Supplementary information

Guest-Host Modulation of Multi-Metallic (Oxy)hydroxides for Superb Water Oxidation

Cheng Tang,[a] Hao-Fan Wang,[a] Han-Sen Wang,[a] Fei Wei,[a] Qiang Zhang*[a]

[a]Beijing Key Laboratory of Green Chemical Reaction Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

E-mail: zhang-qiang@mails.tsinghua.edu.cn (Q. Zhang)

I. Supplementary texts

1.1. Synthesis of G/NiFe (oxy)hydroxide composites

1.1.1. Synthesis of porous MgO templates

Firstly, porous MgO templates were fabricated. PEG-2000 (2.12 g) was dissolved in deionized water (200.0 mL), and then commercial MgO powders (99.5%, 1.0 g) were added slowly under magnetic stirring at 25.0 ^{o}C. Then, the dispersion was transferred into a 250.0 mL Teflon-lined stainless steel autoclave to treat at 200 ^{o}C for 48.0 h. After filtering, washing, freeze-drying, and calcination at 650 ^{o}C for 5.0 h, the as-prepared porous MgO templates were achieved.

1.1.2. Synthesis of graphene framework

The graphene framework was synthesized *via* MgO-templated CVD method. MgO template (1.0 g) was dispersed uniformly into a quartz boat and then placed in the center of a horizontal quartz tube. The tube was inserted into the furnace at atmospheric pressure. Under the protection of Ar (flow rate: 200.0 mL min^{-1}), the reactor was heated to 950 ^{o}C, and then CH_4 (50.0 mL min^{-1}) was introduced into the reactor for 10 min. After the CVD growth of graphene, the furnace was cooled down to room temperature in the atmosphere of H_2 (10.0 mL min^{-1}) and Ar (100.0 mL min^{-1}). The as-obtained product was then treated with 6.0 mol L^{-1} hydrochloric acid (500 mL) at 80.0 ^{o}C for 24.0 h to remove the MgO template. After washing, vacuum filtering, and freeze-drying, the mesoporous graphene sample was fabricated.

1.1.3. Oxidation of graphene framework

The as-obtained graphene was mildly oxidized following a modified Hummers' method. 100.0 mg graphene was firstly dispersed in 25.0 mL concentrated H_2SO_4. Then, the mixture was transferred into an ice-water bath to maintain its temperature under 10 ^{o}C and stirred for 4.0 h. After that, 25.0 mL 10 % dilute H_2SO_4 was gradually added in 1.0 h, followed by slow addition of 75.0 mL deionized water in another 2.0 h. To end the reaction, 2.0 mL H_2O_2 was added into the solution until no gas bubble was released. The moderately oxidized sample was finally obtained after filtering, washing, and freeze-drying.

1.1.4. *In situ* growth of NiFe hydroxides in graphene framework

NiFe (oxy)hydroxides were *in situ* grown inside the mesopores of the as-prepared graphene framework using a urea-assisted co-precipitation reaction for the preparation of G/NiFe (oxy)hydroxide composites. Taken G/NiFe-0.30 as example, the as-prepared oxidized-graphene (25.0 mg) was first ultrasonically dispersed in N-methylpyrrolidone (NMP, 40.0 mL) for 30 min. $Ni(NO_3)_3$ $6H_2O$ (735.0 mg), $Fe(NO_3)_3$ $9H_2O$ (340.0 mg) and urea (9.0 g) were dispersed in deionized water (50.0 mL) to form another solution. The as-obtained solution was mixed with the graphene/NMP dispersion and then kept at 100 ^{o}C in oil bath under continuous magnetic stirring for 6.0 h in a 250 mL flask, which was equipped with a reflux condenser in ambient atmosphere. G/NiFe-0.30 can be obtained after filtering, washing, and freeze-drying of the as-obtained suspension. The other catalysts in this family can be prepared by changing the Fe and Ni nitrate dosage under otherwise identical conditions. To be specific, we use $Ni(NO_3)_3$ $6H_2O$ (980.0 mg) for the preparation of Ni/Fe (4:0), $Ni(NO_3)_3$ $6H_2O$ (245.0 mg), $Fe(NO_3)_3$ $9H_2O$ (1021.0 mg) for Ni/Fe (1:3) and $Fe(NO_3)_3$ $9H_2O$ (1361.0 mg) for Ni/Fe (0:4). Bulk NiFe hydroxides were also fabricated under the same conditions without the graphene addition.

1.2. Characterizations

The morphology and structure of the samples were characterized using a JSM 7401F (JEOL Ltd., Tokyo, Japan) scanning electron microscope (SEM) operated at 3.0 kV and a JEM 2010 (JEOL Ltd., Tokyo, Japan) transmission electron microscope (TEM) operated at 120.0 kV. The mass ratio of LDHs and graphene was obtained through thermalgravimetric analysis (TGA) by a TGA/DSC1 STAR^e system under O_2 flow. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer at 40.0 kV and 120 mA with Cu-K_α radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out by Escalab 250Xi with a monochromated Al-K_α source (1486.6 eV). Elemental analyses were also conducted using an inductively coupled plasma optical emission spectrometer (IRIS Intrepid II XSP, ThermoFisher, USA). The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer using a KBr disk.

1.3. Electrocatalytic Performance Measurements

Electrochemical measurements were performed on an RRDE configuration (Pine Research Instrument, USA) in a three-electrode electrochemical setup using a computer-controlled potential station (CHI 760D, CH Instrument, USA). A platinum sheet electrode and a saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. A rotating ring disk electrode with a disk diameter of 5.0 mm served as the substrate for the working electrode. All electrochemical measurements were performed using a 0.10 M KOH electrolyte.

The fabrication of working electrode was carried out as follows: Taken G/NiFe-0.30 as example, 5.0 mg catalyst was dispersed in 0.95 mL ethanol, then 0.05mL Nafion solution (5 wt%) was added. After sonication for 1.0 h, 10.0 μL suspension was pipetted onto the glass carbon disk electrode surface at twice (each time 5.0 μL), which was polished mechanically with 0.050 μm alumina slurry and then washed with deionized water and acetone to obtain a mirror-like clean surface prior to use. After solvent evaporation for 10 min in air, the working electrode has been fabricated and measurements can be performed.

Linear sweep voltammetry (LSV) was performed with a potential range scanned from 0.0 to 1.0 V versus SCE at the scan rate of 5.0 mV s^{-1} in O_2 -saturated 0.10 M KOH solution. All polarization curves were corrected with 95% iR-compensation. During the tests, the disk electrode was rotating at a speed of 1600 rpm. The stability was measured *via* chronoamperometric tests at potentials for an initial OER current density of 1.0 mA cm^{-2}. The catalyst loading was about 0.25 mg cm^{-2} for all tests. Electrochemically active surface areas (ECSA) was measured by cyclic voltammetry (CV) using the same working electrodes at a potential window of 0.2 - 0.3 versus SCE. CV curves were obtained at different scan rates of 40.0, 60.0, 80.0, 100.0, and 120.0 mV s^{-1}. Then linear fitting of charging current density differences ($\Delta j = j_a - j_c$ at the potential of 250 mV versus SCE) versus the scan rates was done. The double-layer capacitance C_{dl}, half of the slope of the line in number, can be used to represent ECSA.

The overpotential was calculated by the following equation: Overpotential = measured value (*vs.* SCE) + 0.241 + 0.0592 pH - 1.229 (*vs.* RHE). The Tafel slope was derived according to the Tafel equation $\eta = b \log(j/j_0)$, where η is the overpotential, b is the Tafel slope, j is the current density, and j_0 is the exchange current density. The current density j and overpotential η are obtained from the LSV curves with a potential range slightly higher than the onset potential.

Turn over frequency (TOF) is calculated based on the following equation: TOF = $JA/(4Fn)$, where J is the current density at an overpotential of 35 mV; A is the surface area of the 5 mm-diameter electrode; F is faraday constant; n is supposed to be number of moles of active metal species on the electrode. As the real active sites and the number of active sites that actually take part in the catalyzing process are difficult to confirm. Herein, we systematically calculated TOF based on the number of Ni and Fe atoms respectively or together (denoted as TOF_{Ni}, TOF_{Fe}, TOF_{total}), assuming only Ni or Fe or all of them were involved in the catalysis.

II. Supplementary figures

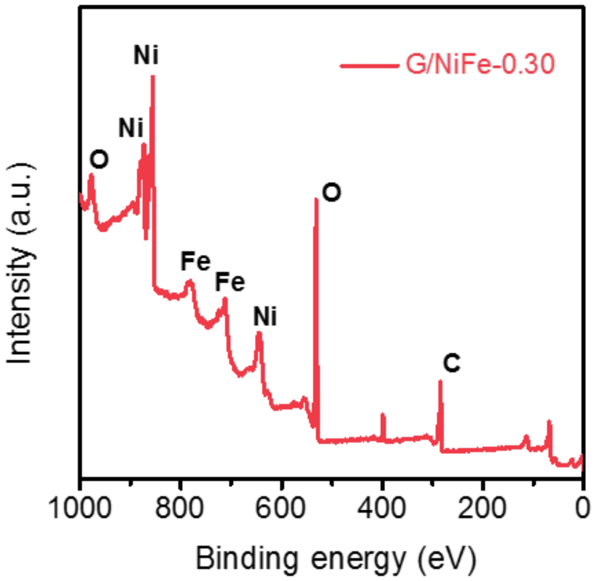

Fig. S1 XPS survey spectrum of G/NiFe-0.30 material.

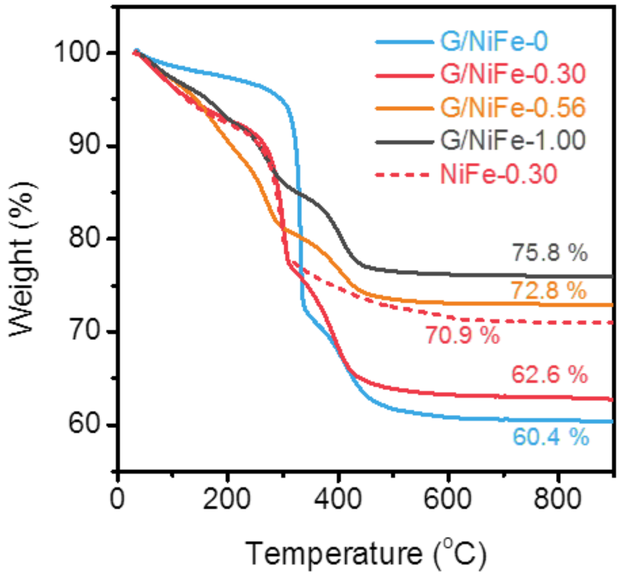

Fig. S2 TGA curves of G/NiFe materials under the O_2 atmosphere. Bulk NiFe hydroxides without graphene were fabricated and tested to obtain the mass ratio of the NiFe hydroxides and graphene in composites. Taken G/NiFe-0.30 as example, the TGA curve of the bulk NiFe-0.30 sample is shown as the dashed line in Fig. S2, with a weight reservation of 70.9 %. Then, the mass content of NiFe-0.30 in G/NiFe-0.30 is calculated to be (62.6/70.9 =) 88.2 % (the mass ratio of NiFe-0.30: G ≈ 7.5), based on the reasonable assumption that the weight loss ratio for hydroxide materials is consistent in the bulk hydroxides and complexes. Analogously, the mass ratios of other hydroxides against graphene are calculated to be 4.8 for G/NiFe-0, 8.9 for G/NiFe-0.56, and 10.5 for G/NiFe-1.00, indicating an increase of metal hydroxide nanoparticles with the increase of Fe ratios.

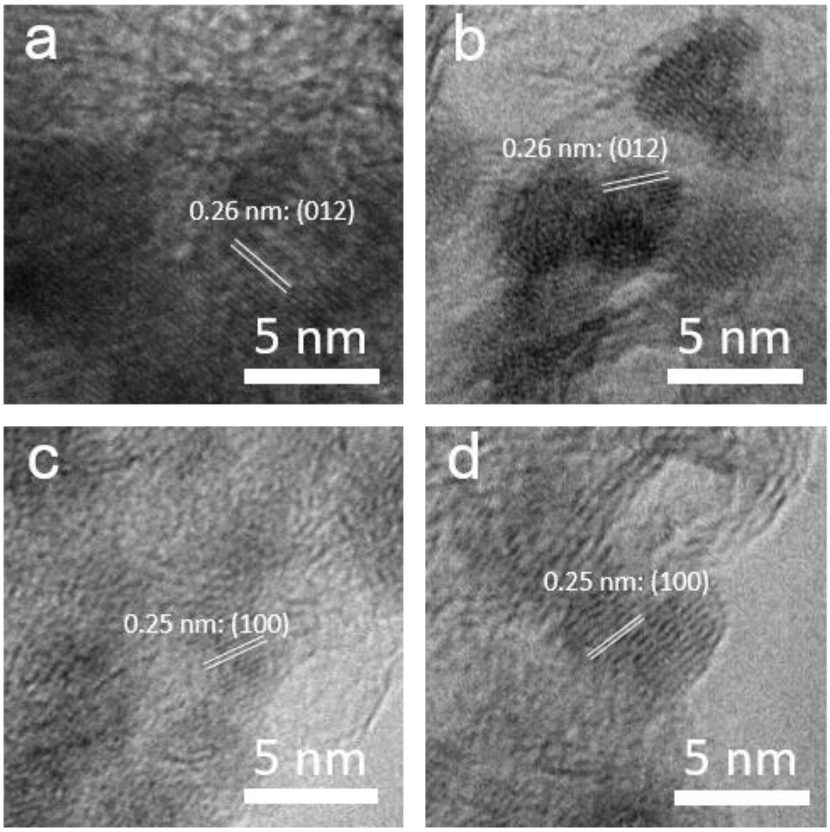

Fig. S3 HRTEM images of G/NiFe materials. (a) G/Ni and (b) G/$NiFe_{0.30}$ exhibit a set of lattice fringes with a spacing of 0.26 nm, corresponding to the (012) lattice planes of the α-$Ni(OH)_2$ structure. (c) G/$NiFe_{0.56}$ and (d) G/Fe show the lattice fringes with a spacing of 0.25 nm, which is assigned to the (100) lattice planes of the FeO(OH) structure.

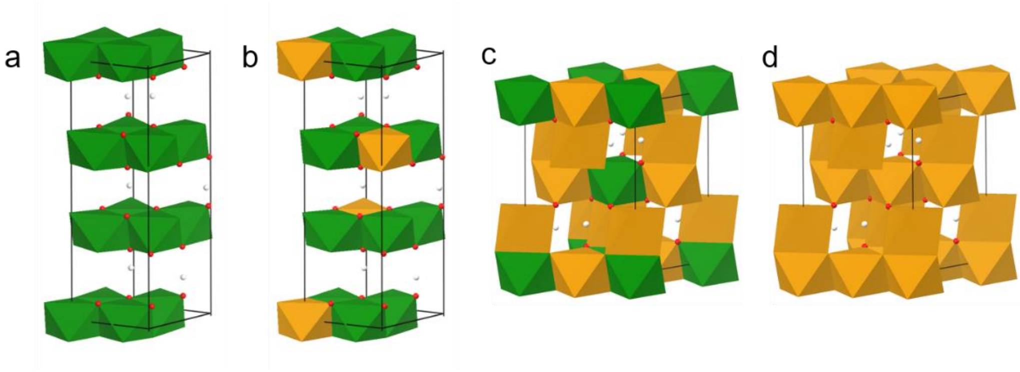

Fig. S4 The model structures showing the physical structure evolution. With the Fe content increased, the resultant materials are transformed from well-crystallized hydroxides: (a) γ-NiO(OH) derived from α-Ni(OH)$_2$, and (b) NiFe LDHs, to amorphous oxyhydroxides; (c) Ni substituted FeO(OH), and (d) FeO(OH) polymorph, dominantly δ-FeO(OH).

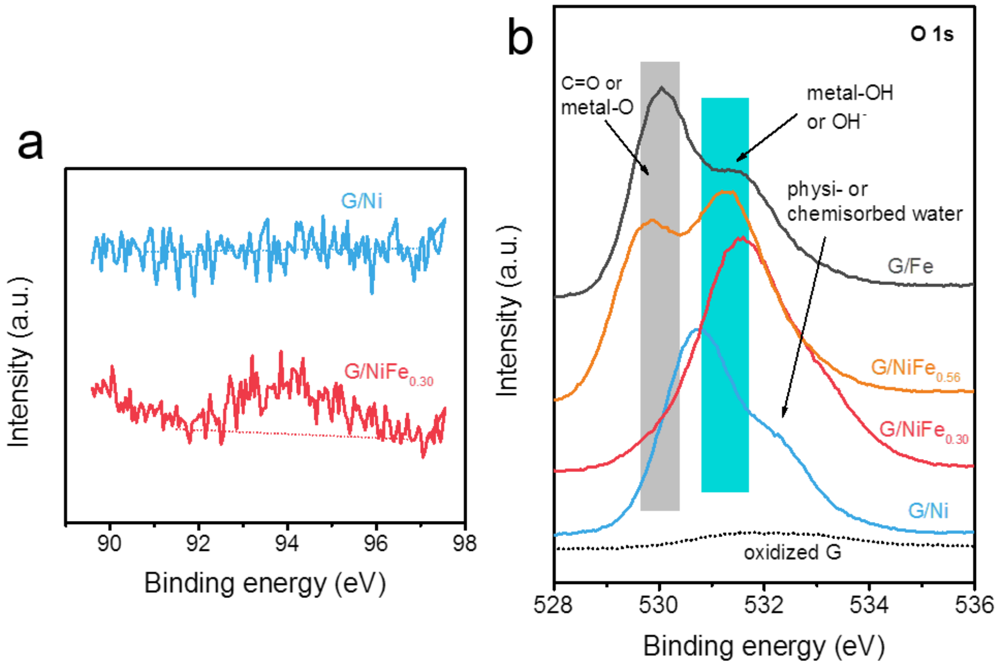

Fig. S5 (a) High resolution Fe 3s spectra of G/Ni and G/NiFe$_{0.30}$ with unrecognizable peaks for the G/Ni sample, indicating the absence of Fe in the G/Ni material. (b) High resolution O 1s spectrum of all G/NiFe materials.

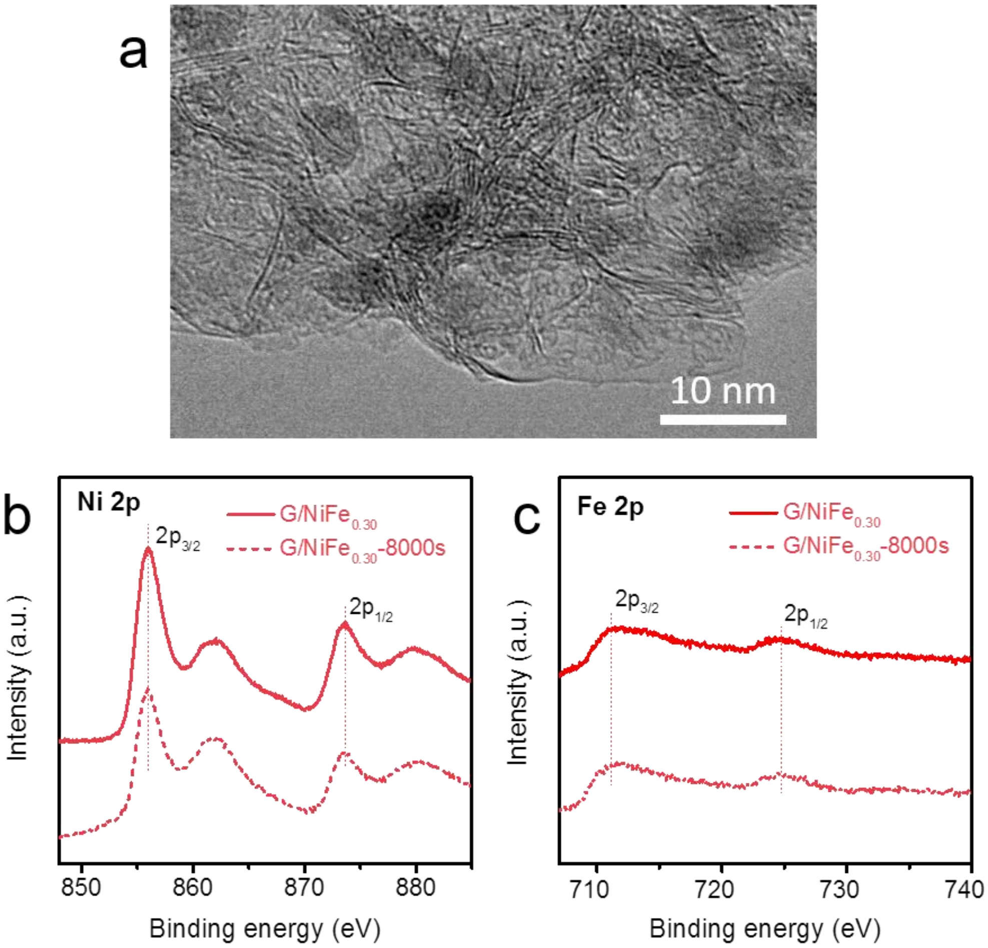

Fig. S6 Characterization of G/NiFe$_{0.30}$ after a 8000 s test at a constant overpotential of 305 mV. (a) TEM image with the preservation of uniformly decorated NiFe LDH nanoplates, indicating the structural stability during the OER catalysis. (b) High resolution Ni 2p and (c) Fe 2p spectra without no change after cycling. As the overpotential for G/Fe is respectively high compared with other samples, the test condition is set with a small initial current density of 1.0 mA cm^{-2}, so that the durability tests can be carried out for all samples. The operation overpotential are 360, 305, 342, and 400 mV for G/Ni, G/NiFe$_{0.30}$, G/NiFe$_{0.56}$, and G/Fe samples.

III. Supplementary tables

Table S1. The compositions of G/NiFe materials based on XPS results.

Sample		G/Ni	G/NiFe$_{0.30}$	G/NiFe$_{0.56}$	G/Fe
Mole ratio of different elements (at. %)	C	30.10	35.17	35.33	52.93
	O	44.74	38.50	44.22	34.77
	Ni	25.16	18.42	9.02	0.00
	Fe	0.00	7.91	11.43	12.31
Fe content (mole ratio of Fe/(Ni+Fe))		0.00	0.30	0.56	1.00