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Amorphous Fe-Ni-P-B-O nanocages as efficient electrocatalysts for oxygen evolution reaction

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ABSTRACT

Electrocatalysts are one of the most important parts for oxygen evolution reaction (OER) to overcome the sluggish kinetics. Herein, amorphous Fe-Ni-P-B-O (FNPBO) nanocages as efficient OER catalysts are synthesized by a simple low-cost and scalable method at room temperature. The samples are chemically stable, in clear contrast to reported unstable or even pyrophoric boride samples. The Fe/Ni ratio of the FNPBO nanocages can be continuously adjusted to optimize the OER catalytic performance. The FNPBO nanocages composed of multi-component elements can weaken the metal-metal bonds thus rearranging the electron density around the catalytic metal atom centers and reducing the energy barrier for intermediate formation. Hence the optimized FNPBO ($\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$) catalyst shows superior intrinsic electrocatalytic activity for OER. The low overpotential to afford the current density of 10 mA cm^{-2} (236 mV), the small Tafel slope (39 mV dec^{-1}), and the high specific current density (26.44 mA cm^{-2}) at a given overpotential of 300 mV make a sharp contrast to state-of-the-art RuO_2 (327 mV, 136 mV dec^{-1} , and 0.028 mA cm^{-2} , respectively).

Clean energy is highly desired for clean and sustainable future.¹⁻³ Hydrogen has been considered as an ideal alternative fuel to replace gasoline, which is environmental friendly with a

high energy density.⁴⁻⁷ Water electrolysis is one of the most practical and effective way to generate hydrogen.⁸⁻¹¹ However, as a four electron-proton coupled reaction, the OER hinders full water electrolysis due to the sluggish kinetics.¹²⁻¹⁴ IrO₂ and RuO₂ have been investigated and proved to be state-of-the-art catalysts for OER.¹⁵⁻¹⁷ However, the high cost and earth scarcity are inevitable obstacles for large-scale applications. Regarding this issue, a new pavement has been attempted for OER by using materials without precious elements including sulfides, selenides, phosphides, carbides, metal oxides, layered double hydroxides, and nitrides etc.¹⁸⁻²⁸ Metal-boron species have been investigated for several decades and recently some metal borides as OER catalysts in alkaline media have been explored.²⁹⁻³¹ The electron transfer from boron to metal could weaken the metal-metal bonds thus diminishing the energy barriers for intermediate formation during the OER catalysis.^{32,33} However, the borides usually suffer from highly unstable or even pyrophoric issues under ambient conditions.^{33,33} Compared to borides, borates may be beneficial for OER.²⁹ The stability is much better not only under ambient conditions but also during the OER catalytic reaction. Meanwhile, the incorporated oxygen atoms may lead to better wettability and higher O affinity strengthening the O* adsorption.^{34,35} Furthermore, the catalytic activity still has great potential to be pushed forward. Recently, phosphorus materials have been demonstrated to be effective adsorption centers for oxygen-containing intermediates decreasing the energy barrier of the OER path.³⁶⁻³⁸ Reasonably, incorporating metal-boron-oxygen species with phosphorus is expected to be a promising way to further boost the OER catalytic activity, in which the metal-metal bonds could be weakened to decrease the energy barriers of intermediate formation and both metal and phosphorus could act as more active centers. In addition, amorphous nanomaterials turn out to be attractive with more active sites for reaction due to abundant defects, which results in improved OER performance.³⁹⁻⁴¹ Considering

the aforementioned factors, to develop amorphous metal-phosphorus-boron-oxygen (M-P-B-O) nanomaterial as OER electrocatalyst can be a promising approach while remaining unexplored.

Herein, we prepared amorphous Ni-P-B-O (NPBO) and Fe-Ni-P-B-O (FNPBO) nanocages by a simple low-cost self-catalytic process at room temperature, which could be easily scale-up. These samples present as nanocages with diameters around 80 nm and shell thicknesses of ~12 nm. The hollow structures may be attributed to the released hydrogen bubbles during the reaction forming gas-liquid interface as templates for the resultant particles. By controlling the reagent source ratio, the P/B ratio and Fe/Ni ratio of the samples could be continuously adjusted. As OER electrocatalyst, the overpotential (η) of the optimized FNPBO ($\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$) nanocages to acquire the current density of 10 mA cm^{-2} (j_{10}) is 236 mV only and the Tafel slope is dramatically reduced to 39 mV dec^{-1} only, as compared to Ni-B-O ($\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, 335 mV at j_{10} , 91 mV dec^{-1}). The outstanding OER catalytic performance outperforms state-of-the-art RuO_2 catalyst with an overpotential of 327 mV at j_{10} . Moreover, the specific current density (j_s) at a given overpotential of 300 mV (26.44 mA cm^{-2}) greatly increases up to 53 folds compared with the Ni-B-O catalyst (0.49 mA cm^{-2}), and is much higher than that of state-of-the-art RuO_2 (0.028 mA cm^{-2}), indicating superior intrinsic electrocatalytic activity. This low-cost nanomaterial by a scalable preparation method set an important step towards effective and practical application for electrocatalytic H_2 generation.

RESULTS AND DISCUSSION

The NPBO nanocages have been synthesized via a precipitation process of metal cations with sodium borohydride (NaBH_4) and sodium hypophosphite (NaH_2PO_2) under oxygen bubbling, as illustrated in **Figure 1**. NaBH_4 can easily reduce metal cations generating metal borides at

ambient conditions while pure NaH_2PO_2 cannot. However, in the presence of NaBH_4 and oxygen, the released heat during the reaction and the generated metal boride/borate are believed to catalyze the redox reaction between NaH_2PO_2 and metal cations. The hollow structures may be ascribed to the released hydrogen bubbles during the reaction, which will form gas-liquid interface and act as templates for the resultant particles. Meanwhile, the bubbled oxygen can involve in the reaction stabilizing the final products. This produced M-P-B-O is highly stable under ambient conditions in contrast to the pyrophoric boride samples. When the molar ratio of P/B of the reagent sources is 1:1, the sample is amorphous as confirmed by powder X-ray diffraction (XRD) pattern (**Figure S1a**). The inductively coupled plasma optical emission spectrometry (ICP-OES) results (**Table S1**) and the X-ray photoelectron spectroscopy (XPS) results (**Figure S2**) reveal the composition of the sample to be $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$. The transmission electron microscopy (TEM) micrograph (**Figure S1b**) demonstrates that the $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ product presents as nanocages with diameters of around 100 nm and wall thickness of about 20 nm. Moreover, the P/B ratios of the NPBO nanocages have been controlled easily by adjusting the reagent ratio of NaH_2PO_2 to NaBH_4 . With the P/B ratios of the reagents varied from 1:4 to 4:1, the nanocage structures can be maintained well (**Figure S1c-f**), and the actual P/B ratio increases continuously from 0.1167 to 0.8881 as indicated by the ICP-OES data (**Table S1**). The XRD patterns (**Figure S1a**) show that the NPBO nanocages with different P/B ratios are still amorphous. As a control, NBO ($\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$) without phosphorus are prepared, which are amorphous nanosheets as revealed by scanning electron microscopy (SEM), XRD and XPS (**Figure S3a-d**).

Moreover, we find that Fe element can be introduced into the NPBO to form FNPBO nanocages while we fix the P/B ratio of the reagents to be 1:1, which shows a reasonably low

overpotential and small Tafel slope as OER catalyst. Furthermore, the ICP-OES results (**Table S2**) show that the molar ratio of Fe to Ni could be continuously tuned from 0.0096 to 7.16 by varying the Fe/Ni ratio of the reagent sources from 1:10 to 10:1. Taking the sample with actual Fe/Ni ratio of 6.4:16.1 as an example, the XPS survey spectrum in **Figure 2a** shows the Fe, Ni, P, B, O and adventitious C element peaks, confirming the elemental composition, which matches the ICP-OES results (**Table S2**). The high-resolution XPS spectra of the Fe 2p, Ni 2p, P 2p and B 1s have been deconvoluted and shown in **Figure 2b-e**. The peak at 706.5 eV for the Fe 2p_{3/2} spectrum in **Figure 2b** indicates the presence of some residual metallic Fe which are not thoroughly oxidized. While the peak at 712.4 is indexed to higher-oxidation state species along with a satellite peak.³¹ Similar to the Fe 2p spectrum, the Ni 2p spectrum shows a peak at 852.7 eV for Ni 2p_{3/2}, corresponding to the residual metallic nickel, and the peak at 855.7 eV for Ni 2p_{3/2} is indexed to higher-oxidation state species with several satellites (**Figure 2c**).^{32,42,43} The P 2p spectrum in **Figure 2d** presents two peaks at 133.1 eV and 128.7 eV. The peak at 133.1 eV is attributed to the oxidized phosphorus and the peak at 128.7 eV is from phosphorus shifted to lower energy. The lower P 2p binding energy may be attributed to the bonding to iron/nickel metals which are not fully oxidized.⁴⁴ The B 1s spectrum in **Figure 2e** can be deconvoluted into two peaks, corresponding to the interaction of boron with residual iron/nickel at 187.3 eV and boron-oxo species at 190.8 eV, respectively.^{32,44,45} The formula is determined to be Fe_{6.4}Ni_{16.1}P_{12.9}B_{4.3}O_{60.2} by the XPS and ICP-OES results (**Table S2**). All in all, the XPS results not only confirm the co-existence of Fe, Ni, P, B and O, but also verify the bonding between metals and P/B, metals and O, P/B and O, which may rearrange the electron distribution of the elements.

X-ray absorption spectroscopy (XAS) has been carried out to further investigate the chemical state. The X-ray absorption near-edge spectra (XANES) of the typical $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ and $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ samples are shown in **Figure 2f**, with $\text{Ni}(\text{OH})_2$ and Ni foil as references. The peaks of the samples located at approximately 8334 eV in the pre-edge region are assigned to the dipole-forbidden but quadrupole-allowed transition from 1s to 3d, which are in agreement with the $\text{Ni}(\text{OH})_2$ reference.^{46,47} The rising-edge positions of the $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ and $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ samples are between the $\text{Ni}(\text{OH})_2$ and the Ni foil references indicating that the Ni oxidation states are between Ni(0) and Ni(II).^{48,49} The rising-edge position of the $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ shifts positively compared to the $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, while that of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ shows larger shift. This indicates the oxidation states are higher after the introduction of P and Fe, respectively. It might result from the interaction of Ni with other elements causing the rearrangement of the electron distribution. This is in consistence with the XPS results (**Figure 2c** and **Figure S2b** and **Figure S3c**).

The samples are still amorphous after the introduction of Fe as shown in **Figure 3a** by the XRD pattern. The SEM micrograph in **Figure 3b** shows the spherical shape of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ sample. Some cracked nanocages in the inset of **Figure 3b** demonstrate the hollow feature. The TEM micrographs (**Figure 3c** and **d**) clearly verify the specific nanocages with diameters of around 80 nm and shell thickness of about 12 nm. No distinguishable heterolayer is observed, indicating uniform sample structures. The selected area electron diffraction (SAED) pattern (inset of **Figure 3c**) shows weak diffuse rings, indicating the amorphous nature of the sample. This is in consistence with the XRD results (**Figure 3a**). The high-resolution TEM image (**Figure S4**) also confirm the amorphous feature. The scanning TEM (STEM) energy dispersive X-ray spectroscopy (EDS) elemental mapping images (**Figure S5** and

Figure 3e-j) and the EDS spectrum (**Figure S6**) prove the uniform distribution of Fe, Ni, P, B and O in the sample. The SEM and TEM micrographs of the FNPBO samples with other Fe/Ni ratios (**Figure S7** and **Figure 4**) show that there is a morphology evolution from nanocages to nanosheets when the Fe/Ni ratio increases. When the ratio is above 1.81, the hollow structure disappears (**Figure 4d-f**). With high content of Fe, the samples tend to form γ -maghemite nanosheets (**Figure S8a and b**).

The OER performance of the NPBO nanocages have been evaluated in oxygen-saturated 1 M KOH aqueous solution at room temperature. After optimization of the mass loading (**Figure S9a and b**), as shown by the linear sweep voltammetry (LSV) (**Figure 5a**), the overpotentials to afford j_{10} for the NPBO nanocages are effectively reduced as compared to that of NBO. Among the NPBO catalysts with different P/B ratios, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ shows the lowest overpotential of only 300 mV to acquire j_{10} , which is better than that of RuO_2 catalyst with an overpotential of 327 mV. Furthermore, the Tafel slope related to the OER kinetics is greatly improved to 67.4 mV dec^{-1} for $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ as compared to 91 mV dec^{-1} for NBO and 136 mV dec^{-1} for RuO_2 (**Figure 5b**).

The electrochemical behaviors of the FNPBO products also have been investigated in an oxygen-saturated 1 M KOH aqueous solution at room temperature. The mass loadings of three typical $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ and $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalysts on the glassy carbon electrodes are firstly optimized to obtain the best OER performance (**Figure S9a-b and Figure S10**). As shown in **Figure 6a**, with the mass loadings of the catalysts increase, the overpotentials to achieve j_{10} are greatly decreased first and reach nearly stable values when the mass loading is approximately $0.2264 \text{ mg cm}^{-2}$. This optimized mass loading is used afterwards. Prior to the OER activity measurements, the prepared catalyst electrodes have been activated by

continuous cyclic voltammetry (CV) scans (Methods section for details). The activation CV curves of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst (**Figure S11**) apparently show a couple of reversible redox peaks at about 1.5 V and 1.3 V corresponding to the oxidation and reduction processes of nickel species between Ni^{2+} and Ni^{3+} , respectively.^{50,51} The OER performance have been subsequently evaluated by LSV at different scan rates (**Figure S12**). The curves are almost the same at different scan rates except stronger oxidation peaks of Ni^{2+} to Ni^{3+} are observed at higher scan rates, which conceal the actual overpotential at low current densities. For easy comparison with other works, i.e. η to afford j_{10} in most reports,⁵²⁻⁵⁵ the scan rate of LSV hereafter is fixed to 1 mV s^{-1} in order to eliminate the interference of the oxidation peak. The iR -corrected (Nyquist plots in **Figure S13**) polarization curves in **Figure 6b** present the OER behaviors of the FNPBO with different Fe/Ni ratios. With the increase of the Fe content, the overpotential to acquire j_{10} starts to decrease and reaches a minimum value at the Fe/Ni ratio = 0.3984. When the Fe content is further increased, the overpotential increases (**Figure 6b, Figure S14 and Table 1**). The overpotential required to afford j_{10} for the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocage catalyst is 236 mV only, which is the smallest among the FNPBO catalysts with different Fe/Ni ratios. The corresponding Tafel curves presented in **Figure 6c** have been employed to investigate the OER kinetics of the FNPBO catalysts. The $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst exhibits the smallest Tafel slope of 39 mV dec^{-1} as compared to 67.4 mV dec^{-1} for $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ (**Figure 5b**), which indicates that appropriate introduction of Fe into NPBO improves the OER kinetics greatly. The electrochemical impedance spectroscopy (EIS) results (**Figure S13**) show that the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst presents the smallest semicircle related to charge-transfer resistance, which is also a proof of the best electrocatalytic kinetics. The OER overpotentials and Tafel slopes of all the catalysts have been summarized (**Table 1**).

For intuitive comparison, the plot of Tafel slope versus potential has been presented in **Figure 6d**. Obviously, the OER performance is improved when P is introduced into the NBO catalyst, and introduction of appropriate ratio of Fe can further enhance the OER performance. Moreover, the P/B ratio is further tuned with the Fe/Ni ratio of the reagents fixed at 1:2, while the optimized $\text{Fe}_{6.9}\text{Ni}_{17.4}\text{P}_{9.3}\text{B}_{8.0}\text{O}_{58.4}$ nanocages only show negligible improvement of the OER performance (**Figure S15** and **Figure S16**).

The electrochemically active surface area (ECSA) and electrocatalytic activity have been estimated via the benchmarking proposed by other report.⁵⁶ The electrochemical double-layer capacitances have been measured by evaluating the non-Faradaic capacitive current from the CV curves of the $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$, $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ and commercial RuO_2 catalysts at various scan rates (**Figure S17** and **Figure S18a**). By taking the charging current density, i_c , from the CV curves, a plot of i_c as a function of scan rate (v) leads to a fitted straight line (**Figure 7a** and **Figure S18b**). The specific double-layer capacitances (C_{dl}) of the FNPBO, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ and $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$ catalysts are equal to the slopes of the fitted straight lines. The C_{dl} values are between 0.224 and 0.52 mF cm^{-2} without obvious trend. Consequently, the resulting ECSAs don't show obvious trend either (**Table S3**). The C_{dl} and ECSA of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ are the smallest among the compared catalysts, while the OER catalytic performance is the best. Considering this, it is inferred that the intrinsic catalytic activity of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ is the best. In order to verify this, the electrocatalytic activities have been evaluated by the specific current density (j_s) at a given overpotential (Methods section for details). The current density per geometric area, j_g , at a given overpotential of 300 mV (1.53 V vs. RHE, which is the potential to afford j_{10} for the $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ catalyst.) is used for calculation. From the results (**Figure 7b** and **Table S3**), the j_s of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$

catalyst is 26.44 mA cm^{-2} , which is about 27 times higher than that of $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ (0.96 mA cm^{-2}) and even 53 folds compared with the $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$ catalyst (0.49 mA cm^{-2}). It is also much higher than that of state-of-the-art RuO_2 (0.028 mA cm^{-2}). The highest j_s among the investigated catalysts verifies the highest electrocatalytic activity, indicating the introduction of Fe can effectively boost the OER activity besides the improvement promoted by P. The $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocage catalyst is among the top reported OER catalysts, and it is much better than state-of-the-art RuO_2 .^{30-33,57-61}

According to the mostly accepted mechanism proposed, OER includes several steps involving formation of oxide (MO), hydroxide (MOH) and oxyhydroxide (MOOH) intermediates in alkaline media.¹² Previous reports about Co_2B and Ni_xB ascribe the good OER activity to the diminished energy barrier for the OOH intermediate formation since the interaction between metal and boron can weaken the M-M bonds.^{32,33} Here for amorphous NPBO nanocages, the additional existence of phosphorus and oxygen besides boron also form interaction with the metal atoms as confirmed by the XPS and XANES results in **Figure 2**. Consequently, this may further weaken the metal bonds rearranging the electron density around the catalytic metal atom center and reducing the energy barrier for intermediate formation, which results in better kinetics compared to NBO. In addition, the introduced phosphorus may act as effective adsorption center for oxygen-containing intermediates decreasing the energy barrier of the OER path and catalyzing the OER.³⁷ Besides, the amorphous hollow structure can provide abundant defects accompanied by large interfacial contact with electrolyte, which is an advantage for ion transport and intermediate transition.^{40,62,63} Furthermore, it is investigated that appropriate amount of co-existed Fe can stabilize Ni atoms in the oxidation state Ni^{2+} under the OER catalytic conditions leading to faster oxygen evolution kinetics at the expense of the oxidation of Ni^{2+} .^{64,65}

Consequently, the amorphous $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocages perform superior OER catalytic activities.

The stability of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst has been carried out by long-term electrolysis at a given overpotential of 236 mV as shown in **Figure 7c**. The current density is stable over 50 h without obvious drop, indicating excellent stability. Moreover, even continuously to deliver a high current density of about 100 mA cm^{-2} for 40 h, it still shows excellent stability, as shown in **Figure 7d**. In addition, the galvanostatic long-term durability is also conducted at the constant j_{10} . The potential to maintain j_{10} is almost unchanged over 30 h continuous electrolysis (**Figure S19**). The excellent OER catalytic performance makes the amorphous $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocage a potential candidate as catalyst for OER.

The $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst is characterized after the OER stability evaluation at an overpotential of 236 mV. Some hollow structures can still be maintained as shown by the SEM and TEM images (**Figure S20a** and **b**), although the long-term test causes some change of the hollow structures. The amorphous feature of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst is unchanged, as indicated by the SAED pattern and XRD pattern (**Figure S20c** and **d**). The co-existence of the Fe, Ni, P, B and O is confirmed by the elemental mapping analysis (**Figure S21a-f**). After the OER stability evaluation, the low valence state Ni, P and B species are oxidized to higher oxidation state, as indicated by the high resolution XPS spectra of the Ni 2p, P 2p and B 1s (**Figure 8a-c**), while the low state Fe species are almost unchanged (**Figure 8d**). The introduction of Fe should be beneficial to the stabilization of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst during the OER process. XAS is also performed to investigate the chemical state of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst after the OER. The rising-edge of the Ni K-edge XANES (**Figure 8e**) shows slight positive shift as compared to the pristine catalyst, indicating the

oxidation of Ni, which is in consistence with the XPS result (**Figure 8a**). From the Fourier transformations of the extended X-Ray absorption fine structure (FT-EXAFS) (**Figure 8f**), all the corresponding peaks show enhanced intensities after the OER stability evaluation, which indicates the increased coordination number. It may be ascribed to the partial transformation of the catalyst to metal oxides or (oxy)hydroxides during the OER. This corresponds to the mostly accepted proposed mechanism for OER.¹² The $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalyst after the OER stability evaluation at a much higher current density of about 100 mA cm^{-2} show similar results by XRD, TEM and XPS as shown in **Figure S22-24**.

CONCLUSION

In summary, amorphous Ni-P-B-O nanocages with adjustable P/B ratio and Fe-Ni-P-B-O nanocages with adjustable Fe/Ni ratio have been synthesized by a simple low-cost method. The introduction of P and Fe can effectively improve the OER catalytic performance. When optimized P is introduced into Ni-B-O catalyst, the overpotential to afford j_{10} is reduced to 300 mV from 335 mV and the corresponding Tafel slope is decreased to 67.4 mV dec^{-1} from 91 mV dec^{-1} . Furthermore, when appropriate amount of both P and Fe are introduced into Ni-B-O catalyst, the overpotential to achieve j_{10} can be as low as 236 mV and the Tafel slope can be greatly reduced to 39 mV dec^{-1} only. The j_s at a given overpotential related to the intrinsic electrocatalytic activity is also apparently improved as compared to state-of-the-art RuO_2 . The excellent intrinsic OER catalytic activity is ascribed to several advantages. Firstly, the introduced P and O may weaken the metal-metal bonds rearranging the electron density around the catalytic metal atom center and reducing the energy barrier for intermediate formation. Secondly, the introduced phosphorus may act as effective adsorption center for oxygen-containing

intermediates decreasing the energy barrier of the OER path. Thirdly, the doped Fe can stabilize the electrocatalytic active Ni centers. Lastly, the unique amorphous hollow structure with abundant defects benefit to provide many active sites. Considering the simple scalable approach and the outstanding OER performance, it can be a promising candidate as an OER catalyst for widespread application.

METHODS

Chemicals: Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 97\%$), sodium borohydride (NaBH_4 , $\geq 98\%$), ruthenium (IV) oxide (RuO_2 , 99.9%), and Nafion[®] 117 (~5 wt% in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich. The conductive Super P[®] Carbon black ($>99\%$) and iron (II) acetate ($\text{Fe}(\text{CH}_3\text{COO})_2$, anhydrous, 95%) were bought from Alfa Aesar. Sodium hypophosphite (NaH_2PO_2 , 99.0%) and potassium hydroxide (KOH , 95%) were bought from Aladdin. The chemicals purchased were directly used for experiments.

Synthesis of amorphous Ni-P-B-O (NPBO) nanocages: De-ionized (DI) water (18.2 M Ω) was used as solvent for the synthesis. Taking $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ (molar ratio of the NaH_2PO_2 to NaBH_4 reagents is 1:1) as an example here, a nickel ion solution was made by dissolving 1.74 g of nickel (II) nitrate nonahydrate in DI water (20 mL) in a three-neck round-bottomed flask with continuous oxygen flushing at room temperature (RT). The oxygen was flushed throughout the whole synthesis process. 2.11 g of sodium hypophosphite was then added to the above solution with stirring. After 5 min, fresh-made 20 mL of sodium borohydride aqueous solution (1.2 M) was added into the above solution with vigorous stirring. Precipitate was formed instantaneously, indicating the reduction of nickel cations coupled with oxidation by oxygen. After 1 h, the precipitate was collected by centrifuge and washed with DI water and ethanol, followed by

vacuum drying at 60 °C overnight. The molar ratio of P to B was adjusted by varying the sodium hypophosphite and sodium borohydride amount while keeping the total concentration as a constant.

Synthesis of amorphous Fe-Ni-P-B-O (FNPBO) nanocages: Similar to the synthesis of amorphous Ni-P-B-O nanocages except that iron (II) acetate and nickel (II) nitrate nonahydrate were used simultaneously as metal ion sources. The molar ratio of iron to nickel was adjusted by varying the concentration of metal salt sources while keeping the total concentration of metal cations as a constant. The P/B ratio can also be optimized by fixating the Fe/Ni ratio of the reagents.

Material characterization: The X-ray diffraction (XRD) patterns were recorded by a Bruker D8 Advance X-ray diffractometer equipped with a Cu-K α radiation source ($\lambda=1.5406$ Å) operated at 40 kV and 40 mA in a 2- θ range between 10° and 80°. The morphology of the samples was acquired by a field emission scanning electron microscope (JEOL JSM 7600F) at an accelerating voltage of 5 kV. The TEM images and SAED patterns were acquired by transmission electron microscopes (TEM, JEOL JEM 2010UHR and JEOL JEM 2100F) at an accelerating voltage of 200 kV. The STEM images and the STEM-EDS elemental composition and distribution analysis were performed by the JEOL JEM 2100F TEM equipped with an EDS detector (FEI) at an accelerating voltage of 200 kV. An ICP-OES spectrometer (PerkinElmer Optima 8300) was used to analyze the elemental composition. A Kratos AXIS Supra equipped with an automated dual anode (Al/Ag K α) X-ray monochromatic source was used to collect the XPS data. The binding energies were calibrated by the C 1s peak at 284.8 eV. The Ni K-edge XANES of the Ni_{33.3}B_{14.7}O_{52.0}, Ni_{33.7}P_{3.2}B_{10.2}O_{52.9} and Fe_{6.4}Ni_{16.1}P_{12.9}B_{4.3}O_{60.2} samples were acquired at beamline 5.2 at Synchrotron Light Research Institute (SLRI), Thailand. The XANES and EXAFS of the

Fe_{6.4}Ni_{16.1}P_{12.9}B_{4.3}O_{60.2} nanocages before and after OER stability evaluation were measured at the beamline 14W1 and monochromatized with Si(111) double-crystals in Shanghai Synchrotron Radiation Facility (SSRF), China. The ATHENA software from the Demeter Suite was used to do the XAS analysis.⁶⁶

Electrochemical characterization: Electrochemical measurements of the catalysts were carried out in a three-electrode configuration cell with a Solartron electrochemical station. All the measurements were carried out at RT. The working electrode was made by depositing catalysts onto a disc-shaped glassy carbon (GC) electrode with a diameter of 3.0 mm. A carbon rod electrode (purity > 99.999%) and a Ag/AgCl/3 M KCl were used as the counter and reference electrodes. The measured potentials *vs.* Ag/AgCl were converted to *vs.* reversible hydrogen electrode (RHE) according the equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.207 + 0.059\text{pH}$. O₂-saturated 1.0 M KOH aqueous solution was used as the electrolyte. A Hg/HgO/1 M KOH reference electrode was used instead, to estimate the long-term stability. The measured potentials *vs.* Hg/HgO were converted to *vs.* reversible hydrogen electrode (RHE) according the equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.059\text{pH}$.

The catalyst powder (4 mg) and carbon black (Super P[®], 0.5 mg) were dispersed into a solution containing 700 μL of ethanol and 50 μL of 5 wt% Nafion solution by ultrasonication for 1 h to form a homogeneous catalyst ink. Before the catalyst loading, the GC electrodes were polished with 0.05 μm alumina suspension on felt polishing pads, rinsed with DI water, ultrasonicated for 5 min in a mixture of ethanol and DI water ($v/v=1:1$), and rinsed with ethanol again. After the GC electrodes were dried naturally in air, 3 μL of the ink was deposited onto each GC electrode using a pipette, resulting in a mass loading of 0.2264 mg/cm^2 . The working electrodes were ready to measure after dried under ambient condition for at least 2 h.

The EIS was conducted at the potential of 0.45 V *vs.* Ag/AgCl with a perturbation of 10 mV in a frequency range of 1 MHz to 1 Hz. The resistance of the solution, R_s , resulted from the Nyquist plot was used to correct the ohmic drop (iR -correction) based on the equation $E = E_{RHE} - iR_s$ for the oxygen evolution reaction (OER) measurement. Before the OER measurement, continuous cyclic voltammetry (CV) at a scan rate of 100 mV s⁻¹ from 0 V to 0.8 V *vs.* Ag/AgCl was conducted until a reproducible CV is obtained, which turns out to be around 20 cycles. The linear sweep voltammetry (LSV) from 0 V to 0.8 V *vs.* Ag/AgCl at a scan rate of 1 mV s⁻¹ under stirring at 1200 rpm was conducted to measure the OER activity. The overpotential (η) is calculated by subtracting 1.23 V which is the theoretical potential for oxygen evolution *vs.* RHE from the iR -corrected E (*vs.* RHE). The corresponding Tafel curve is constructed by the equation: $\eta = a + b \log j$, where j is the current density and b is the Tafel slope. The chronopotentiometry at a fixed current density of 10 mA cm⁻² under stirring at 1200 rpm was recorded to estimate the long-term performance. Besides, the long-term stability was also performed by chronoamperometry at a fixed overpotential of 236 mV. While the long-term stability at 290 mV to achieve a higher current density of about 100 mA cm⁻² was conducted by depositing the catalyst ink onto carbon fiber paper.

The electrochemical surface area (ECSA) was determined by CVs at various scan rates (20, 25, 30, 40, 50, 60, 80, and 100 mV s⁻¹) in a potential window without obvious Faradaic process in static solution, prior to which the activation process was carried out by 20 CV scans at a scan rate of 100 mV s⁻¹ from 0 V to 0.8 V *vs.* Ag/AgCl. The following calculations are conducted by the proposed benchmarking in other report.⁵⁶ The charging current density, i_c , as a function of scan rate (ν) leads to a fitted line where the slope is equal to the specific double-layer capacitance (C_{dl}). The double-layer capacitance (C) is obtained by the equation: $C = C_{dl} \times S_{GC}$, where S_{GC} is

the geometric area of the GC surface (0.07065 cm^2 in our case). ECSA is calculated by the equation: $\text{ECSA} = C/C_s$, where C_s is the specific capacitance of the catalyst or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions. Here a general specific capacitance of $C_s=0.040\text{ mF cm}^{-2}$ in 1 M NaOH is applied according to other reports.⁵⁶ The equation: $\text{RF} = \text{ECSA}/S_{\text{GC}}$ is used to calculate the roughness factor (RF). The specific current density j_s is calculated by the equation: $j_s = j_g/\text{RF}$, where j_g is the current density per geometric area at a given overpotential. The j_g at $\eta = 300\text{ mV}$ (1.53 V vs. RHE) is used for the j_s evaluation, which is the overpotential for the optimized Ni-P-B-O catalyst ($\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$) to afford j_{10} .

ASSOCIATED CONTENT

Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

XRD patterns and TEM micrographs of the NPBO nanocages with various ratios of P to B, XPS spectra of the $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ nanocages, SEM image and XPS spectra of the $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$ nanosheets, HRTEM images and STEM elemental analysis of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocages, SEM micrographs of the FNPBO products with various Fe/Ni ratios, SEM image and XRD pattern of the FPBO product, *iR*-corrected LSV curves of the typical $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$, and $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalysts with different mass loadings, additional electrochemical characterization of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocage catalyst, SEM, TEM, XRD and elemental mapping of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocage catalyst after OER stability evaluation, ICP-OES data and the additional electrochemical results of the NBO, NPBO and FNPBO products.

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Notes

The authors declare no competing financial interest.

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Figure 1. Schematic illustration of the synthesis of amorphous Ni-P-B-O and Fe-Ni-P-B-O nanocages.

Figure 2. (a) Survey XPS spectrum; high-resolution XPS spectra of (b) Fe 2p, (c) Ni 2p, (d) P 2p and (e) B 1s of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocages. (f) The Ni K-edge XANES spectra of the $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ and $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ with Ni foil and $\text{Ni}(\text{OH})_2$ as references.

Figure 3. (a) XRD patterns of the FNPBO products with different ratios of Fe to Ni. (I) $\text{Fe}_{0.3}\text{Ni}_{28.6}\text{P}_{6.8}\text{B}_{8.7}\text{O}_{55.6}$, (II) $\text{Fe}_{4.0}\text{Ni}_{20.9}\text{P}_{11.6}\text{P}_{4.5}\text{O}_{58.9}$, (III) $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$, (IV) $\text{Fe}_{10.2}\text{Ni}_{12.0}\text{P}_{12.3}\text{B}_{4.9}\text{O}_{60.6}$, (V) $\text{Fe}_{10.0}\text{Ni}_{5.5}\text{P}_{15.5}\text{B}_{5.8}\text{O}_{63.1}$, (VI) $\text{Fe}_{16.8}\text{Ni}_{6.1}\text{P}_{9.3}\text{B}_{7.7}\text{O}_{60.1}$, and (VII) $\text{Fe}_{23.3}\text{Ni}_{3.3}\text{P}_{5.1}\text{B}_{9.8}\text{O}_{58.5}$. (b) SEM micrograph, (c) and (d) TEM micrographs, inset of (c) SAED pattern of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocage. (e-j) STEM elemental analysis of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocage. (e) Dark field STEM image, (f) Fe $K\alpha$, (g) Ni $K\alpha$, (h) P $K\alpha$, (i) B $K\alpha$ and (j) O $K\alpha$.

Figure 4. TEM micrographs of FNPBO with different Fe/Ni ratios: (a) $\text{Fe}_{0.3}\text{Ni}_{28.6}\text{P}_{6.8}\text{B}_{8.7}\text{O}_{55.6}$, (b) $\text{Fe}_{4.0}\text{Ni}_{20.9}\text{P}_{11.6}\text{P}_{4.5}\text{O}_{58.9}$, (c) $\text{Fe}_{10.2}\text{Ni}_{12.0}\text{P}_{12.3}\text{B}_{4.9}\text{O}_{60.6}$, (d) $\text{Fe}_{10.0}\text{Ni}_{5.5}\text{P}_{15.5}\text{B}_{5.8}\text{O}_{63.1}$, (e) $\text{Fe}_{16.8}\text{Ni}_{6.1}\text{P}_{9.3}\text{B}_{7.7}\text{O}_{60.1}$ and (f) $\text{Fe}_{23.3}\text{Ni}_{3.3}\text{P}_{5.1}\text{B}_{9.8}\text{O}_{58.5}$.

Figure 5. (a) The *i*R-corrected LSV curves and (b) the corresponding Tafel curves of NPBO with different P/B ratios, NBO and RuO₂.

Figure 6. (a) The overpotentials of the $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ and $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalysts with various mass loading on the glassy carbon electrodes. (b) The *iR*-corrected LSV curves and (c) the corresponding Tafel slopes of the FNPBO catalysts with different Fe/Ni ratios. (d) Tafel slope–potential plot of the $\text{Ni}_{33.3}\text{B}_{14.7}\text{O}_{52.0}$, $\text{Ni}_{33.7}\text{P}_{3.2}\text{B}_{10.2}\text{O}_{52.9}$ and $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ catalysts as compared with that of RuO_2 .

Figure 7. (a) Current density as a function of scan rate derived from the CV curves at different scan rates for the NBO, NPBO and FNPBO catalysts. (b) The comparison of the j_g , corresponding j_m (current density based on mass) and j_s at a given overpotential of 300 mV. (I) Ni_{33.3}B_{14.7}O_{52.0}, (II) Ni_{33.7}P_{3.2}B_{10.2}O_{52.9}, (III) Fe_{6.4}Ni_{16.1}P_{12.9}B_{4.3}O_{60.2}, and (IV) RuO₂. Potentiostatic long-term durability performance of the Fe_{6.4}Ni_{16.1}P_{12.9}B_{4.3}O_{60.2} nanocages at an overpotential of (c) 236 mV and (d) 290 mV.

Figure 8. High-resolution XPS spectra of (a) Ni 2p, (b) P 2p, (c) B 1s and (d) Fe 2p of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ nanocages after OER stability measurement. (e) The Ni K-edge XANES spectra and (f) FT-EXAFS of the $\text{Fe}_{6.4}\text{Ni}_{16.1}\text{P}_{12.9}\text{B}_{4.3}\text{O}_{60.2}$ after OER stability measurement.

Table 1. OER overpotentials and Tafel slopes of the as-prepared catalysts.

Sample	Overpotential (mV) at 10 mA cm ⁻²	Tafel slope (mV dec ⁻¹)
RuO ₂	327	136
Ni _{33.3} B _{14.7} O _{52.0}	335	90.8
Ni _{33.6} P _{1.5} B _{12.6} O _{52.4}	330	80.9
Ni _{35.0} P _{2.7} B _{9.8} O _{52.5}	308	81.7
Ni _{33.7} P _{3.2} B _{10.2} O _{52.9}	300	67.4
Ni _{34.0} P _{3.4} B _{9.8} O _{52.9}	328	66.7
Ni _{31.2} P _{6.8} B _{7.6} O _{54.5}	313	124
Fe _{0.3} Ni _{28.6} P _{6.8} B _{8.7} O _{55.6}	297	67
Fe _{4.0} Ni _{20.9} P _{11.6} P _{4.5} O _{58.9}	263	50
Fe _{6.4} Ni _{16.1} P _{12.9} B _{4.3} O _{60.2}	236	39
Fe _{10.2} Ni _{12.0} P _{12.3} B _{4.9} O _{60.6}	253	73
Fe _{10.0} Ni _{5.5} P _{15.5} B _{5.8} O _{63.1}	326	80
Fe _{16.8} Ni _{6.1} P _{9.3} B _{7.7} O _{60.1}	344	67
Fe _{23.3} Ni _{3.3} P _{5.1} B _{9.8} O _{58.5}	383	69

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Amorphous Fe-Ni-P-B-O nanocages with tunable composition synthesized by a simple low-cost and scalable method at room temperature show enhanced catalytic activity as electrocatalysts for oxygen evolution reaction after the optimized introduction of P and Fe, making a sharp contrast to high-cost RuO₂ catalyst.