

Supporting Information

Constructing Hierarchical Wire-on-Sheet Nanoarrays in Phase-Regulated Cerium-Doped Nickel Hydroxide for Promoted Urea Electrooxidation

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1. Experimental section

1.1 Materials

The chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.. All chemicals were used as received without further purification.

1.2 Synthesis of the hierarchical α -Ni(OH)₂ wire-on-sheet nanoarrays

The α -Ni(OH)₂/NF nanoarray catalysts with variable concentrations of Ce were synthesized via a one-step hydrothermal process. Typically, Ni(NO₃)₂·6H₂O and CeCl₃·7H₂O with total metal amount of 0.9 mmol were dissolved in 90 mL distilled water which contains 2.4 mmol urea, and stirred for 20 min to form a transparent solution. The nickel foam (3cm × 1cm × 1 mm, 100 mesh) was carefully cleaned with acetone by ultrasonication for 5 min to remove the surface organics, rinsed in 1% HCl solution to remove the surface oxide layer, and washed with deionized water for several times. After that, the nickel foam was placed in a 100 mL Teflon-lined stainless-steel autoclave and the precursor solution was added. The autoclave was sealed and maintained at 120 °C for 12h, and then allowed to cool to room temperature. The product was rinsed with distilled water and ethanol for several times and finally dried under vacuum overnight. By changing the Ce:Ni ratio of the precursors, the hierarchical undoped and Ce-doped α -Ni(OH)₂ wire-on-sheet nanoarrays were obtained.

1.3 Synthesis of the β -Ni(OH)₂ nanosheet arrays

The pristine and Ce-doped β -Ni(OH)₂ nanosheet arrays grown on Ni foam were prepared via a one-step hydrothermal route. In a typical procedure, Ni(NO₃)₂·6H₂O and CeCl₃·7H₂O with total metal of 0.9 mmol were dissolved in 90 ml of deionized water and stirred for 20 min to form a transparent solution. Then, the aqueous solution and a piece of Ni foam were transferred to a 100 ml Teflon-lined stainless-steel autoclave, which was sealed and maintained at 140 °C. After reacting for 24h, the system was allowed to cool down to room temperature, and the products were washed with water and ethanol for several times and then dried in vacuum. By changing the starting concentrations of Ce and Ni precursors, the undoped, 1%, and 2% Ce-doped β -Ni(OH)₂ nanosheet arrays grown on Ni foam were fabricated.

1.4 Fabrication of the hierarchical β -Ni(OH)₂ wire-on-sheet nanoarrays

To constructing the hierarchical wire-on-sheet morphology for the β -Ni(OH)₂ phase, the as-obtained undoped and Ce-doped β -Ni(OH)₂ nanosheet arrays were immersed in 90 mL 0.1 M urea solution, and sealed in a 100 mL Teflon-lined stainless-steel autoclave for hydrothermal treatment. After reaction at 120 °C for 12h, the self-supported products were rinsed with distilled water and absolute ethanol for several times and finally dried under vacuum.

1.5 Structural characterizations

X-ray diffraction (XRD) was performed on a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) was carried out on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. The high-resolution TEM (HRTEM) was performed on a JEOL-2010 transmission electron microscope at an acceleration voltage of 200 kV. The atomic force microscopy (AFM) was conducted on a Cypher VRS AFM equipment (Oxford Instruments, Asylum Research) in tapping mode by using an AC240TS probe at a scan rate of 1 Hz. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding elemental mapping analyses were carried out on an FEI Tecnai G2 F20 TEM. A Perkin Elmer Optima 7300DV ICP emission spectroscope was used for the inductively coupled plasma optical emission spectrometry (ICP-OES) analyses to identify the concentration of cerium dopant as Ce/(Ce+Ni)%. X-ray photoelectron spectroscopy (XPS) analyses were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an excitation source of Mg K $\alpha = 1253.6 \text{ eV}$, and the resolution level was lower than 1 atom%.

1.6 Electrocatalytic study

All the electrochemical measurements were performed in a three-electrode system linked with an electrochemical workstation (CHI660E) at room temperature. All potentials were calibrated to a reversible hydrogen electrode (RHE) and the data are presented without iR correction. The cyclic voltammetry (CV) tests with a scan rate of 50 mV s^{-1} were conducted in the electrolyte containing 1 M KOH and 0.33 M urea. A Hg/HgO electrode was used as the reference electrode, a platinum gauze electrode ($2 \text{ cm} \times 2 \text{ cm}$, 60 mesh) was used as the counter electrode, and the nanoarray catalyst was served as the working electrodes which was fixed with an electrode holder connected by a glassy carbon plate. The electrochemical impedance spectroscopy (EIS) measurements were operated at variable potentials from 10^{-2} - 10^5 Hz .

2. Additional physical characterizations

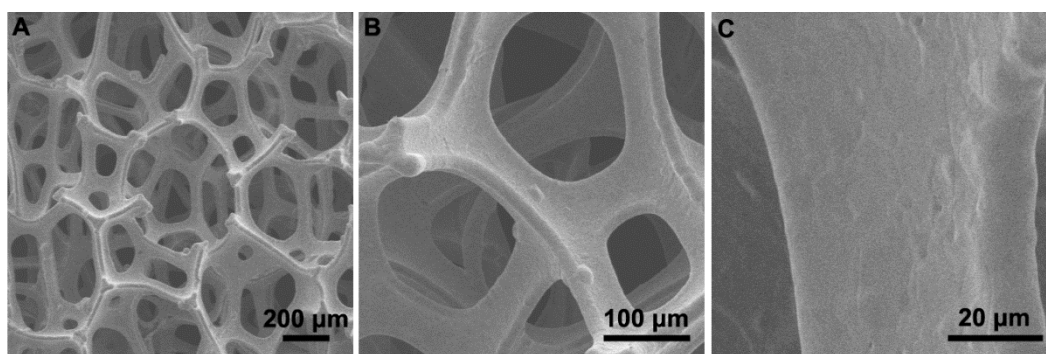


Figure S1. SEM images of the bare nickel foam.

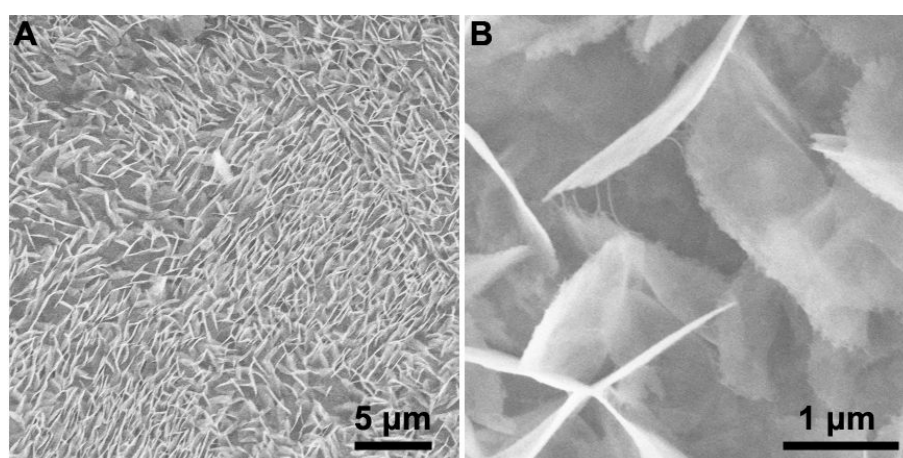


Figure S2. SEM images of the pristine hierarchical α -Ni(OH)₂ wire-on-sheet nanoarrays.

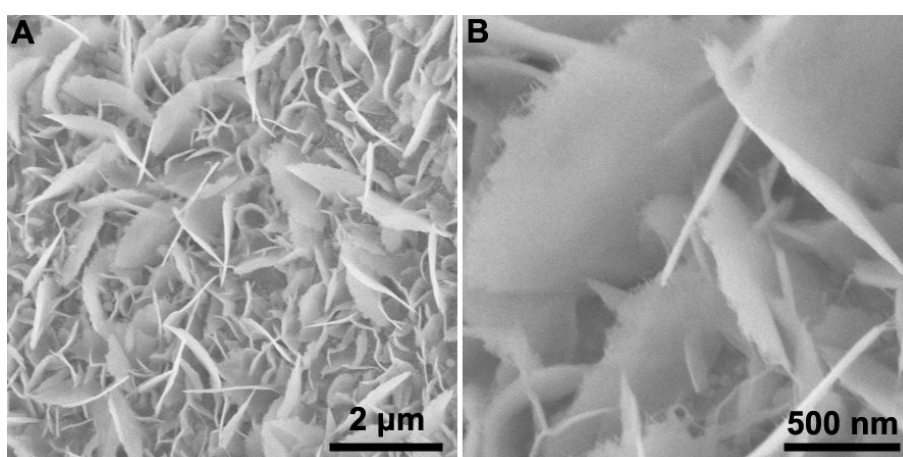


Figure S3. SEM images of the hierarchical 2%Ce:α-Ni(OH)₂/NF nanoarrays.

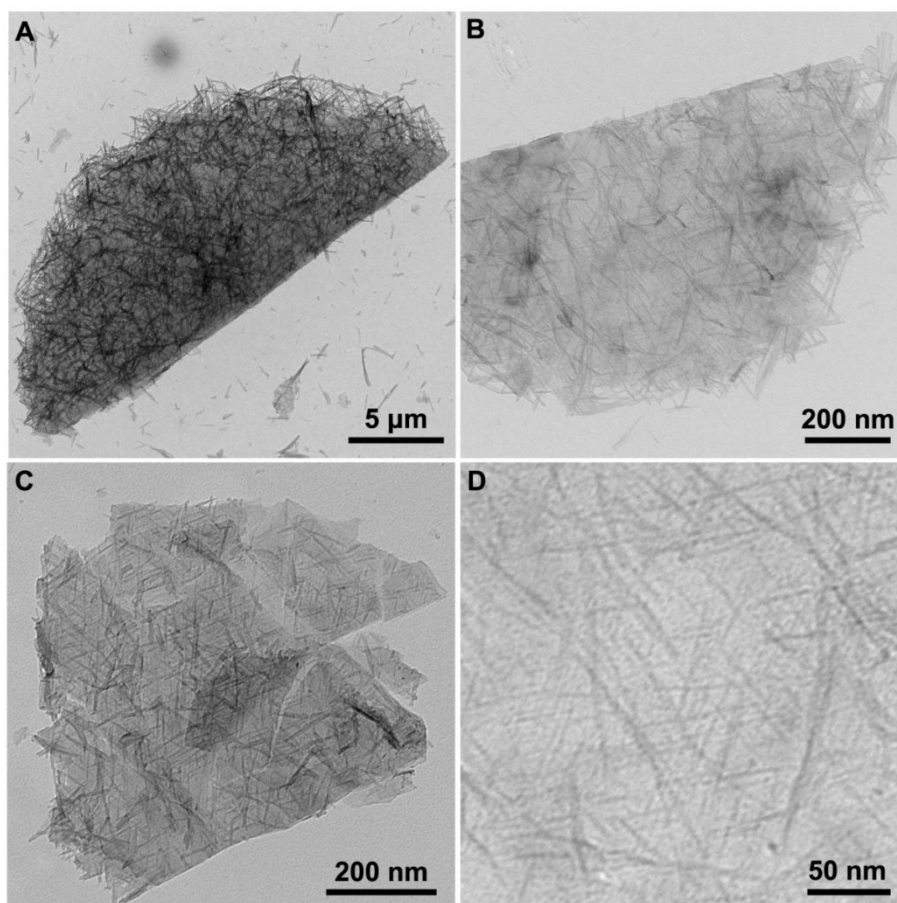


Figure S4. TEM images of the pristine hierarchical α -Ni(OH)₂ nanosheets.

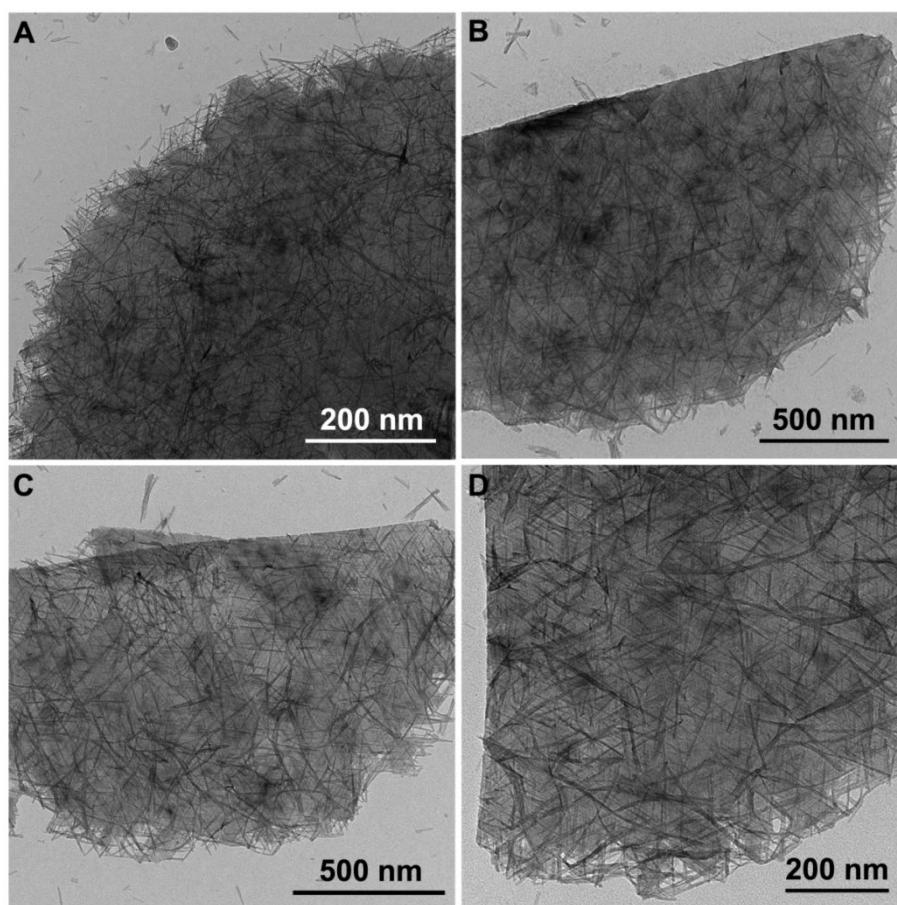


Figure S5. TEM images of the hierarchical 1%Ce:α-Ni(OH)₂ nanosheets.

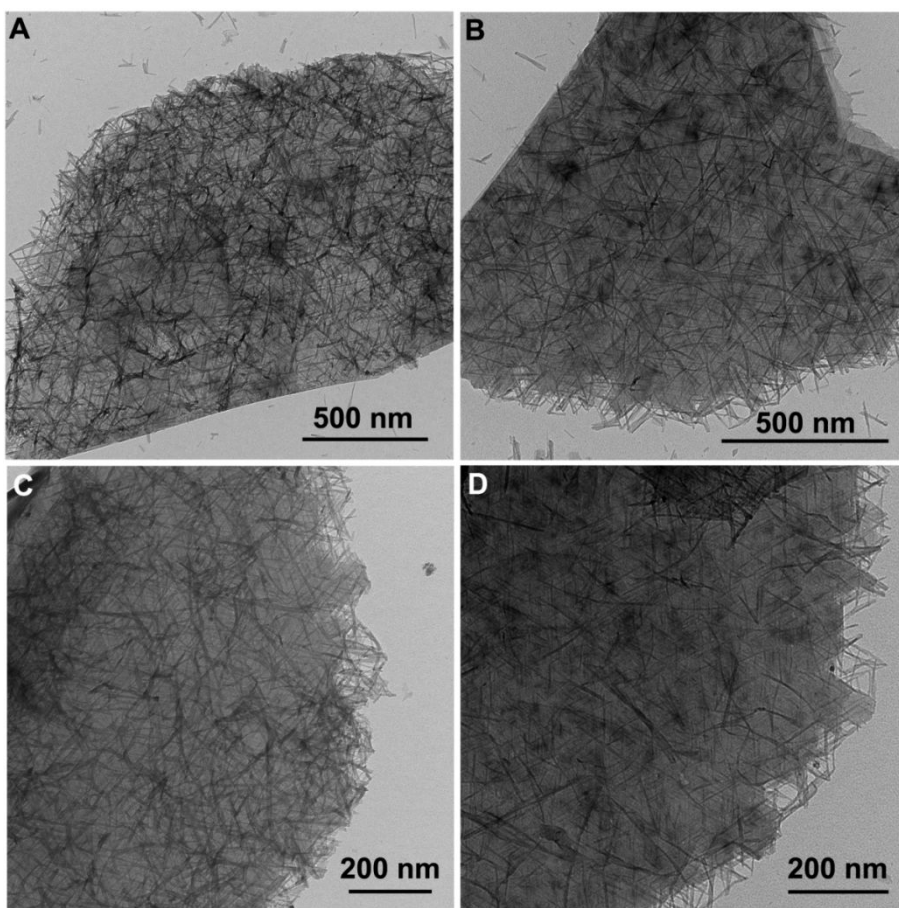


Figure S6. TEM images of the hierarchical 2%Ce:α-Ni(OH)₂ nanosheets.

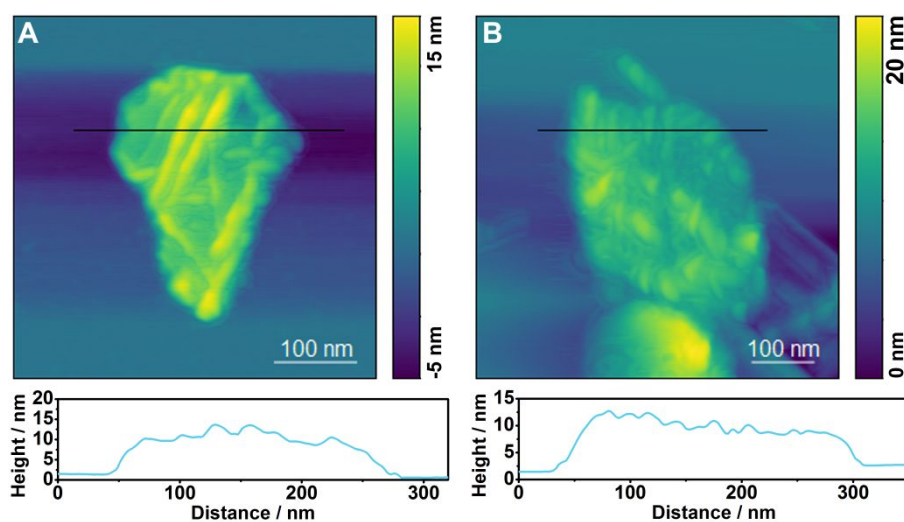


Figure S7. The AFM images and corresponding height profiles. (A) The pristine hierarchical α-Ni(OH)₂ nanosheet. (B) The hierarchical 2%Ce:α-Ni(OH)₂ nanosheet.

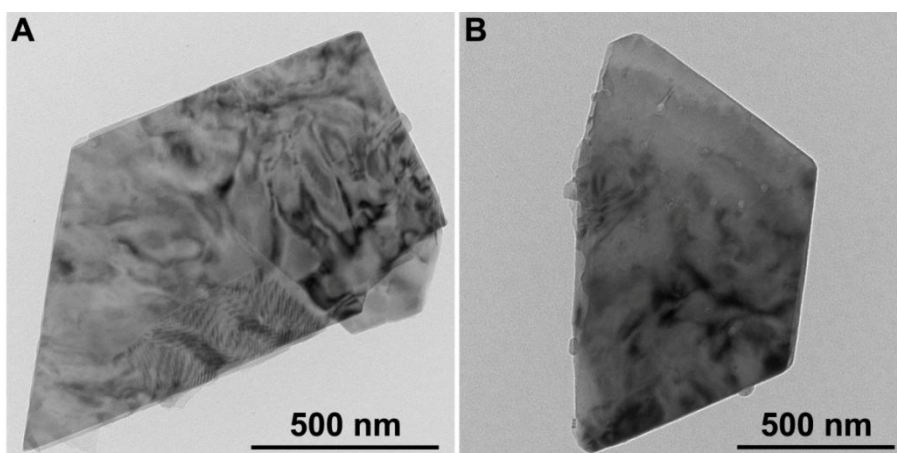


Figure S8. TEM images of (A) the undoped and (B) 2%Ce doped β -Ni(OH)₂ nanosheet.

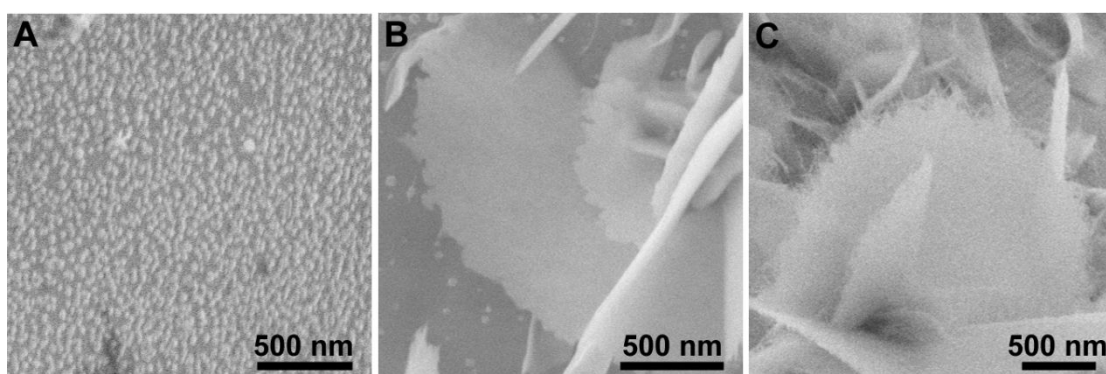


Figure S9. SEM images reveal the time-dependent morphology evolution during the synthesis of the 1%Ce: α -Ni(OH)₂/NF for (A) 0.5 h, (B) 1 h and (C) 4 h.

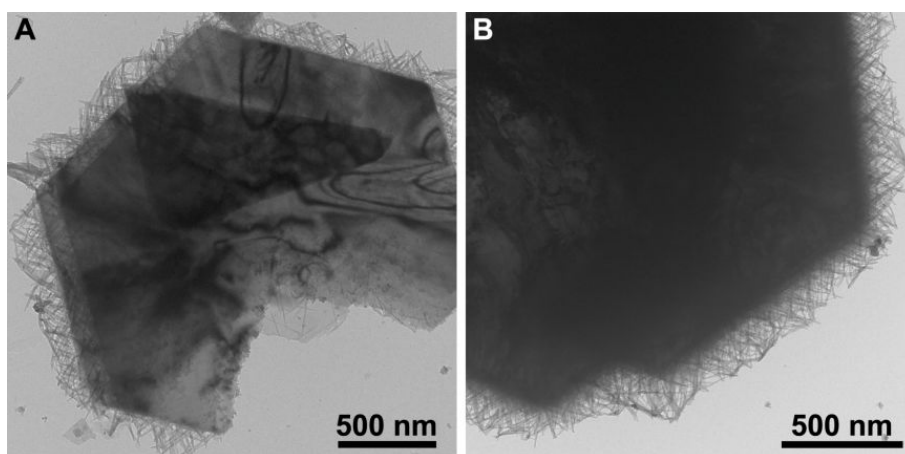


Figure S10. TEM images of (A) the pristine hierarchical β -Ni(OH)₂ nanosheet with surface nanowires and (B) the hierarchical β -Ni(OH)₂ nanosheet with 2% Ce doping.

3. Additional electrochemical measurements

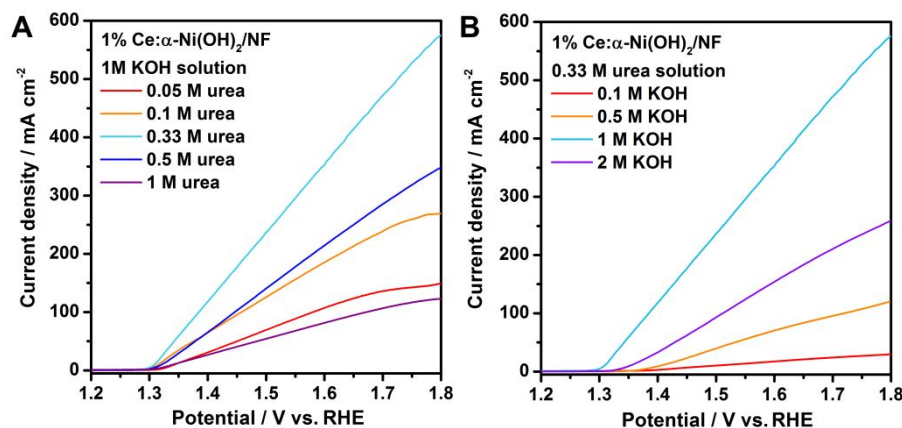


Figure S11. LSV curves in variable concentrations of (A) urea and (B) KOH for the identification of optimal electrolyte for 1%Ce:α-Ni(OH)₂/NF.

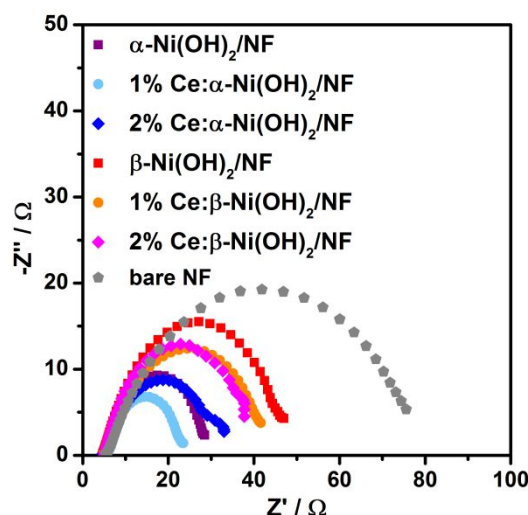


Figure S12. The EIS data of the hierarchical phase-regulated Ce-doped Ni(OH)₂ wire-on-sheet nanoarrays measured in the electrolyte with 1 M KOH and 0.33 M urea at 1.35 V vs. RHE.

The estimation of the electrochemically active surface area of the samples was carried out according to literature.¹⁻² CV measurements were taking in the region of 1.0-1.1 V vs. RHE without redox reactions at various scan rates (2, 4...20 mV s⁻¹, etc.), which are mainly considered as the double-layer capacitive behavior (Figure S13). The electrochemical double-layer capacitance (C_{dl}) of various catalysts can be determined from the CV plots, which is expected to be linearly proportional to the effective surface area. The double-layer capacitance is estimated by plotting the Δj ($j_a - j_c$) at 1.05 V vs. RHE against the scan rate, where the slope is twice C_{dl} . The as-calculated C_{dl} values of the catalysts are listed in Table S1.

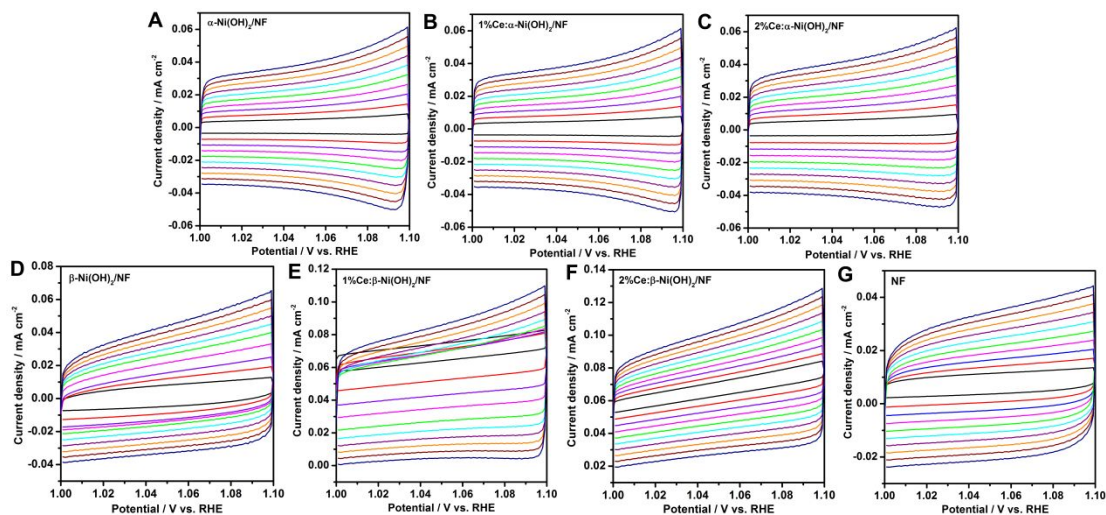


Figure S13. CV curves in the non-redox region for the estimation of C_{dl} .

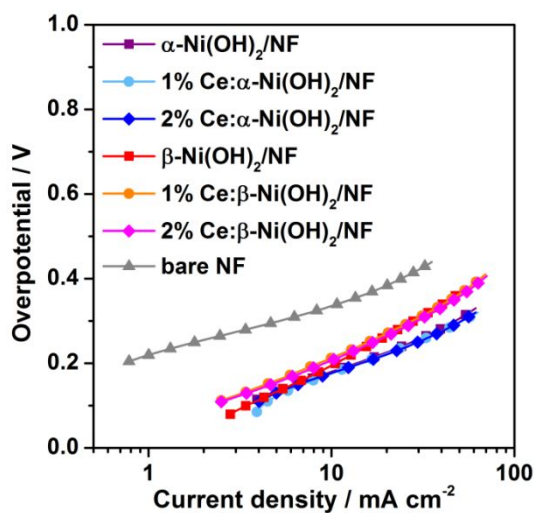


Figure S14. Tafel plots of HER for the phase-regulated nanoarray catalysts with variable Ce concentrations.

Table S1. Summary of the C_{dl} values and the Tafel slopes of UOR and HER.

	C_{dl} [mF cm ⁻²]	Tafel slope of UOR [mV decade ⁻¹]	Tafel slope of HER [mV decade ⁻¹]
α -Ni(OH) ₂ /NF	1.89	29	149
1%Ce: α -Ni(OH) ₂ /NF	2.14	25	148
2%Ce: α -Ni(OH) ₂ /NF	1.93	28	152
β -Ni(OH) ₂ /NF	1.76	51	212
1%Ce: β -Ni(OH) ₂ /NF	1.96	52	153
2%Ce: β -Ni(OH) ₂ /NF	1.86	54	152
bare NF	1.33	27	112

Reference

- (1) Xie, J.; Zhang, J.; Li, S.; Grote, F.; Zhang, X.; Zhang, H.; Wang, R.; Lei, Y.; Pan, B.; Xie, Y., Controllable Disorder Engineering in Oxygen-Incorporated MoS₂ Ultrathin Nanosheets for Efficient Hydrogen Evolution. *J. Am. Chem. Soc.* **2013**, *135*, 17881-17888.
- (2) Lukowski, M. A.; Daniel, A. S.; Meng, F.; Forticaux, A.; Li, L.; Jin, S., Enhanced Hydrogen Evolution Catalysis from Chemically Exfoliated Metallic MoS₂ Nanosheets. *J. Am. Chem. Soc.* **2013**, *135*, 10274-10277.