Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Tuning the Morphological and Electronic Structure of Amorphous Nickel Based Electrocatalysts by Anion Regulation for Water Oxidation in Neutral Media

Gang Yuan, [a,b] *Yujie Hu,* [a] *Qiwei Wang,* [a] *Zihan Wang,* [a] *Li Wang,* [a,b,*] *Xiangwen Zhang,* [a,b] *Qingfa Wang* [a,b,*]

[a] Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, 92 Weijin Road, Tianjin 300072, P. R. China.

[b] Collaborative Innovation Centre of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, P. R. China.

Corresponding Author

[*] E-mail：qfwang@tju.edu.cn

1. Experimental

1.1 Chemicals

Nickel foam (110 pores per inch; mass density of 350 g m^{-2}) was purchased from Suzhou jiashide metal foam Co., Ltd., China. Sodium hypophosphite (NaH_2PO_2), sodium acetate (CH_3COONa), potassium hydroxide (KOH), nickel (II) acetate ($Ni(CH_3COO)_2$) are all at 99 %, purchased from Aladdin and used without further purification. Ultrapure water (18.2 MΩ cm^{-1}; home made by a Millipore, Milli-Q Advantage A10 system) and anhydrous ethanol (99.9%, Jiangtian, China) were used for solution preparation and/or wash work.

1.2 Synthesis of Ni-based electrocatalysts

Amorphous nickel hydroxide phosphide/phosphate on Ni foam, referred to as Ni-OH/P/PO_4, were prepared by a simple one-step hydrothermal process. A piece of Ni foam, which was pretreated by ultrasonicating in acetone, 6M HCl, ethanol and ultrapure water successively for 5 minutes each, was immersed into a Teflon-lined stainless steel autoclave containing a 30 mL aqueous solution of 5 mM $Ni(CH_3COO)_2$, 5 mM CH_3COONa, and 0.5 M NaH_2PO_2. Then, the autoclave was sealed for hydrothermal reaction at 180 °C for 4 h to obtain Ni-OH/P/PO_4. After the autoclave was cooled down to room temperature, the samples were rinsed with copious distilled water and then dried in an electric oven at 60 °C for 12 h.

1.3 Physical characterization

The X-ray diffraction (XRD) spectra of samples was identified by an X'Pert Pro X-ray diffractometer (Panalytical, Netherlands), using Cu Kα radiation at 40 kV, 40 mA. The morphology and thickness of the film were examined by scanning and transmission electronic microscopy (SEM, S-4800, and TEM, JEOL JEM-2100F, respectively), and high-resolution TEM (HRTEM). Energy dispersive X-ray spectroscopy (EDS) was carried out to determine the compositions and elemental dispersion. X-ray photoelectron spectroscopy (XPS, PHI QUANTERA-II SXM) was performed to confirm the elemental composition and examine their surface states. Inductively-coupled plasma optical emission spectroscopy (ICP-OES) was conducted for quantitative analysis of element content.

1.4 Electrochemical measurements

The electrochemical tests were conducted with an Autolab 302N electrochemical workstation (Nova, Netherland) in 25 °C water bath. A typical three-electrode setup was used for all the tests with platinum gauze as a counter electrode. An Hg/HgO (1M KOH) or a SCE electrode was used as a reference electrode, when the experiment was carried out in an alkaline (1M KOH) or a neutral (1M PBS) electrolyte respectively. Prior and during all the electrochemical tests, O_2 was continuous bubbled over the electrolyte to ensure the O_2/H_2O equilibrium (1.23 V vs RHE). The reference electrode was calibrated in H_2-saturated electrolyte over a reverse hydrogen electrode (RHE). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were performed at sweeping rates of 5 mV s^{-1}.

2. Supplementary Figures

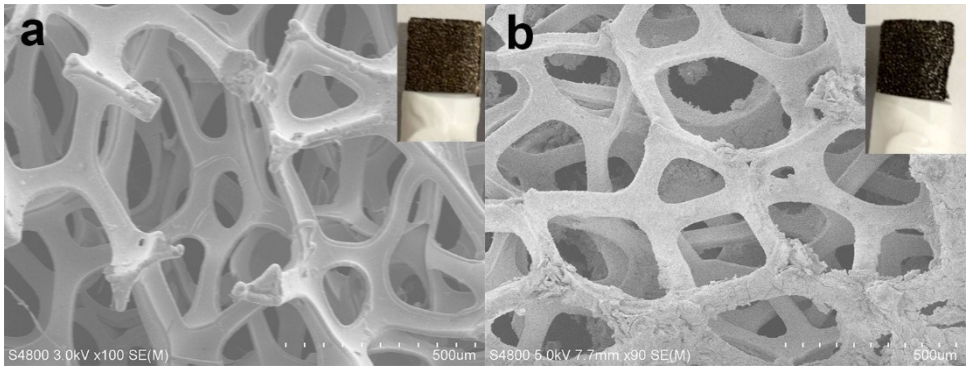

Fig. S1. SEM images of (a) bare NF, and (b) $Ni(OH)_2$/Ni:Pi. The insets are the corresponding bulk sample.

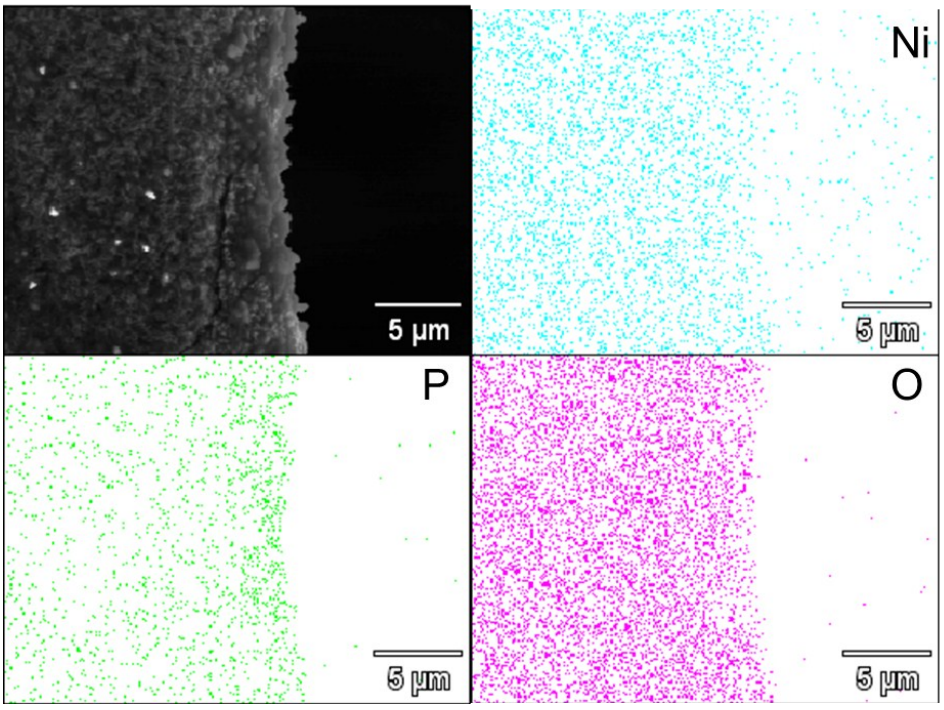

Fig. S2 EDS elemental mapping of $Ni(OH)_2$/Ni:Pi. Ni: blue, P: green, and O: red.

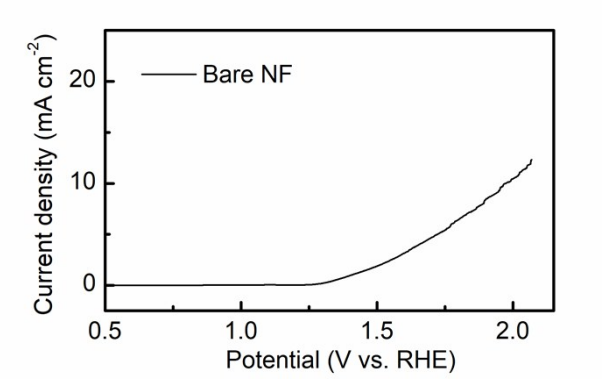

Fig. S3 LSV plots of bare NF at a scan rate of 2 mV s^{-1} in a 1.0 M PBS solution.

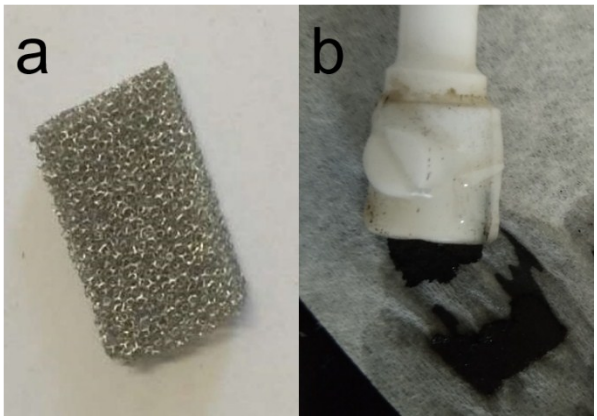

Fig. S4 Digital photos of (a) bare NF and (b) NF tested in a 1.0 M PBS solution from 0 to 2 V at a scan rate of 2 mV s^{-1}.

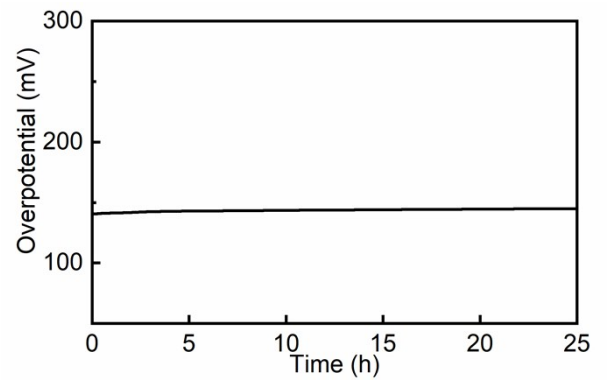

Fig. S5 Chronopotentiometric curves of $Ni(OH)_2$/Ni:Pi at a constant current density of 1 mA cm^{-2} in a 1.0 M PBS solution for 25 h.