

***Supporting Information (SI) for:***

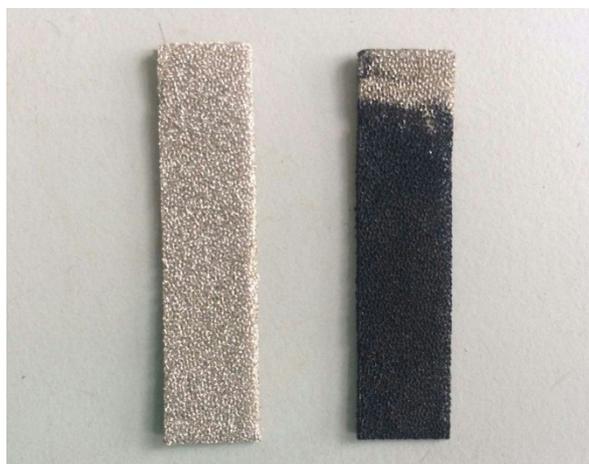
**In Situ electrochemical formation of NiSe/NiO<sub>x</sub> core/shell  
nano-electrocatalysts for superior oxygen evolution activity**

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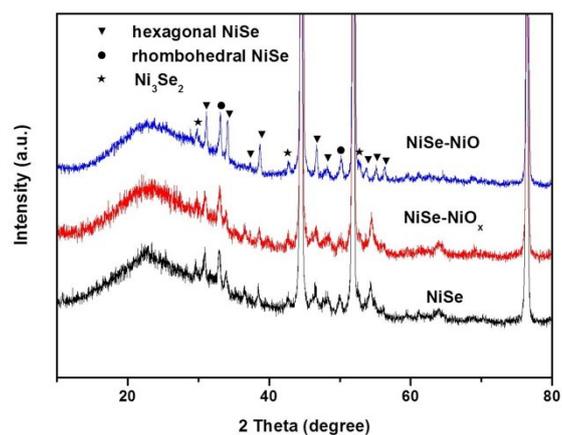
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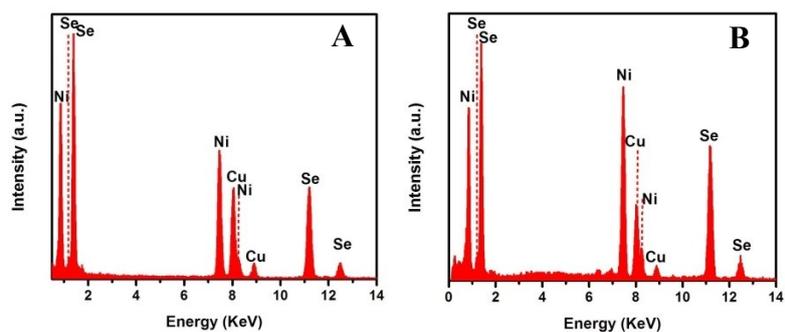
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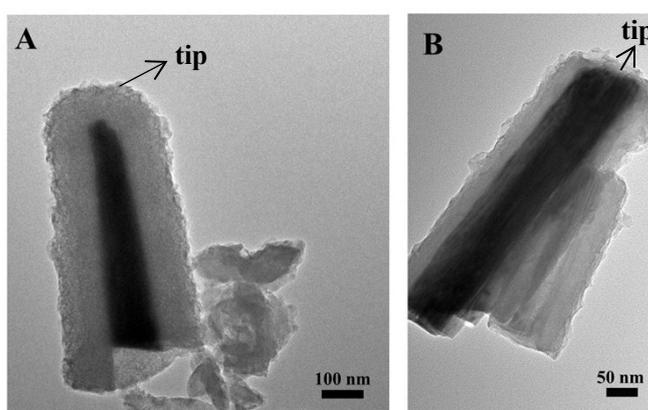
**Figure S1.** Photograph of NF (left) and NiSe/NF (right).



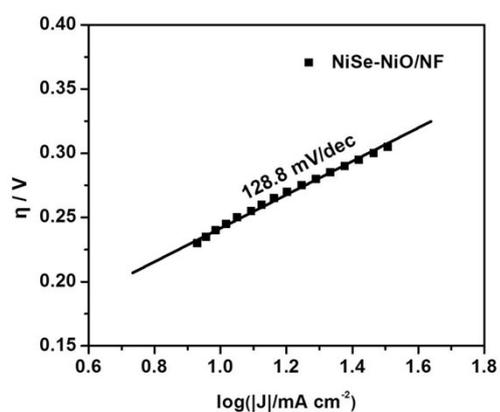
**Figure S2.** XRD patterns of the NiSe-NiO (blue), NiSe-NiO<sub>x</sub>/NF (red) and NiSe/NF (black). ▼, ● and ★ represent NiSe in hexagonal phase (PDF#65-3425), in rhombohedral phase (PDF#18-0887) and Ni<sub>3</sub>Se<sub>2</sub> (PDF#19-0841), respectively.



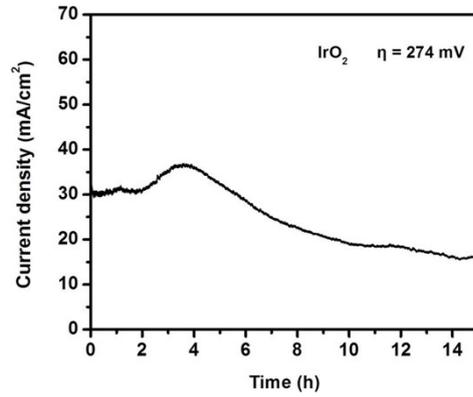
**Figure S3.** EDX spectrum of the NiSe nnaorod for NiSe/NF (The peak locating at 6.3KeV in figure B comes from background).



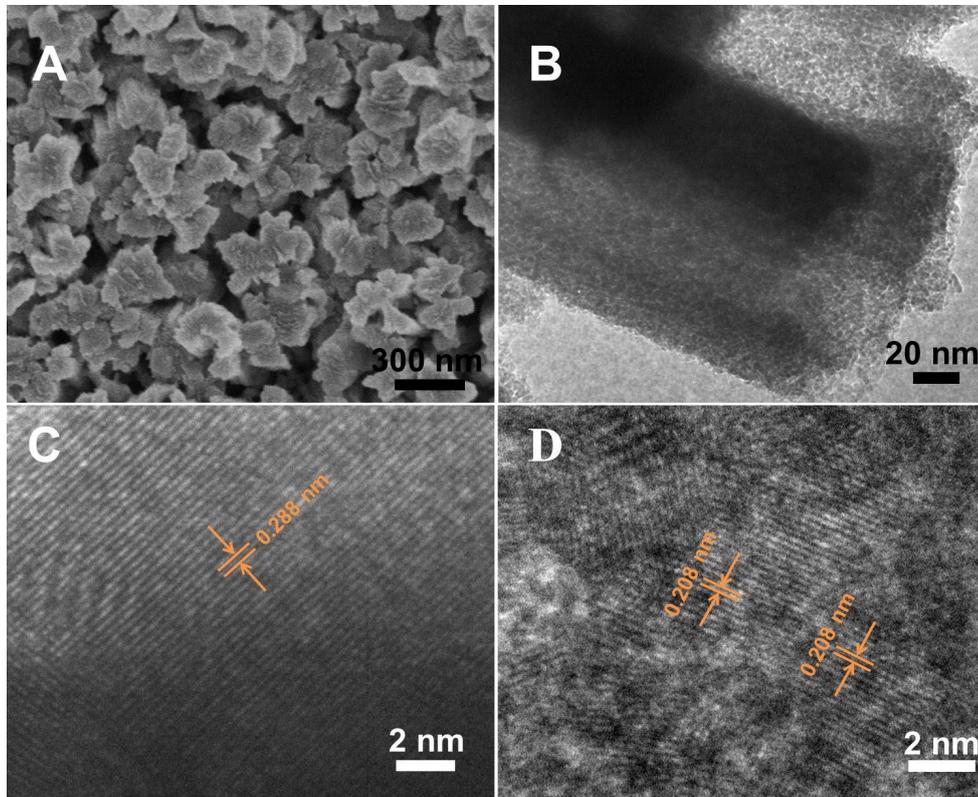
**Figure S4** TEM images of NiSe-NiO<sub>x</sub>. NiSe core is densely coated with NiO<sub>x</sub> layer.



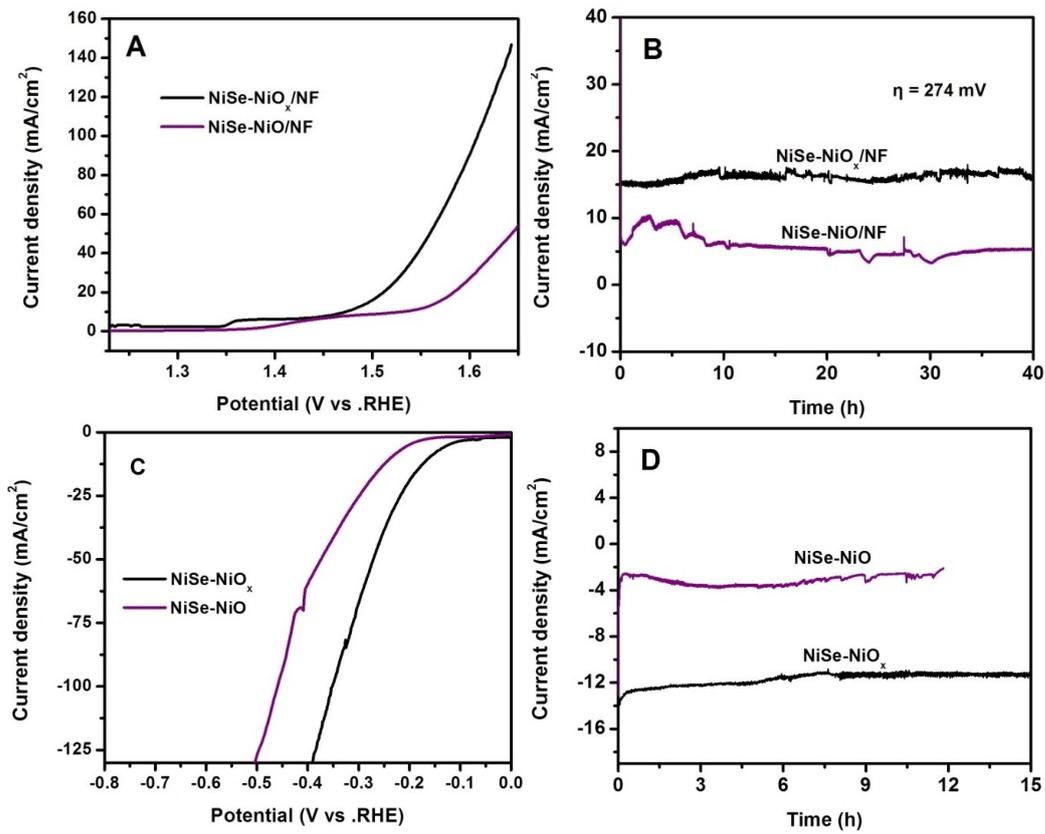
**Figure S5.** Tafel plots for OER over NiSe-NiO<sub>x</sub>/NF.



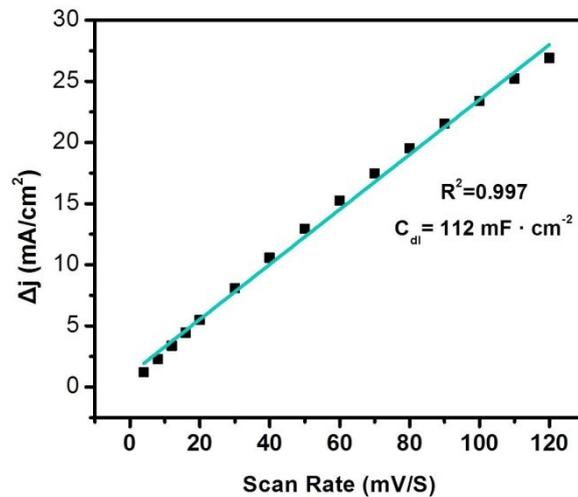
**Figure S6** Constant potential electrolysis with IrO<sub>2</sub> at an overpotential of 274 mV in 1M KOH.



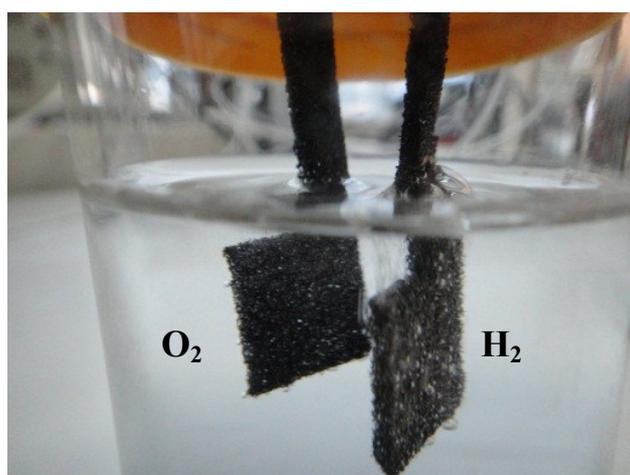
**Figure S7.** (A) SEM image of NiSe-NiO/NF, (B) TEM image of NiSe-NiO/NF, (C) HRTEM taken from the core of NiSe-NiO/NF, (D) HRTEM taken from the shell of NiSe-NiO/NF.



**Figure S8.** (A) Polarization curves of NiSe-NiO<sub>x</sub>/NF and NiSe-NiO/NF for OER, (B) I-t curves of NiSe-NiO<sub>x</sub>/NF and NiSe-NiO/NF at an overpotential of 274 mV, (C) Polarization curves of NiSe-NiO<sub>x</sub>/NF and NiSe-NiO/NF for HER, (D) I-t curves of NiSe-NiO<sub>x</sub>/NF and NiSe-NiO/NF at an overpotential of 150 mV. All the measurements were carried out in 1M KOH.



**Figure S9** Plots showing the extraction of the double-layer capacitive ( $C_{dl}$ ) for IrO<sub>2</sub>.



**Figure S10.** Photograph showing the generation of  $H_2$  and  $O_2$  bubbles on NiSe-NiO<sub>x</sub>/NF electrodes.

**Table S1.** Comparison of the electrocatalytic activity of NiSe-NiO<sub>x</sub>/NF reported here under alkaline medium via-a-via some good NiO-related OER catalysts that have been recently reported for alkaline solution.

| Catalyst  | Current density (mA/cm <sup>2</sup> ) | Overpotential (mV) | Reference  |
|---|---------------------------------------|--------------------|--|
| NiSe-NiO <sub>x</sub>                                   | 10                                    | 243                | <b>This work</b>   |
| NiFeO <sub>x</sub> /CFP                                 | 10                                    | 230                | <i>Nat. Commun.</i> <b>2015</b> , 6, 7261.               |
| Ni-NiO/N-rGo  | 10                                    | 240                | <i>Adv. Funct. Mater.</i> <b>2016</b> ,25,5799           |
| Fe <sub>6</sub> Ni <sub>10</sub> O <sub>x</sub>         | 10                                    | 286                | <i>Angew. Chem. Int. Ed.</i> <b>2014</b> ,53,7547        |
| Ni <sub>2</sub> P/NiO                                   | 10                                    | 290                | <i>Energy Environ. Sci.</i> <b>2015</b> , 8, 2347.       |
| Ni <sub>0.71</sub> Fe <sub>0.29</sub> (OH) <sub>x</sub> | 10                                    | 296                | <i>Nanoscale</i> , <b>2016</b> , 8, 5015.                |
| Ni(OH) <sub>2</sub>                                     | 10                                    | 299                | <i>Faraday Discuss.</i> , <b>2014</b> , 176, 363.        |
| NiO/TiO <sub>2</sub>                                    | 10                                    | 320                | <i>J. Am. Chem. Soc.</i> <b>2016</b> , 138, 6517.        |
| NiCo <sub>2</sub> O <sub>4</sub>                        | 10                                    | 320                | <i>Angew. Chem. Int. Ed.</i> <b>2015</b> , 127, 7507     |
| Ni@C/NF   | 10                                    | 330                | <i>J. Mater. Chem. A</i> <b>2016</b> , 4, 7297.          |
| α-Ni(OH) <sub>2</sub>                                   | 10                                    | 331                | <i>J. Am. Chem. Soc.</i> <b>2014</b> , 136, 7077.        |
| NiO/NF  | 10                                    | 345                | <i>J. Mater. Chem. A</i> <b>2016</b> , 4, 9797.          |
| Ni-NG   | 10                                    | 400                | <i>Energy Environ. Sci.</i> <b>2013</b> , 6, 3693.       |
| NiO <sub>x</sub> /Ni                                    | 10                                    | 390                | <i>Applied Surface Science</i> , <b>2015</b> , 359, 172. |