Ir-Pd nanoalloys with enhanced surface-microstructure-sensitive catalytic activity for oxygen evolution reaction in acidic and alkaline media

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ABSTRACT Ir-based electrocatalysts have been systematically studied for a variety of applications, among which the electrocatalysis for oxygen evolution reaction (OER) is one of the most prominent. The investigation on surface-microstructure-sensitive catalytic activity in different pH media is of great significance for developing efficient electrocatalysts and corresponding mechanism research. Herein, shape-tunable Ir-Pd alloy nanocrystals, including nano-hollow-spheres (NHSs), nanowires (NWs), and nanotetrahedrons (NTs), are synthesized *via* a facile one-pot solvothermal method. Electrochemical studies show that the OER activity of the Ir-Pd alloy nanocatalysts exhibits surface-microstructure-sensitive enhancement in acidic and alkaline media. Ir-Pd NWs and NTs show more than five times higher mass activity than commercial Ir/C catalyst at an overpotential of 0.25 V in acidic and alkaline media. Post-XPS analyses reveal that surface Ir(VI) oxide generated at surface defective sites of Ir-Pd nanocatalysts is a possible key intermediate for OER. In acidic medium, the specific activity of Ir-Pd nanocatalysts has a positive correlation with the surface roughness of NWs > NHSs > NTs. However, the strong dissociation of surface Ir(VI) species (IrO_4^{2-}) at surface defective sites is a possible obstacle for the formation of Ir(VI) oxide, which reverses the activity sequence for OER in alkaline medium.

Keywords: Ir-Pd alloy nanocatalysts, shape control, oxygen evolution reaction, defective sites, surface effects

INTRODUCTION

Hydrogen is one of the most promising clean fuel and energy carrier due to its highest mass energy density and zero carbon emission [1,2]. With dozens of million tons

of total global production each year, hydrogen has also been playing a vital role in the ammonia manufacturing and petrochemical industries for a long time. However, a great majority of hydrogen is produced by fossil fuel-based methods, such as gasification and thermocatalytic processes of natural gas, from which carbon dioxide is also generated as the byproduct [2]. Since carbon dioxide has been recognized to be the chief culprit of global greenhouse effect, the development of hydrogen economy will not be achieved without an effective and clean method of hydrogen production. As a clean, potentially cost-effective and renewable source of hydrogen, water splitting in proton exchange membrane (PEM) electrolyzer has attracted extensive attention [1–4]. The oxygen evolution reaction (OER), the anode reaction of PEM electrolyzer, produces the overpotential in the electrochemical reaction due to a complex four electron transfer mechanism [3,4]. To decrease the overpotential as much as possible, appropriate oxygen electrode catalyst is essential in the typical water splitting process.

Active and durable Ir-based electrocatalysts have been studied as a benchmark catalyst for OER [5–13]. Reier and his co-workers [6] confirmed that Ir nanoparticles should be a class of high potential OER nanocatalysts, since their OER activity and durability were comparable to those of bulk catalysts. Strasser *et al.* [9] and Jaramillo *et al.* [10], respectively, applied different catalyst supports to improve the stability of Ir-based oxide catalysts for OER. Recently, ultrathin laminar Ir superstructure was synthesized as OER electrocatalysts in both acidic and alkaline conditions due to their fully exposed active sites [11]. Ir-rich oxidized surfaces, often caused by the surface

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segregation, were found to significantly improve the catalytic performance of Ir-based alloy catalysts [13–15]. Moreover, when Ir is alloyed with another transition metal, the catalytic performances for OER would be further improved owing to the electronic and lattice induced surface effects [13–16]. Theoretical calculations have shown that Pd would have a good performance in water adsorption and dissociation [17–19]. It has also been considered that possible phase separation systems, such as Pt–Ir or Ir–Pd alloy, contain intrinsic strain which has a significant impact on the catalytic process [20,21]. Actually, as an ordinary noble metal alloy, Ir–Pd nanocatalysts have been widely used in plenty of heterogeneous catalytic reactions, e.g. selective hydrogenation [22,23], hydrazine decomposition [24,25] and electrocatalysis [26–29]. However, to the best of our knowledge, in-depth research of Ir–Pd nanocatalysts for OER with surface-sensitive catalytic properties is seldom to be studied. Although the OER activity of Ir-based catalysts in alkaline media is inferior to some Ni- and Fe-based oxide catalysts, the catalytic properties of Ir-based alloy catalysts under extreme pH conditions are still worthy of study to understand the catalytic mechanism and develop efficient and durable OER catalysts [7,11,30,31].

In this article, we report a surface-microstructure-sensitive catalytic activity of Ir–Pd alloy nanocatalysts for OER in both acidic and alkaline media. Ir–Pd alloy nano-hollow-spheres (NHSSs), worm-like nanowires (NWs) and nanotetrahedrons (NTs) were synthesized as efficient OER catalysts *via* a facile one-pot solvothermal method. Ir–Pd NWs and NTs, respectively, exhibit high OER performance which shows more than five times higher mass activity than commercial Ir/C catalyst at an overpotential of 0.25 V in acidic and alkaline media. Post-XPS analyses after a constant potential treatments determine the key intermediate, surface Ir(VI) oxide, is possibly responsible for the high performance of Ir–Pd alloy nanocatalysts. The surface defective sites of Ir–Pd alloy nanocrystals are critical to the formation of surface Ir(VI) oxide which is sensitive to the pH of the electrolyte.

EXPERIMENTAL SECTION

Chemicals

Poly(vinylpyrrolidone) (PVP, $M_w \sim 29,000$, Sigma-Aldrich), ethylene glycol (EG, 99.0%, Sinopharm Chemical Reagent Co. Ltd., China), $\text{IrCl}_3 \cdot \text{H}_2\text{O}$ (A.R., TCI), PdCl_2 (A.R., Shenyang Institute of Nonferrous Metal, China), tetraethylammonium bromide (TEAB, A.R., Sigma-Aldrich), KI, $\text{Na}_2\text{C}_2\text{O}_4$, NaOH (A.R., Beijing Chemical

Works, China), carbon black (Vulcan XC-72R, Cabot), commercial Ir/C catalyst (20 wt.% Ir, Premetek), commercial Pd/C catalyst (30 wt.% Pd, Sigma-Aldrich), formaldehyde solution (40%, A.R., Beijing Yili Fine Chemical Reagent Corp., China), HCl, H_2SO_4 (A.R., Beijing Chemical Reagent Corp., China), cyclohexane (A.R., Beijing Tong Guang Fine Chemicals Corp., China), acetone, ethanol (A.R., Beijing Chemical Works, China) and Nafion (5% ethanol solution, Alfa Aesar) were used as received. The water used in all experiments was ultrapure (Millipore, 18.2 M Ω cm).

Synthesis of Pd–Ir alloy nanocrystals

Synthesis of Pd–Ir nano-hollow-spheres (NHSSs)

In a typical synthesis of Pd–Ir NHSSs, 0.03 mmol $\text{IrCl}_3 \cdot \text{H}_2\text{O}$, 0.03 mmol PdCl_2 , 0.6 mmol TEAB, 0.012 mmol KI and 100 mg PVP were dissolved in 15 mL of EG upon stirring for 1 h. The solution was then transferred to a 25 mL Teflon-lined stainless autoclave and heated at 180°C for 24 h. After the autoclave was cooled down, the black products were centrifuged with adding 30 mL acetone and 2 mL cyclohexane at 7,800 rpm for 10 min, and then washed by a mix of ethanol/cyclohexane for three times.

Synthesis of Pd–Ir worm-like nanowires (NWs)

The synthesis of Pd–Ir NWs was similar to that of Pd–Ir hollow spheres except for removing TEAB and simultaneously increasing the amount of KI from 0.012 mmol to 0.06 mmol.

Synthesis of Pd–Ir nanotetrahedrons (NTs)

In a typical synthesis of Pd–Ir NTs, 0.045 mmol of $\text{IrCl}_3 \cdot \text{H}_2\text{O}$, 0.045 mmol PdCl_2 , 150 mg $\text{Na}_2\text{C}_2\text{O}_4$, 0.3 mL formaldehyde solution and 16.6 mg PVP were added. The pH value of the solution was adjusted to three by 1:1 HCl solutions and the total volume of the solution was kept at 15 mL. After stirring for 1 h, the solution was then transferred to a 25 mL Teflon-lined stainless autoclave and heated at 180°C for 3 h. The post-treatment was just the same as the above-mentioned nanocrystals.

Preparation of Pd–Ir alloy nanocrystals/carbon black composites

The as-synthesized black Pd–Ir alloy nanocrystals and about 30 mg carbon black were dispersed in 4 mL ethanol and treated ultrasonically for 8 h. The carbon black supported nanocatalysts were centrifuged at 7,800 rpm for 10 min and washed by ethanol for three times. The as-

obtained catalysts were then heated in a muffle furnace at 250°C for 8 h to remove excess PVP. After annealing, 4 mg composites were dispersed in 1 mL ethanol for further electrochemical tests. The mass of metal loadings was determined by ICP-AES analysis.

Characterization

Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) line scan and element mapping were conducted on a FEG-TEM (JEM-2100F, JEOL, Japan) operated at 200 kV. The TEM samples were made from drying a drop of nanoparticle dispersion in ethanol on carbon-coated copper grids. Powder X-ray diffraction (PXRD) analysis was performed on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of 0.5° at a 2 θ scanning speed of 4° min⁻¹ under Cu K α radiation (λ = 1.5406 Å). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was conducted on a Profile Spec ICP-AES spectrometer (Leeman, USA). X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra Imaging Photoelectron Spectrometer (Kratos Analytical Ltd., UK) with a monochromatic Al K α (1486.7 eV) X-ray source operated at 225 W with 15 kV acceleration voltage. The C 1s line at 284.8 eV was used to calibrate the binding energies (BE).

Electrochemical tests

Electrochemical measurements were conducted on a CHI 850C electrochemical analyzer (CH Instrument, TX, USA) in a standard three electrode cell. In the three-electrode system, a rotating disk electrode (RDE) with a glassy carbon disk (0.196 cm²) was used as the working electrode; a Pt foil was used as the counter electrode; a KCl-saturated Ag/AgCl electrode was used as the reference electrode. In a typical OER test, about 4 μ g of as-obtained catalyst composites or 8 μ g of commercial catalysts were dropped on the RDE and dried naturally. Then 5 μ L Nafion (0.5 wt.% ethanol solution) was dropped on RDE and dried, followed by rinsing the RDE with ultrapure water. The electrochemical characterization studies were performed in both 0.5 mol L⁻¹ H₂SO₄ and 1.0 mol L⁻¹ NaOH solutions. The *i*R-compensated OER polarization curves were collected in N₂-saturated electrolyte in the anodic voltammetric scan with a speed of 10 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was carried out to evaluate the charge transfer during OER on an Autolab PGSTAT302N (Autolab Corp.

Figure 1 TEM image with size distribution statistics (a), HRTEM image (b), and HAADF-STEM image (c) of Ir-Pd alloy NHSs. EDS line scan profile for corresponding STEM image (d) and EDS element mapping images for Ir (e), Pd (f), and overlay (g) of Ir-Pd NHSs with the scale bar of 10 nm.

Switzerland) electrochemical analyzer with a frequency range of 100 kHz–50 MHz. All the measurements were performed at room temperature, and the electrolyte used was freshly made. The Ag/AgCl electrode in this work was calibrated against a reversible hydrogen electrode (RHE) in the same electrolyte. All the potentials were reported against the RHE with the following equation: $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.199 \text{ V} + 0.0591 \text{ pH}$.

RESULTS AND DISCUSSION

Solvothermal synthesis of Ir-Pd alloy nanocrystals

Ir-Pd alloy NHSs, NWs, and NTs were synthesized *via* a facile one-pot solvothermal method. By introducing TEAB and KI as the facet-selective agents, Ir-Pd NHSs were obtained with a hollow structure (Fig. 1). The size of most of the hollow spheres is about (7.3 $\pm$ 1.0) nm. HRTEM images show the lattice spacings of 2.24 Å, 1.93 Å, 1.37 Å, and 1.17 Å, corresponding to (111), (200), (220), and (311) facets, respectively (Fig. 1b and S1). Fig. 1c shows the HAADF-STEM image of Ir-Pd NHSs/carbon black composites exhibits a hollow structure after annealing for 8 h at 250°C in air, indicating good thermal stability of the Ir-Pd NHSs. EDS line scan and element mapping images (Fig. 1d–g) proved that Ir-Pd NHSs have an alloy structure.

Figure 2 TEM image with size distribution statistics (a), HRTEM image (b), and HAADF-STEM image (c) of Ir-Pd alloy NWs. EDS line scan profile for corresponding STEM image (d) and EDS element mapping images for Ir (e), Pd (f), and overlay (g) of Ir-Pd NWs with the scale bar of 20 nm.

Figure 3 TEM image with size distribution statistics (a), HRTEM image (b), and HAADF-STEM image (c) of Ir-Pd alloy NTs. EDS line scan profile for corresponding STEM image (d) and EDS element mapping images for Ir (e), Pd (f), and overlay (g) of Ir-Pd NTs with the scale bar of 20 nm.

Time-dependent experiments were conducted under the same reaction conditions to clarify the growth mechanism of Ir-Pd NHSs. At the beginning, solid nanoparticles also maintain in the system except for a part of hollow particles (Fig. S2a, b). Several hours later, the hollow structure of Ir-Pd NHSs forms gradually *via* the galvanic replacement while solid particles disappear in the field of view (Fig. S2c, d). As shown in Fig. S3, if the reaction time is reduced to only 15 min, transparent yellow solution will be obtained. Both HAADF-STEM and EDS element mapping images confirm that Pd nanoparticles and IrCl₃ precursors coexist at this moment (Fig. S3). Based on the time-dependent experiments above, the growth of Ir-Pd NHSs is attributed to galvanic replacement and Kirkendall effect. In a typical synthesis, Pd precursor reduces first and forms polyhedral nanoparticles, and then Ir precursor reduces *via* the galvanic replacement. As the surface enrichment of Ir, the interdiffusion between Ir and Pd takes place. Due to the much faster diffusion rate of Pd, Kirkendall effect in Ir-Pd alloy nanoparticles leads to the hollow structure finally [32,33].

Because TEAB has been proved to slow down the reduction rate of Ir precursor, both precursors are more consumed by removing TEAB. Therefore, polycrystalline Ir-Pd alloy worm-like NWs with twinned defects were synthesized with the help of I⁻ as an oriented agent (Fig.

2). The formation mechanism of Ir-based worm-like NWs has been systematically studied in our previous work [15,34]. The cross section diameter of Ir-Pd NWs is about (2.9±0.4) nm. HRTEM images show the lattice spacings of 2.24 Å, 1.93 Å, and 1.37 Å, which equal to (111), (200), and (220) facets, respectively. Twinned defects (dotted black lines shown in Fig. 2b) can also be clearly observed from corresponding HRTEM images of Ir-Pd worm-like NWs (Fig. 2b and Fig. S4). As shown in the STEM image of Fig. 2c, the worm-like structure is kept after annealing for 8 h at 250°C in air, which also indicates high thermal stability of the Ir-Pd NWs. Similarly, Ir-Pd NWs display an alloy structure according to the EDS line scan and element mapping images (Fig. 2d–g).

Ir-Pd NTs were synthesized hydrothermally using Na₂C₂O₄ as a capping agent and formaldehyde as reductant for 3 h and showed an average size of (5.7±0.8) nm (Fig. 3). Most of the nanoparticles (~70%) exhibit a tetrahedral structure (top right corner of Fig. 3b) except for a few twin crystals (bottom left corner of Fig. 3b). Both expose mostly (111) facets due to the stabilization effect of C₂O₄²⁻ on the (111) facets. However, high concentration of C₂O₄²⁻ will coordinate with metal precursors, slow down their reduction rate and lead to the formation of twin crystals [35]. EDS line scan and ele-

Scheme 1 Synthetic pathways of Ir-Pd alloy nanocrystals *via* one-pot solvothermal method.

Figure 4 XRD patterns of as-synthesized Ir-Pd alloy nanocrystals. Standard XRD pattern of bulk palladium (JCPDS 05-0681) and iridium (JCPDS 06-0598) are shown in the panel for reference.

ment mapping images also confirm the alloy structure of Ir-Pd NTs (Fig. 3d–g). As a summary, the synthetic pathways of Ir-Pd alloy nanocrystals are concisely described in Scheme 1.

Structure and composition characterization of Ir-Pd alloy nanocrystals

The XRD patterns of as-synthesized Ir-Pd nanocrystals are shown in Fig. 4. For each sample, all the diffraction peaks fall between the standard card of bulk Ir and Pd, confirming the face-centered-cubic (fcc) alloy structure of Ir-Pd nanocrystals. Compared with Ir-Pd NHSs and NWs, the (111) peak of Ir-Pd NTs is closer to the (111) peak of bulk Pd. ICP-AES, and XPS results of the corresponding samples are shown in Table 1. According to the ICP-AES results, the total Ir/Pd atomic ratio of both Ir-Pd NHSs and NWs is about 2:3 while that of Pd-rich Ir-Pd NTs is about 1:4. However, different from the internal composition, XPS results demonstrate that all Ir-Pd nanocrystals have relatively Ir-rich surfaces. Ir/Pd atomic

Table 1 Atomic ratio of as-synthesized Ir-Pd alloy nanocrystals determined from ICP-AES and XPS methods

Sample (%)	ICP-AES		XPS	
	Ir	Pd	Ir	Pd
NHS	40.3	59.7	52.3	47.7
NW	41.6	58.4	46.2	53.8
NT	21.0	79.0	25.6	74.4

ratios at the surface rise to about 1:1 for Ir-Pd NHSs and NWs and 1:3 for Ir-Pd NTs. The atomic ratio difference between the interior and surface confirms a concentration gradient of Ir in the Ir-Pd alloy nanocrystals, which also confirms our hypothesis about the surface-segregated structure due to the reduction order of the noble metal precursors.

The surface of Ir-Pd alloy nanoparticles is partially oxidized to the high valences because all the syntheses were conducted in the presence of oxygen. XPS full spectra of annealed Ir-Pd alloy nanoparticles (Fig. S5) show that no obvious peaks of surface-capping agents (i.e. Br^- , I^- , and Na^+) can be found on the surface of the sample. Therefore, the Ir and Pd XPS peaks of can be deconvoluted by only considering different species of oxides. The proportions of different metal oxidation states are summarized in Table S1 by the deconvolution of XPS data in Ir 4f and Pd 3d regions (Fig. S6). Pd exhibits two peaks corresponding to the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ core electrons. The peaks, deconvoluted from $3d_{5/2}$ band, are from 335.2 to 335.4 eV for Pd(0), 335.5 to 335.8 eV for native oxide [Pd(Ntv)], 336.1 to 336.5 eV for PdO [Pd(II)], and 337.7 to 338.3 eV for PdO₂ [Pd(IV)], while the bonding energies of $3d_{3/2}$ region are about 5.26 eV higher [36,37]. However, the deconvolution of Ir 4f region is more complex due to presence of a series of Ir oxides. Since it has been proved that the L_3 edge shift of octahedral Pt–O bonding is 0.7 eV per formal charge and it could be promoted to other noble elements [38–40], in the case of only oxygen to be the ligand, the Ir 4f_{7/2} region is deconvoluted into three peaks: 60.8 to 61.2 eV for Ir(0), 61.8 to 62.3 eV for IrO₂ [Ir(IV)], and 62.7 to 63.3 eV for IrO_x [mostly Ir(VI)], respectively, and the bonding energies of 4f_{5/2} region are about 2.98 eV higher [36,41].

For as-synthesized Ir-Pd nanocrystals, Ir atoms at the surface exist in form of metallic state Ir(0) as well as a small part of surface Ir(IV) species, while Pd(0), Pd(Ntv), and Pd(IV) coexist on the surface. Ir-Pd NHSs and NWs show almost the same ratio of Ir(IV)/Ir(tot) but that of Ir-Pd NTs is about 10% higher. After the annealing treatment, obvious changes are found on the part of surface

Figure 5 *iR*-compensated polarization curves of Ir-Pd alloy nanocatalysts and commercial catalysts in a N₂-saturated (a) 0.5 mol L⁻¹ H₂SO₄ and (b) 1.0 mol L⁻¹ NaOH electrolytes with a rotation rate of 1,600 rpm at a sweep rate of 10 mV s⁻¹. Mass activity (c) normalized by the total metal mass and specific activity (d) of Ir-Pd nanocatalysts and commercial Ir/C catalyst for OER at an overpotential of 0.25 V in acidic and alkaline media. The carbon oxidation current was corrected by deducting the current of Vulcan XC-72R carbon black from the total current.

oxidation of Ir-Pd nanocrystals. The powder XRD patterns of annealed Ir-Pd nanocrystals (Fig. S7) show some obvious peaks of oxides in all samples, especially in the Ir-Pd NTs, indicating they are almost completely turned into oxides. Because some peaks of oxides can hardly be identified in Fig. S7, the detailed structure was also analysed by XPS. From the data in Table S1, Ir-Pd NWs have the best thermal stability with the least change of Ir oxidation states. For the annealed Ir-Pd NHSSs, only about 7% Ir(IV) indicates the surface of Ir-Pd NTs is completely oxidized with the appearance of Ir(VI). For all the samples, the native oxide of Pd is replaced by Pd(II) after the annealing. Considering the change of Ir content at the surface of oxide, the surface oxidation resistance of Ir-Pd nanocrystals is NWs > NHSSs > NTs, which greatly influences their OER properties.

OER tests of Ir-Pd alloy nanocatalysts in acidic and alkaline media

The acidic OER tests of the Ir-Pd alloy nanocatalysts were carried out using a rotating disk electrode (RDE) with a

rotation rate of 1,600 rpm in a N₂-saturated 0.5 mol L⁻¹ H₂SO₄ electrolyte (pH = 0) at room temperature. Linear sweep voltammetry (LSV) techniques were used to evaluate the OER activity of carbon black supported Ir-Pd nanocatalysts (Fig. 5a). All the data were obtained after a stable cyclic voltammetry (CV) scanning from 0 to 1.2 V in N₂-saturated electrolyte at a sweep rate of 50 mV s⁻¹. According to the TEM and HRTEM images in Fig. S8, no obvious morphology changes of Ir-Pd nanoparticles were observed after the stable CV scanning in both acidic and alkaline media, compared with the as-synthesized nanoparticles in Figs 1–3. Each polarization curve was normalized by the surface area of RDE (0.196 cm²) with essential *iR*-compensation. The polarization curves of commercial Ir/C and Pd/C catalysts were also plotted in Fig. 5a. In this work, the recent works by McCrory and Jaramillo *et al.* [7,42] were used as the benchmark to compare the performance of the catalysts.

An overpotential of 0.25 V (1.479 V vs. RHE) was used as a reference potential (Table 2 and Fig. 5c). All the data were normalized by the total metal mass of the catalysts

Table 2 Mass activities normalized by the total mass of catalysts at an overpotential of 0.25 V and Tafel slopes of Ir-Pd alloy nanocatalysts and commercial catalysts for OER in acidic and alkaline media

Sample	Acidic		Alkaline	
	Mass activity (A g ⁻¹ _{metal})	Tafel slope (mV dec ⁻¹)	Mass activity (A g ⁻¹ _{metal})	Tafel slope (mV dec ⁻¹)
NHS	44.4	58	22.3	103
NW	74.9	60	9.3	118
NT	20.5	76	75.0	44
Ir/C	12.0	63	15.1	43
Pd/C	–	244	–	226

and the contribution of carbon oxidation current was also considered by deducting the current of Vulcan XC-72R carbon black from the total current. As shown in Fig. 5c, in acidic medium, the mass activity sequence of Ir-Pd alloy nanocatalysts is NWs (74.9 A g⁻¹) > NHSs (44.4 A g⁻¹) > NTs (20.5 A g⁻¹) at the overpotential of 0.25 V. The Ir-Pd NTs have a comparative mass activity to as-reported Pt-Ir nanooctahedrons (NOs) (21.3 A g⁻¹) [15] and much higher activity than commercial Ir/C catalyst (12.0 A g⁻¹) and reported nanosized IrO_x-Ir catalyst (~8 A g⁻¹) [8]. Ir-Pd NHSs and NWs exhibit better mass activities for about 3.7 and 6.2 times than commercial Ir/C catalyst. Since the catalytic activity of commercial Pd/C catalyst is comparable to Vulcan XC-72 R carbon black, the contribution of Pd to the catalytic activity for OER can be ignored.

Analogously, the alkaline OER tests of Ir-Pd alloy nanocatalysts were conducted under the same conditions except for changing the electrolyte to 1.0 mol L⁻¹ NaOH (pH = 14). The LSV polarization curves with *iR*-compensation are shown in Fig. 5b and reveal that the OER activity is quite different from the data in acidic medium. The mass activities of the catalysts at an overpotential of 0.25 V are also displayed in Table 2 and Fig. 5c. Commercial Ir/C catalyst show a mass activity of 15.1 A g⁻¹, higher than that in acidic medium. The activity sequence of Ir-Pd nanocatalysts reverses completely towards NTs (75.0 A g⁻¹) > NHSs (22.3 A g⁻¹) > NWs (9.3 A g⁻¹). The mass activities of Ir-Pd NHSs and NWs decrease significantly while Ir-Pd NTs show five times the mass activity of commercial Ir/C catalyst. If the mass activities were normalized by the mass of Ir, the activity sequences for OER in different pH media should not be changed (Table S2 and Fig. S9). In this case, the mass activity of Ir-Pd NWs in 0.5 mol L⁻¹ H₂SO₄ (133.1 A g⁻¹_{Ir} at an overpotential of 0.25 V) is much higher than rutile IrO₂ NPs (~30 A g⁻¹_{ox} at η =0.30 V) and rutile RuO₂ NPs (~50

A g⁻¹_{ox} at η =0.30 V) in 0.1 mol L⁻¹ HClO₄ [30], but lower than Ir-Ni mixed oxide thin film (79% Ni, ~375 A g⁻¹_{Ir} at η =0.30 V) in 0.1 mol L⁻¹ HClO₄ [14]. Furthermore, the mass activity of Ir-Pd NTs in 1.0 mol L⁻¹ NaOH (231.7 A g⁻¹_{Ir} at η =0.25 V) is also higher than rutile IrO₂ NPs (~10 A g⁻¹_{ox} at η =0.30 V) and rutile RuO₂ NPs (~12 A g⁻¹_{ox} at η =0.30 V) in 0.1 mol L⁻¹ NaOH [30]. In this work, Ir-Pd NWs and NTs exhibit about 11.1 and 15.3 times enhanced mass activities as commercial Ir/C catalyst for OER in different pH, respectively, which indicates pH greatly affects the surface adsorption states of reaction intermediates during OER.

To further compare the activity of single active sites, specific activities of Ir-Pd nanocatalysts normalized by the electrochemically active surface area (ECSA) are shown in Table S2 and Fig. 5d. The ECSA was estimated by the electrochemical double-layer capacitance of the catalysts in both acidic and alkaline media [7,11,43]. The electrochemical capacitance *C*_{DL} is determined by the non-Faradaic capacitive current which is related to the double-layer charging from the scan-rate dependent CVs (Fig. S10, S11). Generally, the charging current *i*_c is given by the following equation:

$$i_c = \nu C_{DL} \quad (1)$$

where ν is the scan rate of CV, the value of *C*_{DL} comes from the slope of the plot. Hence, the ECSA of each catalyst is obtained via Equation (2):

where the specific capacitance *C*_s is analogously set to 0.035 mF cm⁻² for 0.5 mol L⁻¹ H₂SO₄ or 0.040 mF cm⁻² for 1.0 mol L⁻¹ NaOH [7,43]. The ECSA and the roughness factor (RF) of the catalysts are calculated in Table S2 by deducting the contribution of Vulcan XC-72R carbon black (Fig. S12). RF is the ratio of ECSA and geometric surface area (GSA) of the electrode (0.196 cm²). The data in Table S2 confirmed that both the ECSA and specific activity, which respectively represent the number and activity of a single active site for OER, is pH dependent. For commercial Ir/C catalyst, the influence of pH in specific activity seems not so obvious. However, the specific activity sequences of Ir-Pd nanocatalysts for OER are also reverse in acidic and alkaline media. The reverse specific activity of Ir-Pd nanocatalysts also demonstrates the surface-microstructure-sensitive activity for OER.

To explain the change in specific activity of the catalysts, *iR*-compensated Tafel curves were plotted in Fig. 6. The Tafel slopes around 0.25 V overpotential for OER were collected in Table 2. As a well-accepted conclusion, the reaction mechanism for OER on an active oxide

Figure 6 *iR*-compensated Tafel curves of Ir-Pd alloy nanocatalysts and commercial catalysts for OER in a N₂-saturated (a) 0.5 mol L⁻¹ H₂SO₄ and (b) 1.0 mol L⁻¹ NaOH electrolytes.

electrode can be described as the following steps [44–46]:

where S stands for the active sites on the surface, and S-OH_{ads}^{*}, S-OH_{ads}, and S-O_{ads} are three possible adsorption intermediates. Tafel slope corresponds to a specific rate-determining step. For OER, if the rate-determining step is Equation (3), the predicted Tafel slope is above 120 mV dec⁻¹, by analogy, 60 mV dec⁻¹ for Equation (4), 40 mV dec⁻¹ for Equation (5), 30 mV dec⁻¹ for Equation (6), and 15 mV dec⁻¹ for Equation (7), respectively [45–47]. From the data in Table 2, the Tafel slope of Ir-Pd NHSSs, Ir-Pd NWs, and commercial Ir/C catalyst is about 60 mV dec⁻¹ in acidic medium, whose rate-determining step is related to the change in the adsorption state of intermediates. The Tafel slope of Ir-Pd NTs between 60 and 120 mV dec⁻¹ indicates that the OER process is affected by the dissociation of water. In this way, as shown in Table S3, Ir-Pd NHSSs and NWs show similar overpotential at 10 mA cm⁻² compared with other recently reported high-performance electrocatalysts in acidic media, except for Ir-Pd NTs. However, in alkaline medium, since the Tafel slopes of Ir-Pd NHSSs and NWs increase to 110 and 125 mV dec⁻¹, their activities are deeply restricted by the water dissociation step. The Tafel slopes of Ir-Pd NTs and commercial Ir/C catalyst are quite close to 40 mV dec⁻¹ due to a rate-determining step of hydroxyl dissociation. Compared with other high-performance electrocatalysts in Table S4, Ir-Pd NHSSs and NWs show both higher overpotentials and larger Tafel slopes for

OER in alkaline medium, whereas Ir-Pd NTs perform comparable lower overpotential and Tafel slope with other high-performance catalysts. All the analyses above confirm the surface-microstructure sensitive OER activity of Ir-Pd alloy nanocatalysts in extreme pH media. Since the catalytic activity of Pt-Ir nanocatalysts is closely related to the surface effect, the reverse OER activity is attributed to the specific surface structures of Ir-Pd alloy nanocatalysts[15].

The electrochemical stability of Ir-Pd alloy nanocatalysts for OER was tested using the chronopotentiometry technique at a constant current density of 10 mA cm⁻² per geometric area at a constant rotation rate of 1600 rpm [7,42]. Fig. 7 displays the chronopotentiometry curves of Ir-Pd alloy catalysts in both acidic and alkaline media. The electrode potentials of Ir-Pd alloy catalysts increased gradually in different pH media due to catalytic activity degradation [9]. The overpotentials necessary to achieve 10 mA cm⁻² per geometric area for Ir-Pd alloy catalysts at time = 0 ($\eta(t=0)$) and at time = 2 h ($\eta(t=2\text{h})$) as well as the overpotential change ($\Delta\eta$) within 2 h are summarized in Table S5. In acidic medium, the order of overpotential change for Ir-Pd alloy catalysts within 2 h is NWs < NHSSs < NTs, suggesting the stability sequence of NWs > NHSSs > NTs. Similarly, Ir-Pd alloy catalysts exhibit the opposite stability sequence of NTs > NHSSs > NWs. It is noteworthy that the catalytic activity and stability of Ir-Pd alloy catalysts behave the same sequence in both acidic and alkaline media, implying some intrinsic structural factors likely influence the catalytic properties of Ir-Pd alloy nanocatalysts.

Surface effect of Ir-Pd alloy nanocatalysts for OER

The post-XPS measurements were conducted for the corresponding catalysts after a constant potential treat-

Figure 7 *iR*-compensated chronopotentiometry curves of Ir-Pd alloy nanocatalysts at a constant current density of 10 mA cm^{-2} in N_2 -saturated $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ (solid line) and $1.0 \text{ mol L}^{-1} \text{ NaOH}$ (dash dot line) electrolytes with a constant rotation rate of 1,600 rpm.

ment at an overpotential of 0.25 V for 10 min. As shown in Fig. S13, Ir-Pd alloy nanoparticles basically maintain the original morphology after the constant potential treatment. However, the rather rough surface of the nanoparticles indicates the leaching of nanocatalysts. By studying the dissolution of iridium for OER in acidic media, Cherevko and Mayrhofer *et al.* [48–50] considered that the existence of instable intermediates or mixture of crystalline and amorphous Ir oxide phases would cause the dissolution of iridium at a high positive potential. Herein, ICP-AES results in Table S6 indicate that obvious mass loss takes place during the constant potential treatment. In acidic medium, the leaching rate of Ir is higher than Pd, while those in alkaline medium are similar. In acidic media, it has been proved that PdO formed after heat treatment is effective in protecting Ir oxides at high potential OER, which agrees well with our experiment [51]. In both acidic and alkaline media, the extent of leaching is consistent with the order of activity and stability for OER, which is also related to the surface microstructures. The deconvoluted XPS results are shown in Table 3, 4 and Fig. S14. Compared with commercial Ir/C catalyst, Ir-Pd alloy nanocatalysts seem easier to be oxidized to higher valence after the treatment. In particular, Ir(VI) oxide at the surface, which widely presents in high performance Ir-Pd alloy nanocatalysts after the treatment in both acidic and alkaline media, is a possible key intermediate during the catalytic reaction cycle. Since it has been observed and considered that Ir(V) is a key intermediate species for OER [40,41,52]. Accordingly, building a reaction cycle of $\text{Ir(VI)} \rightarrow \text{Ir(V)} \rightarrow \text{Ir(IV)} \rightarrow \text{Ir}$

Table 3 Proportions of metal oxidation states and surface total atomic ratios of Ir-Pd alloy nanocatalysts determined from deconvolution of XPS after a constant potential treatment at an overpotential of 0.25 V for OER in acidic media

(%)	Ir(0)	Ir(IV)	Ir(VI)	Pd(0)	Pt (Ntv)	Pd(II)	Pd (IV)	Ir _{tot}	Pd _{tot}
NHS	4.9	23.2	20.4	–	12.0	–	39.5	48.5	51.5
NW	5.6	20.9	19.6	–	–	20.1	33.8	46.1	53.9
NT	–	7.4	5.9	22.4	44.1	–	20.2	13.3	86.7
Ir/C	56.8	43.2	–	–	–	–	–	100.0	–

Table 4 Proportions of metal oxidation states and surface total atomic ratios of Ir-Pd alloy nanocatalysts determined from deconvolution of XPS after a constant potential treatment at an overpotential of 0.25 V for OER in alkaline media

(%)	Ir(0)	Ir(IV)	Ir(VI)	Pd(0)	Pd(II)	Pd(IV)	Ir _{tot}	Pd _{tot}
NHS	22.4	30.5	–	16.2	16.6	14.3	52.9	47.1
NW	18.2	21.8	–	12.0	14.2	33.8	40.0	60.0
NT	1.7	7.4	17.5	18.8	37.7	16.9	26.7	73.3
Ir/C	52.8	47.2	–	–	–	–	100.0	–

(VI) may greatly improve the catalytic activity of Ir-Pd nanocatalysts. The surface composition data after the stable CV scanning in Table S7 and Fig. S15 demonstrate that the high activity of Ir-Pd alloy nanocatalysts is related to the formation of Ir(VI) oxide at the surface during the electrocatalytic process.

Generally, the existence of Pd decreases the *d*-band state density of Ir and improves the binding energy between Ir and O, which makes Ir(VI) oxide easier to be produced [20,21]. In acidic medium, although Ir(VI) oxide widely appears on the surface of all kinds of Ir-Pd nanocatalysts (Tables 3, 4 and Fig. S14), the fantastic activity for OER is mainly attributed to the Ir(VI) oxide at the surface. The improvement in the OER activity of Ir-Pd NTs seems to be fairly limited with the most flat surface. As it is considered that defective surface is more likely to be oxidized and is beneficial to the OER activity [18,53], the specific structure of Ir-Pd alloy nanocatalysts is the cause of reverse activity sequence in different pH media. Ir-Pd NWs have the roughest surface with large amounts of surface defective sites (including twinned defects) due to the oriented attachment polycrystalline structure while Ir-Pd NTs that expose almost all (111) surface result in the lowest activity. Therefore, the specific activity of Ir-Pd nanocatalysts is consistent with the sequence of surface roughness, which provides Ir-Pd NHSs and NWs more recyclable surface Ir(VI) oxide and better OER activity in acidic medium. More importantly, as

mentioned above, the existence of PdO would improve the stability of surface Ir oxides [51]. According to the mass loss in Table S6, surface Pd(II) proportions in Table 3 and the chronopotentiometry curves in Fig. 7, Ir-Pd NWs with the highest PdO proportion are the most stable catalyst in acidic medium for OER.

Nevertheless, the situation seems different under alkaline OER conditions. Both the mass and specific activities of Ir-Pd alloy nanocatalysts show completely reverse trends from those in acidic medium. After the constant potential treatment, surface Ir(VI) oxide can be only observed on the surface of Ir-Pd NTs. Pourbaix has noted that Ir(IV) oxide transitions to soluble Ir(VI) species (IrO_4^{2-}) in alkaline medium [12,54]. The activity and stability of Ir-Pd NHSs and NWs are greatly limited by the soluble surface Ir(VI) oxide, but, during the annealing treatment, it is stable enough to maintain a high OER activity of Ir-Pd NTs in alkaline medium. Moreover, as shown in Fig. S16, electrochemical impedance spectroscopy (EIS) analysis is performed to evaluate the charge transfer during OER. The diameter of the semicircular arc stands for the charge transfer resistance (R_{ct}). A small R_{ct} always provides faster charge transfer in the rate-determining step for OER [7,42,55]. According to Fig. S16, the charge transfer sequence of Ir-Pd nanocatalysts is NHSs > NWs > NTs in acidic medium but NHSs > NTs > NWs in alkaline medium, which also indicates a surface-microstructure-sensitive activity of Ir-Pd alloy nanocatalysts for OER.

CONCLUSIONS

In this work, Ir-Pd alloy NHSs, NWs, and NTs were synthesized *via* a facile one-pot solvothermal method. Ir-Pd NHSs were obtained by galvanic replacement and Kirkendall effect according to time-dependent experiment results. Electrochemical tests for OER exhibit that the catalytic activity and stability of Ir-Pd nanocatalysts are surface-microstructure-sensitive in different pH media. Post-XPS analysis demonstrates that surface Ir(VI) oxide is a possible key intermediate to active Ir-Pd nanocatalysts. Ir-Pd NWs exhibit a mass activity of 74.9 A g^{-1} , more than six times higher than that of commercial Ir/C catalyst in acidic medium. The specific activity sequence of Ir-Pd nanocatalysts behave a positive correlation with the surface roughness, since surface defective sites are beneficial to the formation of surface Ir(VI) oxide. However, in alkaline medium, the catalytic activity of Ir-Pd nanocatalysts exhibits a completely reverse trend. Ir-Pd NTs exhibit a mass activity of 75.0 A g^{-1} , five times higher than that of commercial Ir/C

catalyst. The corresponding Tafel slopes reveal the OER performance of Ir-Pd NHSs and NWs are obviously restricted by the water dissociation due to the soluble Ir(VI) species (IrO_4^{2-}) in alkaline medium.

Both the surface alloying effect and oxidation effect are proved to be beneficial to enhancing the OER activity of Ir-Pd nanocatalysts in different pH media. The electron transfer between Ir and Pd enhances the bonding of Ir and O so that surface Ir(VI) oxide is more likely to be produced. In acidic medium, surface defective sites facilitate the generation of surface Ir(VI) oxide on Ir-Pd alloyed surfaces. However, the strong dissolution of surface Ir(VI) species (IrO_4^{2-}) newly formed at surface defective sites of Ir-Pd NHSs and NWs obstructs the formation of surface Ir(VI) oxide, resulting in a decrease in the specific activity for OER. Ir-Pd NTs with more stable surface Ir(VI) oxide deserve the best OER catalyst in alkaline medium. In this sense, the OER performance of Ir-Pd alloy nanocatalysts is surface-microstructure-sensitive. This work also provides a feasible method to study the surface microstructure-sensitive catalytic properties of heterogeneous catalysts and design high performance metal alloy nanocatalysts for OER.

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details are available in the online version of the paper.

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在酸碱性介质中具有增强的表面微观结构敏感性的氧析出催化活性的铱-钯纳米合金研究

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摘要 近年来铱基催化剂已经在一系列电催化反应中被广泛研究, 氧析出反应(OER)是其中最突出的代表. 研究不同pH介质中表面微观结构敏感的催化活性对于开发高效电催化剂及其反应机理研究具有重要意义. 本文作者通过简单的一步溶剂热法合成了纳米空心球(NHSs), 纳米线(NWs)和纳米四面体(NTs)等形貌可调的Ir-Pd合金纳米晶. 通过电化学研究表明, Ir-Pd合金纳米催化剂在酸性和碱性介质中的OER活性增强表现出表面微观结构敏感性. Ir-Pd NWs和NTs在酸性和碱性介质中0.25 V过电势下表现出商业Ir/C催化剂五倍以上的质量活性. XPS结果表明, 在Ir-Pd纳米催化剂表面缺陷位置产生的Ir(VI)物种可能是反应中的一种关键中间体. 在酸性介质中, Ir-Pd纳米催化剂的比活性与Ir-Pd纳米催化剂表面粗糙度呈正相关, 即NWs > NHSs > NTs. 而碱性介质中由于位于表面缺陷位点的IrO₄²⁻物种快速分解阻碍了Ir(VI)物种的形成, 改变了Ir-Pd纳米催化剂的OER活性顺序.