

Materials and Methods

Materials. Sodium ferrocyanide decahydrate ($\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), hydrochloric acid (HCl), and trisodium citrate dihydrate were purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan) and used without further purification.

Synthesis of Ni–Fe NCs. $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ (0.2425 g, 0.5 mmol) was dissolved in water (25 mL) to form a clear solution. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (58.7 mg, 0.25 mmol) and trisodium citrate dihydrate (0.375 g, 1.28 mmol) were dissolved in water (25 mL) to form another clear solution. The two solutions were mixed under magnetic stirring and the resulting mixture was then allowed to age at room temperature for overnight. The precipitate was collected by centrifugation, washed several times with water and ethanol, and dried at 25 °C in a vacuum oven for 24 h to afford a green powder.

Synthesis of the NF-X samples. 0.4 M HCl (2 mL) were added to as-prepared Ni–Fe NCs (5 mg) and the resulting solution was subjected to probe sonication (Sonics, 130 Watt, 20 kHz) for 30 min. The resulting product NF-30 was collected by centrifugation, washed several times with water and ethanol under ultrasonication (Sansyo, US-2KS), and dried at room temperature overnight. For comparison, the as-prepared Ni–Fe NCs were also subjected to ultrasonication for 10 and 20 min under the same experimental conditions to obtain NF-10 and NF-20 (NF-X, where X denotes the etching time), respectively. In addition, samples were etched in 0.1 and 1 M HCl for 30 min.

Characterization. Wide-angle XRD patterns of the samples were collected on a Rigaku RINT 2500X diffractometer with monochromated Cu-K α radiation (40 kV, 40 mA). The sample morphologies were characterized by scanning electron microscopy (SEM) on a Hitachi SU8000 system. Transmission electron microscopy (TEM) and high-angle annular dark field scanning TEM (HAADF-STEM) observations were performed on a JEOL JEM-2100F system operated at 200 kV and equipped with an energy-dispersive spectrometer. Thermogravimetry/differential thermal analysis was conducted on a Hitachi HT-Seiko Instrument Exter 6300 TG/DTA system from room temperature to 500 °C under air at a fixed heating rate of 10 °C min⁻¹. N₂ adsorption–desorption isotherms of the samples were recorded on a Quantachrome Autosorb gas sorption system at 77 K. Fourier-transform infrared (FTIR) spectra were collected at room temperature on a Thermo Scientific Nicolet 4700 instrument.

Electrochemical measurements. Electrodes were prepared by polishing a glassy carbon rotating disk electrode (ϕ 3 mm) with Al₂O₃ powder (0.05 μm) then rinsing with distilled water under ultrasonication. Catalyst dispersions of the Ni–Fe NCs and NF-30 were prepared by mixing the corresponding catalyst powder (4 mg) and 5% Nafion perfluorinated resin solution (100 μL , mixture of lower aliphatic alcohols and containing 45% water) and a mixture of 2-propanol and distilled water (1:2 v/v, 900 μL) under ultrasonication. The catalyst dispersion (6 μL) was then drop cast onto the glassy carbon electrode and allowed to dry at room temperature to obtain a catalyst loading of 0.34 mg cm⁻². Next, 0.05% Nafion solution (3 μL) was drop cast onto the electrode to suppress detachment of the catalyst. All electrochemical measurements were carried out in a three-electrode cell on a CHI842B workstation equipped with an RRDE-3A rotating ring disk electrode (ALS Co., Ltd). A 0.1 M aqueous KOH solution, a glassy carbon rod, and Hg/HgO (1 M NaOH, 905 mV vs. RHE) were used as the electrolyte, counter electrode, and reference electrode, respectively. N₂ was bubbled

through the system for >30 min before pretreatment of the electrodes for OER measurements. Linear voltammetry was conducted for 250 scans from 0.345 to 0.845 V *vs.* Hg/HgO (1 M NaOH) at a scan rate of 100 mV s⁻¹ in N₂-saturated 0.1 M KOH. To estimate the double-layer capacitance, cyclic voltammetry was performed at various scan rates (10, 25, 50, and 100 mV s⁻¹) around the open circuit potential (± 0.1 V) in N₂-saturated 0.1 M KOH solution. O₂ was bubbled through the system for >30 min before the OER measurements. Cyclic voltammetry was performed at a scan rate of 10 mV s⁻¹ in the potential range of 0.245–0.845 V *vs.* Hg/HgO (1 M NaOH), corresponding to 1.15–1.75 V *vs.* RHE, with electrode rotation at 1600 rpm. The catalyst stability was evaluated by chronoamperometry at 1.66 V *vs.* RHE in O₂-saturated 0.1 M KOH with electrode rotation at 1600 rpm. The chronoamperometry measurements were conducted with the rotating disk electrode tilted by approximately 7.5° to facilitate removal of the generated bubbles.

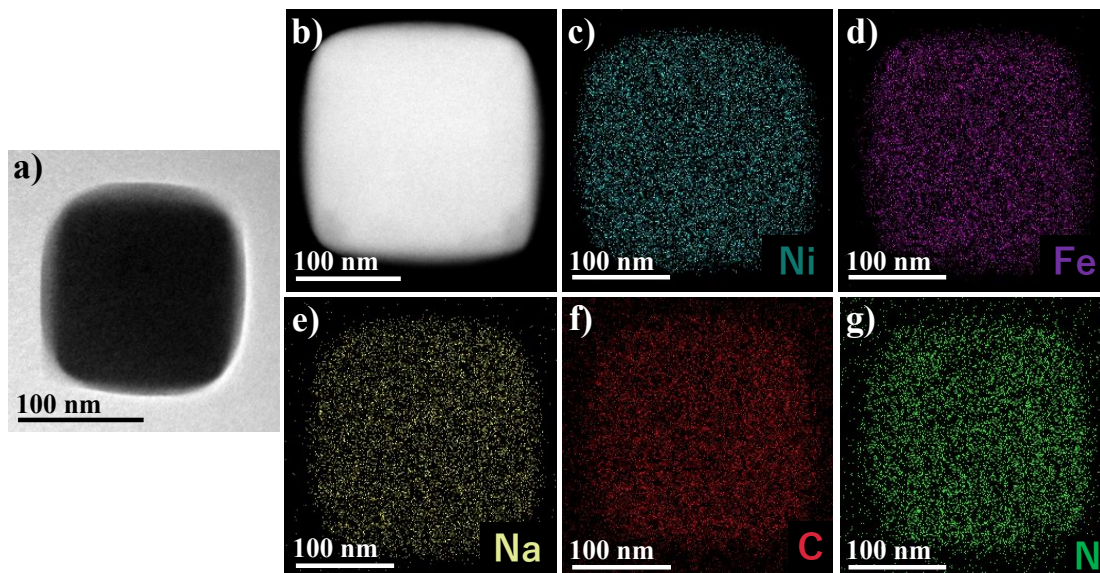


Fig. S1 Microscopy images of the Ni–Fe NCs: (a) TEM, (b) HAADF-STEM, and (c)–(g) elemental mapping for (c) nickel, (d) iron, (e) sodium, (f) carbon, and (g) nitrogen.

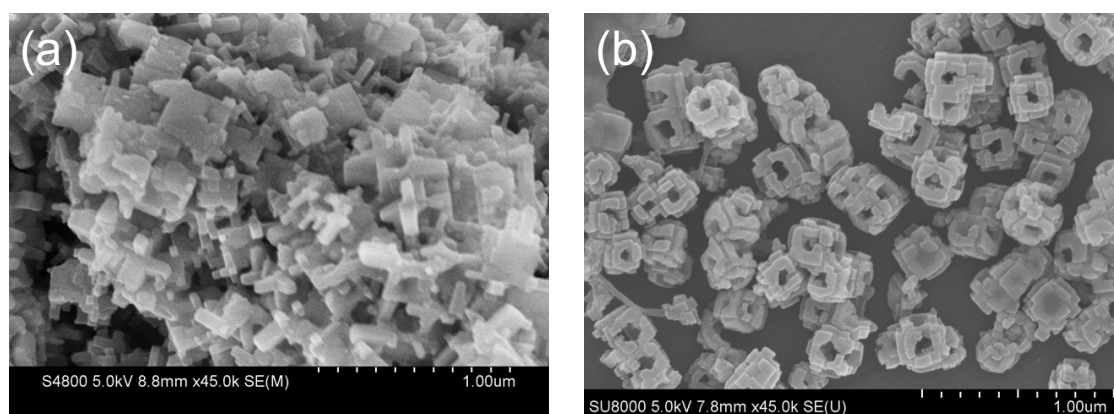


Fig. S2 SEM images of the Ni–Fe NCs after etching for 30 min (a) without sonication and (b) with sonication.

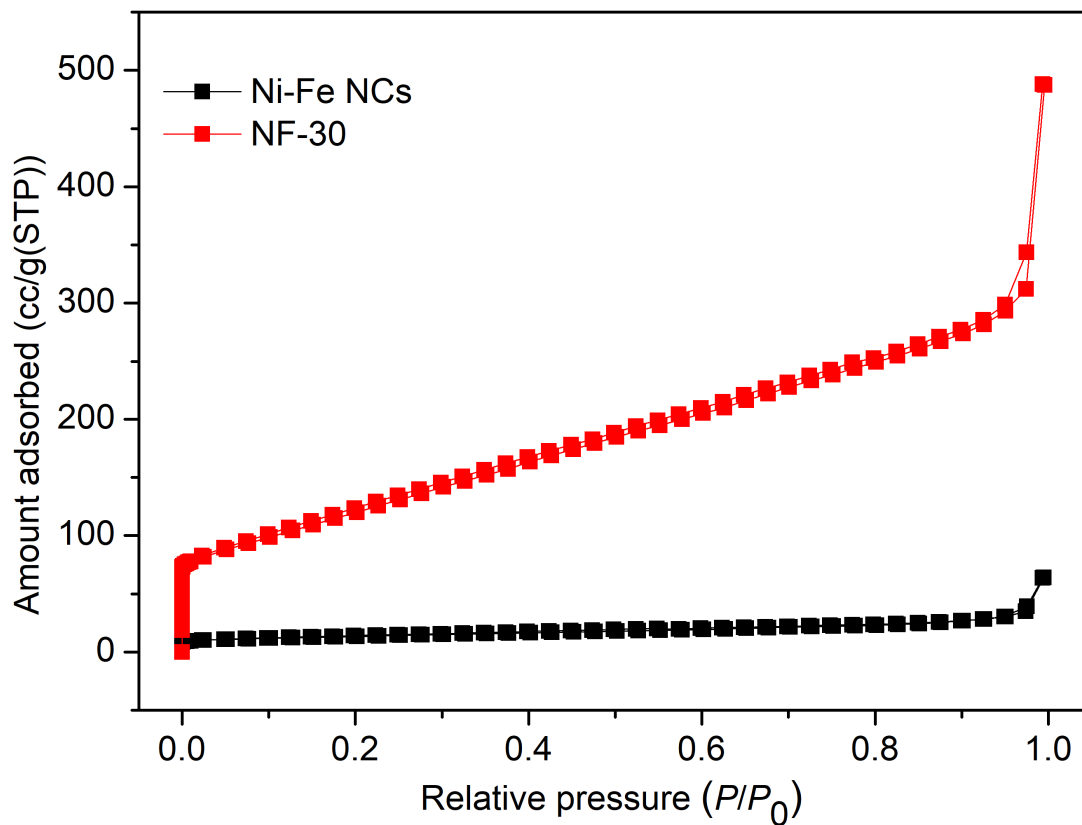


Fig. S3 N_2 adsorption–desorption isotherms for (a) the Ni–Fe NCs and (b) NF-30.

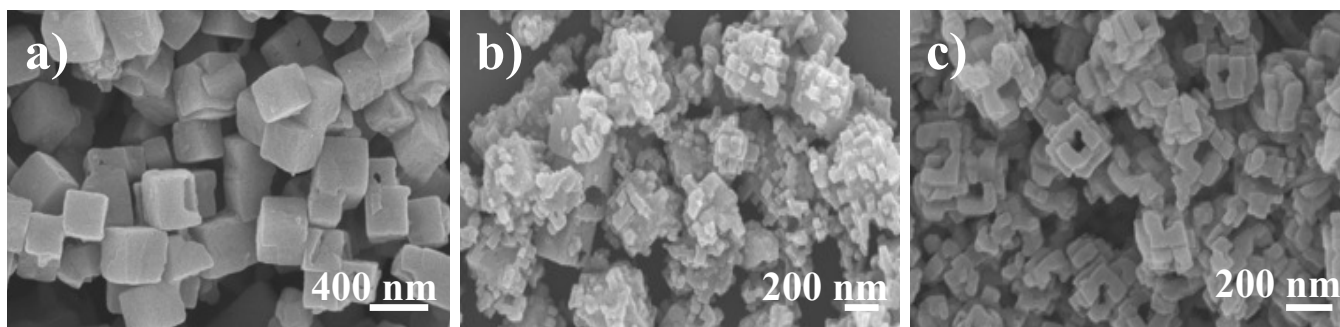


Fig. S4 SEM images of the Ni–Fe NCs after etching in (a) 0.1 M HCl solution for 30 min, (b) 1 M HCl solution for 30 min, and (c) 0.4 M HCl solution for 1 h.

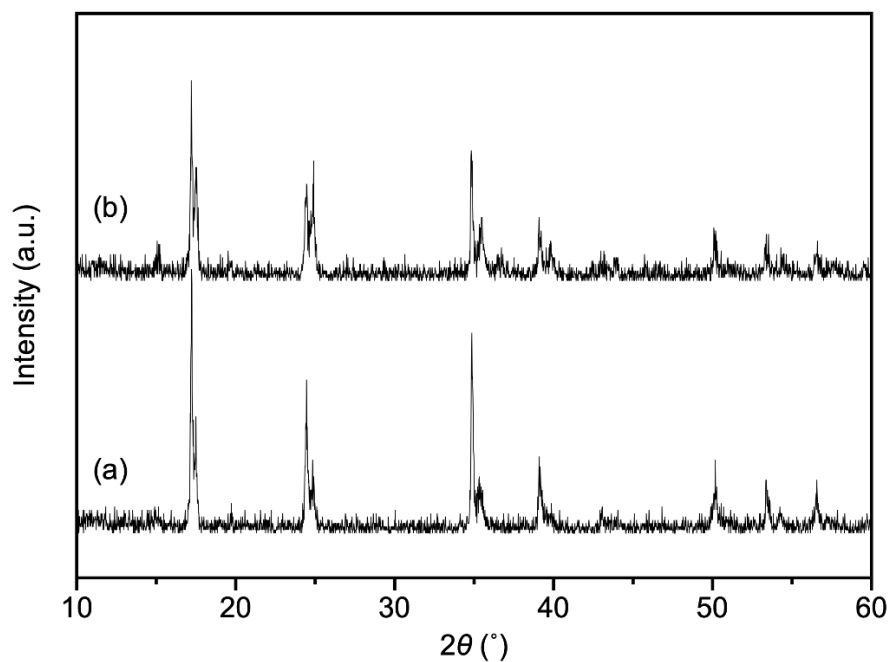


Fig. S5 XRD patterns of the Ni-Fe NCs after etching for 30 min in (a) 0.1 M HCl solution and (b) 1 M HCl solution.

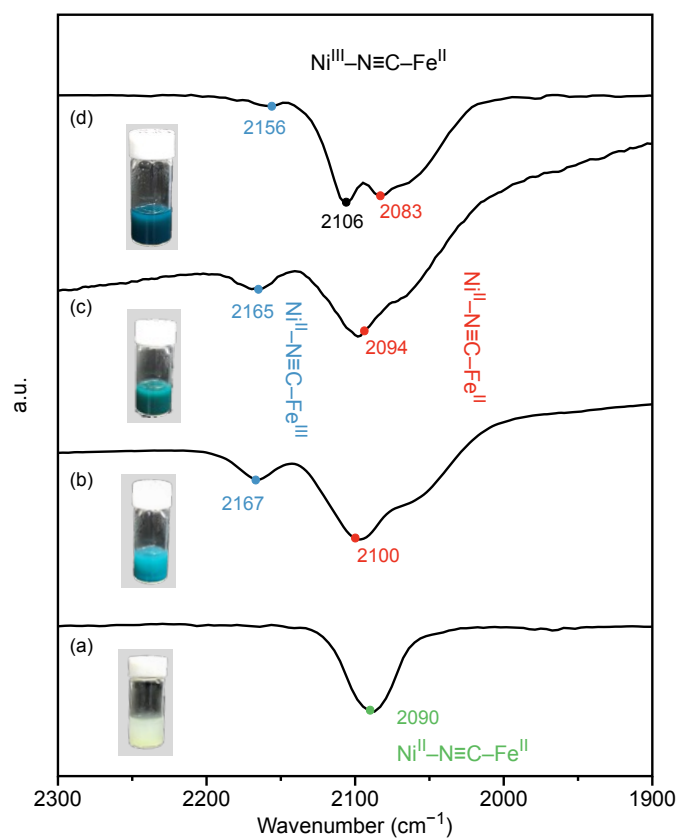


Fig. S6 FTIR spectra of (a) the Ni-Fe NCs, (b) NF-10, (c) NF-20, and (d) NF-30. The insets show photographs demonstrating the color changes with increasing etching time.

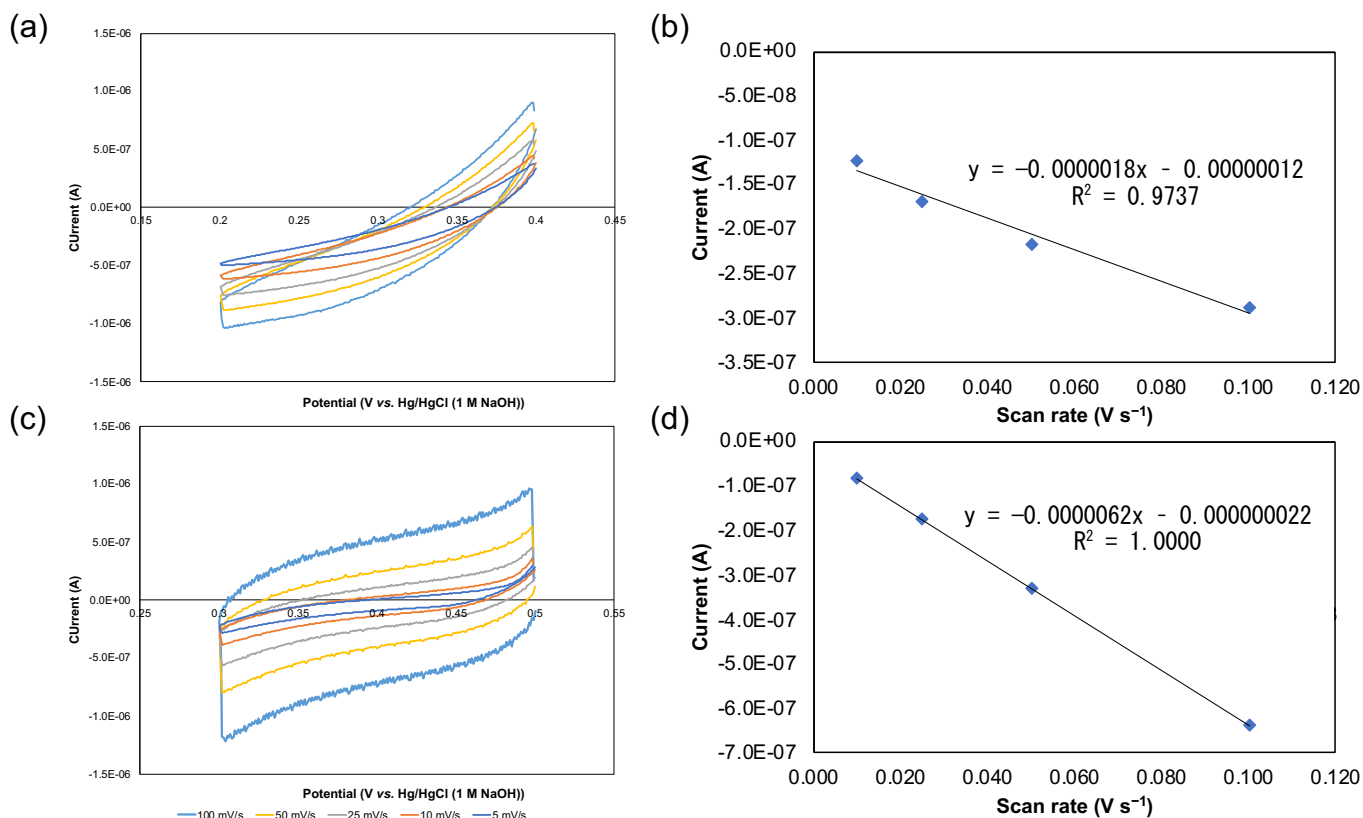


Fig. S7 (a), (c) Cyclic voltammograms (iR-corrected) for (a) the Ni-Fe NCs and (c) NF-30 recorded at scan rates of 10, 25, 50, and 100 mV s⁻¹ in N₂-saturated 0.1 M KOH solution. (b), (d) Half current of the difference of anodic and cathodic current of the cyclic voltammograms for (b) the Ni-Fe NCs (at 0.35 V vs. Hg/HgO (1 M NaOH solution)) and (d) NF-30 (0.40 V vs. Hg/HgO (1 M NaOH solution)) against the scan rate.

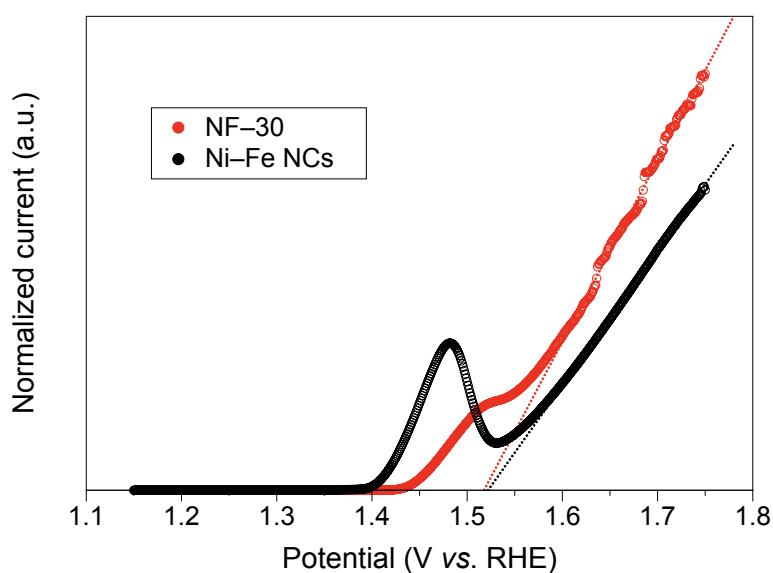


Fig. S8 Anodic cyclic voltammograms (iR-corrected) for the Ni-Fe NCs and NF-30 recorded at a scan rate of 10 mV s⁻¹ in 0.1 M KOH solution. The current was normalized with respect to the double-layer capacitance, which is proportional to the electrochemically active surface area. The potential was converted from the potential of Hg/HgO (1 M NaOH) (905 mV vs. RHE).

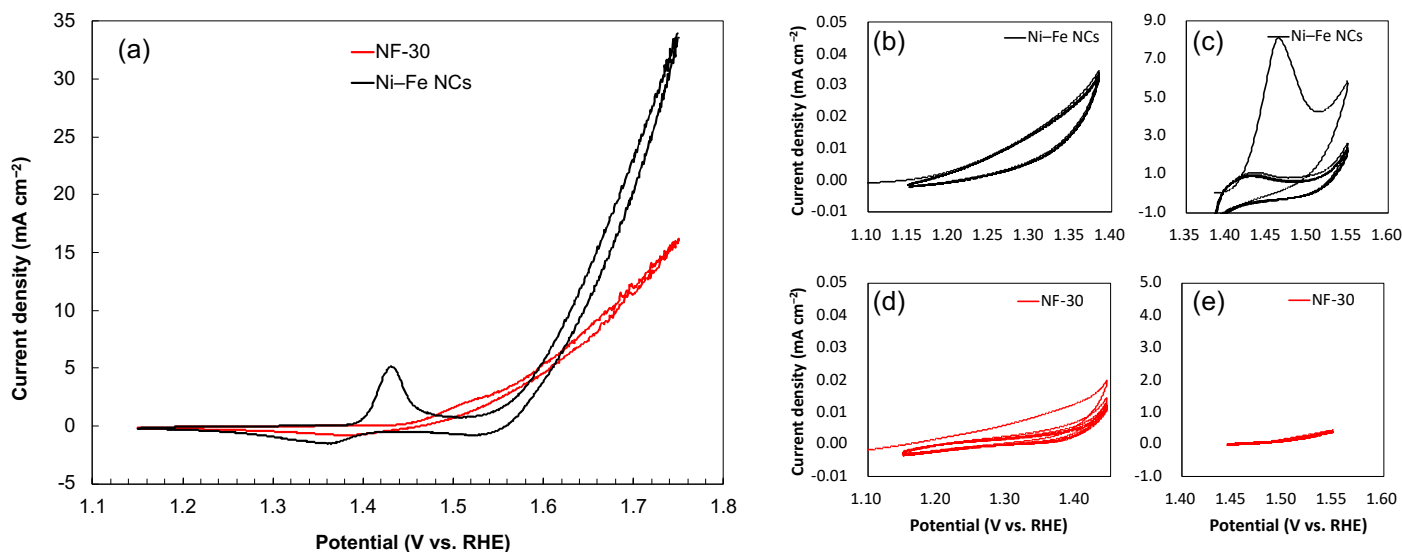


Fig. S9 (a) Cyclic voltammograms (iR-corrected) for the Ni-Fe NCs and NF-30 recorded at a scan rate of 10 mV s⁻¹ in 0.1 M KOH solution. (b)–(e) Cyclic voltammograms for (b) the Ni-Fe NCs between 1.15 and 1.385 V vs. RHE, (c) the Ni-Fe NCs between 1.385 and 1.55 V vs. RHE, (d) NF-30 between 1.15 and 1.445 V vs. RHE, and (e) NF-30 between 1.445 and 1.55 V vs. RHE. The potential was converted from the potential of Hg/HgO (1 M NaOH solution) (905 mV vs. RHE). The catalyst loading amount was 0.28 mg cm⁻², and the electrodes were pretreated by performing cyclic voltammetry scans at a scan rate of 100 mV s⁻¹ for 50 cycles.

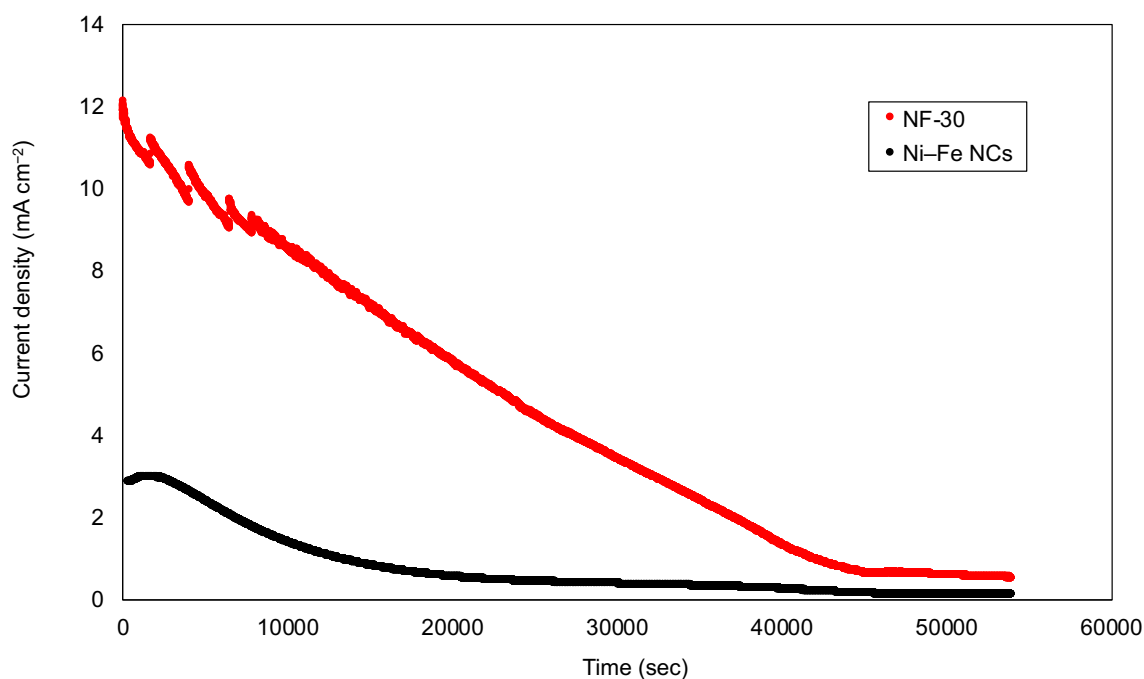


Fig. S10 Chronoamperograms for the Ni-Fe NCs and NF-30 held at 0.75 V vs. Hg/HgO (1 M NaOH solution) (1.66 V vs. RHE). (Note: Sudden current recovery of NF-30 is due to a bubble removal on the disk electrode.)