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Monitoring Oxygen Production on Mass-Selected Iridium-Tantalum Oxide Electrocatalysts

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1 Development of low-cost and high-performance oxygen evolution reaction catalysts is key to 2 implementing polymer electrolyte membrane water electrolyzers for hydrogen production. Iridiumbased oxides are the state-of-the-art acidic oxygen evolution reactio catalysts but still suffer from 3 4 inadequate activity and stability, and iridium's scarcity motivates the discovery of catalysts with 5 lower iridium loadings. Here we report a mass-selected iridium-tantalum oxide catalyst prepared 6 by a magnetron-based cluster source with considerably reduced noble-metal loadings beyond a commercial IrO₂ catalyst. A sensitive electrochemistry/mass-spectrometry instrument coupled with 7 8 isotope labelling was employed to investigate the oxygen production rate under dynamic operating 9 conditions to account for the occurrence of side reactions and quantify the number of surface active sites. Iridium-tantalum oxide nanoparticles smaller than 2 nm exhibit a mass activity of 1.2 ± 0.5 10 kA g_{1r}^{-1} and a turnover frequency of 2.3 ± 0.9 s⁻¹ at 320 mV overpotential, which are two and four 11 times higher than those of mass-selected IrO₂, respectively. Density functional theory calculations 12 reveal that special iridium coordinations and the lowered aqueous decomposition free energy might 13 be responsible for the enhanced performance. 14

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Water electrolysis $(2H_2O \rightarrow 2H_2 + O_2)$ driven by renewable power sources (for example, solar and wind) offers a sustainable strategy to store energy in the form of hydrogen fuel^{1,2}. The polymer electrolyte membrane water electrolyzer (PEM-WE) operating in acidic media serves as a promising technology for such energy conversion and is preferable to alkaline conditions for hydrogen production because of its high current density, fast response, stable operation performance and low cross-over under pressurized operating conditions³. However, the sluggish anodic oxygen evolution reaction (OER), along with the
challenge of materials' stability under the harsh working conditions (low pH, high potentials > 1.4 V, high
oxygen concentration on the anode), severely limits the choice of electrocatalyst and hinders the device
applications on a large scale⁴.

5 As of now, anode catalysts are primarily built on scarce iridium (Ir)⁵⁻⁷. Either searching for earthabundant alternatives or developing catalysts with a minimized Ir loading could be a feasible strategy. 6 Considering the global Ir resource and its catalytic performance towards the OER, a 40 times reduction of 7 the Ir loading (from currently ~ 2 mg_{Ir} cm⁻² to less than 0.05 mg_{Ir} cm⁻²) and an enhanced intrinsic activity 8 9 are highly needed to facilitate the widespread implementation of PEM-WE⁸. Many approaches have been 10 conducted to reduce the Ir consumption and improve the activity of Ir-based catalysts, such as dispersing Ir into inexpensive supports^{9,10}, manipulating the surface area by nanostructuring¹¹ and engineering the 11 reconstructed IrOx surfaces by leaching^{12,13}. Nevertheless, to preserve a reasonable activity and 12 conductivity, loadings of > 20 wt% are still required^{10,14,15}. In addition, further performance improvement 13 of Ir-based catalysts is limited by finding an acid-stable matrix that has a good electronic conductivity 14 even at high anodic potentials. Inspired by the electron tunnelling phenomenon in semiconductors, 15 16 corrosion-resistant metal oxides (Ta₂O₅, Sb₂O₅, and HfO₂) in the subnanoscale could be sufficiently conductive for electrocatalysis, despite having a wide bandgap in bulk^{16,17}. More important, it is critical 17 to unambiguously evaluate the intrinsic oxygen evolution activity. The OER is a rather complex process, 18 always accompanied by other side reactions, for example, oxidation of adventitious carbon, 19 catalyst/support oxidation, material dissolution and capacitive current effects, which could lead to an 20

overestimation of the actual OER activity of a catalyst^{18,19}. Therefore, the OER should always be
 quantified by measuring the actual oxygen production.

Here, we develop a catalyst of iridium-tantalum oxide (Ir-Ta-O) for OER by using a stable Ta₂O₅ 3 4 nanocluster as the matrix. The mass-selected Ir-Ta-O catalysts with sizes ranging from cluster to particle 5 regime have been precisely synthesized by an ultrahigh-vacuum cluster source technique²⁰. The actual OER activity of mass-selected catalyst has been accurately evaluated based on a silicon (Si) microchip-6 based electrochemistry/mass-spectrometry (EC-MS) instrument, developed by our prior work, which has 7 a time resolution of seconds and 100 % collection efficiency²¹. We find that the catalyst within a small 8 size regime (< 2 nm) exhibits a mass activity of $1.2 \pm 0.5 \text{ kA}_{O_2} \text{ g}_{Ir}^{-1}$ and a turnover frequency (TOF) of 2.3 9 \pm 0.9 s⁻¹ at 320 mV overpotential, along with an enhanced stability in acidic media. Density functional 10 theory (DFT) calculations further uncover the key factors dictating these improved activity and stability. 11

Preparation and characterization of mass-selected Ir-Ta-O. Herein, we synthesized up to 12 12 distinctive masses from 6.0×10^3 to 6.0×10^5 atomic mass unit (amu) particles, using our well-established 13 ultrahigh-vacuum cluster source system²⁰. The charged particles were focused and mass selected in flight 14 prior to deposition onto a polycrystalline gold support for electrochemical measurements and onto 15 transmission electron microscope (TEM) grids for morphology investigations (Fig. 1a, Methods and 16 Supplementary Fig. 1)²⁰. Annular dark-field scanning transmission electron microscope (ADF-STEM) 17 images show that the prepared Ir-Ta nanoparticles (NPs) with a selected mass of 6.0×10^3 , 1.2×10^4 and 18 6.0×10⁵ amu are homogeneous and well dispersed on the TEM grid (Fig. 1b Supplementary Fig. 2). The 19 particle size distributions of 6.0×10³, 1.2×10⁴, and 6.0×10⁵ amu Ir-Ta NPs were first estimated according 20 to the ADF-STEM images (Fig. 1c and Supplementary Fig. 3). The measured sizes of 6.0×10^3 , 1.2×10^4 21

and 6.0×10^5 amu particles are 1.1 ± 0.4 , 1.4 ± 0.5 and 6.4 ± 0.8 nm, respectively. Compared to the calculated diameter (Supplementary Table 1), assuming a perfectly spherical particle with metal bulk density²⁰, the measured sizes are slightly larger, which could be due to the surface oxidation of Ir-Ta NPs after exposure to air. Notably, the morphology of the 6.0×10^3 and 1.2×10^4 amu particles shows a platelike structure, suggesting that the discrepancy of smaller particles of 6.0×10^3 and 1.2×10^4 amu might also result from the deviation of the particle shape from the ideal sphere.

To gauge the accuracy of mass-selected synthesis, the particle sizes of 6.0×10^3 and 1.2×10^4 amu Ir-7 8 Ta NPs were further quantified via an atom-counting method utilizing the total amount of intensities 9 scattered by each atomic column. Details are described in Supplementary Fig. 4. As such, the total number of Ir and Ta atoms in a particle could be obtained, as shown in Fig. 1d,e. Based on the investigations, the 10 number of atoms in a 6.0×10^3 or 1.2×10^4 amu Ir-Ta NP has been estimated to be 31 ± 2 or 67 ± 6 atoms, 11 12 respectively (Supplementary Figs. 5 and 6), which is consistent with the estimated numbers of 33 and 66 13 atoms based on their individual atomic masses, respectively. STEM energy-dispersive X-ray spectroscopy (STEM-EDS) elemental mapping (Supplementary Figs. 7 and 8) confirms that Ir and Ta are 14 homogeneously distributed within each particle. 15

Prior to the electrochemical measurements, the as-deposited mass-selected Ir-Ta NPs on the gold support were thermally annealed in air at 400 °C for 5 min (Supplementary Figs. 9 and 10). An elemental composition of Ta/Ir = 9:1 and the overall distribution of the deposited NPs were characterized by X-ray photoelectron spectroscopy (XPS; Supplementary Figs. 11-14). Figure 1f shows the XPS spectra of the Ta 4*f* and Ir 4*f* core-level regions of the as-deposited Ir-Ta NPs and oxidized Ir-Ta-O NPs. The Ta 4f_{7/2} spectrum of the as-deposited sample shows a double set of peaks, suggesting a mixed oxidation state of

1 Ta, which is likely induced by trace amounts of water in the XPS chamber. The O 1s spectrum of the asdeposited sample is shown in Supplementary Fig. 15. The high-resolution spectrum of the Ir 4f core-level 2 region of the as-prepared sample, after data processing due to Au 5p peak overlaps (Supplementary Figs. 3 4 11 and 12), suggests that Ir is in a metallic state. After oxidation, a clear positive shift in binding energy can be observed for the Ta $4f_{7/2}$ and Ir $4f_{7/2}$ to 26.3 eV and 61.3 eV, which are consistent with Ta⁵⁺ and 5 Ir⁴⁺, respectively. In this work, the oxidized Ir-Ta-O is denoted as Ir_{0.1}Ta_{0.9}O_{2.45}. To avoid the particle 6 overlap, the loading of the electrode is controlled to be 5% projected surface area coverage. The total mass 7 loadings of 60 to 275 ng cm⁻² corresponding to an Ir loading of ~6 to 29 ng cm⁻² (according to the elemental 8 9 ratio of Ta/Ir = 9:1) was precisely controlled by monitoring the particle beam current during the deposition (Supplementary Table 1). 10

Monitoring oxygen evolution on Ir_{0.1}Ta_{0.9}O_{2.45} electrocatalysts. The oxygen evolution performances of 11 the thermally oxidized Ir_{0.1}Ta_{0.9}O_{2.45} catalysts were investigated in 0.1 M perchloric acid electrolyte 12 13 (HClO₄, pH = 1.08) by a Si-microchip-based EC-MS, which is schematically depicted in Fig. 2a. To avoid the oxidation of the carbon support causing the overestimation of the OER activity (Supplementary Fig. 14 16), the polycrystalline gold with good conductivity and high corrosion resistance in acid was used as the 15 working electrode in this study. However, the formation of the tunnelling barrier of gold oxide with a wide 16 bandgap of 1.90 eV (Supplementary Fig. 17) at high anodic potential above 1.5 V versus a reversible 17 hydrogen electrode (RHE)²² would compromise the electron transfer during OER working conditions, 18 19 resulting in a sluggish activity of the catalyst.

1	To investigate the OER activity of the catalysts without the influence of the tunnelling barrier of gold
2	oxide, the working potential range of the cyclic voltammetry (CV) tests was conducted between a cathodic
3	potential limit of 0.75 V versus RHE, near the initial the open-circuit potential (OCP) of the sample and
4	an anodic potential limit of 1.7 V versus. RHE. The low cathodic potential limit could inhibit the formation
5	of the tunnelling barrier and ensure a well-conductive electrode surface (Supplementary Figs. 18-20).
6	Figure 2b shows the CV of gold-supported 1.2×10^4 amu Ir _{0.1} Ta _{0.9} O _{2.45} catalyst with the corresponding
7	electrochemical current (I_E) and the O ₂ current (I_{O_2} , the current equivalent of the MS signal of the mass-
8	to-ratio $m/z=32$). It can be readily seen that I_E is relatively higher than I_{O_2} at anodic working potentials,
9	which is mostly due to the gold oxidation during OER (Supplementary Fig. 21). By integrating the MS O ₂
10	currents ($m/z=32$) and Au reduction currents, we calculated the faradaic efficiency (FE) of the OER and
11	Au oxidation. The mass spectrometer signals of O2 and CO2, were calibrated internally for each
12	experiment, as shown in Supplementary Fig. 22. As shown in Fig. 2c, the FE values of the OER and Au
13	oxidation are 50 ± 4 % and 45 ± 4 %, respectively. The residual current goes towards adventitious carbon
14	decomposition and Au dissolution (Supplementary Fig. 23) ²³ .

Due to mass-transport effects, the measured MS currents do not directly correspond to the partial current of the analyte under the dynamic conditions of CV measurements. This effect, however can be eliminated by back calculating the partial current density from a measured MS current by a mathematical deconvolution method (Supplementary Figs. 24 and 25), which has been demonstrated and validated in our recent work²⁴. After deconvolution (Fig. 2d), the obtained oxygen partial current presents the real interfacial oxygen production rate under dynamic operating conditions. The lower activity of the cathodic sweep of the deconvoluted O₂ current can most likely be ascribed to the formed tunnelling barrier of the Au support at high working potentials. We therefore assessed the oxygen evolution activity of mass selected catalysts by using the forward-moving, anodic sweep of the deconvoluted O₂ current
 (Supplementary Figs. 26 and 27).

Oxygen evolution performance of Ir_{0.1}Ta_{0.9}O_{2.45} catalysts. The OER activity of mass-selected 4 Ir_{0.1}Ta_{0.9}O_{2.45} catalysts was evaluated using the mass activity (normalized to the total Ir loading) at 320 5 mV overpotential. Three different sizes of mass-selected IrO2 catalysts within 1-2 nm were also studied 6 for comparison (Supplementary Fig. 28), which shows an average mass activity of 650 \pm 150 $A_{O_2}\,g_{Ir}^{-1}$ at 7 320 mV overpotential. As shown in Fig. 3a, the mass activity of Ir_{0.1}Ta_{0.9}O_{2.45} catalysts exhibit a marked 8 enhancement of $1.2\pm0.5~kA_{O_2}~g_{Ir}^{-1}$ over pure IrO2 within the same size range. Notably, the particle size of 9 Ir_{0.1}Ta_{0.9}O_{2.45} has a profound impact on the OER activity; a rapid decline of the OER activity is observed 10 when the particle mass is higher than 4.4×10^4 amu (equivalent diameter, 2 nm). This lower activity is 11 likely due to a compromised electrical conductivity in larger particles or surface segregation of Ta oxide. 12 In addition, the pure Au electrode and mass-selected Ta₂O₅ catalysts were also studied, which are 13 unsurprisingly inactive for the OER at low overpotentials (Supplementary Fig. 29). 14

A comprehensive comparison with other reported ruthenium- (Ru-) and Ir-based acidic OER catalysts is shown in Fig. 3b. Although the Ru-based catalysts are more active, the narrow potential region of the catalysts' stability (~0.7 to 1.4 V versus RHE, pH=1) severely hinders its practical applications²⁵. The mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} with a highly reduced Ir loading exhibits a high mass activity in acid and comparable to state-of-the-art Ir-based catalysts. Several studies in the literature report higher activities. However, most of these studies have not actually measured the amount of evolved oxygen at the high activity. Relying only on the measured CV will introduce large errors in the catalytic activity due to the
 capacitance effect, redox couples, and corrosion. Therefore, a proper quantification of the OER activity is
 to measure the oxygen evolution rate, as done in this work.

4 Stability of mass-selected $Ir_{0.1}Ta_{0.9}O_{2.45}$ catalysts. The operating stability of a catalyst is another important metric for practical application. We investigated the stability of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} 5 catalyst by a long-term measurement at 1.6 V versus RHE for 24 h in 0.1 M HClO₄ (Fig. 4a). The working 6 electrode was initially held at OCP and stepped up for chronoamperometry at 1.6 V for 4 h; the OER 7 activity of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} catalyst dropped quickly, within minutes (Supplementary Fig. 30), 8 9 in line with the deactivation observed for the gold-supported Ir-Au-TiO₂ catalyst²⁶. We found the OER activity of our catalyst could be recovered with negligible changes even after repeating five cycles by 10 reducing the Au electrode at OCP. Our recent work on the Pt electrode for OER shows that the tunnel 11 barrier for electron transfer by the formation of PtO₂ reduces the faradaic reaction rate of oxygen 12 13 evolution²⁴. We therefore speculate that the gradual degradation of the OER activity during chronoamperometry measurement is attributed to the formation of an insulating gold oxide layer rather 14 than the catalyst deactivation. 15

The stability number (*S*-number) of an electrocatalyst has been proposed as a metric to assess the stability of catalysts, which compares the evolved oxygen (n_{O_2} , calculated according to the total charge (Q_{total}) or MS O₂ currents) to the amount of dissolved Ir (n_{Ir} ; ref. ²⁷). As shown in Fig. 4b, the *S*-numbers of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} NPs and sputtered Ir_{0.1}Ta_{0.9}O_{2.45} thin film are calculated to be approximately 10⁶ (Supplementary Fig. 31), which is comparable with the reported rutile IrO₂ (~10⁶, AlfaAesar) and one order of magnitude higher than the rutile IrO₂ (~10⁵, Sigma-Aldrich) and other reported
Ir-based perovskites (~10⁵)²⁷⁻²⁹. In addition, STEM and XPS characterizations of mass-selected 1.2×10⁴
amu Ir_{0.1}Ta_{0.9}O_{2.45} particles were performed after the electrochemical measurements, which show no
significant changes in the morphology, distribution or composition of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45}
catalysts (Supplementary Figs. 32 and 33), confirming the robust stability. Together, these results suggest
the Ir_{0.1}Ta_{0.9}O_{2.45} catalysts have an excellent OER activity and stability in acid.

Investigation of intrinsic activities. To evaluate the potential for scalability and compare the intrinsic 7 8 activity of our catalysts to the literature, it is essential to assess the TOF, which quantifies how many 9 molecules O₂ are evolved per second per site at a specific overpotential⁴. Besides capacitive cycling and porosimetry techniques, the CO stripping analysis is commonly used to determine the electrochemically 10 active surface area, especially for noble-metal catalysts³⁰. In contrast with metallic noble-metal catalysts, 11 where the active site can be carefully explored, the assessment of oxides is rather complex due to the 12 13 pseudocapacitance charging processes during CO adsorption and oxidation³¹. Additionally, the loading level of our system, below nanomolar, makes an accurate and precise characterization even more 14 15 challenging.

To overcome these difficulties, we employed the highly sensitive in-situ EC-MS technique to determine the active sites rather than relying on the electrochemical current changes²¹. Furthermore, an isotope-labelled ¹³CO gas was introduced as a probe molecule, to exclude the interference of the adventitious carbon from the system. According to the MS-monitored ¹³CO₂ signal, which comes from only the oxidation of the adsorbed ¹³CO on the active Ir sites, the number of surface active sites of the Ir_{0.1}Ta_{0.9}O_{2.45} catalyst can be quantified by integrating the corresponding MS current of ¹³CO₂ (*m/z* = 45)

signal for the intrinsic activity evaluation. The catalyst was brought to a potential of 0 V versus RHE to 1 reduce the surface iridium atoms for CO adsorption³². In addition, pure mass-selected Ta_2O_5 NPs on a Au 2 support do not show any ¹³CO stripping signal, which indicates that all of the ¹³CO₂ signal must be 3 4 associated with iridium. We assumed one ¹³CO molecule adsorbed per surface iridium atom as supported 5 by DFT (Supplementary Fig. 34). The experimental details are presented in Supplementary Figs. 35 and 6 36. For instance, the total Ir loading of 1.2×10^4 amu Ir_{0.1}Ta_{0.9}O_{2.45} NPs with 5 % coverage on a Au support is ~8.0 pmol (4.8×10^{12} Ir atoms), and the number of surface Ir sites determined from the ¹³CO stripping is 7 1.5×10^{12} , which means ~31 % Ir atoms are exposed on the surface. As shown in Fig. 5a, the mass-selected 8 $Ir_{0.1}Ta_{0.9}O_{2.45}$ NPs in a small size regime (< 2 nm) have a similar surface Ir ratio of ~20-40 %, since 9 10 essentially all atoms are residing at the surface. Contrarily when the particle size increases, more Ir atoms are trapped inside the particles during oxidation process³³, which results in a low surface Ir ratio of 3 % 11 for 6.0×10^5 amu (equivalent diameter: 4.8 nm) particles. 12

13 Based on the MS-determined O₂ production rate, the TOF values were calculated according to the total Ir mass (TOF_{bulk}) and ¹³CO-stripping-determined surface active sites (TOF_{surface}) of mass-selected 14 Ir_{0.1}Ta_{0.9}O_{2.45} NPs at 320 mV overpotential, displayed in Fig. 5b. We find that mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} 15 NPs within a smaller size range (1-2 nm) yield similar intrinsic activities with a high average TOF_{surface} 16 value of 2.3 s⁻¹, which is four times higher than that of TOF_{bulk} (~0.6 s⁻¹); the $TOF_{surface}$ of 6.0×10⁵ amu 17 $(\sim 0.37 \text{ s}^{-1})$ is about 40 times higher than that of TOF_{bulk} ($\sim 0.01 \text{ s}^{-1}$), indicating the crucial impact of the 18 particle size on the OER activity. As shown in Fig. 5c, the average TOF_{surface} of mass-selected 19 Ir_{0.1}Ta_{0.9}O_{2.45} NPs within a smaller size range (1-2 nm) was compared to the state-of-the-art Ir/Ru-based 20 OER catalysts in acidic media, the reported OER catalysts with superior activities need to be further 21

1 confirmed by measuring the evolved O_2 at certain potentials. Contrary to those Ir-based thin-film catalysts, 2 the mass-selected $Ir_{0.1}Ta_{0.9}O_{2.45}$ NPs with considerably reduced Ir loading possess an intrinsic activity of 3 2.3 ± 0.9 s⁻¹ at 320 mV overpotential, placing them among the most active Ir-based OER catalysts in acid.

4 DFT calculations. We further performed DFT calculations to gain insight into the OER activity and stability of the Ir_{0.1}Ta_{0.9}O_{2.45} catalysts. The OER activity was evaluated using the theoretical overpotential 5 calculation based on the acidic OER mechanism (Supplementary Fig. 37 and Supplementary Note 1)^{34,35}. 6 Due to the low Ir surface concentration of our catalysts, Ir_{0.1}Ta_{0.9}O_{2.45} was first modelled using an Ir-doped 7 8 Ta_2O_5 (200) surface with three distinct Ir-doping concentrations at the topmost surface (Fig. 6a). The Au-9 supported Ir-doped Ta₂O₅, pure IrO₂, pure Ta₂O₅ and Au-supported Ta₂O₅ were calculated for comparison (Fig. 6b,c and Supplementary Fig. 38). The calculated theoretical overpotentials of these structures as a 10 function of the usual OER activity descriptor, the adsorption free energy difference between *O and *OH, 11 are shown in Fig. 6d (ref. ³⁴). By comparing the calculated theoretical overpotentials of Ir-doped Ta₂O₅ 12 13 (200) (0.45 V) and Ta_2O_5 (200) (0.93 V) to the Au-supported Ir-doped Ta_2O_5 (0.44 V) and Ta_2O_5 (200) (0.91 V), we find that the Au support has little effect on the OER catalytic activity. In addition, Ir-doped 14 Ta₂O₅ (200) surfaces with different Ir-doping concentrations yield a theoretical overpotential similar to 15 that (0.49 V) of IrO₂ (110) and the lowest Ir-doping surface (0.08 monolayer) possesses a favorable 16 activity with a theoretical overpotential of 0.43 V. 17

We also investigated the OER activity for some cluster models and their calculated theoretical overpotentials are similar to those of Ir-doped Ta₂O₅ (200) and IrO₂(110). (Supplementary Fig. 39, Supplementary Note 2 and Supplementary Tables 3 and 4). These results suggest Ir-doped Ta₂O₅ would

have an OER activity as good as IrO₂. Note that we do not expect a direct quantitative comparison of the 1 experimental and calculated theoretical overpotentials to match. The former is a potential-scale measure 2 3 of the activity, while the latter is a function of the current density. Previous studies reported that higher 4 octahedral distortion and undercoordinated Ir atoms are beneficial for catalytic activity^{36,37}. We thus 5 examined the local environment of the active Ir sites of modelled structures (Supplementary Fig. 40). We 6 find that the structural motif of Ir in Ta₂O₅ (200) surface shows a distorted octahedron (IrO₆), which is similar to that in rutile IrO₂ (110). These results indicate that these special Ir local coordinations of 7 Ir_{0.1}Ta_{0.9}O_{2.45} catalysts may be responsible for the excellent OER activity, confirming the experimental 8 9 observations.

10 In addition, the stability of the Ir_{0.1}Ta_{0.9}O_{2.45} catalysts was evaluated by the calculated Pourbaix 11 decomposition free energy (ΔG_{pbx}) using the DFT-calculated bulk Pourbaix diagram (Supplementary Fig. 41 and Supplementary Note 3)³⁸. The calculated ΔG_{pbx} involves contributions from the phase stability and 12 13 aqueous dissolution energy, the latter of which mainly determines the catalyst stability in the aqueous solution. Whether using the Ir-doped Ta_2O_5 bulk or surface/cluster phase of Ir-doped Ta_2O_5 will only 14 affect the calculated phase stability, not the aqueous dissolution energy. Figure 6f shows the calculated 15 16 aqueous decomposition free energies (ΔG_{pbx}) of Ir-doped Ta₂O₅ and IrO₂. Comparing with the calculated ΔG_{pbx} of IrO₂ (ref. ²⁵), the Ir-doped Ta₂O₅ has a non-zero ΔG_{pbx} (~0.2 eV per atom) at the potential 1.23 17 18 V to 1.60 V, which is attributed to its metastability (phase stability) compared to the stable phases of IrO₂ 19 and Ta₂O₅. At the potential range of 1.60 to 1.82 V, the Ir-doped Ta₂O₅ decomposes to $IrO_4^- + Ta_2O_5(s)$ with a marginal increase of ΔG_{pbx} , suggesting that Ir-doped Ta₂O₅ could be stabilized by the slow phase 20 21 transition to Ta₂O₅(s) at room temperature. At potentials higher than 1.82 V, ΔG_{pbx} significantly increases,

and Ir-doped Ta₂O₅ decomposes to $IrO_4^- + Ta_2O_7$ (s). In this scenario, the Ir-doped Ta₂O₅ would suffer from a very large thermodynamic decomposition driving force and consequently becomes unstable in the aqueous solution. In the experiment, $Ir_{0.1}Ta_{0.9}O_{2.45}$ catalysts show much better stability than IrO_x catalysts, which can therefore be attributed to the smaller ΔG_{pbx} . Finally, although the exact structure of the $Ir_{0.1}Ta_{0.9}O_{2.45}$ NP is unknown, we believe these theoretical insights could shed light on the underpinning mechanisms of the enhanced OER performance.

7 Conclusions

In summary, we have synthesized a series of mass-selected $Ir_{0,1}Ta_{0,9}O_{2,45}$ acidic OER catalysts with an Ir 8 9 loading of 9 wt% with an ultrahigh-vacuum cluster source. We have unambiguously evaluated the real 10 OER activity of the gold-supported Ir_{0.1}Ta_{0.9}O_{2.45} NPs using the microchip-based EC-MS instrument. We have found that mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} NPs with a size smaller than 2 nm exhibit an enhanced OER 11 activity in 0.1 M HClO₄ with remarkable stability over 24 hours at 1.6 V versus RHE. The number of 12 surface active Ir atoms was determined by the isotope-labelling combined EC-MS technique, and the 13 mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} catalyst also demonstrates high intrinsic activity with a TOF value of 2.3 \pm 14 0.9 s⁻¹ at 320 mV overpotential. The good OER performance of our catalyst in acid can be explained by 15 16 the favorable particle size and good Ir dispersion on the surface, as well as the favorable atomic configuration of the OER active center. We anticipate that our findings may apply to other wide-bandgap 17 18 and corrosion-resistant metal oxides with well-controlled structures, thus accelerating the development of 19 new low-cost, stable, and efficient acidic OER electrocatalysts.

20 Methods

Preparation of mass-selected Ir, Ta, and Ir-Ta particles. Pure Ir sputtering target (99.9%, Kurt J. 1 Lesker), pure Ta target (99.95%, Kurt J. Lesker), and alloy Ir-Ta (Ir/Ta = 10:90 at%; 99.95%, ACI Alloys) 2 were used to prepare the Ir, Ta, and Ir-Ta NPs, respectively. The NPs were prepared by a cluster source 3 4 based on a direct current magnetron plasma sputtering and gas-aggregation (Teer Coating). The charged 5 NPs of different sizes were extracted and focused by electrostatic lenses, and then passed through a lateral 6 time-of-flight mass filter (with a mass resolution of $m/\Delta m = 20$). The distribution of available particle sizes can be tuned by changing the experimental parameters. The mass-selected NPs were deposited on TEM 7 grids coated with ultra-thin carbon membrane (3 nm, Agar Scientific) or on 5-mm-diameter polycrystalline 8 gold electrodes. For using Au supports, the polished surface was cleaned by 1.5 kV Ar⁺ sputtering for 2 h 9 to remove any residual contaminations, and XPS was used to check the cleanness before the deposition. 10 The whole process including the precleaning, preparation and deposition, weas conducted in a 11 multichamber under ultrahigh vacuum with a base pressure in the low 10⁻⁹ mbar region. Here, we assume 12 each charged particle carries 1e charge, and thus the total loading of the deposited particles could be 13 14 calculated according to the deposition current:

15

$$M_{Total} = mIt$$

Where M_{total} is the total loading of the deposited particles, *m* is the single NP mass, *I* is the deposition current and *t* is the deposition time. For the calculation of particle size, we assume a sphere structure of generated particle with bulk density²⁰. In this study, the loading of the electrode is 5% projected surface area coverage.

20 Material characterizations. ADF-STEM images and STEM-EDS elemental maps were acquired using 21 an aberration-corrected 'cubed' Thermo Fischer Scientific Titan electron microscope, operated at 200 kV, 22 equipped with the ChemiSTEM system³⁹. The probe convergence semi-angle and the detector collection 23 inner semi-angle were set to 21.4 mrad and 38 mrad, respectively. From each investigated atomic cluster, 24 series of 512×512 images were acquired, using a scan time of 0.5 s per frame. XPS measurements were 25 performed using a non-monochromatized Al K α source (XR-50; 1486.7 eV) and concentric hemispheric 26 analyser (Phoibos 100), manufactured by SPECS. The as-prepared NPs were directly analysed under ultrahigh-vacuum conditions after the deposition. The thermal annealed NPs, as well as the NPs after
electrochemical testing, were measured on the same XPS set-up mentioned above. The employed pass
energy was 100 eV for the overview and 20 eV for the high-resolution spectra. All spectra were charged
reference against the Au 4*f* peak at 84 eV and a Shirley background was chosen for the elemental
quantification. CasaXPS software was used for all the XPS analysis. Details of XPS data analysis can be
found in the Supplementary Figs. 11 and 12. Inductively coupled plasma MS was performed on a Thermo
Scientific iCAP Q ICP-MS (Thermo Fisher Scientific) in the Kinetic Energy Discrimination mode.

8 EC-MS measurements. Electrolyte solutions (0.1 M HClO₄) were prepared from perchloric acid (70 %, Sigma-Aldrich) by addition of ultrapure water (18.2 MΩ.cm at 25 °C; Merck). The Hg/HgSO₄ reference 9 electrode was calibrated by measuring the OCP of a cleaned platinum disc in H₂-purging 0.1 M HClO₄ 10 electrolyte. To avoid the oscillations from potentiostat and easy-to-correct ohmic losses, we introduced a 11 conventional ohmic resistor of 100 Ω with the working electrode. Unless otherwise stated, helium (6.0, 12 Air Liquide) was used as an auxiliary gas during EC-MS experiments. The isotope-labeled ¹³CO (≥99 13 atom %; Sigma-Aldrich) stripping measurements were conducted in 0.1 M HClO₄ solution. The catalysts 14 were firstly cycled in He-saturated electrolyte between 0 to 1 V versus RHE. After obtaining stable cyclic 15 voltammogram, the carrier gas was exchanged from He to ¹³CO while holding the potential at 0 V versus 16 RHE for 2 min (ref. ³²). Then, ¹³CO was removed by purging pure He gas into the electrolyte for 2 h, and 17 18 continuous CVs were measured at a scan rate of 5 mV s⁻¹, with the first one being the CO stripping process. The raw data for the ¹³CO stripping experiment is shown in Supplementary Fig. 35a. After the ¹³CO 19 stripping measurements, the OER activity was measured by cycling the working electrode between OCP 20 and 1.7 V versus RHE with a scan rate of 20 mV s⁻¹ until a stable CV was obtained. 21

DFT calculations. Density functional theory calculations were performed using Vienna Ab initio Simulation Package (VASP)⁴⁰. The revised Perdew-Burke-Ernzerhof was used for adsorption energy calculations⁴¹. The plane-wave energy cut-off was set to 400 eV. The electronic energy and structure relaxation were converged within 10^{-5} eV and 0.05 eV Å⁻¹, respectively. The crystal structure of orthorhombic λ -Ta₂O₅ was used to study the surface catalytic activity of Ir-doped Ta₂O₅ (ref. ⁴²). Surface models with a slab thickness of at least 10 Å were generated with a maximum Miller index of two using

the Python Materials Genomics (pymatgen) package⁴³. A vacuum separation of 12 Å was added to the 1 direction perpendicular to the surface. Two four-layers (200) surface models with cell sizes of 2×1 and 2 3×2 were used for Ir-doped Ta₂O₅. The Brillouin zone was sampled using a gamma-center k-point grid 3 of $3 \times 3 \times 1$ and $2 \times 1 \times 1$ for the 2×1 and 3×2 supercell surface models, respectively. A four-layers 4 rutile IrO₂(110) surface with a *k*-point grid of $3 \times 3 \times 1$ was used. The bottom two layers of the slab models 5 6 were fixed at the bulk position. For the $Ta_2O_5(200)/Au(111)$ interface, a slab model with a four-layer 7 $Ta_2O_5(200)$ and three-layer Au(111) interface was constructed to investigate the gold support effect on the OER activity. The lattice mismatch between $Ta_2O_5(200)$ and Au(111) is about 0.14%. The Brillouin zone 8 was integrated using a gamma center k-point grid of $1 \times 2 \times 1$. The topmost two layers were relaxed, and 9 the rest were fixed at the bulk position. The OER activity was evaluated by calculating the theoretical 10 overpotential of the reaction mechanism proposed in refs. ^{34,35} and detailed in Supplementary Note 1. The 11 computational results of cluster models are provided in the Supplementary Note 2. The bulk Pourbaix 12 diagram was calculated using the Strongly Constrained and Appropriately Normed (SCAN) functional, 13 which has been recently shown to accurately predict the aqueous stability of solids^{44,25}. In SCAN 14 calculations, the plane-wave energy cut-off was 520 eV. The electronic energy and structure relaxation 15 were converged to 10⁻⁵ eV and 0.02 eV Å⁻¹, respectively. 16

17 Data availability.

The authors declare that all data supporting the findings of this study are available within the paper and
its Supplementary Information files and on DTU Data (<u>https://doi.org/10.11583/DTU.16818703.v1</u>).

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3 Author Contributions

- 4 I.C., J.K., and J.K.N. conceived and supervised the project. Y.-R.Z. and Z.W co-wrote the manuscript. Y.-
- 5 R.Z. performed electrochemical tests and collected and analyzed the data. J.V., K.Z., T.-W.L., F.P., and
- 6 N.M. S. performed the mass-selected nanoparticles preparation and XPS measurements. Z.W., A.C., M.A.,
- 7 and J.K.N. performed DFT calculations. K.K., D.H., and S.B. S., assisted EC-MS data analysis. T.A., P.L.,
- 8 and S.B. preformed STEM experiments. J.F. and S.V.A. performed quantitative analysis of STEM data.
- 9 C.M. performed the inductively coupled plasma MS measurements. All authors discussed the results and
- 10 assisted during manuscript preparation.

11 Competing interests

- 12 The authors declare no competing interests.
- 13

1 Figure Captions





3 Fig. 1 | Preparation and characterization of mass-selected Ir-Ta NPs. a, Schematic illustration of the ultrahighvacuum mass-selected cluster source technology, which comprises of a magnetron sputtering head, a noble gas-4 5 aggregation chamber, a focusing and acceleration chamber and a time-of-flight mass filter. Mass-selected Ir-Ta NPs were deposited on a polycrystalline gold electrode or TEM grids for further measurement. b. Representative ADF-6 STEM images of three different masses of 6.0×10^3 , 1.2×10^4 and 6.0×10^5 amu Ir-Ta NPs after exposure to air. c, 7 Size distributions of 6.0×10^3 , 1.2×10^4 and 6.0×10^5 amu Ir-Ta NPs, which were determined by measuring the size in 8 9 the STEM images. d.e., Atomic scale high-magnification ADF-STEM images and corresponding optimized models including atom counts for a 6.0×10^3 and 1.2×10^4 amu particle, respectively. The number of atoms was determined 10 by analyzing 12 and 26 different particles for the 6.0×10^3 and 1.2×10^4 amu Ir-Ta NPs respectively. **f**, XPS spectra 11 12 of Ta 4f and Ir 4f of 1.2×10^4 amu as-deposited sample and oxidized Ir_{0.1}Ta_{0.9}O_{2.45} NPs. Background subtraction is described in Supplementary Figs.11 and 12. The dots are the raw data and the grey line is the overall fitting envelope. 13 The same colours are used to indicate each couple of spin-orbit split components corresponding to a different 14 15 oxidation state.





Fig. 2 | Monitoring oxygen evolution on gold supported mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} NPs. a, Schematic diagram 2 3 of the electrochemical cell and Si-microchip assembly, which connects to the mass spectrometer. The distance 4 between the working electrode and the microchip is ~100 μ m. **b**, Comparison of the electrochemical current (I_E) and the O₂ current (I_{O_2} , back-calculated from MS signal of m/z = 32) of the 1.2×10⁴ amu Ir_{0.1}Ta_{0.9}O_{2.45} during 5 potential (E) cycling between OCP and 1.7 V versus RHE with a scan rate of 20 mV s⁻¹ in 0.1 M HClO₄. c, FE of 6 7 each reaction of the $Ir_{0.1}Ta_{0.9}O_{2.45}$ catalyst during water oxidation within a working potential range of ~0.75-1.7 V 8 versus RHE. The carbon decomposition is calculated from the MS monitored CO2 products during potential cycling (Supplementary Fig. 23). The Au oxidation is calculated from the electrochemical Au reduction peak. The dissolved 9 Au amount is ~ 10 ng cm⁻² per cycle with an anodic limiting potential of 1.7 V versus RHE²³. The error bars represent 10 the Standard deviations of FE values of three independent samples $(1.2 \times 10^4, 1.26 \times 10^4 \text{ and } 4.4 \times 10^4 \text{ amu})$. The scatter 11 12 dots represent the individual values of the three experiments. d, Deconvoluted O₂ partial current in comparison to 13 the measured O_2 current of the $Ir_{0.1}Ta_{0.9}O_{2.45}$ catalyst.

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2 Fig. 4. | Stability of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} NPs. a, Stability performance of the 4.4×10⁴ amu Ir_{0.1}Ta_{0.9}O_{2.45} catalyst at 1.6 V versus RHE for 24 h in 0.1 M HClO₄. After every 4 h, the working electrode was reduced at OCP 3 4 for 10 min, and then stepped up to 1.6 versus RHE. The grey line is the smoothed curve derived from the MS O₂ 5 currents (black line). b, Calculated S-number at 570 mV overpotential of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} catalysts and other Ir-based thin film and powder OER catalysts in acid. Reference data are extracted from the literature: rutile 6 IrO₂ (Sigma-Aldrich) and SrCo_{0.9}Ir_{0.1}O_{3-δ} (ref. ²⁸); rutile IrO₂ (Alfa-Aesar), hydrous IrO_x, Ir metal, SrIrO₃ film and 7 Ba₂SrIrO₆ (ref. ²⁷); Sr₂IrO₄ (ref. ²⁹). The error bars of the Ir_{0.1}Ta_{0.9}O_{2.45} thin film represent the standard deviation of 8 the average S-number of three independent experiments. The scatter dots represent the individual values of the 9 10 experiments. The evolved O₂ generated (n_{O_2}) during OER on mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} NPs is obtained from MS 11 O₂ currents.



2 Fig. 5 | Isotope-labelling coupled with EC-MS determined surface active sites and TOF values of massselected Ir_{0.1}Ta_{0.9}O_{2.45} NPs. a, In-situ ¹³CO-stripping-determined surface Ir ratio and particle density as a function 3 4 of the average particle mass of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} NPs on a Au support. The particle density is calculated 5 according to the deposition current; the linear fit line shown in orange has a slope of -0.67 and an R^2 value of 1. 6 Under the same coverage (5%) on the Au support, the smaller the sample size, the higher the particle densities. b, 7 TOF values calculated from total Ir mass (TOF_{bulk}, green) and the determined surface Ir atoms (TOF_{surface}, black) of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} at 320 mV overpotential as a function of particle mass. Electrolyte, 0.1 M HClO₄. Scan 8 rate, 20 mV s⁻¹. The dotted lines are guides to the eye. c, Comparison of TOF values between the mass-selected 9 Ir_{0.1}Ta_{0.9}O_{2.45} NPs, mass-selected IrO₂ NPs and reference noble-metal OER catalysts in acid, including Li-IrO_x (ref. 10 ⁵⁵), 30 h SrIrO₆ (ref. ²⁸), SrCo_{0.9}Ir_{0.1}O_{3-δ} (ref. ²⁸), activated PtNi axis and IrNi edge frame catalyst (*a*-PN-IN 11 frame/C)⁵⁶, amorphous Ir nanosheets (Ir NSs)¹¹ and Y₂Ru₂O_{7- δ} (ref. ⁵⁷). The colored columns represent the intrinsic 12

- 1 activity, which was determined by collecting the actually generated oxygen products, whereas the grey columns
- 2 represent the number of O_2 molecules (N_{O2}) that is obtained from the measured electrochemical currents. Solid and
- 3 hatch columns refer to experimentally/theoretically determined TOF_{surface} and TOF_{bulk}, respectively. The error bars
- 4 of the $TOF_{surface}$ values at 300 mV and 320mV overpotential of mass-selected $Ir_{0.1}Ta_{0.9}O_{2.45}$ represent the standard
- 5 deviation of 16 independent samples with sizes smaller than 4.4×10^4 amu. The error bar of TOF_{bulk} at 320 mV
- $\ \ \, \text{samples with sizes smaller than } 4.4 \times 10^4 \ \text{amu. The error bars of mass-selected } IrO_2 \ \text{represent the standard deviation}$
- 8 of the average TOF of three independent samples (6×10^4 , 9×10^4 and 1.27×10^4 amu). The scatter dots represent the
- 9 individual values of the three experiments.



2 Fig. 6 | Theoretical analysis of OER activity and stability. a-c, Structure models used for catalytic activity 3 calculations of Ir-doped Ta₂O₅(200) (a), Ir-doped Ta₂O₅(200)/Au(111) (b) and IrO₂(110) (c). The Ir-doping 4 concentration at the topmost surface was represented by the fraction of a monolayer (ML). d, Theoretical 5 overpotential volcano plot as a function of the OER activity descriptor characterized by the adsorption free energy 6 difference between *O and *OH. The labelled data points correspond to the modelled structures in a-c. e, Calculated aqueous decomposition free energy (ΔG_{pbx}) of Ir-doped Ta₂O₅ and IrO₂ from the potential 1.0 to 2.0 V versus RHE 7 8 at pH = 0. The projection of ΔG_{pbx} onto the potential axis presents the stable chemical species at the corresponding 9 regions. The arrow is drawn to show the decreasing trend of ΔG_{pbx} with respect to the applied potential.

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- 36 Additional information
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