

1 ***Supporting Information***

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3 **Oxide-supported Ir nanodendrites with high activity and**
4 **durability for the oxygen evolution reaction in acid PEM water**
5 **electrolyzers**

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1 ***Experimental***

2 ***1. Preparation of Ir/C***

3 In a synthesis of Ir supported on carbon (Ir/C), 0.2 mmol of $Ir(CH_3COO)_3$ and 80 mg of
4 $NaOH$ were dissolved in 20 mL of ethylene glycol under vigorous stirring for 30 min. 29.5
5 mg of carbon black (Vulcan) was added to the mixture to produce 20 wt.% of Ir/C. The
6 resulting solution was ultrasonicated for 20 min and then refluxed for 30 min at 160 °C under
7 nitrogen condition. The solution was allowed to cool down to room temperature and left for
8 24 hour with continuous stirring. The reaction solution was centrifuged (8200 rpm, 15 min)
9 and washed several times with ultrapure water. The collected Ir/C slurry was dried in a freeze
10 dryer followed by heat treated at 250 °C in nitrogen atmosphere for 2 hour.

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12 ***2. Physical property of metal oxide:***

13 ***Transmission electron microscopy (TEM):*** The prepared Ir-ND nanoparticles dispersed in
14 ethanol and deionized water (D.I. water) (1:1), and then deposited onto carbon coated copper
15 grids and dried at 50 °C in convection oven. These samples were observed under a FEI
16 TECNI G2 20 S-TWIN equipped with LaB6 cathode by an acceleration voltage of 200 kV.
17 An energy dispersive X-ray (EDX) spectroscopy detector and a GATAN MS794 P CCD
18 camera were employed to investigate the Ir-ND particle morphology and overall elemental
19 composition of Ir-ND/ATO and Ir-ND/C.

20

21 ***Wide-angle X-ray Diffraction (XRD):*** Powder X-ray diffraction patterns (XRD) of the
22 prepared samples were obtained with a D8 Advanced Bruker AXS diffractometer using Cu
23 $K\alpha$ radiation. Data were collected in a 2θ range of 20° to 95° and the XRD profiles were
24 fitted with the Pearson VII function using the software Jade 8. Particle sizes (D) were

1 calculated from X-ray diffraction data using the Scherrer formula:

2

$$Particle\ size\ (D) = K \cdot \lambda / FWHM \cdot \cos\theta$$

3

4 where K = Scherrer constant, which is generally taken to have the value 0.9,

5 λ = wavelength of x-rays,

6 $FWHM$ = full width at half maximum of the reflection peak that has the same
7 maximum intensity in the diffraction pattern,

8 θ = diffraction angle of x-rays

9

10 **Physisorption:** The textural property of the prepared Ir-ND was obtained by nitrogen
11 adsorption and desorption measurements at 77 K using a Quatachrome Autosorb-1-C system.
12 For comparison, commercial Ir black was also measured under same condition. Samples were
13 outgassed at 150 °C under vacuum line for at least 2 h before each measurement. The surface
14 area was calculated by the Brunauer-Emmett-Teller (BET) method, by using the
15 Quantachrome™ AS1Win™ software. The Brunauer-Emmett-Teller (BET) method was
16 utilized to calculate the surface area, according to the bellow equations (E1) – (E2):

17

$$\frac{p/p_0}{n(p_0-p)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \frac{p}{p_0} \quad (E1)$$

19

$$A_s(BET) = n_m N_A a_m \quad (E2)$$

21

22 Here, p is the measured pressure, p_0 is the saturation pressure of the adsorptive, C is the

23 BET constant, n_m is the monolayer capacity, n is the amount of the adsorbent, A_s is the

24 BET surface area, N_A is the Avogadro constant, a_m is the cross-sectional area of the

1 adsorptive molecules. The pore-size distribution was also calculated by using the
2 Quantachrome™ AS1Win™ software. The calculation model was the hybride
3 cylindrical/sphere pore, non-local density functional theory (NLDFT) adsorption model. This
4 simulation is achieved by fitting the adsorption isotherm and using a fast non-negative least-
5 square algorithm to solve the generalized adsorption isotherm equation (E3).

6

$$7 \quad N(P/P_0) = \int_{r_{min}}^{r_{max}} N(P/P_0, r) f(r) dr \quad (E3)$$

8

9 This gives the experimental isotherm $N(P/P_0)$ where, r is the pore width, $f(r)$ is the pore-
10 size distribution function, and $N(P/P_0, r)$ is the isotherm on a single pore of r .

11

12 **3. Electrochemical study:**

13 **Preparation of sample ink:** The sample ink was prepared by blending the 5.0 mg of
14 electrocatalysts ultrasonically in a solution containing 2.49 mL of isopropyl alcohol (IPA, \geq
15 99.7 %, Sigma-Aldrich), 2.49 mL of deionized water (D.I. water) and 20 μ L of 5 wt.% Nafion
16 ionomer (Nafion® 117 solution, Sigma-Aldrich). A sample loading of 10.2 μ g_{Ir}cm⁻² was
17 achieved by depositing the appropriate amount of the suspension on the glassy carbon
18 electrode and then drying in a convection oven at 50 °C.

19

20 **The measurement of voltammetric charge and electrochemical porosity:** According to
21 Ardizzone and Trasatti, total charge (q_T^*) and outer charge (q_o^*) of metal oxide can be
22 calculated by integration of voltammograms at different scan rates (2 – 300 $mV s^{-1}$).^{1,2} Total
23 charge (q_T^*) corresponds with the whole active surface area of electrocatalyst, and can be
24 obtained as the scan rate approaches to the zero. Outer charge (q_o^*) shows the outer

1 accessible active surface during OER, and can be extrapolated as the scan rate approaches the
 2 infinite. The difference between q_T^* and q_o^* is the inner charge (q_i^*) which is attributed
 3 to inner active surface area of oxide layer. Moreover, the ratio q_i^*/q_T^* gives the information
 4 of electrochemical porosity which is related with the pore structure of electrocatalyst. To
 5 measure the voltammetric charge and electrochemical porosity, potential cycling was
 6 performed between 0.4 to 1.4 V vs. RHE at different scan rates (3000, 2000, 1000, 750, 500,
 7 250, 100, 50, 20, 10 $mV s^{-1}$). The voltammetric charge corresponding to the total surface
 8 area (q_T^*) can be calculated plotting the reciprocal of q^* against the square root of the
 9 potential scan rate by using the following equation:

$$(q^*)^{-1}(v) = (q_T^*)^{-1} + kv^{1/2} \quad (E4)$$

10

12

13 The total voltammetric charge (q_T^*) calculated by extrapolation of the linear plots at $v = 0$.
 14 The values of outer charge (q_o^*) can be calculated from the extrapolation to $v \rightarrow \infty$ in the
 15 plot of q^* versus $v^{-1/2}$ according to the following equation.

16

$$q^{-1}(v) = q_o^* + k'v^{-1/2} \quad (E5)$$

18

19 From (q_T^*) and (q_o^*) data, the inner voltammetric charge (q_i^*) contribution of less
 20 accessible surface sites of the oxide layer to the total charge can be calculated.

21

$$q_T^* = q_i^* + q_o^* \quad (E6)$$

23

$$q_i^* = q_T^* - q_o^* \quad (E6')$$

24

1 The electrochemical property defined as the relation between the inner and total charge as a
2 function of the total charge.

3

$$4 \quad \text{Electrochemical porosity} = \frac{q_i^*}{q_T^*} \quad (\text{E7})$$

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6 ***Electrochemical stability test protocols:*** The stability test was performed by using the
7 galvanostatic mode of 1 mA cm^{-2} for 15 hour, under nitrogen condition. The rotating speed
8 was 1600 rpm to remove the evaluated oxygen.

9

10 **4. MEA test:**

11 ***Membrane electrode assembly fabrication:*** To prepare the membrane electrode assemblies
12 (MEAs), a commercial 46% Pt/C catalyst purchased from TKK was used as the cathode, and
13 the prepared catalysts were employed as the anode catalyst. The anode and cathode catalyst
14 inks were prepared by ultrasonically blending with Nafion® solution (5% Sigma Aldrich) and
15 isopropanol (IPA). This mixture was sprayed onto a NR-212 membrane (DuPont™, Nafion®
16 PFSA Membrane) with 5 cm^2 of the geometric area. The total loading of Pt was fixed at 0.4
17 $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$ on the cathode and Ir loading was controlled at $1.0 \text{ mg}_{\text{Ir}} \text{ cm}^{-2}$ on anode. After
18 spraying the catalysts, the catalyst-coated membrane was hot pressed at $140 \text{ }^\circ\text{C}$ for 2.5 min.

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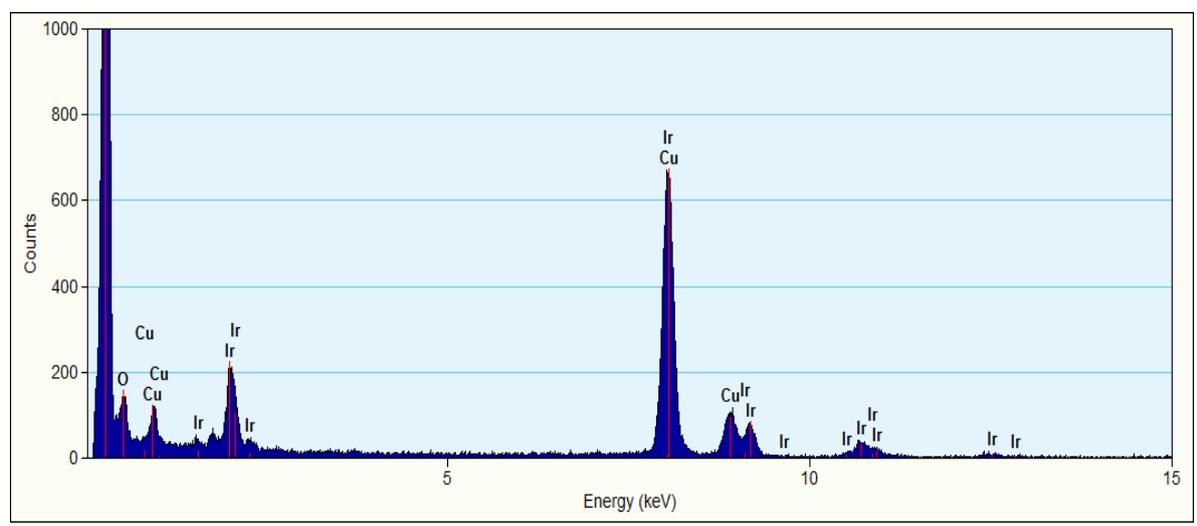
20 ***Cell operation:*** The graphite bipolar-plate was used on cathode side and that of anode side
21 was made from gold-coated titanium. The flow channel was designed to form serpentine type
22 of flow field with a surface area of 5 cm^2 . The depth and width of the channel in the flow-
23 field were both 1 mm. A gold-coated Ti-foam and carbon paper was used as current collectors

1 for anode and cathode respectively. The detail single cell structure was described in **Figure**
2 **S7**. The prepared MEA was sandwiched between the current collectors and assembled in the
3 cell body using 8 screws with a torque of $140 \text{ kg}_f \text{ cm}$. PEMWE single cells were tested
4 using a potentiostat (Bio-logic). The operation temperature of the cell was $80 \text{ }^\circ\text{C}$. The
5 preheated de-ionized water at $80 \text{ }^\circ\text{C}$ supplied to both the anode and cathode compartments at
6 a constant flow rate of 1.5 mL min^{-1} without back pressure. The linear voltammetry
7 profiles were performed for a range of potentials from 1.0 to $2.0 V_{RHE}$ at a 5 mV s^{-1} scan
8 rate.

12 **References**

- 13 (1) De Pauli, C. P.; Trasatti, S. *Journal of Electroanalytical Chemistry* **1995**, 396, 161.
14 (2) Hu, J.-M.; Zhang, J.-Q.; Cao, C.-N. *International Journal of Hydrogen Energy* **2004**,
15 29, 791.

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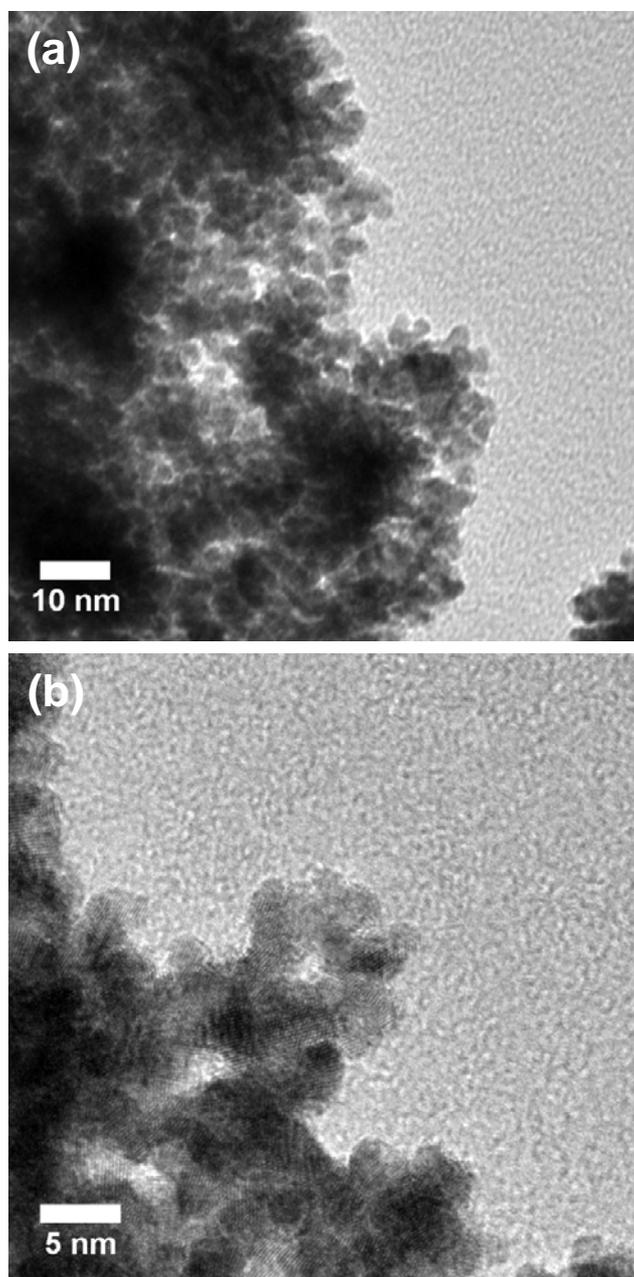
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9 Figure S1. Energy dispersive X-ray spectroscopic (EDX) pattern of Ir nanodendrite (Ir-ND).

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4 Figure S2. TEM images of commercial Ir black (Alfa Aesar, 99.8% metals basis) with
5 different magnifications. (a) low and (b) high magnification.

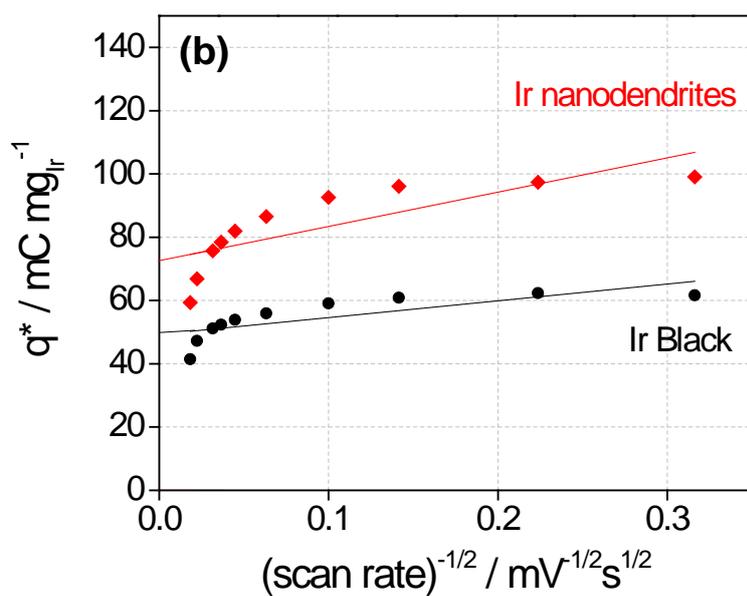
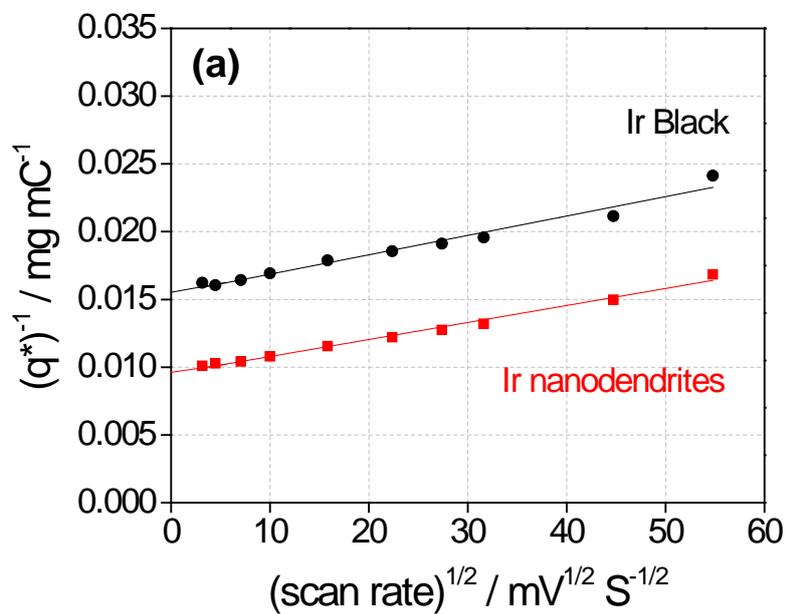
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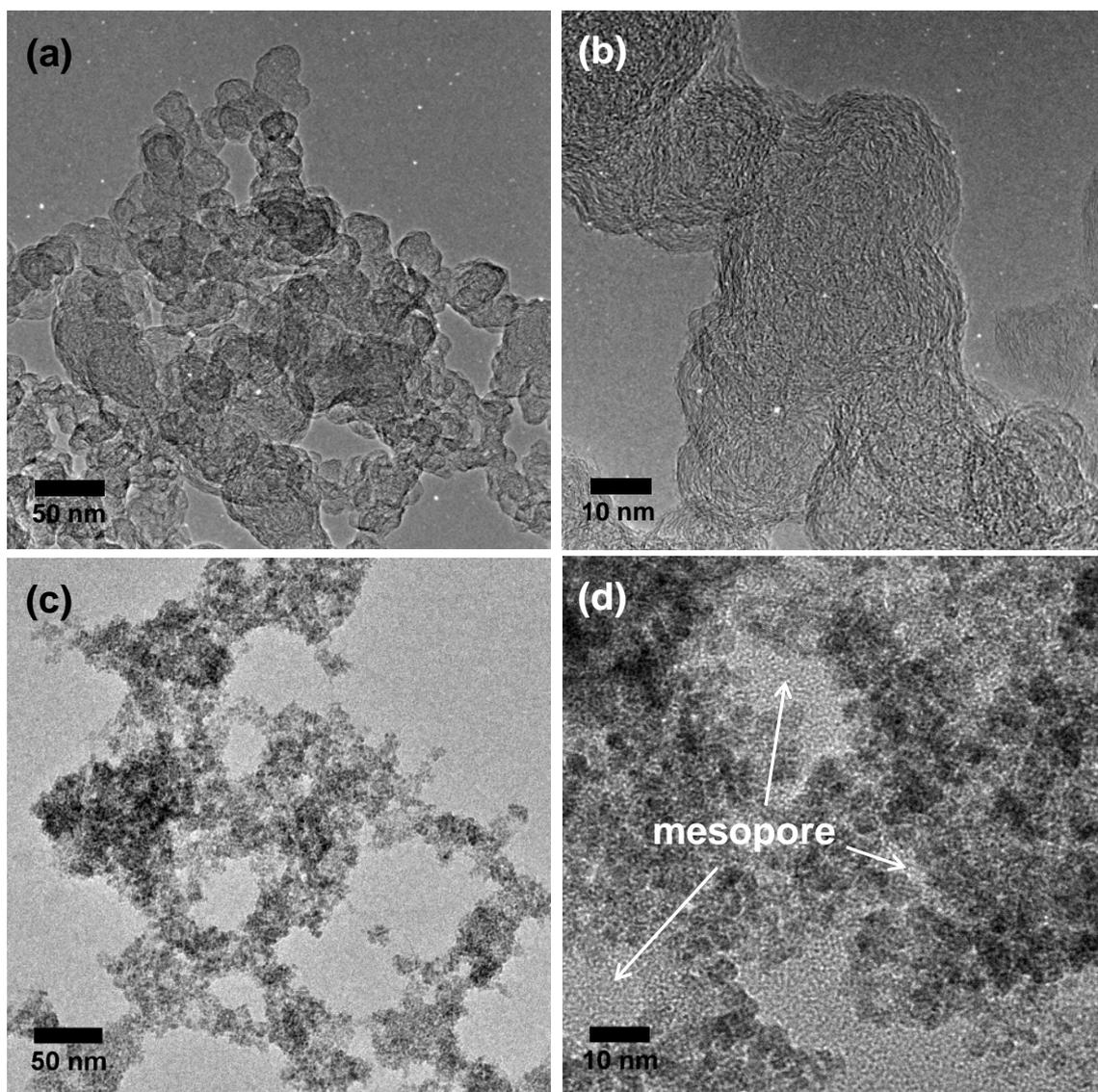
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4 Figure S3. (a) Reciprocal voltammetric charge $(q^*)^{-1}$ versus the square root of the
5 voltammetric scan rate $(v^{1/2})$. (b) Voltammetric charge (q^*) versus the reciprocal square
6 root of the voltammetric scan rate $(v^{-1/2})$ for Ir black and Ir nanodendrites (Ir-ND).

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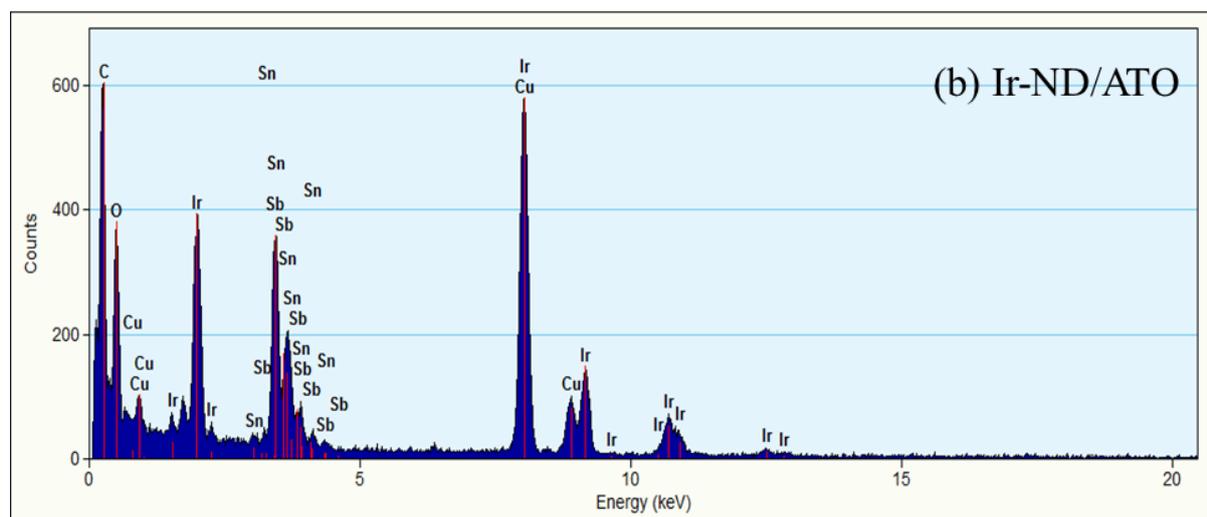
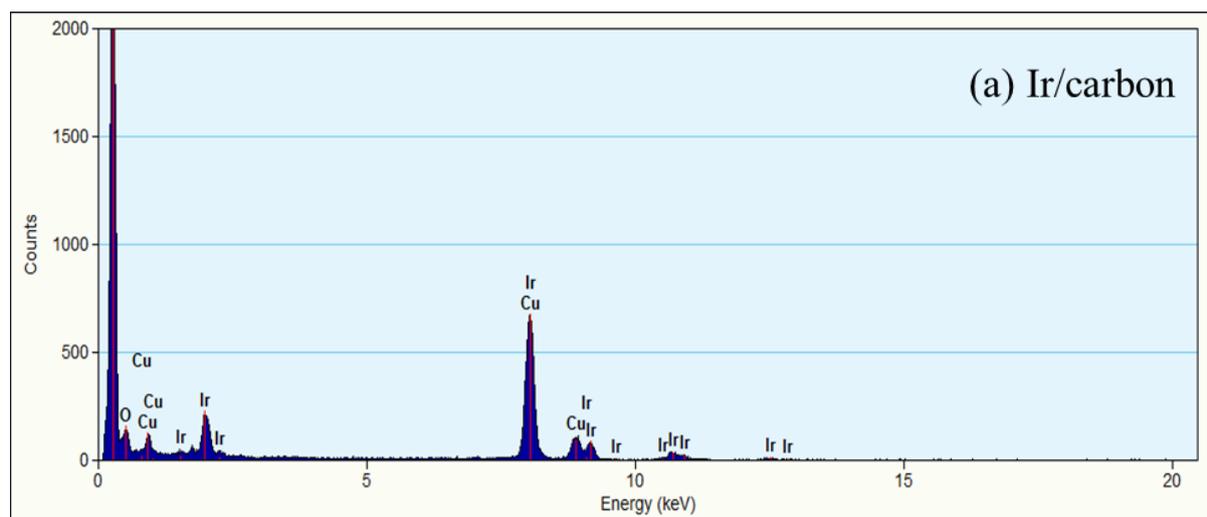
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Figure S4. TEM images of bare catalyst supports. (a, b) carbon black (Vulcan® XC72R) and (c, d) synthesized antimony doped tin oxide (ATO).

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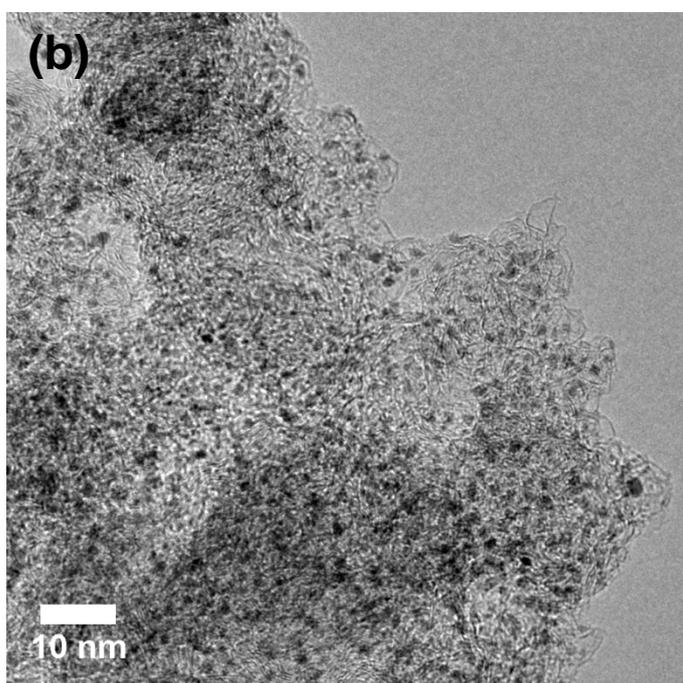
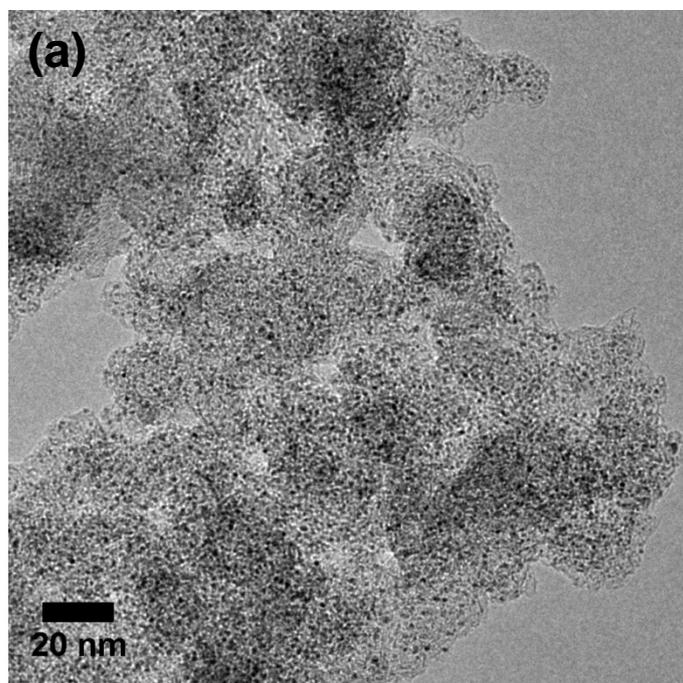


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Figure S5. TEM based EDX patterns of (a) Ir/carbon and (b) Ir-ND/ATO.

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4 Figure S6. TEM images of synthesized Ir nanoparticles supported on carbon black with
5 different magnifications. (a) low and (b) high magnification.

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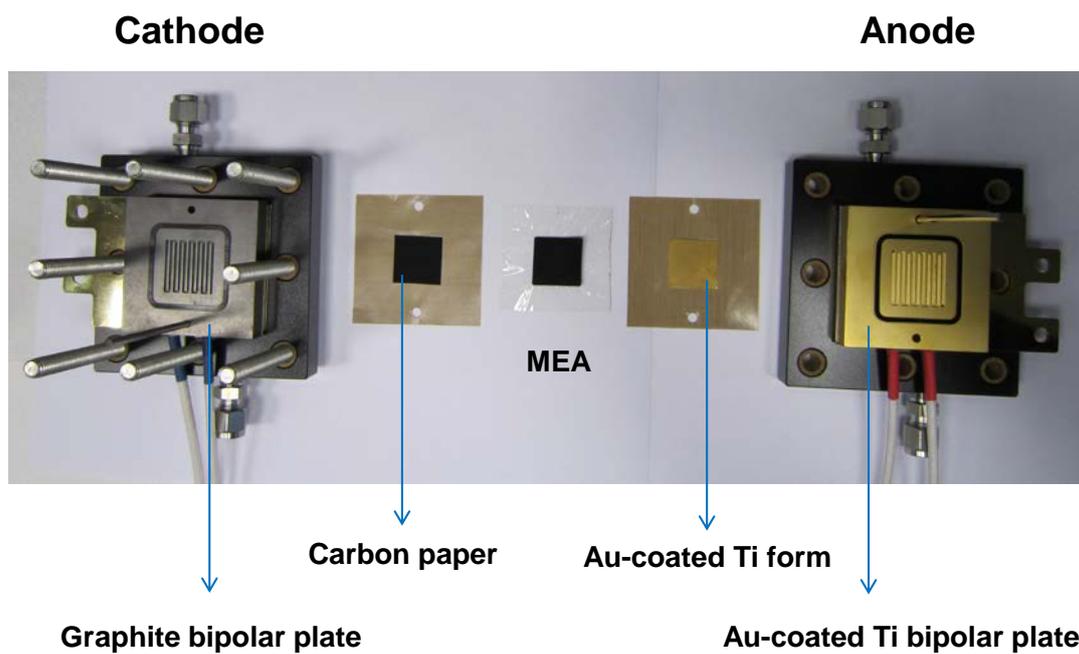
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1 Table S1. Electrochemical properties of synthesized Ir-ND, Ir-ND/C and Ir-ND/ATO. For
2 comparison, Ir black and Ir/C are also shown.

Sample	Tafel slops (mV dec ⁻¹)	Mass activity @ 1.51 V _{RHE} (A g _{Ir} ⁻¹)
Ir black	56.8	8.0
Ir/C	55.6	31.1
Ir-ND	56.5	64.5
Ir-ND/C	57.7	67.9
Ir-ND/ATO	56.4	69.8

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Figure S7. The picture of single cell for PEM water electrolysis. In the anode side, Au-coated Ti foam and plate were used as current collector and bipolar plate, respectively.