Supporting Information for

## Shape-tunable Pt-Ir Alloy Nanocatalysts with High Performance in Oxygen Electrode Reactions

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*Table S1.* Surface atomic ratios, proportions of oxidation states and OER mass activities of Pt-Ir NOs with different annealing temperatures.

| Sample | Pt (%) | Ir (%) | Pt <sup>n+</sup> /Pt | Ir <sup>n+</sup> /Ir | Mass activity |
|--------|--------|--------|----------------------|----------------------|---------------|
|        |        |        | (%)                  | (%)                  | $(A g^{-1})$  |
| NO-300 | 68.3   | 31.7   | 44.1                 | 68.2                 | 15.7          |
| NO-350 | 70.9   | 29.1   | 50.1                 | 78.8                 | 21.3          |
| NO-400 | 69.4   | 30.6   | 67.9                 | 100.0                | 27.9          |

*Table S2.* Surface atomic ratios of Pt-Ir alloy nanocrystals after annealing or working potential treatment determined from XPS analysis.

| Sample | Annealed |      | Treated |      |  |
|--------|----------|------|---------|------|--|
| (%)    | Pt       | Ir   | Pt      | Ir   |  |
| NO     | 74.5     | 25.5 | 70.9    | 29.1 |  |
| NTO    | 70.4     | 29.6 | 68.7    | 31.3 |  |
| NC     | 76.3     | 23.7 | 83.1    | 16.9 |  |
| NSC    | 65.6     | 34.4 | 62.4    | 37.6 |  |
| NW     | 74.1     | 25.9 | 70.8    | 29.2 |  |

*Table S3.* Electrochemically active surface area (ECSA) from the Cu-UPD and high frequency impedance of the catalysts.

| Sample | $\frac{\text{ECSA}}{(\text{m}^2 \text{ g}^{-1})}$ | $R\left(\Omega\right)$ | Sample    | $\frac{\text{ECSA}}{(\text{m}^2 \text{ g}^{-1})}$ | R (Ω) |
|--------|---|------------------------|-----------|---|-------|
| NO     | 25.5  | 4.0                    | NW        | 7.5   | 4.1   |
| NTO    | 20.4  | 4.0                    | Ir/C      | 23.3  | 4.1   |
| NC     | 25.7  | 4.0                    | Pt/C      | 64.8  | 3.7   |
| NSC    | 11.6  | 4.1                    | Pt/C-Ir/C | 48.9  | 4.0   |

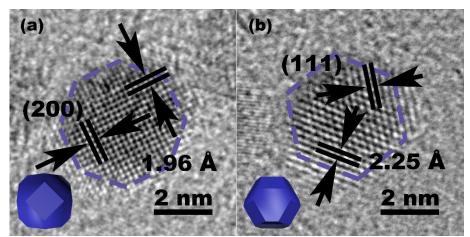
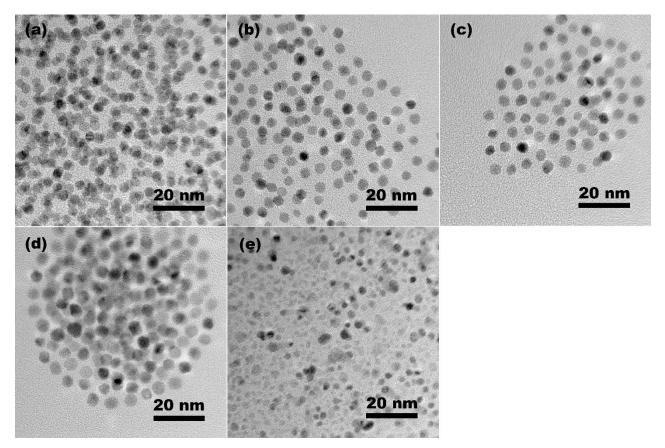
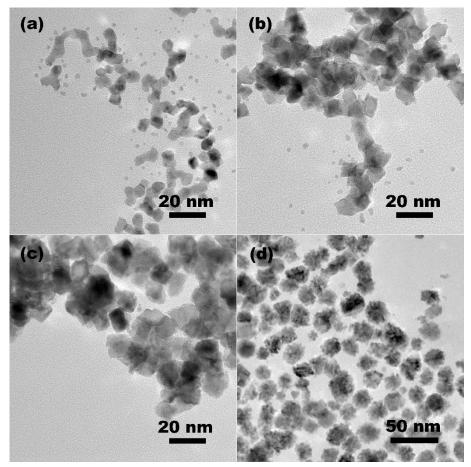


Fig. S1. HRTEM images of Pt-Ir alloy NTOs from the (a) (100) and (b) (111) facets view.



*Fig. S2.* TEM images of Pt-Ir nanoparticles obtained with different amounts of KBr: (a) without KBr, (b) 70 mg, (c) 700 mg, (d) 1400 mg. (e) TEM images of Pt-Ir nanoparticles obtained with 99 mg of TEAC. All the other conditions were the same as those of Pt-Ir alloy single-crystalline nanocrystals.



*Fig. S3.* TEM images of Pt-Ir nanoparticles obtained under different reaction conditions: (a) with 4 mg KI (b) with 20 mg KI (c) with 100 mg KI (d) with 500 mg KI. All the other conditions were the same as those of Pt-Ir alloy single-crystalline nanocrystals.

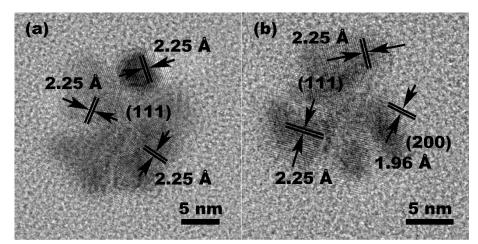


Fig. S4. HRTEM images of as-synthesized Pt-Ir NCFs.

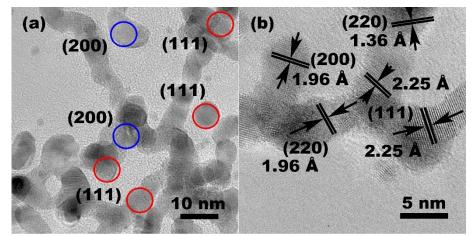
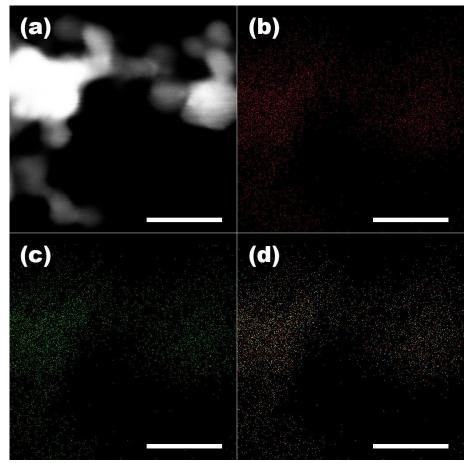


Fig. S5. HRTEM images of as-synthesized Pt-Ir worm-like NWs.



*Fig. S6.* HAADF-STEM image (a) and EDS mapping images: (b) Pt, (c) Ir, (d) overlay of as-synthesized Pt-Ir worm-like NWs with the scale bar of 20 nm.

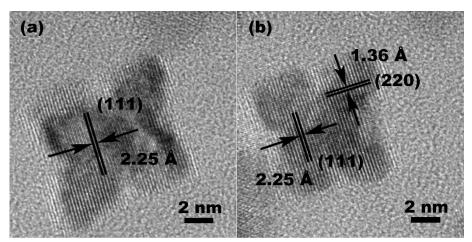
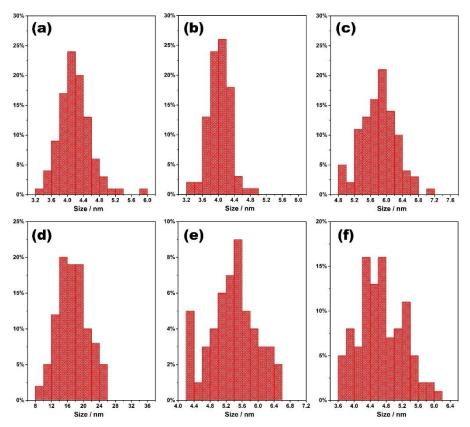


Fig. S7. HRTEM images of as-synthesized Pt-Ir NOSs.



*Fig. S8.* Particle size statistics for as-synthesized Pt-Ir alloy nanocrystals: (a) NOs, (b) NTOs, (c) NCs, (d) NCFs, (e) NWs, and (f) NOSs.

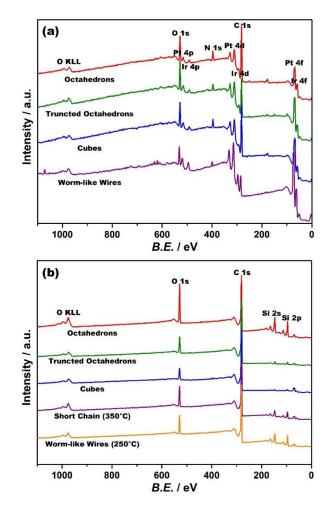


Fig. S9. XPS full spectra of Pt-Ir alloy nanocrystals (a) before and (b) after the annealing treatment.

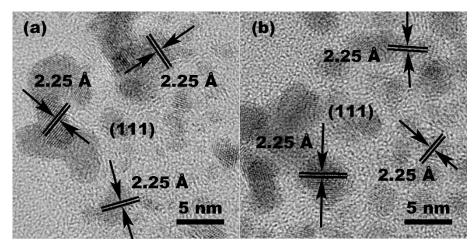
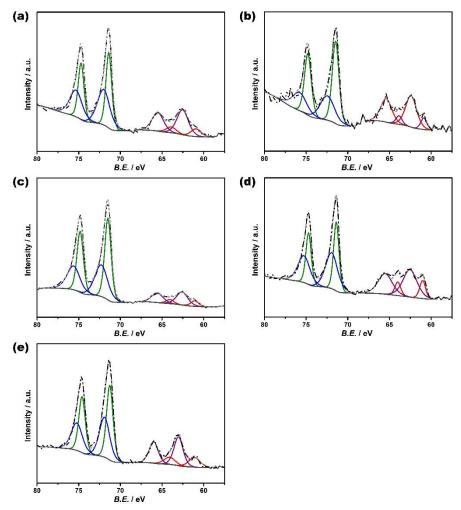
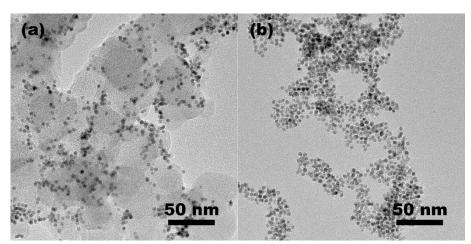


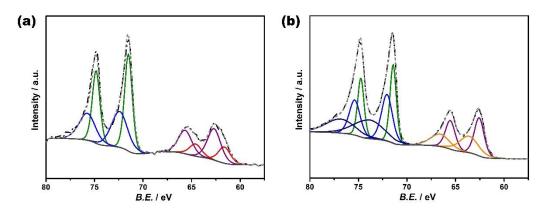
Fig. S10. HRTEM images of commercial Pt/C catalyst.



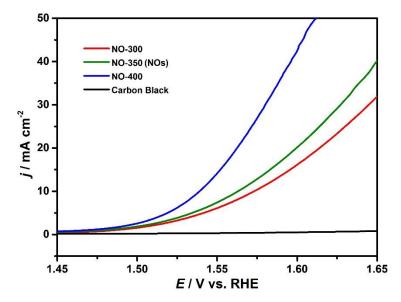
*Fig. S11.* XPS spectra of Pt-Ir alloy nanocrystals in Pt and Ir 4f regions after a working potential treatment at 1.479 V: (a) NOs, (b) NTOs, (c) NCs, (d) NSCs, and (e) NWs.



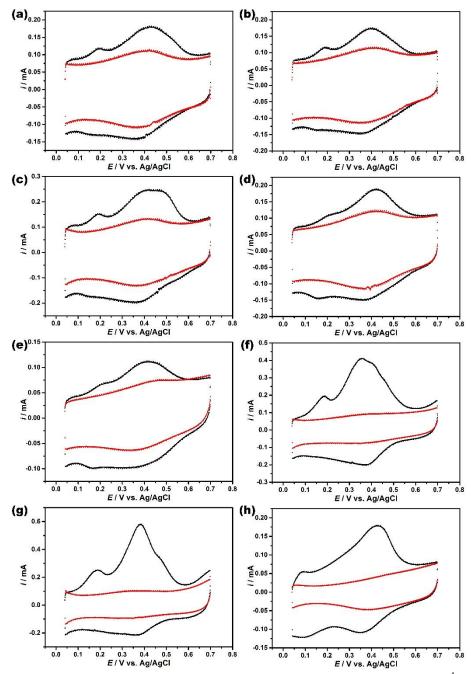
*Fig. S12.* TEM images for Pt-Ir NOs catalyst with different annealing temperatures: (a) NO-300, (b) NO-400.



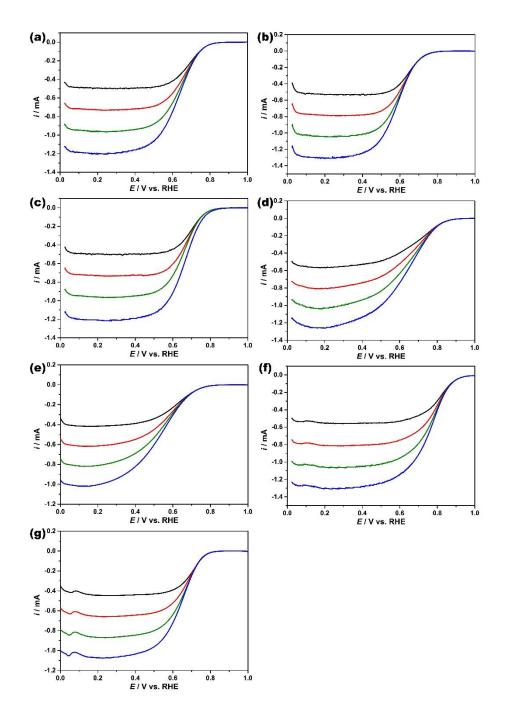
*Fig. S13.* XPS spectra of Pt-Ir NOs in Pt and Ir 4f regions after a working potential treatment at 1.479 V: (a) NO-300, (b) NO-400.



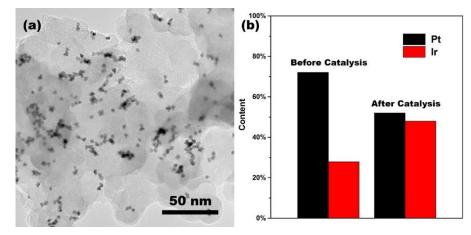
*Fig. S14.* IR-compensated polarization curves of carbon black and Pt-Ir NOs with different annealing temperatures in a N<sub>2</sub>-saturated 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> electrolyte with a rotation rate of 1600 rpm at a sweep rate of 10 mV s<sup>-1</sup>.



*Fig. S15.* Cu-UPD stripping curves measured at 0.3 V for 100 s in 2 mmol L<sup>-1</sup> CuSO<sub>4</sub> and 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution (black curves) or 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution (red curves), followed by the collection of CV curves from 0.04 V to 0.7 V vs. Ag/AgCl with the sweep rate of 50 mV s<sup>-1</sup>: (a) NOs, (b) NTOs, (c) NCs, (d) NSCs, (e) NWs, (f) Pt/C-Ir/C mixture, (g) commercial Pt/C catalyst, and (h) commercial Ir/C catalyst. The ECSA of the sample was calculated from the stripping charge with the coefficient of 420  $\mu$ C·cm<sup>-2</sup>.



*Fig. S16.* Polarization curves for ORR on carbon black supported Pt-Ir alloy nanocatalysts and commercial Pt/C catalyst with different rotations (black: 400 rpm; red: 900 rpm; green: 1600 rpm; blue: 2500 rpm): (a) NOs, (b) NTOs, (c) NCs, (d) NSCs, (e) NWs, (f) commercial Pt/C catalyst, and (g) Pt/C-Ir/C mixture.



*Fig. S17.* TEM image (a) of Pt-Ir NSCs after 5000 cycles of voltage sweeps in the range of 0.6-1.0 V vs. RHE with a scan speed of 200 mV s<sup>-1</sup> in O<sub>2</sub>-saturated mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> electrolyte. (b) Comparison of atomic content of Pt-Ir NSCs (from EDS) before and after the voltage sweeps.