# *Supporting Information*

**A Highly Efficient and Durable Water Splitting System: Platinum Sub-Nanoclusters Functionalized Nickel Iron Layered Double Hydroxide as the Cathode and Hierarchical Nickel Iron Selenide as the Anode**

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**Experimental Section**

*Chemicals and Materials*: Chloroplatinic acid hexahydrate ($H_2PtCl_6·6H_2O$), sodium borohydride ($NaBH_4$) and selenium (Se) were served by Sinopharm Chemical Reagent co., Ltd. (Shanghai, China), iron (II) sulfate heptahydrate ($FeSO_4·7H_2O$) and urea ($CO(NH_2)_2$) were purchased from Tianli Chemical Reagent Co., Ltd. (Tianjin, China). Nickel nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$) and ammonium fluoride ($NH_4F$) were obtained from Fuchen Chemical Reagent Factory (Tianjin, China). All the chemicals were of analytical grade and used without further purification. All the solutions were prepared with Milli-Q water (18.2 MΩ·cm). The hydrophilic carbon cloth (Type: HCP330N, Thickness: 0.32±0.02 mm) was bought from Shanghai hesen electric co. Ltd. The commercial Pt/C (Type: HPT020, Platinum content: 19.30-20.70%) was bought from Shanghai hesen electric co. LTD. The commercial $RuO_2$ (Type: K901828, Ruthenium content: Ru⩾75.2%) was bought from Shanghai dibai biotechnology co. LTD.

*Synthesis of NiFe LDH/CC*: $Ni(NO_3)_2·6H_2O$ (2.0 mmol), $FeSO_4·7H_2O$ (0.5 mmol), $NH_4F$ (10 mmol) and urea (25 mmol) were dissolved in 40 mL deionized $H_2O$. Then, one piece of carbon fiber cloth (24 mm × 36 mm) (13.5 mg $cm^{-2}$) was put into the above solution. The mixture was sealed in a 45 ml Teflon-lined stainless-steel autoclave and heated under 120 °C for 16 h. After that, the obtained product was washed with distilled water and ethanol.

*Synthesis of Pt-NiFe LDH/CC Electrode*: The Pt-NiFe LDH/CC electrode was synthesized *via* a simple wet chemical reduction method. Typically, one piece of the NiFe LDH/CC was immersed into 50 mL $H_2O$. Subsequently, 0.65 mL $H_2PtCl_6·6H_2O$ (20 mM) was added, and the mixture was heated under 90 °C with continuous stirring for 30 min. After cooling to room temperature, the product was washed with deionized water several times. The mass loadings of Pt-NiFe LDH and Pt on carbon fiber cloth are 3.50 and 0.266 mg $cm^{-2}$, respectively (Pure carbon fiber cloth: 13.5 mg $cm^{-2}$). For comparison, the Pt/CC was prepared by replacing the FeNi LDH/CC with a piece of pure carbon fiber cloth.

*Synthesis of ($Ni_{0.77}Fe_{0.23}$)$Se_2$/CC Electrode*: Se (2 mmol) and $NaBH_4$ (4 mmol) were dissolved in 2 mL $H_2O$. Next, the mixture was diluted into 38 mL $H_2O$, and a piece of the FeNi LDH/CC was immersed into above solution. The mixture was then transferred into a 45-mL Teflon-lined stainless-steel autoclave and heated under 160 °C for 6 h. The obtained product was washed with deionized water several times.

*Synthesis of Com-Pt/C and Com-$RuO_2$ Electrodes*: Typically, the mixture containing 10 mg commercial 20 wt% Pt/C catalysts, 0.5 mL $H_2O$, 0.5 mL ethanol, and 0.032 mL 5% Nafion were mixed to form catalyst slurry. The Com-Pt/C electrode was fabricated by casting the slurry onto one piece of carbon fiber cloth (10 mm × 10 mm). The mass loading of active material (20 wt% Pt/C) was controlled to be 3.50 mg $cm^{-2}$ (same as the Pt-NiFe LDH/CC electrode). The Com-$RuO_2$ electrode was prepared by just replacing the commercial 20 wt% Pt/C catalyst with the commercial $RuO_2$ catalyst.

*Characterizations*: The morphologies of all the samples were examined by SEM (JEOL JSM-6480) and TEM (FEI Teccai G2 S-Twin, Philips). The phase compositions were characterized by XRD (Rigaku TTR III) using Cu Kα radiation (λ = 0.17889 nm) in a 2θ range of 20°-80°. The surface chemical states of samples were investigated by XPS using Al Kα radiation (Thermo ESCALAB 250). The element contents of samples were measured using ICP-MS (Thermo X Series II) and EDS.

*Electrochemical Measurements*: The electrochemical performance in a standard three-electrode system was tested with cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronopotentiometry (CP) controlled by a computerized potentiostat (Autolab PGSTAT 302, Eco Chemie company in Holland). The catalysts of Pt-NiFe LDH/CC, ($Ni_{0.77}Fe_{0.23}$)$Se_2$/CC, Com-Pt/C, Com-$RuO_2$, NiFe LDH/CC, Pt/CC or CC were served as the working electrode, a Ag/AgCl (saturated KCl) electrode was served as the reference electrode, and a carbon rod was served as the counter electrode. All tests were carried out in a 1.0 M KOH solution. EIS measurements were

accomplished in the frequency range of $10^5$ Hz to 0.01 Hz. For overall water splitting, a two-electrode electrolyzer was constructed using the Pt-NiFe LDH/CC electrode as cathode and the $(Ni_{0.77}Fe_{0.23})Se_2$/CC electrode as anode. Overall water splitting performance was evaluated using the LSV and CP in a 1.0 M KOH. All measured LSV and CP curves were IR-corrected. All potentials *vs.* RHE are obtained by converting the measured potentials *vs.* Ag/AgCl according to the following equation: $E_{(RHE)} = E_{(Ag/AgCl)} + 0.197 + 0.0592*pH$.

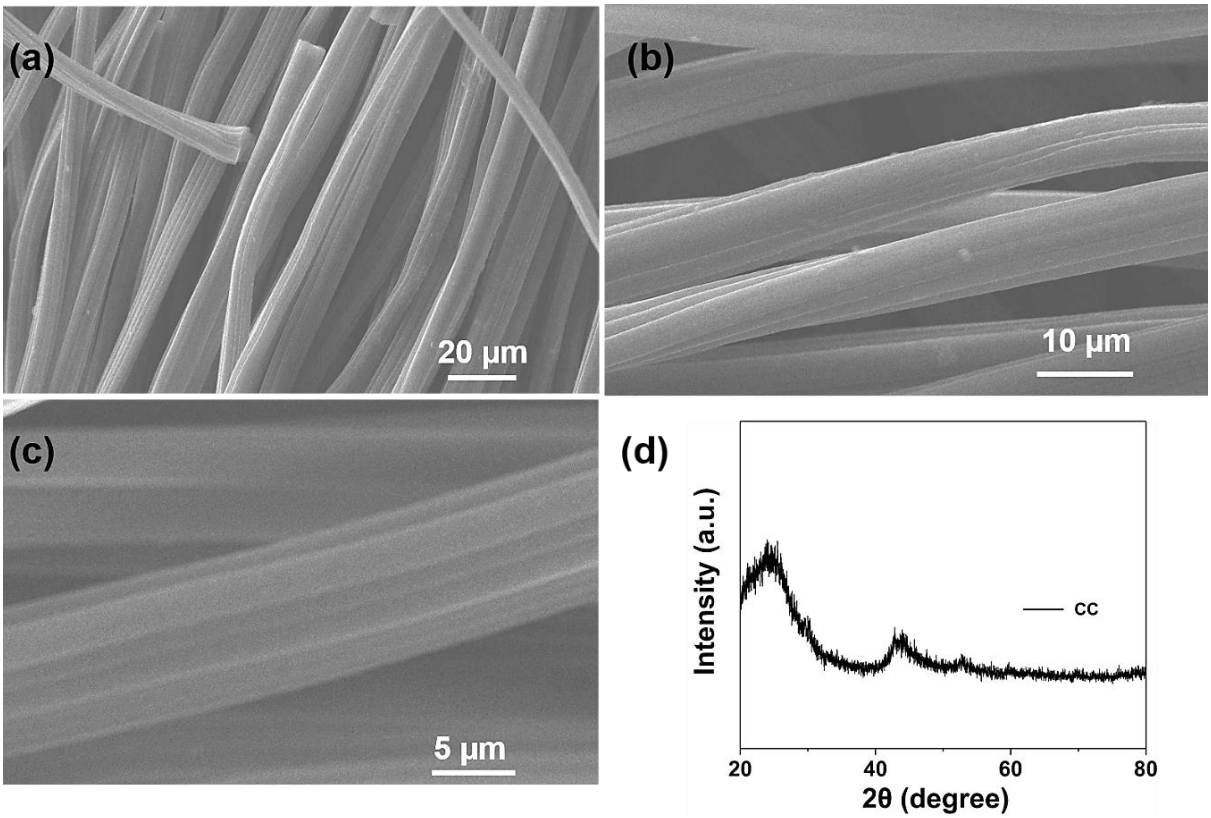


**Figure S1.** SEM images at different magnifications (a-c) and XRD pattern (d) of CC.

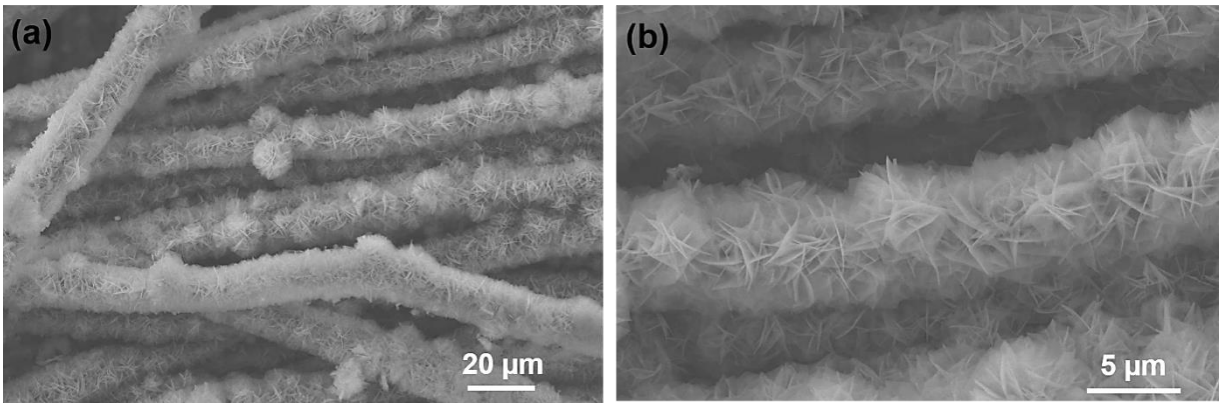


**Figure S2.** SEM images of the NiFe LDH/CC at low (a) and high (b) magnifications.

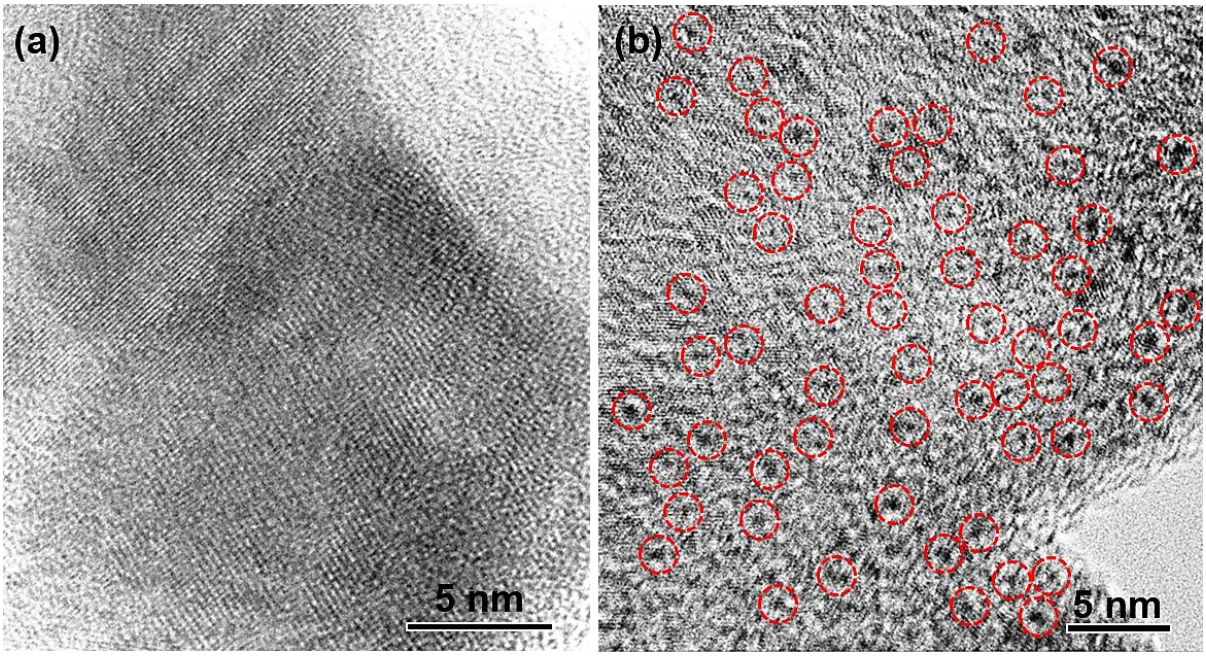


**Figure S3**. HRTEM images of the NiFe LDH (a) and Pt-NiFe LDH nanosheets (b).

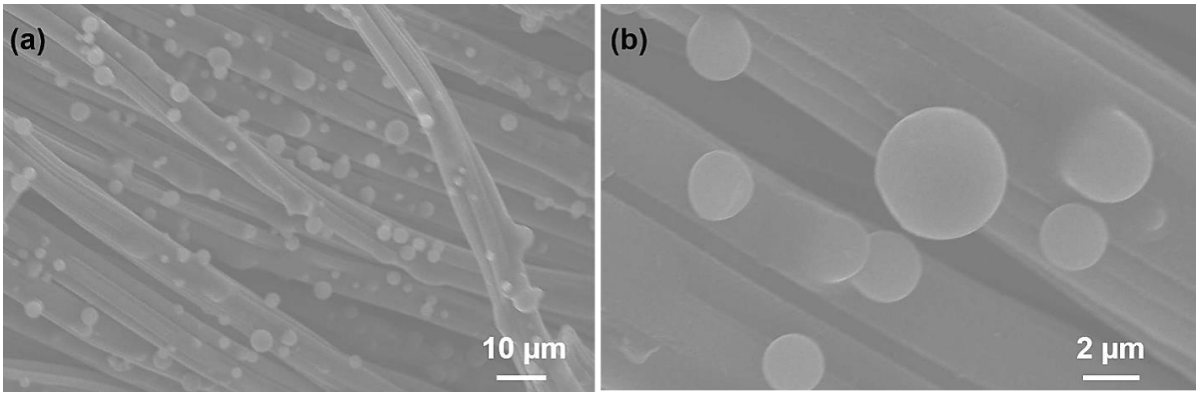


**Figure S4.** SEM images of the Pt/CC electrode at different magnifications.

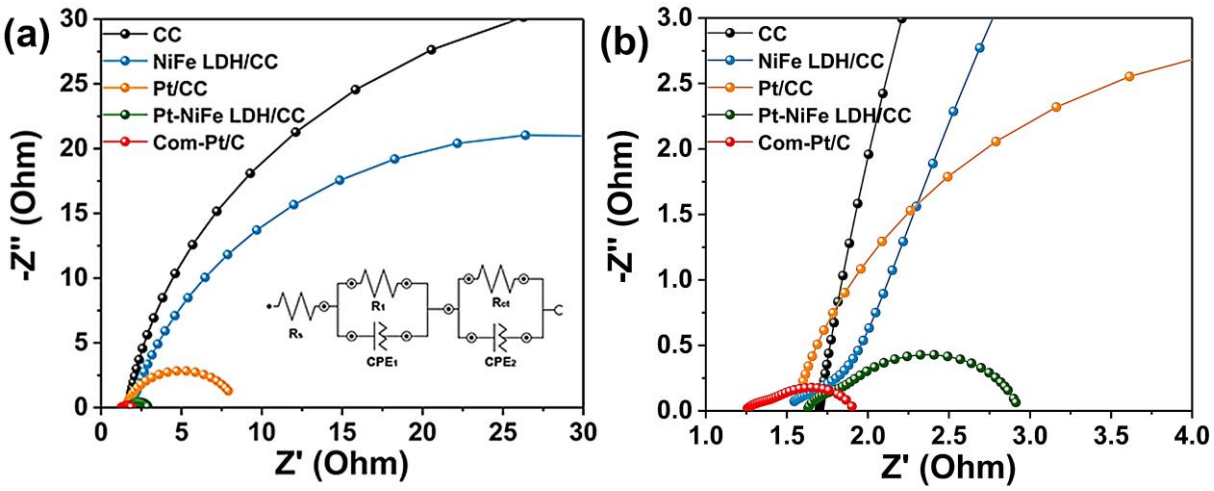


**Figure S5.** Nyquist plots of different HER catalysts measured at an overpotential of 200 mV in the frequency range of $10^5$-0.01 Hz. Inset in Figure S5a showing the modified Randle equivalent circuit model.

**Table S1.** Summary of $R_s$ and $R_{ct}$ for different HER catalysts by fitting the Nyquist plots using the equivalent circuit model.

| | $R_s$ (Ohm) | $R_{ct}$ (Ohm) |
|---|---|---|
| Pt-NiFe LDH/CC | 1.62 | 1.1 |
| Com-Pt/C | 1.24 | 0.49 |
| Pt/CC | 1.55 | 6.91 |
| NiFe LDH/CC | 1.47 | 36.5 |
| CC | 1.75 | 52.4 |

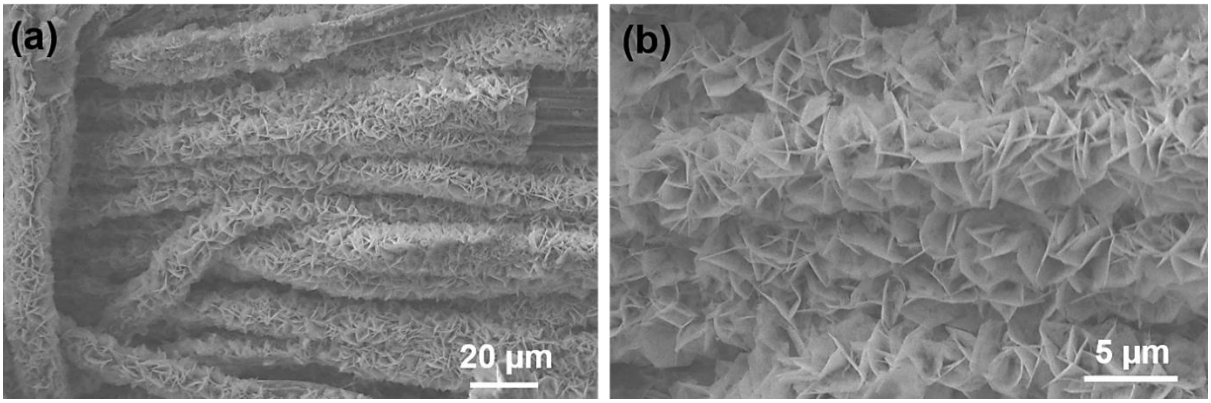


**Figure S6.** SEM images of the Pt-NiFe LDH/CC electrode at different magnifications after HER stability test.

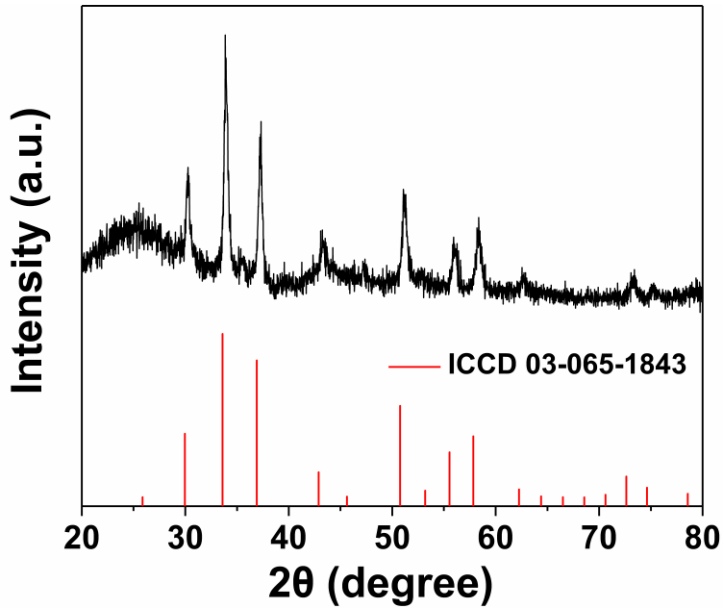


**Figure S7.** XRD pattern of the $(Ni_{0.77}Fe_{0.23})Se_2$/CC composite electrode.

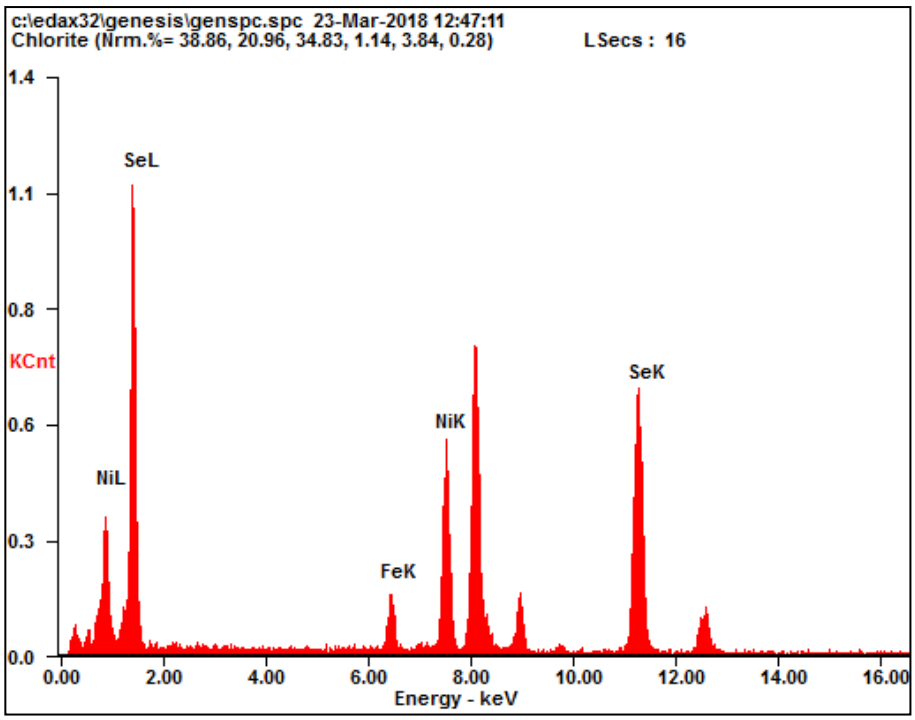


**Figure S8**. EDS plot of the $(Ni_{0.77}Fe_{0.23})Se_2$/CC.

**Table S2.** Elemental summary of the $(Ni_{0.77}Fe_{0.23})Se_2$/CC.

| | **Atomic %** |
|---|---|
| **Fe** | 8.31 |
| **Ni** | 27.79 |
| **Se** | 63.90 |

**Table S3.** Atomic ratio of Ni/Fe in the $(Ni_{0.77}Fe_{0.23})Se_2$/CC sample determined by ICP-MS.

| | **Atomic %** |
|---|---|
| **Fe** | 21.68 |
| **Ni** | 78.32 |

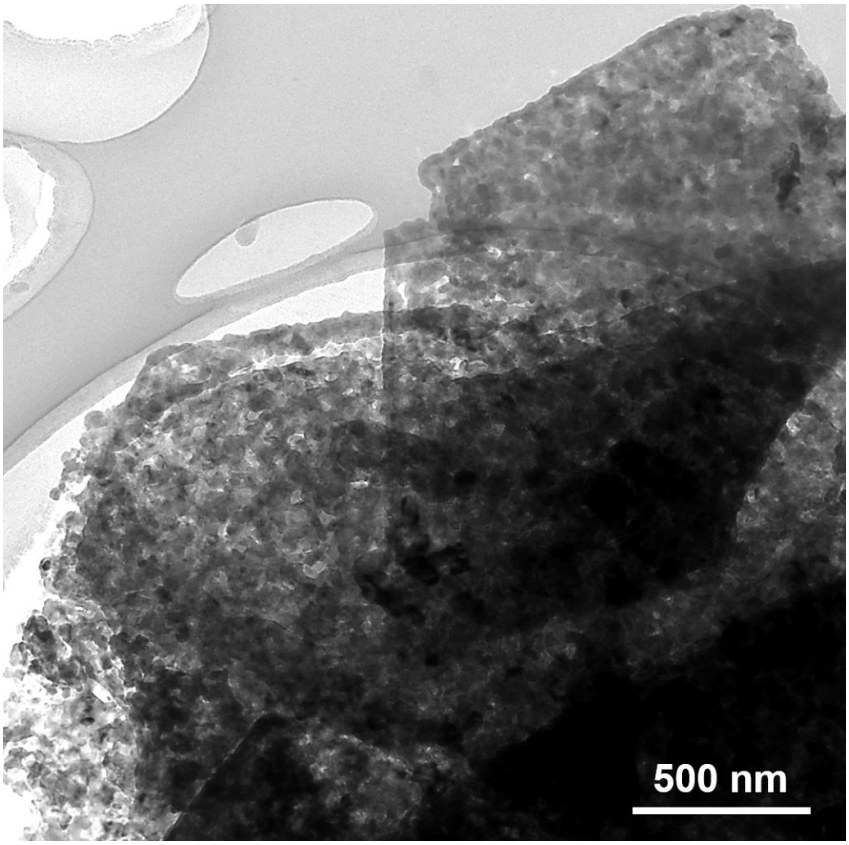


**Figure S9.** TEM image of the $(Ni_{0.77}Fe_{0.23})Se_2$ nanosheets.

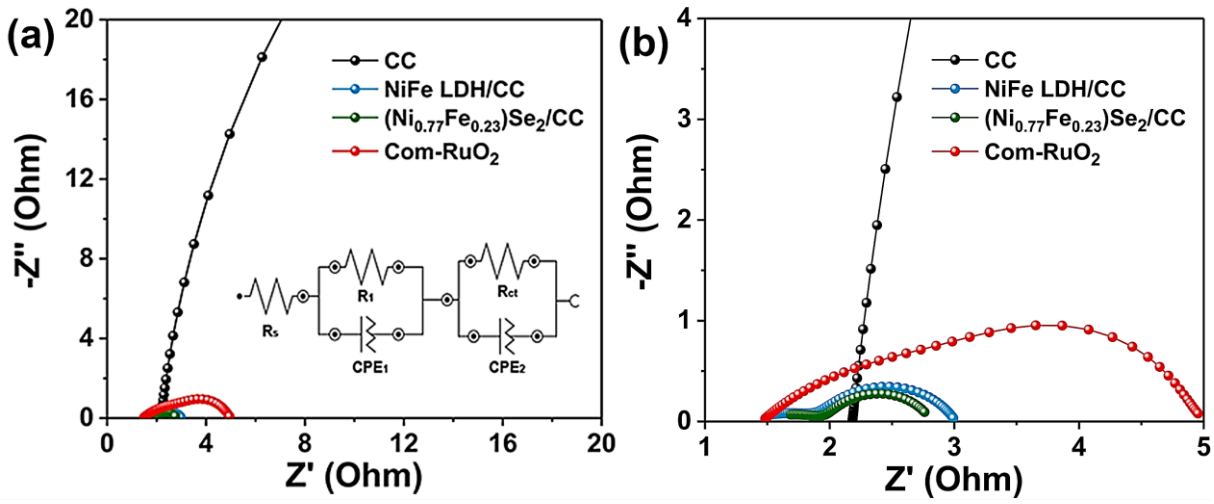


**Figure S10.** Nyquist plots of different OER catalysts measured at an overpotential of 300 mV in the frequency range of $10^5$-0.01 Hz. Inset in Figure S10a showing the modified Randle equivalent circuit model.

**Table S4.** Summary of $R_s$ and $R_{ct}$ for different OER catalysts by fitting the Nyquist plots using the equivalent circuit model.

| | $R_s$ (Ohm) | $R_{ct}$ (Ohm) |
|---|---|---|
| $(Ni_{0.77}Fe_{0.23})Se_2$/CC | 1.41 | 0.788 |
| Com-$RuO_2$ | 1.46 | 1.07 |
| NiFe LDH/CC | 1.34 | 1.02 |
| CC | 2.18 | 138 |

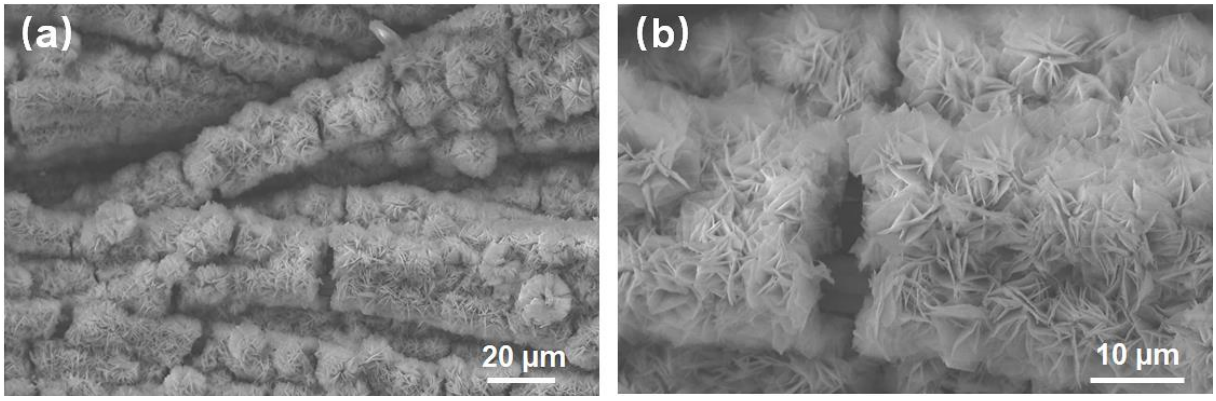


**Figure S11.** SEM images of the $(Ni_{0.77}Fe_{0.23})Se_2$/CC at different magnifications after OER stability test.

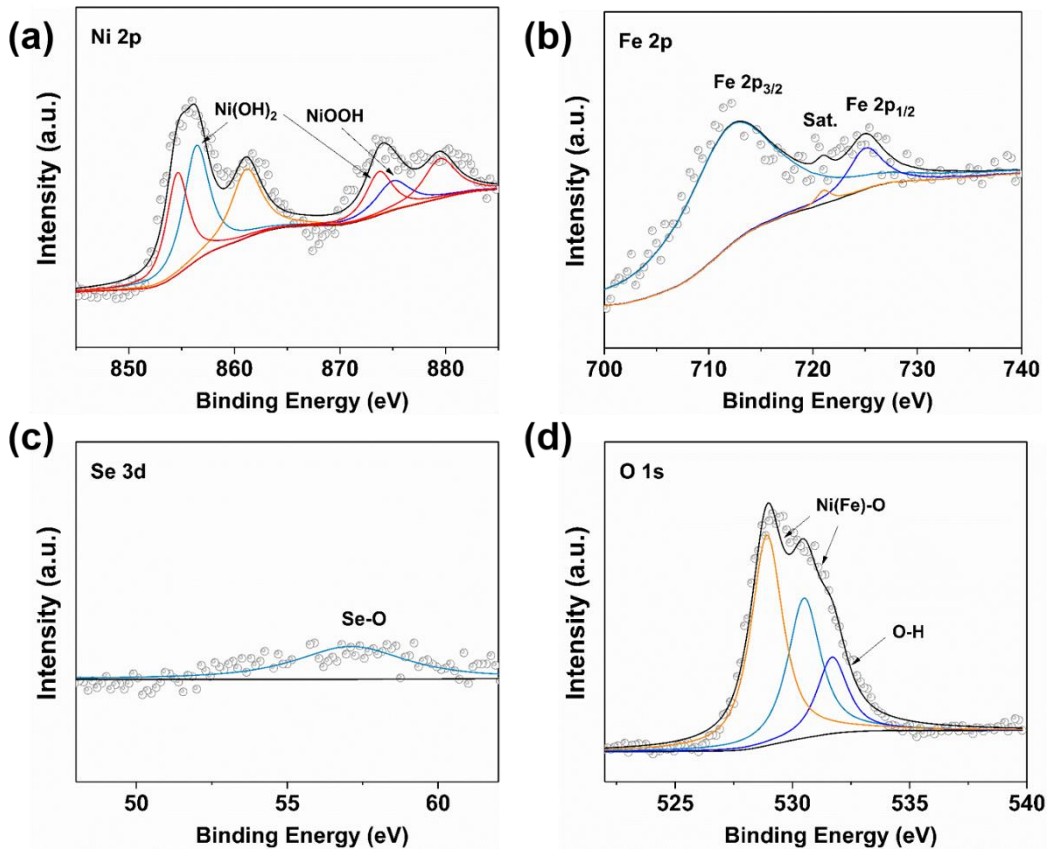


**Figure S12.** (a) Ni 2p, (b) Fe 2p, (c) Se 3d and (d) O 1s XPS spectra of the $(Ni_{0.77}Fe_{0.23})Se_2$/CC after OER stability test.

**Table S5.** Performance comparison of our Pt-NiFe LDH/CC || $(Ni_{0.77}Fe_{0.23})Se_2$/CC water electrolyzer with other water splitting systems.

| Water splitting system (HER catalyst \|\| OER catalyst) | Support | Electrolyte | Voltage (V)@ 10 mA $cm^{-2}$ | Reference |
|---|---|---|---|---|
| CoP NS-2 \|\| $Co_3O_4$ NS-2 | NF | 1 M KOH | 1.63 | [1] |
| NiFe LDHs/NF \|\| NiFe LDHs/NF | NF | 1 M KOH | 1.7 | [2] |
| $NiFe_2O_4$/NiFe LDH \|\| $NiFe_2O_4$/NiFe LDH | NF | 1 M KOH | 1.535 | [3] |
| PA-NiO \|\| PA-NiO | NF | 1 M KOH | 1.56 | [4] |
| $NiCo_2S_4$@NiFe LDH/ NF \|\| $NiCo_2S_4$@NiFe LDH/ NF | NF | 1 M KOH | 1.6 | [5] |
| $Ni_{0.75}Fe_{0.125}V_{0.125}$-LDHs/NF \|\| $Ni_{0.75}Fe_{0.125}V_{0.125}$-LDHs/NF | NF | 1 M KOH | 1.591 | [6] |
| (Ni,Co)$Se_2$-GA \|\| (Ni,Co)$Se_2$-GA | NF | 1 M KOH | 1.60 | [7] |
| $Co_5Mo_{1.0}P$ NSs@NF \|\| $Co_5Mo_{1.0}O$ NSs@NF | NF | 1 M KOH | 1.68 | [8] |
| $Ni_3S_2$-300\|\| $Ni_3S_2$-300 | NF | 1 M NaOH | 1.611 | [9] |
| VOOH nanospheres\|\|VOOH nanospheres | NF | 1 M KOH | 1.62 | [10] |
| $Co_1Mn_1$CH/NF \|\| $Co_1Mn_1$CH/NF | NF | 1 M KOH | 1.68 | [11] |
| $Mo_2C$@C \|\| $Mo_2C$@C | NF | 1 M KOH | 1.73 | [12] |
| NiFe-MOF/NF \|\| NiFe-MOF/NF | NF | 0.1 M KOH | 1.55 | [13] |
| Ni@NC-800/NF \|\| Ni@NC-800/NF | NF | 1 M KOH | 1.6 | [14] |
| Fe-$H_2$cat \|\| Fe-$O_2$cat | IF | 1 M KOH | 1.65 | [15] |
| $Co_3Se_4$/CF \|\| $Co_3Se_4$/CF | CF | 1 M KOH | 1.59 | [16] |
| EG/$Co_{0.85}$Se/NiFe-LDH \|\| EG/$Co_{0.85}$Se/NiFe-LDH | GF | 1 M KOH | 1.67 | [17] |
| Cu@NiFe LDH \|\| Cu@NiFe LDH | CuF | 1 M KOH | 1.54 | [18] |

| | | | | |
|---|---|---|---|---|
| CoP/NCNHP \|\| CoP/NCNHP | CP | 1 M KOH | 1.64 | [19] |
| $Co_2P$/CNT \|\| $Co_2P$/CNT | CP | 1 M KOH | 1.53 | [20] |
| Pt-$CoS_2$/CC \|\| Pt-$CoS_2$/CC | CC | 1 M KOH | 1.55 | [21] |
| $NiCoSe_2$ \|\| $NiCoSe_2$ | CC | 1 M KOH | 1.62 | [22] |
| **Pt-NiFe LDH/CC \|\| $(Ni_{0.77}Fe_{0.23})Se_2$/CC** | **CC** | 1 M KOH | **1.52** | **This work** |

Notes: NF-Nickel foam; IF-Iron foam; CF-Cobalt foam; GF-Graphite foil; CuF-Cu foam; CP-Carbon paper; CC-Carbon fiber cloth.

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