Boron-doped amorphous iridium oxide with ultrahigh mass activity for acidic oxygen evolution reaction

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ABSTRACT Oxygen evolution reaction (OER), as the primary anodic reaction, plays a critical role in many electrochemical energy conversion processes. As the state-of-the-art OER catalysts, iridium-based materials are largely hindered from practical applications mainly due to the extreme scarcity of iridium. Here we demonstrate the successful fabrication of boron-doped amorphous iridium oxide ($\text{IrO}_x\text{-B}$) via a facile boric acid-assisted method, which realizes an ultrahigh OER mass activity of $2779 \text{ A g}^{-1}_{\text{Ir}}$ at 300 mV overpotential, representing one of the best acidic OER catalysts reported so far. It is found that boric acid can not only facilitate the exposure of Ir, but also dope the amorphous IrO_x with a form of metaborate, which could further modify the electronic and local ligand structure of Ir for the improved intrinsic activity. Interestingly, the reported strategy is universal that can be applied to improve other metal oxide OER catalysts, highlighting a versatile strategy for creating high-performance electrocatalysts with ultrahigh mass activity for OER and beyond.

Keywords: amorphous, boron, iridium oxide, oxygen evolution reaction, mass activity

INTRODUCTION

Electrocatalytic oxygen evolution reaction (OER) is a critical component of various energy-conversion systems, such as water splitting and CO_2 reduction, by providing electrons and protons needed for these processes [1–5]. However, the sluggish kinetics of OER largely limits the energy conversion efficiency of such devices [6,7]. Up to date, Ir-based materials are considered as the state-of-the-art OER catalysts especially in acidic conditions, which possess both appealing activity and stability [8–10]. Unfortunately, the commercialization of Ir-based materials is still hindered by the extreme scarcity and high price of Ir. Therefore, it is highly urgent to develop advanced Ir-

based materials with superior OER activity as well as largely reduced Ir usage.

Increasing the atomic utilization of Ir is a conventional solution to enhance the mass activity. For example, low-dimensional Ir-based nanomaterials (e.g., nanosheet, nanowire) [11–14] and even single-atom catalysts [15–17] have been successfully synthesized. Apart from simply exposing more Ir active sites, optimizing the activity of each active site will be a more intrinsic improvement in mass activity. Due to the harsh condition of acidic OER, most of the reported highly active Ir-based catalysts are essentially comprised of the same active species: disordered iridium oxide with active oxygen species (IrO_x) [18–20]. Therefore, designing and constructing disordered iridium oxide with randomly connected $[\text{IrO}_6]$ octahedrons can facilitate releasing abundant highly active oxygen species. Moreover, regulating the local environment and electronic structure of the disordered IrO_x is highly critical for the further enhancement of OER performance. Multi-component catalyst as well as atom-doping method is one of the most effective strategies to optimize its local structure [21], while few of the common doping elements (e.g., Fe, Co, Ni) can sustain under the acidic and oxidizing environment.

Inspired by the above issues, a boron-doped amorphous iridium oxide ($\text{IrO}_x\text{-B}$) was successfully synthesized by a facile boric acid-assisted method. The $\text{IrO}_x\text{-B}$ exhibits ultrahigh OER mass activity, which is 4.1 times higher than that of amorphous IrO_x and even 44 times higher than that of commercial IrO_2 . Detailed studies show that boric acid helps to expose more Ir sites in the synthesis process. In addition, the introduced boron species facilitate decreasing the Ir oxidation state and increasing the amorphization, which lead to the enhanced OER activity. We also found that the boric acid-assisted

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method is beneficial for upgrading other metal-based OER catalysts, showing the high generality of the method reported herein.

METHODS

Synthesis of Ir-0B (IrO_x), Ir-4B, Ir-8B, Ir-12B (IrO_x-B) and Ir-16B

In a typical preparation of Ir-12B (IrO_x-B), H₂IrCl₆·H₂O (10 mg), H₃BO₃ (12 mg), NaOH (8.4 mg) and H₂O (10 mL) were mixed in a glass vial and heated at 90°C for 10 h. The products were collected *via* centrifugation and washed with water (1 mL) and ethanol (8 mL). The synthesis of Ir-0B (IrO_x), Ir-4B, Ir-8B and Ir-16B was the same to that of Ir-12B (IrO_x-B) except that 0, 4, 8 and 16 mg of H₃BO₃ was added, respectively.

Synthesis of RuO_x, RuO_x-B, CoO_x, CoO_x-B, NiFeO_x and NiFeO_x-B

In a typical preparation of boron-doped oxide, RuCl₃·H₂O (7.5 mg), CoCl₂·6H₂O (5.9 mg), FeCl₃·6H₂O (3.4 mg) or NiCl₂·6H₂O (3.0 mg) was mixed with H₃BO₃ (12 mg), NaOH (8.4 mg) and H₂O (10 mL) in a glass vial and heated at 90°C for 10 h. The products were collected *via* centrifugation and washed with water (1 mL) and ethanol (8 mL). Boron-free oxide was synthesized by the same method except for the addition of boric acid.

Electrochemical measurements

A three-electrode cell was used to conduct the electrochemical measurements by CHI 660E, in which a saturated calomel electrode (SCE) was used as the reference electrode, a carbon rod electrode was used as the counter electrode and a glassy carbon electrode (GCE) (diameter: 5 mm, area: 0.196 cm²) was used as the working electrode. IrO_x-B (2.8 mg, 8.9 wt%, measured by thermogravimetric analysis test) was dispersed in 1 mL of solvent containing 20 μL of water, 970 μL of isopropanol, and 10 μL of 5 wt% Nafion to form a homogeneous ink by sonication for 30 min (0.25 mg_{Ir} mL⁻¹). Then 4, 8 or 40 μL of the catalyst ink (5.1, 10.2, 51 μL cm⁻²) was loaded onto a GCE.

The OER measurements were carried out in N₂-saturated 0.1 mol L⁻¹ HClO₄. The cyclic voltammogram (CV) was carried out between +1.0 and +1.7 V_{RHE} at 50 mV s⁻¹ for 20 cycles to activate catalysts. Linear-sweep voltammetry (LSV) tests were recorded in the same potential range at a scan rate of 5 mV s⁻¹ with 95% *iR* compensation.

The CV tests for measuring the number of electrochemically active Ir sites were carried out between +0.4

and +1.4 V_{RHE} at 20 mV s⁻¹ for 3 cycles in 0.1 mol L⁻¹ HClO₄. The number of active sites was calculated from the anodic charge of Ir^{3+/4+} peak with capacitance current subtraction.

The CV tests for measuring the double layer capacitance (*C_{dl}*) were carried out between -0.05 and +0.05 V_{SCE} at different scan rates (100, 200, 300, 400, 500 mV s⁻¹) in 0.1 mol L⁻¹ HClO₄. *C_{dl}* is the slope value of the fitting linear.

The Nyquist plots for OER were recorded at 1.53 V_{RHE} in N₂-saturated 0.1 mol L⁻¹ HClO₄.

The reference electrode SCE was calibrated by using a reversible hydrogen electrode (RHE). A Pt electrode was cleaned and used as the working electrode. Calibration was conducted in the H₂-saturated electrolyte by LSV. The resulting potential is the potential of zero net current. In this work, the potential of zero net current was found at -0.310 V *vs.* SCE in 0.1 mol L⁻¹ HClO₄ (Fig. S1).

E vs. RHE = E vs. SCE + 0.310 V (0.1 mol L⁻¹ HClO₄).

RESULTS AND DISCUSSION

The schematic illustration for synthesizing IrO_x-B is shown in Fig. 1a. Briefly, dihydrogen hexachloroiridate (IV) hydrate, boric acid and sodium hydroxide were mixed in water to form a tawny solution. The mixture was heated at 90°C with stirring for 10 h. It was observed that the tawny color faded quickly and blue suspension formed gradually (Fig. S2). IrO_x-B was collected by centrifugation and washed with water and ethanol. IrO_x was also synthesized for comparison by the same approach but without introducing boric acid. The morphological information was examined by scanning electron microscopy (SEM) and transition electron microscopy (TEM), which show that IrO_x-B is composed of well-dispersed sphere particles with an average size of ~45 nm (Fig. 1b, Fig. S3). High-resolution TEM (HRTEM) was applied to further investigate the atomic structure. As exhibited in Fig. 1c, no clear lattice fringes can be observed and the corresponding Fourier transfer pattern shows the typical diffuse ring, indicating the amorphous structure. The crystal structure was also examined by powder X-ray diffraction (PXRD) and commercial IrO₂ was used for comparison. As shown in Fig. 1e, all the peaks of IrO₂ can be indexed to the typical rutile IrO₂ (PDF 86-0330). In contrast, no obvious sharp diffraction peaks can be seen in IrO_x-B, which further improves the amorphous feature. The Raman spectrum of IrO_x-B shows the similar peaks as that of commercial IrO₂, which arises from the typical Ir-O vibrations (Fig. 1f) [22]. Therefore, we could conclude that amorphous iridium oxide species were suc-

Figure 1 Characterization of $\text{IrO}_x\text{-B}$. (a) Schematic illustration for the synthesis, (b) TEM image, (c) HRTEM image, and (d) HAADF-STEM-EDS elemental mappings of $\text{IrO}_x\text{-B}$. The inset in (c) shows the corresponding Fourier transform pattern. (e) PXRD spectra and (f) Raman spectra of $\text{IrO}_x\text{-B}$ and IrO_2 . (g) B 1s XPS spectra of $\text{IrO}_x\text{-B}$, boric acid and sodium metaborate.

successfully obtained. According to the high-angle annular dark-field scanning TEM energy dispersive X-ray spectroscopy (HAADF-STEM-EDS) element mapping (Fig. 1d), both Ir and B distribute evenly among the particle, indicating the successful introduction of boron species. Inductively coupled plasma optical emission spectroscopy (ICP-OES) test shows that the molar ratio of Ir:B is $\sim 1:1.46$ (Table S1). Furthermore, X-ray photoelectron spectroscopy (XPS) was applied to identify the local structure of boron species (Fig. 1g). The B 1s spectrum of $\text{IrO}_x\text{-B}$ exhibits an obvious peak at ~ 191.9 eV, which is close to the signal of sodium metaborate, indicating that boron species exist in the form of

metaborate. The IrO_x synthesized without boric acid was also characterized for comparison. According to the PXRD pattern as well as the typical Ir–O vibration signals in Raman spectrum (Fig. S4a, b), we can conclude that IrO_x is also amorphous.

In order to uncover the role of boric acid in the synthesis process, controlled experiments were performed. As shown in Fig. S5 and Table S1, with the increase of mass of boric acid ($M_{\text{H}_3\text{BO}_3}$), the obtained products tend to be more dispersed and regularly shaped with a higher molar ratio of B. The difference in number of electrochemically active Ir sites ($N_{\text{active Ir site}}$) was also investigated by measuring the anodic charge between Ir^{3+}

and Ir^{4+} (Fig. S6) [23,24]. A positive correlation exists between $M_{\text{H}_3\text{BO}_3}$ and $N_{\text{active Ir site}}$ in the range of 0–12 mg, while further increasing of $M_{\text{H}_3\text{BO}_3}$ does not have any marked effect. All these experiments indicate that boric acid facilitates increasing the dispersity of product and exposing more active Ir sites. In addition, 12 mg of boric acid is the optimal condition to obtain the well-dispersed uniform morphology and the largest $N_{\text{active Ir site}}$.

The OER activity of $\text{IrO}_x\text{-B}$ was evaluated in $0.1 \text{ mol L}^{-1} \text{HClO}_4$. All the $\text{IrO}_x\text{-B}$, IrO_x and commercial IrO_2 were loaded on carbon black with the loading amount of Ir fixed at $5.1 \mu\text{g cm}^{-2}$ (Fig. S7). The LSV curves show that the overpotential of $\text{IrO}_x\text{-B}$ for reaching 10 mA cm^{-2} is 292 mV, which is much smaller than those of IrO_x (328 mV) and IrO_2 (457 mV) (Fig. 2a). Additionally, $\text{IrO}_x\text{-B}$ also has the lowest Tafel slope (39.2 mV dec^{-1}) (Fig. 2b), indicating the enhanced kinetics for OER. Due to the scarcity and high cost of Ir, mass activity becomes a more critical factor in practical application. We can see that the mass activity at 300 mV overpotential ($1.53 \text{ V}_{\text{RHE}}$) of $\text{IrO}_x\text{-B}$ is $2779 \text{ A g}_{\text{Ir}}^{-1}$, which is 4.1 and 44 times higher than those of IrO_x and IrO_2 , respectively (Fig. 2c and Fig. S8). The OER performance of $\text{IrO}_x\text{-B}$ was also examined by loading other amounts of Ir (i.e., 10.2 and $51 \mu\text{g cm}^{-2}$). As shown in Fig. S9, with the increase of Ir loading, the overpotentials for reaching 10 mA cm^{-2} reduce to 276 mV ($10.2 \mu\text{g cm}^{-2}$) and 256 mV ($51 \mu\text{g cm}^{-2}$), while the mass activities at $1.53 \text{ V}_{\text{RHE}}$ also reduce to $2155 \text{ A g}_{\text{Ir}}^{-1}$ ($10.2 \mu\text{g cm}^{-2}$) and $803 \text{ A g}_{\text{Ir}}^{-1}$ ($51 \mu\text{g cm}^{-2}$), respectively. By comparing both the overpotential and mass activity with the same Ir loading, we find that the $\text{IrO}_x\text{-B}$ readily outperforms most reported Ir-based catalysts so far (Table S2).

Although Ir-mass-based activity is highly relevant to the cost of practical application, the active-site-normalized activity can be a better descriptor for intrinsic activity. We then measured the electrochemically accessible $\text{Ir}^{3+/4+}$ sites by CV, which can be considered as an upper bound of OER active sites (Fig. 2d) [25]. As shown in Fig. S8c, $\text{IrO}_x\text{-B}$ possesses ~ 1.7 times and ~ 13 times more active sites than IrO_x and IrO_2 , respectively. We also generated the specific activity by normalizing the activity to $N_{\text{active Ir site}}$ (J_{specific}) (Fig. 2e and Fig. S8d). In detail, $\text{IrO}_x\text{-B}$ reaches $\sim 632 \text{ A mmol}_{\text{Ir site}}^{-1}$ at $1.53 \text{ V}_{\text{RHE}}$, doubling IrO_x and ~ 4.5 time higher than IrO_2 . C_{dl} was measured to compare the electrochemically active surface area. As shown in Fig. S10, $\text{IrO}_x\text{-B}$ exhibits the largest C_{dl} of 0.55 mF cm^{-2} , which is 1.4 and 8.1 times higher than those of IrO_x and IrO_2 . After normalizing the current to C_{dl} , $\text{IrO}_x\text{-B}$ still possesses the highest specific activity,

which is 2.8 and 5.5 times higher than those of IrO_x and IrO_2 at $1.53 \text{ V}_{\text{RHE}}$. The nitrogen adsorption-desorption isotherms were also collected to generate the surface area (Fig. 2f). The Brunauer-Emmett-Teller (BET) surface area of $\text{IrO}_x\text{-B}$ is ca. $62.6 \text{ m}^2 \text{ g}^{-1}$, much higher than those of IrO_2 ($11.5 \text{ m}^2 \text{ g}^{-1}$) and IrO_x ($22.3 \text{ m}^2 \text{ g}^{-1}$) (Fig. S8e). After normalizing activity to BET surface area ($J_{\text{BET surface}}$), $\text{IrO}_x\text{-B}$ still possesses the highest $J_{\text{BET surface}}$, which is 1.4 and 8.4 times higher than those of IrO_x and IrO_2 , respectively (Fig. 2g). Combining all these site- and surface-normalized activities together, we could conclude that $\text{IrO}_x\text{-B}$ has an edge over IrO_x and IrO_2 in both number of active sites and intrinsic activity, which finally contributes to the ultrahigh mass activity. The enhanced activity of $\text{IrO}_x\text{-B}$ could also be verified by the much smaller interfacial charge-transfer resistance, indicating faster electron transport during the electrocatalytic process (Fig. 2h).

Compared with activity, stability may be more critical in real applications. The high activity of amorphous iridium oxide, however, always comes with the price of stability problems during catalysis [26,27]. Therefore, we also investigated the stability of our catalysts. Both $\text{IrO}_x\text{-B}$ and IrO_x were tested at a constant current density of 10 mA cm^{-2} for 10 h, while IrO_2 quickly deactivated in $\sim 30 \text{ min}$ (Fig. 2i). The dissolved iridium in electrolyte was tested by ICP mass spectroscopy (ICP-MS) (Table S1). No iridium can be detected in the electrolyte of IrO_2 , so the rapid deactivation could not represent the intrinsic stability of IrO_2 , which may contribute to the degradation of backing electrode [28]. For $\text{IrO}_x\text{-B}$ and IrO_x , ~ 59.4 and $120.4 \mu\text{g L}^{-1}$ iridium was dissolved in 30 mL of electrolyte. The stability number (S-number) (defined as the ratio between the amount of evolved oxygen and the amount of dissolved iridium) has been considered as a fair metrix for characterizing the activity *versus* stability. The S-number was calculated from ICP-MS and chronopotentiometry (CP) results, which is $\sim 1.01 \times 10^5$ for $\text{IrO}_x\text{-B}$ and 4.96×10^4 for IrO_x . The doubled S-number indicates the enhanced stability of $\text{IrO}_x\text{-B}$ than common IrO_x . Samples after 10 h CP were also collected and characterized. According to the ICP-OES results (Table S1), the molar ratio of Ir:B maintains $\sim 1:1.28$, close to the pristine state ($1:1.46$). No obvious morphology change and agglomeration can be observed in the TEM image (Fig. S11a). The PXRD pattern, Ir 4f XPS spectrum and CV curves also indicate the structure and valence state are retained during OER catalysis (Fig. S11b–d). All these characterizations confirm the excellent structure stability of $\text{IrO}_x\text{-B}$.

To investigate the origin of improved intrinsic activity

Figure 2 OER performances of IrO_x-B, IrO_x and IrO₂. (a) LSV curves scanned at 5 mV s⁻¹ with 95% *i*R compensation and (b) the corresponding Tafel plots. (c) Ir-mass-normalized activity at 1.53 V_{RHE} (*J*_{mass@1.53 V}). (d) CV curves for measuring the active Ir sites. (e) Ir-site-normalized activity (*J*_{specific}) at 1.53 V_{RHE}. (f) Nitrogen adsorption-desorption isotherms. (g) BET-surface-area-normalized activity (*J*_{BET surface}) at 1.53 V_{RHE}. (h) Nyquist plots recorded at 1.53 V_{RHE}. (i) CP test at a constant current density of 10 mA cm⁻². The electrochemical measurement conditions: 0.1 mol L⁻¹ HClO₄; iridium loading of 5.1 μg cm⁻².

of IrO_x-B, XPS and X-ray adsorption spectroscopy (XAS) were carried out to understand the local atomic and electronic structures. As shown in Fig. 3a, the Ir 4f XPS spectrum is deconvoluted into Ir⁴⁺ (61.7 eV) and Ir³⁺ (62.3 eV) [29,30]. IrO₂ consists of Ir⁴⁺ only, fitting well with the rutile phase. Differing from IrO₂, both IrO_x and IrO_x-B are comprised of Ir³⁺ and Ir⁴⁺. The Ir³⁺ concentration is ~32.6% in IrO_x and increases to ~39.1% in IrO_x-B (Fig. S12). The O 1s XPS spectra could be deconvoluted into the lattice oxygen (O_{lattice}, 529.9 eV), the coordinatively unsaturated oxygen in hydroxyl group

(O_{OH}, 531.1 eV) and the oxygen in adsorbed water (O_{H₂O}, 532.7 eV) (Fig. 3b). Excluding the signals of H₂O, the surface oxygen species are dominated by O_{OH} (~90.3% for IrO_x and ~91.7% for IrO_x-B), except for IrO₂ (~23.1%) where the major contribution comes from O_{lattice}. Combining all the XPS results together, we could find the positive correlation between Ir³⁺ and O_{OH} species, which arises from the formation of Ir-OH species. The local atomic and electronic structures in bulk phase was then examined by X-ray absorption near-edge structure (XANES) and Fourier transformed extended X-ray ab-

Figure 3 Structure characterizations of IrO_x-B and IrO_x. (a) Ir 4f and (b) O 1s XPS spectra of IrO₂, IrO_x and IrO_x-B. (c) XANES and (d) EXAFS spectra of Ir, IrO₂, IrO_x and IrO_x-B. (e) Wavelet transform plots of IrO₂ (left), IrO_x (middle) and IrO_x-B (right). (f) Structure schematics of IrO₂, IrO_x and IrO_x-B.

sorption fine structure (EXAFS) spectroscopy. According to the Ir L₃ edge XANES spectra (Fig. 3c), the edge positions of IrO_x and IrO_x-B locate between that of metallic Ir and rutile IrO₂, indicating a moderate valence state between 0 and +4. In addition, IrO_x-B possesses slightly lower peak energy than IrO_x, indicating a lower average valence state. This can be explained by the presence of metaborate: B-O covalent bonding has been reported to be able to decrease the electron-attracting ability of the oxygen in metal oxide, leading to the decrease of metal valence state [31]. The XANES results also fit well with XPS spectra (Ir valence state: IrO₂ > IrO_x > IrO_x-B), confirming the uniformity between the surface and bulk phase. The Fourier-transformed k³-weighed EXAFS spectra for Ir and the corresponding wavelet transfer plots are compared in Fig. 3d, e. Commercial IrO₂, IrO_x and IrO_x-B all show the typical Ir-O bond at ~1.6 Å. In detail, both IrO_x and IrO_x-B show typical reduction in bond intensity and extension in bond length compared with rutile IrO₂ (Fig. 3e, Fig. S13 and Table S3), which can be

explained by the increased degree of disorder and decreased Ir valence state. Compared with IrO_x, IrO_x-B exhibits the even weaker intensity and longer length.

Considering all the information above, we summarize the structure features of IrO₂, IrO_x and IrO_x-B in Fig. 3f. Commercial IrO₂ is composed of periodically interconnected [IrO₆] octahedron, making Ir⁴⁺ and O_{lattice} the dominant species. According to the flat PXRD pattern and large reduction of peak intensity in EXAFS spectra, [IrO₆] octahedron are randomly interconnected in both IrO_x and IrO_x-B, leading to the exposure of coordinatively unsaturated oxygen species, which can be reflected by the increase in concentration of Ir³⁺ and O_{OH}. Furthermore, the introduced metal borate in IrO_x-B successfully moderates the electronic and atomic structure of Ir, leading to a higher concentration of Ir³⁺ and O_{OH} and a more disordered structure than IrO_x. According to previous report, both Ir³⁺ and O_{OH} have been discussed as the precursors for active sites in the *in situ* characterization [32,33]. Their concentration has even been considered as

an *ex situ* activity descriptor for OER [34]. Therefore, the higher concentration of Ir^{3+} and O_{OH} as well as the increased amorphization caused by the introduction of metaborate contributes to the largely enhanced intrinsic activity.

Significantly, the boric acid-assisted method for creating high-performance $\text{IrO}_x\text{-B}$ is versatile, which can be readily extended to other OER catalysts, such as $\text{RuO}_x\text{-B}$, $\text{CoO}_x\text{-B}$ and $\text{NiFeO}_x\text{-B}$, by simply changing the metal precursors. The boron-free RuO_x , CoO_x and NiFeO_x were also prepared for comparison. As shown in Fig. 4a–

c, no clear diffraction peaks can be observed, indicating low crystallinity feature of all the metal oxide species. According to the B 1s XPS spectra (Fig. 4d–f), metaborate has been successfully introduced. All these metal oxides were loaded on carbon black and examined for OER performance. Specifically, RuO_x and $\text{RuO}_x\text{-B}$ were tested under $0.1 \text{ mol L}^{-1} \text{ HClO}_4$. $\text{RuO}_x\text{-B}$ surpasses RuO_x with a 10 mV-improvement in overpotential (Fig. 4g). The other non-noble metal oxides were tested in $1 \text{ mol L}^{-1} \text{ KOH}$ and exhibited the same trend: $\text{CoO}_x\text{-B}$ possesses an overpotential of 348 mV, better than that of CoO_x

Figure 4 Universality display of the boron-introducing method. PXRD patterns of (a) RuO_x and $\text{RuO}_x\text{-B}$, (b) CoO_x and $\text{CoO}_x\text{-B}$, and (c) NiFeO_x and $\text{NiFeO}_x\text{-B}$. B 1s XPS spectra of (d) RuO_x and $\text{RuO}_x\text{-B}$, (e) CoO_x and $\text{CoO}_x\text{-B}$, and (f) NiFeO_x and $\text{NiFeO}_x\text{-B}$. LSV curves of (g) RuO_x and $\text{RuO}_x\text{-B}$, (h) CoO_x and $\text{CoO}_x\text{-B}$, and (i) NiFeO_x and $\text{NiFeO}_x\text{-B}$.

(380 mV) (Fig. 4h); the overpotential of NiFeO_x-B (277 mV) is much lower than that of NiFeO_x (347 mV) (Fig. 4i). The obvious enhancement of OER regardless of pH value and components clearly shows the universality of the method reported herein, which deserves further investigation.

CONCLUSIONS

In conclusion, we reported a boric acid-assisted method to synthesize B-doped amorphous IrO_x. The use of boric acid facilitates the preparation of well dispersed nanoparticles with largely improved active sites. Moreover, the metaborate converted from boric acid is incorporated into the amorphous IrO_x. This successfully increases the concentration of Ir³⁺ and O_{OH}, making the structure more disordered and finally leading to the enhanced intrinsic activity. As a result, the optimized IrO_x-B shows one of the highest mass activities reported to date. We believe that the synthesized IrO_x-B can act as an ideal OER catalyst and the boron-introducing method may be instructive for designing advanced catalysts with ultrahigh mass activity.

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Supplementary information Experiment details and supplementary data are available in the online version of the paper.

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硼掺杂无定形氧化铱增强酸性析氧反应质量活性

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摘要 析氧反应(OER)作为一种主要的阳极反应, 在许多电化学能量转换过程中起到了重要的作用. 尽管铱(Ir)基材料是目前最先进的OER催化剂, 其稀缺性很大程度上限制了该类材料的实际应用. 在此, 我们利用简便的硼酸辅助法成功制备了硼掺杂的无定形氧化铱($\text{IrO}_x\text{-B}$). 该催化剂在300 mV过电位处展现出 2779 A g^{-1} 的超高OER质量活性, 是已报道的最佳酸性OER催化剂之一. 我们发现硼酸不仅可以促进Ir位点的暴露, 还能够以偏硼酸根的形式掺杂进入无定形 IrO_x 中, 并进一步优化Ir的电子与配位结构, 进而实现本征活性的提升. 有趣的是, 这种方法具有一定的普适性, 能够提升其他金属氧化物催化剂的OER催化活性. 这为制备高质量活性的OER电催化剂提供了一种通用的策略.