Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Highly crystalline β-FeOOH(Cl) nanorod catalysts doped with transition metals for efficient water oxidation

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Supplementary results

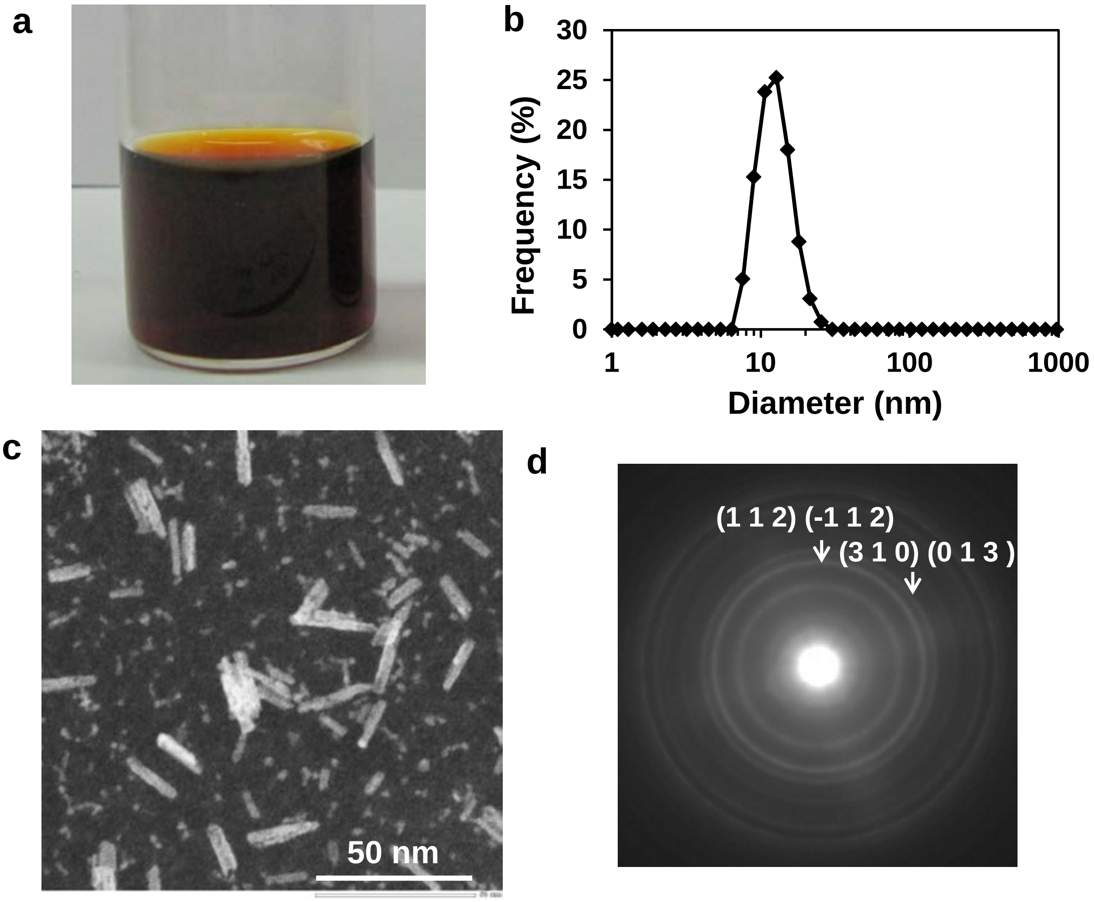

Fig. S1 a) Photographic image and **b)** size distribution of a non-doped β-FeOOH colloidal solution (pH 2.2, stored for one month at room temperature)**,** and **c)** STEM image and **d)** TEM diffraction image of these same particles**.**

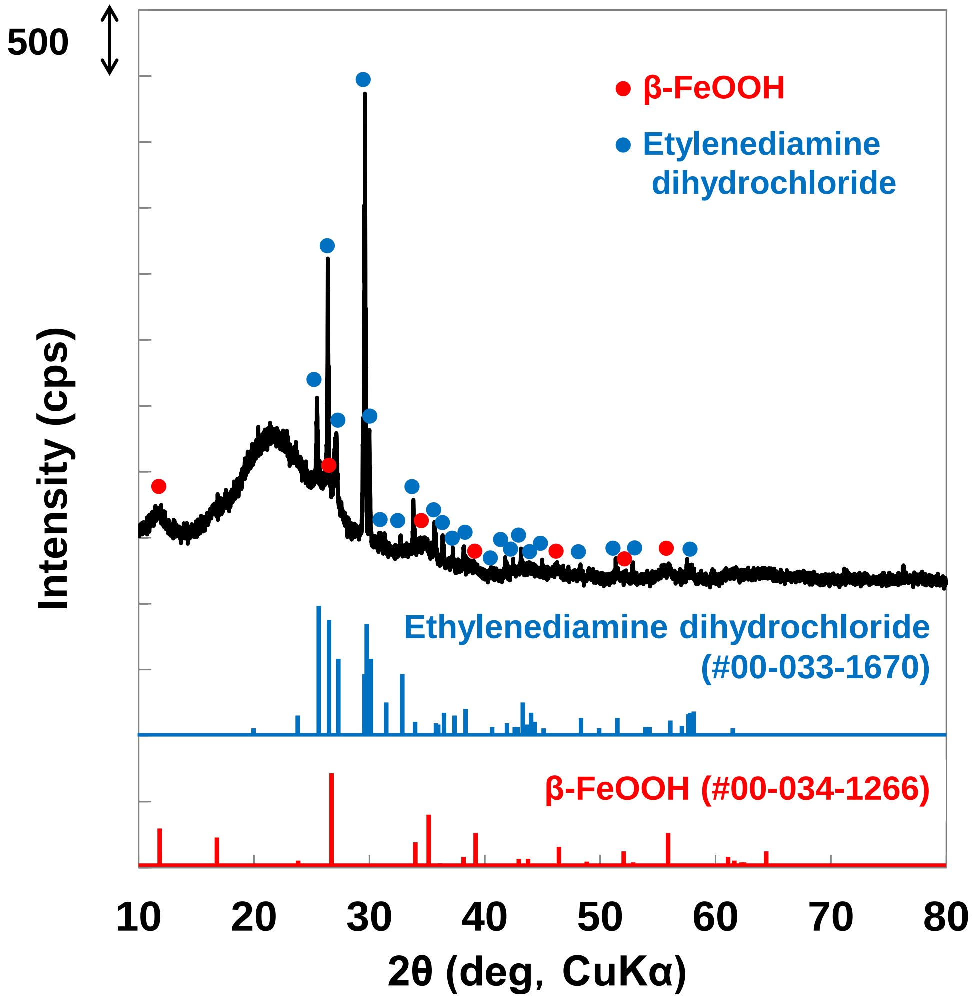

Fig. S2 XRD patterns of β-FeOOH:Ni (1.2 at%) colloidal solution. The sample was measured by RINT-TTR II (Rigaku) using Cu Kα radiation at 50kV and 300mA. A very broad peak at 2θ=22° arises from the glass holder. Although the peaks of originating from ethylendiamine dihydrochoride for pH adjustment of the solution were dominant, a broad peak of β-FeOOH was also confirmed.

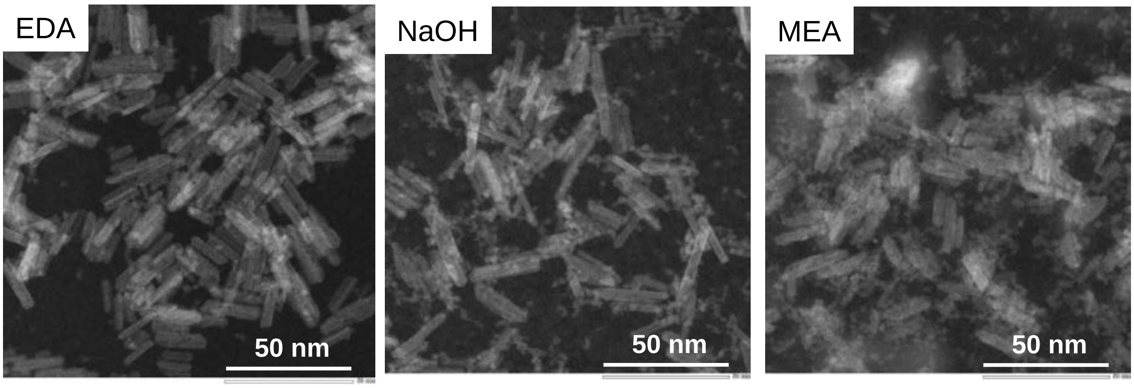

Fig. S3 STEM images of various β-FeOOH:Ni colloidal particles synthesized by utilization of various base reagent, ethylenediamine (EDA), NaOH, or monoethanolamine (MEA) under pH adjustment. All samples were synthesized in a condition of 4 at%-Ni addition.

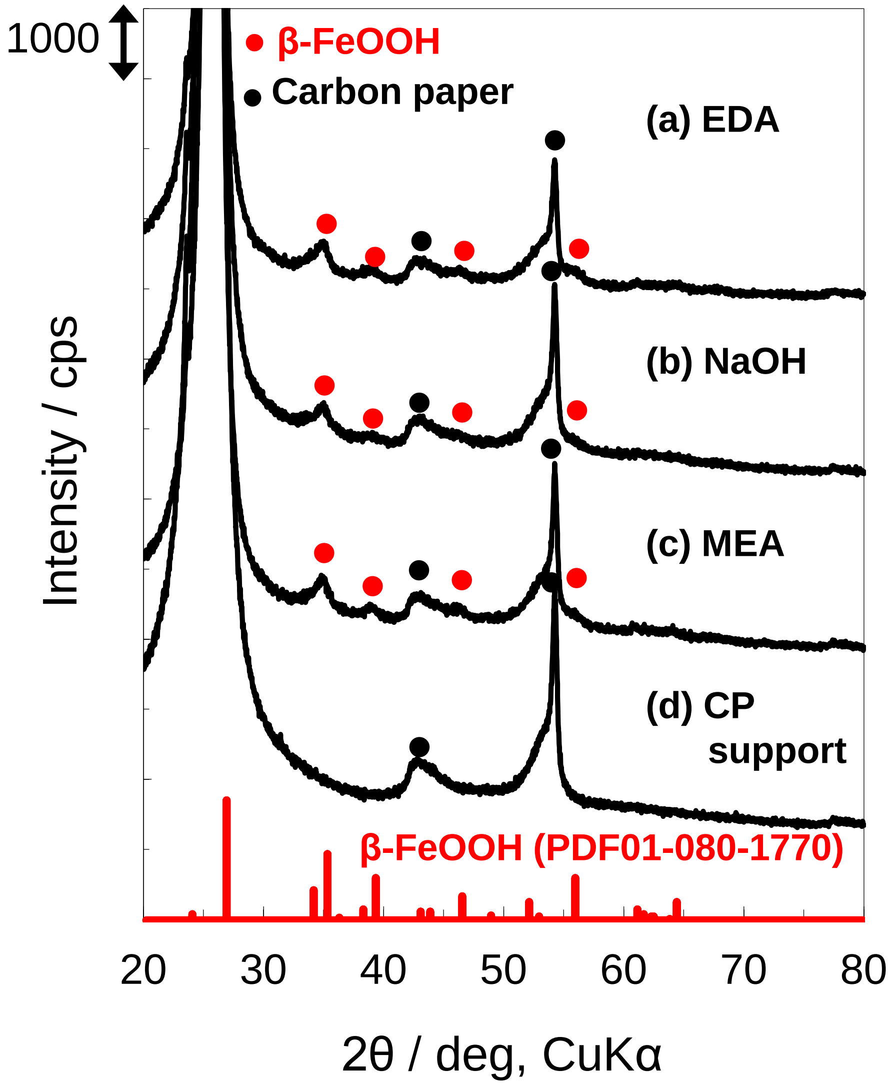

Fig. S4 XRD patterns of various β-FeOOH:Ni nanorod synthesized with additives of (a) EDA, (b) NaOH, and (c) MEA /CP samples and (d) CP support. All samples were synthesized at pH 2.2 in a condition of 4 at%-Ni addition.

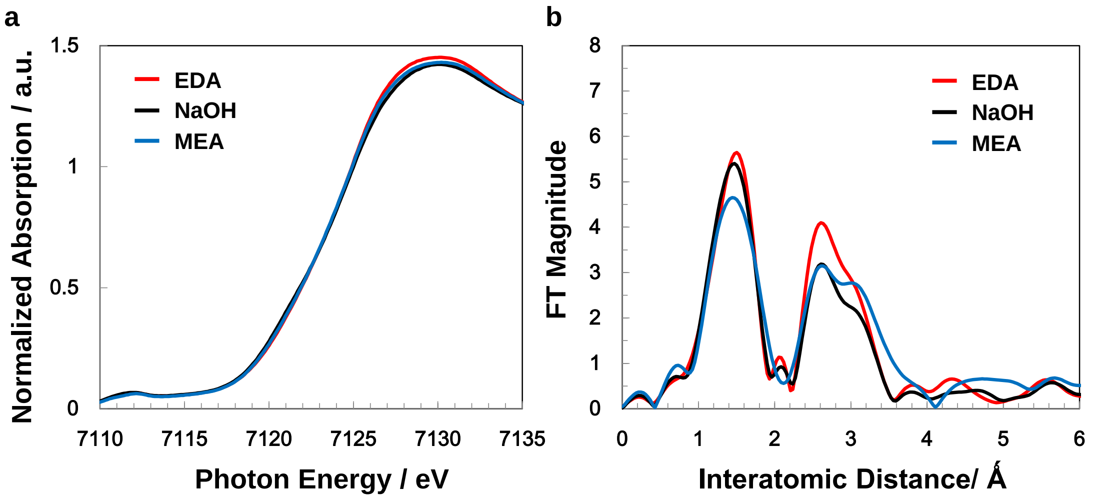

Fig. S5 XANES and k^3-weighted FT-EXAFS spectra for Fe K-edge of various β-FeOOH:Ni nanorods synthesized with additives of EDA (red), NaOH (black), and MEA (blue)/CP. All samples were synthesized at pH 2.2 in a condition of 4 at%-Ni addition.

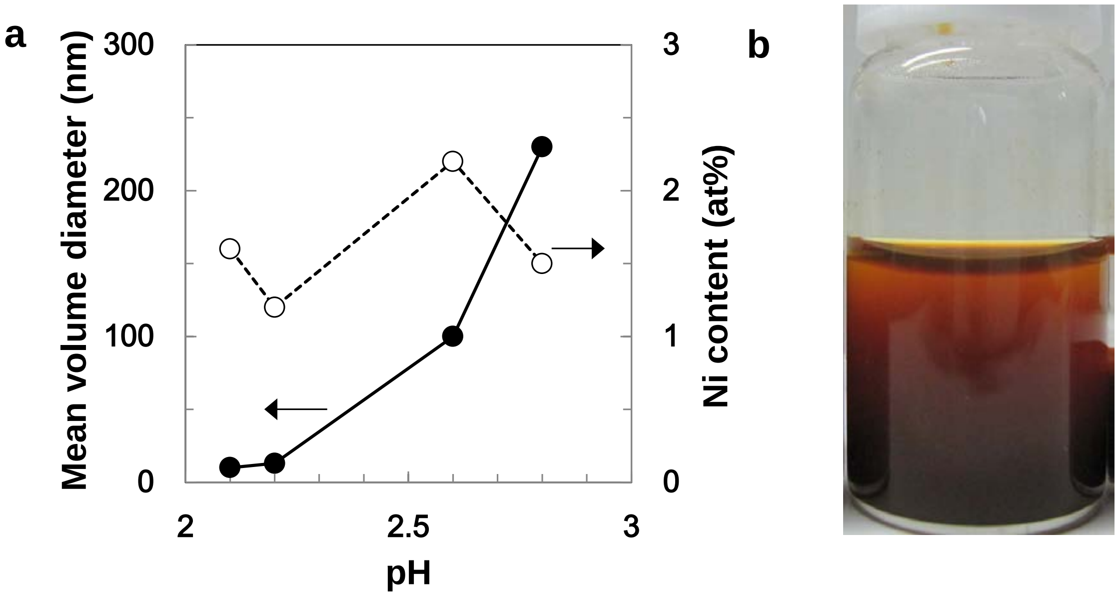

Fig. S6 a) The relationship between the pH of the preparation solution and the properties of the resulting β-FeOOH:Ni colloidal solutions (added 4 at%-Ni^{2+}) and **b)** photographic image of a β-FeOOH:Ni colloidal solution prepared at pH 2.8.

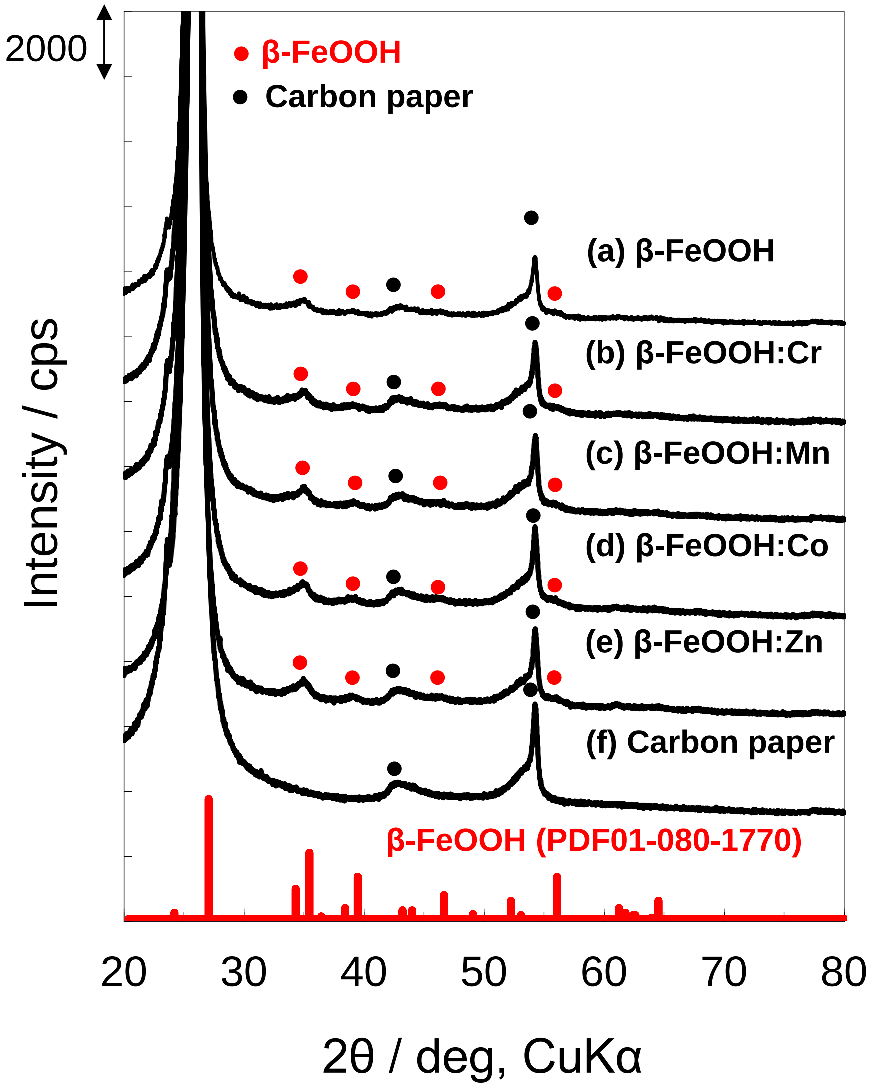

Fig. S7 XRD patterns of metal doped-β-FeOOH nanorod/CP samples (each transition metal (4 at.%) was added).

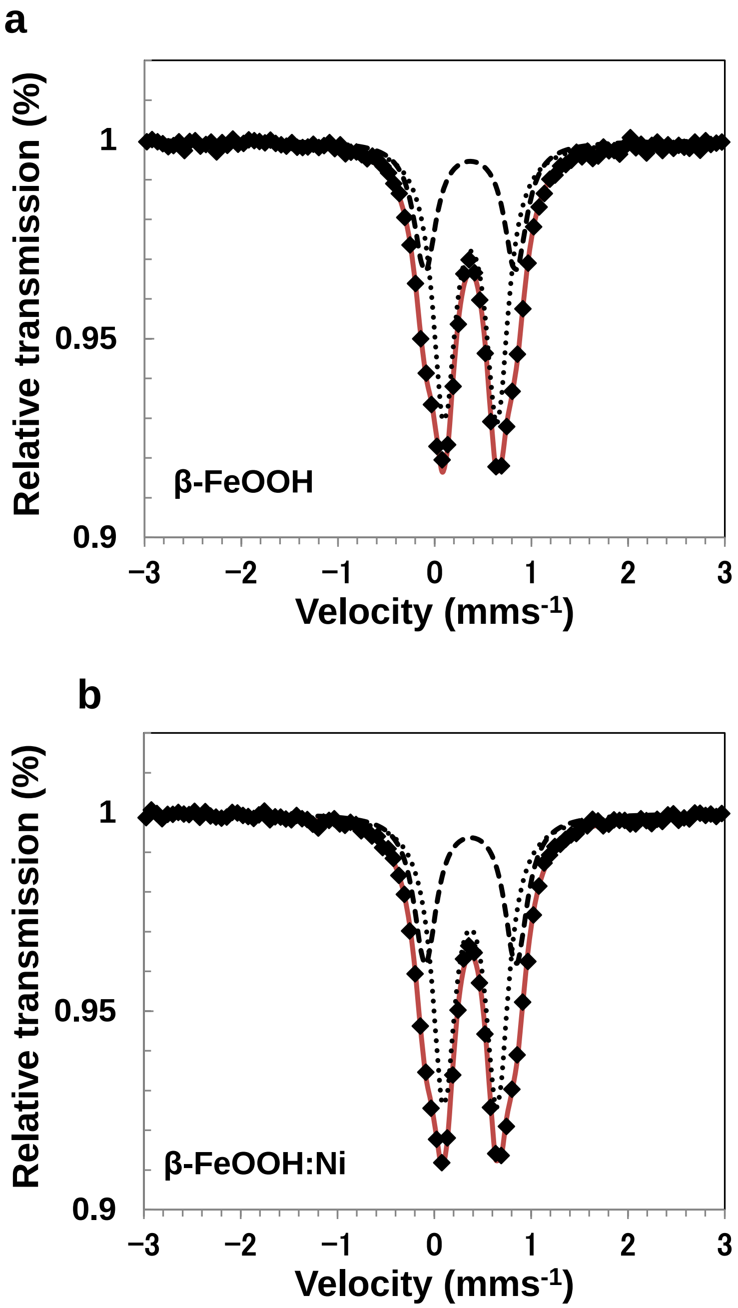

Fig. S8 Room temperature ^{57}Fe Mössbauer spectra of **a)** β-FeOOH nanorods and **b)** β-FeOOH:Ni (1.2 at%) nanorods (stored for one month at room temperature). The square symbols represent experimental data, whereas the solid lines show the applied fits.

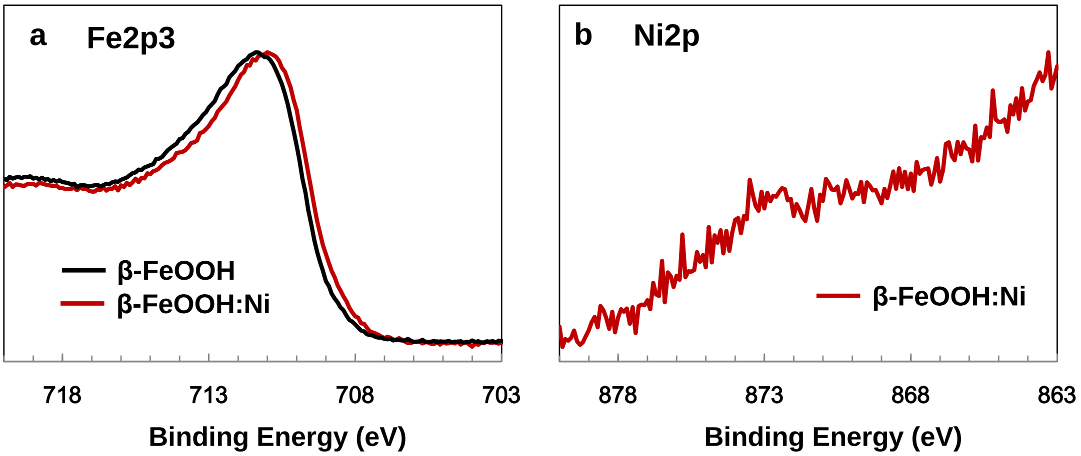

Fig. S9 a) Fe2*p*3 XPS spectra for β-FeOOH and β-FeOOH:Ni (1.2 at%) nanorod/CP samples and **b)** Ni2*p* XPS spectrum for a β-FeOOH:Ni (1.2 at%) nanorod/CP sample.

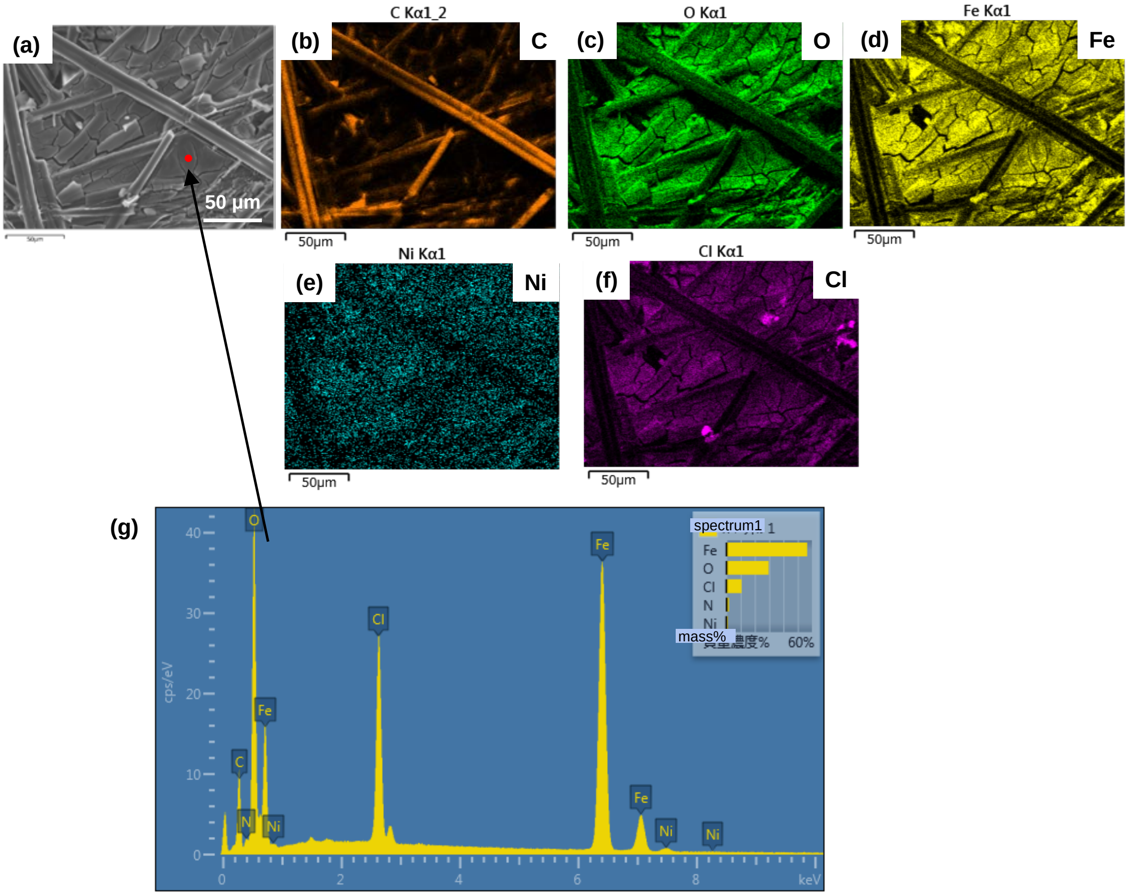

Fig. S10 a) SEM image and **b to g)** SEM-EDX data for a β-FeOOH:Ni (1.2at%) nanorod/CP specimen.

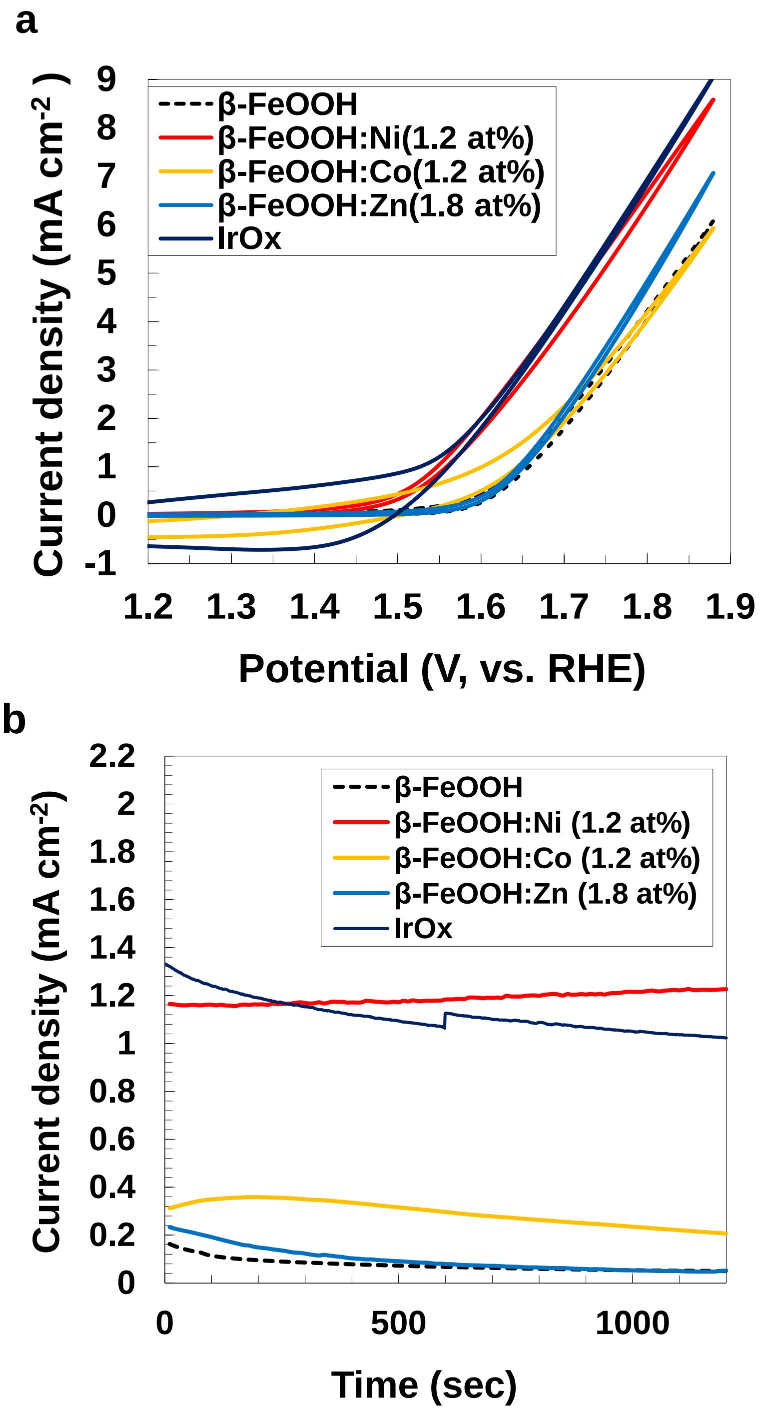

Fig. S11 **a)** Current-potential characteristics and **b)** time courses for the currents generated by various metal-doped FeOOH samples. These data were acquired in a 0.1 M aqueous KOH solution at +1.56 V (vs. RHE).

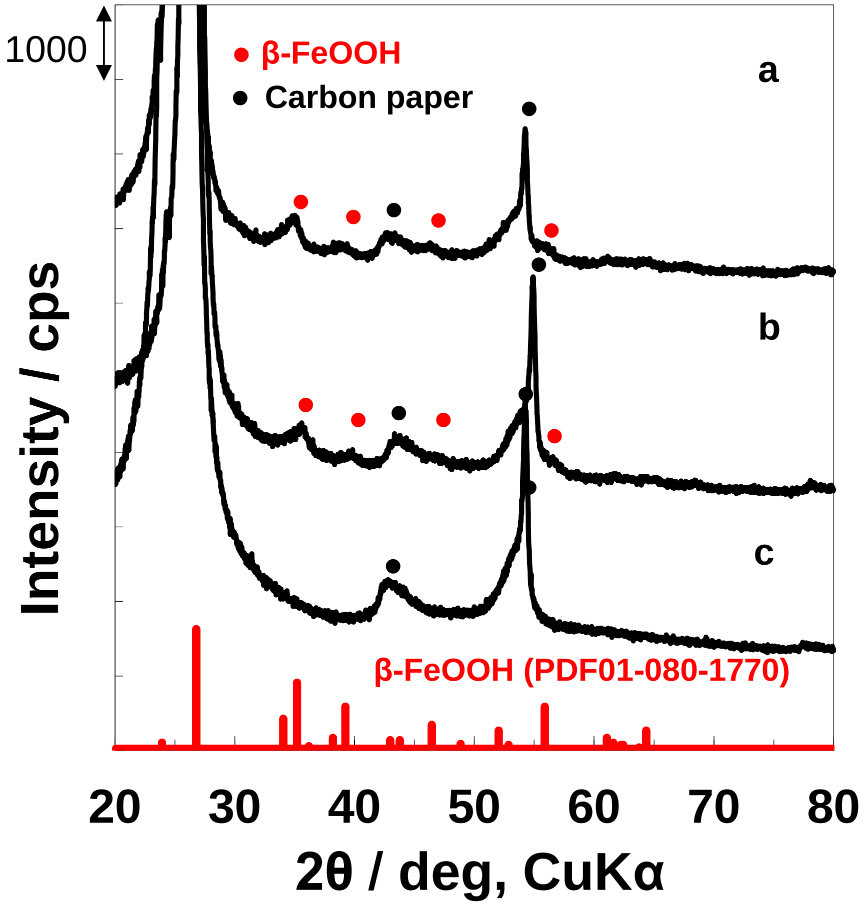

Fig. S12 XRD patterns of a β-FeOOH:Ni (1.2 at%) nanorod/CP sample a) before and b) after current-time measurements over 20 min (as in Figure S7), and c) of the CP support.

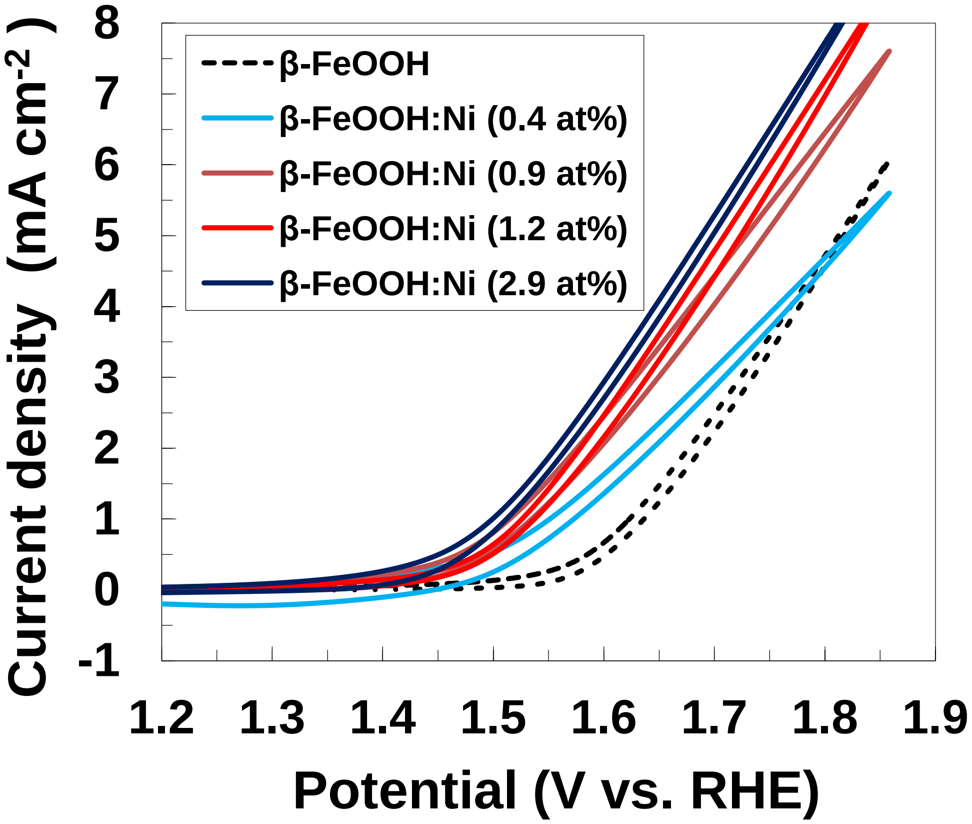

Fig. S13 Current-potential characteristics of β-FeOOH:Ni particle/CP electrodes with varying levels of Ni doping, acquired in a 0.1 M aqueous KOH solution (pH 12.8).

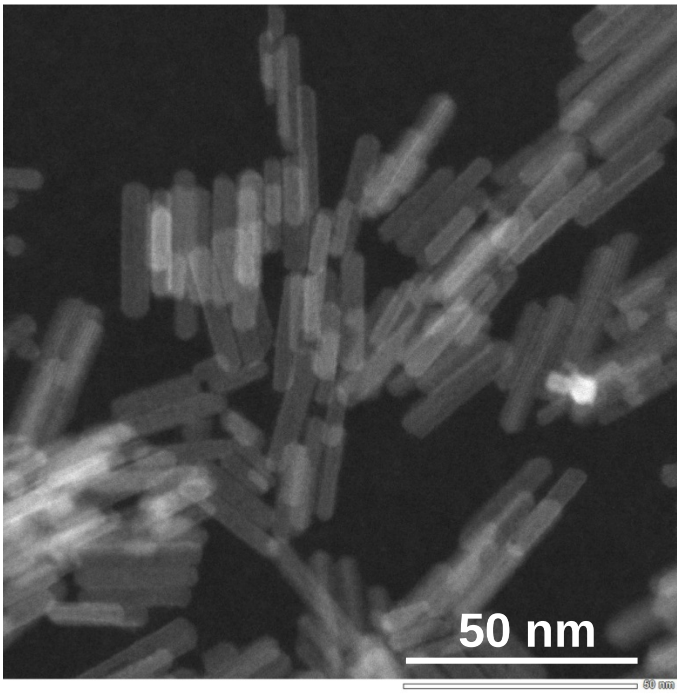

Fig. S14 STEM image of β-FeOOH nanorods (poorly crystalline) prepared by previous method. These β-FeOOH nanords synthesized at 70 ℃ for 7 days according to the report. [1, 2]

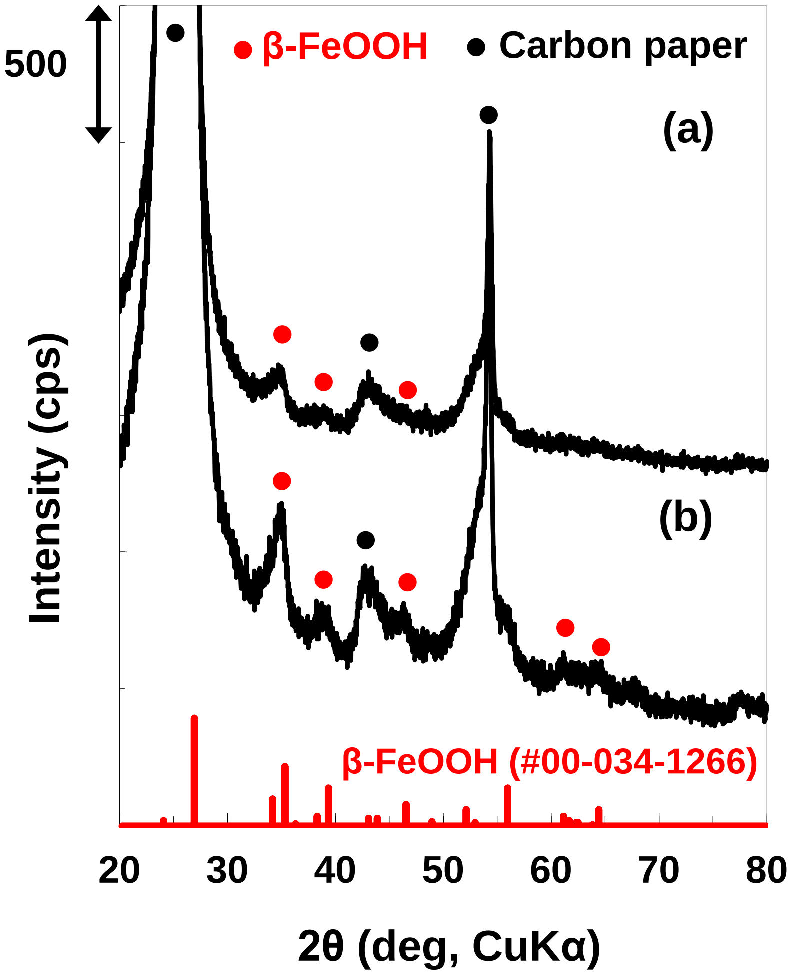

Fig. S15 XRD patterns of (a) β-FeOOH (poor crystalline, prepared by previous method)/CP and (b) β-FeOOH nanorods (this work)/CP. The poorly crystalline β-FeOOH synthesized at 70 ℃ for 7 days according to the report. [1, 2] Both samples contains β-FeOOH:Ni of *ca.* 1.0 mg in 1 cm^2 -CP. Whereas full width at half maximum are almost same, intensity (crystallinity) of previous β-FeOOH was lower than that of the present this study.

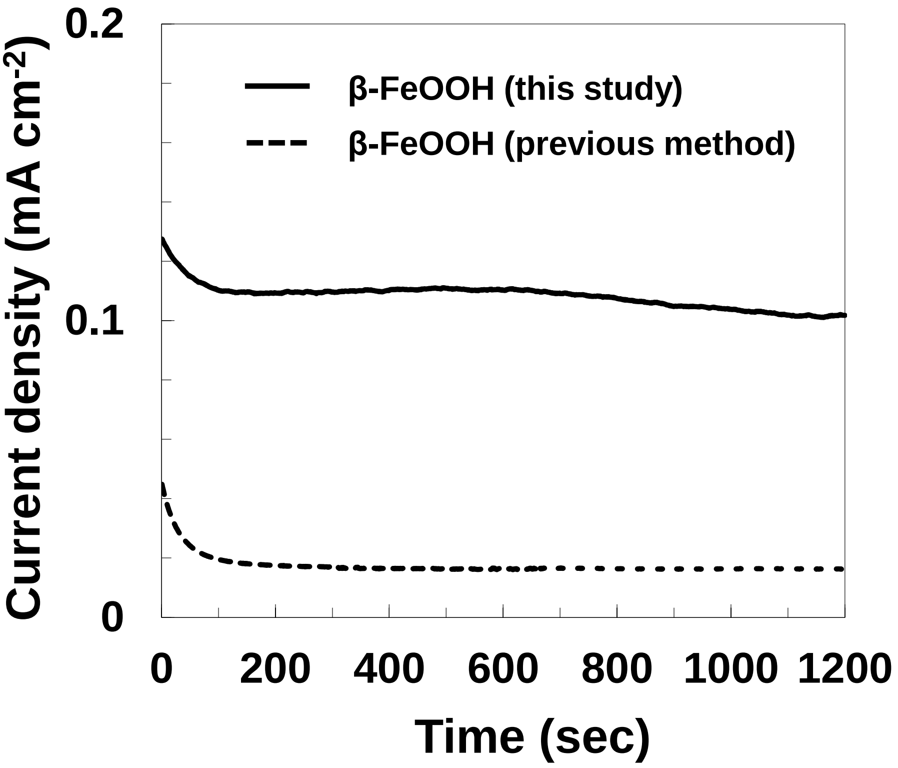

Fig. S16 Time courses for the currents generated by β-FeOOH (this study) and β-FeOOH (synthesized by previous method, poor crystalline)/CP samples. These data were acquired in a 0.1 M aqueous KOH solution at +1.56 V (vs. RHE). The poor crystalline β-FeOOH synthesized at 70 ℃ for 7 days according to the report.[1, 2] Both samples contain β-FeOOH of *ca.* 1.0 mg in 1 cm^2 -CP.

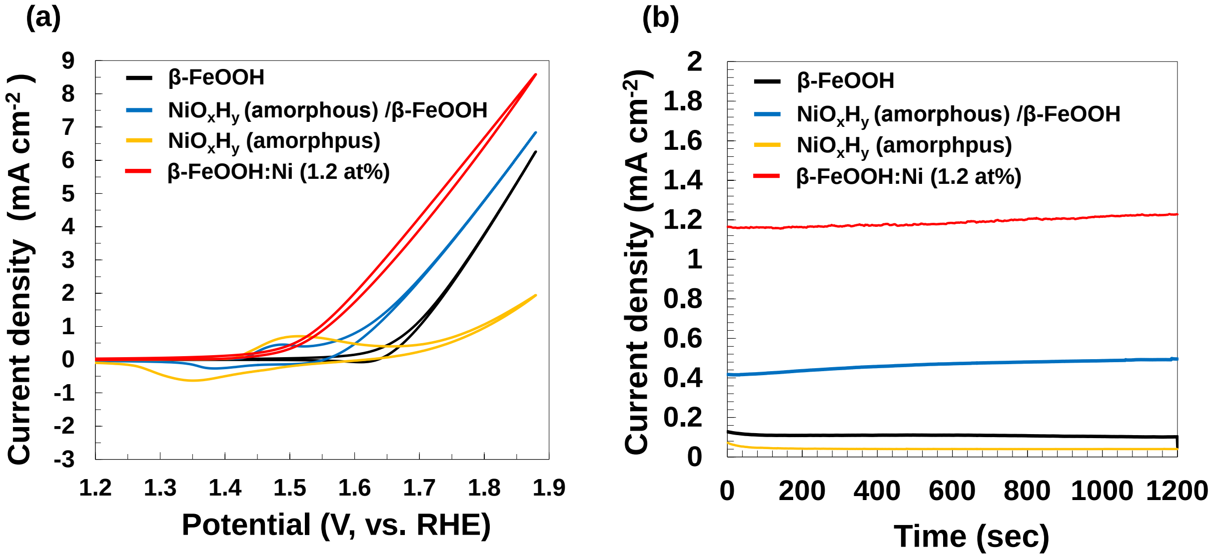

Fig. S17 a) Current-potential characteristics and b) time courses for the currents generated by β-FeOOH nanorods/CP (black line), NiO_xH_y (amorphous) coated β-FeOOH nanorods/CP (blue), NiO_xH_y (amorphous)/CP (orange) and β-FeOOH:Ni (1.2 at%) nanorods/CP (red). The modification of NiO_xH_y (amorphous) was performed by coating of pH-adjusted (pH 2.3) $Ni(NO_3)_2$ solution onto pure β-FeOOH(Cl) nanorods/CP. These data were acquired in a 0.1 M aqueous KOH solution at +1.56 V (vs. RHE). The average value of Ni/Fe of NiO_xH_y (amorphous) coated β-FeOOH/CP was estimated to be 1.9 at% by SEM-EDX.

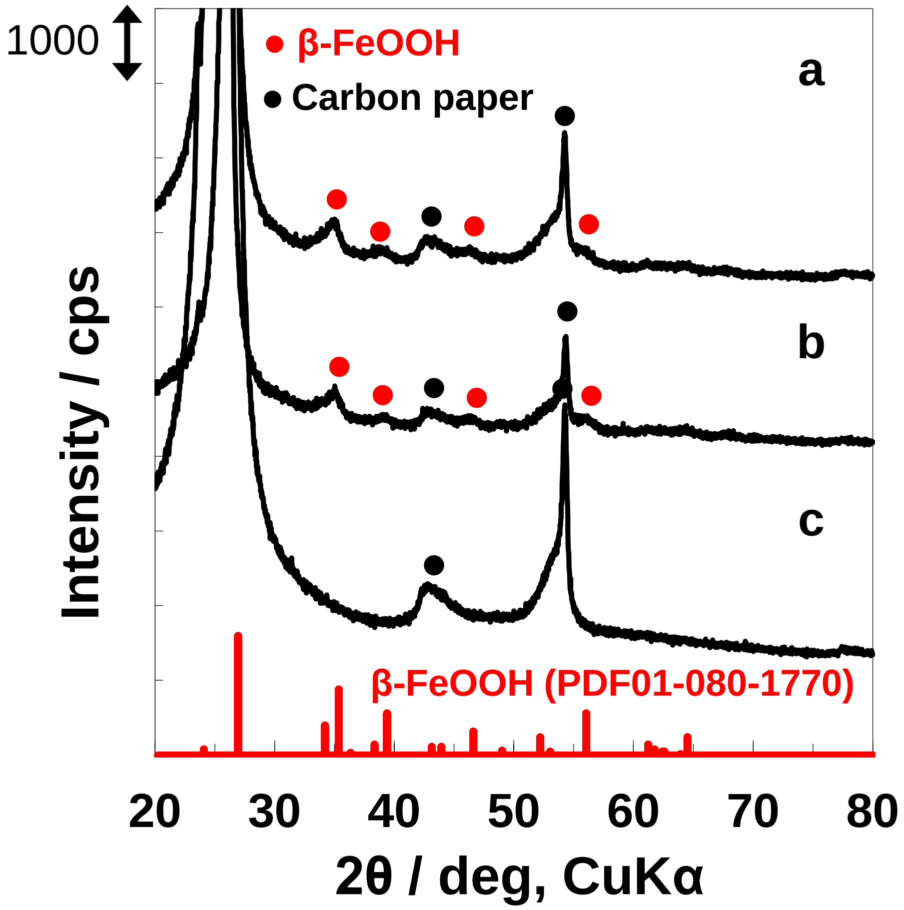

Fig. S18 XRD patterns of β-FeOOH:Ni (1.2 at%) anode (a) before and (b) after electrochemical water splitting reaction for 4 h (Fig. 6) at +1.56 V (vs. RHE) in a 0.1M aqueous KOH solution with a Pt cathode. The crystalline structure of the sample remained β-FeOOH after the water splitting reaction.

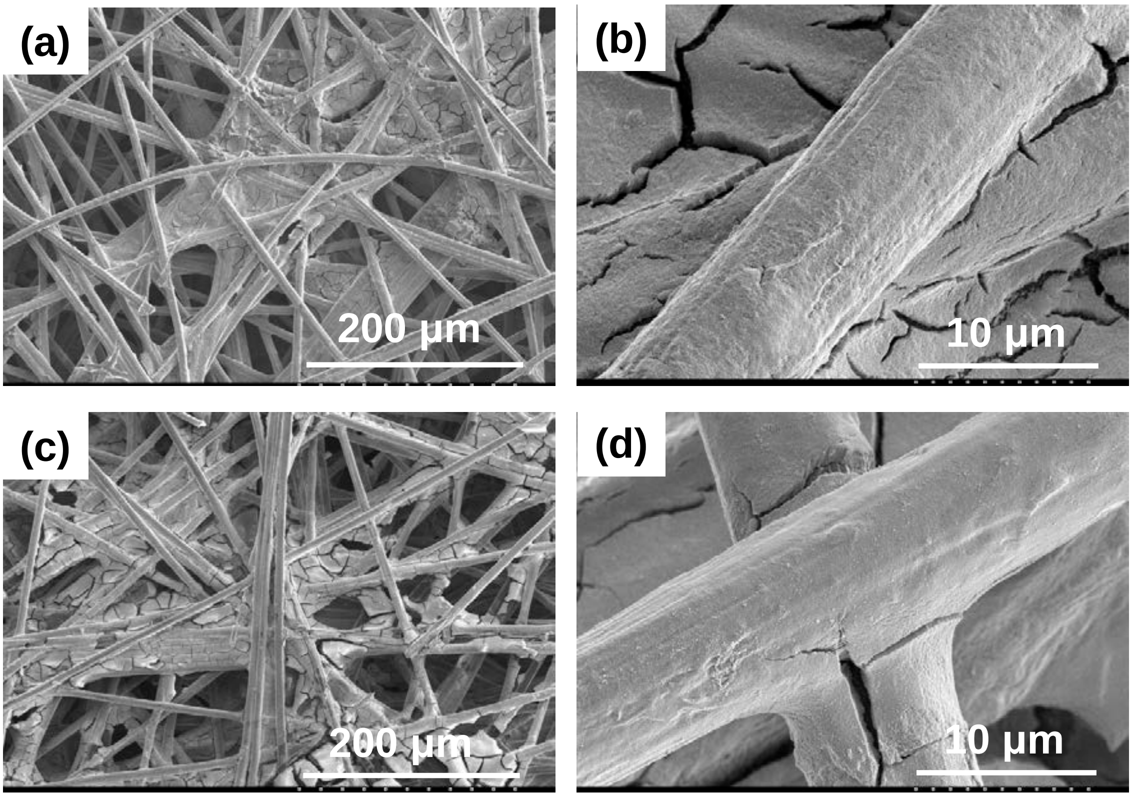

Fig. S19 Top view of SEM images of β-FeOOH:Ni (1.2 at%)/CP: (a) (b) before and (c) (d) after 4 h electrochemical water splitting reaction (Fig. 6) at +1.56 V (vs. RHE) in a 0.1M aqueous KOH solution with a Pt cathode. The morphology after the water splitting reaction was almost unchanged, while cracking partially took place.

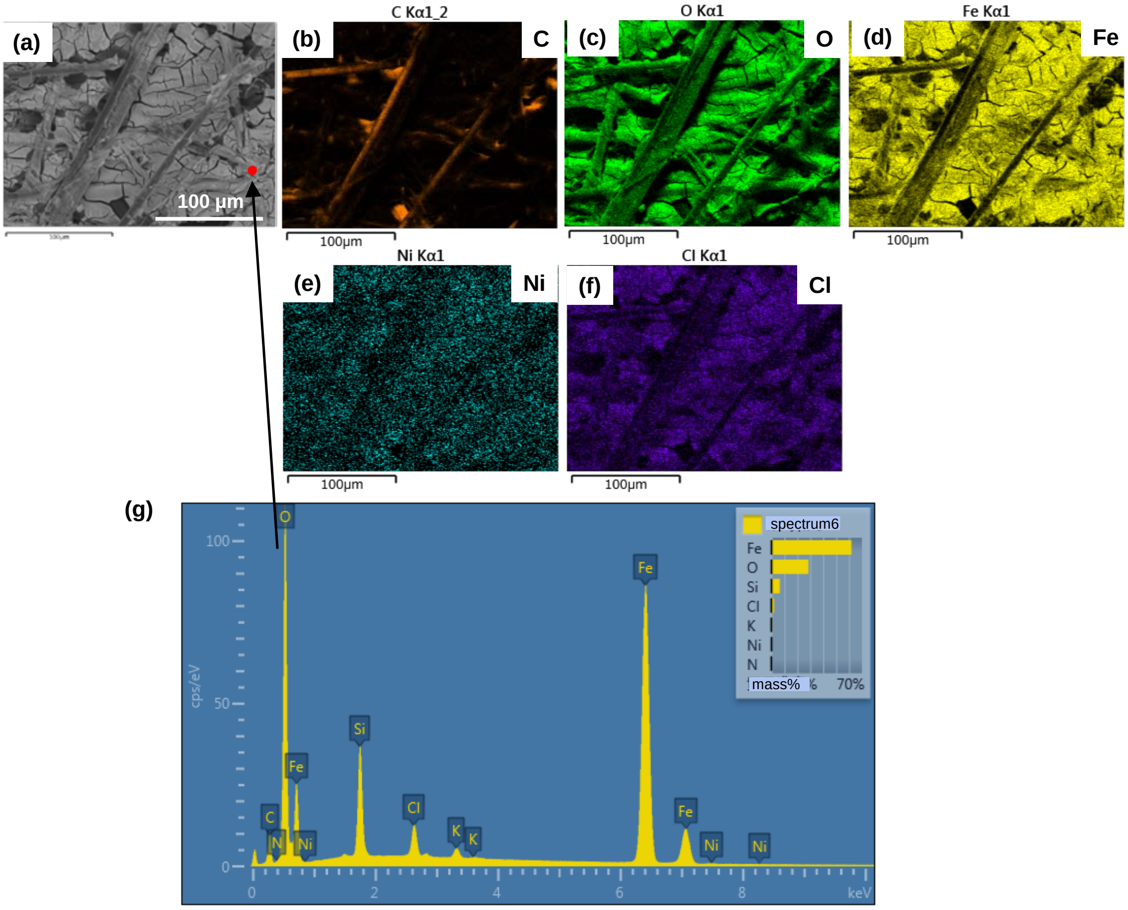

Fig. S20 a) SEM image and **b)-g)** SEM-EDX data for β-FeOOH:Ni (1.2at%) nanorod/CP after electrochemical water splitting reaction for 4 h (Fig. 6) at +1.56 V (vs. RHE) in a 0.1M aqueous KOH solution with a Pt cathode. Large quantity of Si component originated from silicon rubber used for fixing the electrode was also detected.

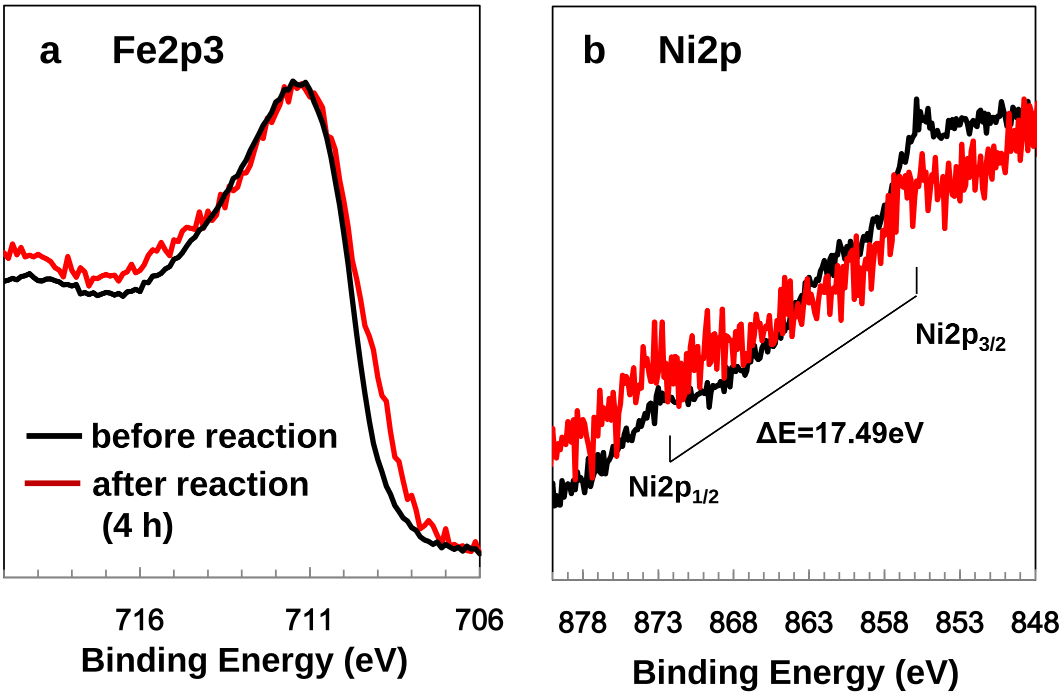

Fig. S21 XPS spectra of (a) Fe 2p3 and (b) Ni 2p for β-FeOOH:Ni (1.2 at%)/CP before (black line) and after (red) electrochemical water oxidation reaction for 4 h (Fig. 6) at +1.56 V (vs. RHE). The weak peaks originating from low concentration can be assigned to Ni because energy difference ΔE between them was 17.49 eV.

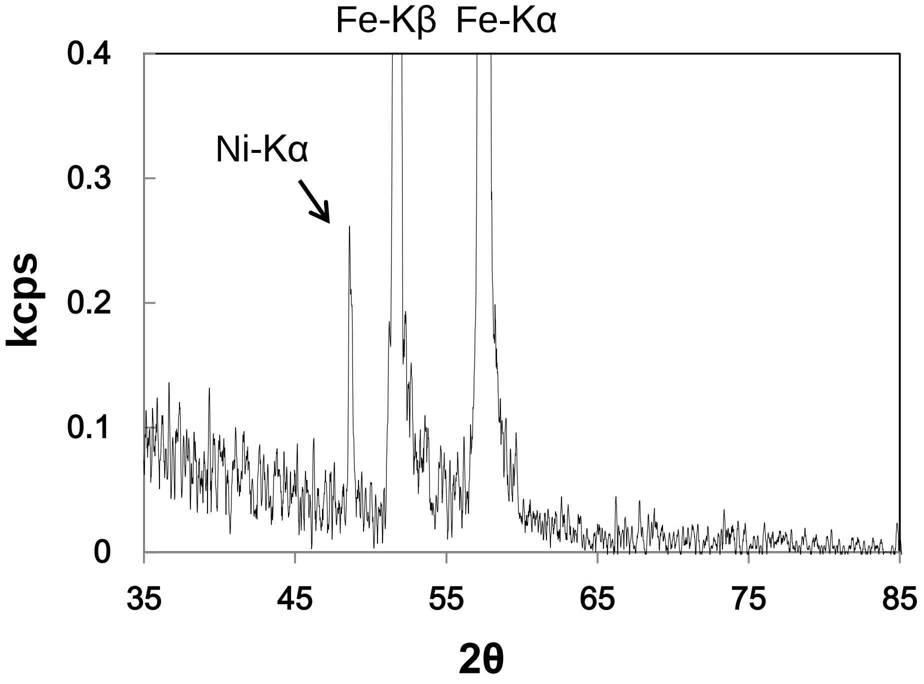

Fig. S22 X-ray fluorescence analysis (XRF: Rigaku, ZSX PRIMUS II) pattern of β-FeOOH:Ni (1.2 at%) after electrochemical water splitting reaction for 4 h (Fig. 6) at +1.56 V (vs. RHE).

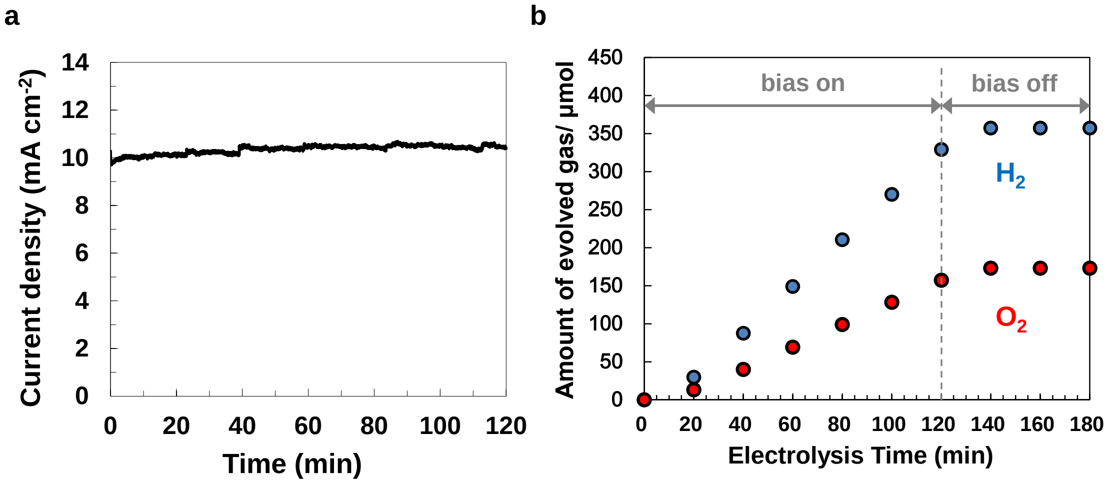

Fig. S23 Electrochemical water splitting by β-FeOOH:Ni (1.2 at%) nanorods/CP measured at +1.95 V (vs. RHE) in a 0.1 M $K_2B_4O_7$/0.2M K_2SO_4 solution (pH 6.9) with a Pt counter electrode. a) anodic water oxidation current and b) time course of hydrogen and oxygen generation by water splitting reaction.

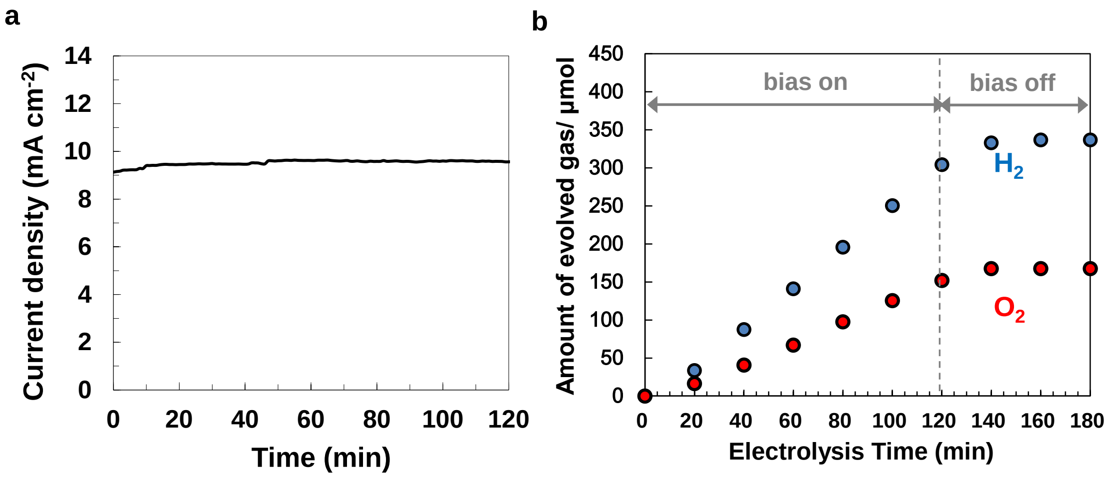

Fig. S24 Electrochemical water splitting by β-FeOOH:Ni (1.2 at%) nanorods/CP measured at +1.91 V (vs. RHE) in a 0.1 M KOH solution (pH 12.8) with a Pt counter electrode. a) anodic water oxidation current and b) time course of hydrogen and oxygen generation by water splitting reaction.

Table S1. Properties of Ni doped β-FeOOH colloidal solutions synthesized by utilization of various base reagent (4 at%-Ni addition).

Base[a)]	pH	Mean volume diameter (nm)[b)]	Ni content (at%)[c)]
Ethylendiamine (EDA)	2.2	13	1.2
NaOH	2.1	13	3.8
Monoethanolamine (MEA)	2.2	14	3.0

a) pH adjusted by utilization of the base, b) estimated by dynamic light scattering (DLS) measurement, c) estimated by ICP measurement

Table S2. Properties of transition metal doped β-FeOOH colloidal solutions (4 at% transition metal added).

Dopant	pH [a)]	Mean volume diameter (nm)[b)]	Transition metal content (at%)[c)]
None	2.4	11	0.0
Cr^{3+}	2.5	19	4.0
Mn^{2+}	2.3	14	1.9
Co^{2+}	2.2	11	1.2
Zn^{2+}	2.2	13	1.8

a) pH adjusted by ethylenediamine, b) estimated by dynamic light scattering (DLS) measurement, c) estimated by ICP measurement

Table S3. Atomic ratio evaluated by XPS for β-FeOOH:Ni (1.2 at%)/CP before and after electrochemical water splitting reaction for 4 h shown in Fig. 6 (average value of 2 points, analysis area: 800 μmΦ).

Atomic ratio			
Before reaction		After reaction	
Ni/Fe	Cl/Fe	Ni/Fe	Cl/Fe
0.014	0.17	0.020	0.14

References

[1] S. Jiang, S. Park, Y. Yoon, J-H. Lee, W-M. Wu, N. P. Dan, M. J. Sadowsky and H-G. Hur, *Environ. Sci. Technol.*, 2013, **47**, 10078-10084.

[2] S. Jiang, M-G. Kim, I. Y. Kim, S-J. Hwnag and Hur, H-G. *J. Mater. Chem. A.*, 2013, **1**, 1646-1650.