Grain Boundary Defect Engineering in Rutile Iridium Oxide Boosts Efficient and Stable Acidic Water Oxidation

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Proton exchange membrane water electrolysis (PEMWE) is considered a promising technology for coupling with renewable energy sources to achieve clean hydrogen production. However, constrained by the sluggish kinetics of the anodic oxygen evolution reaction (OER) and the acidic abominable environment, the grand challenges in developing the active and stable OER electrocatalyst, leading to low efficiency of PEMWE. Herein, we develop the rutile-type IrO$_2$ nanoparticles with abundant grain boundaries and the continuous nanostructure through the joule heating and sacrificial template method. The optimal candidate (350-IrO$_2$) demonstrates remarkable electrocatalytic activity and stability during the OER, presenting a promising advancement for efficient PEMWE. DFT calculations verified that grain boundaries can modulate the electronic structure of Ir sites and optimize the adsorption of oxygen intermediates, resulting in the accelerated kinetics. 350-IrO$_2$ affords a rapid OER process with 20 times higher mass activity (0.61 A mg$^{-1}$) than the commercial IrO$_2$ at 1.50 V vs. RHE. Benefiting from the reduced overpotential and the preservation of the stable rutile structure, 350-IrO$_2$ exhibits the stability of 200 h test at 10 mA cm$^{-2}$ with only trace decay of 11.8 mV. Moreover, the assembled PEMWE with anode 350-IrO$_2$ catalyst outputs the current density up to 2 A cm$^{-2}$ with only 1.84 V applied voltage, long-term operation for 100 h without obvious performance degradation at 1 A cm$^{-2}$.

1. Introduction

Hydrogen is a vital carrier for efficiently utilizing renewable energy.[1] Proton exchange membrane water electrolysis (PEMWE) in acidic media offers advantages including high current density, fast system response, and low resistance losses for large-scale hydrogen generation.[2] However, the sluggish four-electron transfer process for oxygen evolution reaction (OER) leads to high catalytic overpotentials, severely limiting the efficiency of water electrolysis.[3] The previous works have made significant progress in enhancing the OER performance via using Ir-based electrocatalysts, however, it is still difficult to realize the underlying improvement in activity.[4] Moreover, their poor stability in acidic environments and high oxidation potentials severely limit the practical PEMWE application.[5] The serious issues of low mass activity and durability persist in current industrial Ir-based catalysts, for which it is urgent to develop OER electrocatalysts with high catalytic activity and stability.

IrO$_2$ with thermodynamically suitable interaction with oxygen intermediates, is regarded as the promising OER electrocatalyst.[6] Attributed to the strong connectivity between [IrO$_x$]$_n$ cells in the rutile structure, rutile IrO$_2$ has the lower metal cation leaching rate and higher stability in acidic media.[7] Therefore, numerous efforts are dedicated to improve the activity of rutile IrO$_2$ while maintaining its superiority in durability. For metal oxides, optimizing the surface electronic structure and the absorption of intermediates through the well-designed strategies is explored to improve the catalytic performance, such as foreign atoms doping,[8] defects engineering,[9] etc. Doping with foreign metal atoms, such as Ce,[10] Re,[11] and Ta[12] in rutile IrO$_2$ has been effective in enhancing activity for the Ir active sites. In addition, constructing defects related to both anionic[13] (O$^{2-}$) and cationic[14] (Ir$^{4+}$ or foreign atoms) species, will alter the covalency of Ir–O bonds and thereby affect the adsorption free energy of *OH and *O intermediates. Grain boundaries (GBs) are a special type of defect, which can be introduced into crystalline materials through kink nucleation and propagation.[15] The irregular arrangement of the atoms near GBs can significantly impact the intrinsic properties of the materials and enhance the OER activity. Inspired by the above facts, IrO$_2$ electrocatalysts with stable rutile structure and rich GBs defects may potentially possess high mass activity and stability for acidic OER and

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enhance the overall efficiency of PEMWE. However, the controlled synthesis of this IrO$_2$ and well understanding of the GBs in boosting the acidic OER remain challenges.

Herein, we develop the rutile IrO$_2$ electrocatalysts with interconnected nanostructure and abundant GBs by using rapid joule heating pyrolysis and sacrificial template strategy. The target 350-IrO$_2$ exhibits a high acidic OER activity with a low overpotential of 246 mV at 10 mA cm$^{-2}$, which is significantly more active than IrO$_2$ without GBs (477 mV) and commercial IrO$_2$ (377 mV). Density function theory (DFT) calculations reveal that the electronic structure of Ir and the covalency of Ir–O are adjusted by engineering rich GBs, and the enhanced activity is attributed to the reduced energy barriers for the adsorption intermediates on these optimized Ir sites. Benefiting from the advantage of stable rutile structure, 350-IrO$_2$ also presents high stability without the obvious potential degradation under 200 h continuous operation at 10 mA cm$^{-2}$. Importantly, the assembled PEMWE device with the anode 350-GBs–IrO$_2$ catalyst achieves a current density of 2 A cm$^{-2}$ at 1.84 V voltage and demonstrates the potential for practical application.

2. Results and Discussion

2.1. Synthesis and Characterization

The synthesis process of rutile IrO$_2$ with rich GBs is illustrated in Figure 1a and can be summarized in four steps of electrospinning, wetness impregnation, joule heating, and calcination. First, a modified electrospinning method$^{[16]}$ (details in Experimental 2.2) was employed to prepare the high surface area porous carbon nanofibers (PCNFs), which are used as the substrate for the subsequent synthesis. The field-emission scanning electron microscope (SEM, Figure S1) shows the fiber morphology of PCNF. And transmission electron microscope (TEM, Figure S2) image reveals that PCNFs with a uniform diameter of approximately 500 nm were successfully prepared. IrCl$_3$ was distributed on the surface of PCNFs through a simple wetness impregnation process. Subsequently, a programmable temperature-controlled joule heating method was used for the pyrolysis of IrCl$_3$ in which the high temperature and appropriate insulation time can ensure the complete decomposition of IrCl$_3$. Notably, the ultrafast pyrolysis process via joule heating with the temperature up to 1750°C within 0.1 seconds and rapid cooling (Figure S3) in the Ar atmosphere is conducive to the generation of the extremely small metallic Ir nanoparticles.$^{[17]}$ The SEM of Ir-PCNF (Figure S1b) indicated the maintenance of PCNFs during joule heating. Combined with TEM images and the X-ray diffraction (XRD) results in Figures S4a and S5, ultrasmall nanoparticles uniformly loaded onto PCNFs with a diameter of approximately 1.6 nm and clear lattice fingers are assigned to the metallic Ir. The XPS spectra of Ir-PCNF show a lower binding energy compared to commercial IrO$_2$ (C–IrO$_2$) in Figure S6a, further confirming the metallic state of Ir. The possible Cl$^-$ preservation of Ir-PCNFs was not detected according to the Cl 2p X-ray photoelectron spectroscopy (XPS, Figure S6b) results, which confirms the complete transformation of IrCl$_3$ into Ir nanoparticles.

Figure 1. (a) The schematic routes for synthesizing 350-IrO$_2$. (scar bar, 200 nm) (b) SEM image of 350-IrO$_2$. (c) HR-TEM image of 350-IrO$_2$ (inset graph is SAED image of 350-IrO$_2$). (d) The XRD patterns of 350-IrO$_2$, 400-IrO$_2$, and 450-IrO$_2$. 

IrO$_2$ is obtained from Ir-PCNFs after calcination at different temperatures in air and the 350-IrO$_2$ is prepared at 350°C. The lower temperature as 300°C is not sufficient to drive the conversion of elemental Ir into IrO$_2$ and the oxidative removal of PCNF, so the precursors (Ir-PCNF) is unchanged after calcination at 300°C (TEM image, Figure S7). 350-IrO$_2$ sample also inherited the fiber morphology of PCNF template except with rough surface (SEM image, Figure 1b). The high-resolution resolution-transmission electron microscope (HR-TEM) image of 350-IrO$_2$ (Figure 1c) reveals that the metallic Ir was oxidized into rutile IrO$_2$ nanoparticles with a slightly increased particle size, along with generating abundant grain boundaries (GBs) during the crystal propagation process. Distinct polycrystalline diffraction rings attributed to IrO$_2$ nanoparticles are observed in the selected area electron diffraction (SAED, Figure 1c inset) diagram of 350-IrO$_2$. The uniform distribution of Ir and O elements in energy-dispersive X-ray spectroscopy (EDX, Figure S8) further indicates the oxidation of Ir nanoparticles into IrO$_2$ at 350°C. As shown in the TEM profiles (Figure S9) and XRD patterns (Figure 1d), when the sinttering temperature is increased (400 and 450°C), the resultant 400-IrO$_2$ and 450-IrO$_2$ exhibit similar oxidation and propagation processes with 350-IrO$_2$. Among them, the size of IrO$_2$ nanoparticles significantly increases upon the increase in sinttering temperature, which might lead to a reduction in GBs content. Interestingly, the (110) crystal plane of rod-shaped rutile-phase iridium dioxide was observed in 450-IrO$_2$, whereas this specific orientation was absent in 350-IrO$_2$ and 400-IrO$_2$, which is consistent with the XRD results. The broadening of full width at half maximum (FWHM) of prepared electrocatalyst in XRD patterns further verified the size growth of IrO$_2$ nanoparticles with the increase in calcination temperature, in accordance with the TEM results. Moreover, the increased intensity of the (110) diffraction peak indicates the beneficial growth of the thermodynamically stable (110) crystal face in 450-IrO$_2$. However, this oriented growth is not observed in 350-IrO$_2$ and 400-IrO$_2$. It is thus clear that the GBs between crystal faces in these synthesized IrO$_2$ will be enriched upon decreasing the pyrolysis temperature, which likely facilitates the OER process on IrO$_2$.

The electronic configuration and local coordination information of prepared electrocatalysts were collected by XPS and synchrotron X-ray absorption spectroscopy (XAS) spectra. As displayed in Figure 2a, the high-resolution O 1s XPS spectra can be deconvoluted into three peaks: the oxygen in adsorbed water (O$_{ads}$) at 529.8 eV, the lattice oxygen (O$_{lat}$) at 526.0 eV and the adsorbed oxygen (O$_{ads}$) at 528.0 eV. The result indicates (Table S1) the lowest surface O$_{lat}$ content (12.42%) in 350-IrO$_2$, which is likely attributed to the unsaturated coordination Ir sites formed by the abundant GBs defects. The white line peak intensity in X-ray absorption near edge structure (XANES, Figure 2b) spectrum at Ir $L_3$-edge is proportional to the oxidation state of Ir, indicating the reduction in valence state caused by unsaturated coordination sites. As shown in Ir $4f$ XPS spectra (Figure 2c), the lower binding energy of 350-IrO$_2$ further verified the lower Ir valence state compared to the controlled samples and C–IrO$_2$. Furthermore, the analyses of the

![Figure 2](image_url)

**Figure 2.** (a) O 1s XPS spectra of 350-IrO$_2$, 400-IrO$_2$, and 450-IrO$_2$. (b) Ir $L_3$-edge XANES spectra of 350-IrO$_2$, 400-IrO$_2$, 450-IrO$_2$, Ir foil, and C–IrO$_2$. (c) Ir 4f XPS spectra of 350-IrO$_2$, 400-IrO$_2$, 450-IrO$_2$, and C–IrO$_2$. (d) EXAFS spectra of 350-IrO$_2$, 400-IrO$_2$, 450-IrO$_2$, and C–IrO$_2$. 

extended X-ray absorption fine structure (EXAFS, Figure 2d) spectra are conducted. The corresponding fitting results of the first shell Ir–O (Figure S10 and Table S2) reveal the coordination structures of 350-IrO$_2$, 400-IrO$_2$, 450-IrO$_2$, and C-IrO$_2$. The series electrocatalysts of IrO$_2$ with GBs exhibit nearly similar Ir–O bond lengths compared to the commercial rutile IrO$_2$ (C-IrO$_2$), indicating the preservation of the stable rutile structure, which is comprised of the Ir atom as the coordination center and the IrO$_6$ octahedra serves as the basic hexacoordinated structural units.\(^{19}\) Differently, the coordination number (CN) of Ir for 350-IrO$_2$, 400-IrO$_2$, and 450-IrO$_2$, decreases along with reducing the sintering temperature. The decrease in the CN value is ascribed to a large population of surface and corner Ir atoms arising from the GBs,\(^{20}\) which agrees well with the morphology and XPS analysis.

The control samples (350-no GBs and 450-no JH (JH: joule heating) are also prepared to evaluate the influence of GBs and joule heating pretreatment, respectively. It is worth noting that the PCNF as a sacrificed template is important for generating IrO$_2$. For comparison, carbon nanotubes (CNTs) are chosen as the template due to their feature of higher graphitization, providing enhanced oxidation resistance in air. Similarly, after wet impregnating and joule heating to load Ir nanoparticles, the 350-no GBs is obtained after calcination at 350 °C. TEM and XRD (Figure S11) analysis confirms the successful synthesis of IrO$_2$ nanoparticles with approximately 2 nm in diameter independently distributed on the surface of CNTs. Differently, GBs were not observed in 350-no GBs. In addition, the counterpart (450-no JH) synthesized by the traditional heating process rather than the joule heating was also synthesized. A minimum pyrolysis temperature of 450 °C is required for the complete conversion of iridium salts into IrO$_2$ during the slow heating process because of the fact that the decomposition and oxidation temperature of IrCl$_3$ is higher than the direct oxidation temperature of metallic Ir nanoparticles. Compared to 450-IrO$_2$, the uneven distribution of IrO$_2$ nanoparticles is observed in 450-no JH as indicated by the TEM results (Figure S12). Thus, the rapid pyrolysis via the joule heating pretreatment is effective in reducing the phase transition temperature of iridium salts into the IrO$_2$, resulting in finer nanoparticles and facilitating the enrichment of GBs.

2.2. Electrochemical Acidic OER Analysis

The electrocatalytic OER activities of the synthesized samples were evaluated in 0.5 M H$_2$SO$_4$ with a three-electrode system. As shown in the OER polarization curves in Figure 3a, 350-IrO$_2$ only requires a lower overpotential of 246 mV than that of commercial IrO$_2$ (C-IrO$_2$) with 376 mV to achieve the benchmark current density of 10 mA cm$^{-2}$. Along with the reduced pyrolysis temperature (450–350 °C), overpotential at 10 mA cm$^{-2}$ for these samples under various pyrolysis temperatures is decreased with the order of 350-IrO$_2$ (246 mV) < 400-IrO$_2$ (260 mV) < 450-IrO$_2$.
(273 mV), which are all lower than 350-no GBs (477 mV) and 450-no JH (287 mV) as shown in Figure S14. These results verify a positive correlation between the content of GBs defects and OER activity. Moreover, 350-IrO2 exhibits a lower Tafel slope (Figure 3b and S15) of 49.51 mV dec
\(^{-1}\), compared to the 400-IrO2 (54.87 mV dec
\(^{-1}\)), 450-IrO2 (60.18 mV dec
\(^{-1}\)), and C–IrO2 (100.53 mV dec
\(^{-1}\)), which indicated the fast reaction kinetics on the active surface. Additionally, the mass activity normalized by the Ir mass at 1.5 V vs. RHE (overpotential = 270 mV) is shown in Figure 3c and S14. The activity superiority of 350-IrO2 is further gleaned from its highest mass activity as 0.61 A mg
\(^{-1}\) compared to the counterparts. After excluding the influence of factors such as particle size and synthesis temperature, 350-no GBs shows obviously lower mass activity (0.31 A mg
\(^{-1}\)), which strongly indicates that GBs significantly enhance the OER activity. The double-layer capacitance (C
\text{dl}\) Figure S16) of all the electrocatalysts is estimated by voltammetry (CV) curves measured at different scan rates in non-faraday potential regions to evaluate their electrochemically active surface areas (ECSA).

The 350-IrO2 shows the highest C
\text{dl}\) value as 162.2 mF cm
\(^{-2}\), suggesting its higher ECSA with exposure to more accessible active sites. The better acidic OER activity of 350-IrO2 is further confirmed by the electrochemical impedance spectroscopy (EIS) measurements in Figure S17. The charge transfer resistance (R
\text{ct}\) of 350-IrO2 is as low as 10 Ω, indicating the fast charge transfer on the surface, which can contribute to the fast reaction kinetics.

To evaluate the stability of the 350-IrO2 under the corrosive acidic and oxidation conditions, chronopotentiometry (CP) is carried out in 0.5 M H
\text{2}SO\text{4}\ as shown in Figure 3d, only a trace potential increase of 11.8 mV for 350-IrO2 is observed after the continuous OER operation for 200 h. However, the activity of C–IrO2 experienced terrible decay after operating for 1.5 h CP test (Figure S18), indicating better acidic OER durability for 350-IrO2. In addition, 350-IrO2 exhibits high activity and stability compared with other advanced Ir based catalysts in Table S3. The S-number, which is defined as the ratio of the amount of generated oxygen and the dissolved iridium into the electrolyte, was further utilized to illustrate the stability of the catalyst.

According to the inductively coupled plasma-mass spectroscopy (ICP-MS, Table S3), it is calculated to be 2.50×10
\(^{4}\) for 350-IrO2, revealing its good acidic corrosion and stability during OER process. Furthermore, TEM (Figure S19a) results after the OER test of 350-IrO2 show no significant changes in structure and morphology, highlighting the good stability of 350-IrO2. Similarly, 350-IrO2 maintains the rutile structure after the long-term OER tests as indicated by the XRD pattern (Figure S19b) results.

Encouraged by the high activity and stability of acidic OER in a three-electrode configuration, a catalyst-coated membrane (CCM) using 350-IrO2 as anode is employed to evaluate its performance in a PEMWE device. The polarization curve (Figure 4a) operated at 80 °C exhibits high activity of the output voltage of 1.68 V and 1.84 V at 1 A cm
\(^{-2}\) and 2 A cm
\(^{-2}\), respectively. The long-term stability (Figure 4b) could be operated at 1 A cm
\(^{-2}\) for at least 100 h without obvious performance decay. And the S-number (Table S4) of 350-IrO2 is 5.33×10
\(^{7}\) in the PEMWE configuration. The high performance of 350-IrO2 in PEMWE highlights the feasibility of 350-IrO2 in practical application.

2.3. DFT Calculations

Density functional theory (DFT) calculations are conducted to further understand the origin of the OER activity of 350-IrO2 with rich GBs as compared to rutile IrO2. The thermodynamically stable (110) facet is chosen to model the rutile IrO2(Figure S20a). Given the complexity of crystal facets of the synthesized IrO2, the predominant (110) and (101) facets are selected for 350-IrO2, (Figure S20b).

Based on the computed projected density of state (PDOS, Figure 5a and 5b) results, the electrons near the Fermi level become delocalized in rutile IrO2 with GBs compared to rutile IrO2, indicating the role of GBs engineering in tuning the electronic structure of IrO2. The proximity of the Ir 5d-band center (\(\epsilon_p\) to the Fermi level in the GBs model (−2.165 eV) demonstrates the enhanced binding ability between Ir active sites and oxygen intermediates.

Additionally, with the Fermi level energy lowering the energy and moving closer to O 2p states in rutile IrO2 with GBs (\(\epsilon_p = −3.37\ eV\) compared to the rutile IrO2 (\(\epsilon_p = −4.39\ eV\)), the covalency of the Ir–O bond is

**Figure 4.** (a) Polarization curve of the PEMWE using 350-IrO2 as anode electrocatalyst. (b) Chronopotentiometry curve of the PEMWE using 350-IrO2 as anode electrocatalyst operated at 1 A cm
\(^{-2}\) (inset shows the schematics of PEMWE).
enhanced by the presence of GBs wherein strong covalency of Ir–O is associated with the high OER activity. Therefore, when the O 2p states approach the Fermi level, water decomposition becomes more thermodynamically favorable.\textsuperscript{[24]} It is thus clear that GBs can modulate the electronic structure of surface Ir active sites, thereby influencing the adsorption behavior of oxygen intermediates and enhancing OER activity through an increase in covalency.\textsuperscript{[25]}

The adsorbate evolution mechanism (AEM) is widely accepted for the crystallized IrO$_2$ and it was confirmed with numerous experimental investigations.\textsuperscript{[26]} In this mechanism, OER at applied electrocatalysts proceeds via four proton-coupled electron transfer (PCET) steps (Figure 5c and S21) with OH*, O*, and *OOH intermediates, respectively. Figure 5d illustrates the free energy diagrams calculated on both the surfaces of rutile IrO$_2$ with and without GBs. The second proton-couple electron transfer step (OH* \rightarrow O*) with the highest energy uptake (\(\Delta G_2 = 2.1\) eV, Table S5) is the potential determined step (PDS) on rutile IrO$_2$. The introduction of GBs significantly decreases \(\Delta G_2\) for 350-IrO$_2$ (1.5 eV) and thus changes the PDS to the last step (OOH* \rightarrow slab*) with the energy barrier as 1.6 eV. Combining the PDOS results, it is evident that GBs optimize the adsorption capacity of Ir active sites for oxygen species, thereby lowering the reaction barrier. Thus, it requires only 1.63 V to drive the OER reaction for rutile IrO$_2$ with GBs. The free energy calculations suggest that GBs effectively contribute to optimizing the adsorption of oxygen intermediates at Ir sites toward fast OER kinetics.

3. Conclusions

In summary, we optimized the pathway from iridium chloride pyrolysis into IrO$_2$ by joule heating pretreatment, resulting in ultrasmall IrO$_2$ nanoparticles with abundant GBs and uniform particle size. The optimal 350-IrO$_2$ exhibits high activity and stability with a low overpotential of 246 mV and stability of 200 h at 10 mA cm$^{-2}$. DFT calculations reveal that GBs modify the surface electronic structures, thus leading to the appropriate adsorption ability on Ir sites and enhancing the OER activity. Benefiting from the controllable synthesis and the introduction of GB defects, the prepared 350-IrO$_2$ enables highly efficient and stable hydrogen production in PEMWE under 1 A cm$^{-2}$. This work not only presents one promising OER electrocatalyst for the efficient PEMWE but also provides ideas for engineering grain boundary defects in nanocatalysts and understanding the correlation between the surface structure and OER performance.

4. Supporting Information

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

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Conflict of Interests
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: water electrolysis · acidic oxygen evolution reaction · electrocatalysts · joule heating · rutile-type IrO$_2$ · grain boundary

Joule heating pretreatment and carbon templates are used to construct grain boundary-rich IrO$_2$ nanoparticles for promoting acidic oxygen evolution reaction (OER). The assembled proton exchange membrane water electrolysis (PEMWE) with the optimized catalyst (350-IrO$_2$) exhibits high activity (1.68 V at 1 A cm$^{-2}$, 1.84 V at 2 A cm$^{-2}$) and stability (100 h at 1 A cm$^{-2}$).


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