

## Supporting Information

### **Engineering active sites on hierarchical transition bimetal oxides/sulfides heterostructure array enabling robust overall water splitting**

Panlong Zhai,<sup>1,5</sup> Yanxue Zhang,<sup>2,5</sup> Yunzhen Wu,<sup>1,5</sup> Junfeng Gao,<sup>2</sup> Bo Zhang,<sup>1</sup> Shuyan Cao,<sup>1</sup> Yanting Zhang,<sup>1</sup> Zhuwei Li,<sup>1</sup> Licheng Sun,<sup>1,3,4</sup> Jungang Hou<sup>1\*</sup>

<sup>1</sup>State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China.

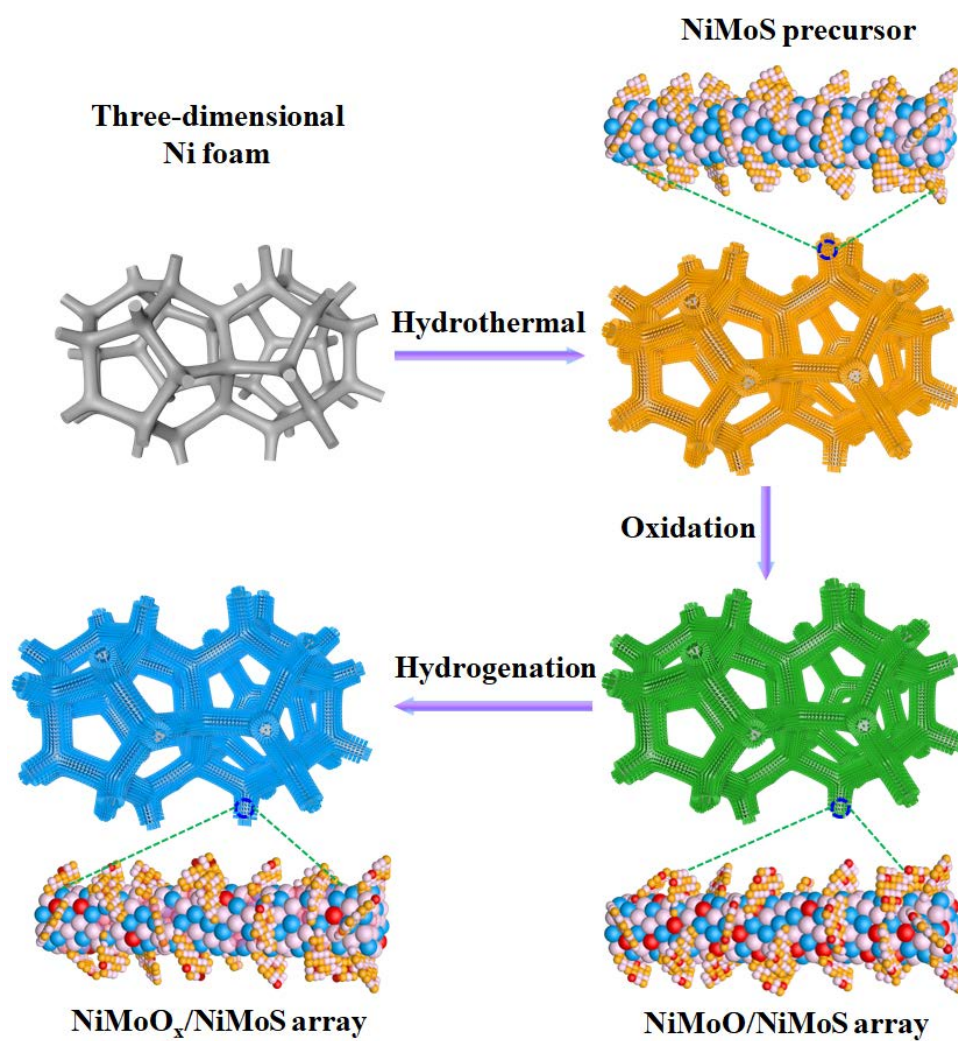
<sup>2</sup>Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Ministry of Education, Dalian 116024, P. R. China.

<sup>3</sup>College of Science, Westlake University, Hangzhou 310024, P. R. China.

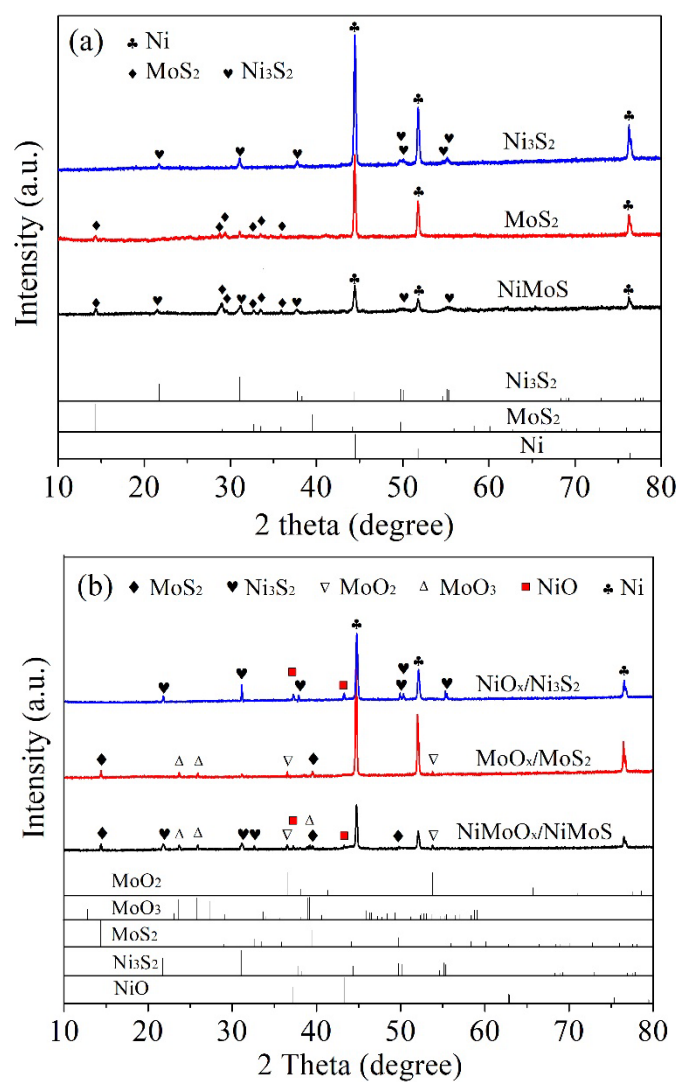
<sup>4</sup>Department of Chemistry, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, 10044 Stockholm, Sweden.

<sup>5</sup>These authors contributed equally: Panlong Zhai, Yanxue Zhang and Yunzhen Wu.

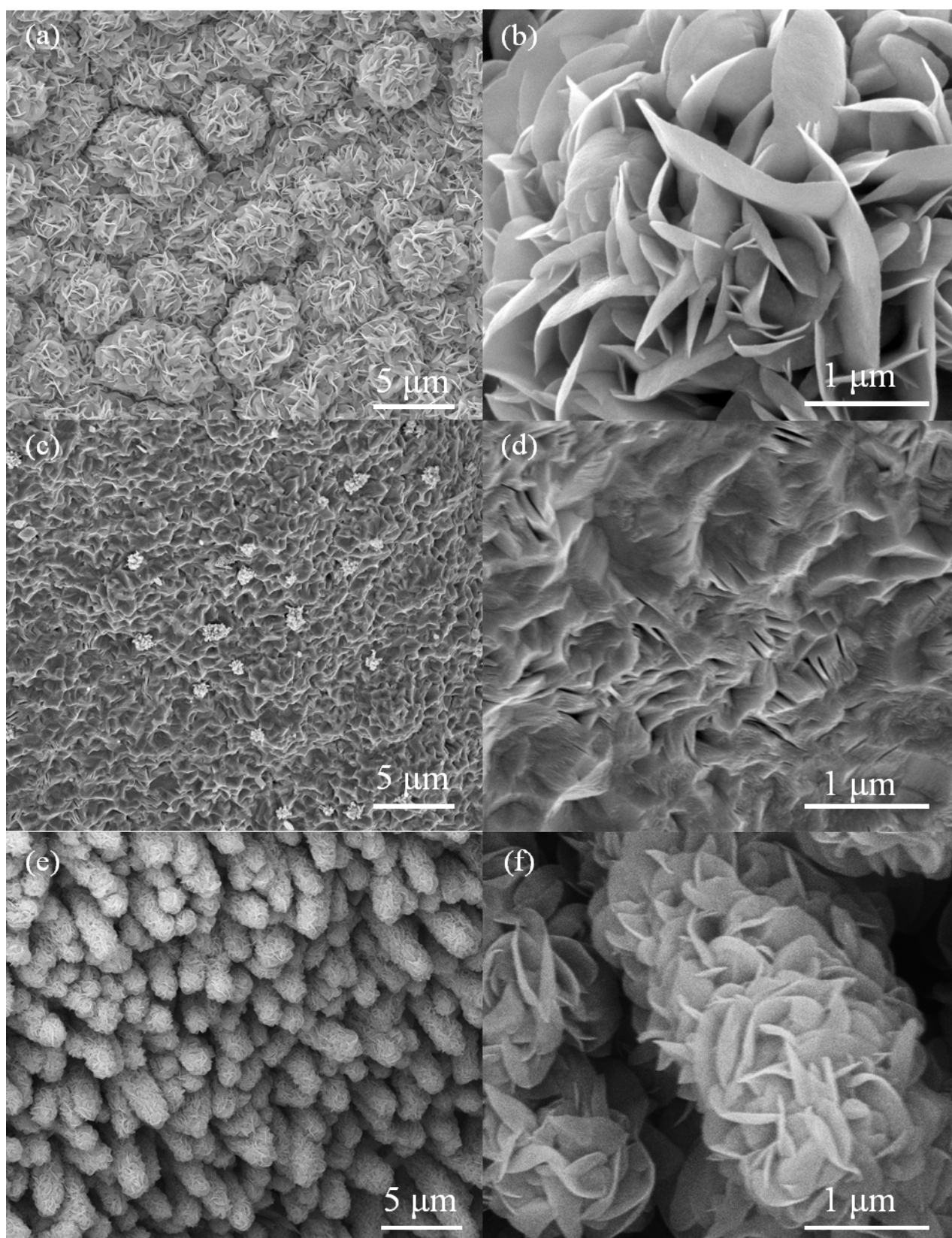
\*E-mail: jhou@dlut.edu.cn



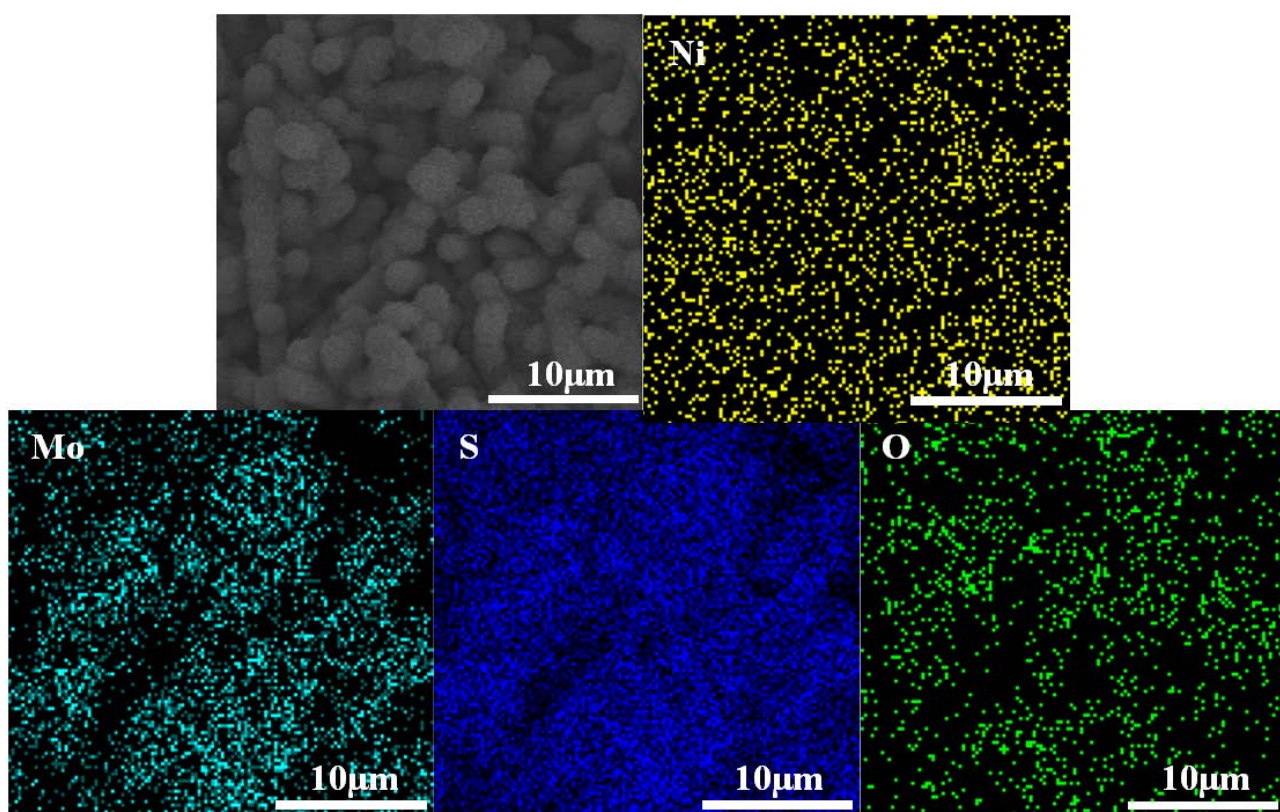
**Supplementary Figure 1.** Synthesis illustration of NiMoO<sub>x</sub>/NiMoS heterostructure array by oxidation/hydrogenation-induced surface reconfiguration strategy.



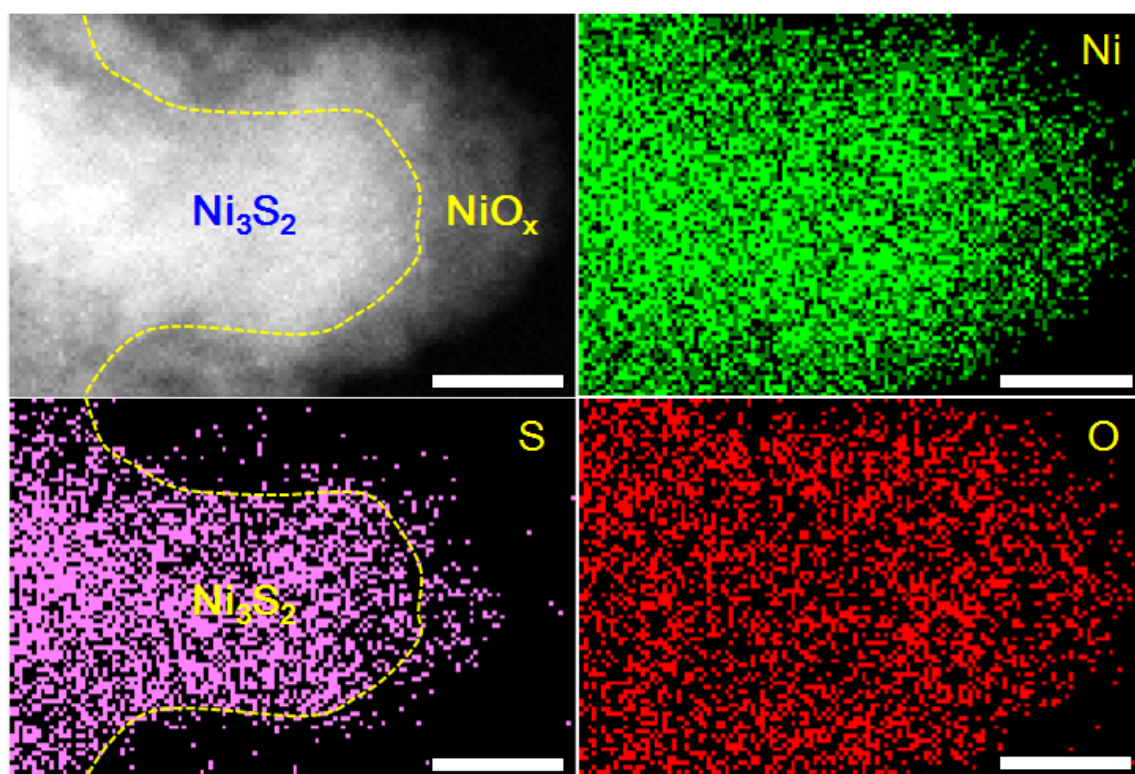
**Supplementary Figure 2.** XRD patterns of different arrays. (a) MoS<sub>2</sub> and Ni<sub>3</sub>S<sub>2</sub> as well as MoS<sub>2</sub>/Ni<sub>3</sub>S<sub>2</sub>, (b) NiO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>, MoO<sub>x</sub>/MoS<sub>2</sub> and NiMoO<sub>x</sub>/NiMoS.



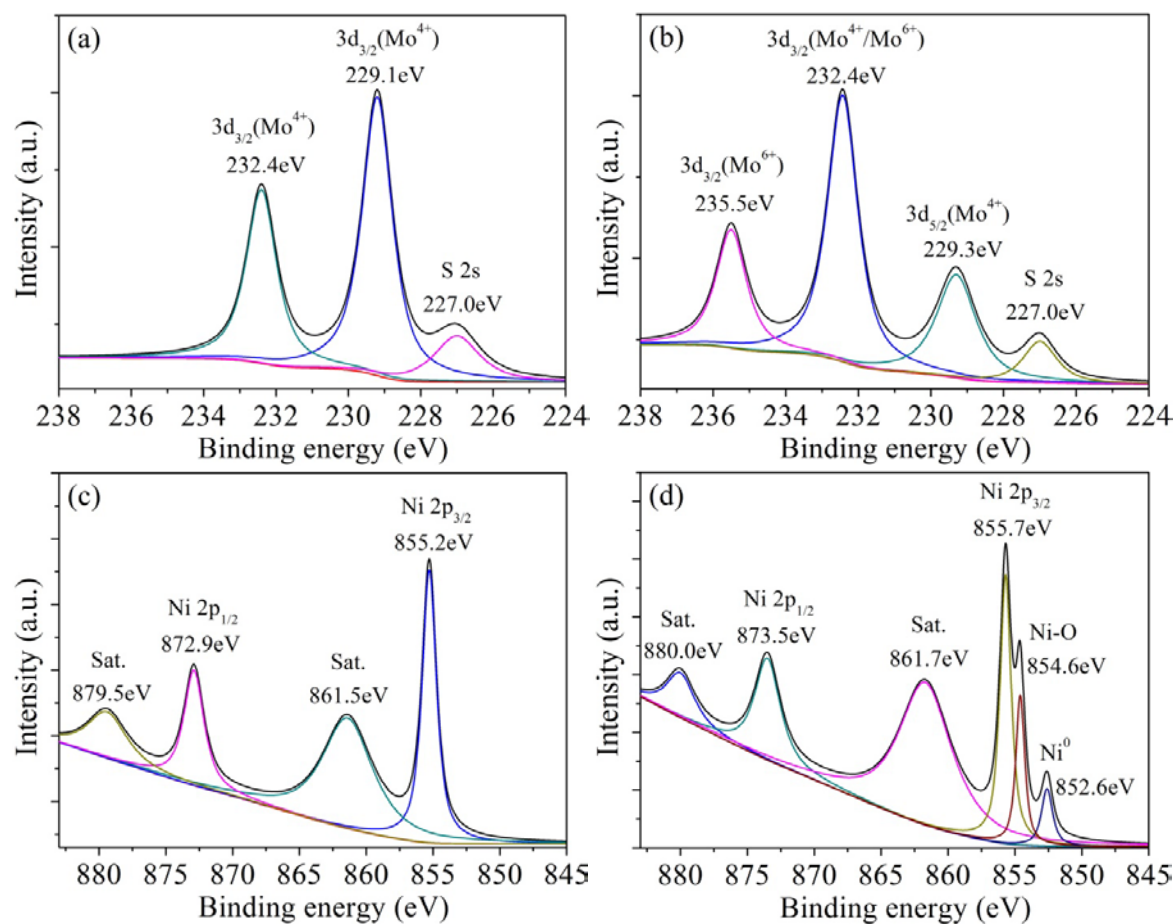
**Supplementary Figure 3.** SEM images of (ab) MoS<sub>2</sub>, (cd) Ni<sub>3</sub>S<sub>2</sub> and (ef) NiMoS arrays.



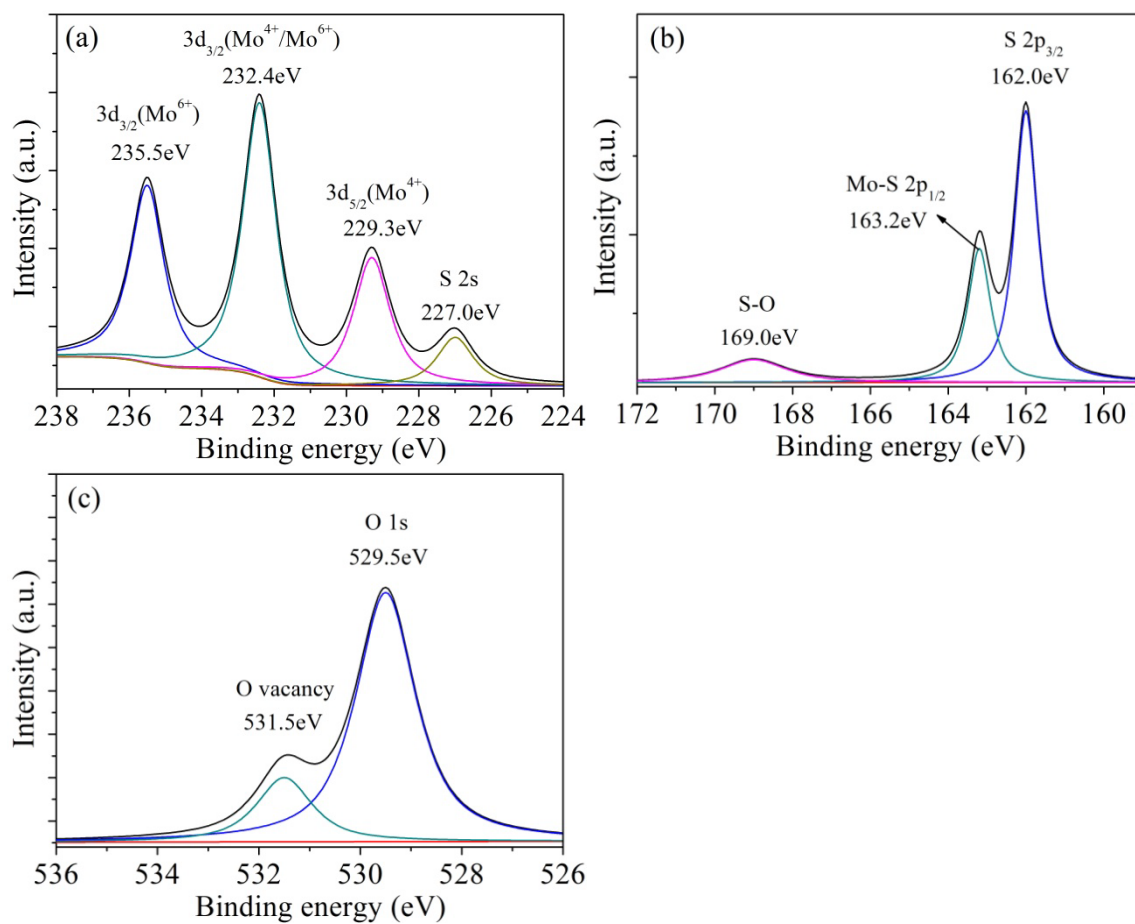
**Supplementary Figure 4.** Element mapping of NiMoO<sub>x</sub>/NiMoS heterostructure array by use of oxidation/hydrogenation-induced surface reconfiguration treatment.



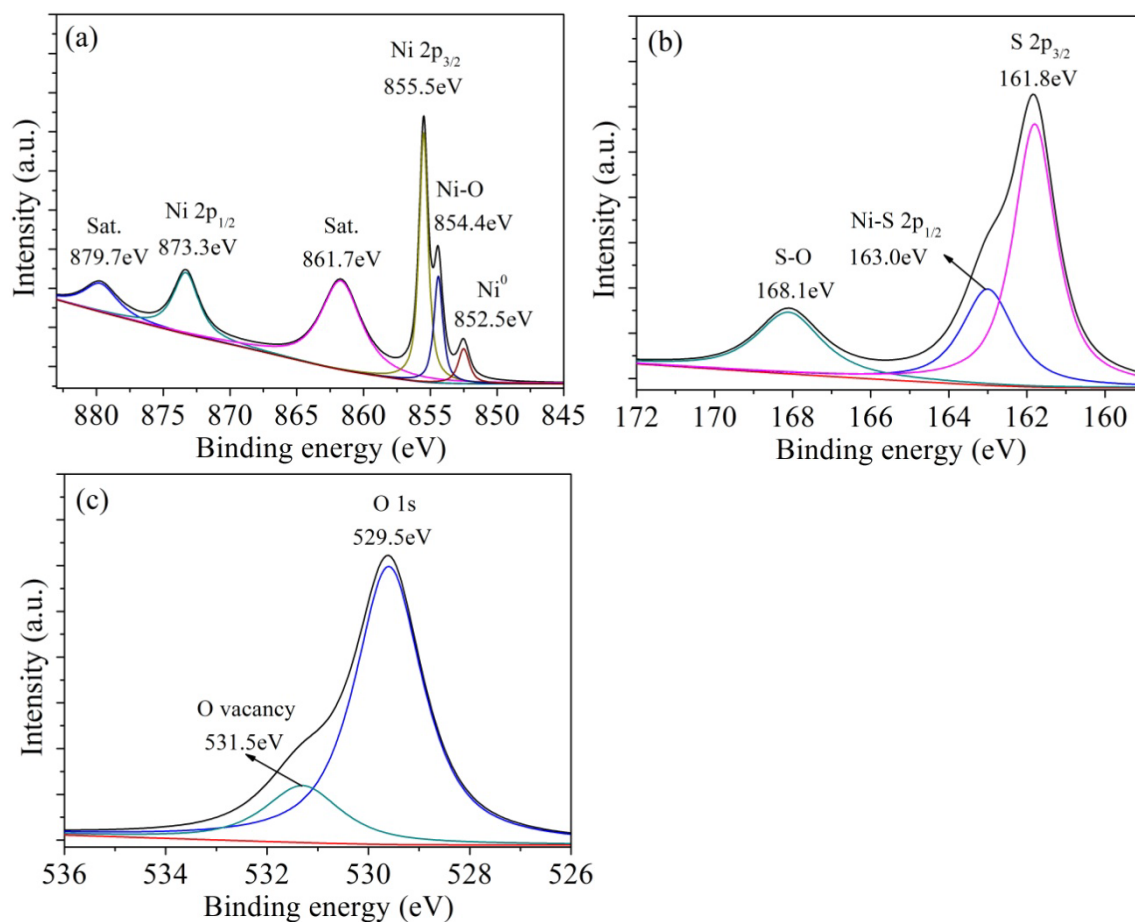
**Supplementary Figure 5.** HAADF-STEM image and the corresponding EDX elemental mapping of  $\text{NiO}_x/\text{Ni}_3\text{S}_2$  from  $\text{NiMoO}_x/\text{NiMoS}$ . Scale bar, 10 nm.



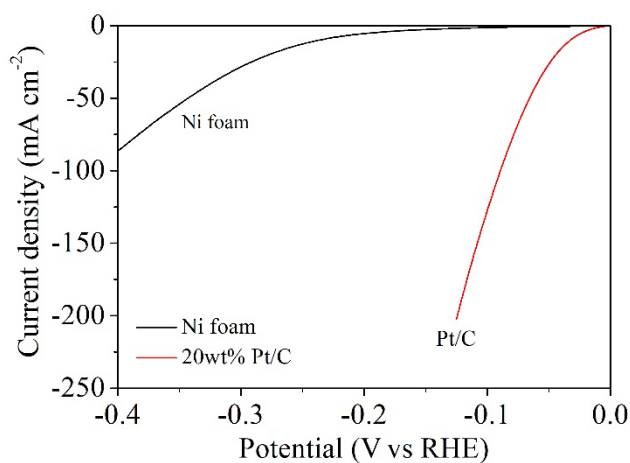
**Supplementary Figure 6.** XPS spectra of NiMoS and NiMoO<sub>x</sub>/NiMoS arrays. (ab) Mo 3d and (cd) Ni 2p.



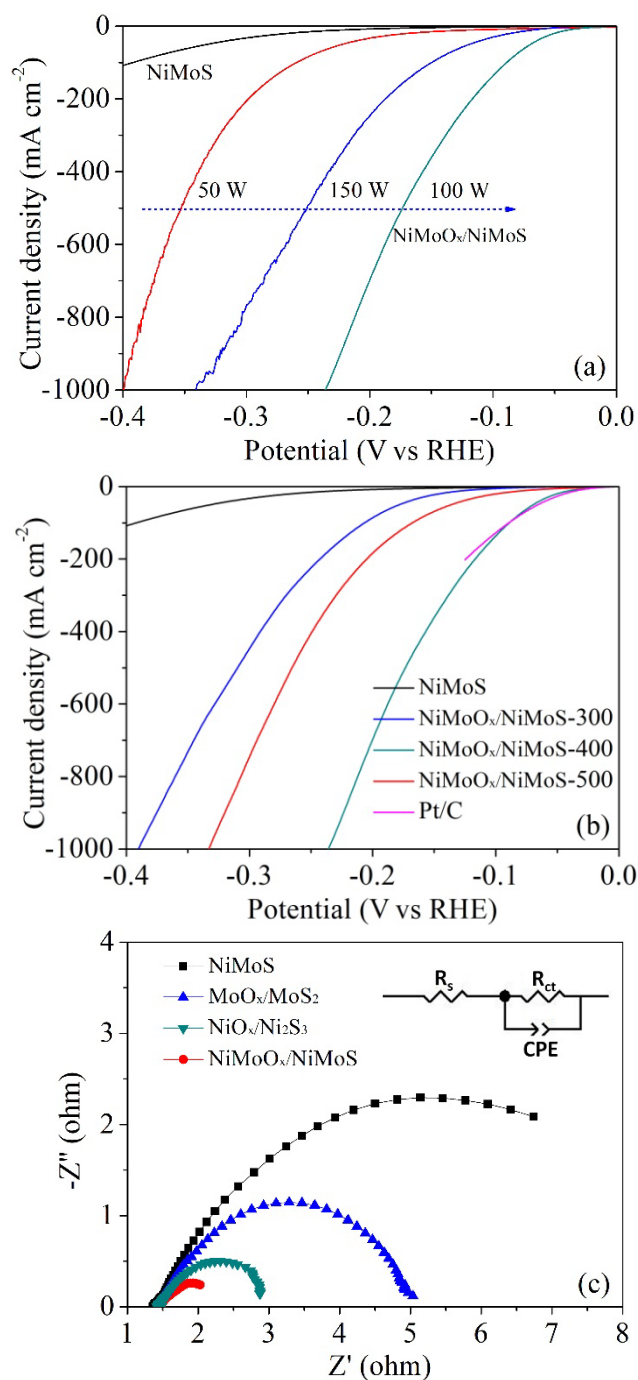
**Supplementary Figure 7.** XPS spectra of MoO<sub>x</sub>/MoS<sub>2</sub> array. (a) Mo 3d, (b) S 2p and (c) O 1s.



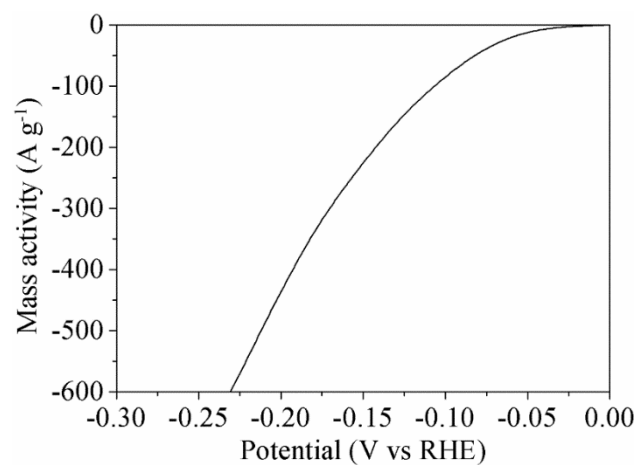
**Supplementary Figure 8.** XPS spectra of  $\text{NiO}_x/\text{Ni}_3\text{S}_2$  array. (a) Ni 3d, (b) S 2p and (c) O 1s.



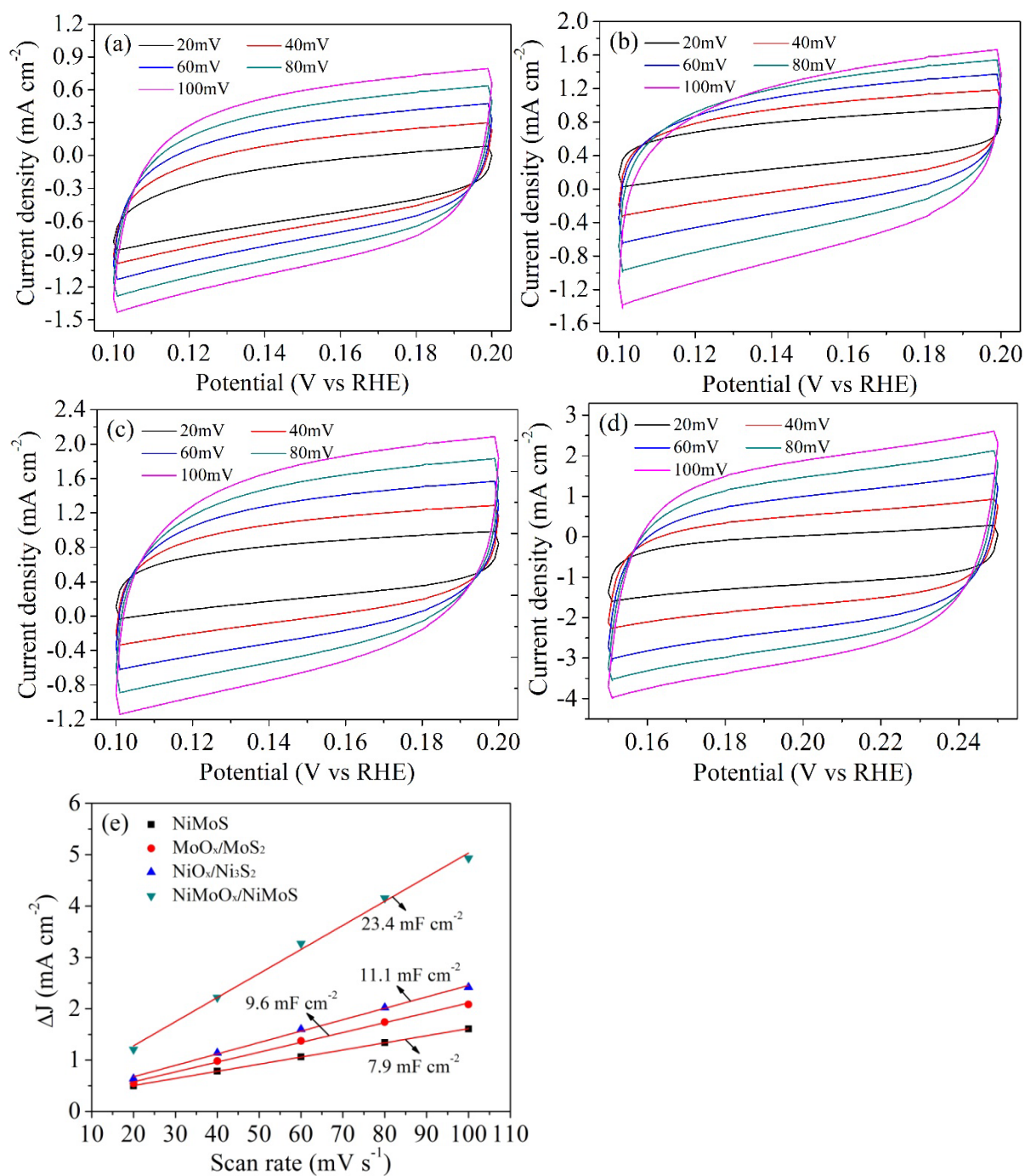
**Supplementary Figure 9.** HER polarization curves of commercial Pt/C supported on Ni foam in comparison of pristine Ni foam in 1 M KOH.



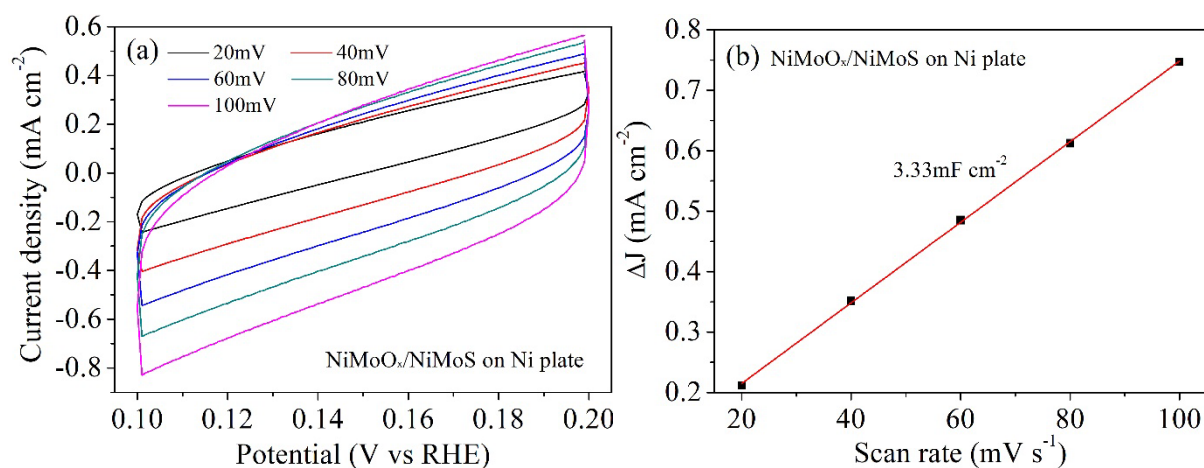
**Supplementary Figure 10.** (ab) LSV curves of different arrays for HER by tunable power and (b) hydrogenation temperatures, (c) electrochemical impedance spectroscopy tests.



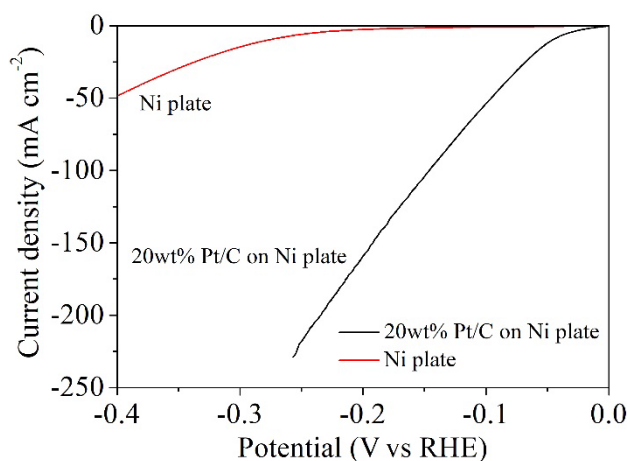
**Supplementary Figure 11.** Calculated mass activity of NiMoO<sub>x</sub>/NiMoS array for HER in 1 M KOH.



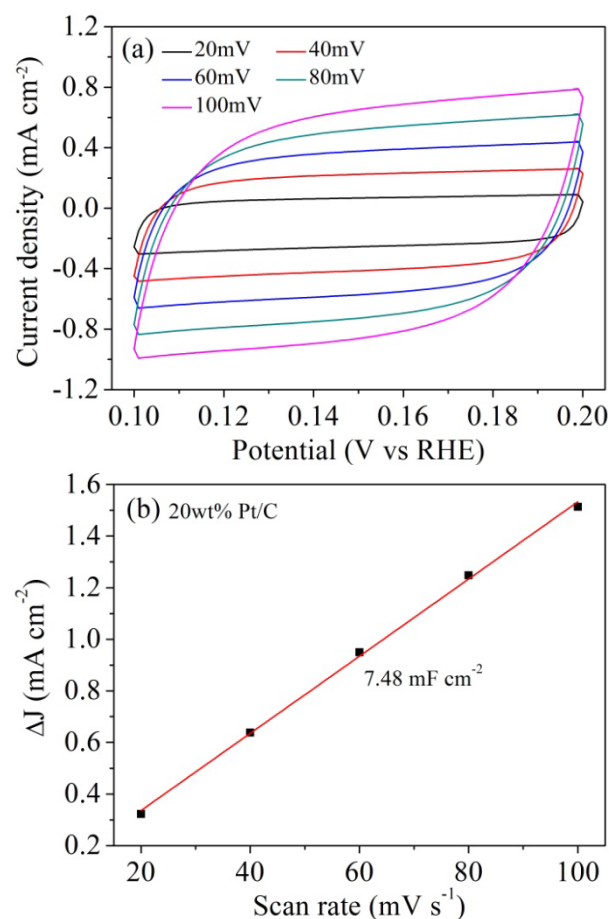
**Supplementary Figure 12.** (abcd) Cyclic voltammetry curves and (e) electrochemical double-layer capacitances of various catalysts supported on Ni foam during HER process.



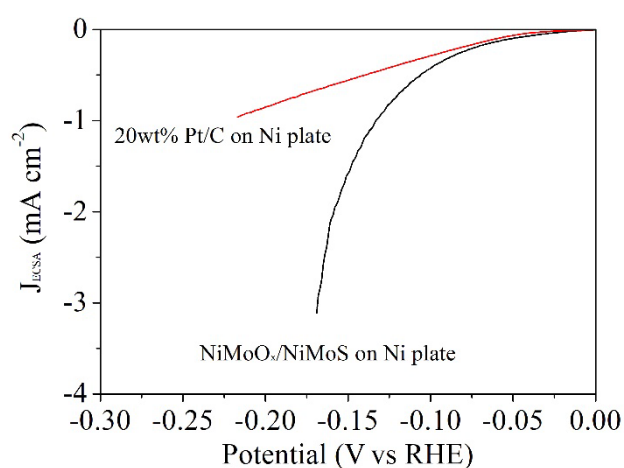
**Supplementary Figure 13.** (a) Cyclic voltammetry curves and (b) electrochemical double-layer capacitance of NiMoO<sub>x</sub>/NiMoS supported on Ni plate.



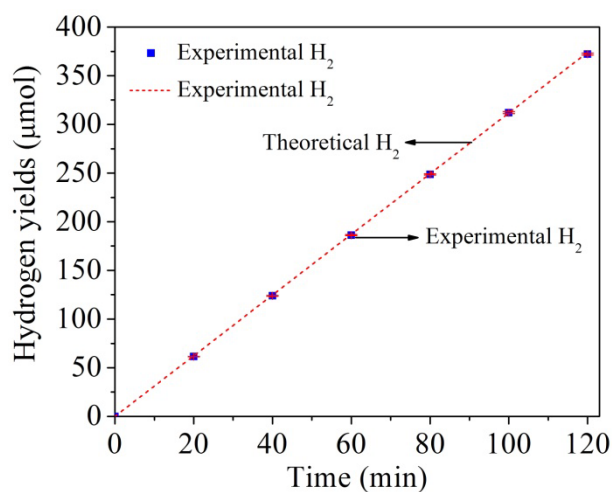
**Supplementary Figure 14.** HER polarization curves of commercial Pt/C supported on Ni plate in comparison of pristine Ni plate in 1 M KOH.



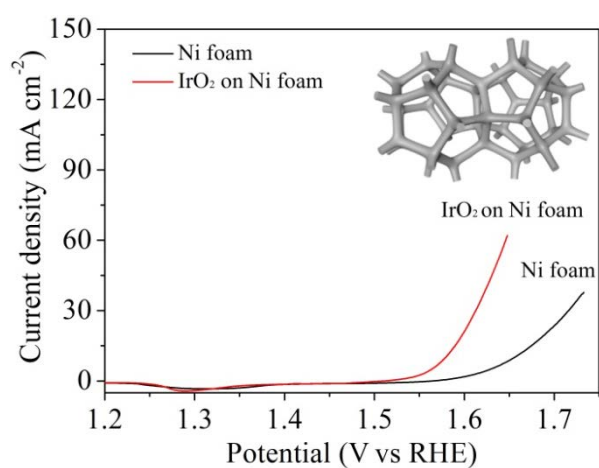
**Supplementary Figure 15.** (a) Cyclic voltammetry curves and (b) electrochemical double-layer capacitance of Pt/C supported on Ni plate.



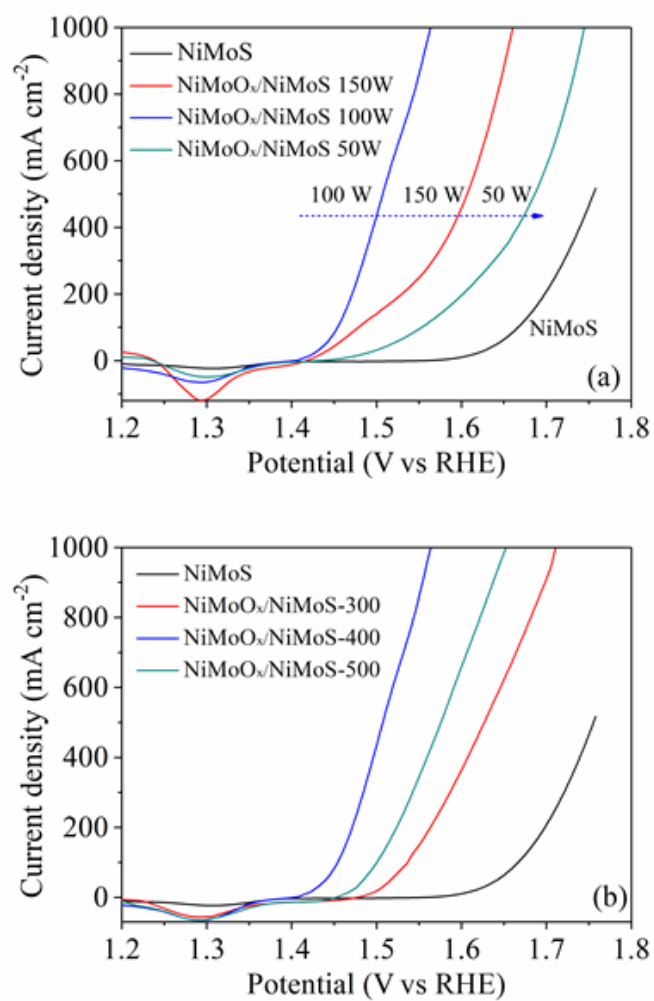
**Supplementary Figure 16.** Polarization curves of NiMoO<sub>x</sub>/NiMoS and commercial Pt/C supported on Ni plate with the relative current normalized to ECSA.



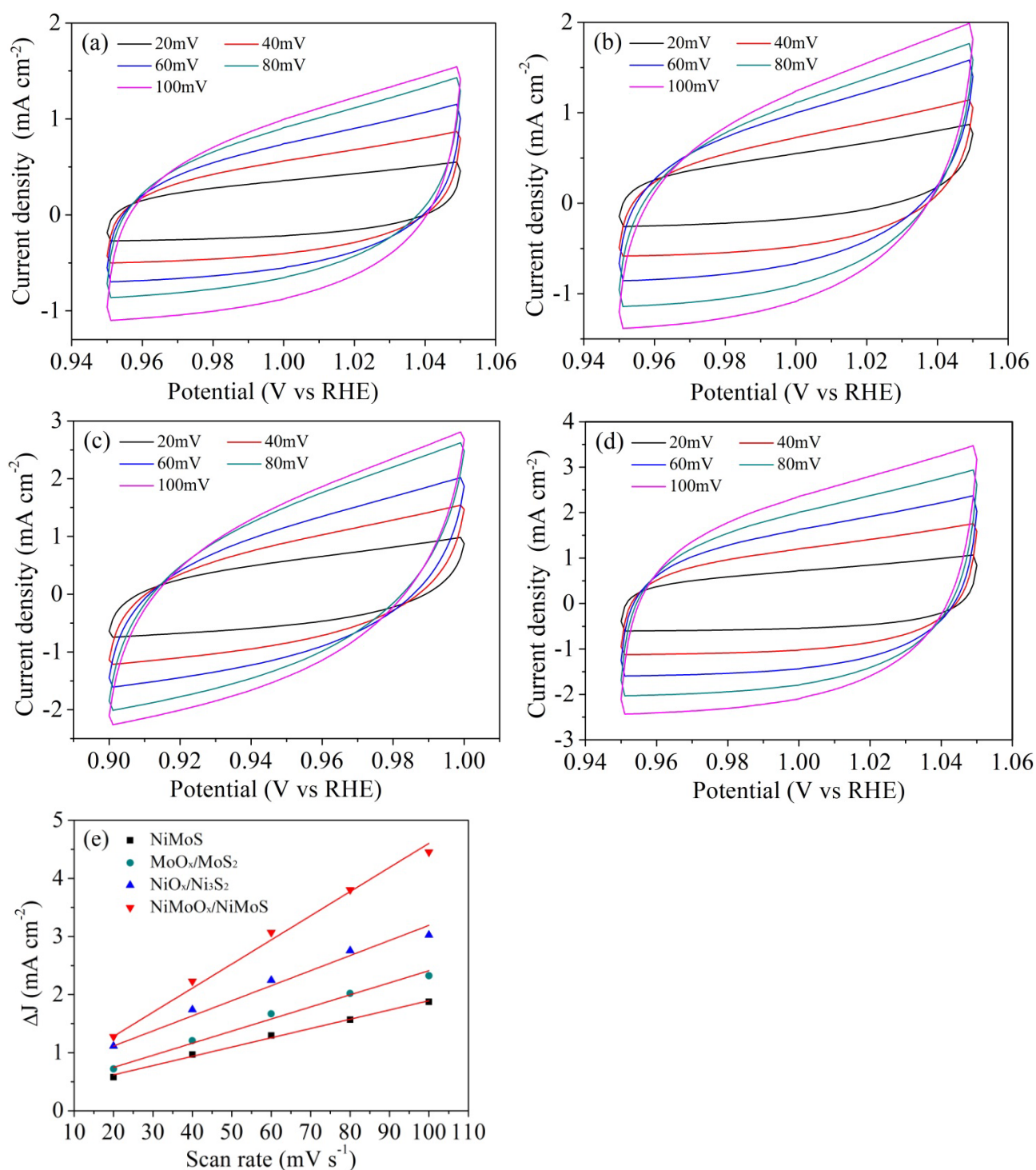
**Supplementary Figure 17.** The yields of hydrogen theoretically calculated from HER current and tested from gas chromatography by NiMoO<sub>4</sub>/NiMoS at 10 mA cm<sup>-2</sup>.



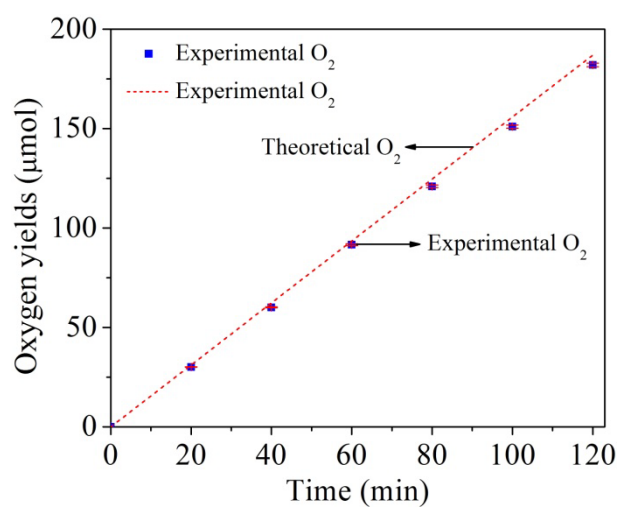
**Supplementary Figure 18.** OER polarization curves of commercial IrO<sub>2</sub> supported on Ni foam in comparison of pristine Ni foam in 1 M KOH.



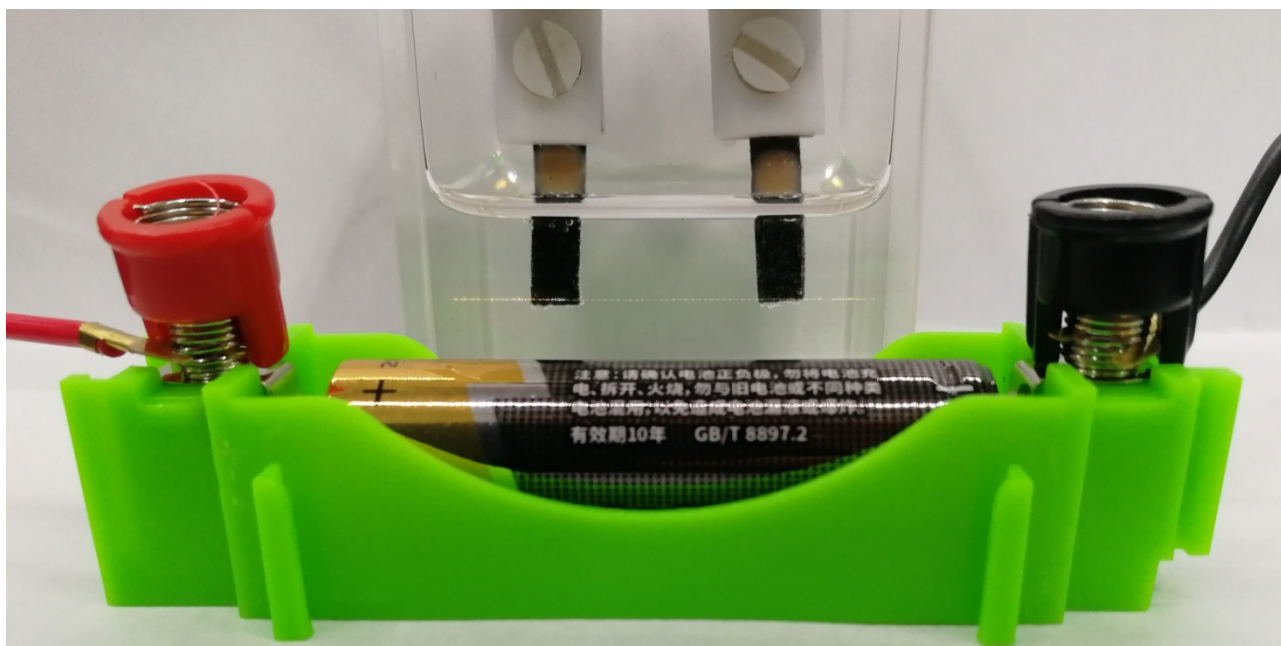
**Supplementary Figure 19.** LSV curves of different arrays for OER by (a) tunable power and (b) different hydrogenation temperatures.



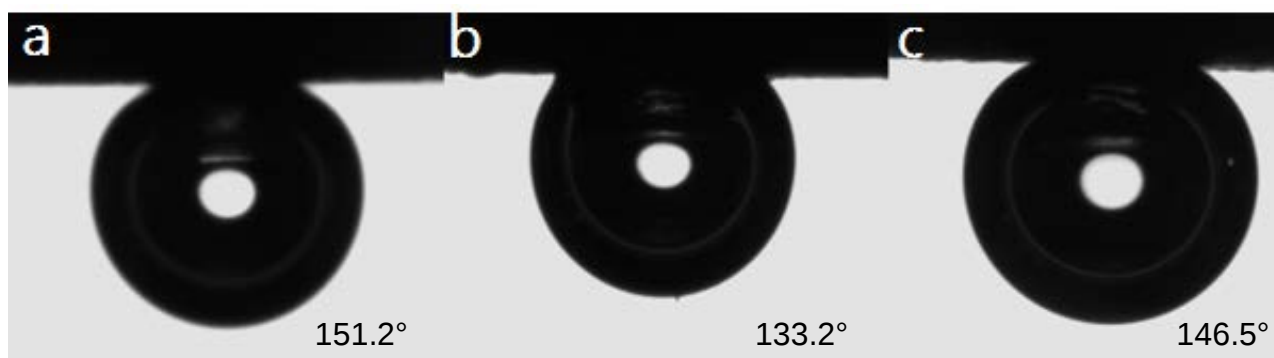
**Supplementary Figure 20.** (abcd) Cyclic voltammety curves and (e) electrochemical double-layer capacitances of various catalysts supported on Ni foam during OER process.



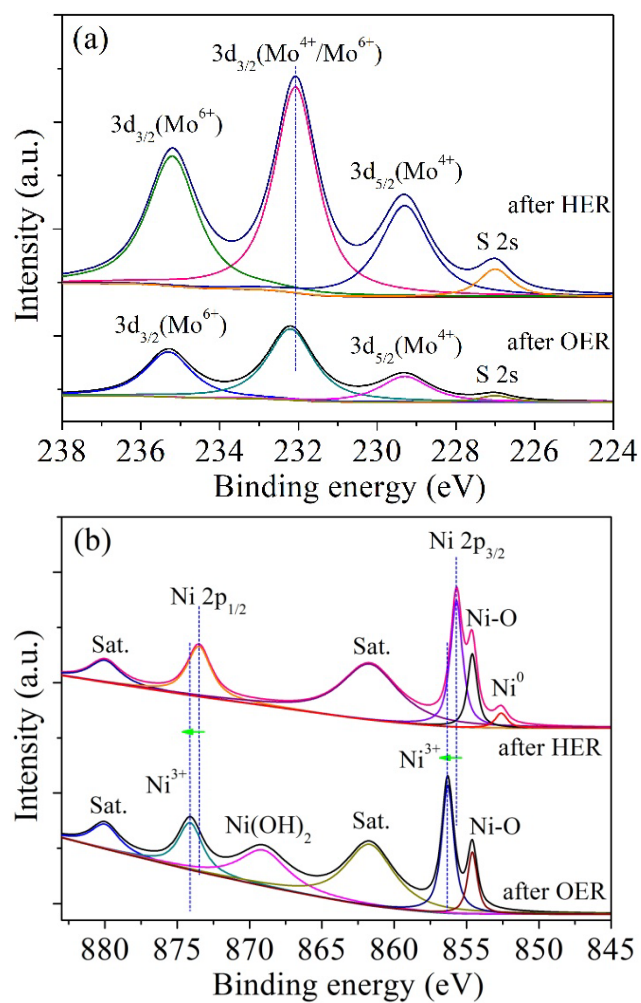
**Supplementary Figure 21.** The yields of hydrogen theoretically calculated from OER current and tested from gas chromatography by NiMoO<sub>x</sub>/NiMoS at 10 mA cm<sup>-2</sup>.



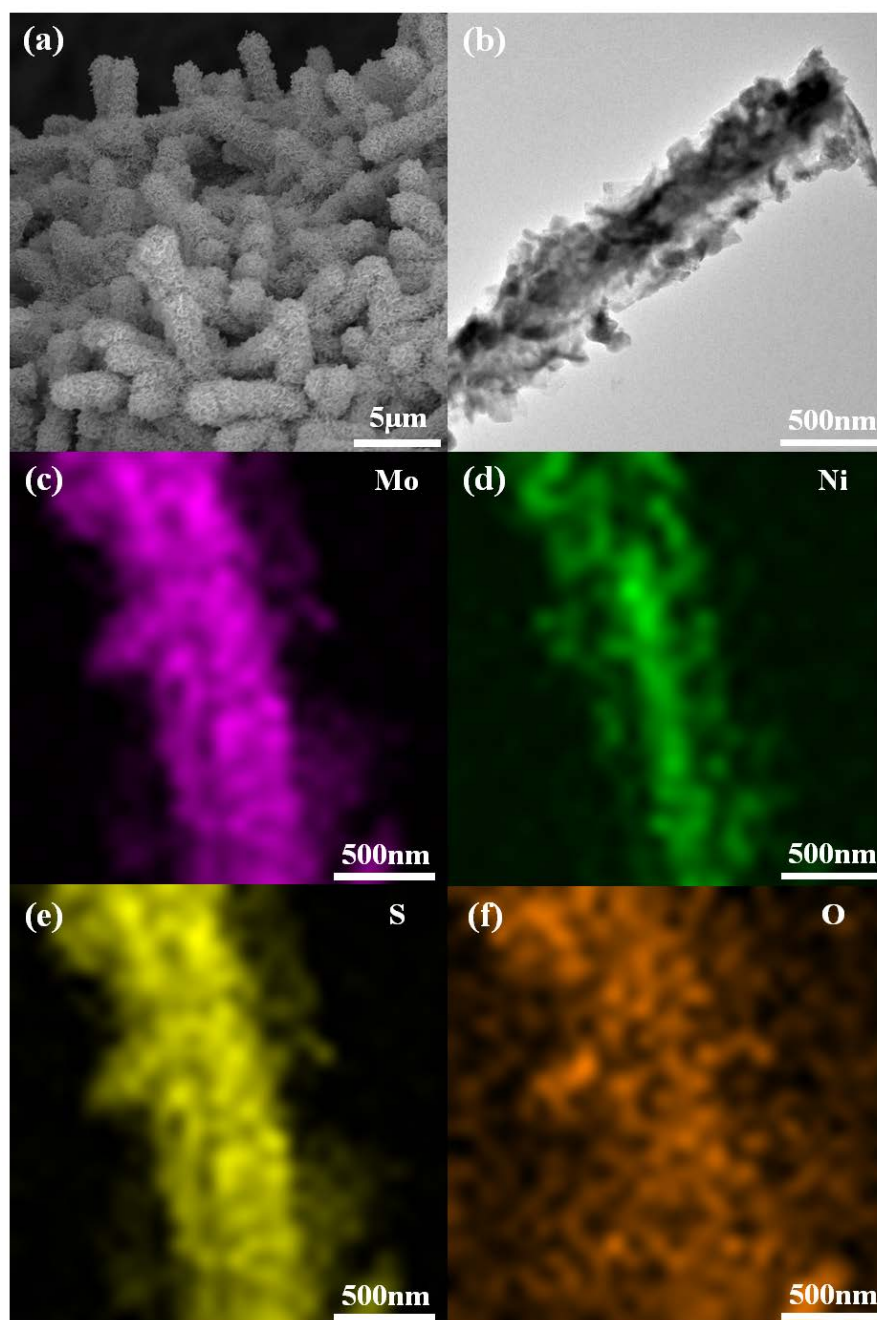
**Supplementary Figure 22.** H<sub>2</sub> and O<sub>2</sub> bubbles on its respective NiMoO<sub>x</sub>/NiMoS heterostructure electrode for two-electrode overall water splitting by a 1.5 V AAA battery.



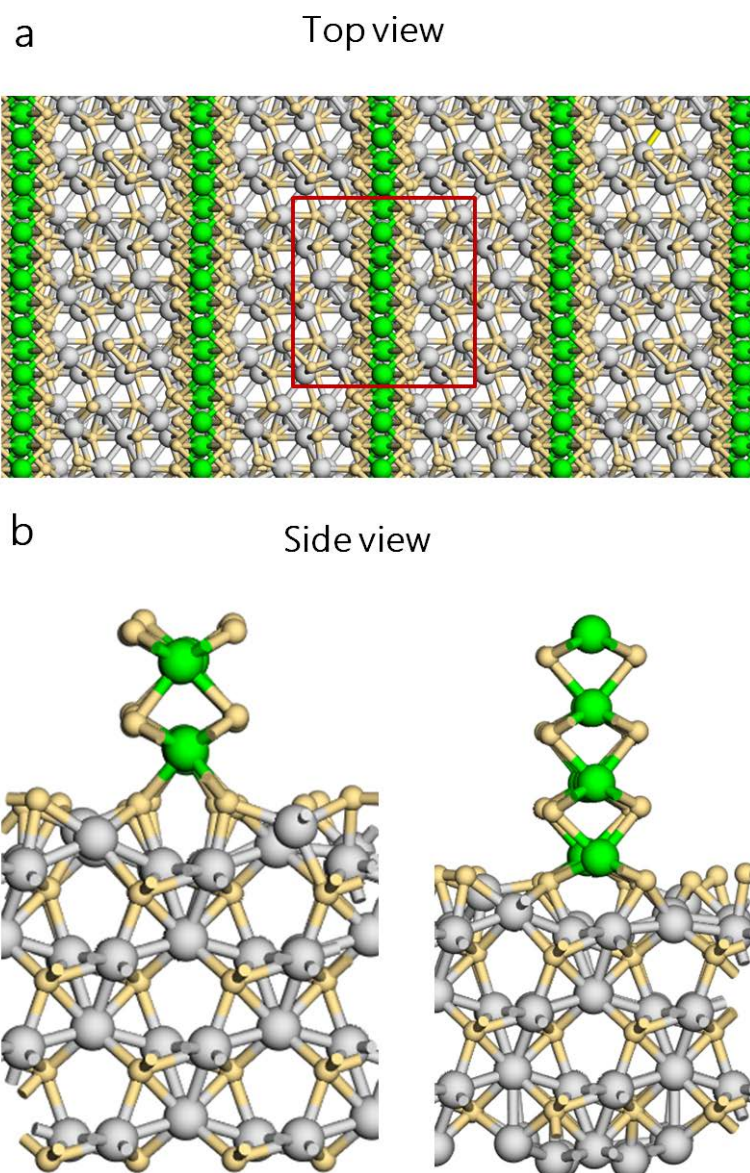
**Supplementary Figure 23.** Air-bubble contact angles under water for (a) NiMoO<sub>x</sub>/NiMoS, (b) NiO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>, (c) MoO<sub>x</sub>/MoS<sub>2</sub>.



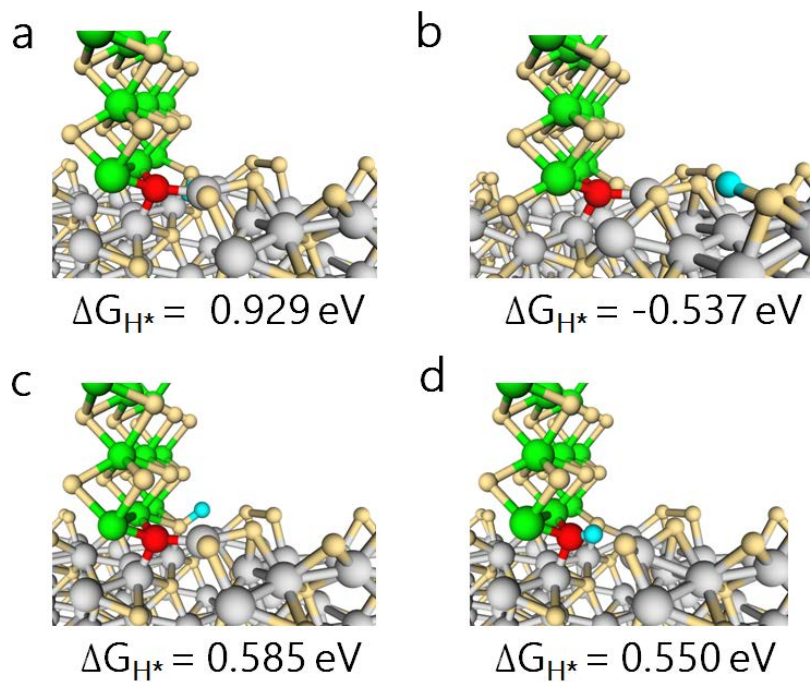
**Supplementary Figure 24.** XPS spectra of NiMoO<sub>x</sub>/NiMoS array after HER and OER reactions.



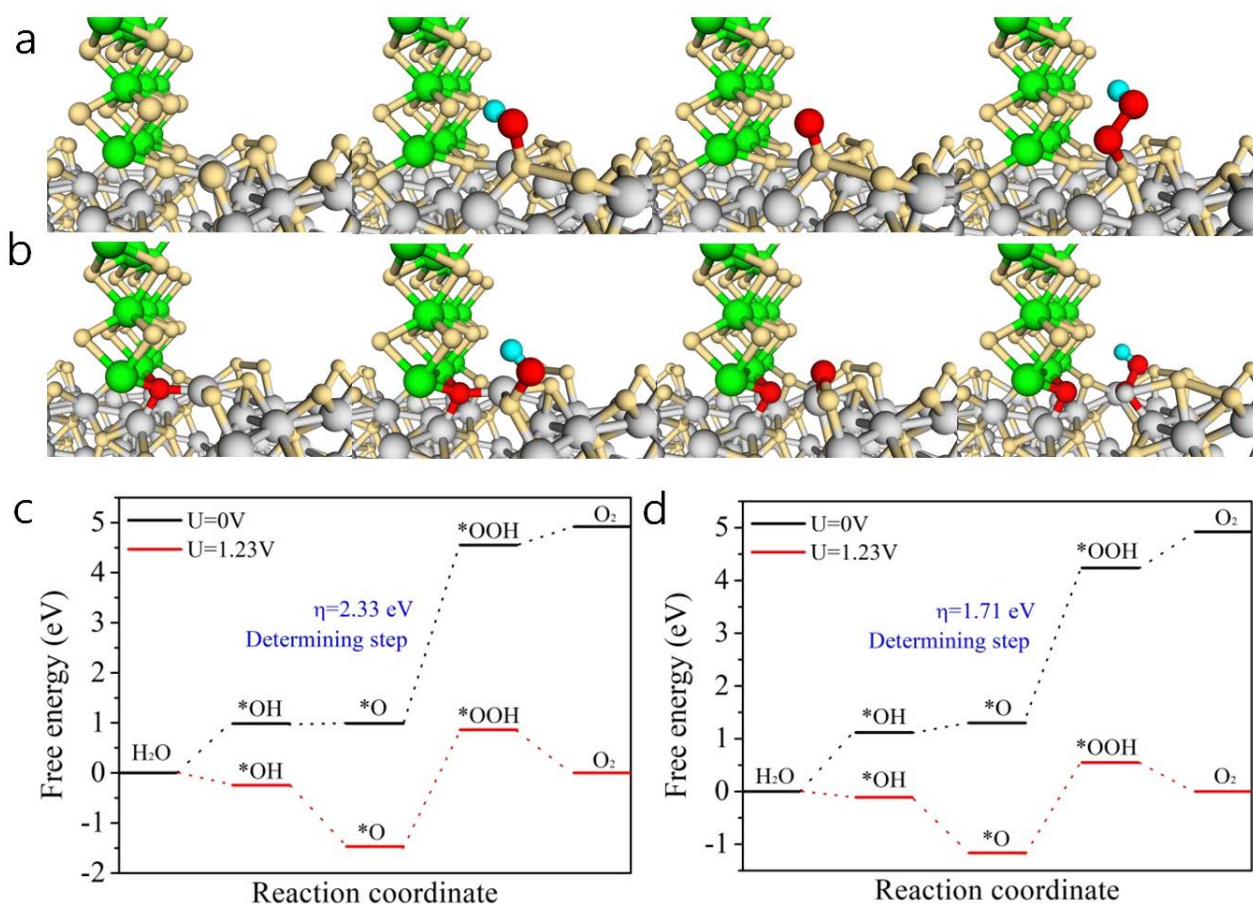
**Supplementary Figure 25.** SEM, TEM images and elements mapping of  $\text{NiMoO}_x/\text{NiMoS}$  array after electrocatalytic water splitting by two-electrode system.



**Supplementary Figure 26.** (a) Top and (b) side view of DFT simulated  $\text{Ni}_3\text{S}_2/\text{MoS}_2$  interface model. The unit cell is marked in the dark red boxes.

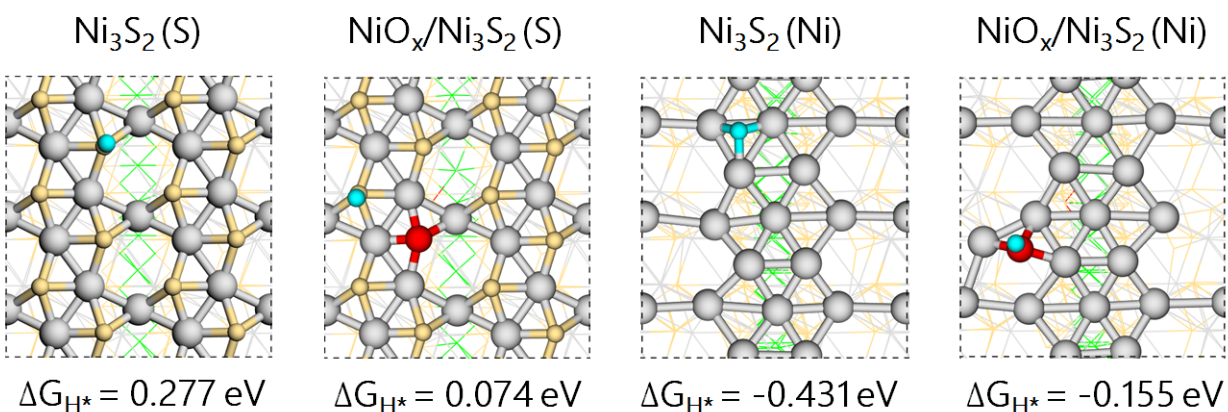


**Supplementary Figure 27.** Possible H\* adsorption sites on the interface of NiMoO<sub>x</sub>/NiMoS and corresponding free energies.

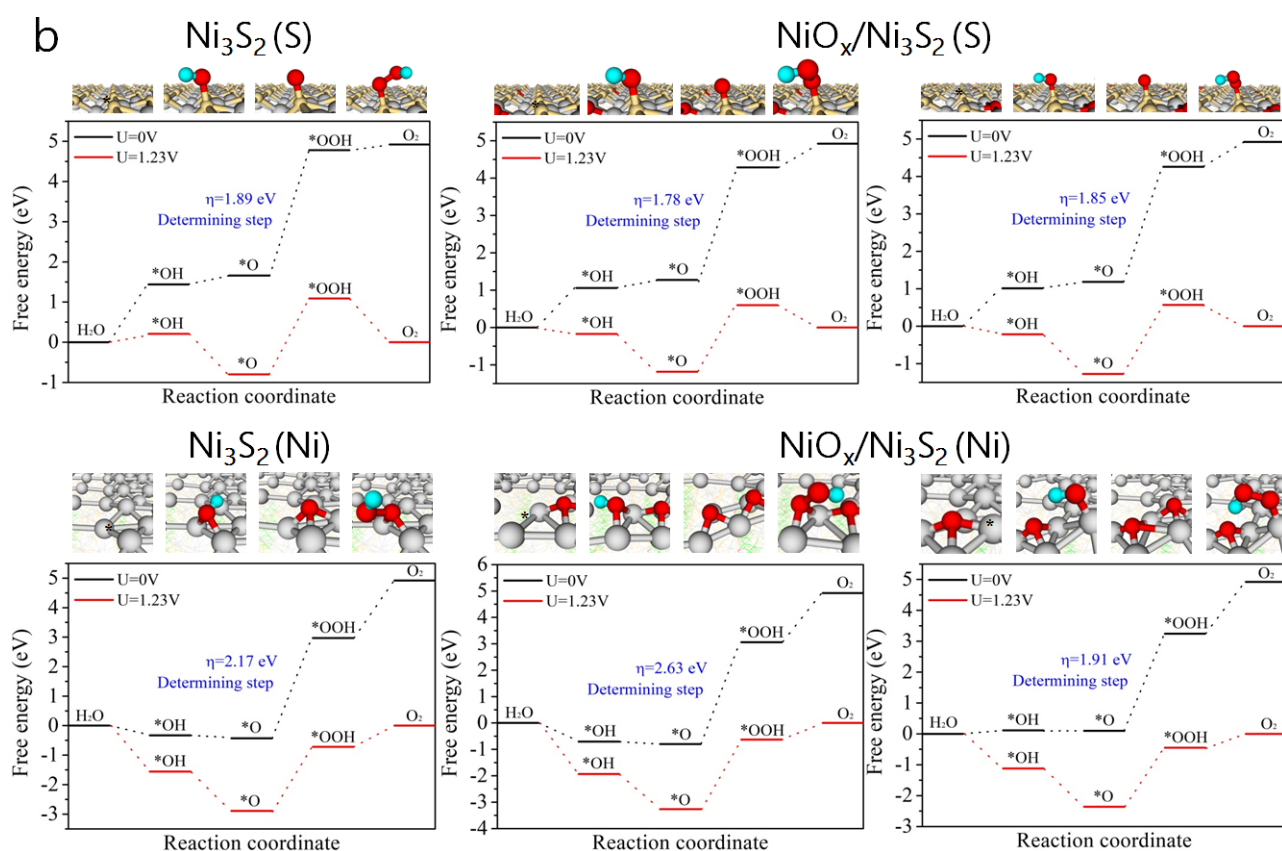


**Supplementary Figure 28.** (ab) OH, O and OOH adsorption configurations and (cd) free energy diagrams for OER on the surface of (ac) NiMoS and (bd) NiMoO<sub>x</sub>/NiMoS.

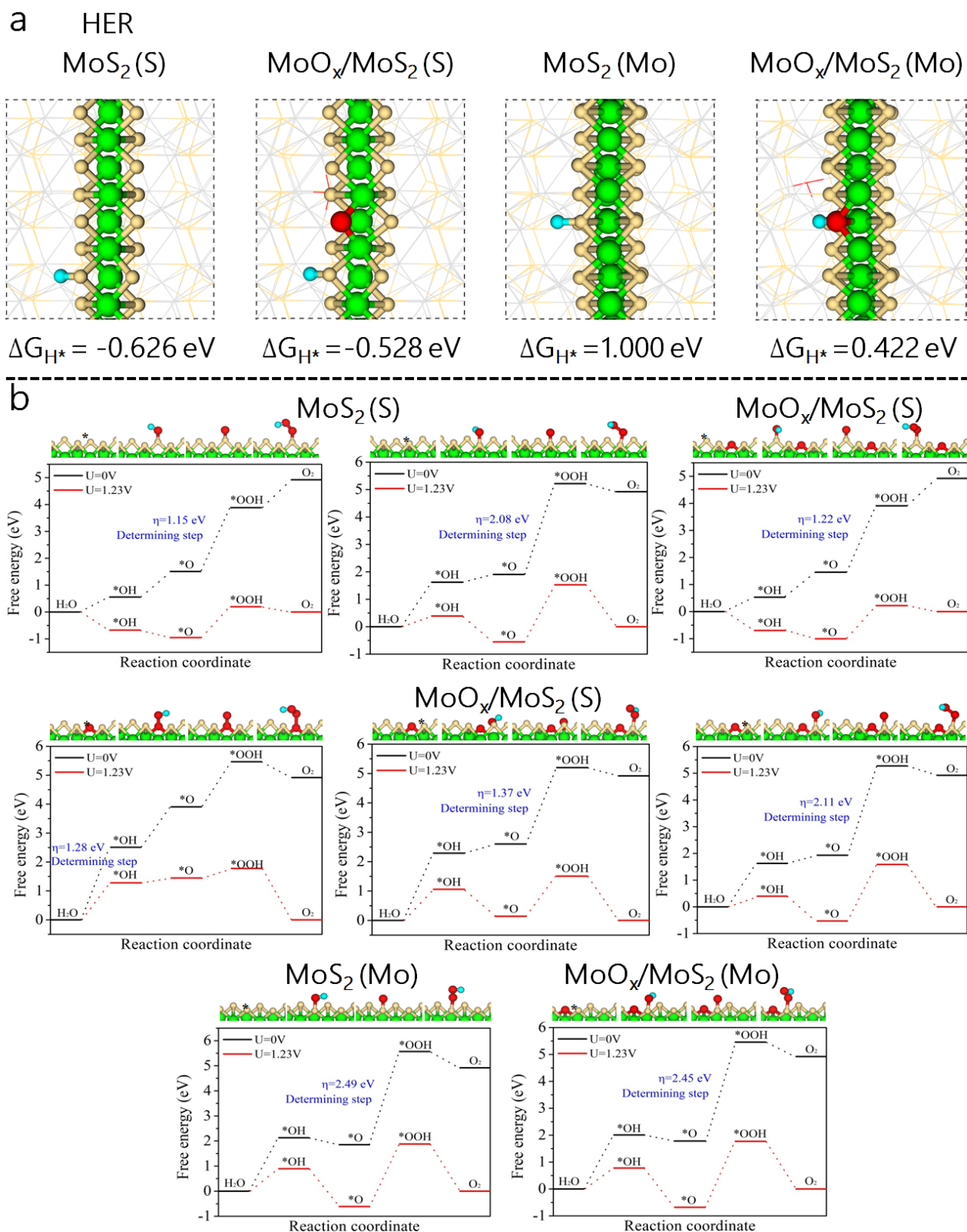
a HER



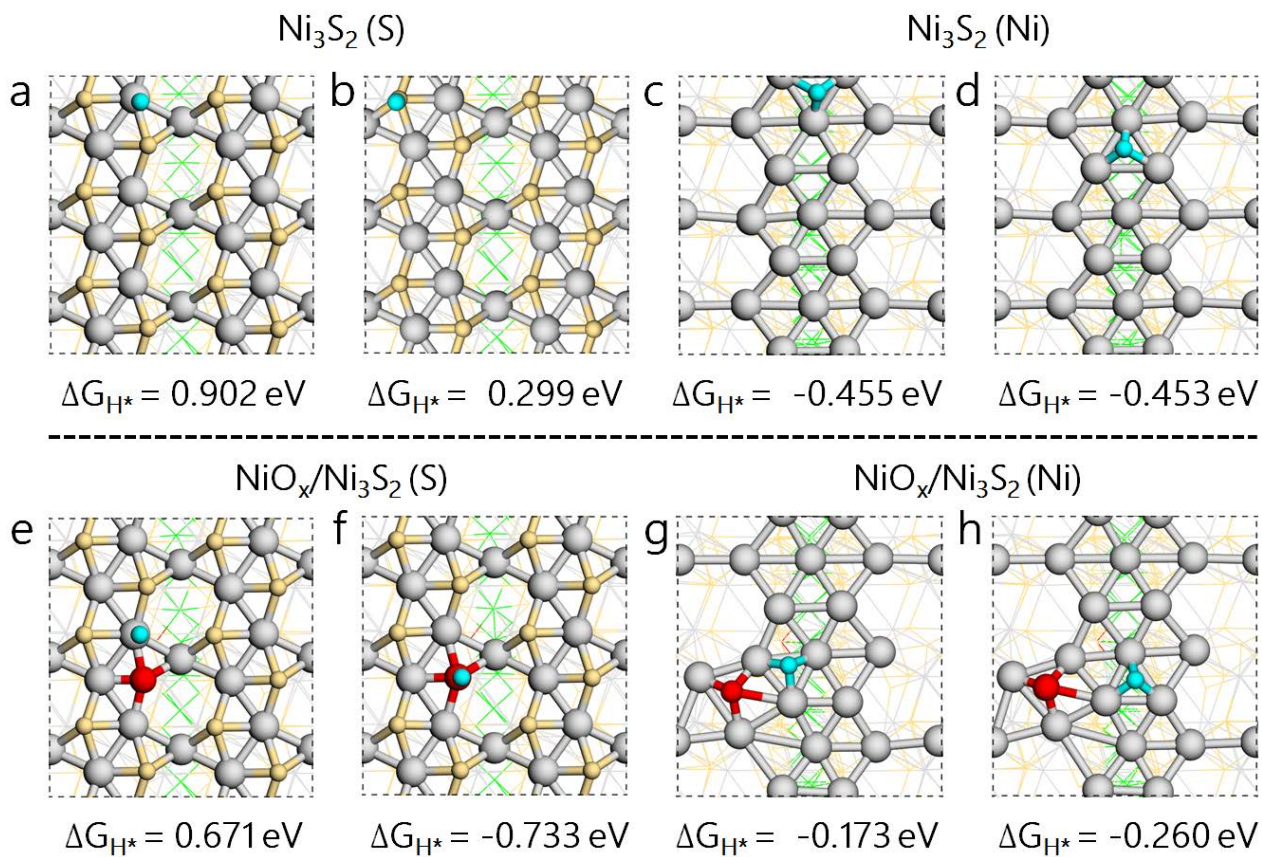
b



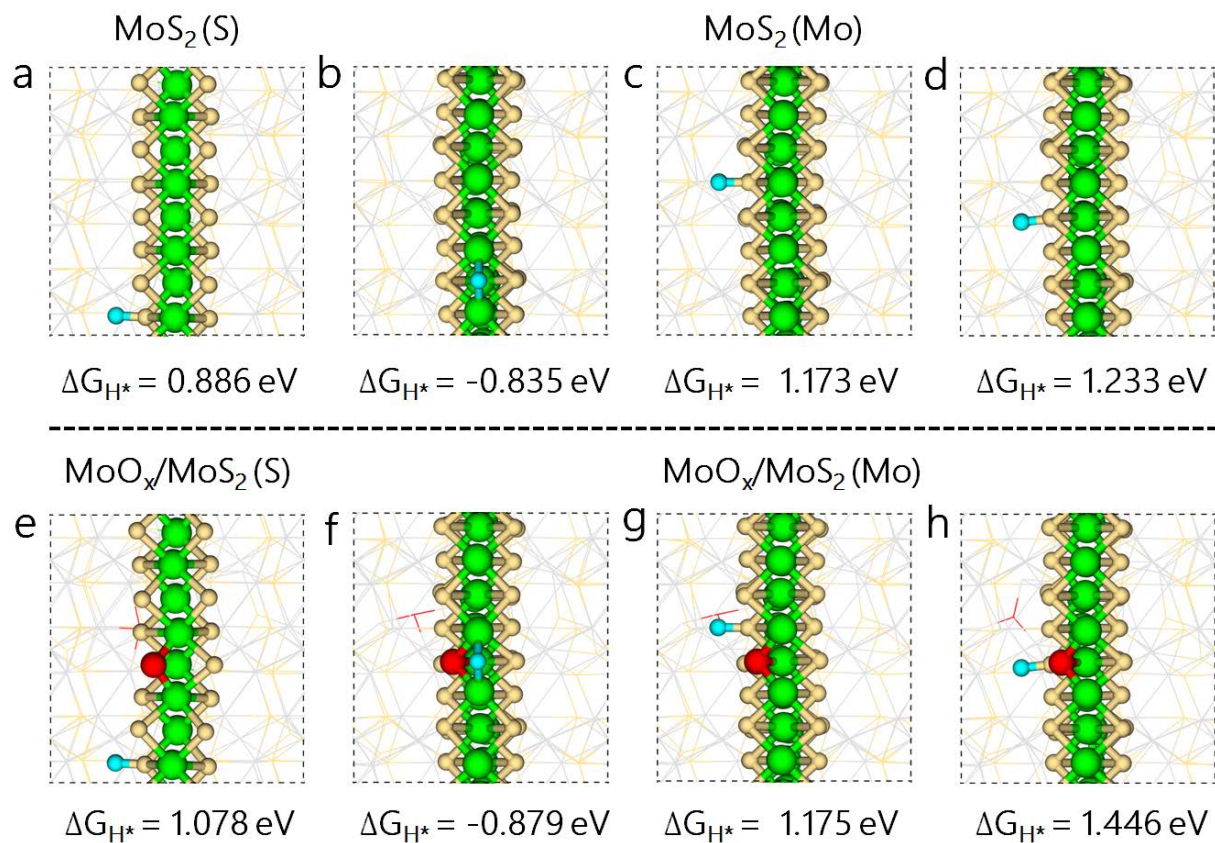
**Supplementary Figure 29.** (a) Chemisorption models and Gibbs free energies of H on the surface of  $\text{Ni}_3\text{S}_2(\text{S})$ ,  $\text{NiO}_x/\text{Ni}_3\text{S}_2(\text{S})$ ,  $\text{Ni}_3\text{S}_2(\text{Ni})$  and  $\text{NiO}_x/\text{Ni}_3\text{S}_2(\text{Ni})$ . (b) OH, O and OOH adsorption configurations for OER on the surface of  $\text{Ni}_3\text{S}_2(\text{S})$ ,  $\text{Ni}_3\text{S}_2(\text{Ni})$ ,  $\text{NiO}_x/\text{Ni}_3\text{S}_2(\text{S})$  and  $\text{NiO}_x/\text{Ni}_3\text{S}_2(\text{Ni})$  and free energy diagrams.



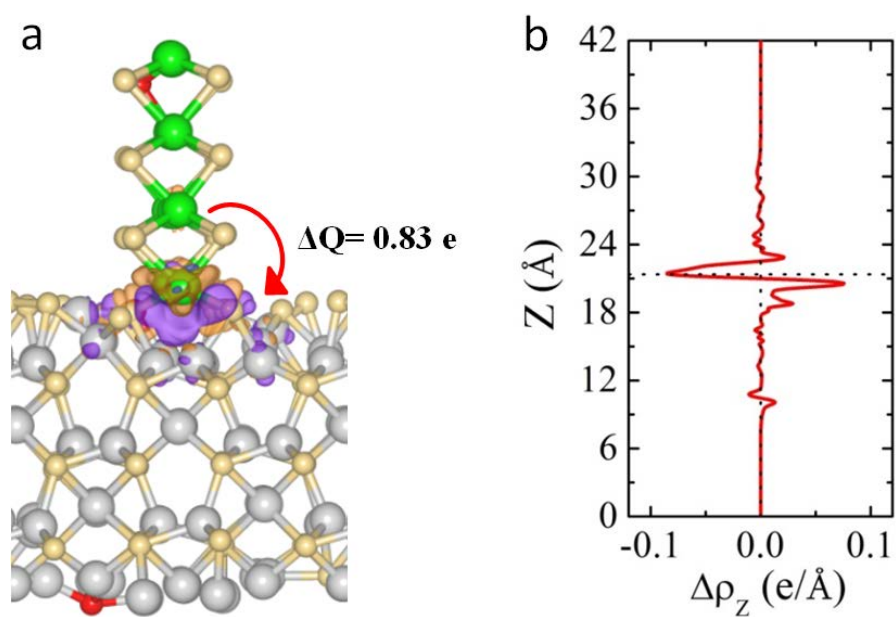
**Supplementary Figure 30.** (a) Chemisorption models and Gibbs free energies of H on the edge of MoS<sub>2</sub> (S), MoO<sub>x</sub>/MoS<sub>2</sub> (S), MoS<sub>2</sub> (Mo) and MoO<sub>x</sub>/MoS<sub>2</sub> (Mo). (b) OH, O and OOH adsorption configurations for OER on the edge of MoS<sub>2</sub> (S), MoO<sub>x</sub>/MoS<sub>2</sub> (S), MoS<sub>2</sub> (Mo) and MoO<sub>x</sub>/MoS<sub>2</sub> (Mo) and free energy diagrams.



**Supplementary Figure 31.** Possible H adsorption sites on the surface of (a,b) Ni<sub>3</sub>S<sub>2</sub> (S), (c,d) Ni<sub>3</sub>S<sub>2</sub> (Ni), (e, f) NiO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub> (S) and (g,h) NiO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub> (Ni) and free energies.



**Supplementary Figure 32.** Possible H adsorption sites on the edge of (a) MoS<sub>2</sub>(S), (b-d) MoS<sub>2</sub>(Mo), (e) MoO<sub>x</sub>/MoS<sub>2</sub>(S) and (f-h) MoO<sub>x</sub>/MoS<sub>2</sub>(Mo) and free energies.



**Supplementary Figure 33.** (a) The charge density difference and (b) the plane-averaged charge density difference  $\Delta\rho_z$  along the Z direction of NiMoO<sub>x</sub>/NiMoS. The purple and orange regions represent the charge accumulation and depletion, respectively.

**Supplementary Table 1.** Comparison of HER activities for various electrocatalysts.

| Catalysts                                                                            | Overpotential @10mA cm <sup>-2</sup> | Tafel slope (mV/dec) | Reference |
|--------------------------------------------------------------------------------------|--------------------------------------|----------------------|-----------|
| Pt <sub>1</sub> /N-C                                                                 | 46 mV                                | 36.8                 | [1]       |
| P,W co doped Co <sub>3</sub> N                                                       | 41 mV                                | 40                   | [2]       |
| C-doped MoS <sub>2</sub>                                                             | 45 mV                                | 46                   | [3]       |
| FeCoNi-HNTAs                                                                         | 58 mV                                | 37.5                 | [4]       |
| Ni-Co with 1T MoS <sub>2</sub>                                                       | 70 mV                                | 38.1                 | [5]       |
| MoS <sub>2</sub> /Co <sub>9</sub> S <sub>8</sub> /Ni <sub>3</sub> S <sub>2</sub> /Ni | 113 mV                               | 85                   | [6]       |
| (Ru-Co)O <sub>x</sub>                                                                | 44.1 mV                              | 23.5                 | [7]       |
| sc-Ni <sub>2</sub> P <sup>δ-</sup> /NiHO                                             | 60 mV                                | 75                   | [8]       |
| Ni-MoS <sub>2</sub>                                                                  | 98 mV                                | 60                   | [9]       |
| MoO <sub>3</sub> /Ni-NiO                                                             | 62 mV                                | 59                   | [10]      |
| Co-Ni <sub>3</sub> N                                                                 | 194 mV                               | 156                  | [11]      |
| R-MoS <sub>2</sub> @NF                                                               | 71 mV                                | 100                  | [12]      |
| Co@N-CNTs@rGO                                                                        | 108 mV                               | 55                   | [13]      |
| O-CoMoS                                                                              | 97 mV                                | 70                   | [14]      |
| Ni(OH) <sub>2</sub> /MoS <sub>2</sub>                                                | 80 mV                                | 60                   | [15]      |
| MoS <sub>2</sub> /NiS <sub>2</sub>                                                   | 62 mV                                | 50.1                 | [16]      |
| MoS <sub>2</sub> /NiS NCs                                                            | 92 mV                                | 113                  | [17]      |
| NiMoO <sub>x</sub> /NiMoS                                                            | 38 mV                                | 38                   | This work |

**Supplementary Table 2.** The turnover frequency (TOF) per site for various HER electrocatalysts at different overpotentials in alkaline condition.

| Catalysts                                        | TOF values            |                        |                       |
|--------------------------------------------------|-----------------------|------------------------|-----------------------|
|                                                  | $\eta=50$ mV          | $\eta=100$ mV          | $\eta=200$ mV         |
| NiMoO <sub>x</sub> /NiMoS                        | 0.28 s <sup>-1</sup>  | 1.97 s <sup>-1</sup>   | 10.08 s <sup>-1</sup> |
| NiO <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> | 0.16 s <sup>-1</sup>  | 0.59 s <sup>-1</sup>   | 3.80 s <sup>-1</sup>  |
| MoO <sub>x</sub> /MoS <sub>2</sub>               | 0.007 s <sup>-1</sup> | 0.027 s <sup>-1</sup>  | 0.35 s <sup>-1</sup>  |
| NiMoS                                            | 0.004 s <sup>-1</sup> | 0.0435 s <sup>-1</sup> | 0.13 s <sup>-1</sup>  |

**Supplementary Table 3.** Comparison of TOF values of HER catalysts in alkaline condition.

| Catalysts                                     | TOF (H <sub>2</sub> s <sup>-1</sup> @ mV) | Reference                 |
|-----------------------------------------------|-------------------------------------------|---------------------------|
| NiCo <sub>2</sub> P <sub>x</sub>              | 0.056 s <sup>-1</sup> at 100 mV           | <a href="#">18</a>        |
| MoNi <sub>4</sub> /MoO <sub>3-x</sub>         | 1.13 s <sup>-1</sup> at 100 mV            | <a href="#">19</a>        |
| N-NiCo <sub>2</sub> S <sub>4</sub>            | 1.0 s <sup>-1</sup> at 125 mV             | <a href="#">20</a>        |
| NiO@1T MoS <sub>2</sub>                       | 0.7 s <sup>-1</sup> at 130 mV             | <a href="#">21</a>        |
| Mo <sub>1</sub> N <sub>1</sub> C <sub>2</sub> | 1.46 s <sup>-1</sup> at 150 mV            | <a href="#">22</a>        |
| Co-NiS <sub>2</sub>                           | 4.1 s <sup>-1</sup> at 200 mV             | <a href="#">23</a>        |
| MoO <sub>3</sub> @MoS <sub>2</sub>            | 1.93 s <sup>-1</sup> at 250 mV            | <a href="#">24</a>        |
| NiMoO <sub>x</sub> /NiMoS                     | 0.28 s <sup>-1</sup> at 50 mV             | <a href="#">this work</a> |
| NiMoO <sub>x</sub> /NiMoS                     | 1.97 s <sup>-1</sup> at 100 mV            | <a href="#">this work</a> |

**Supplementary Table 4.** Comparison of mass activity of HER electrocatalysts.

| Catalysts                                      | Mass activity ( $\text{A g}^{-1}$ ) | Reference                 |
|------------------------------------------------|-------------------------------------|---------------------------|
| Ru@MWCNT                                       | 186 $\text{A g}^{-1}$ at 20mV       | <a href="#">[25]</a>      |
| Co-NiS <sub>2</sub>                            | 100 $\text{A g}^{-1}$ at 185mV      | <a href="#">[23]</a>      |
| NiS <sub>2</sub>                               | 150 $\text{A g}^{-1}$ at 300mV      | <a href="#">[23]</a>      |
| NiCoN/C                                        | 204 $\text{A g}^{-1}$ at 200mV      | <a href="#">[26]</a>      |
| R-MoS <sub>2</sub> @NF                         | 40 $\text{A g}^{-1}$ at 100mV       | <a href="#">[12]</a>      |
| A-MoS <sub>2</sub>                             | 40 $\text{A g}^{-1}$ at 300mV       | <a href="#">[12]</a>      |
| Pt-CoS <sub>2</sub> /CC                        | 2.1 $\text{A g}^{-1}$ at 100mV      | <a href="#">[27]</a>      |
| Pt@PCM                                         | 600 $\text{A g}^{-1}$ at 185mV      | <a href="#">[28]</a>      |
| O <sub>v</sub> -Co <sub>3</sub> O <sub>4</sub> | 2.12 $\text{A g}^{-1}$ at 200mV     | <a href="#">[29]</a>      |
| NiMoO <sub>x</sub> /NiMoS                      | 436 $\text{A g}^{-1}$ at 200mV      | <a href="#">this work</a> |

**Supplementary Table 5.** Comparison of OER activities for various electrocatalysts.

| Catalysts                                                                            | Overpotential @10mA cm <sup>-2</sup> | Tafel slope (mV/dec) | Reference |
|--------------------------------------------------------------------------------------|--------------------------------------|----------------------|-----------|
| np-Ir/NiFeO                                                                          | 197 mV                               | 29.6                 | [30]      |
| CoBDC-FC <sub>0.17</sub>                                                             | 291 mV                               | 61                   | [31]      |
| W-Ni(OH) <sub>2</sub>                                                                | 237 mV                               | 33                   | [32]      |
| Ru/CoFe-LDHs                                                                         | 198 mV                               | 39                   | [33]      |
| Ni-Co with 1T MoS <sub>2</sub>                                                       | 235 mV                               | 45.7                 | [5]       |
| Ir-NiO                                                                               | 215 mV                               | 38                   | [34]      |
| FeOOH(Se)/IF                                                                         | 287 mV                               | 54                   | [35]      |
| MoS <sub>2</sub> /Co <sub>9</sub> S <sub>8</sub> /Ni <sub>3</sub> S <sub>2</sub> /Ni | 166 mV                               | 58                   | [6]       |
| P-Co <sub>3</sub> O <sub>4</sub>                                                     | 280 mV                               | 51.6                 | [36]      |
| Ni/Ni(OH) <sub>2</sub>                                                               | 270 mV                               | 53                   | [37]      |
| W <sub>2</sub> N/WC                                                                  | 320 mV                               | 122.8                | [38]      |
| NiTe/NiS                                                                             | 244 mV                               | 49                   | [39]      |
| Co <sub>1.8</sub> Ni(OH) <sub>5.6</sub>                                              | 274 mV                               | 45                   | [40]      |
| @Co <sub>1.8</sub> NiS <sub>0.4</sub> (OH) <sub>4.8</sub>                            |                                      |                      |           |
| δ-FeOOH NSs/NF                                                                       | 265 mV                               | 69                   | [41]      |
| Co-Ni <sub>3</sub> N                                                                 | 307 mV                               | 57                   | [11]      |
| Porous Ni <sub>3</sub> S <sub>4</sub>                                                | 257 mV                               | 67                   | [42]      |
| O-CoMoS                                                                              | 272 mV                               | 45                   | [14]      |
| NiMoO <sub>x</sub> /NiMoS                                                            | 186 mV                               | 34                   | This work |

**Supplementary Table 6.** Comparison of overall water splitting activities of bifunctional electrocatalysts.

| Catalysts                          | Electrolyte | Potential | Reference            |
|------------------------------------|-------------|-----------|----------------------|
| RuIrO <sub>x</sub>                 | alkaline    | 1.47V     | <a href="#">[43]</a> |
| a-RuTe                             | acid        | 1.52V     | <a href="#">[44]</a> |
| Ni-Fe NPs                          | alkaline    | 1.47V     | <a href="#">[45]</a> |
| IFONFs                             | alkaline    | 1.58V     | <a href="#">[46]</a> |
| NiFe-NiMo/Ni-P                     | alkaline    | 1.51V     | <a href="#">[47]</a> |
| NiFe MOF                           | alkaline    | 1.55V     | <a href="#">[48]</a> |
| NiFeO <sub>x</sub> /CNF            | alkaline    | 1.51V     | <a href="#">[49]</a> |
| CoMoNiS-NF                         | alkaline    | 1.54V     | <a href="#">[6]</a>  |
| EBP@EG                             | alkaline    | 1.54V     | <a href="#">[50]</a> |
| R-NiCo <sub>2</sub> O <sub>4</sub> | alkaline    | 1.61V     | <a href="#">[51]</a> |
| CoP/NCNHP                          | alkaline    | 1.64V     | <a href="#">[52]</a> |
| Ni <sub>3</sub> S <sub>2</sub>     | alkaline    | 1.76V     | <a href="#">[53]</a> |
| CoMnO@CN                           | alkaline    | 1.5V      | <a href="#">[54]</a> |
| MoO <sub>3</sub> /Ni-NiO           | alkaline    | 1.55V     | <a href="#">[10]</a> |
| Ni/Ni(OH) <sub>2</sub>             | alkaline    | 1.59V     | <a href="#">[37]</a> |
| Co <sub>2</sub> P/CoNPC            | alkaline    | 1.64V     | <a href="#">[55]</a> |
| W <sub>2</sub> N/WC                | alkaline    | 1.58V     | <a href="#">[38]</a> |
| CoFeZr oxides                      | alkaline    | 1.63V     | <a href="#">[56]</a> |
| Cr-FeNi-P/NCN                      | alkaline    | 1.50V     | <a href="#">[57]</a> |
| Co/CNFs                            | alkaline    | 1.69V     | <a href="#">[58]</a> |

---

|                                                                           |           |        |                      |
|---------------------------------------------------------------------------|-----------|--------|----------------------|
| Co <sub>3</sub> S <sub>4</sub> /EC-MOF                                    | alkaline  | 1.55V  | <a href="#">[59]</a> |
| Co-RuIr                                                                   | acid      | 1.52V  | <a href="#">[60]</a> |
| Fe <sub>0.09</sub> Co <sub>0.13</sub> -NiSe <sub>2</sub>                  | alkaline  | 1.52V  | <a href="#">[61]</a> |
| Se-(NiCo)S/OH                                                             | alkaline  | 1.6V   | <a href="#">[62]</a> |
| SrCo <sub>0.85</sub> Fe <sub>0.1</sub> P <sub>0.05</sub> O <sub>3-δ</sub> | alkaline  | 1.66V  | <a href="#">[63]</a> |
| Co-MoS <sub>2</sub> /BCCF                                                 | alkaline  | 1.55V  | <a href="#">[64]</a> |
| CoP NC                                                                    | alkaline  | 1.56V  | <a href="#">[65]</a> |
| δ-FeOOH NSs/NF                                                            | alkaline  | 1.62V  | <a href="#">[41]</a> |
| Pt/LiCoO <sub>2</sub>                                                     | alkaline  | 1.54V  | <a href="#">[66]</a> |
| Co/β-Mo <sub>2</sub> C@N-CNTs                                             | alkaliine | 1.64V  | <a href="#">[67]</a> |
| Ir <sub>1</sub> @Co/NC                                                    | alkaline  | 1.603V | <a href="#">[68]</a> |
| RuCu NSs/C                                                                | alkaline  | 1.49V  | <a href="#">[69]</a> |
| CoSn <sub>2</sub>                                                         | alkaline  | 1.55V  | <a href="#">[70]</a> |
| Fe-Ni@NC-CNTs                                                             | alkaline  | 1.58V  | <a href="#">[71]</a> |
| Ni <sub>0.1</sub> Co <sub>0.9</sub> P                                     | neutral   | 1.89V  | <a href="#">[72]</a> |
| Ni <sub>5</sub> P <sub>4</sub>                                            | alkaline  | 1.70 V | <a href="#">[73]</a> |
| Ni/Mo <sub>2</sub> C                                                      | alkaline  | 1.64 V | <a href="#">[74]</a> |
| Pt-CoS <sub>2</sub> /CC                                                   | alkaline  | 1.55 V | <a href="#">[27]</a> |
| Fe-Ni-MoN                                                                 | alkaline  | 1.51 V | <a href="#">[75]</a> |
| N-NiMoO <sub>4</sub> /NiS <sub>2</sub>                                    | alkaline  | 1.6 V  | <a href="#">[76]</a> |
| NC/CuCo/CuCoO <sub>x</sub>                                                | alkaline  | 1.53 V | <a href="#">[77]</a> |
| NC/NiCu/NiCuN                                                             | alkaline  | 1.56V  | <a href="#">[78]</a> |

---

|                                      |          |        |                           |
|--------------------------------------|----------|--------|---------------------------|
| NiCo <sub>2</sub> S <sub>4</sub>     | alkaline | 1.68 V | <a href="#">[79]</a>      |
| O-CoMoS                              | alkaline | 1.60 V | <a href="#">[14]</a>      |
| P-Co <sub>3</sub> O <sub>4</sub> /NF | alkaline | 1.63 V | <a href="#">[80]</a>      |
| NiMoO <sub>x</sub> /NiMoS            | alkaline | 1.46V  | <a href="#">this work</a> |

**Supplementary Table 7.** Comparison of overall water splitting activities of bifunctional electrocatalysts with high current at 500 mA cm<sup>-2</sup>.

| Catalysts                                            | Potential | Reference                 |
|------------------------------------------------------|-----------|---------------------------|
| FeP/Ni <sub>2</sub> P                                | 1.72 V    | <a href="#">[81]</a>      |
| RFNOH-10  NiFe-LDH/NF                                | 1.69 V    | <a href="#">[82]</a>      |
| Cu@NiFe LDH  Ni <sub>2(1-x)</sub> Mo <sub>2x</sub> P | 1.82 V    | <a href="#">[83]</a>      |
| Ni NWs  Ni <sub>0.8</sub> Fe <sub>0.2</sub> -AHNA    | 1.702 V   | <a href="#">[84]</a>      |
| MoNi <sub>4</sub> /SSW  SSW Rs-12h                   | 1.978 V   | <a href="#">[85]</a>      |
| NFN-MOF/NF                                           | 1.9 V     | <a href="#">[86]</a>      |
| NiMoO <sub>x</sub> /NiMoS  NiMoO <sub>x</sub> /NiMoS | 1.6 V     | <a href="#">this work</a> |

**Supplementary Table 8.** Entropy and zero point energy used for calculated the free energy of the intermediate in this work.

|                                   | TS (eV) | TΔS (eV) | ZPE (eV) | ΔZPE (eV) | ΔZPE-TΔS(eV) |
|-----------------------------------|---------|----------|----------|-----------|--------------|
| H <sub>2</sub> O <sup>[1]</sup>   | 0.67    | 0        | 0.56     | 0         | 0            |
| *OH+1/2H <sub>2</sub>             | 0.33    | -0.34    | 0.50     | -0.06     | 0.28         |
| *O+H <sub>2</sub>                 | 0.48    | -0.19    | 0.34     | -0.22     | -0.03        |
| *OOH+3/2H <sub>2</sub>            | 0.75    | -0.59    | 0.87     | -0.25     | 0.34         |
| H <sub>2</sub> <sup>[87,88]</sup> | 0.41    | -        | 0.27     | -         | -            |
| *OH                               | 0.12    | -        | 0.36     | -         | -            |
| *O                                | 0.07    | -        | 0.07     | -         | -            |
| *OOH                              | 0.13    | -        | 0.46     | -         | -            |

### Supplementary Note 1. Calculation of TOF.

The TOF values ( $\text{s}^{-1}$ ) were calculated with the following formula:

$$\text{TOF} = \frac{I}{2nF} \quad (1)$$

I: current density extracted from the LSV curves;

F: Faraday constant;

n: the number of active sites. Cycle voltammetry measurements were conducted between -0.2 V and 0.6 V vs. RHE in 1M PBS (pH=7) at a scan rate of  $50 \text{ mV s}^{-1}$ . The absolute components of the voltammetric charges tested during one CV cycle were calculated. Assuming a one-electron process for both reduction and oxidation, the absolute charges was divided by two and the Faraday constant to get the number of active sites of the catalysts. The upper limit of active sites for NiMoO<sub>x</sub>/NiMoS could be calculated according to the equation:

$$n = Q/2F \quad (2)$$

## Supplementary References

1. Fang, S. et al. Uncovering near-free platinum single-atom dynamics during electrochemical hydrogen evolution reaction. *Nat. Commun.* **11**, 1029 (2020).
2. Liu, Y. et al. Manipulating dehydrogenation kinetics through dual-doping Co<sub>3</sub>N electrode enables highly efficient hydrazine oxidation assisting self-powered H<sub>2</sub> production. *Nat. Commun.* **11**, 1853 (2020).
3. Zang, Y. et al. Tuning orbital orientation endows molybdenum disulfide with exceptional alkaline hydrogen evolution capability. *Nat. Commun.* **10**, 1217 (2019).
4. Li, H. et al. Systematic design of superaerophobic nanotube-array electrode comprised of transition-metal sulfides for overall water splitting. *Nat. Commun.* **9**, 2452 (2018).
5. Li, H. et al. Amorphous nickel-cobalt complexes hybridized with 1T-phase molybdenum disulfide via hydrazine-induced phase transformation for water splitting. *Nat. Commun.* **8**, 15377 (2017).
6. Yang, Y. et al. Hierarchical nanoassembly of MoS<sub>2</sub>/Co<sub>9</sub>S<sub>8</sub>/Ni<sub>3</sub>S<sub>2</sub>/Ni as a highly efficient electrocatalyst for overall water splitting in a wide pH range. *J. Am. Chem. Soc.* **141**, 10417-10430 (2019).
7. Wang, C. and Qi, L. Heterostructured inter-doped ruthenium-cobalt oxide hollow nanosheet arrays for highly efficient overall water splitting. *Angew. Chem. Int. Ed.* **59**, 17219-17224 (2020).
8. You, B. et al. Negative charging of transition-metal phosphides via strong electronic coupling for destabilization of alkaline water. *Angew. Chem. Int. Ed.* **58**, 11796-11800 (2019).
9. Zhang, J. et al. Engineering water dissociation sites in MoS<sub>2</sub> nanosheets for accelerated electrocatalytic hydrogen production. *Energy Environ. Sci.* **9**, 2789-2793 (2016).
10. Li, X. et al. Sequential electrodeposition of bifunctional catalytically active structures in MoO<sub>3</sub>/Ni-NiO composite electrocatalysts for selective hydrogen and oxygen evolution. *Adv. Mater.* **32**, 2003414 (2020).
11. Zhu, C. et al. In situ grown epitaxial heterojunction exhibits high-performance electrocatalytic water splitting. *Adv. Mater.* **30**, 1705516 (2018).
12. Anjum, M. A. R. et al. Efficient hydrogen evolution reaction catalysis in alkaline media by all-in-one MoS<sub>2</sub> with multifunctional active sites. *Adv. Mater.* **30**, 1707105 (2018).
13. Chen, Z. et al. Ultrafine Co nanoparticles encapsulated in carbon-nanotubes-grafted graphene sheets as advanced electrocatalysts for the hydrogen evolution reaction. *Adv. Mater.* **30**, 1802011 (2018).
14. Hou, J. et al. Vertically aligned oxygenated-CoS<sub>2</sub>-MoS<sub>2</sub> heteronanosheet architecture from polyoxometalate for efficient and stable overall water splitting. *ACS Catal.* **8**, 4612-4621 (2018).
15. Zhang, B. et al. Interface engineering: The Ni(OH)<sub>2</sub>/MoS<sub>2</sub> heterostructure for highly efficient alkaline hydrogen evolution. *Nano Energy* **37**, 74-80 (2017).
16. Lin, J. et al. Defect-rich heterogeneous MoS<sub>2</sub>/NiS<sub>2</sub> nanosheets electrocatalysts for efficient overall water splitting. *Adv. Sci.* **6**, 1900246 (2019).

17. Zhai, Z. et al. Dimensional construction and morphological tuning of heterogeneous MoS<sub>2</sub>/NiS electrocatalysts for efficient overall water splitting. *J. Mater. Chem. A* **6**, 9833-9838 (2018).
18. Zhang, R. et al. Ternary NiCo<sub>2</sub>P<sub>x</sub> nanowires as pH-universal electrocatalysts for highly efficient hydrogen evolution reaction. *Adv. Mater.* **29**, 1605502 (2017).
19. Chen, Y. Y. et al. Self-templated fabrication of MoNi<sub>4</sub>/MoO<sub>3-x</sub> nanorod arrays with dual active components for highly efficient hydrogen evolution. *Adv. Mater.* **29**, 1703311 (2017).
20. Wu, Y. et al. Electron density modulation of NiCo<sub>2</sub>S<sub>4</sub> nanowires by nitrogen incorporation for highly efficient hydrogen evolution catalysis. *Nat. Commun.* **9**, 1425 (2018).
21. Huang, Y. et al. Atomically engineering activation sites onto metallic 1T-MoS<sub>2</sub> catalysts for enhanced electrochemical hydrogen evolution. *Nat. Commun.* **10**, 982 (2019).
22. Chen, W. et al. Rational design of single molybdenum atoms anchored on n-doped carbon for effective hydrogen evolution reaction. *Angew. Chem. Int. Ed.* **56**, 16086-16090 (2017).
23. Yin, J. et al. Atomic arrangement in metal-doped NiS<sub>2</sub> boosts the hydrogen evolution reaction in alkaline media. *Angew. Chem. Int. Ed.* **58**, 18676-18682 (2019).
24. Huang, L. B. et al. Self-limited on-site conversion of MoO<sub>3</sub> nanodots into vertically aligned ultrasmall monolayer MoS<sub>2</sub> for efficient hydrogen evolution. *Adv. Energy Mater.* **8**, 1800734 (2018).
25. Kweon, D. H. et al. Ruthenium anchored on carbon nanotube electrocatalyst for hydrogen production with enhanced Faradaic efficiency. *Nat. Commun.* **11**, 1278 (2020).
26. Lai, J. et al. Strongly coupled nickel-cobalt nitrides/carbon hybrid nanocages with Pt-like activity for hydrogen evolution catalysis. *Adv. Mater.* **31**, 1805541 (2019).
27. Han, X. et al. Ultrafine Pt nanoparticle-decorated pyrite-type CoS<sub>2</sub> nanosheet arrays coated on carbon cloth as a bifunctional electrode for overall water splitting. *Adv. Energy Mater.* **8**, 1800935 (2018).
28. Zhang, H. B. et al. Dynamic traction of lattice-confined platinum atoms into mesoporous carbon matrix for hydrogen evolution reaction. *Sci. Adv.* **4**, eaao6657 (2018).
29. Zhang, H. et al. Continuous oxygen vacancy engineering of the Co<sub>3</sub>O<sub>4</sub> layer for an enhanced alkaline electrocatalytic hydrogen evolution reaction. *J. Mater. Chem. A* **7**, 13506-13510 (2019).
30. Jiang, K. et al. Dynamic active-site generation of atomic iridium stabilized on nanoporous metal phosphides for water oxidation. *Nat. Commun.* **11**, 2701 (2020).
31. Xue, Z. et al. Missing-linker metal-organic frameworks for oxygen evolution reaction. *Nat. Commun.* **10**, 5048 (2019).
32. Yan, J. et al. Single atom tungsten doped ultrathin  $\alpha$ -Ni(OH)<sub>2</sub> for enhanced electrocatalytic water oxidation. *Nat. Commun.* **10**, 2149 (2019).
33. Li, P. et al. Boosting oxygen evolution of single-atomic ruthenium through electronic coupling with cobalt-iron layered double hydroxides. *Nat. Commun.* **10**, 1711 (2019).

34. Wang, Q. et al. Ultrahigh-loading of Ir single atoms on NiO matrix to dramatically enhance oxygen evolution reaction. *J. Am. Chem. Soc.* **142**, 7425-7433 (2020)
35. Niu, S. et al. Se-doping activates FeOOH for cost-effective and efficient electrochemical water oxidation. *J. Am. Chem. Soc.* **141**, 7005-7013 (2019).
36. Xiao, Z. et al. Filling the oxygen vacancies in Co<sub>3</sub>O<sub>4</sub> with phosphorus: an ultra-efficient electrocatalyst for overall water splitting. *Energy Environ. Sci.* **10**, 2563-2569 (2017).
37. Dai, L. et al. Ultrathin Ni(0)-embedded Ni(OH)<sub>2</sub> heterostructured nanosheets with enhanced electrochemical overall water splitting. *Adv. Mater.* **32**, 1906915 (2020).
38. Diao, J. et al. Interfacial engineering of W<sub>2</sub>N/WC heterostructures derived from solid-state synthesis: a highly efficient trifunctional electrocatalyst for ORR, OER, and HER. *Adv. Mater.* **32**, 1905679 (2020).
39. Xue, Z. et al. Interfacial electronic structure modulation of NiTe nanoarrays with NiS nanodots facilitates electrocatalytic oxygen evolution. *Adv. Mater.* **31**, 1900430 (2019).
40. Wang, B. et al. A nanosized CoNi hydroxide@hydroxysulfide core-shell heterostructure for enhanced oxygen evolution. *Adv. Mater.* **31**, 1805658 (2019).
41. Liu, B. et al. Iron vacancies induced bifunctionality in ultrathin ferroxhyte nanosheets for overall water splitting. *Adv. Mater.* **30** 1803144 (2018).
42. Wan, K. et al. Hierarchical porous Ni<sub>3</sub>S<sub>4</sub> with enriched high-valence Ni sites as a robust electrocatalyst for efficient oxygen evolution reaction. *Adv. Funct. Mater.* **29**, 1900315 (2019).
43. Zhuang, Z. et al. Three-dimensional open nano-netcage electrocatalysts for efficient pH-universal overall water splitting. *Nat. Commun.* **10**, 4875 (2019).
44. Wang, J. et al. Amorphization activated ruthenium-tellurium nanorods for efficient water splitting. *Nat. Commun.* **10**, 5692 (2019).
45. Suryanto, B. H. R. et al. Overall electrochemical splitting of water at the heterogeneous interface of nickel and iron oxide. *Nat. Commun.* **10**, 5599 (2019).
46. Fan, X. et al. Defect-enriched iron fluoride-oxide nanoporous thin films bifunctional catalyst for water splitting. *Nat. Commun.* **9**, 1809 (2018).
47. Sahasrabudhe, A. et al. Value added transformation of ubiquitous substrates into highly efficient and flexible electrodes for water splitting. *Nat. Commun.* **9**, 2014 (2018).
48. Duan, J. et al. Ultrathin metal-organic framework array for efficient electrocatalytic water splitting. *Nat. Commun.* **8**, 15341 (2017).
49. Wang, H. et al. Bifunctional non-noble metal oxide nanoparticle electrocatalysts through lithium-induced conversion for overall water splitting. *Nat. Commun.* **6**, 7261 (2015).
50. Yuan, Z. et al. Ultrathin black phosphorus-on-nitrogen doped graphene for efficient overall water splitting: dual modulation roles of directional interfacial charge transfer. *J. Am. Chem. Soc.* **141**, 4972-4979 (2019).
51. Peng, S. et al. Necklace-like multishelled hollow spinel oxides with oxygen vacancies for efficient water electrolysis. *J. Am. Chem. Soc.* **140**, 13644-13653 (2018).

52. Pan, Y. et al. Core-shell ZIF-8@ZIF-67-derived CoP nanoparticle-embedded N-doped carbon nanotube hollow polyhedron for efficient overall water splitting. *J. Am. Chem. Soc.* **140**, 2610-2618 (2018).
53. Feng, L. L. et al. High-index faceted Ni<sub>3</sub>S<sub>2</sub> nanosheet arrays as highly active and ultrastable electrocatalysts for water splitting. *J. Am. Chem. Soc.* **137**, 14023-14026 (2015).
54. Li, J. et al. Nanoparticle superlattices as efficient bifunctional electrocatalysts for water splitting. *J. Am. Chem. Soc.* **137**, 14305-14312 (2015).
55. Liu, H. et al. Metal-organic framework-derived Co<sub>2</sub>P nanoparticle/multi-doped porous carbon as a trifunctional electrocatalyst. *Adv. Mater.* **32**, 2003649 (2020).
56. Huang, L. et al. Zirconium-regulation-induced bifunctionality in 3D cobalt-iron oxide nanosheets for overall water splitting. *Adv. Mater.* **31**, 1901439 (2019).
57. Wu, Y. et al. Cr-doped FeNi-P nanoparticles encapsulated into N-doped carbon nanotube as a robust bifunctional catalyst for efficient overall water splitting. *Adv. Mater.* **31**, 1900178 (2019).
58. Yang, Z. et al. Trifunctional self-supporting cobalt-embedded carbon nanotube films for ORR, OER, and HER triggered by solid diffusion from bulk metal. *Adv. Mater.* **31**, 1808043 (2019).
59. Liu, T. et al. Self-sacrificial template-directed vapor-phase growth of mof assemblies and surface vulcanization for efficient water splitting. *Adv Mater* **31**, 1806672 (2019).
60. Shan, J. et al. Transition-metal-doped RuIr bifunctional nanocrystals for overall water splitting in acidic environments. *Adv. Mater.* **31**, 1900510 (2019).
61. Sun, Y. et al. Strong electronic interaction in dual-cation-incorporated NiSe<sub>2</sub> nanosheets with lattice distortion for highly efficient overall water splitting. *Adv. Mater.* **30**, 1802121 (2018).
62. Hu, C. et al. Synergism of geometric construction and electronic regulation: 3D Se-(NiCo)S<sub>x</sub>/(OH)<sub>x</sub> nanosheets for highly efficient overall water splitting. *Adv. Mater.* **30**, 1705538 (2018).
63. Chen, G. et al. A universal strategy to design superior water-splitting electrocatalysts based on fast in situ reconstruction of amorphous nanofilm precursors. *Adv. Mater.* **30**, 1804333 (2018).
64. Xiong, Q. et al. Cobalt covalent doping in MoS<sub>2</sub> to induce bifunctionality of overall water splitting. *Adv. Mater.* **30**, 1801450 (2018).
65. Li, H. et al. Colloidal cobalt phosphide nanocrystals as trifunctional electrocatalysts for overall water splitting powered by a zinc-air battery. *Adv. Mater.* **30**, 1705796 (2018).
66. Zheng, X. et al. Multifunctional active-center-transferable platinum/lithium cobalt oxide heterostructured electrocatalysts towards superior water splitting. *Angew. Chem. Int. Ed.* **59**, 14533-14540 (2020).
67. Ouyang, T. et al. Heterostructures composed of N-doped carbon nanotubes encapsulating cobalt and  $\beta$ -Mo<sub>2</sub>C nanoparticles as bifunctional electrodes for water splitting. *Angew. Chem. Int. Ed.* **58**, 4923-4928 (2019).
68. Lai, W. H. et al. General  $\pi$ -electron-assisted strategy for Ir, Pt, Ru, Pd, Fe, Ni single-atom electrocatalysts with bifunctional active sites for highly efficient water

- splitting. *Angew. Chem. Int. Ed.* **58**, 11868-11873 (2019).
69. Yao, Q. et al. Channel-rich RuCu nanosheets for pH-universal overall water splitting electrocatalysis. *Angew. Chem. Int. Ed.* **58**, 13983-13988 (2019).
  70. Menezes, P. W. et al. Structurally ordered intermetallic cobalt stannide nanocrystals for high-performance electrocatalytic overall water-splitting. *Angew. Chem. Int. Ed.* **57**, 15237-15242 (2018).
  71. Zhao, X. et al. Bifunctional electrocatalysts for overall water splitting from an iron/nickel-based bimetallic metal-organic framework/dicyandiamide composite. *Angew. Chem. Int. Ed.* **57**, 8921-8926 (2018).
  72. Wu, R. et al. A janus nickel cobalt phosphide catalyst for high-efficiency neutral-pH water splitting. *Angew. Chem. Int. Ed.* **57**, 15445-15449 (2018).
  73. Ledendecker, M. et al. The synthesis of nanostructured Ni<sub>5</sub>P<sub>4</sub> films and their use as a non-noble bifunctional electrocatalyst for full water splitting. *Angew. Chem. Int. Ed.* **54**, 12361-12365 (2015).
  74. Li, M. X. et al. Ni strongly coupled with Mo<sub>2</sub>C encapsulated in nitrogen - doped carbon nanofibers as robust bifunctional catalyst for overall water splitting. *Adv. Energy Mater.* **9**, 1803185 (2019).
  75. Zhu, C. L. et al. Fe-Ni-Mo nitride porous nanotubes for full water splitting and zn-air batteries. *Adv. Energy Mater.* **8**, 1802327 (2018).
  76. An, L. et al. Epitaxial heterogeneous interfaces on N-NiMoO<sub>4</sub>-NiS<sub>2</sub> nanowires nanosheets to boost hydrogen and oxygen production for overall water splitting. *Adv. Funct. Mater.* **29**, 1805298 (2019).
  77. Hou, J. et al. Promoting active sites in core-shell nanowire array as mott-schottky electrocatalysts for efficient and stable overall water splitting. *Adv. Funct. Mater.* **28**, 1704447 (2018).
  78. Hou, J. et al. Electrical behavior and electron transfer modulation of nickel-copper nanoalloys confined in nickel-copper nitrides nanowires encapsulated in nitrogen-doped carbon framework as robust bifunctional electrocatalyst for overall water splitting. *Adv. Funct. Mater.* **28**, 1803278 (2018).
  79. Sivanantham, A. et al. Hierarchical NiCo<sub>2</sub>S<sub>4</sub> nanowire arrays supported on Ni foam an efficient and durable bifunctional electrocatalyst for oxygen and hydrogen evolution reactions. *Adv. Funct. Mater.* **26**, 4661-4672 (2016).
  80. Wang, Z. et al. Phosphorus-doped Co<sub>3</sub>O<sub>4</sub> nanowire array a highly efficient bifunctional electrocatalyst for overall water splitting. *ACS Catal.* **8**, 2236-2241 (2018)
  81. Yu, F. et al. High-performance bifunctional porous non-noble metal phosphide catalyst for overall water splitting. *Nat. Commun.* **9**, 2551 (2018).
  82. Xiao, X. et al. In situ growth of Ru nanoparticles on (Fe,Ni)(OH)<sub>2</sub> to boost hydrogen evolution activity at high current density in alkaline media. *Small Methods* **4**, 1900796 (2020).
  83. Yu, L. et al. Ternary Ni<sub>2(1-x)</sub>Mo<sub>2x</sub>P nanowire arrays toward efficient and stable hydrogen evolution electrocatalysis under large-current-density. *Nano Energy* **53**, 492-500 (2018).
  84. Liang, C. et al. Exceptional performance of hierarchical Ni-Fe oxyhydroxide@NiFe

- alloy nanowire array electrocatalysts for large current density water splitting. *Energy Environ. Sci.* **13**, 86-95 (2020).
85. Jothi, V. R. et al. Corrosion and alloy engineering in rational design of high current density electrodes for efficient water splitting. *Adv. Energy Mater.* **10**, 1904020 (2020).
86. Senthil, Raja. D. et al. In situ grown bimetallic MOF-based composite as highly efficient bifunctional electrocatalyst for overall water splitting with ultrastability at high current densities. *Adv. Energy Mater.* **8**, 1801065 (2018).
87. Rossmeisl, J. et al. Electrolysis of water on (oxidized) metal surfaces. *Chem. Phys.* **319**, 178-184 (2005)
88. NIST-JANAF Thermochemical Tables. <http://janaf.nist.gov/>.