Amorphous Metallic NiFeP: A Conductive Bulk Material Achieving High Activity for Oxygen Evolution Reaction in Both Alkaline and Acidic Media

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The intrinsic catalytic activity at 10 mA cm\(^{-2}\) for oxygen evolution reaction (OER) is currently working out at overpotentials higher than 320 mV. A highly efficient electrocatalyst should possess both active sites and high conductivity; however, the loading of powder catalysts on electrodes may often suffer from the large resistance between catalysts and current collectors. This work reports a class of bulk amorphous NiFeP materials with metallic bonds from the viewpoint of electrode design. The materials reported here perfectly combine high macroscopic conductivity with surface active sites, and can be directly used as the electrodes with active sites toward high OER activity in both alkaline and acidic electrolytes. Specifically, a low overpotential of 219 mV is achieved at the geometric current density 10 mA cm\(^{-2}\) in an alkaline electrolyte, with the Tafel slope of 32 mV dec\(^{-1}\) and intrinsic overpotential of 280 mV. Meanwhile, an overpotential of 540 mV at 10 mA cm\(^{-2}\) is attained in an acidic electrolyte and stable for over 30 h, which is the best OER performance in both alkaline and acidic media. This work provides a different angle for the design of high-performance OER electrocatalysts and facilitates the device applications of electrocatalysts.

The oxygen evolution reaction (OER) is a rate-determining process in various renewable energy conversion and storage devices such as water splitting electrolyzer cells, fuel cells, and lithium–air batteries. Currently, the intrinsic OER overpotentials at 10 mA cm\(^{-2}\) are generally above 320 mV in an alkaline medium or 750 mV in an acidic medium, respectively. As the electrocatalytic activity is strongly correlated with active sites, significant efforts have been made to tailor defect densities or architect nanostructures, which can reduce the apparently geometric overpotential for OER below 300 mV at 10 mA cm\(^{-2}\).[2,3] Among various electrocatalytic materials, the first-row transition metals (e.g., Fe and Ni) have smaller d orbitals and thus lower crystal-field activation energies, which makes their compounds more active in OER as compared with noble metal oxides (e.g., RuO\(_2\) and IrO\(_2\)).[1,4–7] The electrocatalytic activities of transition metal oxides, hydroxides, and dichalcogenides, however, turn out to be significantly limited by their low electrical conductivity. For this reason, a variety of novel materials with improved electrical conductivity, including semiconducting...
MoS₂ and WS₂, superconducting NbSe₂ and TaS₂, and metallic/half-metallic WTe₂, TiSe₂, CoSe₂, and Co₄N, have been developed to boost electrocatalytic activity.[3,8–10]

Taken together, the combination of active sites with high conductivity should be a promising approach to design high-performance OER electrocatalysts. The efficiency of energy transfer on a geometric-area basis is usually improved by increasing catalyst loading or exposed surface area. However, this approach would eventually result in the reduced mass transportation, which is caused by the uncontrolled agglomeration, increased series resistance and limited electron transfer from catalyst surface to current collector. Intuitively, the integration of macroscopic conductivity in bulk with dense active sites on surface would provide a solution to address this challenge, paving the way to highly efficient OER electrocatalysts on a geometric-area basis.

In this Communication, we report a class of bulk amorphous NiFeP materials toward high OER activity in both alkaline and acidic electrolytes, from the viewpoint of electrode design. The key to our design is to directly utilize the bulk electrocatalytic materials with high conductivity as electrodes so that the OER no longer suffers from the large resistance between catalysts and current collectors. Although the NiFeP has been synthesized by thermal conversion,[11] temperature-programed H₂ reduction,[12–14] electrodeposition,[15,16] electroless deposition,[17,18] and alloy-quenching techniques,[19] the electrocatalytic performance of bulk amorphous NiFeP remains unexplored. Our investigation reveals that the bulk amorphous NiFeP materials perfectly combine high macroscopic conductivity with surface active sites. The amorphism, credited by their highly free energy, has recently been recognized as a contribution to OER active sites.[6,20] As Ni and Fe sites have been proven synergistic for OER with optimal adsorption and desorption energies,[21,22] we choose Ni and Fe as the metal elements to constitute amorphous solids. In the amorphous NiFeP materials, the element P with appropriate electronegativity is employed to stabilize the Ni and Fe atoms as an amorphous metallic phase with high bulk conductivity, and can also potentially form active species for improving OER performance.[23,24] As a result, the bulk amorphous NiFeP materials achieve the unprecedentedly outstanding OER performance—an η_{geometric} of 219 mV or η_{intrinsic} of 280 mV at the current density of 10 mA cm⁻² in an alkaline medium, and an η of 540 mV at 10 mA cm⁻² in an acidic electrolyte.

Our bulk amorphous NiFeP materials are facilely fabricated through a melting spinning and rapid quenching process, with the capability of readily tailoring chemical compositions. Figure 1a displays the optical photograph of a typical sample Ni₄₀Fe₄₀P₂₀ (namely, NFP40), showing a metallic and flexible appearance. To topographically examine the sample, we have sliced the bulk NFP40 and characterized the cross-section by high-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) mapping, which can reveal the elemental distribution and crystallinity of sample. The characterization indicates the amorphous nature of NiFeP and the uniform distribution of Ni, Fe, and P.
P elements in the bulk. In particular, we have identified an oxide layer on surface with the thickness of 5–7 nm, which can then form NiFeOOH active species on surface in OER solution. The NiFeP sample is further characterized by X-ray diffraction (XRD, Figure S1, Supporting Information), suggesting the nature of amorphous solid.

To precisely resolve local structural information, we have employed synchrotron radiation-based X-ray absorption fine structure (XAFS) spectroscopy to characterize the sample (Figure S2, Supporting Information). Figure 1b,c shows the Ni and Fe K-edge extended XAFS (EXAFS) spectra of NFP40 processed through a Fourier-transform (FT), respectively, using standard Ni foil, Fe foil, NiO, Fe₂O₃, Ni₃P, and Fe₃P as the references. To look into bonding situation, we extract bond lengths and coordination numbers (CNs) from EXAFS curve fitting as listed in Table 1. According to the bond lengths, the NFP40 sample contains two types of Ni–Ni bonds corresponding to the states of metallic Ni and phosphide, respectively. This assignment is further supported by the identification of Ni–P bond for NFP40. The same situation has been observed for the Fe element in NFP40. Thus this amorphous NiFeP solid possesses the characteristics of both metallic Ni/Fe and phosphides. The metallic bonds would facilitate electron transport in long distance, while the phosphides can offer moderate bonding to the intermediates. Moreover, the CNs of Ni and Fe-based bonds in NFP40 are significantly lower than those for the corresponding metal foils and phosphides, suggesting that the Ni and Fe atoms in the NFP40 sample are coordinatively unsaturated. It is anticipated that these two merits would enable a giant enhancement on OER performance owing to the improvement on bulk conductivity and active sites.

Upon acquiring the structural information, we are now in a position to examine the OER activity of amorphous NiFeP samples with various Ni/Fe ratios (Ni₅₀Fe₃₀P₂₀, NFP₃₀; Ni₄₀Fe₄₀P₂₀, NFP₄₀; Ni₃₀Fe₅₀P₂₀, NFP₅₀; and Ni₂₀Fe₆₀P₂₀, NFP₆₀). The catalytic activity toward OER by amorphous NiFeP is measured by linear voltammetry scanning at a potential scan rate of 5 mV s⁻¹ in 1 x NaOH electrolyte. As shown in Figure 2a, the shapes of polarization curves are analogous to each other for various Ni/Fe ratios. At 10 mA cm⁻², the overpotentials of all NiFeP samples are comparable to that of RuO₂ (see the inset of Figure 2a). Among the samples, the NFP40 achieves the lowest overpotential of 319 mV, slightly lower than that of RuO₂ (325 eV). In order to compare the performance of our material with the Ni–Fe materials without phosphorus, the reported performance for similar Ni–Fe materials including NiFe-LDH (layered double hydroxide), NiFeOₓ, NiFe nanospheres, and NiFeOOH is listed in Table S1 (Supporting Information). It demonstrates the superior electrocatalytic OER performance of our bulk amorphous NiFeP to its counterparts.

To gain insights into reaction rates, the Tafel slopes have been analyzed in Figure 2b. The NiFeP samples with different Ni/Fe ratios exhibit the approximately equal Tafel slope of ≈42 mV dec⁻¹, remarkably lower than that of RuO₂ (61 mV dec⁻¹). Note that the Tafel slopes of RuO₂ depend on the type or synthetic process of RuO₂, which are typically in the range of 52–88 mV dec⁻¹.[36–39] It demonstrates that higher OER rates are enabled by amorphous NiFeP catalysts, leading to higher OER efficiency. The Ni/Fe ratios should be an important parameter to OER activity, since the presence of Fe can enhance the electrical conductivity by more than a factor of 30.[7] However, only a small performance variation is observed for the samples with different Ni/Fe ratios in our case, most likely because the metallic nature of our amorphous solid has enabled high bulk conductivity to facilitate the electron transport from catalyst surface to current collector.

It is worth noting that the incorporation of P content should be maintained at ≈20% to form amorphous solids; otherwise, crystalline phosphides (Fe,Ni)₃P or face-centered cubic (fcc) Fe will be produced in the samples (Figure S3, Supporting Information). It has been reported for binary and ternary alloys that the glass-forming process is usually the best achieved at or near the eutectic compositions. [30–34] This trend can be explained by the fact that the smallest temperature gap at the eutectic composition is required for undercooling the sample from the liquid temperature (Tₗ) down below the glass-transition temperature (Tₖ). Moreover, the reduced glass transition temperature (Tₖ, defined as Tₖ = Tₗ/Tₕ) would reach the maximum at the eutectic composition, because the Tₗ is the lowest at the eutectic composition while the Tₖ is usually less dependent on the compositions. According to the binary alloy phase diagrams, the eutectic points of Fe–P and Ni–P are 19 and 17 at%, respectively. In our case, when the P content in the alloy is too high (e.g., 25 at%), the composition of alloy deviates from the eutectic point. As a result, the liquid temperature of alloy would increase, reducing the glass-forming ability. For this reason, amorphous alloy can hardly be formed under the same rapid cooling conditions.

To assess the OER durability of amorphous NiFeP, the V–t relationship is recorded by applying constant current densities as shown in Figure 2c. It manifests that our NiFeP samples can survive the OER for at least 12 h. Our inductively coupled plasma-optical emission spectrometry (ICP-OES)
measurement has not found iron or nickel species in solution after the OER process, indicating that NiFeP is quite stable in alkaline solution. Impressively, only small overpotentials of 46–78 mV are additionally acquired when the OER current density is increased from 10 to 100 mA cm\(^{-2}\), in accordance with the Tafel slope of \(\approx 42\) mV dec\(^{-1}\) (Figure 2b). Figure S4 (Supporting Information) shows the cyclic voltammetry (CV) curves up to 5000 cycles in the overpotential region of 0.10–0.35 V. In this region, a M-OH/M-OOH redox transition between M(OH)\(_2\) at low potentials and MOOH at high potentials can be observed.\(^{[22]}\) Our measurement reveals that the integrated redox area increases by running the CV cycles, while the anodic and cathodic redox waves are anodically moved for \(\approx 42\) mV. This feature is indicative of improved catalytic performance resulting from a decrease in average oxidation states\(^{[35]}\) or a harmonization of electronic structures.\(^{[36,37]}\)

At 100 mA cm\(^{-2}\), we measure the Faradaic efficiency by real-time monitoring the amount of produced oxygen. As shown in Figure 2d, the collected O\(_2\) volume is well fitted with the theoretical calculation for 100% Faradaic efficiency, demonstrating the high efficiency. In sharp contrast, the crystalline NiFeP sample almost exhibits no electrocatalytic activity, as shown in Figure S5 (Supporting Information). At an overpotential of 0.7 V, the sample produces a low current density of 0.02 mA cm\(^{-2}\). The activity can be increased after the crystalline NiFeP is ground into powder and loaded on glass carbon electrode; however, an overpotential of 0.51 V is still required for a current density of 10 mA cm\(^{-2}\).

Strikingly, it turns out that our amorphous NiFeP catalysts also exhibit excellent OER durability in an acidic electrolyte. Nonprecious metals often suffer from the dissolution in acidic media in OER applications. However, Figure 2e shows that the NFP40 sample can be stable in 0.05 M H\(_2\)SO\(_4\) solution for more
than 30 h at 10 mA cm\(^{-2}\) with an OER overpotential of 540 mV. To the best of our knowledge, our sample is one of the most stable nonprecious OER catalysts in acidic media as comparable with IrO\(_2\) or RuO\(_2\).

Then the next question would be which factors enable the excellent OER performance of amorphous NiFeP solids. Given the presence of metallic bonds as indicated by XAFS characterization, we first examine the conductivity of samples in reference to the nanoparticles of Fe\(_2\)P, Ni\(_3\)P, or RuO\(_2\). Figure 2f shows the Nyquist plots obtained from the electrochemical impedance spectroscopy (EIS) measurements that are performed at the overpotentials of 440 and 490 mV. The NFP40 sample exhibits the significantly reduced charge-transfer resistance \(R_{\text{ct}}\) in comparison with Fe\(_2\)P, Ni\(_3\)P, or RuO\(_2\). To gain more information, we have fitted the EIS data with an equivalent circuit model as illustrated in the inset of Figure 2f. Our HRTEM characterization (Figure 1a) reveals the existence of a thin oxide film on the surface of bulk NiFeP. For this reason, it is assumed that the equivalent circuit should include an oxide film (resistance, \(R_{\text{oxide}}\)). The fitting results are listed in Table S2 (Supporting Information). Typically, the high overpotential may trigger the electrochemical transformation of RuO\(_2\) to an infe-
rior conductive RuO\(_{2-x}\). In sharp contrast, our NFP40 sample exhibits relatively constant resistance by altering the overpotentials. Moreover, Fe\(_2\)P and RuO\(_2\) show higher resistance (refer to the larger \(Z'\)), partly owing to the \(O_2\) bubbles that lag on the nanoparticle-composed electrode surface and clog the catalytic sites. These features demonstrate that the macroscopic conductivity of our amorphous NiFeP samples would facilitate the OER process.

In addition to the bulk conductivity, active sites should be the other factor determining the OER activity. The XAFS characterization has revealed the presence of coordinatively unsaturated metal sites which can boost the OER activity. Moreover, we find out that the P element in amorphous NiFeP samples also plays a key role in the OER process. Although the amorphous NiFeP samples well maintain their amorphous nature after the OER at 100 mA cm\(^{-2}\) up to 12 h (Figure S1, Supporting Information), we have observed some notable changes on the Ni, Fe, and P elements as indicated by X-ray photoelectron spectroscopy (XPS) (Figure 3a–d). The amorphous NiFeP adsorbs molecular oxygen and hydroxides on its surface, while the bulk is composed of elemental Fe and Ni, phosphides, and phosphates. This well agrees with our findings from XAFS characterization (Figure 1b,c). After the OER, a significantly increased amount of oxides or hydroxides, which are usually considered as the active sites for OER can be observed. Meanwhile, a large quantity of phosphates is formed at catalyst surface. Interestingly, it turns out that the P 2p binding energy for phosphates positively shifts from 132.5 to 133.1 eV. It has been reported that the phosphates can act as a proton transport mediator at catalyst surface. Accordingly, the Fe 2p binding energy for Fe\(^{3+}\) negatively shifts from 713.2 to 712.5 eV as the OER proceeds, while the Ni 2p binding energy for Ni\(^{2+}\) almost remains unchanged. Thus the Fe sites are most likely the hydroxyl acceptor that accelerates the OER through discharging and desorption, in accordance with the previous observation in FeNi catalysts.

Taken together, the high reaction activity of OER by the amorphous NiFeP should originate from a synergistic effect of Fe, Ni and P elements. The OER is generally associated with O–H bond breaking and attendant O–O bond formation, which undergoes a proton-coupled electron transfer at the high equivalency of 4.\(^{[42-46]}\)

\[
M + OH^- \rightarrow MOH + e^- \quad (1)
\]

\[
(M = \text{Ni and Fe})
\]

\[
MOH + OH^- \rightarrow MO + H_2O + e^- \quad (2)
\]

\[
MO + OH^- \rightarrow MOOH + e^- \quad (3)
\]

\[
MOOH + OH^- \rightarrow M + O_2 + H_2O + e^- \quad (4)
\]

In our case, the Tafel slope for amorphous NiFeP is about 40 mV dec\(^{-1}\), suggesting that Reaction (2) is the rate-determining step. The phosphorus has lone-pair electrons in 3p orbitals and vacant 3d orbitals for accommodating electrons on surface and increasing local charge density.\(^{[47]}\) For this reason, it is assumed that the formation of PO\(_4^{3-}\) may generate a more active state to expedite the kinetics of oxygen evolution.\(^{[24]}\) Meanwhile, the coupled Fe and Ni generate oxhydroxide as revealed by previous characterizations.\(^{[7,48]}\) The MOOH is an efficient species for Reaction (3),\(^{[22,35]}\) which can further react with hydroxyl to produce oxygen (Reaction (4)). Specifically, we assume that the Fe is predominate active sites, according to XPS binding energy shifts (i.e., a negative shift of 1.9 eV for Fe in Figure 3b versus a small negative shift of 0.5 eV for Ni in Figure 3a).

The schematic illustrating the entire process is outlined in Figure 3e. During this process, the thin layer of NiFeOOH, which is formed at the surface of amorphous NiFeP—a conductive material, should be the active material for OER.\(^{[22,35]}\) Meanwhile, the phosphates formed on NiFeP surface can facilitate the oxygen evolution.\(^{[24]}\) As a matter of fact, the electrocatalytic performance of our amorphous NiFeP, with a Tafel slope of 40 mV dec\(^{-1}\) and the overpotential of 280 mV at 10 mA cm\(^{-2}\), is comparable to that of the Au-supported NiFeOOH,\(^{[35]}\) which evidences NiFeOOH as an electrocatalytically active species. In our work, the replacement of precious Au by metallic NiFeP can significantly reduce material costs.

Our measurement indicates that the electrochemically active surface areas (ECSAs) of NFP40 is 40.82 \(\mu F\ cm^{-2}\) as determined from the non-Faradaic electrochemical double-layer capacitance. The OER catalytic performance can be further elevated by increasing the number of surface active sites. By etching the ternary in HNO\(_3\) for 5 min, the surface turns black as the etched cracks (see scanning electron microscopy (SEM) image in Figure S6 in the Supporting Information) can hardly reflect light. To examine the change in surface structures, we have sliced the bulk NFP40 after HNO\(_3\) etching and characterized the cross-section by HRTEM and elemental mapping. As shown in Figure S7 (Supporting Information), some micro-sized pores are formed on surface most likely due to the selective dissolution of Ni and/or Fe species. XPS characterization (Figure 4a) reveals that more phosphates are formed on surface, which would facilitate the OER process. The ECSA estimated from the electrochemical capacitance (\(C_{\text{dl}} = 133.78 \mu F\ cm^{-2}\))
is enlarged 3.3 times after the etching (see Figure 4b). As a result, the OER activity has been substantially improved, in which the overpotentials at the geometric and intrinsic current densities of 10 mA cm\(^{-2}\) are about 219 and 280 mV, respectively, in 1 m NaOH (Figure 4c). As indicated in Figure 4d, the etched NFP40 sample can sustain the OER for 12 h at a current density of 10 mA cm\(^{-2}\). The sample exhibits only a small raise of 31–38 mV in overpotential as the OER current density is increased from 10 to 100 mA cm\(^{-2}\), and achieves a steady current density of 100 mA cm\(^{-2}\) (see Figure 4d).

In addition to the performance in alkaline medium, it is well recognized that the OER catalyst stability in acidic solution is a bottleneck for proton exchange membrane (PEM) water electrolysis. In our assessment, we specifically choose 0.05 m H\(_2\)SO\(_4\) as the electrolyte, because the acidic solution with pH of 1 is an acceptable electrolyzer for PEM water electrolysis.[49–51] The balance between activity and stability is always a key issue to the electrocatalysts in acidic electrolytes.[2,49,52,53] In general, the stability of OER catalysts in acidic electrolytes is enabled by the slow dissolution rate.[2] To investigate the ion leaching, we have monitored the release of nickel and iron species from NFP40 in 0.05 m H\(_2\)SO\(_4\) solution. As shown in Figure S8 (Supporting Information), the concentrations of nickel and iron cations reach 1.35 and 1.17 ppm, respectively, after the electrochemical water splitting in a 100 mL acidic solution at 10 mA cm\(^{-2}\) for 100 min. This feature has been also resolved by running CV in acidic solution. As shown in Figure S4 (Supporting Information), the first scan exhibits a substantially higher current which might be caused by the dissolution of surface oxide at NiFeP. The CV curves from 2 to 5000 cycles are overlapped.

**Figure 3.** High-resolution a) Ni 2p, b) Fe 2p, c) P 2p, and d) O 1s XPS spectra for the surface region, bulk region, and active region of NFP40. The active region denotes the surface species formed during three scans e) Schematic illustrating the working mechanism of amorphous bulk NiFeP for OER.
with the redox peaks at an overpotential around 220 mV. The position of redox peak is very close to that in the alkaline solution, suggesting that they follow a similar catalytic mechanism.

To look into the sample evolution in acidic electrolytes, we have collected XPS data for the NFP40 after OER in acidic condition for 6 h. As shown in Figure S9 (Supporting Information), Ni is more dissolved from surface, in accordance with the ICP-OES results. The dissolution of Ni would leave a thin layer of iron hydroxides or iron phosphates on surface. As evidenced by cyclic voltammetry (Figure S4, Supporting Information), this process is accompanied with the redox reactions from Ni/Fe(II) to Ni/Fe(III). The redox products are prone to be dissolved in acidic solution and to deteriorate NiFeP material. We have also employed ex situ XAFS to tightly monitor the changes in Ni, Fe, and P along with the OER process in acidic medium. As indicated in Figures S10–S12 (Supporting Information), the oxidation states of Ni and Fe have not been changed along with the OER process, but the bond lengths for Ni and Fe have been slightly increased. This feature should be associated with the partial dissolution of Ni and Fe species. Meanwhile, the P K-edge spectra suggest that the sample after the OER for 5 min possesses an increased amount of phosphates, which further supports our finding from XPS. It is worth pointing out that the stability of our NiFeP samples depends on their surface structures. As indicated in Figure S13 (Supporting Information), the durability of the NFP40 etched by HNO₃ lasts about 25 h in 0.05 M H₂SO₄ electrolyte. It is assumed that the HNO₃ treatment forms an oxidation film on the surface of bulk NiFeP, which is prone to be dissolved in acidic solution.

In summary, we have developed a new class of high-performance OER electrocatalysts based on bulk amorphous NiFeP materials. The bulk amorphous NiFeP materials can directly serve as the electrodes for OER device applications, which perfectly combine high macroscopic conductivity with highly active sites. The high macroscopic conductivity from metallic bonds enables fast charge transfer from catalyst surface to current collector. Meanwhile, the synergistic effect of coordinatively unsaturated Ni, Fe, and P constitutes the highly active sites. The formed phosphate can generate active sites to significantly promote the OER reaction kinetics, while the Fe may further improve intrinsic activity. After a surface treatment, the active surface area has been significantly increased to boost the OER activity. The bulk amorphous NiFeP materials exhibit excellent OER activity and durability in both alkaline and acidic media. Strikingly, a low overpotential of 219 mV has been achieved at the geometric current density 10 mA cm⁻² in an alkaline electrolyte, with the Tafel slope of 32 mV dec⁻¹ and intrinsic overpotential of 280 mV. This work opens up new possibilities for designing low-cost, high-performance OER electrocatalysts toward device applications with a simple fabrication method. We envision that it would provide fresh insights into rationally fabricating OER electrocatalysts from the viewpoint of electrode design.

Experimental Section

Sample Preparation and Characterization: The samples of amorphous metallic NiFeP with varied compositions were obtained by melting spinning and rapidly quenching NiFeP ingots in an argon atmosphere.
The NiFeP ingots were first prepared by mixing and melting Fe₂P and Ni₃P lumps (purity of 99%, Kojundo Chemical Laboratory Co., Ltd.), pure Ni and pure Fe with different ratios in an argon atmosphere. The obtained samples were examined using SEM, HRTEM, EDS, XRD, and XPS. SEM images and EDS mapping profiles were collected on a JEOL JEM-ARM200F Cold-Fe high-resolution transmission microscope operated at 20 kV. HRTEM images and EDS mapping profiles were collected on a JEM-2100F. XPS spectra were collected on an ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-Kα X-ray as the excitation source.

XAFS Characterization: Ni and Fe K-edge XAFS measurements were performed at the beamline 1W1B in Shanghai Synchrotron Radiation Facility 1W1B in Beijing Synchrotron Radiation Facility, China. The X-ray was monochromatized by a double-crystal Si(311) monochromator. The acquired XAFS data were processed according to the standard procedures using the WinXAS3.1 program.[14] Theoretical amplitudes and phase-shift functions were calculated with the FEFF8.2 code using the crystal structural parameters of Ni foil, Fe foil, NiO, Fe₃O₄, Ni₃P, and Fe₃P.[15]

Electrochemical Measurement: The OER performance was recorded in a three-electrode system in an alkaline electrolyte of 1 M NaOH or an acidic electrolyte of 0.05 M H₂SO₄ on an electrochemical workstation (bio-Logic, VMP3). A Pt mesh and a Ag/AgCl electrode served as the counter and reference electrodes, respectively. The reference electrode was calibrated to reversible hydrogen potential according to the Nernst equation. Prior to the measurements, the oxygen dissolved in solution was removed by purging with argon for at least 30 min. The bulk NiFeP solid was directly used as a working electrode, which was ultrasonically washed in deionized water (Milli-Q) and ethanol three times for 5 min, respectively, to remove all residuals before the use. The RuO₂ with a purity of 99.9% was purchased from Sigma-Aldrich. The protocol in literature was followed to examine its electrocatalytic activity.[16] Typically, 4 mg of catalyst powder, 1 mL of solvent (water and ethanol, 4:1, v/v) and 80 μL of Nafion solution (5 wt% in water) were mixed. The suspension was immersed in an ultrasonic bath for 30 min to prepare a homogeneous ink. The working electrode was prepared by depositing 5 μL of catalyst ink onto a glass carbon electrode. Linear scan voltammetry was conducted at a scan rate of 5 mV s⁻¹ and corrected for iR losses. The amount of produced oxygen was measured in real-time by a NeoFox Sport Oxygen Sensor (Ocean Optics). EIS was carried out in the frequency range of 100 kHz to 100 mHz with an AC voltage amplitude of 10 mV at potentials of 0–750 mV versus Ag/AgCl. CV curves were recorded with a sweep rate of 50 mV s⁻¹ to collect the capacitance charging and discharging currents. The currents at the OCP were plotted against the scan rates, whose slopes were the double-layer capacitances of the samples. The corrosion products in the alkaline and acidic electrolytes were detected by ICP-OES (Agilent Technologies, 700 Series).

Ex Situ XAFS Characterization: The ex situ Ni, Fe, and P K-edge XAFS measurements were performed at the Advanced Photon Source on the bending-magnet beamline 20-BM-B with electron energy of 7 GeV and average current of 100 mA. The radiation was monochromatized by an Si(111) double-crystal monochromator. Harmonic rejection was accomplished with Harmonic rejection mirror and also 15% detune. All the spectra of samples were collected in fluorescence mode by PIPS detector. All the spectra of standards were collected in transmission mode. Data reduction and analysis were processed by Athena software.

Supporting Information
Supporting information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was financially supported by the 973 Program (2014CB848900), the NSFC (No. 21471411, U1532135, U1532112, 21303251, 21573212, 11375198, 11574280, and 11602011), the Shenzhen Science and Technology Foundation (JCY2014191204621), the Recruitment Program of Global Experts, and the CAS Hundred Talent Program. XAFS measurements were performed at the beamline BL14W1 in the Shanghai Synchrotron Radiation Facility (SSRF) and the Beijing Synchrotron Radiation Facility (BSRF), China. Use of the Advanced Photon Source (9 BM and 20 BM), an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by the Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
amorphous, conductivity, electrocatalysis, oxygen evolution reaction, phosphate

Received: December 5, 2016
Revised: May 1, 2017
Published online:
