Supporting Information

Tuning the electronic structure of NiCoVO$_x$ nanosheets through S doping for enhanced oxygen evolution

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Experimental Section

Chemicals

Co(NO$_3$)$_2$·6H$_2$O, VCl$_3$, urea (CO(NH$_2$)$_2$), NH$_4$F, KOH, thiourea (CS(NH$_2$)$_2$), commercial IrO$_2$, isopropanol, nafion solution were purchased from China National Pharmaceutical Industry Corporation Ltd. NF was purchased from China Kunshan Yizhongtian New Material Corporation Ltd. Carbon paper (CC) was purchased from Taiwan Carbon Energy Technology Corporation Ltd. Deionized water (18.2 MΩ) was utilized in all the experimental procedures. All the reagents were of analytical grade and used as received without further treatment.

Material synthesis

Synthesis of NiCoVO$_x$/NF

NiCoVO$_x$/NF was obtained by the similar procedure as $S_{4.06}$-NiCoVO$_x$/NF without adding thiourea in the hydrothermal process.

Synthesis of $S_m$-NiCoVO$_x$/NF ($m = 0.41, 2.89, 4.13, 6.26$)

$S_{6.26}$-NiCoVO$_x$/NF, $S_{4.13}$-NiCoVO$_x$/NF, $S_{2.89}$-NiCoVO$_x$/NF, $S_{0.41}$-NiCoVO$_x$/NF samples were obtained from the similar procedure with $S_{4.06}$-NiCoVO$_x$/NF with some modifications. Typically, via tuning the atomic ratio of urea/thiourea into 1/4, 2/3, 3/2, 4/1, the resulting sample denoted as $S_{6.26}$-NiCoVO$_x$/NF, $S_{4.13}$-NiCoVO$_x$/NF, $S_{2.89}$-NiCoVO$_x$/NF, $S_{0.41}$-NiCoVO$_x$/NF, respectively, were obtained.

Synthesis of $S_{4.06}$-NiCoVO$_x$/CC and $S_{4.06}$-CoVO$_x$/CC

The $S_{4.06}$-NiCoVO$_x$/CC and $S_{4.06}$-CoVO$_x$/CC were prepared using the similar procedure as $S_{4.06}$-NiCoVO$_x$/NF except substituting NF with CC in the hydrothermal
process.

**Preparation of IrO$_2$/NF**

A total of 10 mg commercial powder IrO$_2$ was ultrasonically dispersed in 0.5 mL deionized water, 0.495 mL isopropanol, 0.05 mL of 5 wt% Nafion solution, then the ink was transferred onto a pre-treated NF electrode via a controlled drop casting method. The mass loading amount of IrO$_2$ kept the same with S$_{4.06}$-NiCoVO$_x$/NF sample.

**Material characterizations**

The morphology and structure of as-synthesis materials were investigated with scanning electron microscope (SEM). The atomic structure of samples was taken on transition electron microscope (TEM) with energy-dispersive X-ray spectroscopy (EDS) with a field emission gun operated at 200 kV. The thickness of nanosheets was measured by atomic force microscopy (AFM) (Bruker Dimension Icon, Germany). The X-ray diffraction data was obtained on a Bruker D8 Advance by X-ray diffractometer (Cu K$\alpha$ radiation, $\lambda=1.54178$ Å). X-ray photoelectron spectroscopy (XPS) was collected with an Escalab 250 X-ray photoelectron spectroscope (15 kV, 6 mA). The energy scale was calibrated with C 1s spectrum at maximum peak of 284.8 eV as reference.

**Computational Methods**

All spin-polarized density functional theory plus Hubbard $U$ (DFT+$U$) calculations were operated with the Vienna ab-initio simulation Package (VASP). The exchange-correlation energy was described by using the generalized gradient
approximation (GGA) functional of Perdew-Burke-Ernzerhof (PBE)\(^2\) and projected augmented wave (PAW)\(^3\) pseudopotential. A plane-wave cutoff energy of 400 eV was adapt for all geometry optimization and energy calculation processes. Meanwhile, the energy and force convergence criteria of geometry optimization were \(10^{-5}\) eV and 0.02 eV \(\AA^{-1}\), respectively. The first Brillouin zone was described by gamma centered \(k\)-points of \(3\times3\times1\) for geometry optimization and \(7\times7\times1\) for PDOS calculation. The solvent effect was considered by the implicit solvation method in VASP\(_\text{sol}\) code.\(^4\)

To describe V, Co and Ni 3\(d\)-electrons accurately, the Hubbard \(U_{\text{eff}}(V)=3.25\) eV, \(U_{\text{eff}}(\text{Co})=3.32\) eV and \(U_{\text{eff}}(\text{Ni})=6.2\) eV obtained from the Materials Project database\(^5\) were added to the GGA functional of PBE via the rotationally invariant approach proposed by Dudarev \textit{et al.}\(^6\) Two 17.3 Å height \(2\times2\) periodic slab models of VNiO\(_3\) (220) and (020) plane with half of Ni replaced uniformly by Co were built as the substrates. A 15 Å vacuum space along the vertical direction was adopted to avoid the interactions between the slab and its period images. Moreover, a surface O atom nearing surface Co atom was substituted by S atom to study the effect of S doping. During all geometry optimization and energy calculation processes, the bottom half of atoms were fixed to their bulk positions, meanwhile the others were allowed to relax.

The computational hydrogen electrode (CHE) model was used to calculate the Gibbs free energy difference \((\Delta G)\),\(^7\) which defined as:

\[
\Delta G = \Delta E + \Delta ZPE - T \Delta S + \Delta G_U
\]

where \(\Delta E\), \(\Delta ZPE\) and \(\Delta S\) are the change of total energy, zero point energy, and entropy respectively, \(T\) is the temperature and \(\Delta G_U\) is the contribution of potential
The OER process can be described by four electrochemical steps, they are

\[
\begin{align*}
\text{OH}^-(aq)+* & \rightarrow \text{OH}^* \\
\text{OH}^*+\text{OH}^-(aq) & \rightarrow \text{O}^*+\text{H}_2\text{O}(aq) \\
\text{O}^*+\text{OH}^-(aq) & \rightarrow \text{OOH}^* \\
\text{OOH}^*+\text{OH}^-(aq) & \rightarrow \text{OO}^*+\text{H}_2\text{O}(aq)
\end{align*}
\]

The four electrochemical steps correspond to four free energy changes, $\Delta G_i$ ($i=1,2,3,4$), which determines the value of overpotential ($\eta$), defined as:

\[
\eta = \max \frac{\Delta G_i}{e^{-1.23V}}
\]

where 1.23V is the equilibrium potential of OER.
Fig. S1 SEM image of $S_{4.06}$-NiCoVO$_x$/NF.
**Fig. S2** Atomic force microscopy results for S$_{4.06}$-NiCoVO$_x$ nanosheets.
Fig. S3 Pore size distribution of the $S_{4.06}$-NiCoVO$_x$/NF.
Fig. S4 (a) SEM and (b) HRTEM images of NiCoVOₓ/NF. (c) HAADF-STEM image and the corresponding elemental mapping of NiCoVOₓ nanosheets.
**RHE calibration**

The potential of calomel electrode was carefully calibrated with respect to the reversible hydrogen electrode. In detail, a calomel electrode (saturated KCl) was calibrated with respect to RHE in high purity hydrogen saturated 1.0 M KOH electrolyte with a Pt plate as the working electrode and platinum gauze as the counter electrode at a scan rate of 1 mV s$^{-1}$. The average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reaction.$^{8,9}$ The CV result was shown in Fig. S5. The potential reported in our work was converted to RHE according to the following equation: $E(\text{RHE}) = E(\text{SCE}) + 0.993$ V.

Fig. S5 RHE calibration in 1.0 M KOH, $E(\text{RHE}) = E(\text{SCE}) + 0.993$ V.
Fig. S6 LSV curves of NF, S-NF, and S$_{4.06}$-NiCoVO$_x$/NF. Sweep rate: 10 mV s$^{-1}$.
**Fig. S7** Turnover frequency (TOF) of \( \text{S}_{4.06}\text{-NiCoVO}_x/\text{NF} \), \( \text{NiCoVO}_x/\text{NF} \) and \( \text{IrO}_2/\text{NF} \) at the overpotential of 300 mV.

TOF was calculated according the equation as follow:\(^{10}\)

\[
\text{TOF} \ (s^{-1}) = \frac{j \times A}{4 \times F \times n}
\]

Where \( j \) (A cm\(^{-2}\)) is the current density at overpotential of 300 mV, \( A \) (cm\(^2\)) is the area of NF, \( F \) is the Faradaic constant, the number 4 is the 4 electrons that were generated during OER process, and \( n \) is the moles of all metal species including Ni, Co and V loaded on NF.
Fig. S8 The cyclic voltammograms at various scan rates of 4, 8, 12, 16, 20 mV/s for
(a) S_{4.06}-NiCoVO_x/NF and (b) NiCoVO_x/NF.
Fig. S9 XPS survey spectra of \( \text{S}_{6.26}\text{-NiCoVO}_x/\text{NF} \), \( \text{S}_{4.13}\text{-NiCoVO}_x/\text{NF} \), \( \text{S}_{4.06}\text{-NiCoVO}_x/\text{NF} \), \( \text{S}_{2.89}\text{-NiCoVO}_x/\text{NF} \), \( \text{S}_{4.06}\text{-NiCoVO}_x/\text{NF} \), \( \text{S}_{0.41}\text{-NiCoVO}_x/\text{NF} \), \( \text{S}_{2.89}\text{-NiCoVO}_x/\text{NF} \) and \( \text{S}_{0.41}\text{-NiCoVO}_x/\text{NF} \).
**Fig. S10** SEM images of (a) $S_{6.26}$-NiCoVO$_x$/NF, (b) $S_{4.13}$-NiCoVO$_x$/NF, (c) $S_{2.89}$-NiCoVO$_x$/NF and (d) $S_{0.41}$-NiCoVO$_x$/NF.
Fig. S11 OER activity tests of $S_{6.26}$-NiCoVO$_x$/NF, $S_{4.13}$-NiCoVO$_x$/NF, $S_{4.06}$-NiCoVO$_x$/NF, $S_{2.89}$-NiCoVO$_x$/NF and $S_{0.41}$-NiCoVO$_x$/NF. (a) LSV curves, (b) Tafel slopes of corresponding samples.
Fig. S12 LSV curves of $S_{4.06}$-NiCoVO$_x$/CC, $S_{4.06}$-CoVO$_x$/CC and $S_{4.06}$-NiCoVO$_x$/NF. 

Scan rate: 10 mV s$^{-1}$. 
Fig. S13 LSV curves of $S_{4.06}$-NiCoVO$_x$/NF for 1st and 3001th cycle.
Fig. S14 SEM image of $S_{4.06}$-NiCoVO$_x$/NF after stability test.
Fig. S15 High resolution XPS spectra of (a) Ni 2p, (b) Co 2p, (c) V 2p, (d) O 1s and (e) S 2p for S_{4.06}-NiCoVO_{3}/NF after stability test.
Fig. S16 The side and top views of NiCoVO$_3$ (020) plane before and after S doping.
Fig. S17 The side and top views of NiCoVO$_3$ (220) plane.
Fig. S18 The Gibbs free energy change diagram for OER pathway on bare NiCoVO₃ (220) and (020) plane.
Fig. S19 The charge density difference of S-NiCoVO\textsubscript{3} (020) plane.
Table S1: Comparison of OER performance of S\(_{4.06}\)-NiCoVO\(_x\)/NF catalyst with recently reported non-noble metal based (hydro)oxides.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Overpotential (mV)@10mA/cm(^2)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(_{4.06})-NiCoVO(_x)/NF</td>
<td>1 M KOH</td>
<td>248</td>
<td>46.2</td>
<td>This work</td>
</tr>
<tr>
<td>Fe-Co(_2)O(_4)</td>
<td>1 M KOH</td>
<td>262</td>
<td>43</td>
<td>11</td>
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<tr>
<td>CoV-Fe(_{0.28})</td>
<td>1 M KOH</td>
<td>215</td>
<td>39.1</td>
<td>12</td>
</tr>
<tr>
<td>Ag/Co(OH)(_2)</td>
<td>1 M KOH</td>
<td>250</td>
<td>76</td>
<td>13</td>
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<tr>
<td>NiFeCr hydroxide/CeO(_2)/Cu</td>
<td>1 M KOH</td>
<td>230.8</td>
<td>32.7</td>
<td>14</td>
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<tr>
<td>CoFe-LDH</td>
<td>1 M KOH</td>
<td>320</td>
<td>53</td>
<td>15</td>
</tr>
<tr>
<td>Fe(<em>x)Co(</em>{1-x})OOH</td>
<td>1 M KOH</td>
<td>266</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>Ir-doped NiV(OH)(_2)</td>
<td>1 M KOH</td>
<td>260</td>
<td>55.3</td>
<td>17</td>
</tr>
<tr>
<td>Gelled FeCo</td>
<td>1 M KOH</td>
<td>277</td>
<td>60</td>
<td>18</td>
</tr>
<tr>
<td>Gelled FeCo (oxy)hydroxides</td>
<td>1 M KOH</td>
<td>225</td>
<td>40.2</td>
<td>19</td>
</tr>
<tr>
<td>Co(<em>{0.73})Ni(</em>{0.25})(OH)(_2)</td>
<td>1 M KOH</td>
<td>235</td>
<td>56</td>
<td>20</td>
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<tr>
<td>Co(<em>{0.8})V(</em>{0.2})OOH</td>
<td>1 M KOH</td>
<td>190</td>
<td>39.6</td>
<td>21</td>
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<tr>
<td>CoFe-LDH-Ar</td>
<td>1 M KOH</td>
<td>266</td>
<td>37.9</td>
<td>22</td>
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<tr>
<td>Au@Co(_3)O(_4) core-shell</td>
<td>1 M KOH</td>
<td>350</td>
<td>60</td>
<td>23</td>
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<tr>
<td>nanocrystals</td>
<td>0.1 M KOH</td>
<td>400</td>
<td>48</td>
<td>24</td>
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<tr>
<td>Material</td>
<td>KOH Concentration</td>
<td>Temperature</td>
<td>Overpotential (%)</td>
<td>Efficiency (%)</td>
</tr>
<tr>
<td>--------------------------------</td>
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<tr>
<td>Cobalt-vanadium (oxy)hydroxide</td>
<td>1 M KOH</td>
<td>250</td>
<td>44</td>
<td>25</td>
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<tr>
<td>CoO/Co$_3$O$_4$</td>
<td>1 M KOH</td>
<td>260</td>
<td>55</td>
<td>26</td>
</tr>
<tr>
<td>Co$_2$Mo$_3$O$_8$@NC-800</td>
<td>1 M KOH</td>
<td>331</td>
<td>87.5</td>
<td>27</td>
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<tr>
<td>Co$_3$O$_4$/CeO$_2$ NHs</td>
<td>1 M KOH</td>
<td>270</td>
<td>60</td>
<td>28</td>
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<tr>
<td>Co$_3$O$_4$/Co-Fe oxide</td>
<td>1 M KOH</td>
<td>297</td>
<td>61</td>
<td>29</td>
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<td>DSNBs</td>
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<tr>
<td>$\gamma$-CoOOH nanosheets</td>
<td>1 M KOH</td>
<td>275</td>
<td>49</td>
<td>30</td>
</tr>
<tr>
<td>NiFeMo oxides</td>
<td>0.1 M KOH</td>
<td>280</td>
<td>49</td>
<td>31</td>
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References


