

Supporting Information

Modulating electronic structure of ultra-thin NiCo-LDH by FeNiCoS₄ for efficient electrocatalytic urea oxidation

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The preparation of Fe_{0.9}Ni_{0.1}Co₂S₄/NF (FeNiCoS₄/NF) is taken as an example: Firstly, activate the nickel foam (NF) with ultrasonic cleaner, take the nickel foam (2*1) to the beaker, take dilute hydrochloric acid, acetone, ethanol, deionized water in turn and add to the beaker until it is not over the nickel foam, and ultrasonic for 10min to remove the surface oxidation layer and other impurities, and then put 0.9mmol Fe(NO₃)₃·9H₂O, 0.1mmol Ni(NO₃)₂·6H₂O, 2 mmol Co(NO₃)₂·6H₂O, 2 mmol CH₄N₂O and 4 mmol NH₄F were dissolved in 60 mL of deionized water and stirred until the solution was completely clear. The treated NF and the solution were transferred to a 100 mL Teflon lined stainless steel autoclave and reacted at 120°C for 10 hours. At the end of the reaction, the precursor was removed, the reactor was cleaned with spent nitric acid for four hours at 150°C, and the precursor was cleaned with deionized water and ethanol for several times to remove residues, and then dried in a vacuum drying oven at 60°C to obtain FeNiCoLDH/NF.

Na₂S·9H₂O was used as the sulfur source. 0.6 g of Na₂S·9H₂O was dissolved in 60 mL of deionized water and stirred until the solution was completely transparent. The precursor was put into the sulphide solution transferred to a 100 mL Teflon lined stainless steel autoclave and vulcanized at 180°C for 6 hours. At the end of the reaction, the product was removed and washed several times with deionized water and ethanol respectively. The samples were dried in vacuum at 60°C and noted as FeNiCoS₄/NF

The electro deposition process was carried out using chronoamperometry modul of station Ivium at 1.2V for 900s. 100 ml electroplating solution contains 1.5 mmol

Ni(NO₃)₂•6H₂O, 1.5 mmol Co(NO₃)₂•6H₂O and 4 mmol NH₄F. After several rinses with deionized water, the obtained product was dried overnight. The final product is NiCo-LDH/FeNiCoS₄/NF.

The catalyst structure was characterized by X-ray diffraction, the basic principle of which is that since the crystal has a very regular spatial structure, when the crystal is irradiated by a beam of monochromatic X-rays, the order of magnitude of the wavelength of the incoming X-rays is the same as that of the distance between these regularly arranged atoms, and therefore the X-rays scattered by different atoms interfere with each other, resulting in the strong X-ray diffraction of some special directions of the crystal, whose intensity is the same as that of the X-ray diffraction. The intensity and spatial distribution of X-rays are related to the structure of the crystal, which can be analyzed to obtain data such as the phase of the substance. In this experiment, the XRD of Fe NiCoS₄ was tested and compared with a standard card.

In this experiment, a three-electrode system electrolytic cell and an electrochemical workstation were used to test the electrochemical properties associated with the prepared catalysts. The electrolyte was 1 M KOH solution. The working electrode was NiCo-LDH/FeNiCoS₄ loaded on nickel foam (1 × 1 cm), the reference electrode was a saturated calomel electrode, and the counter electrode was a carbon rod.

① Linear scanning voltammetry test

The principle of linear scanning voltammetry is that a linear potential is applied between the auxiliary electrode and the working electrode of the electrolytic cell. According to the current-potential curve measured peak current and the concentration of the measured substance, the two show a linear relationship, from which quantitative analysis can be done. Commonly used potential scanning rates are 0.001 to 0.1 V s⁻¹. The tested potentials need to be converted to potential values relative to the standard hydrogen potential (RHE) according to the formula.

$$E_{\text{RHE}} = E_{\text{Hg/Hg}_2\text{Cl}_2} + 0.2415 + 0.0591 \times \text{pH}$$

② Calculation of Tafel slope

Tafel curve is generally obtained by fitting the polarization curve. And the smaller the value of Tafel slope, the stronger the charge transfer ability of the surface catalyst.

The expression is: $\eta = b \log j + a$, (where j is the current density and b is the Tafel slope)

③ Electrochemical impedance test

The principle of electrochemical impedance spectroscopy is to apply an AC signal of small amplitude and different frequency to the electrolytic cell system, and measure the variation of the ratio of voltage to current of the AC signal with the frequency of the sinusoidal waveform ω , or measure the variation of the phase angle Φ of the impedance with ω . The kinetic data of the electrode process is then analyzed. The test frequency of this experiment is 0.1Hz-100kHz.

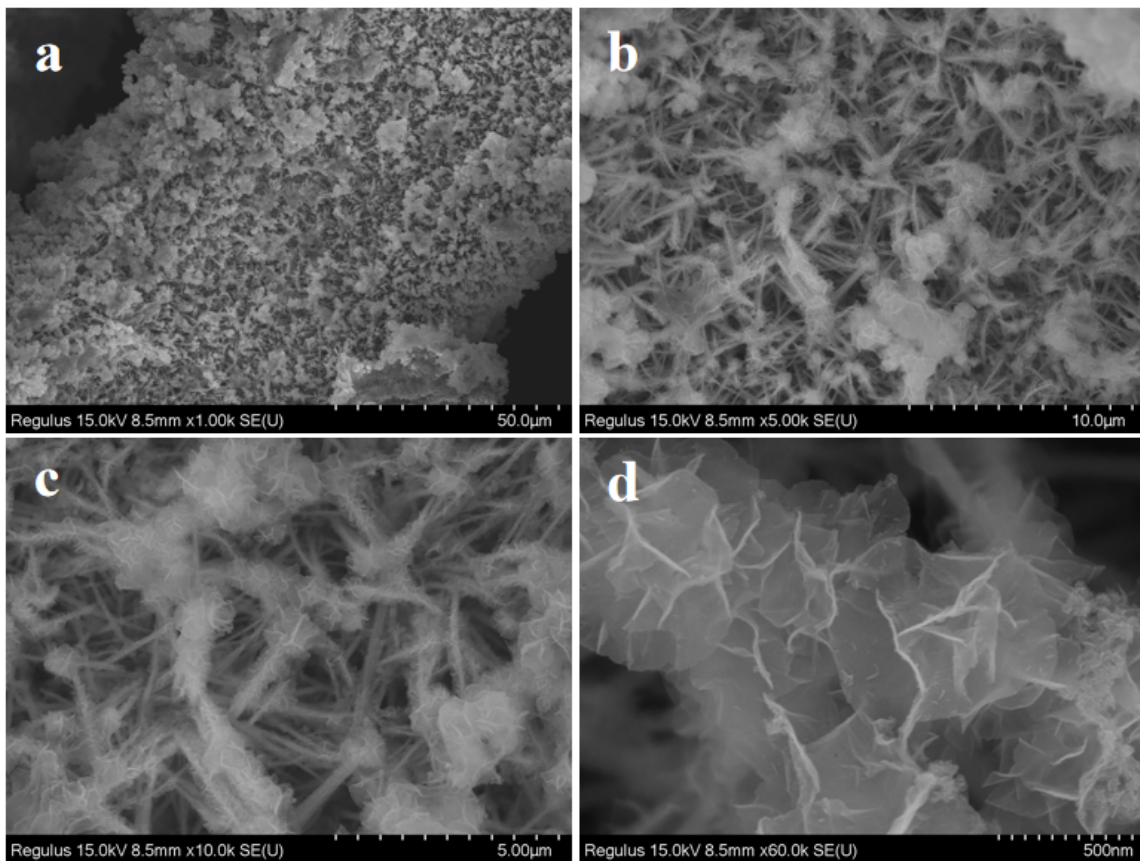


Fig S1. (a-d)SEM images of NiCo-LDH/FeNiCoS₄/NF.

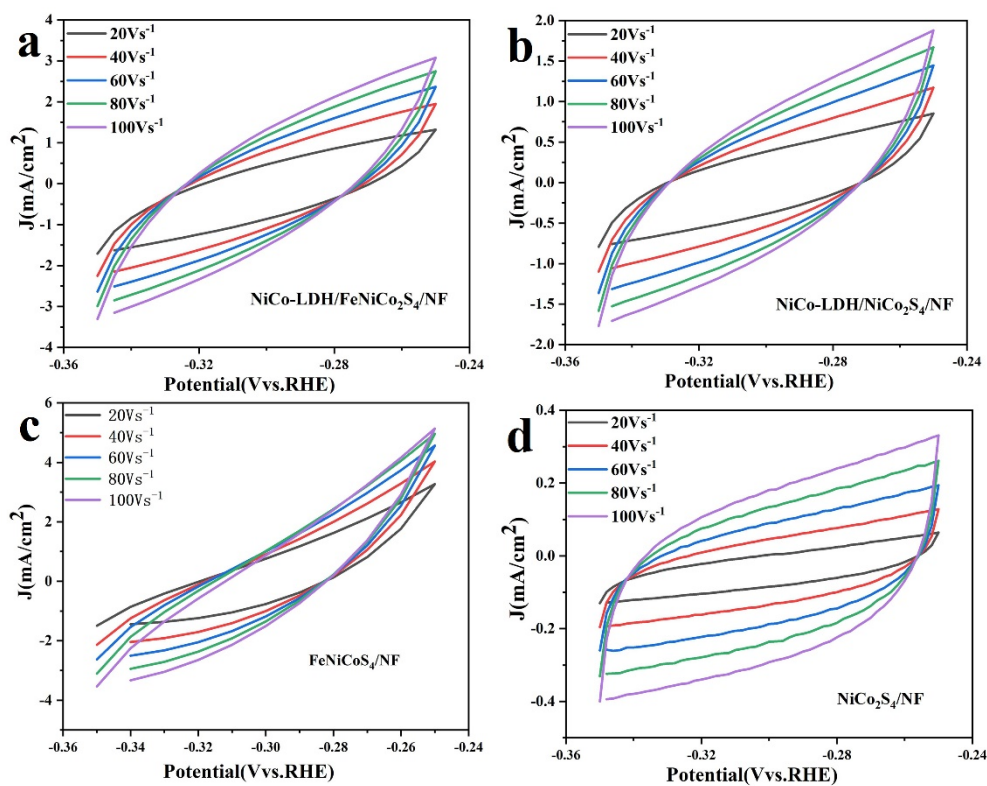


Fig S2. The 20,40,60,80,100 CV cycles of the urea oxidation process of (a)NiCo-LDH/FeNiCoS₄/NF.(b)NiCo-LDH/NiCo₂S₄/NF.(c)FeNiCoS₄/NF.(d)NiCo₂S₄/NF.

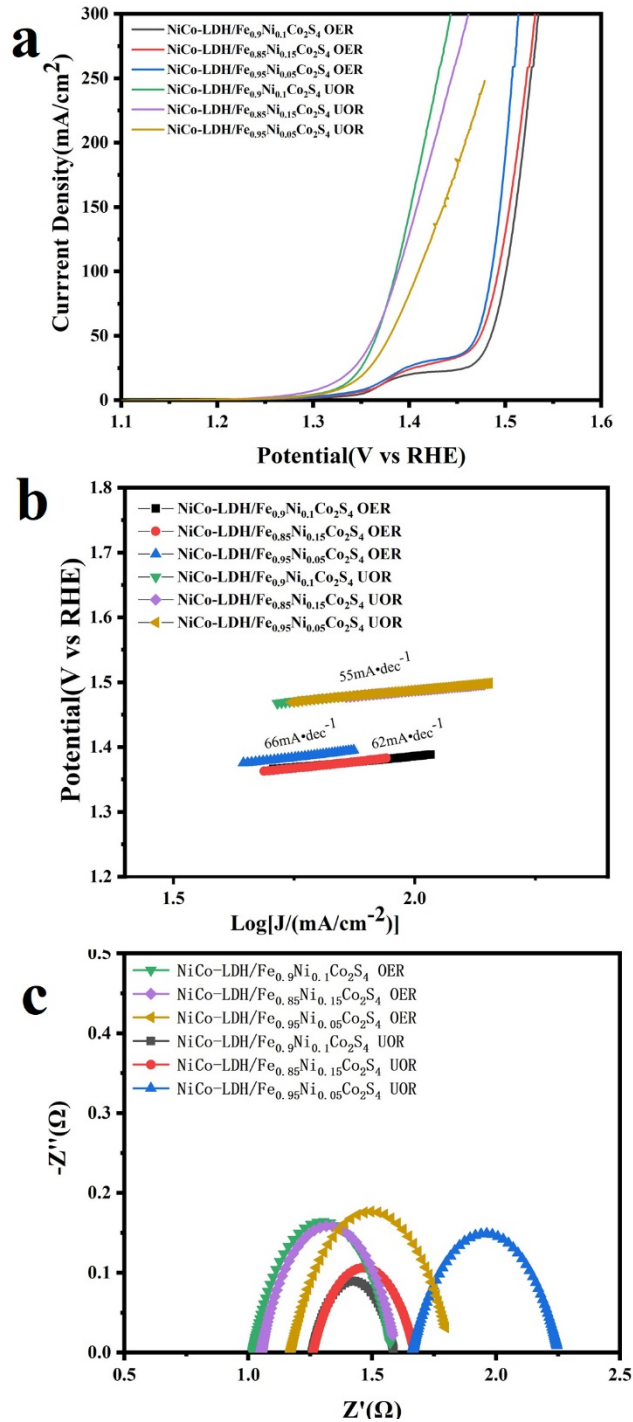


Fig S3. (a)LSV curves of OER and UOR in different proportions .**(b)** Tafel slopes of OER and UOR in different proportions. **(c)**Nyquist plots of OER and UOR in different proportions.

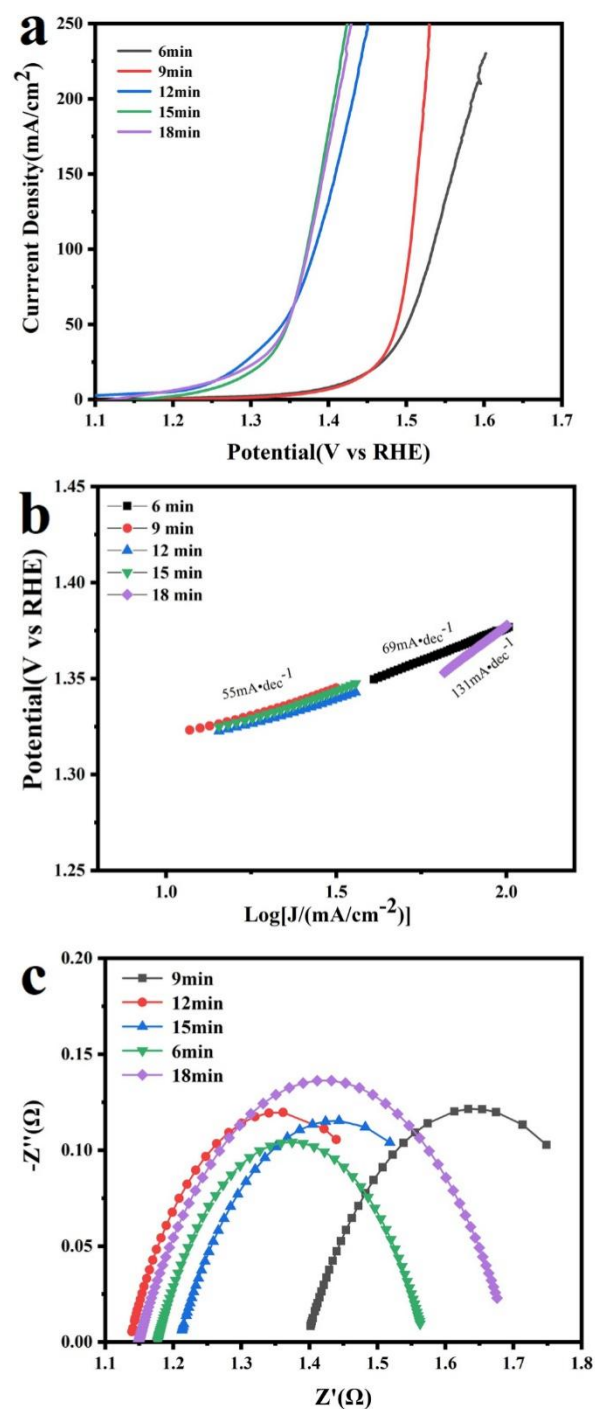


Fig S4. (a)LSV curves of different plating times.**(b)**Tafel slopes of different plating times.**(c)** Nyquist plots of different plating times.

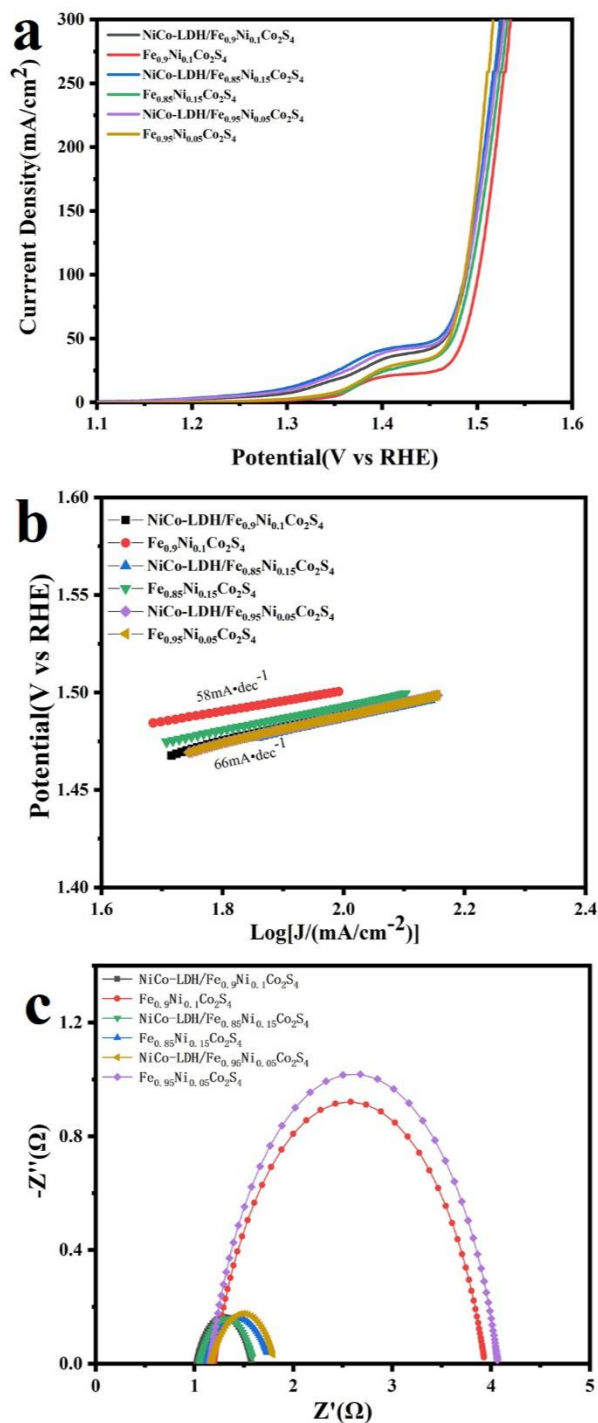
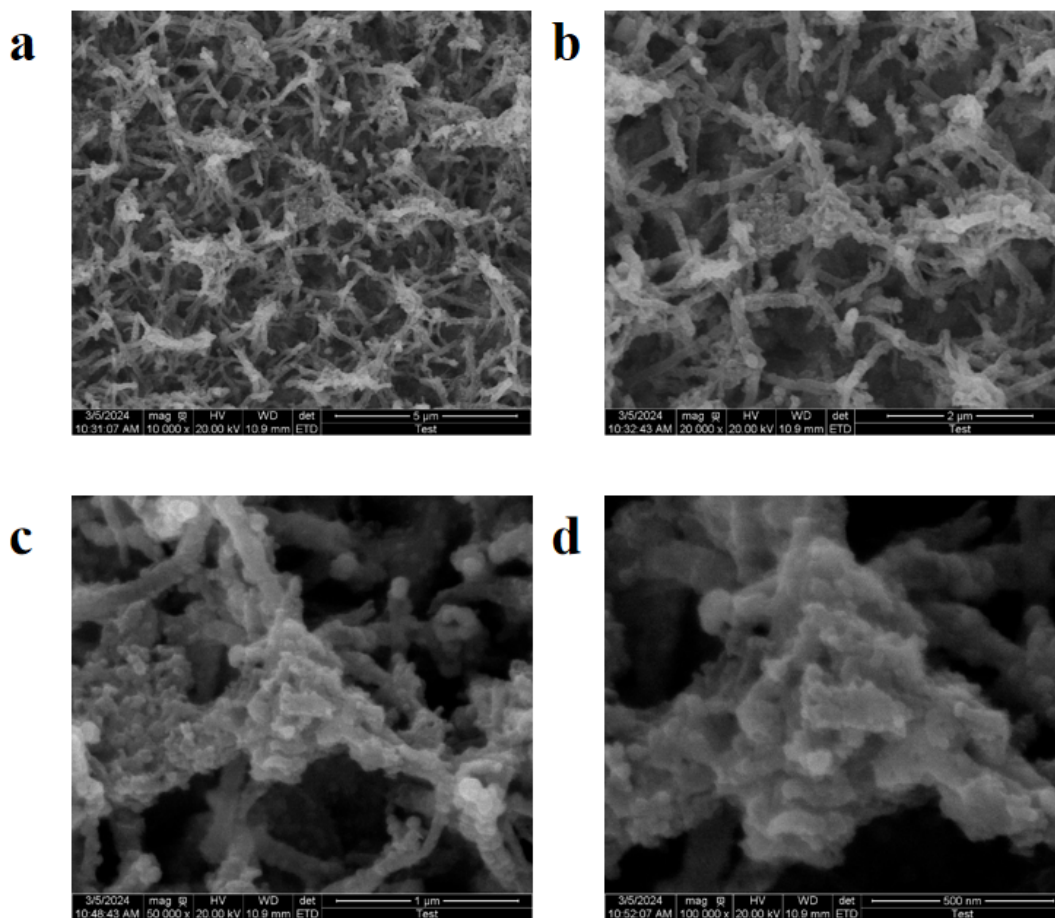


Fig S5. (a)LSV curves of NiCo-LDH/FeNiCoS₄/NF and NiCo-LDH/NiCo₂S₄/NF in different proportions .**(b)**Tafel slopes of NiCo-LDH/FeNiCoS₄/NF and NiCo-LDH/NiCo₂S₄/NF in different proportions.**(c)** Nyquist plots of NiCo-LDH/FeNiCoS₄/NF and NiCo-LDH/NiCo₂S₄/NF in different proportions



. Fig S6. SEM image of NiCo-LDH/FeNiCoS₄/NF after UOR for 12h.

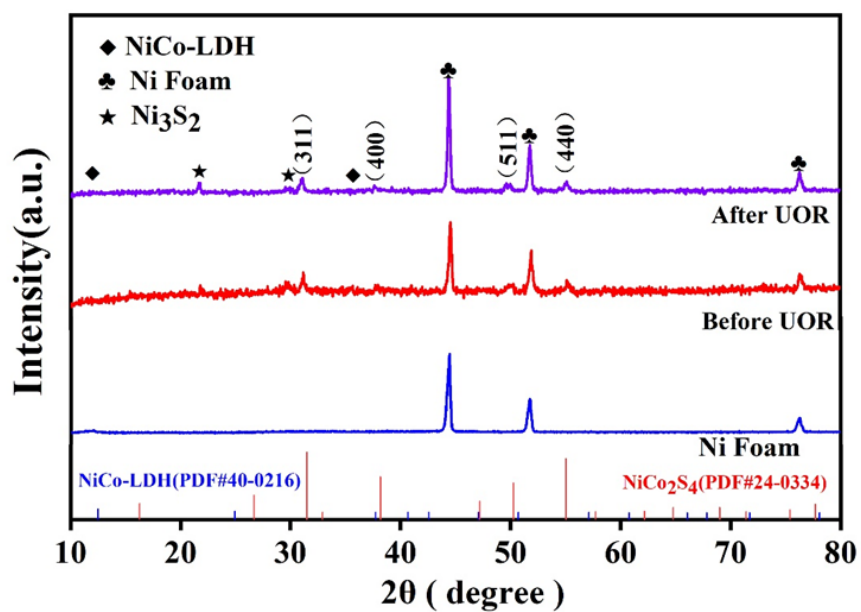


Fig S7. XRD patterns of NiCo-LDH/FeNiCoS₄/NF before and after UOR of 12h

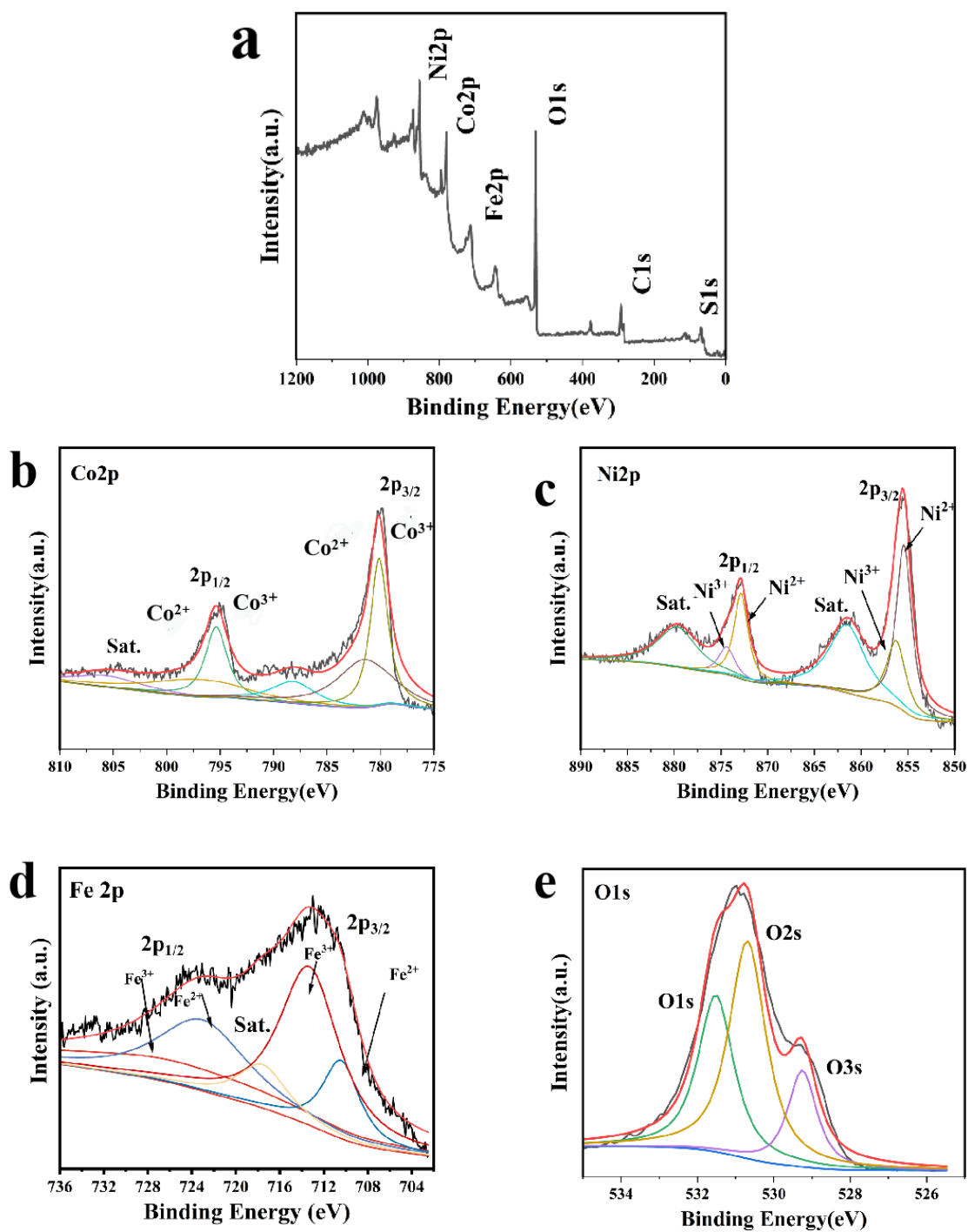


Fig S8. XPS spectra of (a) survey, (b) Co 2p, (c) Ni 2p, (d) Fe 2p and (e) O 1s spectra of NiCo-LDH/FeNiCoS₄/NF after UOR for 12h.

TableS1. The comparison chart of UOR potential at the current density of 50 and 100 mA cm⁻² with the recently reported catalysts.

| Catalysts | UOR potentials V(vs.RHE) (50mA.cm ⁻²) | UOR potentials V(vs.RHE) (100mA.cm ⁻²) | Reference |
|--|---|--|--|
| This work | 1.36V 1.38V | 1.38V | |
| Cr-Ni(OH) ₂ | 1.38 V | | Chem. Catal. 2022 2 3254-3270 |
| NiFe-LDH@Ni(OH) ₂ | 1.44 V | | Alloys Compd. 2022 921 166145 |
| CoFe _{0.75} Mn _{0.25} -LDH | 1.45 V | | J. Alloys Compd. 2022 925166754 |
| NiFeCoSe ₂ | 1.37 V | | Mater. Chem. Phys. 2022 287 126310 |
| NiS/MoS ₂ @FC P | 1.42 V | | J. Solid State Chem. 2020 292121644 |
| FeCo-LDH | 1.35 V | | Applied Catalysis A: General, 2022 118745 |
| Ni(OH) ₂ | | 1.6 V | Applied Catalysis B: Environmental, 2019 259 118020 |
| NiFe(OH) ₂ - SD/NF | | 1.52 V | J. Mater. Chem. A, 2019 7 26364 |
| NiMoV LDH/NF | | 1.4 V | Chemical Engineering Journal, 2022 133100 |
| MoP@NiCo-LDH/NF-20 | | 1.41 V | J. Mater. Chem. A 2020 8 18106- 18116 |
| NF/NiMoO ₄ -S | | 1.66 V | Applied Surface Science, 2023 1 155166 |
| Ni-Mo-O nanorod | | 1.45 V | Energy Environ.Sci, 2018 11 1890-1897 |