NiCo LDH Derived Defect-Engineered Se-Doped NiCoP Mesoporous Nanoflowers for Enhanced Oxygen Evolution Reaction

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1. Experimental Section

1.1. Materials

$Ni(NO_3)_2$, $Co(NO_3)_2$, Se powder, NaH_2PO_2, CTAB, Methanol, Acetone, HCL, KOH and Ni foam (NF) were procured from Sigma-Aldrich. All the chemicals were obtained without further treatment. Deionized water (DI water) obtained from a water purification system (Millipore, Billerica, MA) was used throughout the experiment.

1.2. Synthesis of NiCo LDH/NF (NCL/NF)

The NiCo LDH/NF was synthesized through a solvothermal technique.[1] At first the 7 mM metal nitrate salts of Ni and Co with a ratio of 1:1 was dissolved in a methanol-water (5:1) aqueous solution (36 mL). After that, 0.25 mg of CTAB has been added to the above solution and stirred for 30 minutes. Subsequently, the homogeneous solutions were transferred to a 100 mL Teflon-lined autoclave and then after pre-cleaned NF (1 x 2 cm^2) were immersed in the solution and placed face down with a slanting angle against the wall. The autoclave was sealed and maintained at 180 °C for 24h. The as-obtained NiCo LDH/NF was rinsed with distilled water and ethanol and finally dried at 60 °C for 12 h under a vacuum environment. It was denoted as NCL/NF.

1.3. Synthesis of NiCoP-Se/NF (NCP-Se/NF)

The NiCoP-Se/NF was synthesized through the pyrolysis method in a tubular furnace under a nitrogen atmosphere.[2] The as-obtained NCL/NF was placed in the downstream and a mixture of NaH_2PO_2 (20 times) and Se powder (4 times) was placed in the up-stream of the tube. The phosphor-selenization reaction was performed at 350 °C with 2°/min for 2h under an inert environment in order to obtain the NiCoP-Se/NF catalyst which was then stored in vacuum condition for further use. It was denoted as NCP-Se/NF. A similar procedure was followed to prepare the NiCoP/NF electrocatalyst without taking Se powder and named as (NCP/NF). For comparison study, two more catalyst was prepared by varying the Se powder to parent NCL weight ratio of 3:1 (NCP-Se3) and 5:1 (NCP-Se5). Moreover, a CTAB control material was synthesized named as NCP-Se(WC)/NF.

1.4. Synthesis of RuO_2/NF

According to previous reports, 2 mg of commercial RuO_2 was dispersed in 500μL of ethanol, 485 μL of DI water, and 15 μL of Nafion, and then sonicated for 30 min to obtain a uniform ink mixture. Finally, the mixture was drop-casted on an effective surface area of 1x1 cm^2 of NF and dried overnight in a vacuum oven.

2. Physicochemical characterization technique

The phase purity and crystalline properties of the as-synthesized NiCo LDH/NF, NiCoP/NF, NiCoSe/NF and NiCoPSe/NF have been measured by X-ray diffraction (Rigaku-Ultima IV, CuKα radiation source, scanning window $2\theta = 10^o - 80^o$) at a scan rate of 10 °C min^{-1}. The topological characteristics were measured by Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) (TEM, JEOL-2100) field-emission scanning electron microscopy (FESEM, ZEISS, S-4800) and corresponding selected area electron diffraction (SAED). The electronic environment and oxidation states of the as-synthesized electrocatalyst were analyzed by X-ray photoelectron spectroscopy (XPS) characterization. The functional groups present in the as-synthesized materials have been measured by Fourier Transform Infrared spectrometer (FTIR) technique JASCO FTIR-4600. For Brunauer–Emmett–Teller (BET) surface area measurement, N_2 adsorption–desorption technique was adopted by specific surface area analyzer (NOVA3000, Quanta chrome GmbH, Germany) and Barrett–Joyner–Halenda (BJH) technique was carried out to calculate the pore size distribution and pore volumes. The electron paramagnetic resonance (EPR) spectroscopy was characterised to determine the P-vacancy using a Bruker A300 Germany instrument.

3. Electrochemical characterisations technique

All electrochemical performance was conducted at room temperature by three-electrode configuration performed with IVIUMnSTAT single channel electrochemical analyser in 1M KOH electrolyte (pH= 14). In this three-electrode system, a Pt wire serves as the counter, an Ag/AgCl electrode serves as the reference, and as-synthesized NCL/NF, NCP/NF, NiCoPSe/NF, or NiCoPSe/NF serve as the working electrodes. The active material loading on nickel foam for all as-prepared catalyst was maintained in the range of ~2.1-3.3 mg/cm^2. The Linear sweep voltammetry (LSV) polarization curve was measured at a slow scan rate of 2 mV/sec. 85% iR was corrected manually from the R_S of the EIS study. The continuous accelerated-degradation (AD) cyclic voltametric (CV) was performed at a very high sweep rate of 50 mV/s for 500 cycles in 1 M KOH for OER. Chronoamperometry (CA) was conducted for 10 h at constant potential of 1.65 V vs RHE. Similarly, multi current process (10-50 mA/cm^2) chronopotentiometry (CP) was measured for the optimised electrode.

The whole resulting potential data were taken in Ag/AgCl electrode and later it was converted to the reversible hydrogen electrode (E_{RHE}) scale by using Nernst equation (S1)

$$E_{RHE} = E^{0}_{Ag/AgCl} + E_{Ag/AgCl} + 0.059 \times pH \text{ .... (S1)}$$

Over potential (η) values of all as-prepared electrode at 10, 50 and 100 mA/cm^2 benchmarking current density have been estimated through above equation (S2)

$$Over\ potential(\eta) = E_{RHE} - 1.23V \text{........................}(S2)$$

The iR corrected Tafel slope was calculated by fitting η *vs* log(j) using this Tafel equation

$$\eta = \beta \log\left(\frac{j}{j_0}\right) \text{.....................................} (S3)$$

where β implies the value of Tafel slope, j and j_0 denotes the current density and the exchange current density respectively. Electrochemical impedance spectroscopy (EIS) characterisation was performed from the frequency ranges of 10^5 to 0.1 Hz at 1.56 V *vs* RHE for OER. Then the electrochemically active surface areas (ECSA) can be calculated by analysing the electrochemical double layer capacitance (C_{dl}) as follows:

$$\Delta J = \nu \times C_{dl} \text{...} (S4)$$

$$ESCA = \frac{C_{dl}}{C_s} \text{................................}(S5)$$

where ΔJ signifies the double-layer charging current resulting from the non-faradic potential region of CV outcomes at different scan-rates (ν) , C_s is the specific capacitance value of flat electrode surface i.e., 40 μF/cm^2 depending on the typical reported values. The specific activity of the electrocatalysts was calculated by normalizing the geometric current density with respect to ECSA values i.e.,

$$Specific\ Activity = J_{ESCA} = \frac{J_{geo}}{ESCA} \text{.....................} (S6)$$

Determination of Surface concentration of NCP-Se/NF from the redox features of CV :

The area associated with the oxidation of Ni^{2+} to Ni^{3+} = 0.008967 VA

Henceforth, the associated charge is = 0.0089VA / 0.05 mVs^{-1} = 0.160 C

Now, the number of electrons transferred is = 0.160 C / (1.602 x 10^{-19}) C

= 9.9875 x 10^{17}

Subsequently the reduction of Ni^{3+} to Ni^{2+} is a single electron transfer reaction; the number of electrons calculated above is exactly the same as the number of surface-active sites

Hence, the number of Ni participating in OER is = 9.9875 x 10^{17}

In this present study, the Turnover Frequency (TOF) was determined from OER current density by assuming that the Ni atoms as surface-active sites that underwent the redox reaction just before the onset of OER only participated in OER electrocatalysis.[3] The corresponding expression is

$$TOF = \frac{j \times N_A}{F \times n \times \tau} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (S7)$$

Where, j = current density, N_A= Avogadro number, F = Faraday constant, n = Number of electrons i.e. 4 for OER and τ = Surface concentration.

Hence, we have,

TOF = (74 x 10^{-3}) x (6.023 x 10^{23}) / (9.9875 x 10^{17}4 x 96485) =0.12 s^{-1}

Similarly, the TOF values for pristine NCL/NF and NCP/NF were determined form the redox feature and calculated values are found to be 0.08 and 0.10 s^{-1} respectively.

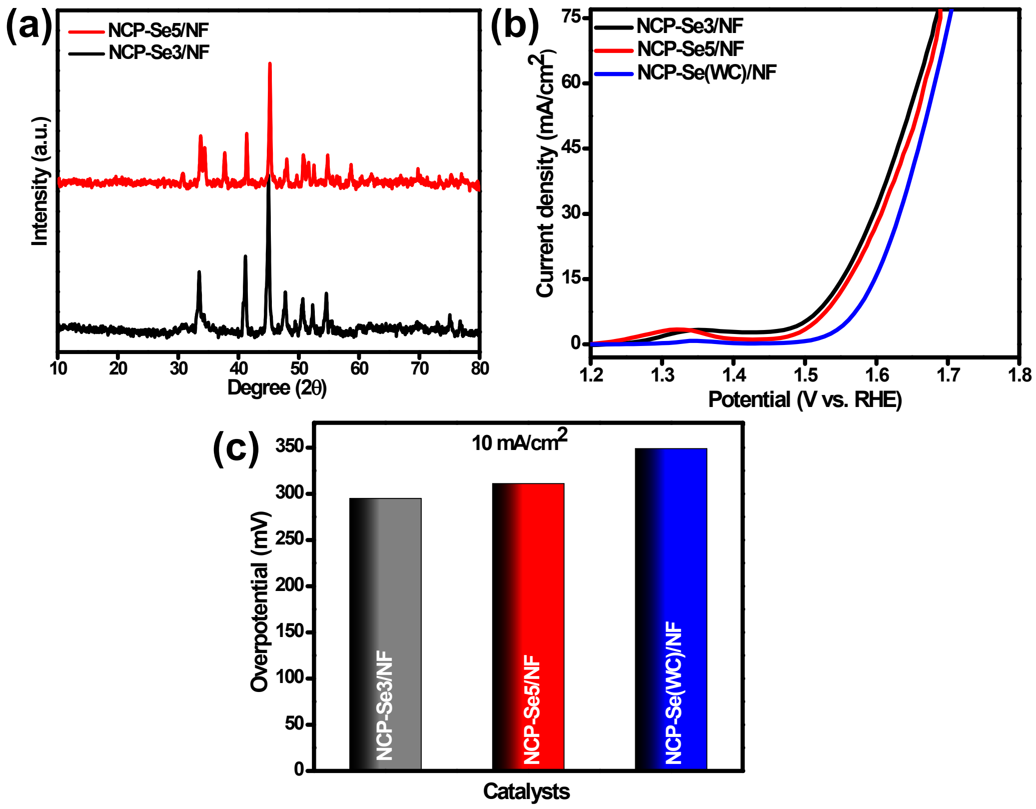

Fig. S1 (a) XRD plot of NCP-Se3/NF and NCP-Se5/NF, (b) LSV, and (c) Overpotential plot of NCP-Se3/NF, NCP-Se5/NF and NCP-Se(WC)/NF materials.

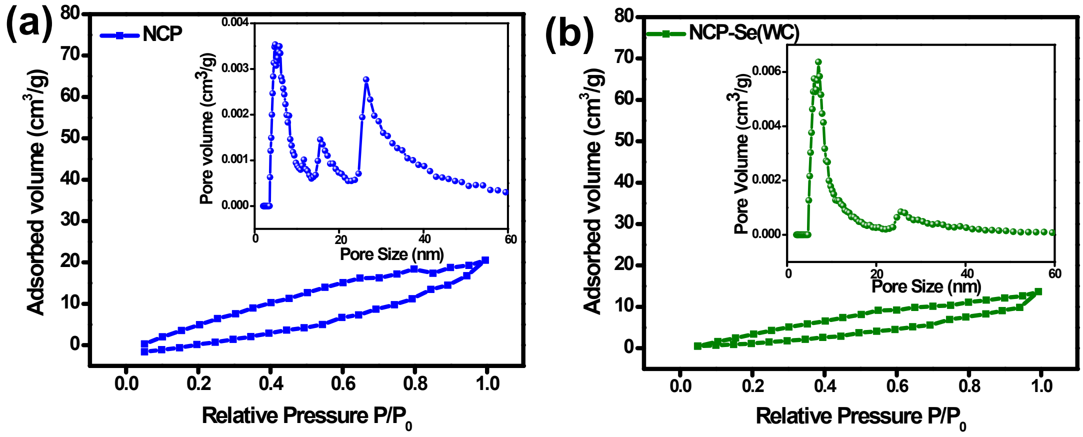

Fig. S2 N_2 adsorption-desorption isotherm of (a) NCP and (b) NCP-Se (WC) nanohybrid. Pore size distribution curve was inserted in their corresponding image.

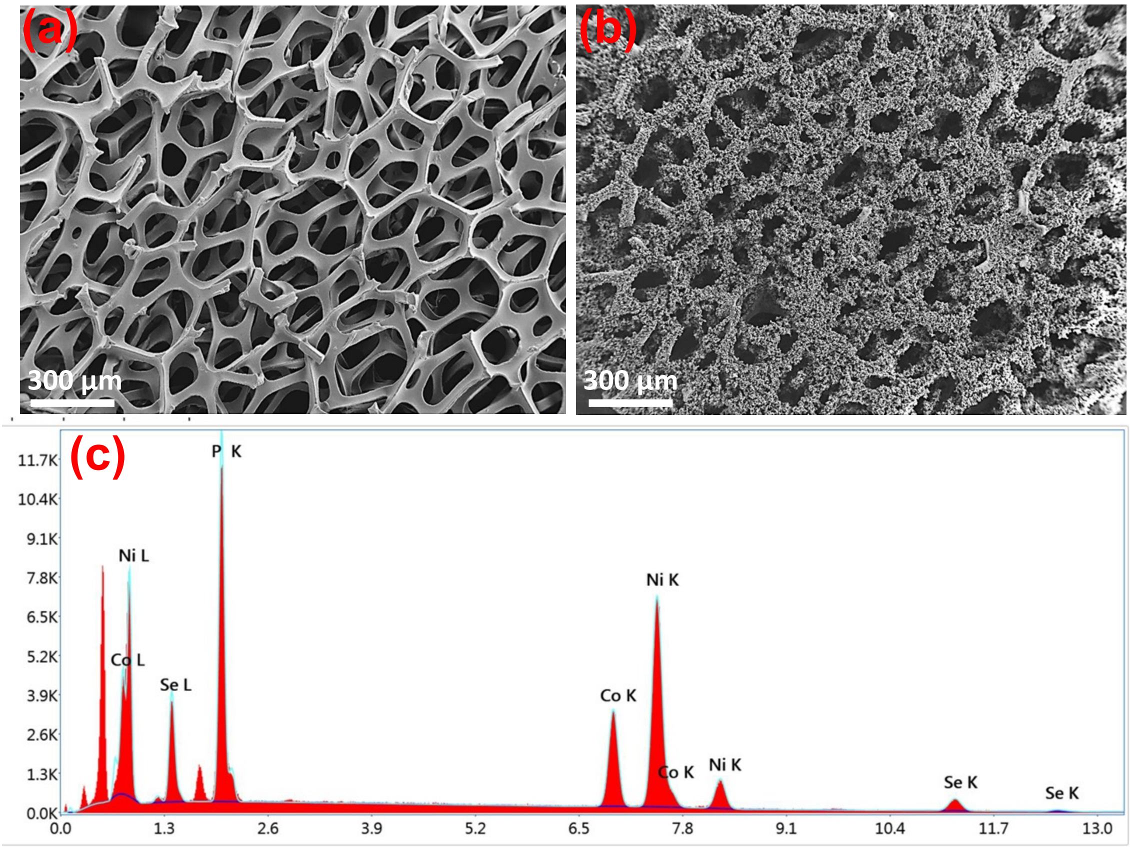

Fig. S3 FESEM image of (a) bare NF, (b) NCL/NF, and (c) EDAX image of NCP-Se/NF catalyst.

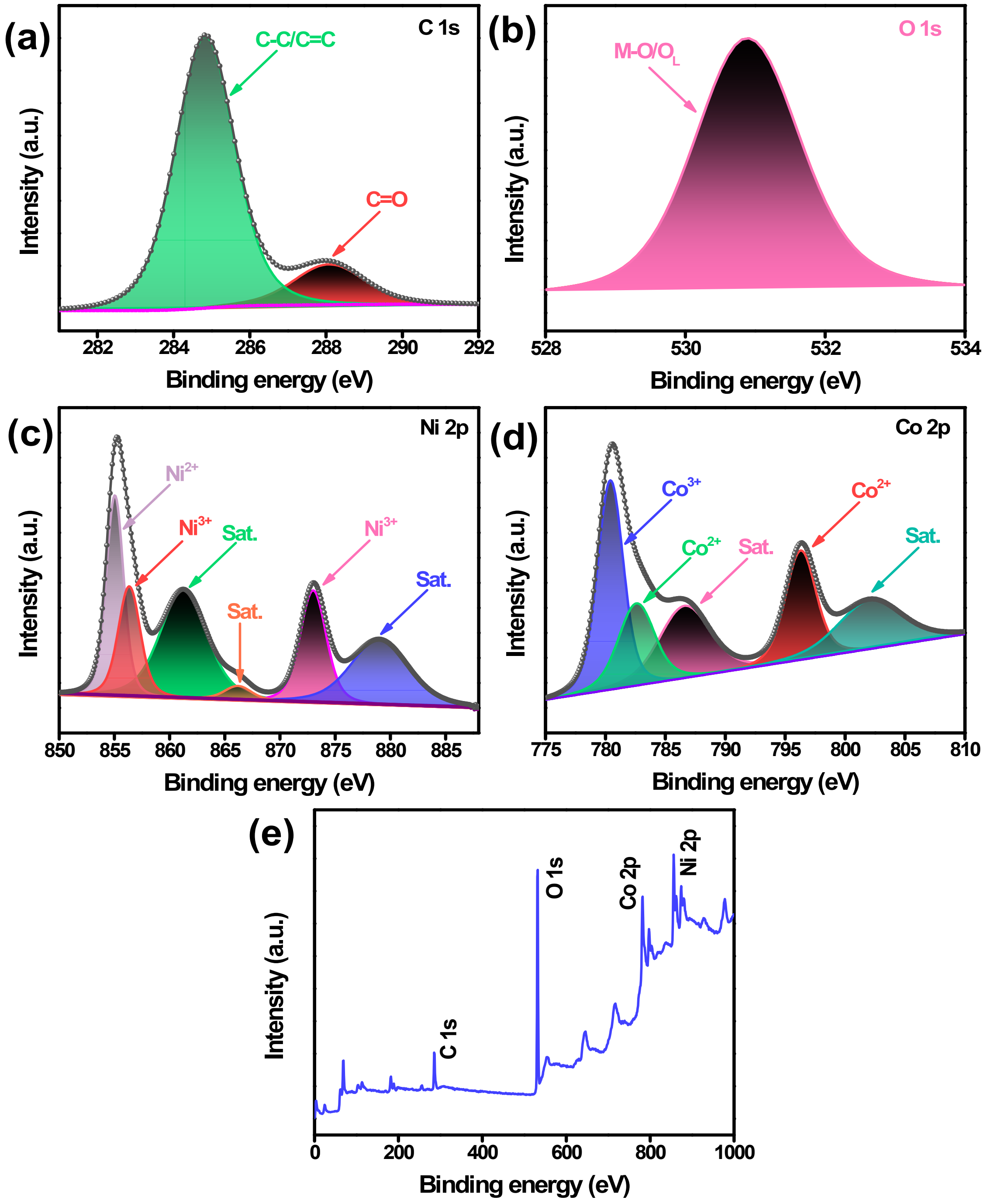

Fig. S4 (a) C 1s, (b) O 1s, (c) Ni 2p, (d) Co 2p, and (e) survey scan XPS spectrum of NCL.

Table S1. Quantitative analysis ratio of Ni^{2+}/Ni^{3+}, $\cdot$ Co^{2+}/Co^{3+}, Ni^{3+}/Ni^{2+} and Co^{3+}/Co^{2+} in Ni 2p and Co 2p XPS spectrum of NCL, NCP and NCP-Se nanohybrid respectively.

Catalysts	**Ni^{2+}/Ni^{3+}**	**Co^{2+}/Co^{3+}**	**Ni^{3+}/Ni^{2+}**	**Co^{3+}/Co^{2+}**
NCL	0.72	2.25	1.38	0.44
NCP	0.62	2.10	1.60	0.47
NCP-Se	0.41	1.16	2.42	0.85

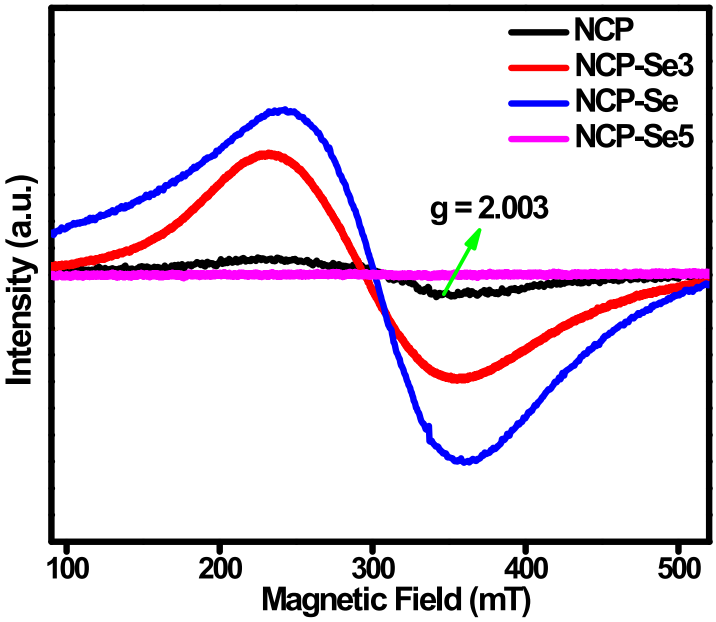

Fig. S5 EPR spectra of NCP, NCP-Se3, NCP-Se and NCP-Se5 catalysts.

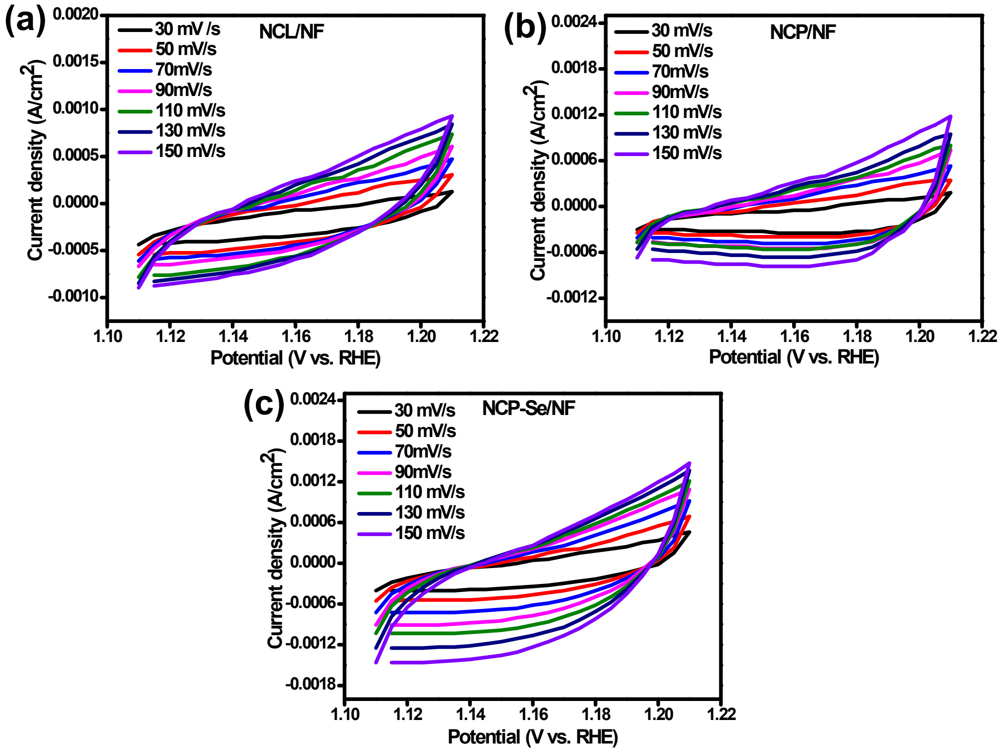

Fig. S6 Cyclic voltammetry feature of (a) pristine NCL/NF, (b) NCP/NF, and (C) NCP-Se/NF with a different applied scan rate value for obtaining the C_{dl} information.

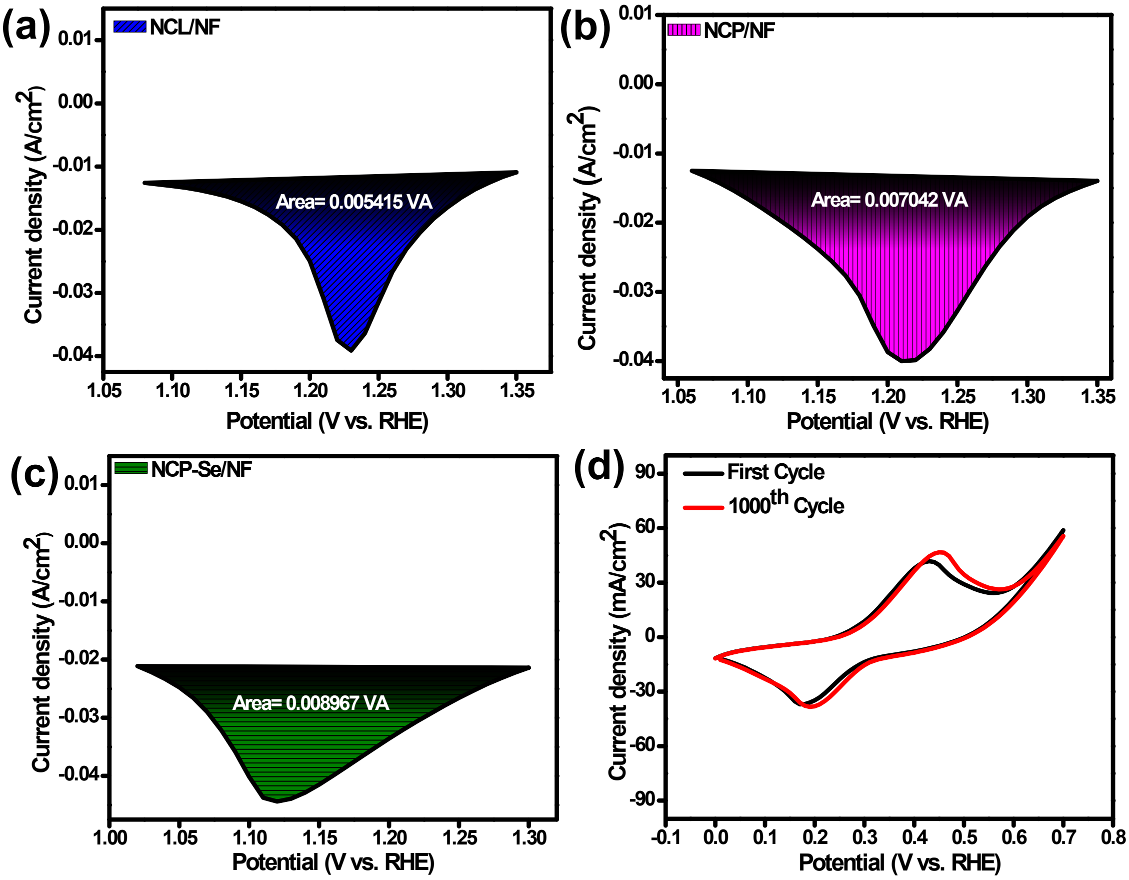

Fig. S7 Reduction area corresponding to Ni^{3+} to Ni^{2+} conversion of (a) NCL/NF, (b) NCP/NF, and (c) NCP-Se/NF materials and (d) First and 1000th CV cycles of NCP-Se/NF catalyst.

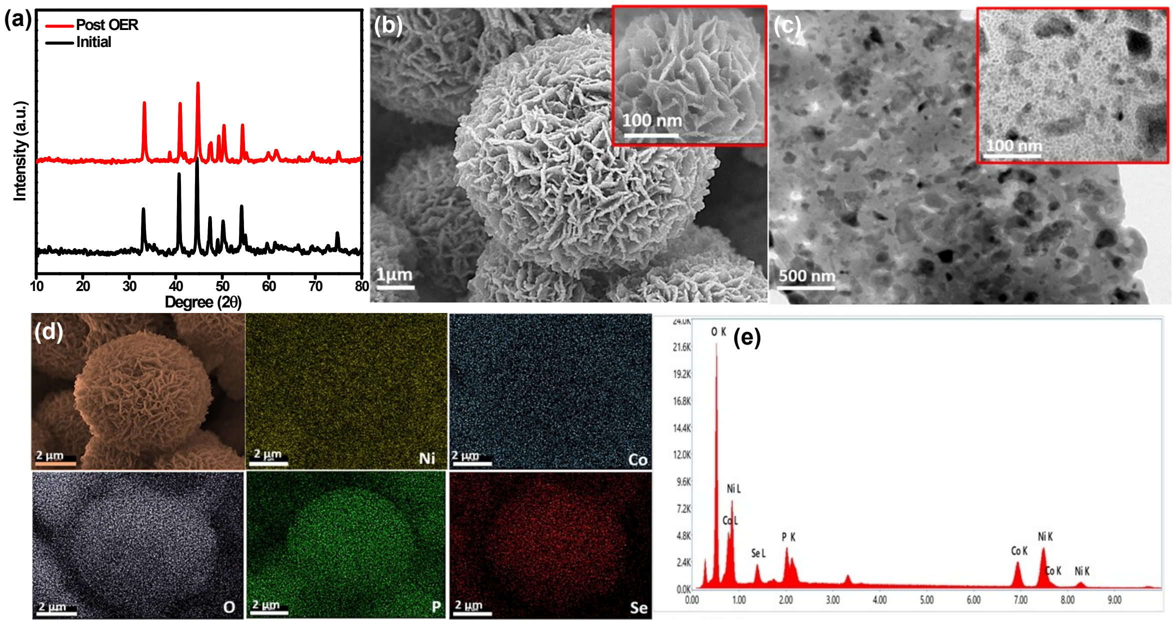

Fig. S8 Post OER characterisation of (a)XRD, (b) FESEM, (c) TEM, (d) elemental colour mapping, and (e) EDAX of NCP-Se material.

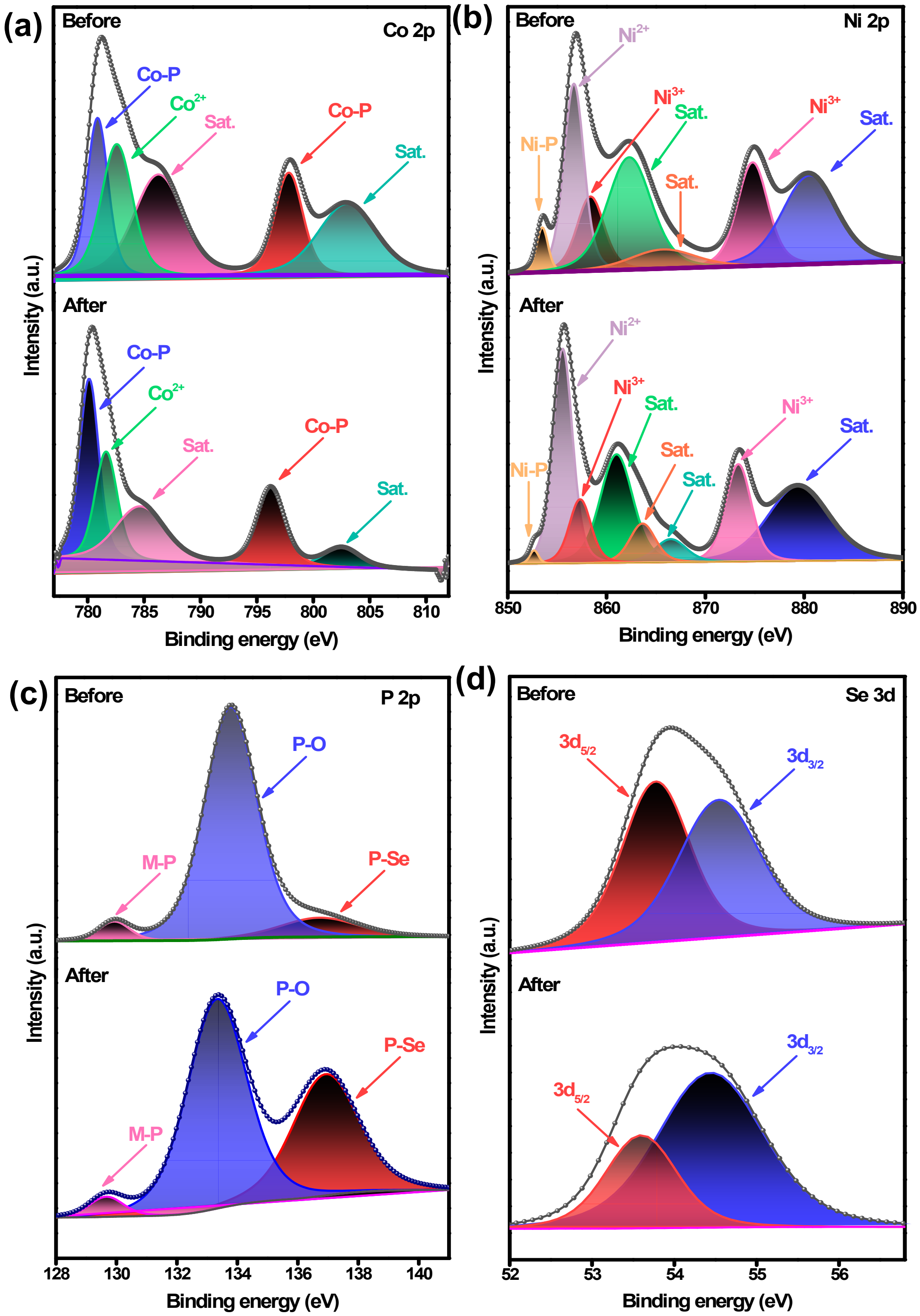

Fig. S9 Comparison of XPS plot before and after OER for (a) Ni 2p, (c) Co 2p, (d) P 2p, and (e) Se 3d, spectra of NCP-Se nanohybrid.

Table S2. The electrocatalytic OER activities of NCP-Se/NF were compared with similar types of catalysts reported in the table.

Electrocatalyst	**Electrolyte**	**Current density (mA cm^{-2})**	**Overpotential (mV)**	**Tafel slope (mV dec^{-1})**	**Ref**
NiCoP-Se	1M KOH	10	280	60.13	4
Ni_2P@NC	1M KOH	10	320	50	5
Fe-Ni_2P	1M KOH	20	260	52.65	6
Ni_2P–CoP@NC	1M KOH	10	267	95	7
O–NiCoP	1M KOH	10	310	84	8
R-CoP_x/rGO(O)	1M KOH	10	268	103	9
CoP-B1	1M KOH	10	297	58.1	10
0.75-NC Fe_xP	1M KOH	10	302	44	11
Fe-Ni_2P-V_P	1M KOH	10	289	54.7	12
Fe_1-NiCoP	1M KOH	50	293	43.6	13
NCP-Se/NF	**1M KOH**	**10**	**260**	**28.17**	**Present work**

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