Strong Oxide-Support Interaction over IrO$_2$/V$_2$O$_5$ for Efficient pH-Universal Water Splitting

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Constructing strong oxide-support interaction (SOSI) is compelling for modulating the atomic configurations and electronic structures of supported catalysts. Herein, ultratine iridium oxide nanoclusters ($\approx$ 1 nm) are anchored on vanadium oxide support (IrO$_2$/V$_2$O$_5$) via SOSI. The as made catalyst, with a unique distorted IrO$_2$ structure, is discovered to significantly boost the performance for pH-universal oxygen evolution reaction (OER). Based on experimental results and theoretical calculations, the distorted IrO$_2$ active sites with flexible redox states in IrO$_2$/V$_2$O$_5$ serve as electrophilic centers balance the adsorption of oxo-intermediates and effectively facilitate the process of O–O coupling, eventually propelling the fast turnover of water oxidation. As a result, IrO$_2$/V$_2$O$_5$ demonstrates not only ultralow overpotentials at 10 mA cm$^{-2}$ (266 mV, pH = 0; 329 mV, pH = 7; 283 mV, pH = 14) for OER, but also high-performance overall water electrolysis over a broad pH range, with a potential of mere 1.50 V (pH = 0), 1.65 V (pH = 7) or 1.49 V (pH = 14) at 10 mA cm$^{-2}$. In addition, SOSI can simultaneously secure the distorted active sites and thus remarkably improving the catalytic stability, making it a promising strategy to develop high-performance catalytic systems.

1. Introduction

Electricity-driven water splitting to produce hydrogen (H$_2$) powered by renewable energy has been considered a prospective strategy to develop sustainable, fossil-free and global-scale energy systems.[1–3] Electro-catalysts are the central part of the hydrogen and oxygen evolution reactions (HER and OER). Significant success has been realized in the field of HER and overpotential at 10 mA cm$^{-2}$ can be lower than 20 mV.[4–6] To date, the large-scale industrial water electrolysis is hindered by the huge energy consumption derived from the large overpotential of OER.[7–10] Basically, producing one oxygen molecule involves the sluggish kinetics of four electrons transfer and the formation of O–O bond.[9,10] Consequently, exploring advanced OER electro-catalysts is vital for improving the energy conversion efficiency of water electrolyzers and has been drawn considerable attention in recent years.[11–13] In principle, the binding energies of multiple intermediates (*OH, *O, and *OOH) in OER are correlated with each other. Typically, the adsorption energy difference between *OOH and *OH is about 3.2 ± 0.2 eV because of scaling relation of the two intermediates without regarding of catalyst type.[14–16] According to the volcano plot of $\eta_{\text{OER}}$ versus ($\Delta G_{\text{OOH}}$ − $\Delta G_{\text{OOH}}$), the catalyst with oxygen binding that is neither too strong nor too weak shows optimal activity.[14,17] To date, several approaches have been reported for modulating oxygen intermediate adsorption energy, including substituting with foreign elements,[18,19] heterostructure modulating,[20,21] strain engineering,[22,23] nanoscopic confinement[24] and so on. So far, the overpotentials values of state-of-the-art OER catalysts at 10 mA cm$^{-2}$ are smaller than 200 mV[25–27] however, most of them can only be applied in a certain pH or specific working scenarios. In order to meet the complicated working conditions, it is highly urgent to develop a high-performance catalyst that is universally compatible to optimize the reliability during operation.

In the past decades, constructing strong metal/metal oxide-support interaction (SMSI/SOSI) has attracted great attentions due to its intriguing capabilities for designing advanced catalysts with unique properties.[28–31] On the one hand, the electron re-location on the interface will modulate electronic properties of active sites,[32] On the other hand, distinctive structure deformation as well as diverse atomic coordination environment would appear at the interface, both of which will significantly affect the electrocatalytic performance.[32] Although the idea of manufacturing supported catalysts seems to be clear-cut, the individual
components must be carefully selected for specific purposes to take advantage of this catalyst design strategy. In term of constructing supported OER electrocatalysts, IrO₂ and VOₓ (1 ≤ x ≤ 2.5) would be appropriate building blocks. Though IrO₂ is an excellent benchmark catalyst for OER in acidic media, the binding between IrO₂ and oxygen-related intermediates is still strong, limiting its OER performance.[14,33] A large space exists for the property enhancement of IrO₂ by modifying geometric and electronic structures, which can lead to optimized interaction between the catalyst and oxygen intermediates.[34] Recently, owing to their excellent interactions with molecules or ions, outstanding catalytic activities, and/or strong electron-electron correlations, nanostructured vanadium oxides-based composite materials have been extensively studied for energy conversion (water splitting, carbon dioxide reduction and alcohol oxidation) reactions in the recent years.[35–39] Benefit from the multiple valence states, V₂O₅ exhibits redox and Lewis acid/base properties, which makes strong interaction with foreign active materials. On the one hand, strong interaction is beneficial to regulate the intrinsic activity of active species, and on the other hand, it also plays a role in stabilizing the substrate. Additionally, vanadium oxide can facilitate the hydrolysis kinetics and provide hydrogen protons during electrochemical process, which has been considered important in surface catalytic reactions.[40] Inspired by the aforementioned discussions, we envisioned whether a rational modification of IrO₂ on VOₓ support could integrally construct a supported catalyst with strong oxide-support interaction, and improve catalytic activity and durability.

Herein, a simple method was developed to prepare highly dispersed IrO₂/V₂O₅ catalysts in which vanadium containing MOF MIL-88B (V) was used as a host. After impregnating with Ir precursor and then annealing under air atmosphere, IrO₂ nanoclusters (∼1 nm), with unique distorted and deformed lattice fringes induced by SOSI, are uniformly embedded in the porous network of V₂O₅. Contrast experiments and theoretical calculations indicated that the SOSI between IrO₂ and V₂O₅, i.e., the SOSI induced lattice fringes’ distortion exposed more catalytic active sites and enhanced the redox states of electrophilic IrO₂, can significantly promote the OER performance of IrO₂ over a wide pH range (pH = 0–14, 1–2 orders of magnitude higher intrinsic and mass activity than commercial IrO₂) as well as durability.

2. Results and Discussion

2.1. Preparation and Structure Characterization of Catalysts

The synthesis of the IrO₂/V₂O₅ hybrid oxides is illustrated in Scheme 1, which includes the synthesis of the Ir(III)/MIL-88B (V) precursors and the subsequent thermal pyrolysis. First of all, MIL-88B (V) was synthesized by scalable hydrothermal method,[41] in which vanadium chloride and p-phthalic acid were used as raw materials. And then Ir(III) ions can be readily hosted within MIL-88B (V) by means of impregnation. An apparent color change from dark green to brown can be observed over the parent MIL-88B (V) and Ir(III)/MIL-88B (V), which indicates the successful incorporation of the Ir(III) ions into MIL-88B (V). The power X-ray diffractions (XRD) patterns of both MIL-88B (V) and Ir(III)/MIL-88B (V) (Figure S1, Supporting Information) show the similar characteristic peaks, suggesting that the presence of Ir(III) (Figure S2, Supporting Information) has no apparent influence on the crystalline structure of MIL-88B (V). Meanwhile, there was no peak for IrCl₃ or other Ir-V mixed materials, indicating that IrCl₃ did not crystalize or interact with MIL-88B (V) to form Ir-V mixed material in the pores of MIL-88B (V) but was adsorbed on the pore surface. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of MIL-88B (V) and Ir-MIL-88B (V) exhibit similar shuttle-like morphology (Figure 1a and Figure S3, Supporting Information), and element distribution analysis of Ir-MIL-88B (V) indicates the Ir and V atoms are uniformly distributed to form the hybrids. Subsequently, black powder IrO₂/V₂O₅ was obtained by annealing Ir(III)/MIL-88B (V) under air atmosphere. As a comparison, MIL-88B (V) was treated in the same condition to produce yellow powder V₂O₅. As shown in Figure 1b, IrO₂/V₂O₅ inherits the original shuttle-like morphology of MIL-88B (V) with rough surface and porous structure. However, SEM and TEM images (Figure S4, Supporting Information) of V₂O₅ exhibit rod-like morphology composed of many nanoplates, affirming that introduction of Ir is beneficial to stabilize the shuttle-like structure and form porous skeleton during postannealing process. Nitrogen adsorption/desorption measurement evidenced that the specific surface area of IrO₂/V₂O₅ is 40 m² g⁻¹, which is higher than that of V₂O₅ (18 m² g⁻¹) as shown in Figure S5 (Supporting Information). XRD measurement (Figure 1c) demonstrates

Scheme 1. Schematic illustration of the preparation of IrO₂/V₂O₅ hybrid oxides electrocatalysts.
Figure 1. Morphology and structural characteristics of catalysts. The SEM images of a) MIL-88B (V) and b) IrO$_2$/V$_2$O$_5$; the inserts show corresponding TEM images. c) XRD patterns of IrO$_2$/V$_2$O$_5$, V$_2$O$_5$, and IrO$_2$. d-e) The HRTEM images of IrO$_2$/V$_2$O$_5$; the insert in (d) is the size distribution pattern. f) The HRTEM image of IrO$_2$/HPC; g) H$_2$-TPR patterns of IrO$_2$/V$_2$O$_5$, IrO$_2$/HPC, and V$_2$O$_5$. h) Ir 4f spectra of IrO$_2$/V$_2$O$_5$, IrO$_2$/HPC, and commercial IrO$_2$. i) V 2p$_{3/2}$ spectra of IrO$_2$/V$_2$O$_5$ and V$_2$O$_5$. j) Top and side views of charge density difference in the interface of Ir$_4$O$_8$/V$_2$O$_5$ and Ir$_5$O$_{10}$/V$_2$O$_5$; the cyan region reflects an electron-deficient state while the yellow region reflects an electron-rich area; the insert shows Ir Bader charge transfer of Ir$_4$O$_8$/V$_2$O$_5$ and Ir$_5$O$_{10}$/C (the cyan region reflects an electron-deficient state while the yellow region reflects an electron-rich area); the insert shows Ir Bader charge transfer of Ir$_4$O$_8$/V$_2$O$_5$ and Ir$_5$O$_{10}$/C. k) The pDOS of d orbitals of Ir and V in Ir$_4$O$_8$/V$_2$O$_5$, and the d orbitals of Ir and p orbitals of C in Ir$_5$O$_{10}$/C, respectively.
signed hierarchically porous carbon-supported IrO2 catalysts,
To systemically investigate the possible SOSI, we delicately detec-
file of IrO2/HPC is characterized by a single and sharp peak at
photoelectron spectroscopy (XPS), and density functional theory
while, the reduction temperature of V2O5 species in IrO2/V2O5
197 °C approximately interacted with the V2O5 support at the interface. Mean-
detected, which may be attributed to iridium oxide species inti-
° 2.2. In-Depth Understanding of SOSI Effect of IrO2/V2O5
To further figure out the effect of SOSI on the properties of cata-
ysts, H2 temperature programmed reduction (H2-TPR), X-ray photoelectron spectroscopy (XPS), and density functional theory
(DFT) calculations were carried out. Figure 1g shows the H2-TPR profiles of IrO2/V2O5, IrO2/HPC and V2O5. The reduction pro-
file of IrO2/HPC is characterized by a single and sharp peak at
197 °C, assigned to the reduction of iridium oxide species,[45,46] which is similar to reduction temperature of commercial IrO2
(210 °C) (Figure S11, Supporting Information). Pure V2O5 mate-
rial presents main hydrogen consumption peaks at about 430–
590 °C, showing high oxidation state (V) of V reduced to low
interaction between IrO2 and V2O5. In contrast, the pDOS curves of
IrO2/C elucidate that less orbitals coupling between Ir d orbitals and C p orbitals leads to the weak interaction.
2.3. Catalytic Activity towards OER
The catalytic properties of IrO2/V2O5 and IrO2/HPC toward
the OER were then systematically evaluated in a typical three-electrode set-up in a wide pH range (0–14), along with commercial rutile IrO2 (consisted of 20–300 nm irregular particles, see Figure S13, Supporting Information) and V2O5 substrate as comparison. Prior to this, by optimizing the synthesis conditions of
IrO2/V2O5, 400 °C and 4 h are suitable calcination temperature and time to obtain optimal OER performance for subse-
quent comparison (Figures S14–S16, Supporting Information). Specially, IrO2/V2O5 gives an extremely low OER overpotential of
266 mV at 10 mA cm−2 (Figure 2a,b) and a Tafel slope of 56 mV
dec−1 in and 0.5 M H2SO4, both significantly lower than that of
IrO2/HPC (307 mV, 83 mV dec−1), commercial IrO2 (379 mV, 93 mV dec−1), and V2O5 support. Notably, the acidic OER catal-
alytic activity is also superior to most of the recently reported landmark catalysts (Figure 2c and Table S4, Supporting Informa-
tion). When electrolyte is switched to 1 M PBS (Figure 2d,e), as expected, IrO2/HPC and commercial IrO2 display almost inert or
pure V2O5. Based on the results of H2-TPR measurement, we
convinced that the strong interaction between IrO2 species and
V2O5 support is successfully constructed.
XPS was carried out to characterize the surface structure of the catalyst. As shown in Figure 1h,i and Figure S12 (Supporting
Information), in the typical Ir 4f spectra of commercial IrO2
and IrO2/HPC fit parameters are provided in Table S2, Supporting
Information), the peaks at around 61.95 and 64.95 eV can be mainly attributed to 4f7/2 and 4f5/2 of Ir4+, respectively, follow-
by three satellite peaks.[24,48] Compared with commercial IrO2
and IrO2/HPC, it is clear that the binding energy of Ir4+
for IrO2/V2O5 is positively shifted by 0.46 eV up to 62.41 and
65.41 eV. Combining with the discussion of H2-TPR, we claimed
that a decreased charge density of Ir is responsible for the higher
binding energy rather than forming Ir5+ with a reverse core level
shft. In the V 2p1/2 XPS spectra (details see Table S3, Supporting
Information), the V5+ peak at 517.30 eV is dominant in the
pure V2O5 sample, accompanied by weak peak of V4+ centered
at 516.05 eV (AV5+:AV4+= 0.087). As excepted, apart from typical
V5+ signal, the intensity of V4+ peak significantly enhances
in IrO2/V2O5 hybrid oxide (AV4+:AV5+= 0.3).[49] These results
point to the highly strong electron coupling effect between IrO2
NCs and V2O5 support with the charge transfer from the IrO2
to V2O5. DFT calculations were additionally performed for ana-
lyzing the charge transfer and internal interactions between IrO2
NCs and V2O5 and C supports, respectively. As shown in Fig-
ure 1j, we obviously observe that the strong charge redistribution
occurs at the interface region of IrO2/V2O5. According to Bader
charge analysis, a partial charge transfer of 1.03 e− from Ir to
the V2O5 was found, while only charge transfer of 0.08 e− is
discovered in IrO2/C system, which is in good agreement with the
XPS analysis. The projected density of states (pDOS) curves of
IrO2/V2O5 (Figure 1k) show that the peaks of Ir d orbitals and V
d orbitals overlap well around Fermi level, affirming the strong
interaction between IrO2 and V2O5. In contrast, the pDOS curves of
IrO2/C elucidate that less orbitals coupling between Ir d orbitals
and C p orbitals leads to the weak interaction.
Figure 2. OER activity comparison (Ir loading with 0.1 mg cm$^{-2}$). a) The steady-state polarization curves were obtained with a low scan rate of 1 mV s$^{-1}$. b) Tafel plots of different electrocatalysts in 0.5 M H$_2$SO$_4$, and c) comparison of acidic OER activity between IrO$_2$/V$_2$O$_5$ and recently reported electrocatalysts. d) The steady-state polarization curves. e) Tafel plots of different electrocatalysts in 1 M PBS, and f) comparison of neutral OER activity between IrO$_2$/V$_2$O$_5$ and recently reported electrocatalysts. g) The steady-state polarization curves, h) Tafel plots of different electrocatalysts in 1 M KOH, and i) comparison of alkaline OER activity between IrO$_2$/V$_2$O$_5$ and recently reported electrocatalysts. j) The number of active sites in IrO$_2$/V$_2$O$_5$, IrO$_2$/HPC, and commercial IrO$_2$ measured with Cu-UPD method. k) TOF values and l) mass activity of IrO$_2$/V$_2$O$_5$, IrO$_2$/HPC, and commercial IrO$_2$ at 1.53 V$_{RHE}$ for OER.
inferior performance as result of intrinsic sluggish kinetics under neutral condition. In stark contrast, IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} still demonstrates unprecedented catalytic capability with a small overpotential of 329 mV at 10 mA cm\textsuperscript{−2}. Tafel slope plots further elucidate the accelerated kinetics of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} (67 mV dec\textsuperscript{−1}) in neutral-pH media, which opens the door to the realization of efficient and biocompatible systems for energy storage and conversion, as well as for direct seawater splitting.\cite{50,51} The comparison of OER activity with state-of-art catalysts also indicates that IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} ranks among the top neutral OER catalysts (Figure 2f and Table S5, Supporting Information). Undoubtedly, IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} performs well in 1 M KOH electrolyte, requiring a low overpotential of 283 mV to attain 10 mA cm\textsuperscript{−2} and an unprecedented low Tafel slope of 34 mV dec\textsuperscript{−1}, far superior to those of IrO\textsubscript{2}/HPC, commercial IrO\textsubscript{2} and IrO\textsubscript{2}/HPC and outstanding reported alkaline OER catalysts (Figure 2g-i and Table S6, Supporting Information). It is worth mentioning that electrocatalytic activity is tightly connected with the capability of charge transfer, the number of active sites and turnover rates.\cite{52–55} Therefore, the electrochemical impedance spectroscopy (EIS) was first performed to investigate the interface charge transfer process of the electrode. The semicircular diameter of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} in Nyquist plots is much smaller than that of IrO\textsubscript{2}/HPC, commercial IrO\textsubscript{2} and V\textsubscript{2}O\textsubscript{5} in all-pH range, as revealed in Figure S17 (Supporting Information), which indicates smaller charge transfer resistance induced by rapid interfacial electron migration between distorted IrO\textsubscript{2} and V\textsubscript{2}O\textsubscript{5} support. The high density of active sites plays an important role in the improvement of catalytic activity. In order to quantitatively analyze the number of active sites, underpotential deposition of copper (Cu-UPD) was then conducted to measure the active site density.\cite{55} As is seen in Figure 2j and Figure S18 (Supporting Information), compared with commercial IrO\textsubscript{2} (4.80 × 10\textsuperscript{−8} mol) and IrO\textsubscript{2}/HPC (4.94 × 10\textsuperscript{−8} mol), an increase in the number of active sites can be observed for IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} (5.51 × 10\textsuperscript{−8} mol). As mentioned above, the small NCs (=1 nm) consists of unique structure distortion, which endows the IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} catalyst with a high exposure of IrO\textsubscript{2} active sites as well as a high accessibility for substrate molecules. The turnover frequencies (TOFs) based on the number of active sites of the catalyst was calculated to evaluate the intrinsic activity of a catalyst. As illustrated in Figure 2k and Figure S19 (Supporting Information), with the overpotential increase to 300 mV of OER, the TOF values of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} even reach 0.27, 0.19, and 0.05 O\textsubscript{2} s\textsuperscript{−1}, which are about 3.0, 6.3, and 2.5 folds of those of IrO\textsubscript{2}/HPC (0.09, 0.03, and 0.02 O\textsubscript{2} s\textsuperscript{−1}), and far surpassing commercial IrO\textsubscript{2} in acidic, alkaline and neutral media, respectively. As one of precious metal, the mass activity of Ir-based electrocatalysts is of great importance for industrial application. Mass activity of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} is 287, 207, and 56 A g\textsubscript{Ir}\textsuperscript{−1}, which is about 3.4, 7.7, and 2.7 folds of those of IrO\textsubscript{2}/HPC (84, 27, and 21 A g\textsubscript{Ir}\textsuperscript{−1}), and 1-2 orders of magnitude larger than those of commercial IrO\textsubscript{2} in acidic, alkaline and neutral media at the overpotential of 300 mV (Figure 2l and Figure S20, Supporting Information), respectively, strongly verifying the enhanced intrinsic activity of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5}. Stability is an important criterion to evaluate the performance of catalysts. The stability of the IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5}, IrO\textsubscript{2}/HPC and commercial IrO\textsubscript{2} catalysts were assessed by using static chronopotentiometry test and transient accelerated degradation test (ADT) protocol on Au electrode (avoiding the influence of back electrode to stability analysis).\cite{56,57} The static chronopotentiometry test (at 10 mA cm\textsuperscript{−2}) is conventional way to evaluate the stability, as plotted in Figure 3a, the IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} catalyst represents a relatively stable horizontal line in different electrolyte (even in the acidic media) during 20 operating hours, while IrO\textsubscript{2}/HPC and commercial IrO\textsubscript{2} exhibit a progressive activity decay within a few hours, demonstrating the outstanding activity retention of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5}, which is competitive to the state-of-art Ir-based OER catalysts reported in literatures (Table S7, Supporting Information). The detailed characterizations of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} and IrO\textsubscript{2}/HPC after durability are conducted to reveal the change of structures. The IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} postcatalyst maintains its original porous skeleton and IrO\textsubscript{2} nanoclusters are slightly aggregated (Figure 3b and Figure S21, Supporting Information). Although the distorted structure is detected, it is not as obvious as the original state, which is ascribed to the loss of V\textsubscript{2}O\textsubscript{5} support confirmed by V\textsubscript{2}p spectra after stability test (Figure S22a, Supporting Information). Ir\textsuperscript{4f} spectra of postcatalyst exhibit the huge change of line-shape (Figure S22b, Supporting Information), and an amount of Ir(III) species (4f\textsubscript{7/2}: 63.02 eV and 4f\textsubscript{5/2}: 66.02 eV) is available on the surface.\cite{58} In sharp contrast, as shown in Figure 3c and Figure S23 (Supporting Information), the IrO\textsubscript{2} NCs loaded on HPC after stability test are obviously agglomerated. Notably, static protocol is not sufficient to evaluate the stability of Ir-based OER catalysts. Therefore, the transient ADT protocol endows the catalyst to distinctly higher currents (double layer charging and fast redox reactions) than the static protocol at same potential, which is benefit to save time to investigate the durability. As seen in the Figure S24a–c (Supporting Information), with increasing the numbers of ADTs, the redox centered at 0.95–1.0 V \textit{RHE} and shifted to lower potential, which represents the typical transition of Ir\textsuperscript{III} to Ir\textsuperscript{IV}.\cite{50} agreeing with above results of Ir\textsuperscript{4f} spectra. The strong change in redox activity during ADTs is reflected by the increase in \( Q_{\text{anodic-final}} = 2.28 \text{ mC} > Q_{\text{anodic-initial}} = 1.92 \text{ mC} \). The same process is performed on IrO\textsubscript{2}/HPC in Figure S25a–c (Supporting Information) for comparison. The leaking extent of Ir or V from the electrode to electrolyte after ADTs test in 0.5 M H\textsubscript{2}SO\textsubscript{4} are determined by ICP-MS measurement. To show this more clearly, when the amount of dissolved Ir is normalized to time and to the geometric surface area, as shown in the Figure 3d, the Ir dissolution rate of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} (0.21 ug h\textsuperscript{−1} or 33.0 ug cm\textsuperscript{−2}) is much smaller than those of IrO\textsubscript{2}/HPC (0.33 ug h\textsuperscript{−1} or 51.3 ug cm\textsuperscript{−2}). Meanwhile, we observed that the V/Ir mass ratio of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} decreases from initial 2.1 to 1.7 due to the faster V dissolution rate (0.59 ug h\textsuperscript{−1} or 93.0 ug cm\textsuperscript{−2}). Furthermore, as displayed in Figure 3e, Figures S24d–f and S25d–f (Supporting Information), the observed activity \( j_{\text{pro-j}_{\text{dyn}}}, \text{and } j_{\text{mass}} \) remaining percentage of IrO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} at 1.53 V \textit{RHE} are 2 times higher than those of IrO\textsubscript{2}/HPC. These results collectively confirm that the SOSI effect between V\textsubscript{2}O\textsubscript{5} and IrO\textsubscript{2} can efficiently reduce the detrimental effects of agglomeration of particles and degradation of intrinsic or mass activity of Ir active sites.

2.4. DFT Calculations

DFT calculations were performed to unveil the mechanism of the OER from the view of atomic and electronic structures. Based on the amorphous and distorted iridium oxide structure observed
in HRTEM, the OER computational model adopt Ir₄O₈ cluster supported on V₂O₅ (001) substrate along with periodically interconnected rutile IrO₂ (110) as comparison. The elementary electrochemical steps for proposed the 4e⁻ mechanism of OER on Ir₄O₈/V₂O₅ and IrO₂ under acid and alkaline media are presented in Figure 4a, b, which is following conventional adsorbate evolution mechanism (AEM) pathway. The Ir atoms in both models serve as the active sites in the OER process. The computed energy landscapes of the OER steps at U = 0 and 1.23 V (acid OER) or 0.408 V (alkaline OER) for Ir₄O₈/V₂O₅ and IrO₂ are shown in Figure 4c, d. For both of the calculated configurations, the OER rate-determining step (RDS) is the formation of Ir-OOH* intermediate from Ir-O* with free energy barriers of 0.38 and 0.58 eV on Ir₄O₈/V₂O₅ and IrO₂ under the equilibrium potential, respectively, indicating that Ir₄O₈/V₂O₅ is more referable for OER. As demonstrated in Figure S26 and Table S8 (Supporting Information), compared with IrO₂ (ΔE_O* = 1.35 eV, L_{Ir-O*} = 1.78 Å), the obvious reduced oxygen adsorption energy (ΔE_O* = 2.02 eV) and enlarged Ir-O* bond length (L = 1.82 Å) on Ir₄O₈/V₂O₅ may result in the relatively higher OER activity. This is consistent with the results by Nørskov and coworkers that catalyst can bind O too strongly and the overall reaction is limited by the O–O coupling process, and appropriately weakening the strength of M–O* is beneficial to reduce the barrier for the formation of M–OOH*.

Obviously, the SOSI between V₂O₅ and IrO₂ weakens the binding of IrO₂ with oxygen. To figure out the surface electronic features of catalyst is conducive to better understanding the discrepancy of oxygen adsorption energy, therefore, the d-band centers of the Ir atoms of Ir₄O₈/V₂O₅ and IrO₂ were calculated (Figure 4e). It is found that the d-band center of Ir atoms (−2.52 eV) of Ir₄O₈/V₂O₅ is far away from the Fermi level compared to that
of IrO$_2$ (−1.75 eV). It is well known that the lower the center of d-band relates, the higher the antibonding states, leading to weak adsorption (Figure 4f). Furthermore, the pDOS curves of Ir d-bands in IrO$_2$/V$_2$O$_5$ suggest that there are the more unoccupied $e_g$ states at 0.2 to 1.2 eV above Fermi level (Figure 4g), which indicated that the V$_2$O$_5$ support regulates the $e_g$ occupancy to affect the bonding of oxygen intermediate in the AEM,$^{[12,60]}$ thus promoting OER. To further quantitatively reveal the interaction between Ir active sites and adsorbed O*, crystal orbital Hamilton population (COHP)$^{[61,62]}$ were calculated to represent the bonding and antibonding filling states of Ir-O*. As illustrated in Figure 4h and Figure S27 (Supporting Information), the values of integrated COHP (ICOHP) for Ir–O* bond is computed on Ir$_4$O$_8$/V$_2$O$_5$ (−2.67 eV) and IrO$_2$ (−2.84 eV) by calculating the energy of COHP integral up to the Fermi level, where the more positive ICOHP value on Ir$_4$O$_8$/V$_2$O$_5$ indicates the weaker bonding. In rutile IrO$_2$, O–O bond formation may be hindered by its “rigid” periodically linked structure, while distorted structures of Ir$_4$O$_8$/V$_2$O$_5$ enables the iridium oxide species more “flexible” during the oxidation-reduction cycles to accelerate the hydroxyl ox-
2.5. Overall Water Splitting Performance

Besides, we also evaluated the HER performance of IrO$_2$/V$_2$O$_5$, IrO$_2$/HPC, commercial IrO$_2$ and V$_2$O$_5$ in all-pH media (Figure S29, Supporting Information). Surprisingly, IrO$_2$/V$_2$O$_5$ displays a small overpotential of 65, 176, and 49 mV to achieve 10 mA cm$^{-2}$ in acidic, neutral and alkaline solution, respectively, surpassing those of IrO$_2$/HPC (129, 252, and 130 mV) and commercial IrO$_2$ (136, 317, and 198 mV). Meanwhile, the IrO$_2$/V$_2$O$_5$ shows lowest Tafel slopes and charge transfer resistance among the catalysts, manifesting its fastest reaction kinetics. Impressively, in all three conditions, IrO$_2$/V$_2$O$_5$ is demonstrated as a “universally compatible” electrocatalyst that simultaneously shows excellent HER and OER performances over the entire pH range. In order to demonstrate the practical applications, we loaded the IrO$_2$/V$_2$O$_5$ electrocatalysts on carbon fiber paper (CP) as anode and cathode to construct a two-electrode water splitting cell in 0.5 M H$_2$SO$_4$, 1 m PBS and 1 m KOH solutions (catalyst loading amount is 1 mg cm$^{-2}$). In the exper-
iments of all-pH overall water splitting, the potential required for two-electrode IrO_2/V_2O_5/CP (±) electrolyzer is only 1.49, 1.65, and 1.50 V to reach a current density of 10 mA cm\(^{-2}\) in alkaline, neutral, and acidic media, exceeding the commercial (−)Pt/C@CP||IrO_2@CP(+) electrolyzer (Figure 5a). Moreover, a commercial AA battery with a nominal voltage of 1.50 V is able to drive overall water splitting with obvious gas bubble release, confirming the high efficiency of the IrO_2/V_2O_5 catalysts toward both HER and OER (Figure 5b and Movie S1, Supporting Information). These results reveal that the IrO_2/V_2O_5/CP electrode has potential applications in low-cost and energy-efficient water electrolysis. Additionally, compared with previously highly active water splitting electrocatalysts, the overall water splitting performance of IrO_2/V_2O_5 catalyst is significantly comparable to the most electrocatalysts in different media (Figure 5c and Table S9, Supporting Information). Besides, IrO_2/V_2O_5/CP (±) system exhibits excellent stability in all-pH condition by chronopotentiometry tests (Figure 5d), the voltage required for maintaining the overall water splitting current density of 10 mA cm\(^{-2}\) remains stable for 30 h. In sharp contrast, (−)Pt/C@CP||IrO_2@CP(+) electrolyzer deactivates rapidly within a few hours. We detected the generated H\(_2\) and O\(_2\) from IrO_2/V_2O_5/CP (±) system by online gas chromatography (Figure S30, Supporting Information). The amounts of produced H\(_2\) and O\(_2\) collected at a current density of 100 mA cm\(^{-2}\) matches well with the theoretically calculated values, corresponding to a faradic efficiency of ≈100% (Figure 5e). The unique compatibility, high-efficiency and good stability performance of the IrO_2/V_2O_5 catalyst enable it expected to develop next-generation water splitting technologies.

3. Conclusion

In summary, we have developed a simple method to synthesize highly effective IrO_2/V_2O_5 catalyst for water splitting in a wide pH range. HRTEM images demonstrated clearly distorted and deformed lattice fringes of IrO_2, corroborating the XRD and XPS results, indicating a SOSI between IrO_2 and V_2O_5. The unique structure distortion endows the IrO_2/V_2O_5 catalyst with a high exposure of IrO_2 active sites. DFT and XPS indicated that the SOSI induced charge transfer from IrO_2 to V_2O_5, therefore, the electrophilic IrO_2 center can effectively promote the hydroxyl oxidation kinetics and the O–O bond coupling process, eventually promoting the fast turnover of water oxidation. Additionally, overall water-splitting system driven by commercial AA battery (1.5 V) is also demonstrated to further promote the application. This work provides a road map in accelerating OER kinetics in different media to boost the efficiency of water electrolysis and shed light on the extension of SOSI to a variety of catalyst systems for enhancing their activity and stability.

4. Experimental Section

Material: Iridium(III) chloride hydrate (IrCl_3·xH_2O, 298.58), vanadium(III) chloride (VCl_3, 157.30), and p-phthalic acid (C_9H_4O_4, 166.13) were purchased from Aladdin Inc. The commercial IrO_2 was purchased from Sigma-Aldrich.

Preparation of MIL-88B (V): In a typical procedure, 314 mg of vanadium (III) chloride (VCl_3) and 332 mg of terephthalic acid (C_8H_4O_4) were mixed in a 50 mL beaker. Then, a solution containing 2 mL of hydrochloric acid (1 M HCl) and 10 mL of ethyl alcohol (C_2H_5OH) was added under vigorous stirring at room temperature. After 30 min, the resulting green suspension was further dispersed with ultrasonic treatment for 15 min. Finally, the mixture was transferred to a 50 mL Teflon-lined stainless-steel autoclave and heated in an electrical oven at 120 °C for 48 h. The prepared MIL-888 (V) was placed at 50 °C under vacuum for 12 h for future use.

Preparation of IrO_2/V_2O_5 Hybrid Oxides: Typically, 50 mg IrCl_3·xH_2O was dissolved in 50 mL ethanol under stirring for 30 min. After that, 0.2 g MIL-888 (V) was slowly added into the IrCl_3 solution under stirring. To ensure the uniform distribution of IrCl_3, the resulting mixture was further kept stirring at room temperature for 12 h to allow the complete loading of IrCl_3 into MIL-888 (V) pores. After impregnation, the product was recovered by centrifugation, and washed four times with ethanol to remove IrCl_3 remained on the outer surface of MIL-888 (V) material. Finally, the resulting Ir(III)/MIL-888 (V) was dried at 50 °C under vacuum for 10 h. Ir(III)/MIL-888 (V) powder was placed in muffle furnace and heated to T (T = 300, 400, 500 °C) at a heating rate of 5 °C min\(^{-1}\) and held for 4 h. After cooling down to room temperatures, the resulting black products were collected, and denoted as IrO_2/V_2O_5-T. Notably, the typical IrO_2/V_2O_5 material was obtained at 400 °C unless otherwise specified. For comparison, V_2O_5 was obtained by annealing MIL-888 (V) powder at 400 °C.

Preparation of IrO_2/HPC and IrO_2/V_2O_5/HM: Typically, in order to ensure the consistent loading of Ir, 0.2 g hierarchically porous carbon (HPC) or synthesized V_2O_5 were impregnated by 6.2 mL of IrCl_3·xH_2O aqueous solution (10 mg mL\(^{-1}\) based on precursor). Then water was evaporated at 60 °C and the powders were dried at 120 °C for 3 h, followed by calcination in muffle furnace at 400 °C for another 4 h.

Characterization: Powder X-ray diffraction patterns (PXRD) of samples were recorded using a Bruker D8 Advance diffractometer (Cu Kr, λ = 1.5418 Å, operating at 40 kV/40 mA). The morphologies were characterized by transmission electron microscope (TEM, Hitachi-7700, 100 kV) and scanning electron microscope (SEM; Hitachi S-4800). The high-resolution transmission electron microscope (HRTEM) were carried out by an FEI Tecnai G2 F20S-Twin HRTEM working at 200 kV. The aberration-corrected high-angle annular darkfield scanning transmission electron microscope (AC HAADF-STEM) images and the corresponding atomic-resolution energy-dispersive X-ray spectroscopy element mappings were recorded by a Titan 80–300 scanning/transmission electron microscope operated at 300 kV. N\(_2\) adsorption–desorption measurements were carried out at 77 K using a Quantachrome SI-MP Instrument. The surface area of the samples was estimated by method of Brunauer–Emmett–Teller ( BET). Elemental analysis of Ir and V in the samples was detected by a Thermo IRIS Intrepid II inductively coupled plasma-optical emission spectrometry (ICP-OES). X-ray photoemission spectroscopy were obtained on an ESCALAB MARK II spherical analyzer with a monochromatized Al Kα source (1486.6 eV) with a base pressure in the lower 2 × 10\(^{-7}\) mbar range. The binding energy (BE) was calibrated by setting the C 1s BE to 284.8 eV with respect to the Fermi level. High-resolution spectra were acquired with an analyzer pass energy of 40 eV. The XPS spectra were fit after subtraction of a Shirley background with the available XPSPEAK 4.1 software. In all fits, the peak separation and the peak area ratios between the Ir 4f\(_{5/2}\) and the Ir 4f\(_{7/2}\) components were constrained to 3 eV and 4.3, respectively. The detailed description about the fitting models, lineshape definition, peak position, restrained parameters summarized in the Tables S2 and S3 (Supporting Information).

H\(_2\)-TPR Measurement: The mobility and redox properties of catalyst samples were evaluated via H\(_2\)-TPR measurement using hydrogen (H\(_2\)) as a reductant. Briefly, 100 mg of catalyst sample with grain sizes of 60–80 mesh were loaded in a quartz reactor and pretreated with a ultrapure Ar gas (with flow rate of 30 mL min\(^{-1}\)) at 200 °C for 2 h to remove the surface-adsorbed species. The pretreated sample was then cooled to room temperature, following which the sample was heated to 800 °C under the mixed gas flow (10 vol% H\(_2\) in Ar with flow rate of 30 mL min\(^{-1}\)) at a heating rate of 2 °C min\(^{-1}\). H\(_2\) consumption was measured using an online thermal conductivity detector (TCD).

Electrochemical Measurement: All the electrochemical measurements were carried out with a three-electrode setup using a CHI 760E electrochemical workstation (Chenhua Instrument Co., Ltd., Shanghai, China) with three electrodes: a glassy carbon as working electrode, a Pt wire as auxiliary electrode, and a saturated calomel electrode as reference electrode. A 0.1 M KOH solution was used as an electrolyte.
for all samples during electronic structure calculation and the structure of the ADT protocol in 0.5 \( \text{m} \times \text{m} \) × 1.0 mm (5 mm diameter) to serve as the working electrode for the electrochemical testing. A saturated calomel electrode (SCE) and carbon rod were used as the reference electrode and the counter electrode, respectively. The reference electrode was also calibrated using the Pt RDE as working electrode in highly pure H$_2$-saturated electrolyte. All potentials were referenced to a reversible hydrogen electrode (RHE). For OER test, linear sweep voltammetry (LSV) was carried out in 1.0 M KOH, 1.0 M PBS, and 0.5 M H$_2$SO$_4$ at a scan rate of 1 mV s$^{-1}$ after purging with O$_2$ (99.999%) for at least 30 min and the HER test was also performed in accordance with above similar operations, except that O$_2$ is replaced with H$_2$ before the test. All the polarization curves are the steady ones after several scans with 95% iR compensation. The current density was calculated against the geometric area (0.196 cm$^2$) of the electrode to obtain the specific activity. Electrochemical impedance spectroscopy (EIS) measurements were performed from 100 kHz to 0.01 Hz with an amplitude of 5 mV at an overpotential of 100 mV for HER and 300 mV for OER. The stability measurements were performed by static chronopotentiometry test in 1.0 M KOH, 1.0 M PBS, and 0.5 M H$_2$SO$_4$ and transient accelerated degradation test (ADT) protocol in 0.5 M H$_2$SO$_4$ on Au electrode (3 mm diameter, 0.0706 cm$^2$). Chronopotentiometry was measured at 10 mAh cm$^{-2}$ to represent typical static long-term stability tests. ADT tests were conducted as follows. Typically, square-wave voltammetry consisted of 10 000 cycles were conducted between a lower potential of 0.05 V RHE and an higher potential of 1.0 V RHE. Each cycle was maintained for 4 s. Every 2500 cycles were interrupted for LSV and CV scans (between 0.4 and 1.4 V RHE at 5 mV s$^{-1}$ to obtain the total anodic charge \( Q_{\text{anodic}} \), of the samples). The leaking extent Ir and V from the electrode to electrolyte was determined by ICP-MS (NextION 2000).

The underpotential deposition of copper (Cu-UPD) on Pt, Ru, and Ir was proven to be an ideal method for quantifying the number of active sites and the electrochemically active surface area (ECSA). Hence, the number of active sites (n) could require based on the generated charges during the UPD copper (Cu) stripping (\( Q_{\text{Cu-UPD}} \rightarrow \text{Cu}^{2+} + 2e^- \)) with that, is \( n = Q_{\text{Cu-UPD}} / 2F \).

The turnover frequency (TOF, s$^{-1}$) was calculated by the equation: TOF = \( I/(znF) \). \( F (C \text{ mol}^{-1}) \) is the Faraday constant, \( I \) is the current (A) at corresponding overpotential and the factor \( z \) means the number of electrons required to form one hydrogen molecule or oxygen molecule (\( z = 2 \) for HER, \( 4 \) for OER).

The full electrolyzer configuration was assembled using two identical IrO$_2$/V$_2$O$_5$ cathodes, IrO$_2$ clusters supported on 4 \( \times \) 4 supercell of V$_2$O$_5$ (001) with 95% iR compensation. The current density was calculated against the IrO$_2$-V$_2$O$_5$ catalyst, the Ir$_4$O$_8$ clusters supported on 4 \( \times \) 4 supercell of V$_2$O$_5$ (001). The theoretical overpotential, which is independent of pH, at standard conditions is then given by following equation.

Supporting Information

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

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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oxides, oxygen evolution reaction, pH-universal electrocatalysts, strong oxides-support interaction, water splitting

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