Supporting Information

Open Hollow Co-Pt clusters Embedded in Carbon Nanoflake Arrays for Highly Efficient Alkaline Water Splitting

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Schem. S1. Schematic illustration of the synthesis of Co-Pt/C nanoflake arrays grown on carbon cloth.
Fig. S1. XRD pattern and SEM images of Co-MOFs.
Fig. S2. SEM images and TEM images of Co/C (a-d), Co-Pt/C-5 (e-h) and Co-Pt/C-10 (i-l).

Fig. S3. (a-c) HRTEM image and the associated fast Fourier transform (FFT) images of Co-Pt/C-5. HRTEM image of (d) Co/C and (e) Co-Pt/C-10.
The HRTEM images and the associated fast Fourier transform (FFT) clearly show that the Co(111) plane with the interplanar distances of 0.203 nm and Pt(111) plane with the interplanar distances of 0.226 nm co-exist in Co-Pt/C-5 and Co-Pt/C-10, but only the Co(111) plane can be observed in Co/C, which confirms that the Co nanoparticles turned into the Co-Pt bimetallic open hollow clusters embedding in carbon after the replacement reaction.

Fig. S4. SEM images and STEM images of Co-Pt/C-20.
Fig. S5 High-resolution Pt 4f XPS spectra of Co-Pt/C-10.

Fig. S6. LSV curves of Co-Pt/C-5, Co-Pt/C-10, Co-Pt/C-20 for (a) HER and (b) OER.
Fig. S7. (a) Stability test curves at -0.2 V for HER in an N$_2$-saturated 1 M KOH solution. (b) Nyquist plots for HER in an N$_2$-saturated 1 M KOH solution.

Table S1. Series resistance and charge transfer resistance from Nyquist plots for HER.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Co/C</th>
<th>Co-Pt/C-5</th>
<th>Co-Pt/C-10</th>
<th>Pt/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series resistance</td>
<td>1.71</td>
<td>1.52</td>
<td>1.38</td>
<td>1.40</td>
</tr>
<tr>
<td>Charge transfer resistance</td>
<td>5.01</td>
<td>4.98</td>
<td>3.50</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Fig. S8. Comparison of HER performances of some typical Co based and MOF derived electrocatalysts in alkaline electrolyte.

Sources:
Fe-CoP/Ti NA: Fe-doped CoP nanoarray on Ti foil $^1$
NiCo$_2$S$_4$/Ni NA: NiCo$_2$S$_4$ nanowire array supported on Ni foam $^2$
Co–Ni–B$^{[3]}$
Co NPs-NC: Co nanoparticles embedded in N-rich carbon
CoO$_x$@CN: Cobalt Oxide/nitrogen-doped Carbon Hybrids
CoP$_x$-NC: MOF derived CoP$_x$ NPs embedded in nitrogen-doped carbon matrices
Ni$_{0.33}$Co$_{0.67}$S$_2$: Ni$_{0.33}$Co$_{0.67}$S$_2$ nanowires
Co-NG: Atomic cobalt on nitrogenitrogen-doped graphene
CoN$_x$/C: Molecular Co–N$_x$ centres in porous carbon
Co(OH)$_2$/Pt(111)
c-CoSe/CC: cubic phase CoSe$_2$ on carbon cloth
Pt$_3$Ni$_2$ NWs-S/C: Pt-Ni sulfide interface nanowires
MoC$_x$: MoC$_x$ nano-octahedrons derived by MOF
NiO/Ni-CNT: nickel oxide/nickel heterostructures on carbon nanotube

Fig. S9. (a) Curves of stability test at 1.6 V for OER in an O$_2$-saturated 1 M KOH solution. (b) Nyquist plots for OER in an O$_2$-saturated 1 M KOH solution.

Table S2. Series resistance and charge transfer resistance from Nyquist plots for OER.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Co/C</th>
<th>Co-Pt/C-5</th>
<th>Co-Pt/C-10</th>
<th>Pt/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series resistance</td>
<td>1.95</td>
<td>1.84</td>
<td>1.61</td>
<td>2.73</td>
</tr>
<tr>
<td>Charge transfer resistance</td>
<td>17.8</td>
<td>7.01</td>
<td>5.60</td>
<td>5.34</td>
</tr>
</tbody>
</table>
Fig. S10. CV curves at scan rates from 1 mV/s to 5mV/s, where no redox peaks are observed in this voltage range, and plots of electrochemical double-layer capacitance.
Fig. S11. Comparison of OER performances of some typical Co based and MOF derived electrocatalysts.

Sources:
NiCo$_2$O$_4$ HNAs: NiCo$_2$O$_4$ hollow nanoarray$^{15}$
Co NPs-NC: Co NPs embedded in porous N-rich carbon$^{4}$
Co/Fe-NC: Spindle-like Co/Fe metal oxides in nitrogen-doped porous carbon$^{16}$
Co$_3$O$_4$-C NAs: Co$_3$O$_4$-C nanoarray$^{17}$
CoP/rGO-L: layered CoP/rGO composite$^{18}$
Co@Co$_3$O$_4$-CNT-NC: Co@Co$_3$O$_4$ encapsulated in CNT grafted nitrogen-doped carbon polyhedral$^{19}$
MOF-NCNT: MOF derived nitrogen-doped carbon nanotube$^{20}$
Co$_3$O$_4$/NiCo$_2$O$_4$ DSNCs: Co$_3$O$_4$/NiCo$_2$O$_4$ double-shelled nanocages$^{21}$
Ni$_2$Co$_{3-x}$O$_4$ NWAs: Ni$_2$Co$_{3-x}$O$_4$ nanowire array$^{22}$
Ni-Co CB: Ni-Co cubes$^{23}$
CoCo-LDH: CoCo layered double hydroxides$^{24}$
CoFe$_2$O$_4$$^{2}$
Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$$^{26}$
CoMoO$_4$ PF: CoMoO$_4$ porous flowers$^{27}$
Fig. S12. XRD patterns of Co-Pt/C-10 after the stability test of HER and OER, respectively.

Fig. S13. High-resolution (a) Co 2p and (b) Pt 4f XPS spectra of Co-Pt/C-10 after HER stability test.
Fig. S14. High-resolution (a) Co 2p and (b) Pt 4f XPS spectra of Co-Pt/C-10 after OER stability test.

Supplementary References: