

# Torsion strained iridium oxide for efficient acidic water oxidation in proton exchange membrane electrolyzers

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**Abstract:** Acidic oxygen evolution reaction (OER) is crucial for practical PEM water splitting electrolyzers, which have been hindered by the high catalytic overpotential and high loading of noble metal catalysts. Here we present torsion strained Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> nanocatalyst with numerous grain boundaries that exhibit a low overpotential of 198 mV at 10 mA cm<sup>-2</sup> toward OER in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Microstructural analyses, X-ray absorption spectroscopy and theoretical calculations reveal that the synergistic effects between grain boundaries that result in torsion strained Ir–O bonds and the doping induced ligand effect collectively tune the adsorption energy of oxygen intermediates, thus enhancing the catalytic activity. A PEM electrolyzer using Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> nanocatalyst with a low mass loading of 0.2 mg cm<sup>-2</sup> can operate stably at 1.5 A cm<sup>-2</sup> for 500 hours with an estimated cost of \$1/kg H<sub>2</sub>, which is much lower than the target (\$2/kg H<sub>2</sub>) by U.S. Department of Energy.

## Main text:

Emerging electrochemical technologies allow the utilization of renewable solar and wind energy for the production of fuels and chemicals<sup>1-3</sup>. Hydrogen generation *via* proton exchange membrane (PEM) water electrolysis in acidic electrolyte can achieve much higher current

densities than the traditional alkaline electrolyzers due to lower resistance losses and less gas crossover<sup>4,7</sup>. The efficiency of water splitting is significantly limited by the oxygen evolution reaction (OER), which has a high catalytic overpotential due to the sluggish four-electron transfer process involving multiple oxygen intermediates<sup>8,9</sup>. Moreover, the poor stability of many OER catalysts in acidic solutions poses even more challenges for PEM electrolyzers, for which  $\text{IrO}_x$  is the only known practical industrial OER electrocatalyst<sup>10,11</sup>. However, the current  $\text{IrO}_x$  catalysts still suffer from low mass activities and cannot meet the requirements of high performance and long-term stability under commercial current densities<sup>3,12</sup>. Further increasing the catalytic performance and decreasing the loading of expensive noble metals yet improving the stability<sup>13</sup> of acidic OER catalysts would make the PEM water electrolysis technology more competitive.

Previous research reveals that the OER catalytic activity can be predicted based on the difference between the adsorption free energies of  $\text{OH}^*$  and  $\text{O}^*$  intermediates<sup>14-16</sup>, which is closely correlated with the electronic structures of the active sites. Doping foreign metals into  $\text{IrO}_x$  or Ir-based perovskite oxides has been effective for enhancing OER activities through tuning the electronic structures of the Ir sites<sup>8,17-19</sup>. The catalytic activity of various types of electrochemical reactions could also be enhanced by strain engineering, usually in the form of compressive or tensile surface strains in carefully engineered core-shell or alloyed nanostructures of noble metal catalysts<sup>20-23</sup>. Extending similar concepts to core-shell metal oxide nanostructures or thin films could enhance the OER activity through tuning the metal–oxygen (M–O) bonds due to the compressive or tensile lattice strains<sup>21,24-26</sup>. However, under the highly anodic and corrosive acidic OER environment, such disordered nanostructured catalysts could be easily dissolved or oxidized, leading to a sharp decrease in activity<sup>18,27</sup>. Achieving enhanced activity yet maintaining catalytic stability under lattice strains has been challenging. On the other hand, fine grain boundaries (GB) could be introduced to crystalline materials by stacking fault movements<sup>28</sup> and/or oriented attachments during materials growth<sup>29</sup>. The presence of GBs has been recently shown to boost the catalytic activity in metals<sup>30,31</sup>. Not only new type of strains beyond the compressive or tensile strains could potentially be introduced and controlled flexibly at such GBs for optimizing catalysis, but also the catalytic stability could be better maintained due to the structural reversibility<sup>28</sup>.

Herein, by using a fast pyrolysis synthesis strategy and doping foreign metals (Ta and Tm) into  $\text{IrO}_{2-\delta}$ , we present a new type of torsion strained  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts with abundant trigeminal GB (referred to as GB- $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$ ) that displays a significantly higher mass activity over that of  $\text{IrO}_{2-\delta}$  with/without GB and commercial  $\text{IrO}_2$  (C- $\text{IrO}_2$ ), and such catalytic enhancement can be understood by careful structural analyses and theoretical calculations. Furthermore, a PEM electrolyzer employing GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  as the anode catalyst with a low mass loading of  $0.2 \text{ mg cm}^{-2}$  has been demonstrated with excellent operating performance for 500 h with an estimated cost of \$1/kg  $\text{H}_2$ .

## Synthesis and characterization of the nanocatalysts

We synthesize torsion strained  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts using a fast pyrolysis approach. We choose dual metal dopants of tantalum (Ta) and thulium (Tm) for their catalytic enhancement and stability after experimental trials with many transition and lanthanide metal

elements. A mixture of the metal salt precursors in a mixed water/ethanol solution is co-precipitated by ammonia and citric acid, and then rapidly heated to 450 °C to yield interconnected mesoporous networks of nanoparticles (Fig. 1a top row, experimental details in Methods). The key for making these nanocatalysts with abundant GB is the rapid heating and pyrolysis process. In contrast,  $\text{IrO}_{2-\delta}$  and  $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalysts without GB are synthesized via the traditional slow pyrolysis (Fig. 1a bottom row to 1d, and Supplementary Figs. 1, 2). Rapid pyrolysis leads to the formation of a large population of nuclei from the precursors<sup>32</sup>, and the kinetically controlled process leads to the non-traditional mesocrystal growth through particle collision and coalescence that result in many twins, stacking faults, dislocations at the nanocrystalline GB<sup>29,33</sup>. In order to match the orientations of the crystallographic facets between numerous neighboring crystalline grains colliding in a short timescale, lattice torsion will be generated<sup>34</sup> (Fig. 1a, and Supplementary Fig. 3). Thus, crystalline grains grow along the axial direction of nanocatalysts via oriented attachment<sup>29</sup> and shear strain due to the lattice torsion emerges at the trigeminal GB, where three or more adjoining crystalline grains meet<sup>35</sup>. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) analyses reveal that GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst synthesized via fast pyrolysis possess an average grain size of ~10 nm and many GBs (Fig. 1e-g, and Supplementary Figs. 4, 5), which are in clear contrast to the nanocatalysts formed via slow pyrolysis (Fig. 1b-d). The misfit strain gliding along the nanocatalyst surface creates many stacking faults (SF) at the trigeminal GB (Fig. 1f, g, examples of trigeminal GB and SF are highlighted with dash lines).

We further employ geometric phase analyses (GPA), a widely used method for strain quantification<sup>36</sup>, to further quantitatively analyze the distribution of strains along the GB (Fig. 1h-k) and SF (Fig. 1l-o) in GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst. Under lattice torsion, both shear strain and axial strain (which can be compressive or tensile strains) can emerge at the GB. GPA analyses show that both axial strain ( $\epsilon_{xx}$ ) and shear strain ( $\epsilon_{xy}$ ) are distributed along both sides of the GB, which could respectively reach a maximum value of  $\epsilon_{xx} = 3\%$  (Fig. 1j) and  $\epsilon_{xy} = 6\%$  (Fig. 1k). The maximum value of  $\epsilon_{xy}$  along the GB is twice as high as that of  $\epsilon_{xx}$ , revealing that the shear strain due to lattice torsion is the dominant strain on the GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst surface (Fig. 1k). There are also considerable axial strain and shear strain along the SF on the (111) planes, which respectively reach a maximum value of  $\epsilon_{xx} = 2\%$  (Fig. 1n) and  $\epsilon_{xy} = 3\%$  (Fig. 1o). This further confirms the dominance of the shear strain along the SF. Thus, the GPA analyses confirm the presence of shear strain along both GB and SF in the GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst formed via fast pyrolysis, which is absent from nanocatalysts of the same compositions formed via slow pyrolysis.

Furthermore, the homogeneous distributions of Ir, Ta, Tm, and O elements in GB- $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts are confirmed by energy dispersive X-ray spectroscopy (EDS) elemental analyses (Supplementary Fig. 4g, and Figs. 6-11), suggesting that Ta and Tm are successfully doped into  $\text{IrO}_{2-\delta}$ . TEM and HRTEM analyses show that all of these samples exhibit multigrain boundaries and strains (Supplementary Figs. 6-11). Both EDS (Supplementary Fig. 12) and inductively coupled plasma mass spectrometry (ICP-MS) (Supplementary Tables 1-6) confirm that the actual ratios of Ir, Ta, and Tm in these catalysts are close to the nominal ratios in the precursor mixtures. The GB- $\text{IrO}_{2-\delta}$ , GB- $\text{Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , GB- $\text{Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , and

GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> nanocatalysts all exhibit the rutile IrO<sub>2</sub> phase with dominant (110), (101), and (211) X-ray diffraction peaks (Supplementary Fig. 13).

### Oxidation state and bond length analyses

To investigate the surface electronic structures and chemical states of these GB-Ta<sub>x</sub>Tm<sub>y</sub>Ir<sub>1-x-y</sub>O<sub>2-δ</sub> nanocatalysts, we use X-ray photoelectron spectroscopy (XPS) to characterize the Ir 4f, Ta 4f, Tm 4d, and O 1s signals. Compared to the Ir 4f signal of C-IrO<sub>2</sub> that indicates Ir<sup>4+</sup> valence state, those of GB-IrO<sub>2-δ</sub> shift to lower binding energies with three sets of doublets at 61.3 and 64.2 eV, 61.8 and 64.8 eV, and 62.7 and 65.7 eV, which could be assigned to Ir<sup><3+</sup>, Ir<sup>3+</sup>, and Ir<sup>4+</sup> valence state<sup>24,37</sup>, respectively (Supplementary Fig. 14a). More significantly, the introduction of Ta and Tm into GB-IrO<sub>2-δ</sub> shifts these three sets of doublets of GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> to even lower binding energies compared to those of GB-IrO<sub>2-δ</sub> (Fig. 2a), suggesting even lower valence states<sup>24</sup> of Ir in GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub>. The binding energies of Ta 4f and Tm 5p for the GB-Ta<sub>x</sub>Tm<sub>y</sub>Ir<sub>1-x-y</sub>O<sub>2-δ</sub> sample also shift from those of GB-Ta<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2-δ</sub> and GB-Tm<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2-δ</sub>, respectively (Supplementary Fig. 15). Moreover, the various percentages of Ir species with different valence states in these nanocatalysts further show that the electronic structure of Ir active sites is tuned through doping and strains (Supplementary Table 7).

Moreover, X-ray absorption near-edge spectroscopy (XANES) reveals the differences in Ir–O bond lengths and Ir valence states in C-IrO<sub>2</sub>, GB-IrO<sub>2-δ</sub>, and GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> due to strain and doping. The intensities of the Ir L-edge white lines of GB-IrO<sub>2-δ</sub> and GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> are between those of Ir foil and C-IrO<sub>2</sub> (Fig. 2b), indicating that the average valence states of Ir in GB-IrO<sub>2-δ</sub> and GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> are lower<sup>24</sup> than +4. Therefore, the surface species are likely Ir<sup><3+</sup> and Ir<sup><4+</sup>. Additionally, the less intense Ir L-edge white line of GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> suggests the valence state of Ir in GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> is slightly lower than that in GB-IrO<sub>2-δ</sub>, consistent with the XPS results discussed earlier. Furthermore, extended X-ray absorption fine structure (EXAFS) spectra reveal the coordination structures of C-IrO<sub>2</sub>, GB-IrO<sub>2-δ</sub>, and GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> (Fig. 2c, d). The length of the first shell Ir–O in GB-IrO<sub>2-δ</sub> is 2.02 Å, slightly longer than that in C-IrO<sub>2</sub> (1.97 Å) due to the strain effect (Fig. 2c). Additionally, the strain effect could also be found by comparing the Ir–Ir lengths in GB-IrO<sub>2-δ</sub> vs. C-IrO<sub>2</sub> (Supplementary Table 8 and Supplementary Fig. 16). Moreover, the length of the first shell Ir–O in GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> (2.06 Å) is even slightly longer than that in GB-IrO<sub>2-δ</sub> (Fig. 2d), suggesting Ta and Tm also tune the Ir–O bond length. These EXAFS results further confirm the presence of strain in GB-IrO<sub>2-δ</sub> and GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> nanocatalysts, in agreement with the earlier HRTEM and GPA analyses. The lengthened Ir–O bonds in GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> nanocatalysts suggest that strain and doping synergistically tune the covalency and electronic structures of Ir–O bonds.

### Electrochemical acidic OER in three-electrode system

The OER catalytic activities of Ta<sub>x</sub>Tm<sub>y</sub>Ir<sub>1-x-y</sub>O<sub>2-δ</sub> nanocatalysts are evaluated in 0.5 M H<sub>2</sub>SO<sub>4</sub> in comparison with other control samples (Fig. 3, and full results in Supplementary Figs. 17, 18). The linear sweep voltammetry (LSV) curves after *i*R correction and geometric area normalization

(see details in Methods) reveal that the activities of these nanocatalysts are enhanced due to both strain and doping.  $\text{IrO}_{2-\delta}$  and  $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanoparticles without GB require a catalytic overpotential ( $\eta_{10}$ ) of 299 mV and 226 mV, respectively, to deliver a current density of 10  $\text{mA cm}^{-2}$ . In contrast, GB- $\text{IrO}_{2-\delta}$  and GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalysts only require a  $\eta_{10}$  of 253 mV and 198 mV, respectively (Fig. 3a, and Supplementary Fig. 19). These results show that strain significantly enhances OER activities of GB- $\text{IrO}_{2-\delta}$  and GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ . Moreover, the OER activities of the series of nanocatalysts with GB but different compositions (Fig. 3b) follow the order of  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta} > \text{GB-Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta} \approx \text{GB-Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta} > \text{GB-IrO}_{2-\delta} (> \text{C-IrO}_2)$ , revealing that introducing of both Tm and Ta into GB- $\text{IrO}_{2-\delta}$  collectively optimizes the OER activity. GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  exhibits a lower Tafel slope of 64  $\text{mV dec}^{-1}$ , compared to the Tafel slopes of C- $\text{IrO}_2$  and  $\text{IrO}_{2-\delta}$  without GB (Supplementary Fig. 17b), which could be due to the fast electron hopping on surface<sup>38, 39</sup>. Tafel slopes calculated from the steady state measurements (Supplementary Fig. 20)<sup>40</sup> are slightly higher than those derived from the LSV data but their sequence is unchanged. Additionally, the mass activities of all synthesized catalysts are calculated at  $\eta = 266$  mV. GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  displays the highest mass activity of 3126  $\text{mA mgIr}^{-1}$ , which is much higher than the values for nanocatalysts without (Fig. 3c left) or with GB (Fig. 3c right, and Supplementary Table 9), confirming that strain and doping significantly enhances the OER activity, respectively. These results clearly confirm that the optimized acidic OER activity of torsion strained GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  is the synergistic result of both strain and doping. Importantly, the OER activity of the optimized GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst is higher than those of the state-of-the-art acidic OER electrocatalysts reported previously (Supplementary Table 10).

To further evaluate the exposed active surface areas of  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts and other control samples, electrochemical double-layer capacitance ( $C_{dl}$ ) (Supplementary Fig. 17d) is extracted from cyclic voltammetry (CV) curves (Supplementary Figs. 21, 22). The most active GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst shows the highest  $C_{dl}$  value, suggesting both strain and foreign metal doping result in more active sites (Supplementary Figs. 17d, 18c). The LSV curves normalized by electrochemically active surface areas (ECSA) and BET (Supplementary Table 11) surface areas (Supplementary Fig. 23) show that the order of catalytic activity of various catalysts is consistent with those normalized by geometric areas presented in Fig. 3. Additionally, the charge-transfer resistance ( $R_{ct}$ ) of GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  is the smallest among these catalysts, indicating the strain and doping collectively tune the intrinsic catalytic activity (Supplementary Figs. 17c, 18d). The measured Faradaic efficiency of  $\text{O}_2$  production from the GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst is 98.6% (Fig. 3d). Catalyst stability is also important for acidic OER due to the anodic potential and corrosive electrolyte. After the GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst is operated in 0.5 M  $\text{H}_2\text{SO}_4$  at 10  $\text{mA cm}^{-2}$  for 500 h, the potential increases by only 3 mV (Fig. 3d pink curve). The calculation of the stability number (S-number)<sup>13</sup> based on the dissolution of metal elements monitored by ICP-MS (Supplementary Fig. 24, and Supplementary Table 12) shows that the various nanocatalysts exhibit high S-number (Supplementary Fig. 25). The stability of GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  is further investigated under CVs in an accelerated degradation test<sup>41</sup> (Supplementary Fig. 26). These results further confirm the excellent stability of the GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst during acidic OER.

## DFT calculations

Theoretical studies reveal that the energetics of the catalytic intermediates on IrO<sub>2</sub> can be tuned through strain and doping induced ligand effects (Fig. 4a) to enhance the electrocatalytic activity<sup>42</sup>. First, the influence of Ta and Tm on the electronic structure and OER process of IrO<sub>2</sub> is studied by density functional theory (DFT) calculations of IrO<sub>2</sub> with the (100), (101), and (110) surface facets (Supplementary Fig. 27). The IrO<sub>2</sub> (110) surface is chosen for the slab models due to stable features<sup>8,11</sup>. The free energy for  $\Delta G_2$  ( $= \Delta G_O - \Delta G_{OH}$ ) on the (110) facet is much higher than 1.23 eV, indicating too weak adsorption ability of active site with oxygen intermediates<sup>43</sup>. The calculations show that substituting Ir with Ta and Tm significantly decreases  $\Delta G_2$  for Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  compared to that for IrO<sub>2</sub> (Supplementary Fig. 28). Moreover, the energetics for the potential-determining step (PDS) of Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  is the lowest compared to that of Ta<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2- $\delta$</sub> , Tm<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2- $\delta$</sub> , and IrO<sub>2</sub> (Fig. 4b, and Supplementary Figs. 27, 28), suggesting that introducing Ta and Tm together into IrO<sub>2</sub> structure could tune electronic structures, thus optimizing the adsorption of oxygen intermediates on Ir sites. The projected density of states (DOS) also reveal that d ( $\epsilon_d$ ) and p ( $\epsilon_p$ ) band centers in Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  moves closer to the Fermi level upon introducing Ta and Tm, respectively (Fig. 4b, and Supplementary Fig. 29), which indicates that the doping effect tunes the electronic structure of active sites.

To further investigate the energetics of oxygen intermediates tuned through the strain caused by GB, we tension the established models of IrO<sub>2</sub>, Ta<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2- $\delta$</sub> , Tm<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2- $\delta$</sub> , and Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  with the amount of strain according to the GPA analyses above (see details in Methods, Supplementary Figs. 30, 31). The DOS reveals the  $\epsilon_p$  for GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  is not too far away or too close to the Fermi level among these catalyst models (Fig. 4c, and Supplementary Fig. 32), suggesting that the torsion strained Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  possesses suitable binding ability with oxygen intermediates. According to DFT results, GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  exhibits the lowest energetic barriers toward OER (Fig. 4b, and Supplementary Fig. 31). Additionally, a linear relationship between  $\Delta G_{OOH}$  and  $\Delta G_{OH}$ <sup>8</sup> is fitted based on these established Ta<sub>x</sub>Tm<sub>y</sub>Ir<sub>1-x-y</sub>O<sub>2- $\delta$</sub>  models:  $\Delta G_{OOH} = 1.1\Delta G_{OH} + 2.46 \pm 0.2$  (Fig. 4d), indicating the calculated sites are at the scaling between  $\Delta G_{OOH}$  and  $\Delta G_{OH}$ <sup>14</sup>. With the application of the strain, GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  shows a  $\Delta G_2 = \Delta G_O - \Delta G_{OH} = 1.24$  eV that is much closer to the theoretical value (1.23 eV) than the other models with various doping and with or without strain. The “volcano-like” relationship between  $\eta$  and  $(\Delta G_O - \Delta G_{OH})$  (Fig. 4e) shows that GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub>  is at the nadir of the inverse volcano (lowest overpotential), indicating that strain and doping synergistically tune the oxygen binding energies on Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2- $\delta$</sub> . These results reveal that the non-optimal oxygen binding ability of IrO<sub>2</sub> and thus the catalytic energy barrier could be tuned by the combination of strain and doping to optimize the acidic OER catalytic activity.

## Electrochemical acidic OER in PEM electrolyzer

Finally, we apply the optimized GB-Ta<sub>x</sub>Tm<sub>y</sub>Ir<sub>1-x-y</sub>O<sub>2- $\delta$</sub>  nanocatalysts with a low mass loading of 0.2 mg cm<sup>-2</sup> together with the comparative catalysts as the anode catalysts in an acidic (0.5 M H<sub>2</sub>SO<sub>4</sub>) PEM electrolyzer using a Nafion 117 membrane (Fig. 5a, and Supplementary Figs. 33, 34). The polarization curves operated at 50 °C show that the performance of these catalysts (Fig.

5b) follows the order of  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta} > \text{GB-Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta} \approx \text{GB-Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta} > \text{GB-IrO}_{2-\delta}$ . The cell voltage required to reach a current density of  $1 \text{ A cm}^{-2}$  using  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  (1.766 V) is substantially lowered over  $\text{GB-IrO}_{2-\delta}$  (1.946 V),  $\text{GB-Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$  (1.915 V), and  $\text{GB-Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$  (1.897 V) (Fig. 5b). The best performing  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  can also reach 1.5 and  $2 \text{ A cm}^{-2}$  at the cell voltage of 1.868 and 1.935 V, respectively. This device also outperforms the PEM electrolyzers using commercial Ir/NSTF and the other reported state-of-the-art  $\text{IrO}_x$  catalysts (Supplementary Table 13). Even if we assume all metal atoms in the  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst are active toward OER, the lower bound estimate of the turnover frequency (TOF) of  $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  at  $1.5 \text{ A cm}^{-2}$  reaches  $2.54 \text{ O}_2 \text{ s}^{-1}$  (Supplementary Table 14). If we assume only the surface atoms (estimated around 7.3%) are active toward OER, the TOF of  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  can be estimated as  $34.8 \text{ O}_2 \text{ s}^{-1}$  (Fig. 5c, and Supplementary Table 15). Moreover, the device efficiency of the PEM electrolyzers using  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  catalyst reaches 67.1% at  $1.5 \text{ A cm}^{-2}$  (Fig. 5c, and Supplementary Table 16). The corresponding energy consumption of the PEM electrolyzer using the  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  catalyst is  $4.5 \text{ kWh/m}^3 \text{ H}_2$  at  $1.5 \text{ A cm}^{-2}$  (calculation details in Supplementary Information), lower than that of the commercial PEM electrolyzers<sup>44</sup>.

Moreover, the PEM electrolyzer employing the optimized  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst could be operated at  $1.5 \text{ A cm}^{-2}$  for at least 500 h without obvious performance decay (Fig. 5d) to produce 0.12 kg of  $\text{H}_2$  (1243 L at standard pressure and temperature) and 0.896 kg of  $\text{O}_2$  (626 L) at the cathode and anode, respectively. According to the calculation from U.S. Department of Energy (DOE)<sup>45</sup>, the estimated cost of one kilogram of hydrogen produced by this PEM electrolyzer is about \$1, which is much lower than the DOE target of \$2/kg  $\text{H}_2$ . After the continuous operation for 500 h, the used  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  catalyst was characterized with XRD, TEM, XPS, and XANES (Supplementary Figs. 35-41, and Supplementary Table 17) to further confirm the stability of the catalyst after the long-term operation. TEM images reveal that the morphology of  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst did not change and still possesses a lot of GBs after 500 h operation in three-electrode system (Supplementary Fig. 36) and PEM electrolyzer (Supplementary Fig. 38). The GPA analyses (Supplementary Figs. 37, 39) show the maximum value of  $\epsilon_{xy}$  along the GB is still twice as high as that of  $\epsilon_{xx}$ , revealing that the shear strain due to lattice torsion is still the dominant strain on the surface of  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  after the OER stability tests. These results confirm the excellent stability of  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst and the preservation of GBs during acidic OER.

## Conclusions

In summary, we present a new type of torsion strained  $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst that exhibits outstanding activity toward acidic OER with excellent stability, and attributes its enhanced catalytic activity to the synergistic effects of strain and doping. The dominant torsion strained along the grain boundaries between nanocrystalline domains of the nanostructured catalysts tunes the Ir–O bond lengths, which optimizes the adsorption energy of oxygen intermediates and lowers the energy barriers for OER, yet maintains excellent catalyst stability. Moreover, the doping effect caused by substituting Ta and Tm into  $\text{IrO}_{2-\delta}$  also tunes the electronic structures of active sites optimizing the binding energetics of catalytic intermediates. The new torsion strained  $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst enables stable and high performance water splitting using a PEM electrolyzer operated under commercially relevant conditions. This work not only demonstrates a robust and highly efficient OER catalyst to promote the industrial applications of PEM electrolyzers, but also introduces a new strategy to use torsion strained

nanostructured catalysts to enhance the catalytic activity for electrochemical and other catalytic reactions.

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**Author contributions:** X.W.Z. and S.J. conceived the idea. X.W.Z. designed experiments. S.Y.H. prepared the samples, characterized them and analyzed the data. H.Y.S. and J.Z.H. helped to analyze the XPS and electrochemical data. M.L. helped to analyze EXAFS data. G.K.Z. and Y.H. performed the DFT calculations. F.Z., X.N.L., Z.W.S., J.J.H., Y.Q., and L.N.Z. assisted in the fabrication of PEM electrolyzers and analyzed the device efficiency. S.Y.H., H.Y.S., J.Z.H., B.S., L.C.L., X.W.Z. and S.J. wrote the manuscript with inputs from all authors.

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## References

1. Stamenkovic, V. R., Strmcnik, D., Lopes, P. P. & Markovic, N. M. Energy and fuels from electrochemical interfaces. *Nat. Mater.* **16**, 57-69, doi:10.1038/nmat4738 (2017).
2. Li, F. *et al.* Molecular tuning of CO<sub>2</sub>-to-ethylene conversion. *Nature* **577**, 509-513, doi:10.1038/s41586-019-1782-2 (2020).
3. Kibsgaard, J. & Chorkendorff, I. Considerations for the scaling-up of water splitting catalysts. *Nat. Energy* **4**, 430–433, doi:10.1038/s41560-019-0407-1 (2019).
4. Carmo, M., Fritz, D. L., Mergel, J. & Stolten, D. A comprehensive review on PEM water electrolysis. *Int. J. Hydrogen Energy* **38**, 4901-4934, doi:10.1016/j.ijhydene.2013.01.151 (2013).
5. Lagadec, M. F. & Grimaud, A. Water electrolyzers with closed and open electrochemical systems. *Nat. Mater.* **19**, 1140-1150, doi:10.1038/s41563-020-0788-3 (2020).
6. Nong, H. N. *et al.* Key role of chemistry versus bias in electrocatalytic oxygen evolution. *Nature* **587**, 408-413, doi:10.1038/s41586-020-2908-2 (2020).
7. Chatti, M. *et al.* Intrinsically stable in situ generated electrocatalyst for long-term oxidation of acidic water at up to 80 °C. *Nat. Catal.* **2**, 457-465, doi:10.1038/s41929-019-0277-8 (2019).
8. Seitz, L. C. *et al.* A highly active and stable IrO<sub>x</sub>/SrIrO<sub>3</sub> catalyst for the oxygen evolution reaction. *Science* **353**, 1011, doi:10.1126/science.aaf5050 (2016).
9. Blasco-Ahicart, M., Soriano-López, J., Carbó, J. J., Poblet, J. M. & Galan-Mascaros, J. R. Polyoxometalate electrocatalysts based on earth-abundant metals for efficient water oxidation in acidic media. *Nat. Chem.* **10**, 24-30, doi:10.1038/nchem.2874 (2018).
10. Yang, L. *et al.* Efficient oxygen evolution electrocatalysis in acid by a perovskite with face-sharing IrO<sub>6</sub> octahedral dimers. *Nat. Commun.* **9**, 5236, doi:10.1038/s41467-018-07678-w (2018).



11. Ping, Y., Nielsen, R. J. & Goddard, W. A., III. The reaction mechanism with free energy barriers at constant potentials for the oxygen evolution reaction at the IrO<sub>2</sub> (110) surface. *J. Am. Chem. Soc.* **139**, 149-155, doi:10.1021/jacs.6b07557 (2017).
12. Bessarabov, D. *et al.* Gas crossover mitigation in PEM water electrolysis: hydrogen cross-over benchmark study of 3M's Ir-NSTF based electrolysis catalyst-coated membranes. *ECS Trans.* **75**, 1165-1173, doi:10.1149/07514.1165ecst (2016).
13. Geiger, S. *et al.* The stability number as a metric for electrocatalyst stability benchmarking. *Nat. Catal.* **1**, 508-515, doi:10.1038/s41929-018-0085-6 (2018).
14. Man, I. C. *et al.* Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem* **3**, 1159-1165, doi:10.1002/cctc.201000397 (2011).
15. Bajdich, M., García-Mota, M., Vojvodic, A., Nørskov, J. K. & Bell, A. T. Theoretical investigation of the activity of cobalt oxides for the electrochemical oxidation of water. *J. Am. Chem. Soc.* **135**, 13521-13530, doi:10.1021/ja405997s (2013).
16. Suen, N. T. *et al.* Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives. *Chem. Soc. Rev.* **46**, 337-365, doi:10.1039/C6CS00328A (2017).
17. Grimaud, A. *et al.* Activation of surface oxygen sites on an iridium-based model catalyst for the oxygen evolution reaction. *Nat. Energy* **2**, 16189, doi:10.1038/nenergy.2016.189 (2016).
18. Gao, J. *et al.* Breaking long-range order in iridium oxide by alkali ion for efficient water oxidation. *J. Am. Chem. Soc.* **141**, 3014-3023, doi:10.1021/jacs.8b11456 (2019).
19. Diaz-Morales, O. *et al.* Iridium-based double perovskites for efficient water oxidation in acid media. *Nat. Commun.* **7**, 12363, doi:10.1038/ncomms12363 (2016).
20. Escudero-Escribano, M. *et al.* Tuning the activity of Pt alloy electrocatalysts by means of the lanthanide contraction. *Science* **352**, 73-76, doi:10.1126/science.aad8892 (2016).
21. You, B. *et al.* Enhancing electrocatalytic water splitting by strain engineering. *Adv. Mater.* **31**, e1807001, doi:10.1002/adma.201807001 (2019).
22. Li, M. *et al.* Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction. *Science* **354**, 1414, doi:10.1126/science.aaf9050 (2016).
23. Luo, M. *et al.* PdMo bimetallic for oxygen reduction catalysis. *Nature* **574**, 81-85, doi:10.1038/s41586-019-1603-7 (2019).
24. Shan, J. *et al.* Charge-redistribution-enhanced nanocrystalline Ru@IrO<sub>x</sub> electrocatalysts for oxygen evolution in acidic media. *Chem* **5**, 445-459, doi:10.1016/j.chempr.2018.11.010 (2019).
25. Petrie, J. R., Jeon, H., Barron, S. C., Meyer, T. L. & Lee, H. N. Enhancing perovskite electrocatalysis through strain tuning of the oxygen deficiency. *J. Am. Chem. Soc.* **138**, 7252-7255, doi:10.1021/jacs.6b03520 (2016).
26. Wang, H. *et al.* Direct and continuous strain control of catalysts with tunable battery electrode materials. *Science* **354**, 1031, doi:10.1126/science.aaf7680 (2016).
27. Tobias Reier, Hong Nhan Nong, Detre Teschner, Robert Schlögl & Strasser, P. Electrocatalytic oxygen evolution reaction in acidic environments - reaction mechanisms and catalysts. *Adv. Energy Mater.* **7**, 1601275, doi:10.1002/aenm.201601275 (2017).

28. Zhu, Y. T., Liao, X. Z. & Wu, X. L. Deformation twinning in nanocrystalline materials. *Progress in Materials Science* **57**, 1-62, doi:10.1016/j.pmatsci.2011.05.001 (2012).
29. Penn, R. L. & Banfield, J. F. Imperfect oriented attachment: dislocation generation in defect-free nanocrystals. *Science* **281**, 969, doi:10.1126/science.281.5379.969 (1998).
30. Mariano, R. G., McKelvey, K., White, H. S. & Kanan, M. W. Selective increase in CO<sub>2</sub> electroreduction activity at grain-boundary surface terminations. *Science* **358**, 1187, doi:10.1126/science.aao3691 (2017).
31. Chhetri, M. *et al.* Mechanochemical synthesis of free-standing platinum nanosheets and their electrocatalytic properties. *Adv. Mater.* **27**, 4430-4437, doi:https://doi.org/10.1002/adma.201501056 (2015).
32. Bøjesen, E. D. & Iversen, B. B. The chemistry of nucleation. *CrystEngComm* **18**, 8332-8353, doi:10.1039/c6ce01489e (2016).
33. De Yoreo, J. J. *et al.* Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science* **349**, aaa6760, doi:10.1126/science.aaa6760 (2015).
34. Morin, S. A., Bierman, M. J., Tong, J. & Jin, S. Mechanism and kinetics of spontaneous nanotube growth driven by screw dislocations. *Science* **328**, 476, doi:10.1126/science.1182977 (2010).
35. Palumbo, G., Thorpe, S. & Aust, K. On the contribution of triple junctions to the structure and properties of nanocrystalline materials. *Scr. Metall. Mater.* **24**, 1347-1350 (1990).
36. Hÿtch, M. J., Snoeck, E. & Kilaas, R. Quantitative measurement of displacement and strain fields from HREM micrographs. *Ultramicroscopy* **74**, 131-146, doi:https://doi.org/10.1016/S0304-3991(98)00035-7 (1998).
37. Freakley, S. J., Ruiz-Esquius, J. & Morgan, D. J. The X-ray photoelectron spectra of Ir, IrO<sub>2</sub> and IrCl<sub>3</sub> revisited. *Surf. Interf. Anal.* **49**, 794-799, doi:10.1002/sia.6225 (2017).
38. Mesa, C. A. *et al.* Multihole water oxidation catalysis on haematite photoanodes revealed by operando spectroelectrochemistry and DFT. *Nat. Chem.* **12**, 82-89, doi:10.1038/s41557-019-0347-1 (2020).
39. Pham, H. H., Cheng, M. J., Frei, H. & Wang, L. W. Surface Proton Hopping and Fast-Kinetics Pathway of Water Oxidation on Co<sub>3</sub>O<sub>4</sub> (001) Surface. *ACS Catal.* **6**, 5610-5617, doi:10.1021/acscatal.6b00713 (2016).
40. Anantharaj, S., Noda, S., Driess, M. & Menezes, P. W. The Pitfalls of Using Potentiodynamic Polarization Curves for Tafel Analysis in Electrocatalytic Water Splitting. *ACS Energy Lett.* **6**, 1607-1611, doi:10.1021/acsenerylett.1c00608 (2021).
41. Cherevko, S., Geiger, S., Kasian, O., Mingers, A. & Mayrhofer, K. J. J. Oxygen evolution activity and stability of iridium in acidic media. Part 2. – Electrochemically grown hydrous iridium oxide. *J. Electroanal. Chem.* **774**, 102-110, doi:https://doi.org/10.1016/j.jelechem.2016.05.015 (2016).
42. Meng, G. *et al.* Strain regulation to optimize the acidic water oxidation performance of atomic-layer IrO<sub>x</sub>. *Adv. Mater.* **31**, e1903616, doi:10.1002/adma.201903616 (2019).

43. Exner, K. S. Design Criteria for Oxygen Evolution Electrocatalysts from First Principles: Introduction of a Unifying Material-Screening Approach. *ACS Appl. Energy Mater.* **2**, 7991-8001, doi:10.1021/acsaem.9b01480 (2019).
44. Wang, M., Wang, Z., Gong, X. & Guo, Z. The intensification technologies to water electrolysis for hydrogen production – A review. *Renew. Sustain. Energy Rev.* **29**, 573-588, doi:10.1016/j.rser.2013.08.090 (2014).
45. Bender, G. & Dinh, H. (Sponsor Org.: USDOE Office of Energy Efficiency and Renewable Energy (EERE), Transportation Office. Fuel Cell Technologies Office).
46. Ravel, B. N. M. & Newville, M. Data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Rad.* **12**, 537-541, doi:10.1107/S0909049505012719 (2005).

## Figure Captions

**Fig. 1 Synthesis and characterization of torsion strained  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts.** **a**, The schematic routes for synthesizing GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalysts via fast pyrolysis (top) vs. nanoparticles without GB via slow pyrolysis (bottom). **b-d**, Low-resolution TEM (**b**), HRTEM (**c**), and magnified HRTEM images (**c**) of  $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanoparticles without GB. **e-g**, Low-resolution TEM (**e**), HRTEM (**f**), and magnified HRTEM (**g**) images of GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst, with some trigeminal GB and SF marked with dashed lines. **h**, Simulated structure of GB due to lattice torsion. **i**, Lattice-resolved HRTEM image of the GB region in (**g**). **j**, **k**, the corresponding GPA images for (**j**) axial strain ( $\epsilon_{xx}$ ) and (**k**) shear strain ( $\epsilon_{xy}$ ) analyses. **l**, Simulated structure of SF due to lattice torsion. **m**, Lattice-resolved HRTEM image of the SF region in (**g**). **n**, **o**, the corresponding GPA images for (**n**) axial strain ( $\epsilon_{xx}$ ) and (**o**) shear strain ( $\epsilon_{xy}$ ) analyses.

**Fig. 2 Surface XPS and bulk XANES, EXAFS analyses of various GB- $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  catalysts.** **a**, Ir 4f XPS spectra for GB- $\text{IrO}_{2-\delta}$ , GB- $\text{Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , GB- $\text{Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , and GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalysts. **b**, Ir L-edge XANES spectra for Ir foil, C- $\text{IrO}_2$ , GB- $\text{IrO}_{2-\delta}$ , and GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalysts, suggesting the distinct Ir valence states in these samples. **c**, EXAFS spectra for Ir foil, C- $\text{IrO}_2$ , and GB- $\text{IrO}_{2-\delta}$ , showing the strain effect on the Ir–O and Ir–Ir bond lengths. **d**, EXAFS spectra for Ir foil, GB- $\text{IrO}_{2-\delta}$ , and GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ , showing the effect of doping on the Ir–O and Ir–metal bond lengths.

**Fig. 3 Electrocatalytic properties of various  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts toward OER in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte.** **a**, LSV curves of GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  and GB- $\text{IrO}_{2-\delta}$  nanocatalysts vs. those without GB. **b**, LSV curves of different doped GB- $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  samples vs. C- $\text{IrO}_2$ . **c**, Mass activities of these nanocatalysts at  $\eta=266$  mV, showing the effects of both strain and doping on enhancing OER activities. **d**, Chronopotentiometry curve of GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst operated at  $10 \text{ mA cm}^{-2}$  (pink), and the Faradaic efficiency (black dots) during the 500 h test.

**Fig. 4 Tuning the electronic structures of  $\text{IrO}_{2-\delta}$  by strain and doping to enhance OER activity.** **a**, The illustration of synergistic strain and doping effects on enhancing catalytic activity. **b**, The correlation of overpotentials and p band center ( $\epsilon_p$ ) for  $\text{IrO}_2$ ,  $\text{Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ ,  $\text{Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , and  $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  with/without strain. **c**, DOS of  $\text{IrO}_2$  vs. GB- $\text{IrO}_2$ , GB- $\text{IrO}_2$  vs. GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ , and  $\text{IrO}_2$  vs.  $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ . **d**, The established correlation between  $\Delta G_{\text{OH}}$  and  $\Delta G_{\text{OOH}}$  at universal scaling relationship and **e**, The volcano plot for the overpotential as a function of  $\Delta G_{\text{O}} - \Delta G_{\text{OH}}$  for various  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  catalyst models through doping and strain effects.

**Fig. 5. Water splitting PEM electrolyzer employing GB- $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts as the anode catalysts in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte at 50 °C.** **a**, Schematic diagram of the PEM electrolyzer (GDL: gas diffusion layer; MEA: membrane electrode assembly; CP: carbon paper; Pt@Ti foam: Pt-plated Ti foam). **b**, Polarization curves of the PEM electrolyzers employing GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ , GB- $\text{Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , GB- $\text{Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , and GB- $\text{IrO}_{2-\delta}$  as anode catalysts. **c**, The efficiency and TOF for these anode catalysts at 50 °C. **d**, Chronopotentiometry curve of the PEM electrolyzer employing GB- $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$  nanocatalyst operated at 1.5 A cm<sup>-2</sup> (Insets show photographs of the PEM electrolyzer device). The small fluctuations in cell voltage might be caused by the generation of bubbles that could not dissipate from the surface of membrane electrode assemblies (MEA).

## Methods

### Materials and Chemicals

Iridium(III) chloride ( $\text{IrCl}_3$ ), tantalum(V) chloride ( $\text{TaCl}_5$ ), thulium(III) nitrate hexahydrate ( $\text{Tm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), ethanol ( $\geq 99.5\%$ ), isopropyl alcohol ( $\geq 99.95\%$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ), and ammonia solution were purchased from Sinopharm Chemical Reagent Co., Ltd without further purification. Commercial iridium(IV) oxide (99.9% metal basis, Ir  $\geq 84.5\%$ ) (denoted as C- $\text{IrO}_2$ ) was purchased from Shanghai Maclean Biochemical Technology Co., Ltd. Ultrapure Milli-Q water (18.2 M $\Omega$ ·cm) was used to prepare samples and electrolyte solutions.

### Preparation of $\text{IrO}_{2-\delta}$ , $\text{Ta}_{0.05}\text{Ir}_{0.95}\text{O}_{2-\delta}$ , $\text{Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , $\text{Ta}_{0.2}\text{Ir}_{0.8}\text{O}_{2-\delta}$ , $\text{Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ , and $\text{Ta}_{0.1}\text{Tm}_{0.2}\text{Ir}_{0.7}\text{O}_{2-\delta}$ precursors

The preparation of precursors for the synthesis of various  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts was based on the sol-gel method. In a typical preparation of precursors for synthesis of  $\text{IrO}_{2-\delta}$ , 0.05 mmol of citric acid was first dissolved in 20 mL of ethanol and 10 mL of  $\text{H}_2\text{O}$  by ultrasonication for 60 min. Then, 1 mmol of  $\text{IrCl}_3$  was added into the mixed water/ethanol solution containing citric acid under vigorous stirring in an ice bath, preventing the hydrolysis of the precursors. After stirring for 2 h, ammonia solution was added drop-wisely into the reaction solution within

1 h to adjust the pH to around 6. After continuously stirring for 6 h, the reaction solution was transferred to a freeze dryer and steam dried at -40 °C.

The preparation of precursors for the synthesis of  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts followed similar protocols except the amounts of metal salts used. For example, to prepare precursors for the synthesis of  $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ , 0.08 mmol of  $\text{IrCl}_3$ , 0.01 mmol of  $\text{TaCl}_5$ , and 0.01 mmol of  $\text{Tm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were added into the mixed water/ethanol solution containing citric acid under vigorous stirring in an ice bath. The other steps were the same as those described above.

### **Synthesis of $\text{GB-IrO}_{2-\delta}$ , $\text{GB-Ta}_{0.05}\text{Ir}_{0.95}\text{O}_{2-\delta}$ , $\text{GB-Ta}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , $\text{GB-Ta}_{0.2}\text{Ir}_{0.8}\text{O}_{2-\delta}$ , $\text{GB-Tm}_{0.1}\text{Ir}_{0.9}\text{O}_{2-\delta}$ , $\text{GB-Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ , and $\text{GB-Ta}_{0.1}\text{Tm}_{0.2}\text{Ir}_{0.7}\text{O}_{2-\delta}$ nanocatalysts**

The synthesis of various  $\text{GB-Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts was carried out using a fast pyrolysis method in a homemade setup. First, both ends of the tube furnace were opened to air, and the tube furnace was heated to 450 °C with a heating rate of 10 °C min<sup>-1</sup>. Then, the quartz boat containing the dried precursors prepared above was pushed into the center of tube furnace heating zone with a fast speed of 20 cm s<sup>-1</sup>. The precursors were inserted into the 450 °C heating zone from room temperature within 2 seconds. After heating the precursors at 450 °C for 2 h in air, the quartz boat was quickly pushed to the cold zone of tube cooled by water. Finally, the  $\text{GB-Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts were obtained.

### **Synthesis of $\text{IrO}_{2-\delta}$ and $\text{Ta}_{0.1}\text{Tm}_{0.1}\text{Ir}_{0.8}\text{O}_{2-\delta}$ nanocatalysts without GB**

The synthesis of  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts without GB was carried out using the traditional slow pyrolysis method. First, the quartz boat containing the dried precursors was put into the center of the tube furnace. Next, the tube furnace was heated to 450 °C with a heating rate of 10 °C min<sup>-1</sup>. After keeping the precursors at 450 °C for 2 h in air, the tube furnace was naturally cooled to room temperature, and  $\text{Ta}_x\text{Tm}_y\text{Ir}_{1-x-y}\text{O}_{2-\delta}$  nanocatalysts without GB were obtained.

### **Characterization**

The X-ray diffraction (XRD) patterns of these synthesized nanocatalysts were obtained on a X-pert Powder X-ray diffractometer (PANalytical B.V., Netherlands) with a PIXcel 1d detector and  $\text{Cu-K}\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) radiation. The  $2\theta$  angle was scanned at a rate of 1° min<sup>-1</sup> from 10° to 80°. The transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high angle annular dark field scanning TEM (HAADF-STEM), and energy dispersive X-ray spectroscopy (EDS) elemental mapping images of these nanocatalysts were obtained on a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI, America) at an acceleration voltage of 200 kV. The TEM samples were prepared by drop-casting dispersed nanocatalysts on TEM grids. Geometric phase analyses (GPA) was carried out using the GPA plug-in software for strain measurement (HREM Research Inc.) in the Digital Micrograph software (Gatan).

X-ray photoelectron spectroscopy (XPS) analyses of various nanocatalysts were performed using a Thermo Scientific Escalab Xi+ X-ray photoelectron spectrometer. The ratios of the metal elements in the nanocatalysts as well as the dissolved metal ions in the tested electrolyte

solutions after OER stability tests were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS, NexIon 300Q, PerkinElmer).

The soft X-ray absorption spectroscopy (XAS) spectra were collected at the BL01C1 Beamline in Shanghai Synchrotron Radiation Facility. A silicon (111) double-crystal monochromator was monochromatized for the X-ray radiation. All samples were scanned in the range of 11015 eV to 12000 eV with 0.1 eV steps to measure the L absorption edge of Ir. The Ir L-edge data were collected in fluorescence mode using a Lytle detector, while the Ir foil was collected in transmission mode. The nanocatalyst samples were ground and uniformly daubed on the special adhesive tape. Additionally, Ir foil and commercial IrO<sub>2</sub> powder were used as references for Ir<sup>0</sup> and Ir<sup>4+</sup> valence states, respectively. Athena and Artemis software were employed to analyze the XANES and EXAFS data, respectively<sup>46</sup>. The coordination number (N), bond distance (R, in the unit of Å), and Debye-Waller factor ( $\sigma^2$ ) were all extracted from EXAFS data.

### Electrochemical measurements in three-electrode system

Typically, 1.6 mg of electrocatalysts were dispersed in a 1 mL mixture of isopropanol and water (1:3, v:v), and 100  $\mu$ L of 5 wt% Nafion solution was added into this mixture. The suspension was ultrasonicated for 1 h until well dispersed catalyst ink was formed. Then, 5  $\mu$ L of the catalyst ink was drop-casted on an Au disk electrode (diameter: 5 mm; geometric area: 0.196 cm<sup>2</sup>) with a mass loading of 8  $\mu$ g, which was used as the working electrode. A platinum column electrode and a Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode were respectively employed as the counter and reference electrodes. The three-electrode system in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution was characterized using a Bio-Logic VSP potentiostat.

Before each OER experiment, the Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode was calibrated using the following method. Two Pt sheet electrodes (0.1-mm thickness) were respectively used as the working and counter electrodes and were immersed in the 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. After purging the electrolyte with O<sub>2</sub> for 30 min, cyclic voltammetry (CV) was collected at a scan rate of 5 mV s<sup>-1</sup> and the average value of the intercept on the potential axis was considered as the thermodynamic equilibrium potential of the reversible hydrogen electrode (RHE).

To evaluate the OER catalytic activities of the electrocatalysts, linear sweep voltammetry (LSV) with *i*R correction was measured using the three-electrode system in 50 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte that was pre-purged with O<sub>2</sub> for 30 min. The electrochemical test of the three-electrode system was carried out on a rotating disk electrode with a rotation speed of 1600 rpm. Double layer capacitances (*C*<sub>dl</sub>) of the electrocatalysts were assessed by collecting CV at different scan rates from 10 to 30 mV s<sup>-1</sup>. *C*<sub>dl</sub> values were calculated from the linear fitting of charging current density as a function of scan rate. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 0.01–100 kHz at onset potential. The stabilities of the electrocatalysts were evaluated by carrying out chronopotentiometry at a constant OER catalytic current density of 10 mA cm<sup>-2</sup>.

To calculate the Faradaic efficiency (FE) of OER, the O<sub>2</sub> gas generated from acidic OER on GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> nanocatalyst in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte in the three-electrode system was detected using a GC-9790II (Fuli Instrument) gas chromatograph (GC) equipped with a 5 Å molecular sieve column (length: 2 m; diameter: 3 mm) and a thermal conductivity detector (TCD). The electrolyte solution under stirring was first purged with Ar gas for 30 min to remove O<sub>2</sub> gas from the solution and the headspace. Then, chronopotentiometry was carried out at a constant OER catalytic current of 10 mA cm<sup>-2</sup>, and the gaseous sample in the headspace was sampled out using a gas tight syringe every 20 min. Each sample injection into GC was repeated to lower the experimental error.

The FE of the O<sub>2</sub> generation could be calculated using equation 1:

$$FE(O_2, \%) = \frac{V_{O_2} * 4 * F}{V_m * i * t} * 100\% \quad (1)$$

where V<sub>O<sub>2</sub></sub> represents the volume of the O<sub>2</sub> gas generated from OER (L), *F* is the Faraday's constant (96485 C mol<sup>-1</sup>), *i* stands for the applied current (A), *t* is the total time of OER operation (s), and V<sub>m</sub> represents the molar volume of O<sub>2</sub> gas (L mol<sup>-1</sup>).

### Electrochemical measurements in PEM electrolyzer

Prior to constructing the membrane electrode assembly (MEA), as-received Nafion 117 membrane (N117, Dupont) was first sequentially treated by 3 wt% H<sub>2</sub>O<sub>2</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub>, and distilled water at 80 °C for 1 h each step. After cooling to room temperature, the treated N117 membrane was preserved in distilled water.

Various synthesized nanocatalysts (namely GB-IrO<sub>2-δ</sub>, GB-Ta<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2-δ</sub>, GB-Tm<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2-δ</sub>, or GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub>) were employed as the anode catalysts, and Pt/C (20 wt%) was employed as the cathode catalyst for the PEM electrolyzer. To prepare the cathode or anode catalyst ink, 0.8 mg of catalyst was suspended into a 1 mL mixture of isopropanol and water (1:3, v:v), 100 μL of 5 wt% Nafion solution was then added into this mixture, the suspension was then ultrasonicated for 1 h until well dispersed catalyst ink was formed. The prepared cathode or anode catalysts ink was sprayed onto sheets of polytetrafluoroethylene (PTFE) (surface area: 2×2 cm<sup>2</sup>). Subsequently, PTFE-supported Pt/C cathode catalyst, pretreated N117 membrane, and PTFE-supported GB-Ta<sub>x</sub>Tm<sub>y</sub>Ir<sub>1-x-y</sub>O<sub>2-δ</sub> anode catalysts were hot pressed together at 100 °C for 3 min under a pressure of 3 MPa. Pretreated carbon paper (CP) and Pt-plated Ti foam were respectively used as cathode and anode gas diffusion layers (GDL). The MEA was constructed by placing the catalyst-supported N117 membrane in the middle of the CP and Pt-plated Ti foam GDLs, followed by hot pressing at 120 °C for 5 min under a pressure of 8 MPa. See representative photographs of these samples in Supplementary Fig. 33. Finally, the constructed MEA could be applied in the PEM electrolyzer (Supplementary Fig. 34).

The PEM electrolyzer was operated at the temperature of 50 °C using 0.5 M H<sub>2</sub>SO<sub>4</sub> as the electrolyte solution under the flowing rate of 400 mL min<sup>-1</sup>. The performance of the PEM electrolyzer was evaluated by measuring polarization curves from 0.1 A cm<sup>-2</sup> to 2.2 A cm<sup>-2</sup>. The

stability of the PEM electrolyzer employing GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> as the anode catalyst was evaluated by measuring chronopotentiometry at 1.5 A cm<sup>-2</sup> for 500 h. The dissolution of metal elements from the GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> anode catalyst into the electrolyte solution during the 500 h test was quantified by ICP-MS. After the 500 h test, the anode catalyst was recovered for additional structural analysis.

### Theoretical calculations

The Vienna Ab Initio Simulation Package (VASP) was used to perform all the spin-polarized density functional theory (DFT) calculations within the generalized gradient approximation (GGA) along with employing the Perdew-Burke-Ernzerhof (PBE) formulation<sup>47-49</sup>. The projected augmented wave (PAW) potentials were used to describe the ionic cores<sup>50,51</sup>. In the calculation process, PAW pseudopotential was chosen for the Tm element. Simultaneously, the valence electrons were taken into account using a plane wave basis set with a kinetic energy cutoff of 550 eV. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10<sup>-5</sup> eV. Hubbard U was not used in the calculation process due to the various values of U for the different configurations in the same element. The shear strain was added to calculate the energetics. The maximum Hellmann-Feynman force for each ionic optimization step as well as for the optimization of equilibrium lattice constants was 0.05 eV/Å.

All modeled catalyst configurations were established using four metal layers, where the metal atoms in the bottom two layers were fixed. The crystal structure of IrO<sub>2</sub> has a space group of *P42/mnm* with lattice constants of *a* = 4.498 Å, *b* = 4.498 Å, *c* = 3.154 Å. According to previous reports, there are various types in IrO<sub>2</sub>. Taking these into consideration, a series of models were established in this work, including undoped IrO<sub>2</sub> (110), (100), (101), Ta-doped Ta<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2-δ</sub> (110), Tm-doped Tm<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2-δ</sub> (110), Ta- and Tm-doped Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub> (110) surfaces. The shear strain ( $\epsilon_{xy}$  = 1%, 2%, 4%, 6%) in the *x* and *y* directions was applied to stretch the unstrained supercell. The supercell was fixed during the relaxation. The atoms in the strained cell are all relaxed and optimized until the maximum atomic forces lowering 10<sup>-2</sup> eV/Å. A stable structure was obtained by optimizing the models employing VASP until the total energy converging within 10<sup>-5</sup> eV during the relaxation. In the electrocatalytic simulation process, the lattice was fixed in these slab models with shear strain. All simulation processes adopt the same optimization parameters and keep the lattice constant. The models with shear strain introduced were named as GB-IrO<sub>2</sub>, GB-Tm<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2-δ</sub>, GB-Ta<sub>0.1</sub>Ir<sub>0.9</sub>O<sub>2-δ</sub>, GB-Ta<sub>0.1</sub>Tm<sub>0.1</sub>Ir<sub>0.8</sub>O<sub>2-δ</sub>, respectively. A 3×3×1 Monkhorst-Pack *k*-point grid for Brillouin zone sampling was used in calculation. This slab was separated by a 20 Å vacuum layer in the *z* direction between the slab and its periodic images. In order to fully consider the catalytic activity of each catalyst, various possible catalytic sites were selected to evaluate the adsorption energetics of oxygen intermediates on each catalyst.

The free energy ( $\Delta G$ ) of OER on those catalysts is defined as<sup>15</sup>:



$$\Delta G = E_{\text{DFT}} + E_{\text{ZPE}} - T \times \Delta S \quad (2)$$

where  $E_{\text{DFT}}$ ,  $E_{\text{ZPE}}$ ,  $T$  and  $S$  are the calculated total energy of \*O, \*OH, or \*OOH intermediate on catalyst surface, the zero-point energy, temperature, and entropy, respectively.

The calculated overpotential ( $\eta_{\text{OER}}$ ) for OER on each catalyst model is defined as<sup>14,15</sup>:

$$\eta_{\text{OER}} = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/e - 1.23 \quad (3)$$

where the  $\Delta G_1 (= \Delta G_{\text{OH}})$ ,  $\Delta G_2 (= \Delta G_{\text{O}} - \Delta G_{\text{OH}})$ ,  $\Delta G_3 (= \Delta G_{\text{OOH}} - \Delta G_{\text{O}})$ ,  $\Delta G_4 (= \Delta G_{\text{O}_2} - \Delta G_{\text{OOH}})$  are the free energies of the four elementary reactions of OER. Many calculations were performed for various possible catalytic sites for various doped or undoped  $\text{IrO}_{2-\delta}$  catalysts with or without GB and the results were used to construct the plots shown in Figs. 4d, 4e in the main text.

## References

14. Man, I. C. *et al.* Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem* **3**, 1159-1165, doi:10.1002/cctc.201000397 (2011).
15. Bajdich, M., García-Mota, M., Vojvodic, A., Nørskov, J. K. & Bell, A. T. Theoretical investigation of the activity of cobalt oxides for the electrochemical oxidation of water. *J. Am. Chem. Soc.* **135**, 13521-13530, doi:10.1021/ja405997s (2013).
47. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15-50, doi:https://doi.org/10.1016/0927-0256(96)00008-0 (1996).
48. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169-11186, doi:10.1103/PhysRevB.54.11169 (1996).
49. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865-3868, doi:10.1103/PhysRevLett.77.3865 (1996).
50. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758-1775, doi:10.1103/PhysRevB.59.1758 (1999).
51. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953-17979, doi:10.1103/PhysRevB.50.17953 (1994).

**Data and materials availability:** All data needed to evaluate the conclusions in the paper are presented in the paper or the Supplementary Information. Extra data are available from the corresponding author upon reasonable request.