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

Ya-Rong Zheng^{1,2†}, Jerome Vernieres^{1†}, Zhenbin Wang^{1†}, Ke Zhang^{1†}, Degenhart Hochfilzer¹, Kevin Kremp¹, Ting-Wei Liao¹, Francesco Presel^{1,3}, Thomas Altantzis^{4,5}, Jarmo Fatermans⁴, Soren Bertelsen Scott¹, Niklas Mørch Secher¹, Choongman Moon¹, Pei Liu⁴, Sara Bals⁴, Sandra Van Aert⁴, Ang Cao¹, Megha Anand¹, Jens K. Nørskov^{1*}, Jakob Kibsgaard¹, and Ib Chorkendorff^{1*}

¹*Department of Physics, Technical University of Denmark, 2800 Kongens Lyngby, Denmark.*

²*Anhui Province Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology, 230009, Hefei, China.*

³*Institute of Physics, NAWI Graz, University of Graz, Universitätsplatz 5, 8010 Graz, Austria.*

⁴*EMAT and NANOLab Center of Excellence, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium.*

⁵*ELCAT, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium.*

[†]These authors contributed equally: Y.-R. Zheng, J. Vernieres, Z. Wang, K. Zhang.

*Corresponding authors, e-mail: ibchork@fysik.dtu.dk and jkno@dtu.dk

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. Iridium-**
3 **based oxides are the state-of-the-art acidic oxygen evolution reactio catalysts but still suffer from**
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**
7 **commercial IrO₂ catalyst. A sensitive electrochemistry/mass-spectrometry instrument coupled with**
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**
10 **sites. Iridium-tantalum oxide nanoparticles smaller than 2 nm exhibit a mass activity of 1.2 ± 0.5**
11 **kA g_{Ir}⁻¹ and a turnover frequency of 2.3 ± 0.9 s⁻¹ at 320 mV overpotential, which are two and four**
12 **times higher than those of mass-selected IrO₂, respectively. Density functional theory calculations**
13 **reveal that special iridium coordinations and the lowered aqueous decomposition free energy might**
14 **be responsible for the enhanced performance.**

15
16 **W**ater electrolysis ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$) driven by renewable power sources (for example, solar and
17 wind) offers a sustainable strategy to store energy in the form of hydrogen fuel^{1,2}. The polymer electrolyte
18 membrane water electrolyzer (PEM-WE) operating in acidic media serves as a promising technology for
19 such energy conversion and is preferable to alkaline conditions for hydrogen production because of its
20 high current density, fast response, stable operation performance and low cross-over under pressurized

1 operating conditions³. However, the sluggish anodic oxygen evolution reaction (OER), along with the
2 challenge of materials' stability under the harsh working conditions (low pH, high potentials > 1.4 V, high
3 oxygen concentration on the anode), severely limits the choice of electrocatalyst and hinders the device
4 applications on a large scale⁴.

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

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

3 Here, we develop a catalyst of iridium-tantalum oxide (Ir-Ta-O) for OER by using a stable Ta₂O₅
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
6 OER activity of mass-selected catalyst has been accurately evaluated based on a silicon (Si) microchip-
7 based electrochemistry/mass-spectrometry (EC-MS) instrument, developed by our prior work, which has
8 a time resolution of seconds and 100 % collection efficiency²¹. We find that the catalyst within a small
9 size regime (< 2 nm) exhibits a mass activity of $1.2 \pm 0.5 \text{ kA}_{\text{O}_2} \text{ g}_{\text{Ir}}^{-1}$ and a turnover frequency (TOF) of 2.3
10 $\pm 0.9 \text{ s}^{-1}$ at 320 mV overpotential, along with an enhanced stability in acidic media. Density functional
11 theory (DFT) calculations further uncover the key factors dictating these improved activity and stability.

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

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

7 To gauge the accuracy of mass-selected synthesis, the particle sizes of 6.0×10^3 and 1.2×10^4 amu Ir-
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
10 of Ir and Ta atoms in a particle could be obtained, as shown in Fig. 1d,e. Based on the investigations, the
11 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,
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
14 (STEM-EDS) elemental mapping (Supplementary Figs. 7 and 8) confirms that Ir and Ta are
15 homogeneously distributed within each particle.

16 Prior to the electrochemical measurements, the as-deposited mass-selected Ir-Ta NPs on the gold
17 support were thermally annealed in air at 400 °C for 5 min (Supplementary Figs. 9 and 10). An elemental
18 composition of Ta/Ir = 9:1 and the overall distribution of the deposited NPs were characterized by X-ray
19 photoelectron spectroscopy (XPS; Supplementary Figs. 11-14). Figure 1f shows the XPS spectra of the
20 Ta 4f and Ir 4f core-level regions of the as-deposited Ir-Ta NPs and oxidized Ir-Ta-O NPs. The Ta 4f_{7/2}
21 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 as-
2 deposited sample is shown in Supplementary Fig. 15. The high-resolution spectrum of the Ir 4f core-level
3 region of the as-prepared sample, after data processing due to Au 5p peak overlaps (Supplementary Figs.
4 11 and 12), suggests that Ir is in a metallic state. After oxidation, a clear positive shift in binding energy
5 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
6 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
7 overlap, the loading of the electrode is controlled to be 5% projected surface area coverage. The total mass
8 loadings of 60 to 275 ng cm⁻² corresponding to an Ir loading of ~6 to 29 ng cm⁻² (according to the elemental
9 ratio of Ta/Ir = 9:1) was precisely controlled by monitoring the particle beam current during the deposition
10 (Supplementary Table 1).

11 **Monitoring oxygen evolution on Ir_{0.1}Ta_{0.9}O_{2.45} electrocatalysts.** The oxygen evolution performances of
12 the thermally oxidized Ir_{0.1}Ta_{0.9}O_{2.45} catalysts were investigated in 0.1 M perchloric acid electrolyte
13 (HClO₄, pH = 1.08) by a Si-microchip-based EC-MS, which is schematically depicted in Fig. 2a. To avoid
14 the oxidation of the carbon support causing the overestimation of the OER activity (Supplementary Fig.
15 16), the polycrystalline gold with good conductivity and high corrosion resistance in acid was used as the
16 working electrode in this study. However, the formation of the tunnelling barrier of gold oxide with a wide
17 bandgap of 1.90 eV (Supplementary Fig. 17) at high anodic potential above 1.5 V versus a reversible
18 hydrogen electrode (RHE)²² would compromise the electron transfer during OER working conditions,
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 $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ 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 O_2 and CO_2 , 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 $50 \pm 4 \%$ and $45 \pm 4 \%$, respectively. The residual current goes towards adventitious carbon
14 decomposition and Au dissolution (Supplementary Fig. 23)²³.

15 Due to mass-transport effects, the measured MS currents do not directly correspond to the partial
16 current of the analyte under the dynamic conditions of CV measurements. This effect, however can be
17 eliminated by back calculating the partial current density from a measured MS current by a mathematical
18 deconvolution method (Supplementary Figs. 24 and 25), which has been demonstrated and validated in
19 our recent work²⁴. After deconvolution (Fig. 2d), the obtained oxygen partial current presents the real
20 interfacial oxygen production rate under dynamic operating conditions. The lower activity of the cathodic
21 sweep of the deconvoluted O_2 current can most likely be ascribed to the formed tunnelling barrier of the

1 Au support at high working potentials. We therefore assessed the oxygen evolution activity of mass-
2 selected catalysts by using the forward-moving, anodic sweep of the deconvoluted O₂ current
3 (Supplementary Figs. 26 and 27).

4 **Oxygen evolution performance of Ir_{0.1}Ta_{0.9}O_{2.45} catalysts.** The OER activity of mass-selected
5 Ir_{0.1}Ta_{0.9}O_{2.45} catalysts was evaluated using the mass activity (normalized to the total Ir loading) at 320
6 mV overpotential. Three different sizes of mass-selected IrO₂ catalysts within 1-2 nm were also studied
7 for comparison (Supplementary Fig. 28), which shows an average mass activity of $650 \pm 150 \text{ A}_{\text{O}_2} \text{ g}_{\text{Ir}}^{-1}$ at
8 320 mV overpotential. As shown in Fig. 3a, the mass activity of Ir_{0.1}Ta_{0.9}O_{2.45} catalysts exhibit a marked
9 enhancement of $1.2 \pm 0.5 \text{ kA}_{\text{O}_2} \text{ g}_{\text{Ir}}^{-1}$ over pure IrO₂ within the same size range. Notably, the particle size of
10 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
11 when the particle mass is higher than 4.4×10^4 amu (equivalent diameter, 2 nm). This lower activity is
12 likely due to a compromised electrical conductivity in larger particles or surface segregation of Ta oxide.
13 In addition, the pure Au electrode and mass-selected Ta₂O₅ catalysts were also studied, which are
14 unsurprisingly inactive for the OER at low overpotentials (Supplementary Fig. 29).

15 A comprehensive comparison with other reported ruthenium- (Ru-) and Ir-based acidic OER catalysts
16 is shown in Fig. 3b. Although the Ru-based catalysts are more active, the narrow potential region of the
17 catalysts' stability (~ 0.7 to 1.4 V versus RHE, pH=1) severely hinders its practical applications²⁵. The
18 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
19 comparable to state-of-the-art Ir-based catalysts. Several studies in the literature report higher activities.
20 However, most of these studies have not actually measured the amount of evolved oxygen at the high

1 activity. Relying only on the measured CV will introduce large errors in the catalytic activity due to the
2 capacitance effect, redox couples, and corrosion. Therefore, a proper quantification of the OER activity is
3 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
5 important metric for practical application. We investigated the stability of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45}
6 catalyst by a long-term measurement at 1.6 V versus RHE for 24 h in 0.1 M HClO₄ (Fig. 4a). The working
7 electrode was initially held at OCP and stepped up for chronoamperometry at 1.6 V for 4 h; the OER
8 activity of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} catalyst dropped quickly, within minutes (Supplementary Fig. 30),
9 in line with the deactivation observed for the gold-supported Ir-Au-TiO₂ catalyst²⁶. We found the OER
10 activity of our catalyst could be recovered with negligible changes even after repeating five cycles by
11 reducing the Au electrode at OCP. Our recent work on the Pt electrode for OER shows that the tunnel
12 barrier for electron transfer by the formation of PtO₂ reduces the faradaic reaction rate of oxygen
13 evolution²⁴. We therefore speculate that the gradual degradation of the OER activity during
14 chronoamperometry measurement is attributed to the formation of an insulating gold oxide layer rather
15 than the catalyst deactivation.

16 The stability number (*S*-number) of an electrocatalyst has been proposed as a metric to assess the
17 stability of catalysts, which compares the evolved oxygen (n_{O_2} , calculated according to the total charge
18 (Q_{total}) or MS O₂ currents) to the amount of dissolved Ir (n_{Ir} ; ref. ²⁷). As shown in Fig. 4b, the *S*-numbers
19 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
20 approximately 10⁶ (Supplementary Fig. 31), which is comparable with the reported rutile IrO₂ (~10⁶, Alfa-

1 Aesar) and one order of magnitude higher than the rutile IrO₂ (~10⁵, Sigma-Aldrich) and other reported
2 Ir-based perovskites (~10⁵)²⁷⁻²⁹. In addition, STEM and XPS characterizations of mass-selected 1.2×10⁴
3 amu Ir_{0.1}Ta_{0.9}O_{2.45} particles were performed after the electrochemical measurements, which show no
4 significant changes in the morphology, distribution or composition of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45}
5 catalysts (Supplementary Figs. 32 and 33), confirming the robust stability. Together, these results suggest
6 the Ir_{0.1}Ta_{0.9}O_{2.45} catalysts have an excellent OER activity and stability in acid.

7 **Investigation of intrinsic activities.** To evaluate the potential for scalability and compare the intrinsic
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
10 porosimetry techniques, the CO stripping analysis is commonly used to determine the electrochemically
11 active surface area, especially for noble-metal catalysts³⁰. In contrast with metallic noble-metal catalysts,
12 where the active site can be carefully explored, the assessment of oxides is rather complex due to the
13 pseudocapacitance charging processes during CO adsorption and oxidation³¹. Additionally, the loading
14 level of our system, below nanomolar, makes an accurate and precise characterization even more
15 challenging.

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

1 signal for the intrinsic activity evaluation. The catalyst was brought to a potential of 0 V versus RHE to
2 reduce the surface iridium atoms for CO adsorption³². In addition, pure mass-selected Ta₂O₅ NPs on a Au
3 support do not show any ¹³CO stripping signal, which indicates that all of the ¹³CO₂ signal must be
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
7 is ~ 8.0 pmol (4.8×10^{12} Ir atoms), and the number of surface Ir sites determined from the ¹³CO stripping is
8 1.5×10^{12} , which means ~ 31 % Ir atoms are exposed on the surface. As shown in Fig. 5a, the mass-selected
9 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
10 essentially all atoms are residing at the surface. Contrarily when the particle size increases, more Ir atoms
11 are trapped inside the particles during oxidation process³³, which results in a low surface Ir ratio of 3 %
12 for 6.0×10^5 amu (equivalent diameter: 4.8 nm) particles.

13 Based on the MS-determined O₂ production rate, the TOF values were calculated according to the
14 total Ir mass (TOF_{bulk}) and ¹³CO-stripping-determined surface active sites (TOF_{surface}) of mass-selected
15 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}
16 NPs within a smaller size range (1-2 nm) yield similar intrinsic activities with a high average TOF_{surface}
17 value of 2.3 s^{-1} , which is four times higher than that of TOF_{bulk} ($\sim 0.6 \text{ s}^{-1}$); the TOF_{surface} of 6.0×10^5 amu
18 ($\sim 0.37 \text{ s}^{-1}$) is about 40 times higher than that of TOF_{bulk} ($\sim 0.01 \text{ s}^{-1}$), indicating the crucial impact of the
19 particle size on the OER activity. As shown in Fig. 5c, the average TOF_{surface} of mass-selected
20 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
21 OER catalysts in acidic media, the reported OER catalysts with superior activities need to be further

1 confirmed by measuring the evolved O₂ 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 $2.3 \pm 0.9 \text{ s}^{-1}$ 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
5 stability of the Ir_{0.1}Ta_{0.9}O_{2.45} catalysts. The OER activity was evaluated using the theoretical overpotential
6 calculation based on the acidic OER mechanism (Supplementary Fig. 37 and Supplementary Note 1)^{34,35}.
7 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
8 Ta₂O₅ (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
10 (Fig. 6b,c and Supplementary Fig. 38). The calculated theoretical overpotentials of these structures as a
11 function of the usual OER activity descriptor, the adsorption free energy difference between *O and *OH,
12 are shown in Fig. 6d (ref. ³⁴). By comparing the calculated theoretical overpotentials of Ir-doped Ta₂O₅
13 (200) (0.45 V) and Ta₂O₅ (200) (0.93 V) to the Au-supported Ir-doped Ta₂O₅ (0.44 V) and Ta₂O₅ (200)
14 (0.91 V), we find that the Au support has little effect on the OER catalytic activity. In addition, Ir-doped
15 Ta₂O₅ (200) surfaces with different Ir-doping concentrations yield a theoretical overpotential similar to
16 that (0.49 V) of IrO₂ (110) and the lowest Ir-doping surface (0.08 monolayer) possesses a favorable
17 activity with a theoretical overpotential of 0.43 V.

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

1 have an OER activity as good as IrO₂. Note that we do not expect a direct quantitative comparison of the
2 experimental and calculated theoretical overpotentials to match. The former is a potential-scale measure
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
7 similar to that in rutile IrO₂ (110). These results indicate that these special Ir local coordinations of
8 Ir_{0.1}Ta_{0.9}O_{2.45} catalysts may be responsible for the excellent OER activity, confirming the experimental
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.
12 41 and Supplementary Note 3)³⁸. The calculated ΔG_{pbx} involves contributions from the phase stability and
13 aqueous dissolution energy, the latter of which mainly determines the catalyst stability in the aqueous
14 solution. Whether using the Ir-doped Ta₂O₅ bulk or surface/cluster phase of Ir-doped Ta₂O₅ will only
15 affect the calculated phase stability, not the aqueous dissolution energy. Figure 6f shows the calculated
16 aqueous decomposition free energies (ΔG_{pbx}) of Ir-doped Ta₂O₅ and IrO₂. Comparing with the calculated
17 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
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 IrO₄⁻ + Ta₂O₅ (s)
20 with a marginal increase of ΔG_{pbx} , suggesting that Ir-doped Ta₂O₅ could be stabilized by the slow phase
21 transition to Ta₂O₅(s) at room temperature. At potentials higher than 1.82 V, ΔG_{pbx} significantly increases,

1 and Ir-doped Ta₂O₅ decomposes to IrO₄⁻ + Ta₂O₇ (s). In this scenario, the Ir-doped Ta₂O₅ would suffer
2 from a very large thermodynamic decomposition driving force and consequently becomes unstable in the
3 aqueous solution. In the experiment, Ir_{0.1}Ta_{0.9}O_{2.45} catalysts show much better stability than IrO_x catalysts,
4 which can therefore be attributed to the smaller ΔG_{pbx} . Finally, although the exact structure of the
5 Ir_{0.1}Ta_{0.9}O_{2.45} NP is unknown, we believe these theoretical insights could shed light on the underpinning
6 mechanisms of the enhanced OER performance.

7 **Conclusions**

8 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
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
11 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
12 activity in 0.1 M HClO₄ with remarkable stability over 24 hours at 1.6 V versus RHE. The number of
13 surface active Ir atoms was determined by the isotope-labelling combined EC-MS technique, and the
14 mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} catalyst also demonstrates high intrinsic activity with a TOF value of $2.3 \pm$
15 0.9 s^{-1} at 320 mV overpotential. The good OER performance of our catalyst in acid can be explained by
16 the favorable particle size and good Ir dispersion on the surface, as well as the favorable atomic
17 configuration of the OER active center. We anticipate that our findings may apply to other wide-bandgap
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**

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

$$15 \quad M_{Total} = mIt$$

16 Where M_{total} is the total loading of the deposited particles, m is the single NP mass, I is the deposition
17 current and t is the deposition time. For the calculation of particle size, we assume a sphere structure of
18 generated particle with bulk density²⁰. In this study, the loading of the electrode is 5% projected surface
19 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

1 ultrahigh-vacuum conditions after the deposition. The thermal annealed NPs, as well as the NPs after
2 electrochemical testing, were measured on the same XPS set-up mentioned above. The employed pass
3 energy was 100 eV for the overview and 20 eV for the high-resolution spectra. All spectra were charged
4 reference against the Au 4f peak at 84 eV and a Shirley background was chosen for the elemental
5 quantification. CasaXPS software was used for all the XPS analysis. Details of XPS data analysis can be
6 found in the Supplementary Figs. 11 and 12. Inductively coupled plasma MS was performed on a Thermo
7 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 %,
9 Sigma-Aldrich) by addition of ultrapure water (18.2 MΩ.cm at 25 °C; Merck). The Hg/HgSO₄ reference
10 electrode was calibrated by measuring the OCP of a cleaned platinum disc in H₂-purging 0.1 M HClO₄
11 electrolyte. To avoid the oscillations from potentiostat and easy-to-correct ohmic losses, we introduced a
12 conventional ohmic resistor of 100 Ω with the working electrode. Unless otherwise stated, helium (6.0,
13 Air Liquide) was used as an auxiliary gas during EC-MS experiments. The isotope-labeled ¹³CO (≥99
14 atom %; Sigma-Aldrich) stripping measurements were conducted in 0.1 M HClO₄ solution. The catalysts
15 were firstly cycled in He-saturated electrolyte between 0 to 1 V versus RHE. After obtaining stable cyclic
16 voltammogram, the carrier gas was exchanged from He to ¹³CO while holding the potential at 0 V versus
17 RHE for 2 min (ref. ³²). Then, ¹³CO was removed by purging pure He gas into the electrolyte for 2 h, and
18 continuous CVs were measured at a scan rate of 5 mV s⁻¹, with the first one being the CO stripping process.
19 The raw data for the ¹³CO stripping experiment is shown in Supplementary Fig. 35a. After the ¹³CO
20 stripping measurements, the OER activity was measured by cycling the working electrode between OCP
21 and 1.7 V versus RHE with a scan rate of 20 mV s⁻¹ until a stable CV was obtained.

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

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

17 **Data availability.**

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

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3 **Author Contributions**

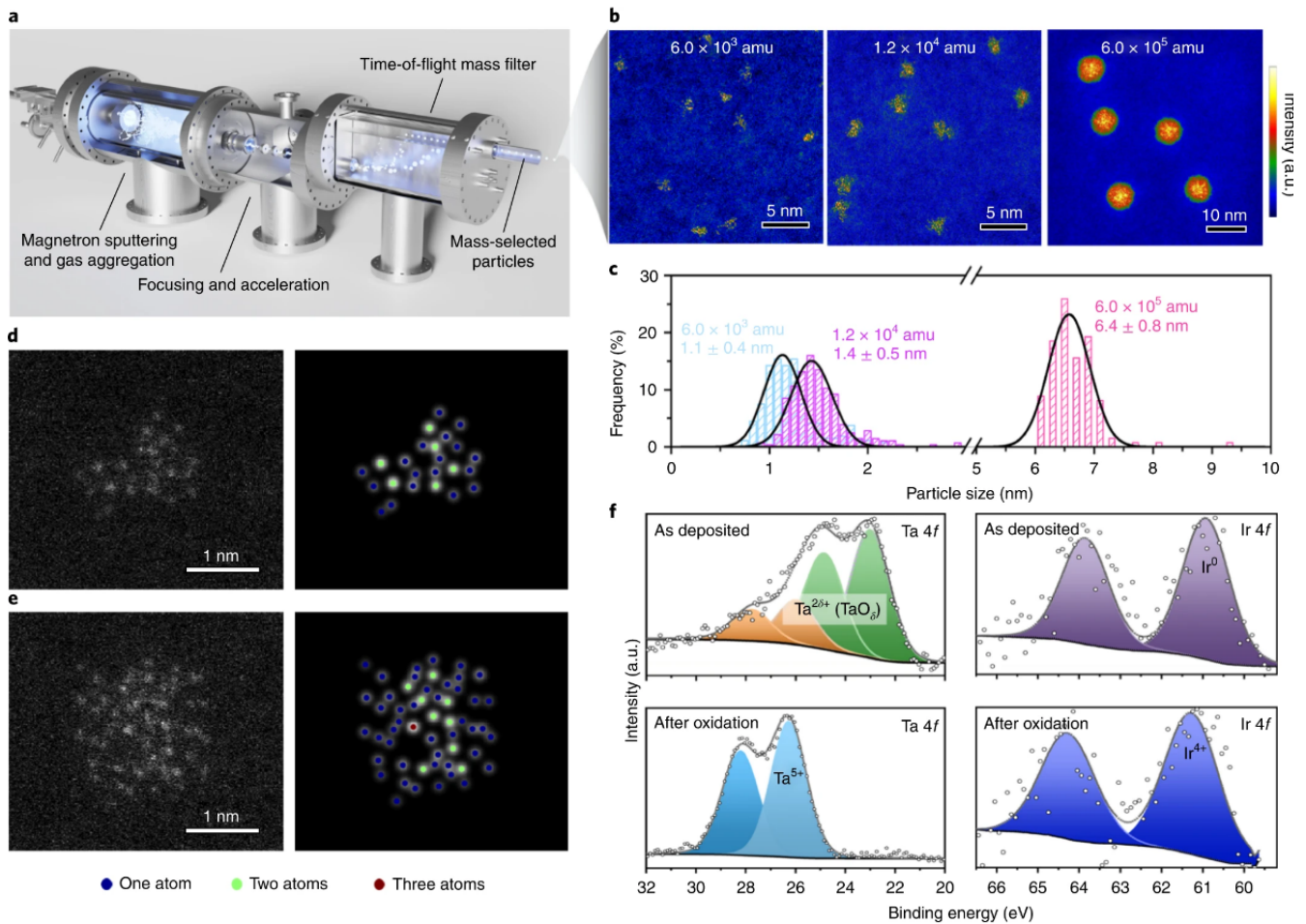
4 I.C., J.K., and J.K.N. conceived and supervised the project. Y.-R.Z. and Z.W co-wrote the manuscript. Y.-
5 R.Z. performed electrochemical tests and collected and analyzed the data. J.V., K.Z., T.-W.L., F.P., and
6 N.M. S. performed the mass-selected nanoparticles preparation and XPS measurements. 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. performed 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

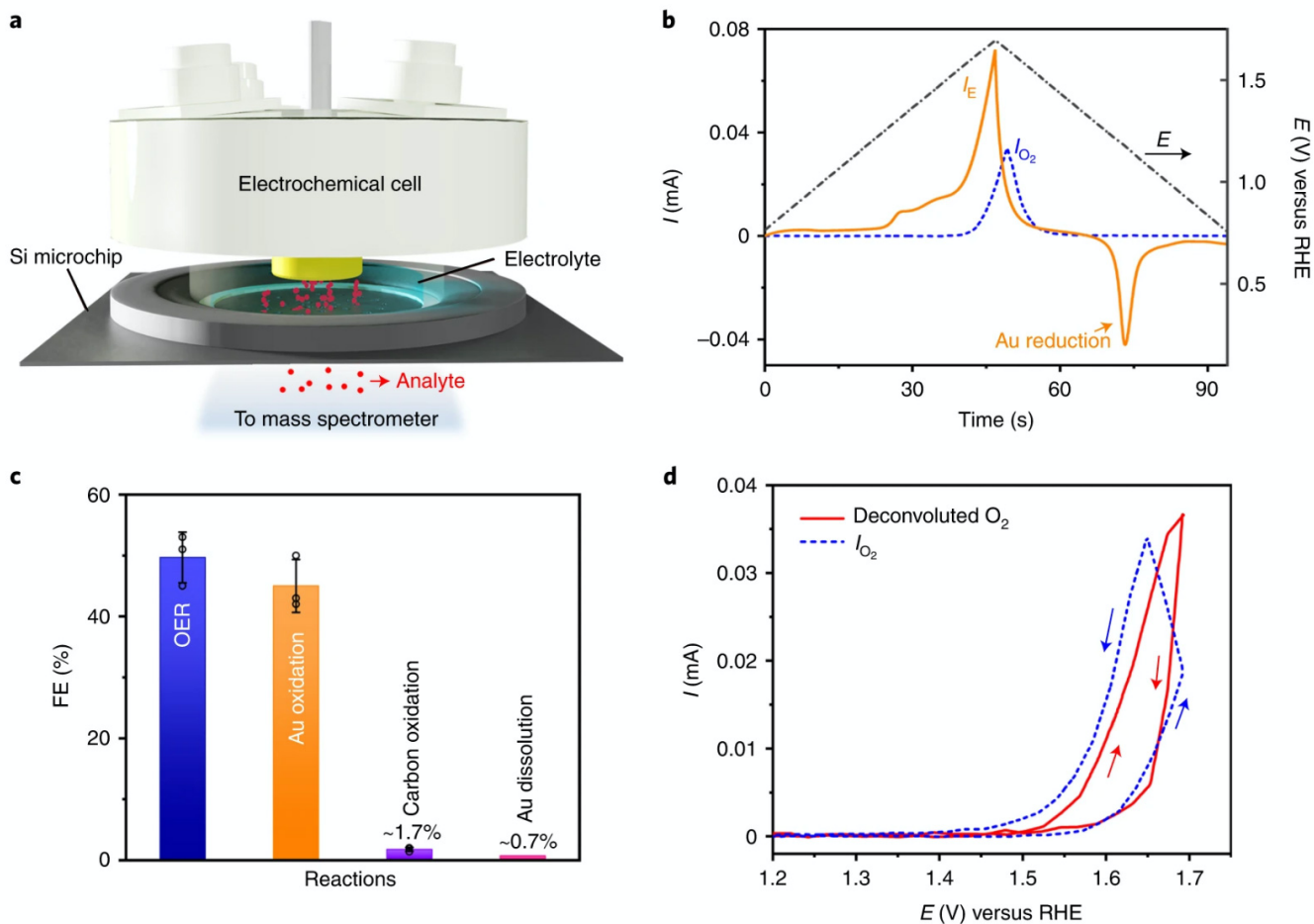
1 Figure Captions



2

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

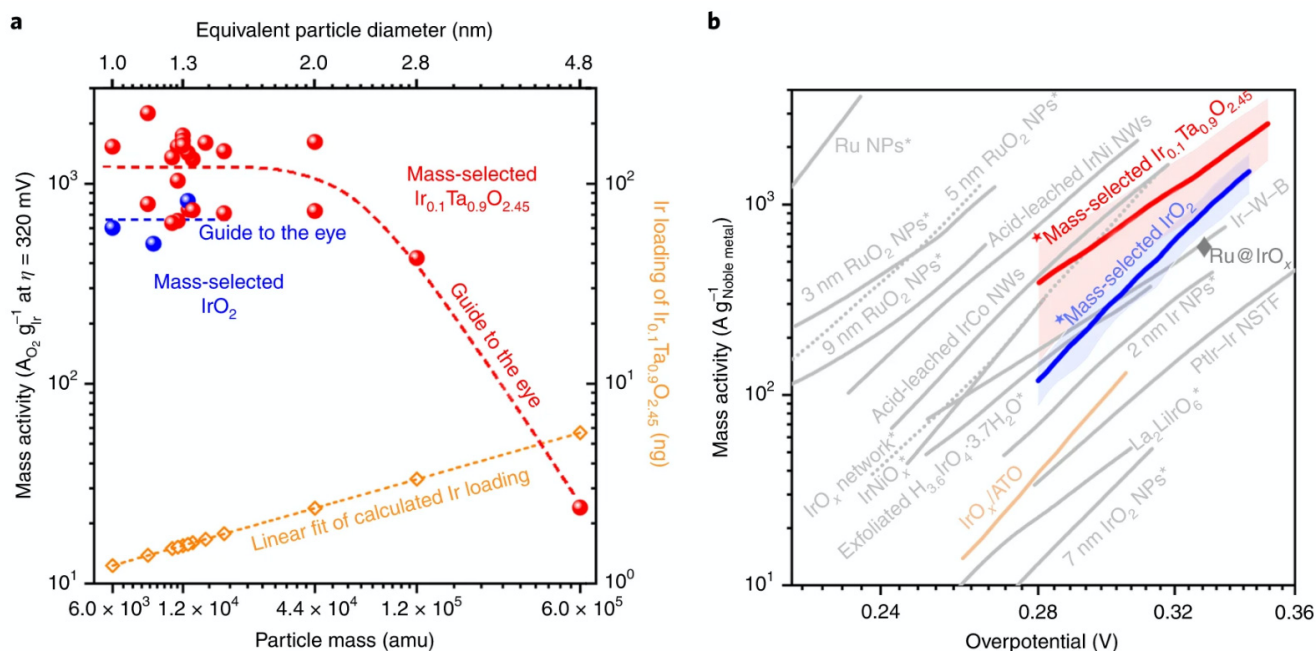
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1

2 **Fig. 2 | Monitoring oxygen evolution on gold supported mass-selected $Ir_{0.1}Ta_{0.9}O_{2.45}$ NPs.** **a**, Schematic diagram
 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 $\sim 100 \mu\text{m}$. **b**, Comparison of the electrochemical current (I_E)
 5 and the O_2 current (I_{O_2} , back-calculated from MS signal of $m/z = 32$) of the 1.2×10^4 amu $Ir_{0.1}Ta_{0.9}O_{2.45}$ during
 6 potential (E) cycling between OCP and 1.7 V versus RHE with a scan rate of 20 mV s^{-1} in 0.1 M HClO_4 . **c**, FE of
 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 CO_2 products during potential cycling
 9 (Supplementary Fig. 23). The Au oxidation is calculated from the electrochemical Au reduction peak. The dissolved
 10 Au amount is $\sim 10 \text{ ng cm}^{-2}$ per cycle with an anodic limiting potential of 1.7 V versus RHE²³. The error bars represent
 11 the Standard deviations of FE value of three independent samples (1.2×10^4 , 1.26×10^4 and 4.4×10^4 amu). The scatter
 12 dots represent the individual values of the three experiments. **d**, Deconvoluted O_2 partial current in comparison to
 13 the measured O_2 current of the $Ir_{0.1}Ta_{0.9}O_{2.45}$ catalyst.

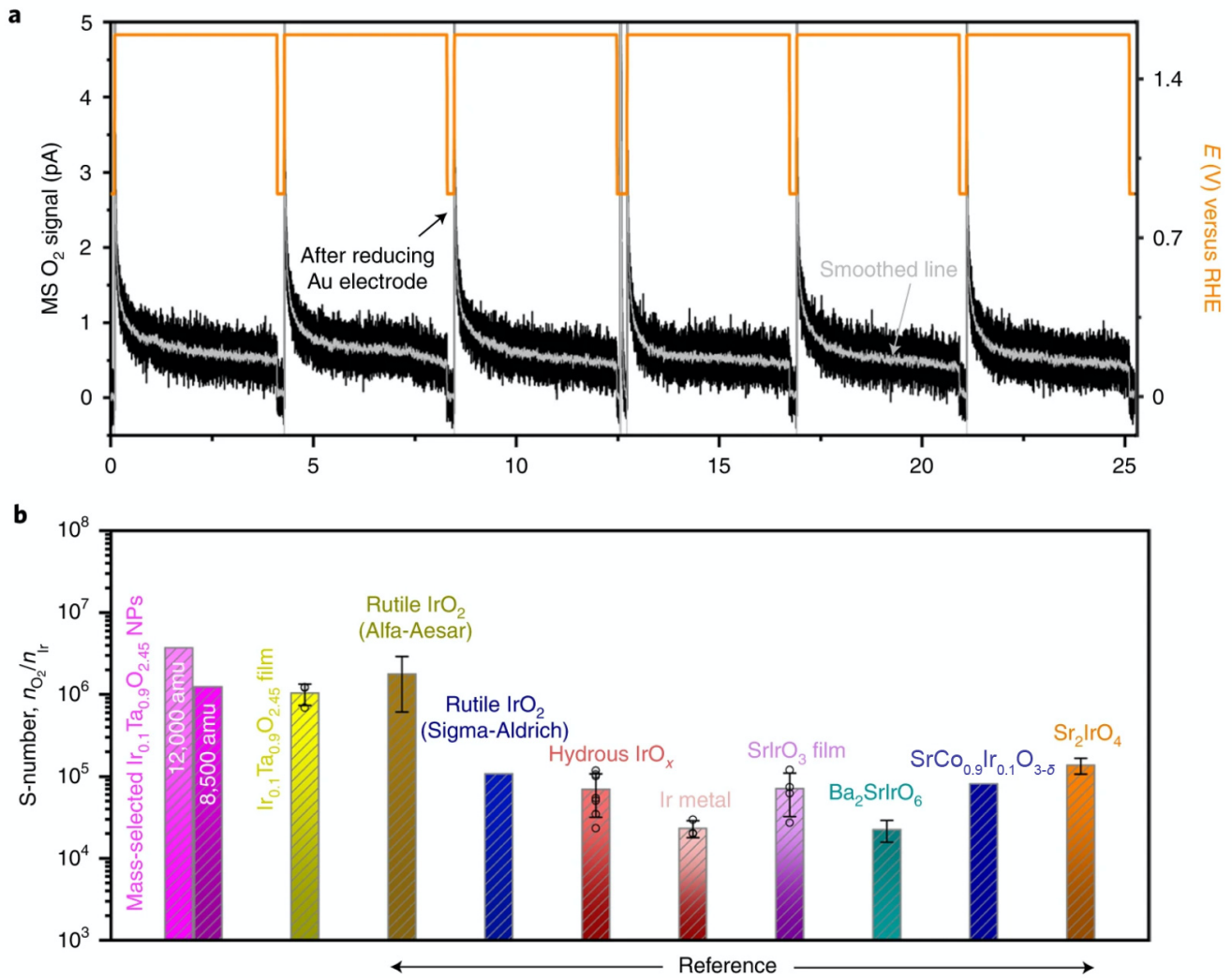
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2 **Fig. 3 | Comparison of OER catalytic performance.** **a**, OER mass activities of mass-selected $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ and
 3 IrO_2 NPs at 320 mV overpotential, and Ir loadings for different mass-selected $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ NPs. The calculated Ir
 4 loading was determined from the deposition current; the linear fit line shown in orange has a slope of 0.33 and an
 5 R -squared (R^2 , coefficient of determination) value of 0.999. The dotted lines shown in blue and red are guides to
 6 the eye. **b**, Comparison of mass activity between mass-selected $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ and other state-of-the-art OER
 7 catalysts in acidic media. The average mass activity and standard deviation of mass-selected $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ is based
 8 on 20 independent samples with sizes smaller than 4.4×10^4 amu (Supplementary Fig. 27). The average mass activity
 9 and standard deviation of mass-selected IrO_2 catalysts are based on three independent samples (6×10^4 , 9×10^4 and
 10 1.27×10^4 amu particles, Supplementary Fig. 28). The gray and orange lines are duplicated from the literatures: Ru
 11 NPs and 3, 5, and 9 nm RuO_2 NPs⁴⁵; acid-leached IrNi and IrCo nanowires⁴⁶; the IrO_x network⁴⁷; Ir-W-B alloy⁴⁸; 2
 12 nm Ir NPs⁴⁹; IrNiO_x (ref. ¹³); exfoliated $\text{H}_{3.6}\text{IrO}_4 \cdot 3.7\text{H}_2\text{O}$ (ref. ²⁹); $\text{IrO}_x/\text{antimony-doped tin oxide (ATO)}$ (ref. ⁵⁰);
 13 PtIr-Ir nanostructured thin film (NSTF)⁵¹; 7 nm IrO_2 (ref. ⁵²); and $\text{La}_2\text{LiIrO}_6$ (ref. ⁵³). Diamond, $\text{Ru}@/\text{IrO}_x$ (644.8 A
 14 $\text{g}_{\text{oxide}}^{-1}$ @ 0.33 V overpotential)⁵⁴. Asterisks, glassy-carbon-supported catalysts. Star, data from this work. The grey
 15 symbols represent the data that did not measure O_2 , whereas the colored symbols represent the data that measured
 16 evolved O_2 .

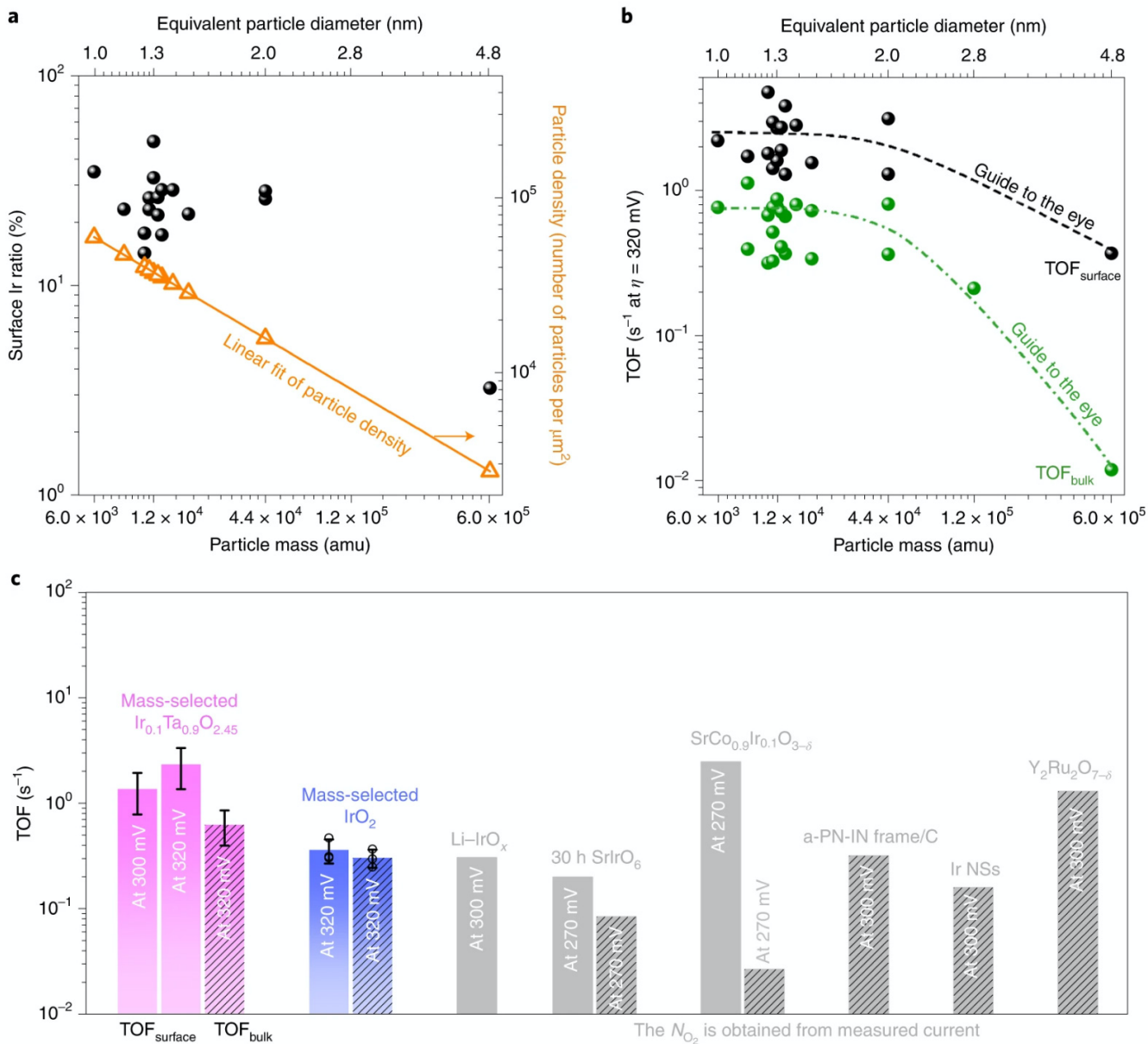
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2 **Fig. 4. | Stability of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} NPs.** **a**, Stability performance of the 4.4×10^4 amu Ir_{0.1}Ta_{0.9}O_{2.45}
 3 catalyst at 1.6 V versus RHE for 24 h in 0.1 M HClO₄. After every 4 h, the working electrode was reduced at OCP
 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
 6 other Ir-based thin film and powder OER catalysts in acid. Reference data are extracted from the literature: rutile
 7 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
 8 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
 9 the average *S*-number of three independent experiments. The scatter dots represent the individual values of the
 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.

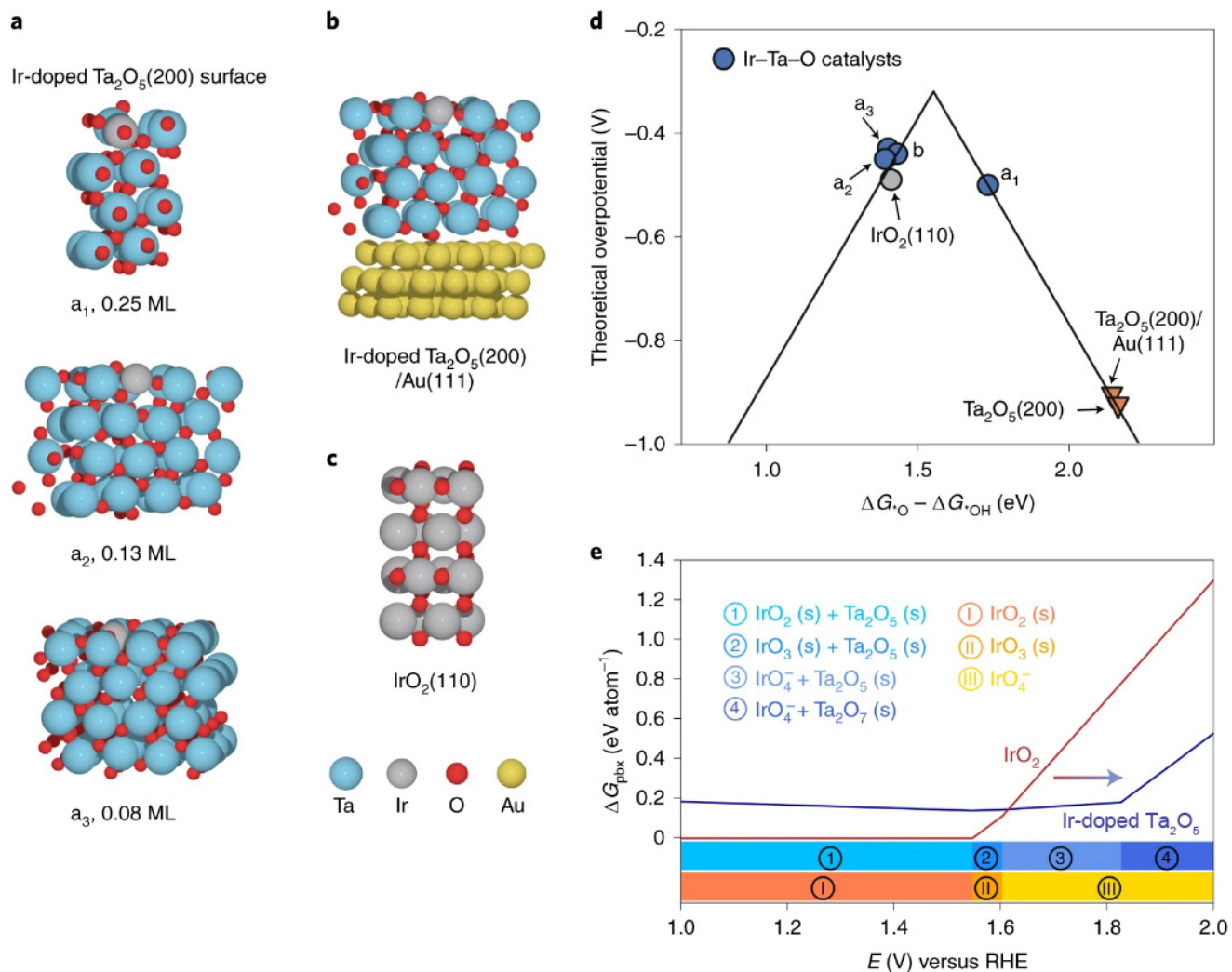
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2 **Fig. 5 | Isotope-labelling coupled with EC-MS determined surface active sites and TOF values of mass-**
 3 **selected $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ NPs. a,** In-situ ^{13}C O-stripping-determined surface Ir ratio and particle density as a function
 4 of the average particle mass of mass-selected $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ 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
 8 mass-selected $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ at 320 mV overpotential as a function of particle mass. Electrolyte, 0.1 M HClO_4 . Scan
 9 rate, 20 mV s^{-1} . The dotted lines are guides to the eye. **c,** Comparison of TOF values between the mass-selected
 10 $\text{Ir}_{0.1}\text{Ta}_{0.9}\text{O}_{2.45}$ NPs, mass-selected IrO_2 NPs and reference noble-metal OER catalysts in acid, including Li-IrO_x (ref.
 11 55), 30 h SrIrO_6 (ref. 28), $\text{SrCo}_{0.9}\text{Ir}_{0.1}\text{O}_{3-\delta}$ (ref. 28), activated PtNi axis and IrNi edge frame catalyst ($a\text{-PN-IN}$
 12 frame/C) 56 , amorphous Ir nanosheets (Ir NSs) 11 and $\text{Y}_2\text{Ru}_2\text{O}_{7-\delta}$ (ref. 57). The colored columns represent the intrinsic

1 activity, which was determined by collecting the actually generated oxygen products, whereas the grey columns
2 represent the number of O₂ molecules (N_{O_2}) 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
6 overpotential of mass-selected Ir_{0.1}Ta_{0.9}O_{2.45} represent the standard deviation of the average value of 18 independent
7 samples with sizes smaller than 4.4×10^4 amu. The error bars of mass-selected IrO₂ 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.



1
 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
 7 aqueous decomposition free energy (ΔG_{pbx}) of Ir-doped Ta₂O₅ and IrO₂ from the potential 1.0 to 2.0 V versus RHE
 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**

37 **Supplementary information** is available for this paper at <http://XXXXXXXXXX>.

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