Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


Supporting Information

# Metallic and superhydrophilic nickel cobalt diselenides nanosheets electrodeposited on carbon cloth as bifunctional electrocatalyst

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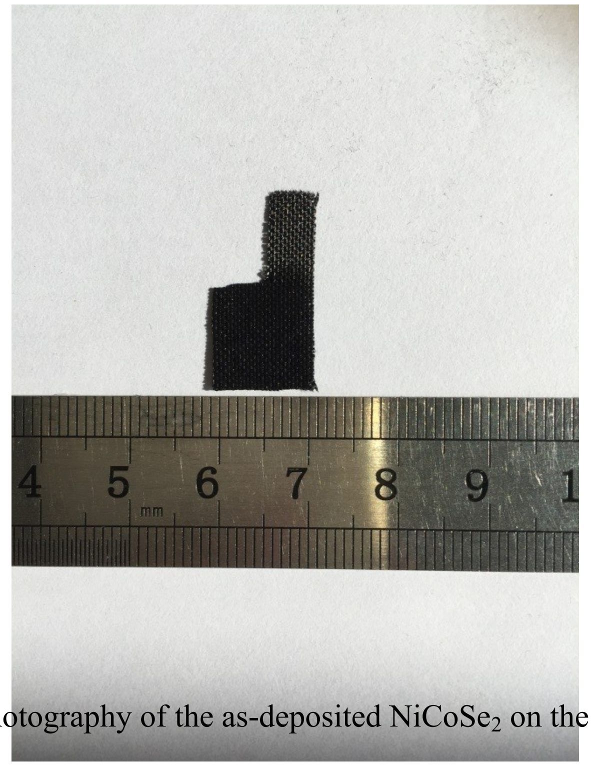


**Fig. S1** Digital photography of the as-deposited $NiCoSe_2$ on the surface of carbon cloth.

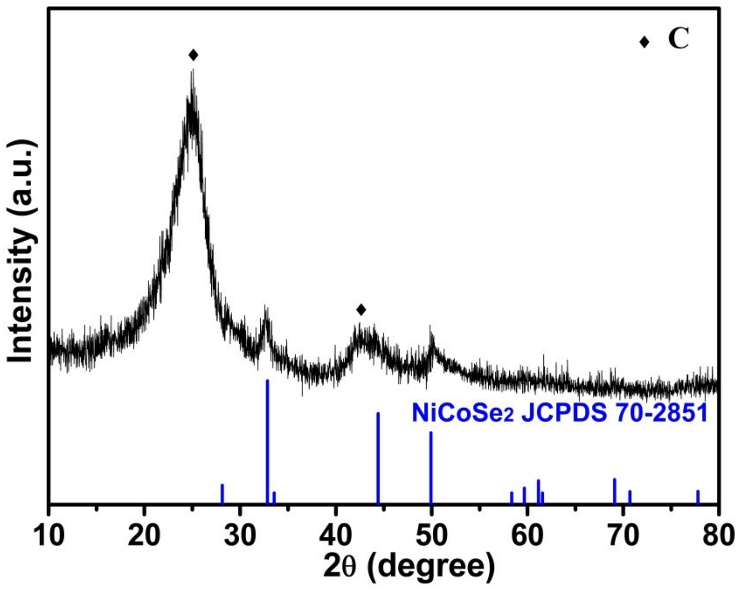


**Fig. S2** XRD pattern of the as-deposited $NiCoSe_2$ on carbon cloth

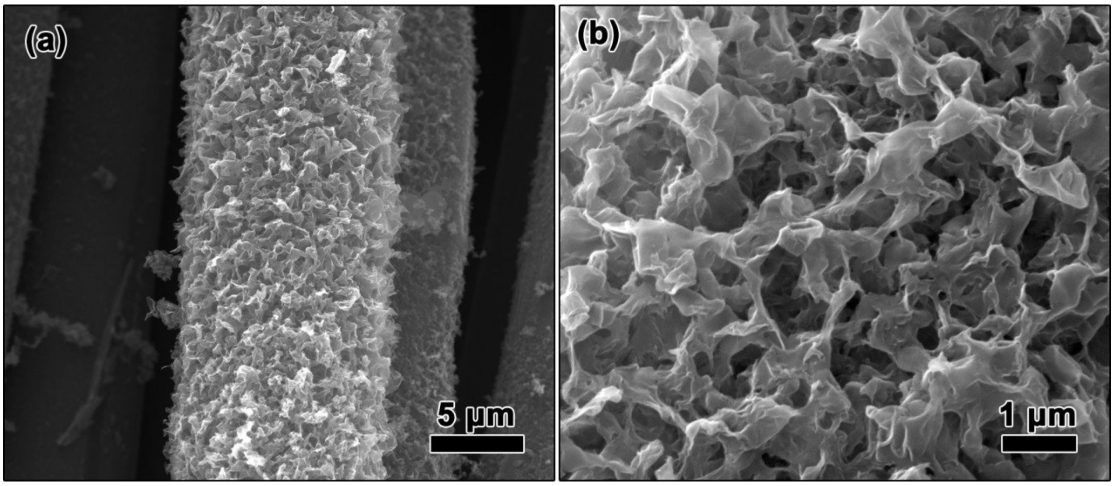


**Fig. S3** SEM images of $NiCoSe_2$ nanosheets with different magnifications.

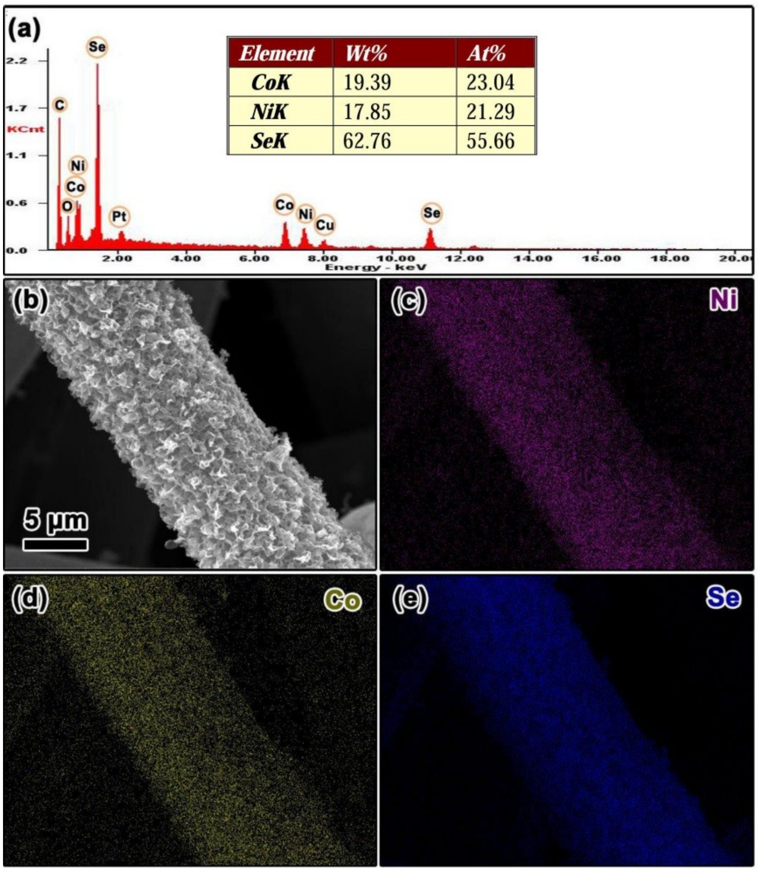


**Fig. S4** (a) SEM-EDS spectrum of $NiCoSe_2$ nanosheets. (b-e) SEM-EDS mappings of $NiCoSe_2$ nanosheets.

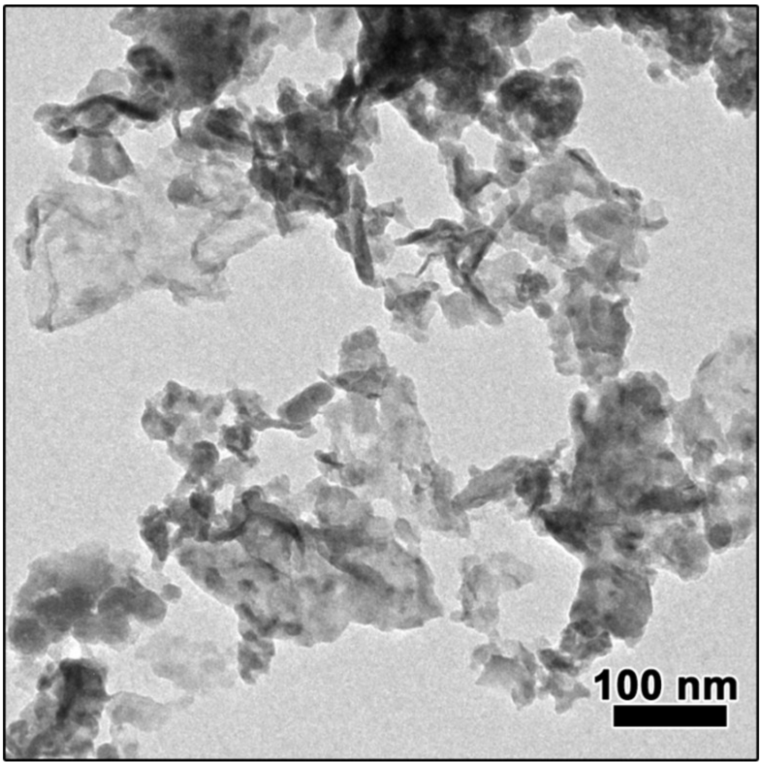


**Fig. S5** TEM image of $NiCoSe_2$ nanosheets.

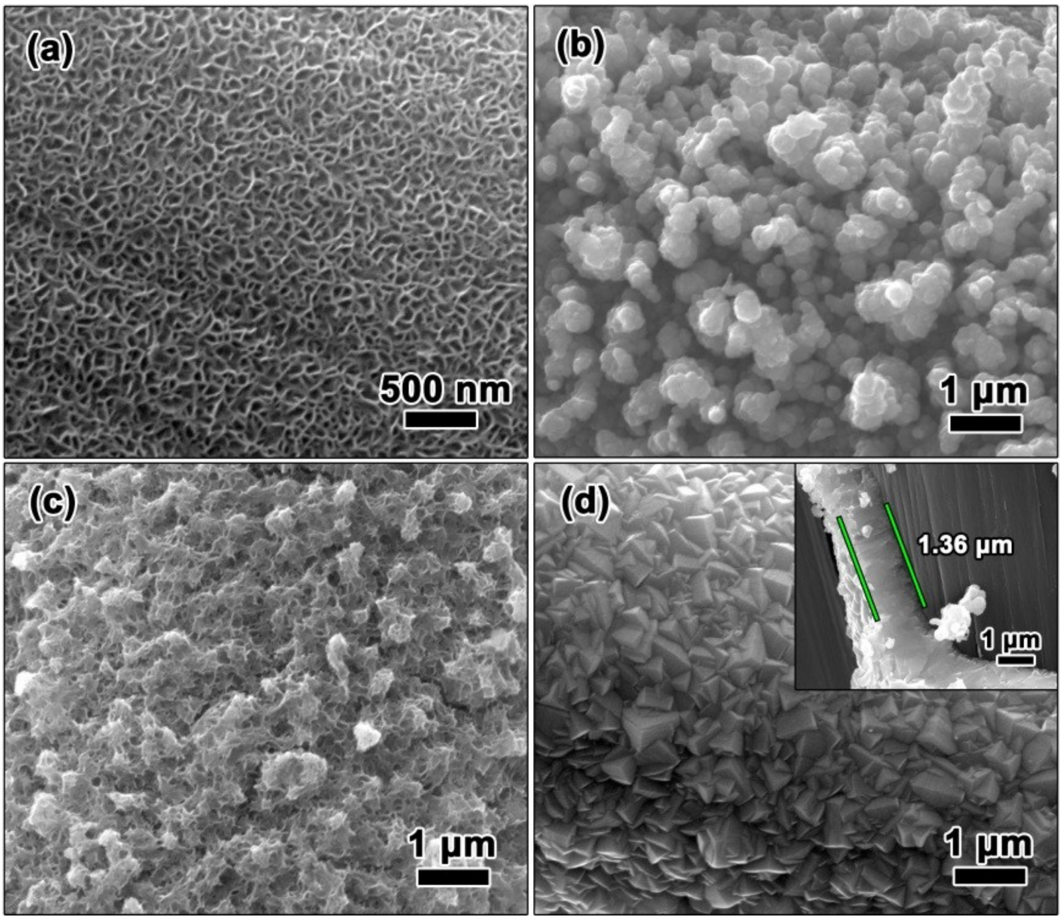


**Fig. S6** SEM images of different samples obtained by electrodedeposition. (a) NiCo-OH, (b) NiSe, (c) CoSe, (d) $NiCoSe_2$ obtained at 0.65 V. Inset of (d) is cross-section SEM image.

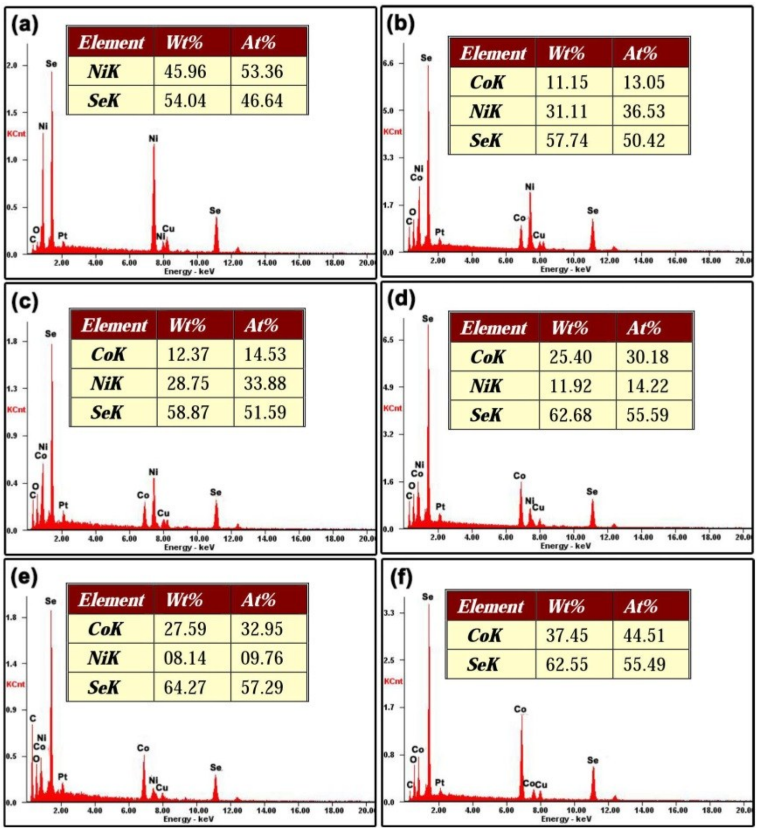


**Fig. S7** SEM-EDS spectra of Ni-Co-Se samples with different Ni/Co ratios. (a) NiSe, (b) $Ni_{1.5}Co_{0.5}Se_2$, (c) $Ni_{1.34}Co_{0.66}Se_2$, (d) $Ni_{0.66}Co_{1.34}Se_2$, (e) $Ni_{0.5}Co_{1.5}Se_2$, (f) CoSe. The Ni/Co ratio in Ni-Co-Se is close to added Ni and Co sources, and the mole ratio of metal and Se is close to 1:1.

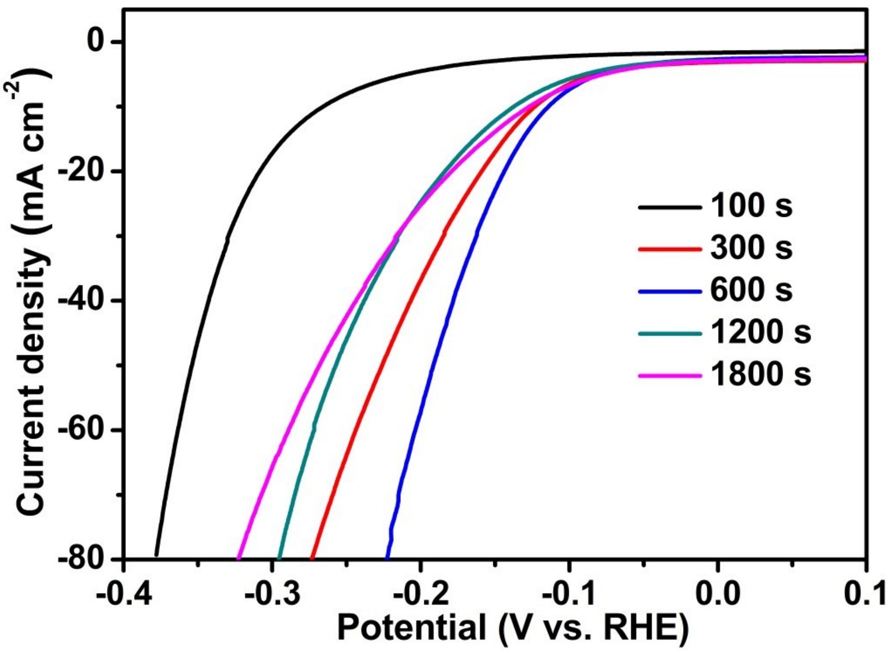


**Fig. S8** HER polarization curves of $NiCoSe_2$ prepared with different deposition durations.

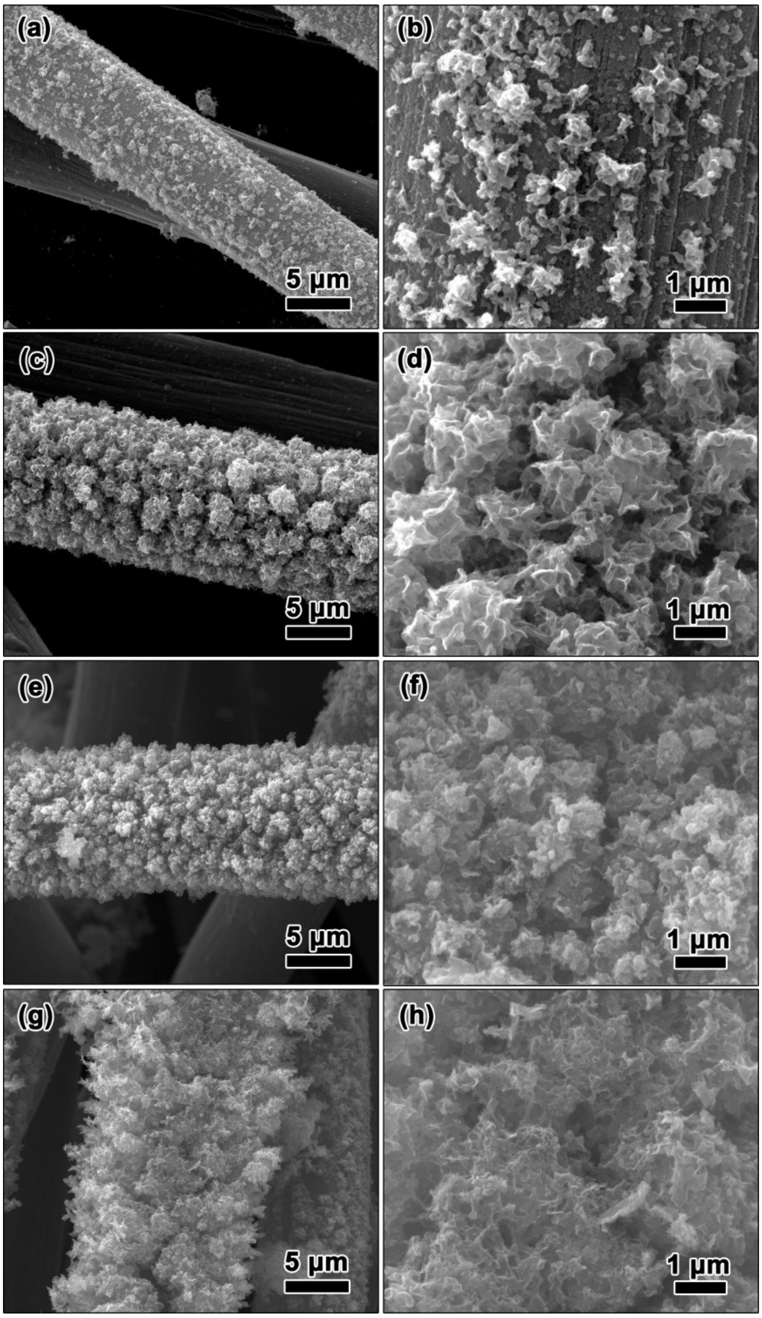


**Fig. S9** SEM images of $NiCoSe_2$ at different electrodeposition durations. (a, b) 100 s, (c, d) 300 s, (e, f) 1200 s, (g, h) 1800 s.

The effect of deposition time on the resultants was investigated to examine the formation process of $NiCoSe_2$ nanosheets. As shown in Figure S8, various of nanoparticles emerged on CC surface and covered CC incompletely with the deposition time of 100 s. Moreover, the nanoparticles exhibited the trend to crimp.

With the increasing time to 300 s, the sample owned the morphology of microflowers comprised of numerous nanosheets. And then these microflowers tended to combine with each other and form interconnected structure. Along with further prolonged deposition time, the sample accumulated densely around CC, which is not favorable to charge diffusion.

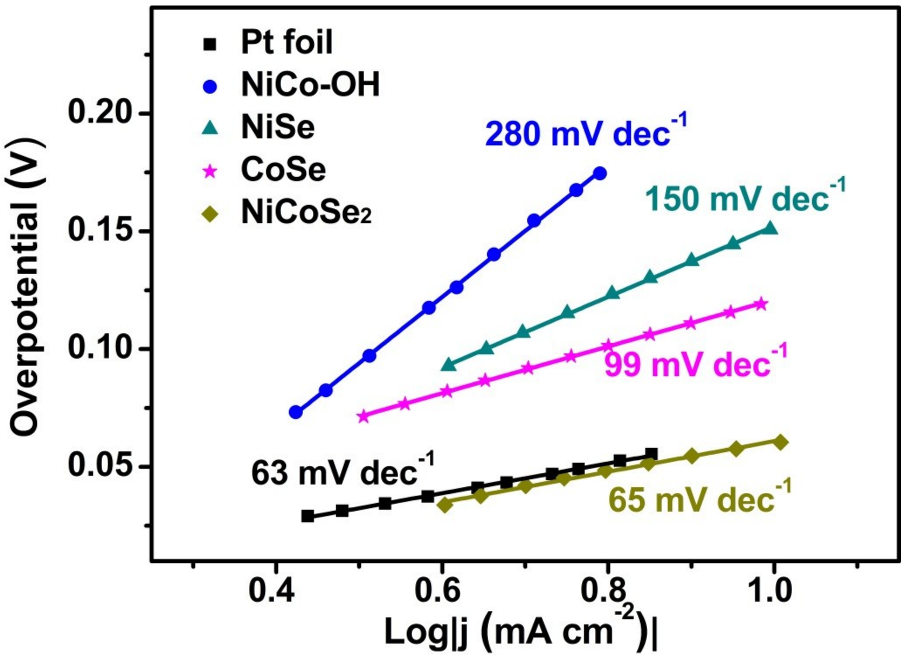


**Fig. S10** The HER Tafel plots of different samples.

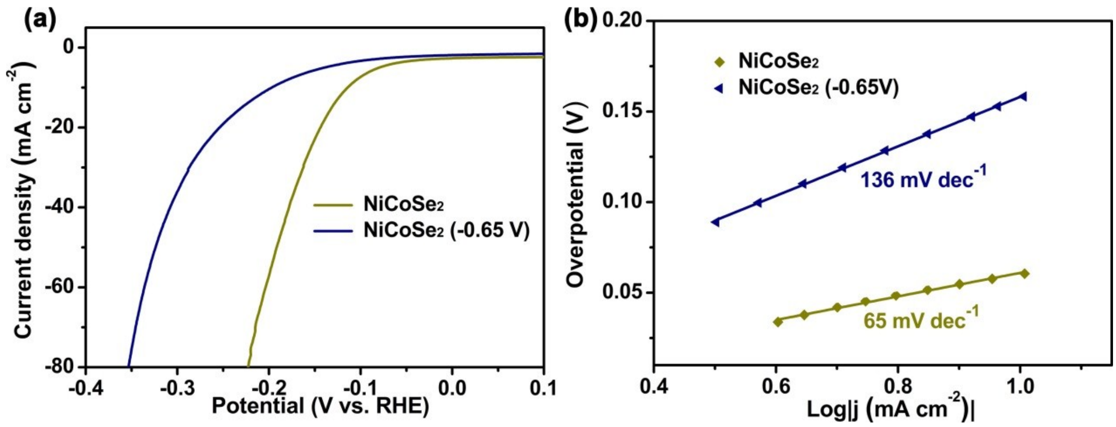


**Fig. S11** (a) LSV polarization curves and (b) corresponding Tafel plots toward HER of $NiCoSe_2$ prepared with different deposition potentials of -0.65 V and -0.8 V.

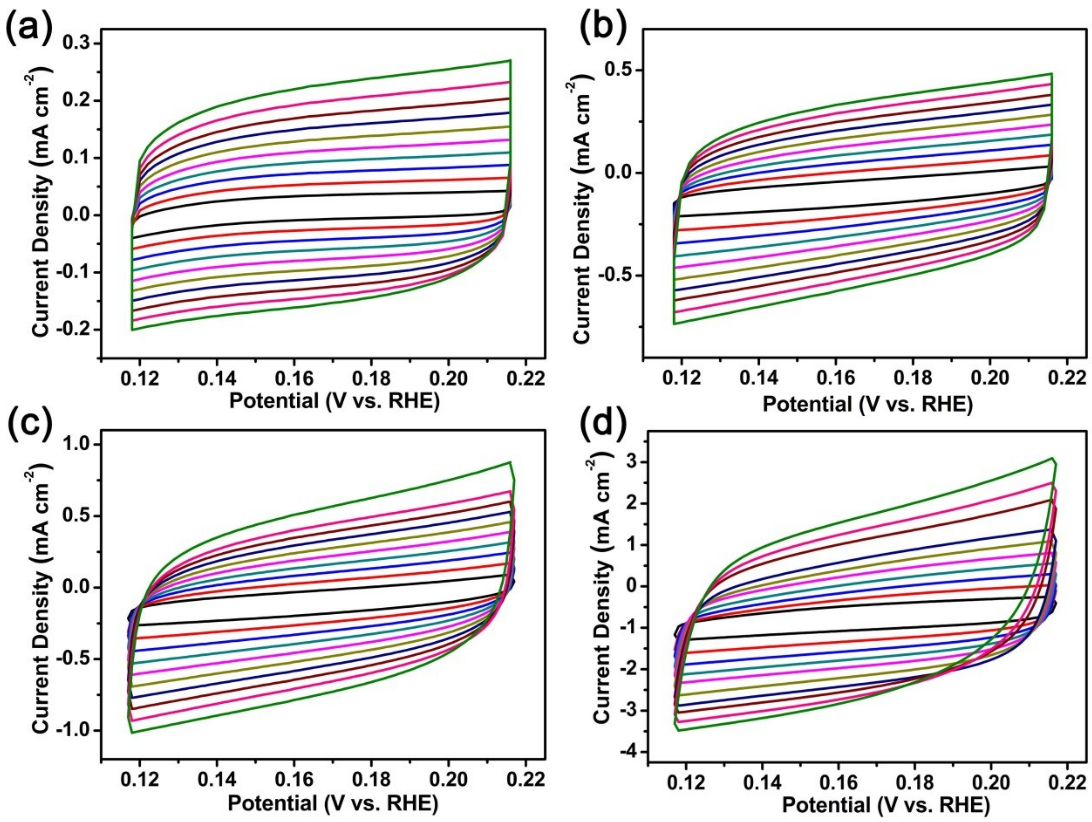


**Fig. S12** Electrochemical cyclic voltammetry curves of (a) NiCo-OH, (b) NiSe, (c) CoSe and (d) $NiCoSe_2$ at different scanning rates. The scanning rates are in the ranges from 20 to 200 mV $s^{-1}$ with an interval point of 20 mV $s^{-1}$.

## Electrochemical active surface area (ECSA)

The active surface area of each catalyst was estimated from their electrochemical capacitances according to the following equation:

$$A(ECSA) = \frac{C_{dl} - catalyst\ (mF\ cm^{-2})}{C_{dl} - carbon\ cloth\ (mF\ cm^{-2})\ per\ ECSA\ cm^2}$$

Consequently, the $A_{ECSA}$ for NiSe, CoSe and $NiCoSe_2$ were calculated as:

$$A_{ECSA}^{NiSe} = \frac{2.14\ mF\ cm^{-2}}{0.7\ mF\ cm^{-2} per\ cm_{ECSA}^2} = 3.06\ cm_{ECSA}^2$$

$$A_{ECSA}^{CoSe} = \frac{3.01 mF\ cm^{-2}}{0.7\ mF\ cm^{-2} per\ cm_{ECSA}^2} = 4.3\ cm_{ECSA}^2$$

$$A_{ECSA}^{NiCoSe_2} = \frac{10.55\ mF\ cm^{-2}}{0.7\ mF\ cm^{-2} per\ cm_{ECSA}^2} = 15.07\ cm_{ECSA}^2$$

## Turnover frequency (TOF) calculations

The TOF values were eliminated according to:

$$TOF = \frac{\#total\ hydrogen\ (or\ oxygen)\ turnovers/geometric\ area(cm^2)}{\#surface\ active\ sites/geometric\ area\ (cm^2)}$$

The number of the total hydrogen or oxygen turnovers is calculated based on the measured current density by the following equations:

$$\#H_2 = |J| \frac{mA}{cm^2} * \frac{1\ C\ s^{-1}}{1000\ mA} * \frac{1\ mol\ e^-}{96495.3\ C} * \frac{1\ mol\ H_2}{2\ mol\ e^-} * \frac{6.022 * 10^{23}\ H_2\ m}{1\ mol\ H_2} \times 10^{15} \frac{H_2\ s^{-1}}{cm^2} per \frac{mA}{cm^2}$$

$$\#O_2 = J\frac{mA}{cm^2} * \frac{1\,C\,s^{-1}}{1000\,mA} * \frac{1\,mol\,e^-}{96495.3\,C} * \frac{1\,mol\,O_2}{4\,mol\,e^-} * \frac{6.022 * 10^{23}\,O_2\,mo}{1\,mol\,O_2}$$

$$\times 10^{15}\frac{O_2\,s^{-1}}{cm^2} per \frac{mA}{cm^2}$$

The upper limit of the surface sites can be calculated as following:

$$\#Surface\ sites_{NiSe} = \left(\frac{4\ atoms\ per\ unit\ cell}{61.15\ A^3\ per\ unit\ cell}\right)^{\frac{2}{3}} = 1.62 \times 10^{15}\ atoms/cm^2\ real\ sur$$

$$\#Surface\ sites_{CoSe} = \left(\frac{4\ atoms\ per\ unit\ cell}{57.84\ A^3\ per\ unit\ cell}\right)^{\frac{2}{3}} == 1.68 \times 10^{15}\ atoms/cm^2\ real\ su$$

$$\#Surface\ sites_{NiCoSe_2} = \left(\frac{4\ atoms\ per\ unit\ cell}{59.72\ A^3\ per\ unit\ cell}\right)^{\frac{2}{3}} = 1.65 \times 10^{15}\ atoms/cm^2\ real\ sur$$

$$TOF_{HER} = \frac{3.12 \times 10^{15}\frac{H_2\,s^{-1}}{cm^2} per \frac{mA}{cm^2} \times |J|}{\#Surface\ active\ sites \times A_{ECSA}}$$

$$TOF_{OER} = \frac{1.56 \times 10^{15}\frac{O_2\,s^{-1}}{cm^2} per \frac{mA}{cm^2} \times J}{\#Surface\ active\ sites \times A_{ECSA}}$$

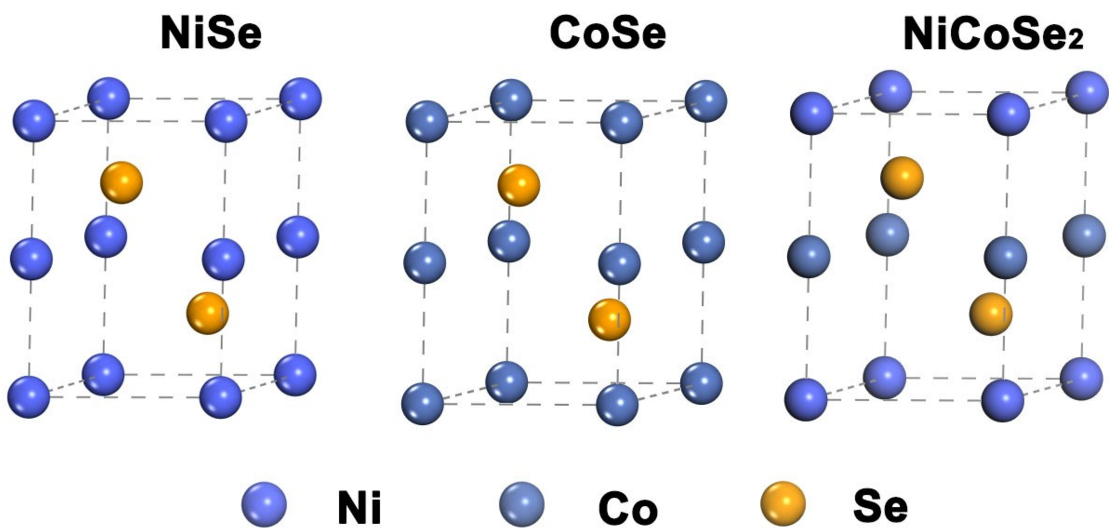


**Fig. S13** Unit cells of NiSe (2 Ni and 2 Se atoms), CoSe (2 Co and 2 Se atoms) and $NiCoSe_2$ (1 Ni, 1 Co and 2 Se atoms), respectively.

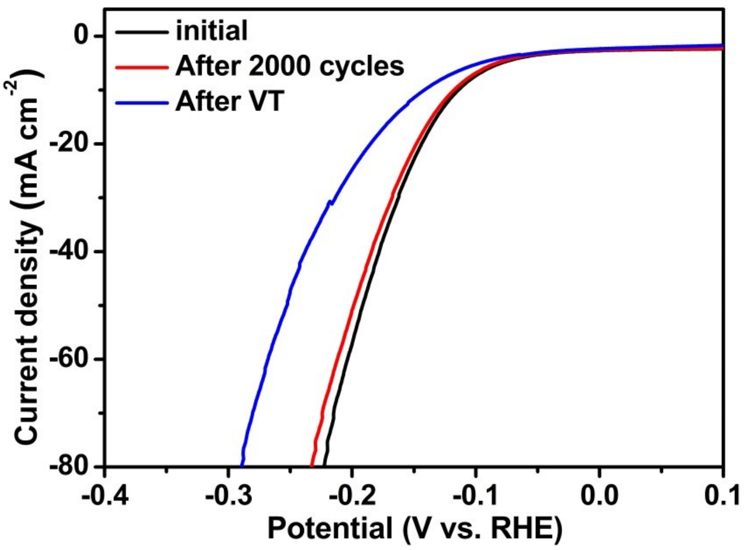


**Fig. S14** HER polarization curves recorded for $NiCoSe_2$ at initial state, after 2000 CV cycles and 24 h of chronopotentiometric test.

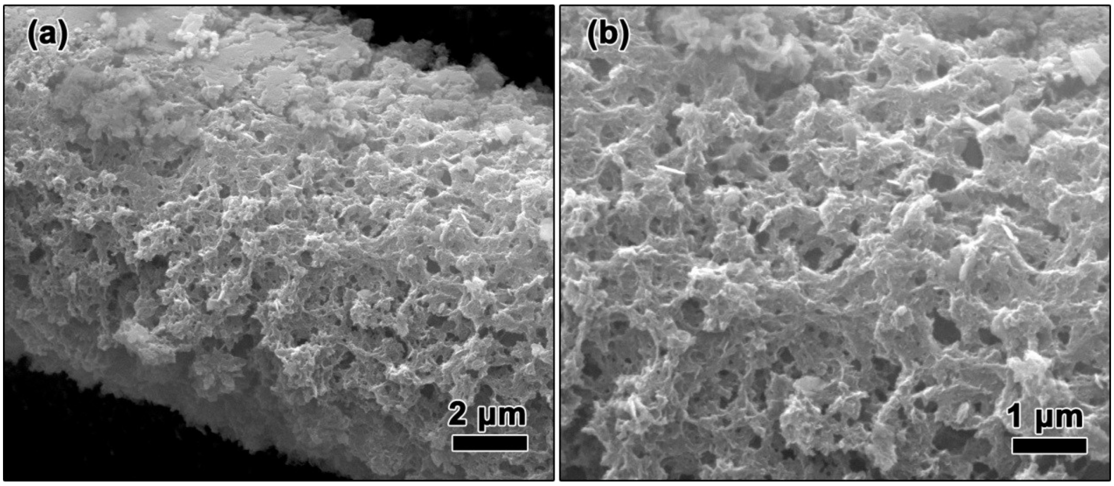


**Fig. S15** SEM images of $NiCoSe_2$/CC electrode after HER measurement.

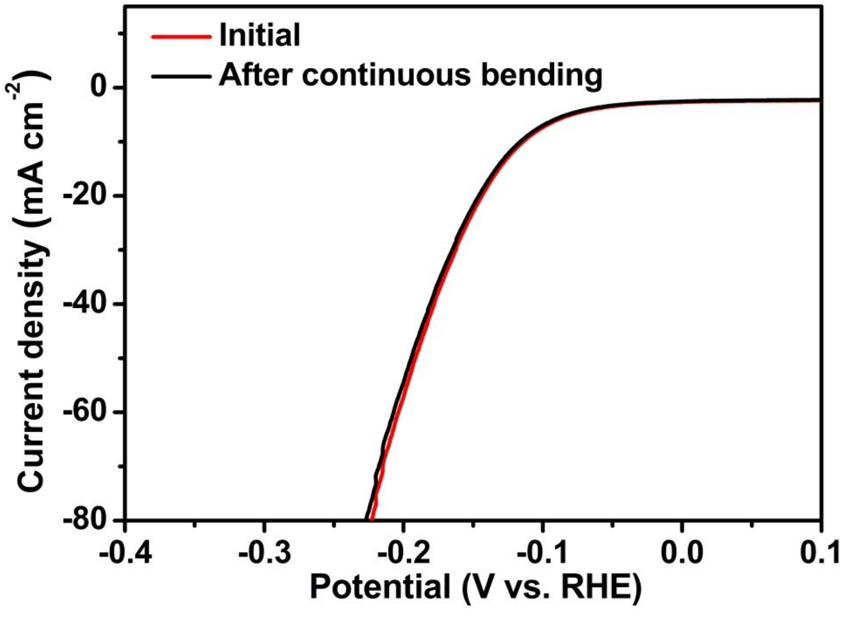


**Fig. S16** HER polarization curves of $NiCoSe_2$/CC electrode before and after the continuous bending for 10 times. The LSV curve after 10 times bending is almost overlapping with the initial curve, indicating excellent mechanical stability of $NiCoSe_2$/CC electrode.

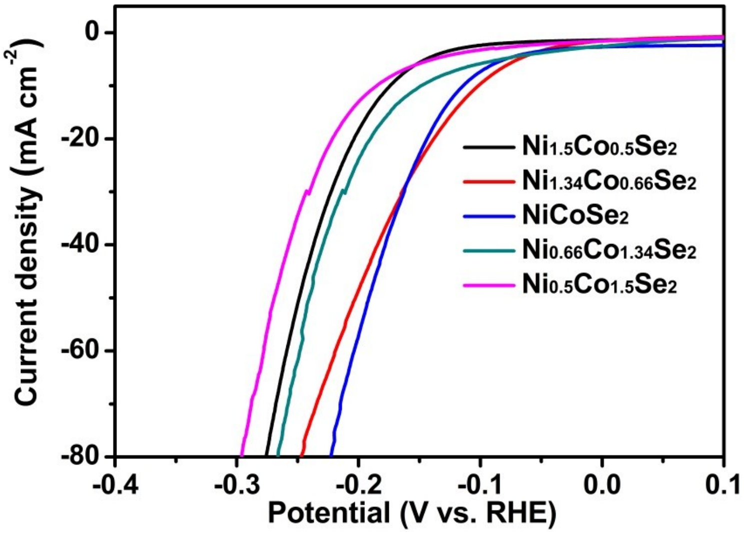


**Fig. S17** LSV polarization curves toward HER of $NiCoSe_2$ with different Ni/Co ratio.

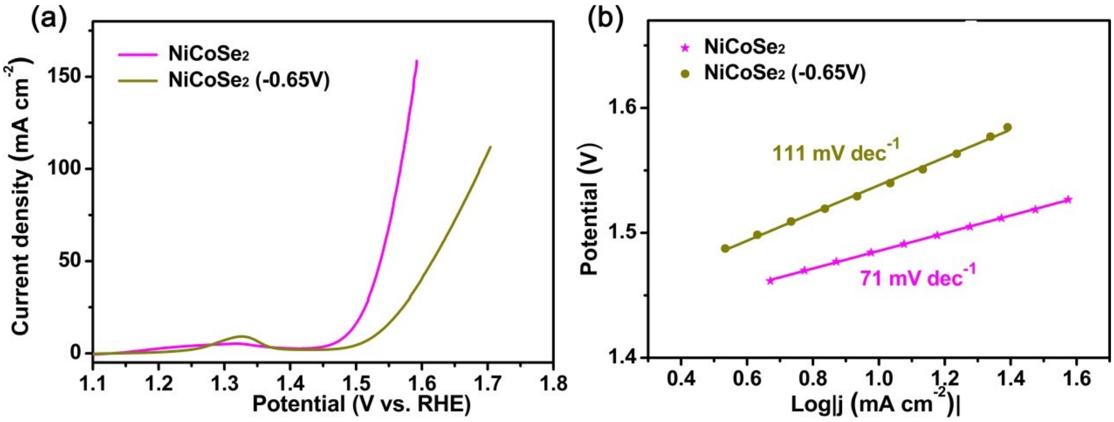


**Fig. S18** (a) LSV polarization curves and (b) corresponding Tafel plots toward OER of $NiCoSe_2$ prepared with different deposition potentials of -0.65 V and -0.8 V.

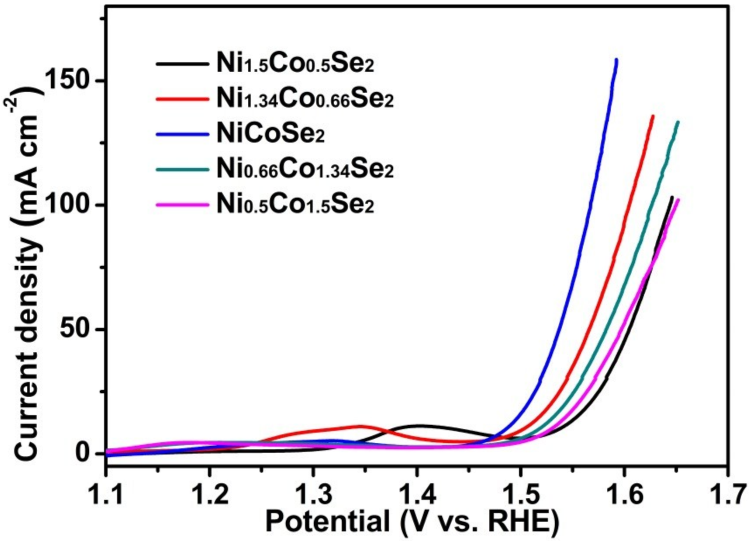


**Fig. S19** LSV polarization curves toward OER of $NiCoSe_2$ with different Ni/Co ratios.

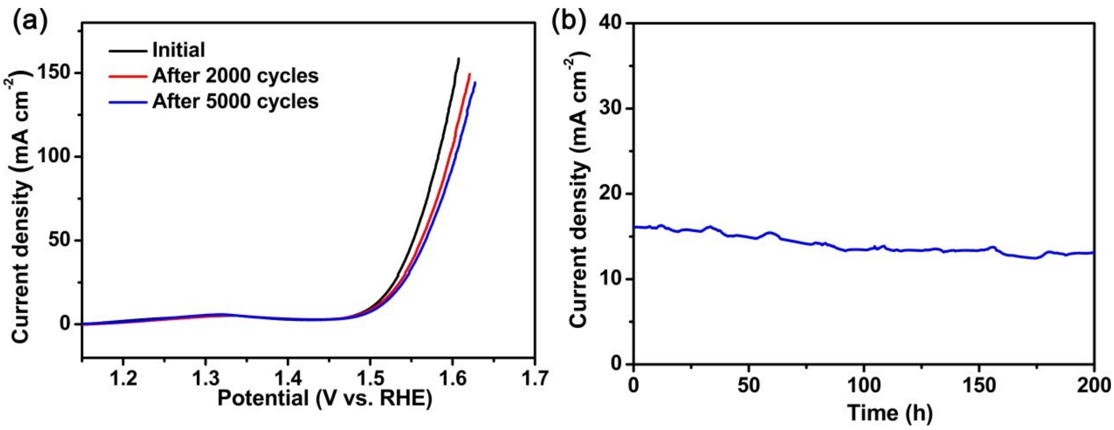


**Fig. S20** (a) OER Polarization curves recorded for $NiCoSe_2$ at initial state, after 2000 and 5000 CV cycles. (b) Chronoamperometric curve of $NiCoSe_2$ at a constant current potential of 1.52 V for 200 h of continuous operation.

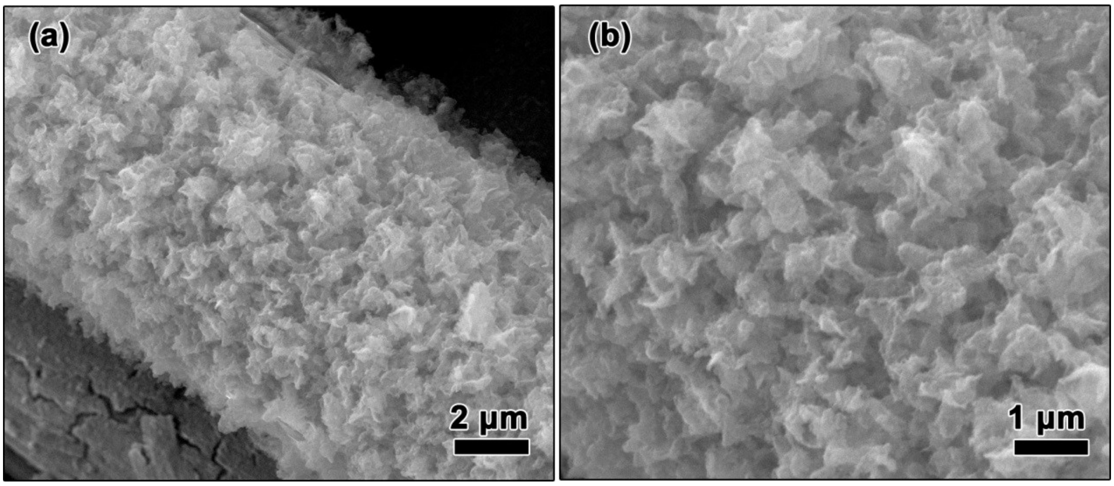


**Fig. S21** SEM images of $NiCoSe_2$/CC electrode after OER measurement.

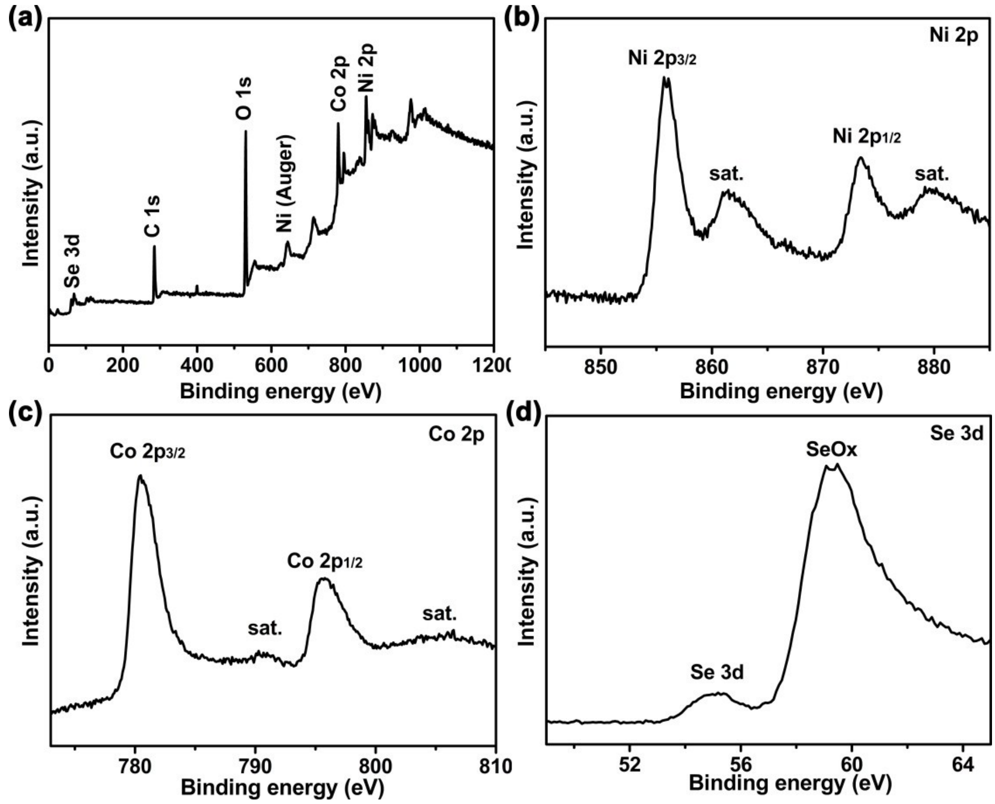


**Fig. S22** XPS spectra of $NiCoSe_2$ after OER test. (a) XPS survey spectrum. (b) High-resolution XPS spectra of (b) Ni 2p, (c) Co 2p and (d) Se 3d. The obviously increasing Se oxide species suggest an oxidation on the surface of $NiCoSe_2$ during the OER process.

**Table S1**. Summary of the electrochemical features and water splitting activities in 1M KOH upon the as-deposited samples.

| Sample | NiCo-OH | NiSe | CoSe | $NiCoSe_2$ |
|---|---|---|---|---|
| $\eta_{10}$ (HER, mV) | 393.8 | 204.8 | 179.5 | 112.7 |
| Tafel slope (HER, mV/dec) | 280 | 150 | 99 | 65 |
| $R_{ct}$ (HER, Ω) | 124.4 | 60.3 | 51.4 | 44.7 |
| $\eta_{10}$ (OER, mV) | 388.1 | 331.4 | 313.1 | 255.8 |
| Tafel slope (OER, mV/dec) | 256 | 143 | 92 | 71 |
| $R_{ct}$ (OER, Ω) | 31.8 | 17.3 | 14.7 | 8.0 |
| $\eta_{10}$ (Full water splitting, V) | 1.88 | 1.82 | 1.68 | 1.62 |
| $C_{dl}$ ($mF/cm^2$) | 0.94 | 2.14 | 3.01 | 10.55 |

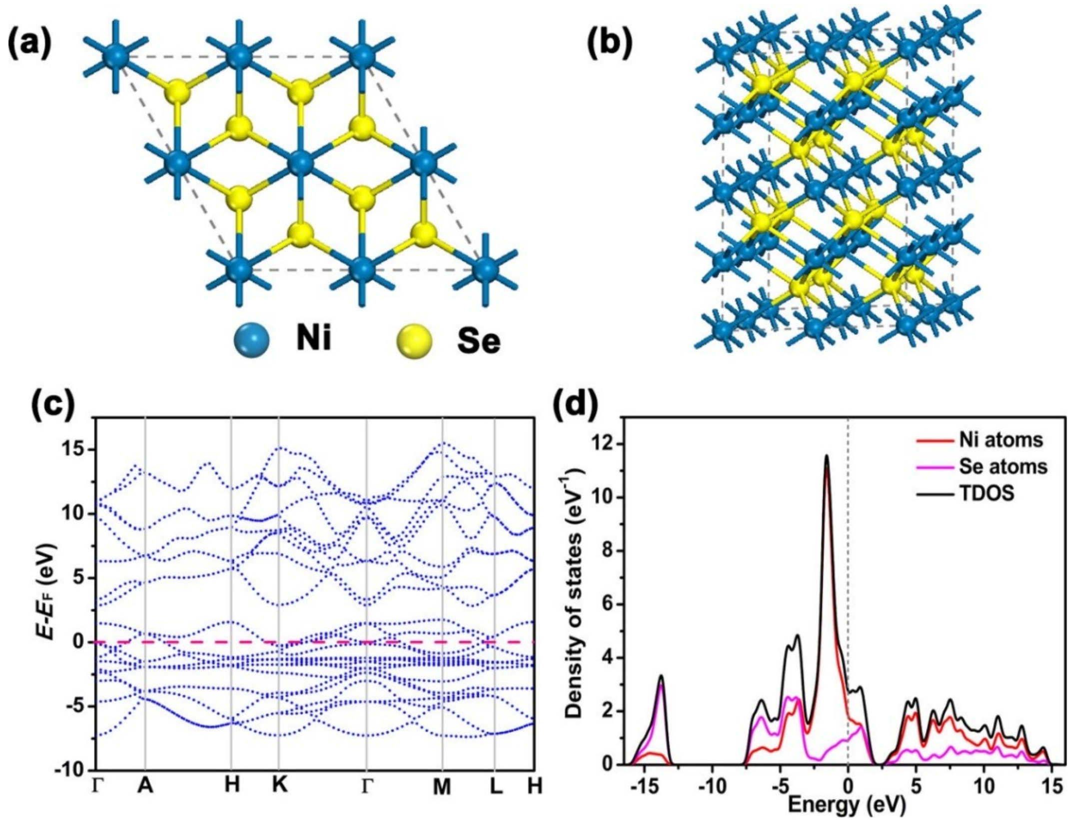


**Fig. S23** Crystal structure of NiSe with (a) top view and (b) side view. Calculated (c) band structures and (d) density of states for NiSe. The Fermi level is set at 0 eV.

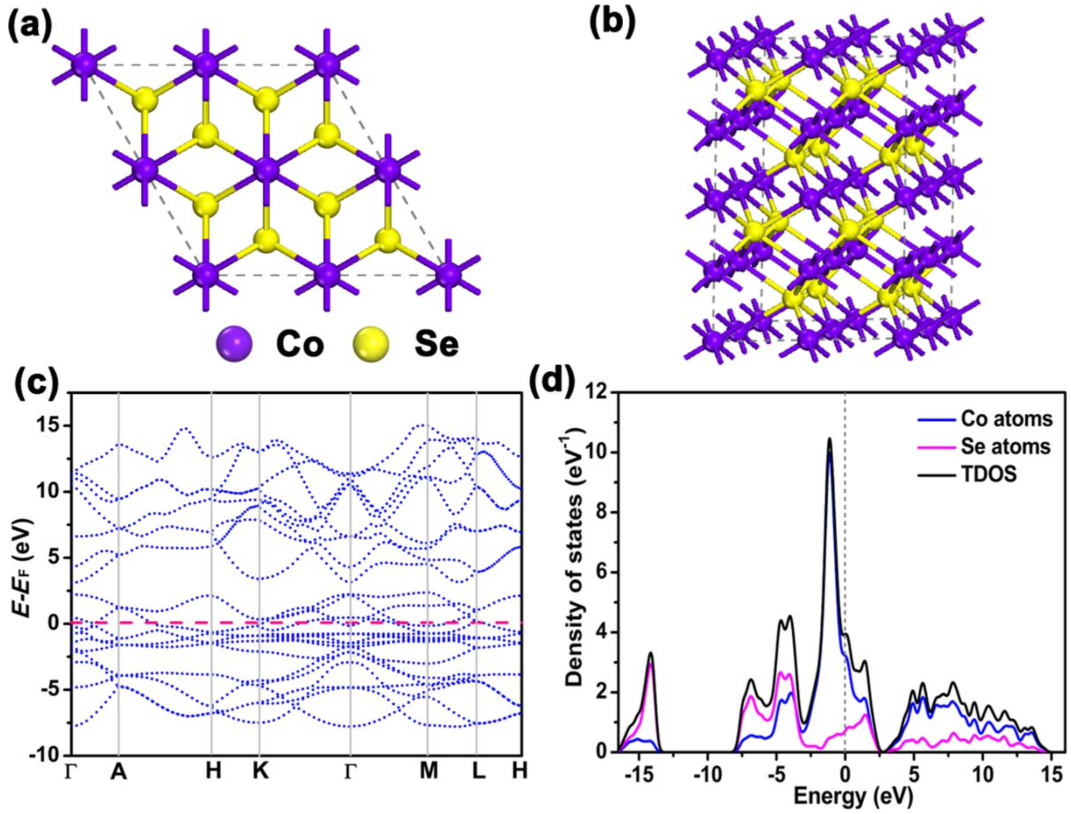


**Fig. S24** Crystal structure of CoSe with (a) top view and (b) side view. Calculated (c) band structures and (d) density of states for CoSe. The Fermi level is set at 0 eV.

**Table S2**. Comparison of electrocatalytic performance for $NiCoSe_2$/CC with the state-of the-art bifunctional electrocatalysts for water splitting in 1M KOH.

| Catalysts | HER $\eta_{10}$ (mV) | OER $\eta_{10}$ (mV) | $E_{10}$ (V)[a] | Ref. |
|---|---|---|---|---|
| **$NiCoSe_2$** | **112.7** | **255.8** | **1.62** | **This work** |
| NiCoP/rGO | 209 | 270 | 1.59 | *Adv. Funct. Mater.*, 2016, **26**, 6785-6796. |
| $(Ni,Co)_{0.85}Se$ | 169 | $\eta_{20}$=287 | 1.65 | *J. Mater. Chem. A*, 2018,**6**, 7585-7591 |
| $NiCo_2P_x$ | 47 | 284 | 1.61 | *J. Mater. Chem. A*, 2018,**6**, 7420-7427 |
| $NiCo_2S_4$ | 210 | 260 | 1.63 | *Adv. Funct. Mater.*, 2016, **26**, 4661-4672 |
| NiFe-Se/C | 160 | 240 | 1.68 | *J. Power Sources*, 2017, **366**, 193-199. |
| Ni-Fe-P | 182 | 271 | 1.67 | *ACS Appl. Mater. Interfaces,* 2017, **9**, 26134-26142. |
| $Ni_{12}P_5/Ni_3(PO_4)_2$ | 114 | 318 | – | *Appl. Catal., B*, 2017, **204**, 486-496. |
| NiCoP/Ti | 97 | 310 | 1.64 | *Adv. Mater. Interfaces*, 2016, **3**, 1500454. |
| $FeSe_2$ | 178 | 245 | 1.73 | *Angew. Chem., Int. Ed.*, 2017, **56**, 10506-10510. |
| $Ni_3FeN$ | 158 | 280 | – | *Adv. Energy Mater.,* 2016, **6**, 1502585. |
| $Ni_{2.5}Co_{0.5}Fe$/NF | ~150 | 275 | 1.62 | *J. Mater. Chem. A*, 2016, **4**, 7245-7250. |
| $Ni_xCo_{3-x}O_4$/NiCo/ $NiCoO_x$ | 155 | 337 | 1.75 | *ACS Appl. Mater. Interfaces*, 2016, **8**, 3208-3214. |

[a] the overall water splitting voltage at the current density of 10 mA $cm^{-2}$.