Electronic Supplementary Information

Accelerating the oxygen evolution reaction kinetics of Co$_3$O$_4$ in neutral electrolyte by decorating RuO$_2$

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Experimental Section

Synthesis of CCH and Ruₓ-CCH
Nickel foam (NF) (2×3 cm²) was first rinsed in 3 M hydrochloric acid for 10 min and then sonicated in ethanol and deionized water for 10 min in succession. In a typical process for the synthesis of cobalt carbonate hydroxide (CCH) nanorod arrays, 5 mmol of Co(NO₃)₂ and 25 mmol of urea were first dissolved in 40 ml of deionized water and the solution was transferred into a 50 ml Teflon-lined stainless-steel reactor. Then, the NF was put into the autoclave and the autoclave was subsequently put into the oven and heated at 90 °C for 7 h. After the hydrothermal reaction is finished, the sample is taken out and washed and dried for use. The synthesis of Ruₓ-CCH is similar to that of CCH except adding 0.05, 0.15, and 0.25 mmol of RuCl₃. The samples obtained with addition of 0.05, 0.15, and 0.25 mmol of RuCl₃ were named as Ru₁-CCH, Ru-CCH, and Ru₂-CCH, respectively.

Synthesis of Co₃O₄, RuO₂/Co₃O₄₋₁, RuO₂/Co₃O₄, and RuO₂/Co₃O₄₋₂
The as-synthesized CCH and Ruₓ-CCH were put in a muffle furnace and heated at 350 °C in air for 3 h at a heating rate of 5 °C per minute. The corresponding metal oxides named as Co₃O₄, RuO₂/Co₃O₄₋₁, RuO₂/Co₃O₄, and RuO₂/Co₃O₄₋₂ were obtained by calcination of CCH, Ru₁-CCH, Ru-CCH, and Ru₂-CCH, respectively. The loading of catalysts on the surface of Ni foam were calculated by weighting the mass change of Ni foam before and after catalysts growth. The loading of Co₃O₄, RuO₂/Co₃O₄₋₁, RuO₂/Co₃O₄, and RuO₂/Co₃O₄₋₂ is around 1200 μg cm⁻². The loading of RuO₂ was then calculated by XPS analysis and was determined to be 54, 146, and 228 μg cm⁻² for RuO₂/Co₃O₄₋₁, RuO₂/Co₃O₄, and RuO₂/Co₃O₄₋₂, respectively.

Material Characterizations
X-ray diffraction (XRD) data were measured by the X-ray diffractometer (DX-2700). The morphology of the sample was observed with Hitachi S4800 scanning electron microscope (SEM). Raman spectra were collected on a Via-Reflex Raman microscope equipped with a 532 nm laser. A FEI tecnai G2F20 S-Twin instrument was used to obtain the transmission electron microscope (TEM) image, elemental mapping images and the electron diffraction pattern of the selected area. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed on ESCALAB-MKII spectrometer (VG Company, UK). The work function of the material is calculated according to the positions of the secondary electron cut-off edge and the Fermi edge of the UPS spectrum. E_Fermi is the abscissa value corresponding to the intersection of the tangent line of the Fermi edge and the baseline, and E_Cutoff corresponds to the abscissa value of the midpoint of the secondary electron cut-off edge curve.¹² The work function can be estimated according to the following formula:³:

\[
hv - \Phi = E_{\text{Fermi}} - E_{\text{Cutoff}}
\]

\[
\Phi = hv + E_{\text{Cutoff}} - E_{\text{Fermi}}
\]

Where hv is the known excitation energy and Φ represents work function.

Electrochemical characterizations
Electrochemical tests were carried out on CHI electrochemical workstation and
Biologic multi-channel potentiostat. Under the standard three-electrode system, the NF with the growth of catalysts (geometric area: 0.5 cm$^2$) was used as the working electrode, the carbon rod was used as counter electrode, and Ag/AgCl was employed as reference electrode. 1 M phosphate buffer solution (PBS) with a pH of 7 was used as the electrolyte. Before the OER performance test, dozens of voltammetry cycles were carried out or $i-t$ test at 10 mA cm$^{-2}$ on the sample until the performance of the material was stable. The range of the voltammetry cycles was 1.1-1.9 V vs. RHE at a scan rate of 50 mV s$^{-1}$. The linear sweep voltammetry curves were tested in the range of 1.1-1.9 V vs. RHE at a scan speed of 5 mV s$^{-1}$. All the LSV curves were $iR$ corrected. 85% $iR$ correction was applied manually to all the as-recorded LSV curves based on the resistance ($R_{OCP}$) at open circuit potential. $0.85 \times i \times R_{OCP}$ was subtracted from the recorded voltage values in the LSV to apply the correction. Conversion relationship between reversible hydrogen electrode and Ag/AgCl electrode is as follows:

$$E_{RHE} = E_{exp} + E_{Ag/AgCl} + 0.059 \times pH$$

Faraday efficiency was calculated by the rotating ring disk electrode (RRDE) test. The RRDE is composed of glassy carbon disk and Pt ring. The catalysts were peeled off from the surface of Ni foam by sonication. Then, 5 mg of the catalysts powders were dispersed into a mixed solution containing 270 μL of ethanol, 200 μL of water, and 30 μL of Nafion solution (5wt%). 2.5 μL of the as-obtained ink was dropped onto the disk electrode. The RRDE ring potential was maintained at 0 V vs. RHE to reduce the O$_2$ produced by the catalyst on the disk electrode. The Faraday efficiency ($\varepsilon$) is calculated according to the following equation:

$$\varepsilon = I_c/(I_d N)$$

Where $I_d$, $I_c$ and $N$ represents the RRDE disk current, ring current and current collection efficiency (here is 0.424), respectively.

Methods of DFT calculations

We have employed the first-principles to perform density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation. We have chosen the projected augmented wave (PAW) potentials to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The 3$\times$3$\times$1 $k$-points has been chosen, and the electronic energy was considered self-consistent when the energy change was smaller than 10$^{-6}$ eV. A geometry optimization was considered convergent when the energy change was smaller than 0.05 eV Å$^{-1}$. In addition, for the Co atoms, the $U$ schemes need to be applied, and the $U$ has been set as 3.1 eV. The spin correction has been employed to describe the electronic properties. The reaction free energies were calculated using the equation:

$$G = E + ZPE - TS$$
Where $G$, $E$, $ZPE$ and $TS$ are the free energy, total energy from DFT calculations, zero-point energy, and entropic contributions, respectively.

**Fig. S1** Adsorption configuration of (a) OH*, (b) O*, and (c) OOH* on CoOOH. The blue, red, and white balls represent Co, O, and H atoms, respectively.

**Fig. S2** Adsorption configuration of (a) OH*, (b) O*, and (c) OOH* on Co site of RuO$_2$/CoOOH; Adsorption configuration of (d) OH*, (e) O*, and (f) OOH* on Ru site of RuO$_2$/CoOOH. The blue, gray, red, and white balls represent Co, Ru, O, and H atoms, respectively.
**Fig. S3** (a,b) XRD patterns and (b,c,e,f) SEM images of CCH (a,b,c) and Ru-CCH (d,e,f).

**Fig. S4** (a) SEM image and (b-e) corresponding EDX elemental mapping images of CCH.
**Fig. S5** (a) SEM image and (b-f) corresponding EDX elemental mapping images of Ru-CCH.

**Fig. S6** (a,b) Large-scale SEM images and (c,d) XRD patterns of Co$_3$O$_4$ (a,c) and RuO$_2$/Co$_3$O$_4$ (b,d) nanorod arrays.
Fig. S7 HRTEM image of RuO$_2$/Co$_3$O$_4$ nanorod.

Fig. S8 Raman spectra of Co$_3$O$_4$ and RuO$_2$/Co$_3$O$_4$ nanorod arrays.

Fig. S9 I-t curve of RuO$_2$/Co$_3$O$_4$ nanorod arrays at 10 mA cm$^{-2}$ before LSV test.
Fig. S10 (a,b) CV curves at different scanning rates in the non-Faraday region and (c,d) plots for $C_{dl}$ calculation of $\text{Co}_3\text{O}_4$ and $\text{RuO}_2/\text{Co}_3\text{O}_4$ nanorod arrays.

Fig. S11 (a) XRD pattern and (b,c) SEM images of $\text{RuO}_2/\text{Co}_3\text{O}_4$-1 nanorod arrays.

Fig. S12 (a) XRD pattern and (b,c) SEM images of $\text{RuO}_2/\text{Co}_3\text{O}_4$-2 nanorod arrays.
Fig. S13 (a) LSV curves, (b) Tafel plots, and (c) Nyquist plots of Co₃O₄, RuO₂/Co₃O₄-1, RuO₂/Co₃O₄, and RuO₂/Co₃O₄-2 nanorod arrays in 1 M PBS; (d) Overpotentials at 10 mA cm⁻² and Tafel slopes of Co₃O₄, RuO₂/Co₃O₄-1, RuO₂/Co₃O₄, and RuO₂/Co₃O₄-2 nanorod arrays.

Fig. S14 (a, b) CV curves at different scanning rates in the non-Faraday region and (c, d) plots for Cₐl calculation of RuO₂/Co₃O₄-1 and RuO₂/Co₃O₄-2 nanorod arrays.
Fig. S15 (a) XRD pattern and (b) SAED pattern of RuO$_2$/Co$_3$O$_4$ nanorod arrays after OER stability test.

Fig. S16 HRTEM images of (a) Co$_3$O$_4$ and (b) RuO$_2$/Co$_3$O$_4$ nanorod arrays after OER stability test.

Fig. S17 (a) Scanning TEM image and (b) corresponding EDX elemental mapping images of RuO$_2$/Co$_3$O$_4$ nanorod arrays after OER stability test.
Fig. S18 (a) Co 2p and (b) O 1s high-resolution XPS spectra of Co$_3$O$_4$ and RuO$_2$/Co$_3$O$_4$ nanorod arrays after OER stability test; (c) Ru 3p high-resolution XPS spectra of RuO$_2$/Co$_3$O$_4$ nanorod arrays after OER stability test.

Fig. S19 (a) LSV curves and (b) Tafel plots of Co$_3$O$_4$, RuO$_2$/Co$_3$O$_4$-1, RuO$_2$/Co$_3$O$_4$, and RuO$_2$/Co$_3$O$_4$-2 nanorod arrays in 1 M KOH; (c) Overpotentials of Co$_3$O$_4$, RuO$_2$/Co$_3$O$_4$-1, RuO$_2$/Co$_3$O$_4$, and RuO$_2$/Co$_3$O$_4$-2 nanorod arrays at 10 and 100 mA cm$^{-2}$; (d) Nyquist plots of Co$_3$O$_4$, RuO$_2$/Co$_3$O$_4$-1, RuO$_2$/Co$_3$O$_4$, and RuO$_2$/Co$_3$O$_4$-2 nanorod arrays; (e) chronoamperometery curve of RuO$_2$/Co$_3$O$_4$ at 100 mA cm$^{-2}$. 
Fig. S20 Polarization curve of full water electrolysis and chronoamperometry curve (inset) of the electrolysis cell by using RuO$_2$/Co$_3$O$_4$ nanorod arrays as anode and commercial Pt/C as cathode in 1 M PBS.
### Table S1 Different atomic content measured by the X-ray photoelectron spectroscopy (XPS) survey spectra.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ru Atomic %</th>
<th>Co Atomic %</th>
<th>C Atomic %</th>
<th>O Atomic %</th>
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<tbody>
<tr>
<td>Co$_3$O$_4$</td>
<td>0</td>
<td>30.16</td>
<td>19.33</td>
<td>49.9</td>
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<tr>
<td>RuO$_2$/Co$_3$O$_4$-1</td>
<td>0.73</td>
<td>28.04</td>
<td>20.3</td>
<td>50.94</td>
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<tr>
<td>RuO$_2$/Co$_3$O$_4$</td>
<td>1.37</td>
<td>18.09</td>
<td>25.12</td>
<td>55.41</td>
</tr>
<tr>
<td>RuO$_2$/Co$_3$O$_4$-2</td>
<td>1.85</td>
<td>20.56</td>
<td>24.21</td>
<td>53.39</td>
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</table>

### Table S2 Comparison of OER performance of RuO$_2$/Co$_3$O$_4$ with the most advanced electrocatalyst in neutral electrolytes.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Electrolyte</th>
<th>Overpotential (mV) at 10 mA cm$^{-2}$</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM@ZIF-8</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>784.19 (@1 mA cm$^{-2}$)</td>
<td>783.62</td>
<td>9</td>
</tr>
<tr>
<td>Co$_4$-bdt</td>
<td>1 M PBS</td>
<td>430</td>
<td>68</td>
<td>10</td>
</tr>
<tr>
<td>Zn,S-CoP NRCs/CP</td>
<td>1 M PBS</td>
<td>391</td>
<td>99.7</td>
<td>11</td>
</tr>
<tr>
<td>CeO$_2$/Co-Bi</td>
<td>0.1 M PBS</td>
<td>453</td>
<td>120</td>
<td>12</td>
</tr>
<tr>
<td>CoO$_3$H$_3$ NSAs</td>
<td>0.1 MPBS</td>
<td>430</td>
<td>121</td>
<td>13</td>
</tr>
<tr>
<td>np-Co$_9$S$_8$P</td>
<td>1 M PBS</td>
<td>483</td>
<td>106</td>
<td>14</td>
</tr>
<tr>
<td>Na$_2$CoP$_2$O$_7$</td>
<td>0.5 M PBS</td>
<td>560 (@1 mA cm$^{-2}$)</td>
<td>90</td>
<td>15</td>
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<tr>
<td>SCN-Ru-RuO$_2$/C$_3$N$_4$</td>
<td>1 M PBS</td>
<td>342</td>
<td>92</td>
<td>16</td>
</tr>
<tr>
<td>Co$_3$(PO$_4$)$_2$@GF</td>
<td>0.1 M PBS</td>
<td>530 (@5 mA cm$^{-2}$)</td>
<td>133</td>
<td>17</td>
</tr>
<tr>
<td>Co$_3$O$_4$ QDs</td>
<td>0.2 M PBS</td>
<td>490</td>
<td>80</td>
<td>18</td>
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<tr>
<td>NiCoO$_2$@CeO$_2$ NBs</td>
<td>0.1 M PBS</td>
<td>501 (@1 mA cm$^{-2}$)</td>
<td>72</td>
<td>19</td>
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<tr>
<td>Co$_3$O$_4$/Ti</td>
<td>1 M PBS</td>
<td>544</td>
<td>88</td>
<td>20</td>
</tr>
<tr>
<td>NaCoO$_4$(PO$_4$)$_3$</td>
<td>0.05 M PBS</td>
<td>373 (@1 mA cm$^{-2}$)</td>
<td>121</td>
<td>21</td>
</tr>
<tr>
<td>Co-Se-S-O NTs</td>
<td>0.1 M PBS</td>
<td>480</td>
<td>86.1</td>
<td>22</td>
</tr>
<tr>
<td>Co$_3$(PO$_4$)$_2$</td>
<td>0.1 M PBS</td>
<td>375 (@5 mA cm$^{-2}$)</td>
<td>59</td>
<td>23</td>
</tr>
<tr>
<td>Co$_3$(BO$_3$)$_2$@CNT</td>
<td>1 M KNO3</td>
<td>487</td>
<td>264</td>
<td>24</td>
</tr>
<tr>
<td><strong>RuO$_2$/Co$_3$O$_4$</strong></td>
<td><strong>1 M PBS</strong></td>
<td><strong>365</strong></td>
<td><strong>53</strong></td>
<td><strong>This work</strong></td>
</tr>
</tbody>
</table>
Supplementary references

17. L. Liu, D. Zhang, D. Duan, Y. Li, Q. Yuan, L. Chen and S. Liu, J. Mater. Chem. C, 2020, 862, 114031