₂-saturated at varied potentials by indophenol blue method for CoPi/HSNPC (a, b), CoPi/NPC (c, d), CoO NPs (e, f), and NPC (g, h). The inset is the photograph of electrolyte treated using the indophenol blue method.

Fig. S14 EIS of CoPi/HSNPC at different cathodic potentials in 0.1 M KOH.

Fig. S15 UV-Vis absorption spectra of the electrolyte after electrolyzation in N₂-saturated at -0.2 V vs. RHE for CoPi/HSNPC sample and the fresh KOH electrolyte containing N₂H₄ by the Watt-Chrisp method.
Fig. S16 UV-Vis absorption spectra (a) and calibration curves (b) for NH$_4^+$ in 1.0 M KOH by indophenol blue method. The fitted curves obtained a good linear relation of absorbance with NH$_4^+$ concentration, $y = 0.4127x + 0.0063$, $R^2 = 0.999$.

Fig. S17 (a) Chronoamperometry curves and (b) UV−vis absorption spectra of electrolyte after electrolyzation in N$_2$-saturated 1.0 M KOH at varied potentials by indophenol blue method for CoPi/HSNPC. (c) NH$_3$ yield rate and Faradaic efficiency of CoPi/HSNPC at varied potentials in 1.0 M KOH. (d) LSV curves of CoPi/HSNPC in 0.1 M and 1.0 M KOH.

Fig. S18 XRD patterns of CoPi/HSNPC before and after NRR recycling tests.
Fig. S19 (a, b) SEM and (c, d) TEM images of CoPi/HSNPC after NRR recycling tests.

Fig. S20 (a) UV-Vis spectra of the electrolyte stained with indophenol indicator before and after 2 h electrolysis for CoPi/HSNPC at the potential of -0.2 V vs. RHE under different electrochemical conditions. (b) NMR analysis of the reacted solution by feeding $^{15}\text{N}_2$ gas after NRR electrolysis.

Fig. S21 (a) XPS survey scan and (d) element content of CoPi/HSNPC catalyst before and after NRR tests.
Fig. S22 CV curves of CoPi/HSNPC (a), CoPi/NPC (b), CoO NPs (c), and NPC (d) under the scan rates from 10 to 20 mV s\(^{-1}\). (e) Plots of the current density as a function against the corresponding scan rates of these samples.

Fig. S23 Nyquist plots of CoPi/HSNPC, CoPi/NPC, CoO NPs, and NPC in 1.0 M KOH. Inset is the corresponding equivalent circuit diagram consisting of an electrolyte resistance \((R_s)\), a charge-transfer resistance \((R_{ct})\), and a constant-phase element (CPE).

Fig. S24 Electrochemical in situ-FTIR spectroscopy of the NRR on CoPi/HSNPC and CoO NPs.
Fig. S25 Typical photograph of this home-made Zn-N₂ battery.

Fig. S26 Galvanostatic discharge curve of CoPi/HSNPC catalyzed Zn-N₂ battery. The energy density (mWh g⁻¹) is calculated according to the equation of \((\text{current} \times \text{service hours} \times \text{average discharge voltage}) / (\text{weight of consumed zinc})\).

Fig. S27 (a) Discharge polarization curves of CoPi/HSNPC-catalyzed battery with different feeding gas. (b) Oxygen reduction reaction polarization curves of CoPi/HSNPC catalysts measured in 0.1 M O₂-saturated 0.1 M KOH with the rotation speed of 1600 rpm.
Fig. S28 (a) Galvanostatic discharge curves of CoPi/HSNPC-catalyzed battery under different voltages in N$_2$-saturated 1.0 M KOH. (b) UV–vis absorption spectra of electrolyte after electrolyzation in N$_2$-saturated at varied voltages for CoPi/HSNPC-catalyzed battery by indophenol blue method.

Fig. S29 UV-Vis absorption spectra of electrolyte after electrolyzation in N$_2$-saturated at 0.6 V vs. Zn$^{2+}$/Zn by the Watt-Chrisp method for CoPi/HSNPC-catalyzed battery.

Fig. S30 (a) Galvanostatic discharge curves of CoPi/HSNPC-catalyzed battery under different voltages in N$_2$-saturated 0.1 M KOH. (b) Charge-discharge polarization curves and the corresponding power density curves of CoPi/HSNPC-catalyzed battery with different electrolyte. Inset is the voltage gap at the current density of 1.0 mA
cm$^{-2}$. (c) UV–vis absorption spectra of electrolyte after electrolyzation in N$_2$-saturated at varied voltages for CoPi/HSNPC-catalyzed battery by indophenol blue method. (d) NH$_3$ yield rate and Faradaic efficiency of CoPi/HSNPC at varied potentials in 0.1 M KOH.

**Fig. S31** High-resolution XPS spectra of N 1s (a), and P 2p (b) region of CoPi/HSNPC before and after Zn-N$_2$ battery cycling tests.

**Fig. S32** (a, b) SEM images of CoPi/HSNPC after Zn-N$_2$ battery cycling tests.
3. Supplementary Tables

**Tables S1.** Summary of the NRR performance of recent reported Co-based and other nonprecious electrocatalysts in alkaline conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH$_3$ yield rate</th>
<th>Faradaic efficiency (%)</th>
<th>Potential</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CoPi/HSNPC</strong></td>
<td>0.1 M KOH</td>
<td>16.48 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>4.46</td>
<td>-0.2 V vs. RHE</td>
<td>This work.</td>
</tr>
<tr>
<td><strong>CoP hollow nanocage</strong></td>
<td>1.0 M KOH</td>
<td>10.78 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>7.36</td>
<td>-0.4 V vs. RHE</td>
<td>[1]</td>
</tr>
<tr>
<td><strong>Fe-N/C-CNTs</strong></td>
<td>0.1 M KOH</td>
<td>34.83 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>9.28</td>
<td>-0.2 V vs. RHE</td>
<td>[2]</td>
</tr>
<tr>
<td><strong>Pd$<em>{0.8}$Cu$</em>{0.2}$/rGO</strong></td>
<td>0.1 M KOH</td>
<td>2.8 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>-4.5</td>
<td>-0.2 V vs. RHE</td>
<td>[3]</td>
</tr>
<tr>
<td><strong>B/N-CN</strong></td>
<td>0.1 M KOH</td>
<td>20.0 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>13.2</td>
<td>-0.5 V vs. RHE</td>
<td>[4]</td>
</tr>
<tr>
<td><strong>γ-Fe$_2$O$_3$ nanoparticles-CNT</strong></td>
<td>0.1 M KOH</td>
<td>0.2 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>1.9</td>
<td>-1.0 V vs. Ag/AgCl</td>
<td>[5]</td>
</tr>
<tr>
<td><strong>ZIF-derived carbon</strong></td>
<td>0.1 M KOH</td>
<td>57.8 µg h$^{-1}$ cm$^{-2}$</td>
<td>10.2</td>
<td>-0.3 V vs. RHE</td>
<td>[6]</td>
</tr>
<tr>
<td><strong>W$_2$N$_3$</strong></td>
<td>0.1 M KOH</td>
<td>11.7 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>11.7</td>
<td>-0.2 V vs. RHE</td>
<td>[7]</td>
</tr>
<tr>
<td><strong>Eex-COF/NC</strong></td>
<td>0.1 M KOH</td>
<td>12.5 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>45.4</td>
<td>-0.2 V vs. RHE</td>
<td>[8]</td>
</tr>
<tr>
<td><strong>Fe-N/C-CNTs</strong></td>
<td>0.1 M KOH</td>
<td>34.8 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>9.3</td>
<td>-0.2 V vs. RHE</td>
<td>[9]</td>
</tr>
<tr>
<td><strong>Fe$_3$O$_5$/CNT</strong></td>
<td>0.5 M KOH</td>
<td>0.26 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>0.164</td>
<td>-2.0 V vs. Ag/AgCl</td>
<td>[10]</td>
</tr>
<tr>
<td><strong>Single-atom-Mo/N-doped porous carbon</strong></td>
<td>0.1 M KOH</td>
<td>34.0 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>14.6</td>
<td>-0.3 V vs. RHE</td>
<td>[11]</td>
</tr>
<tr>
<td><strong>Zr-doped TiO$_2$</strong></td>
<td>0.1 M KOH</td>
<td>8.9 µg h$^{-1}$ cm$^{-2}$</td>
<td>17.3</td>
<td>-0.45 V vs. RHE</td>
<td>[12]</td>
</tr>
<tr>
<td><strong>Co3Fe-MOF</strong></td>
<td>0.1 M KOH</td>
<td>8.79 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>25.64</td>
<td>-0.2 V vs. RHE</td>
<td>[13]</td>
</tr>
<tr>
<td><strong>FeS@MoS$_2$/CFC</strong></td>
<td>0.1 M KOH</td>
<td>2.46 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>0.067</td>
<td>-0.5 V vs RHE</td>
<td>[14]</td>
</tr>
<tr>
<td><strong>Fe$_8$@N-C</strong></td>
<td>0.1 M KOH</td>
<td>7.48 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>56.55</td>
<td>0 V vs. RHE</td>
<td>[15]</td>
</tr>
<tr>
<td><strong>K$_2$TiO$_3$ nanobel</strong></td>
<td>0.1 M KOH</td>
<td>22.8 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>5.9</td>
<td>-0.5 V vs. RHE</td>
<td>[16]</td>
</tr>
<tr>
<td><strong>PdO/Pd/CNTs</strong></td>
<td>0.1 M NaOH</td>
<td>18.2 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>11.5</td>
<td>0.1 V vs. RHE</td>
<td>[17]</td>
</tr>
<tr>
<td><strong>Pd–Co/CuO</strong></td>
<td>0.1 M KOH</td>
<td>10.0 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>2.2</td>
<td>-0.2 V vs. RHE</td>
<td>[18]</td>
</tr>
<tr>
<td><strong>Rh nanosheet</strong></td>
<td>0.1 M KOH</td>
<td>23.88 µg h$^{-1}$ mg$^{-1}$ cat.</td>
<td>0.2</td>
<td>-0.2 V vs. RHE</td>
<td>[19]</td>
</tr>
</tbody>
</table>
Table S2. The comparison of OER performance of as-prepared CoPi/HSNPC and some active nonprecious OER electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Overpotential (mV) @ 10 mA cm(^{-2})</th>
<th>Tafel slope (mV dev(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoPi/HSNPC</td>
<td>1.0 M KOH</td>
<td>341</td>
<td>82</td>
<td>This work.</td>
</tr>
<tr>
<td>CoO(_x)-4h nanoplates</td>
<td>1.0 M KOH</td>
<td>306</td>
<td>67</td>
<td>[20]</td>
</tr>
<tr>
<td>Co(_{3})O(_4)</td>
<td>1.0 M KOH</td>
<td>268</td>
<td>38.2</td>
<td>[21]</td>
</tr>
<tr>
<td>Fe1Co1-ONS</td>
<td>0.1 M KOH</td>
<td>308</td>
<td>36.8</td>
<td>[22]</td>
</tr>
<tr>
<td>CoO/C-500</td>
<td>1.0 M KOH</td>
<td>200</td>
<td>59.5</td>
<td>[23]</td>
</tr>
<tr>
<td>Co(_2)(OH)(_2)BDC nanosheets</td>
<td>1.0 M KOH</td>
<td>263</td>
<td>74</td>
<td>[24]</td>
</tr>
<tr>
<td>Fe-incorporated Co(_x)S(_y)</td>
<td>1.0 M KOH</td>
<td>304</td>
<td>54.2</td>
<td>[25]</td>
</tr>
<tr>
<td>CoO-L</td>
<td>1.0 M KOH</td>
<td>369</td>
<td>46</td>
<td>[26]</td>
</tr>
<tr>
<td>CoFe(_2)O(_4) nanorods</td>
<td>1.0 M KOH</td>
<td>355</td>
<td>96</td>
<td>[27]</td>
</tr>
<tr>
<td>Hierarchical Mn-Co phosphide yolk-shell spheres</td>
<td>1.0 M KOH</td>
<td>330</td>
<td>59</td>
<td>[28]</td>
</tr>
<tr>
<td>Zn-CoSe(_2) NAs</td>
<td>1.0 M KOH</td>
<td>286</td>
<td>37</td>
<td>[29]</td>
</tr>
<tr>
<td>Fe-CoP/CoO</td>
<td>1.0 M KOH</td>
<td>219</td>
<td>52</td>
<td>[30]</td>
</tr>
<tr>
<td>Co(_3)O(_4)/CoO</td>
<td>1.0 M KOH</td>
<td>302</td>
<td>68.6</td>
<td>[31]</td>
</tr>
<tr>
<td>CoO(_4)(Ce)</td>
<td>1.0 M KOH</td>
<td>229</td>
<td>63.7</td>
<td>[32]</td>
</tr>
<tr>
<td>NiMoP@CoCH/CC</td>
<td>1.0 M KOH</td>
<td>267 @40 mA cm(^{-2})</td>
<td>99</td>
<td>[33]</td>
</tr>
<tr>
<td>Fe-CoO</td>
<td>1.0 M KOH</td>
<td>304</td>
<td>38</td>
<td>[34]</td>
</tr>
<tr>
<td>Co@NPC-H</td>
<td>1.0 M KOH</td>
<td>350</td>
<td>57</td>
<td>[35]</td>
</tr>
</tbody>
</table>

Tables S3. Summary of the NRR performance of recent reported Zn-N\(_2\) battery.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Peak power density</th>
<th>Voltage (V vs Zn(^{2+}/Zn)) @ highest NH(_3) yield rate</th>
<th>NH(_3) yield rate</th>
<th>Faradaic efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoPi/HSNPC</td>
<td>1.0 M KOH</td>
<td>0.33 mW cm(^{-2})</td>
<td>0.6</td>
<td>11.58</td>
<td>24.39%</td>
<td>This work.</td>
</tr>
<tr>
<td>nano-Cu</td>
<td>0.1 M KOH</td>
<td>10.1 μW cm(^{-2})</td>
<td>~0.925</td>
<td>~0.125 μg h(^{-1}) cm(^{-2})</td>
<td>~59%</td>
<td>[36]</td>
</tr>
<tr>
<td>exfoliated NbS(_2) nanosheets</td>
<td>N.A.</td>
<td>0.31 mW cm(^{-2})</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>[37]</td>
</tr>
<tr>
<td>VN@NSC-900</td>
<td>0.1 M KOH</td>
<td>16.42 μW cm(^{-2})</td>
<td>~0.525</td>
<td>0.172 μg h(^{-1}) cm(^{-2})</td>
<td>~12%</td>
<td>[38]</td>
</tr>
</tbody>
</table>
4. Supplementary References


nanoparticles embedded carbon nanocages as bifunctional electrocatalysts for oxygen evolution and reduction, Carbon 144 (2019) 492-499.

