Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Shaped Ir-Ni bimetallic nanoparticles for minimizing Ir utilization in oxygen evolution reaction

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Experimental section

Materials Iridium(III) chloride hydrate ($IrCl_3 \cdot xH_2O$), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.999 %), oleylamine (OAm, 70 %), sodium hydroxide (NaOH, ≥ 97.0 %), ethylene glycol (EG, 99.8 %), acetic acid (HOAc, ≥ 99.99 %), and sulfuric acid (H_2SO_4, 99.999 %), were obtained from Sigma-Aldrich. Iridium acetate ($Ir(CH_3COO)_n$, 48-54 % Ir), and iridium black (99.8 %) were obtained from Alfa Aesar. Carbon black (Vulcan, XC-72R) was used as supports. Ethanol (Anhydrous, 99.9 %) and n-hexane (95 %) were obtained from Samchun. Deionized water with resistivity of more than 18.3 MΩ·cm was prepared with Human Power II$^+$ Scholar (Human Corporation).

Synthesis of Ir-Ni bimetallic structures Ir-Ni nanoparticles with thin Ir layers (Ir-Ni TL) were prepared by the following method. $IrCl_3 \cdot xH_2O$ 10.1 mg and 21.9 mg of $Ni(NO_3)_2 \cdot 6H_2O$ were added to 1 mL of deionized water and the solution was then homogenized by heating slightly at 80 °C overnight. Then, 0.8 mL of the prepared homogeneous precursor solution was added to 10 mL of oleylamine at 160 °C, and the mixture was stirred for 5 min to remove water. The solution was then quickly heated up to 280 °C under Ar flow. It took approximately 5 min heating to 280 °C. When the temperature reached 280 °C, the brownish solution suddenly turned into black. After 5 min, the solution was removed from the heating mantle and cooled down to room temperature quickly. The prepared nanoparticles were washed with n-hexane several times. Ir-Ni nanoparticles with a star candy shape (Ir-Ni SC) or Ir lumps (Ir-Ni LP) were prepared using 26.3 mg or 78.7 mg of $IrCl_3 \cdot xH_2O$ in otherwise unchanged conditions. Pure Ni nanoparticles were synthesized without Ir precursor at otherwise identical condition. Pure Ir nanoparticles were also synthesized without Ni precursor using 10.1 mg of $IrCl_3 \cdot xH_2O$ at otherwise identical condition. However, in the absence of a Ni precursor, Ir was not reduced at 280 °C immediately, but the color changed into black in 30 min. The Ir-Ni nanoparticles were supported on the carbon black for electrochemical measurements. The proper amounts of carbon black were added to the above nanoparticle solutions and mixed with 3 mL of ethanol. The mixture was sonicated for 2 hrs and then stirred overnight. The resulting slurry was washed with ethanol several times, dried overnight at 80 °C, and then calcined at 250 °C for 2 hrs under N_2 flow. The weight fraction of Ir and Ni were 0.7 wt% and 14.3 wt% for Ir-Ni TL/C, 4.4 wt% and 5.3 wt% for Ir-Ni SC/C, and 10.4 wt% and 4.8 wt% for Ir-Ni LP/C, respectively. Ir/Ni atomic ratios were 0.015, 0.25, and 0.66 for Ir-Ni TL/C, Ir-Ni SC/C, and Ir-Ni LP/C, respectively.

Synthesis of Ir NP/C for benchmarks Ir nanoparticles supported on carbon black (Ir NP/C) catalysts were prepared by following the previously reported procedure [S1]. First, 125 mg of Ir(CH_3COO)$_n$ was dissolved in 40 mL of 0.15 M NaOH solution in EG. After purging the solution with N_2 sufficiently, the solution was heated to 160 °C with reflux and stirred for 30 min. Ir nanoparticles were formed at this stage. The solution was then cooled down rapidly. Carbon black 200 mg were mixed with 30 mL of deionized water and 5 mL of acetic acid. The prepared carbon suspension was added to the Ir nanoparticle solution. The mixture was sonicated for 2 hrs, stirred overnight, then washed with deionized water sufficiently. The resulting slurry was freeze-dried for a day. The Ir NP/C catalysts were then calcined at 250 °C for 2 hrs under N_2 flow. The weight fraction of Ir was 20 wt% for Ir NP/C. The mixture of Ir black and carbon black was also used for comparison with an Ir weight fraction of 20 wt%.

Electrochemical measurements A typical three electrodes electrochemical cell was used using a potentiostat (CHI 760E, PINE instrument) with a glassy carbon rotating disk electrode (RDE, diameter: 5 mm, PINE instrument). The counter electrode was a Pt wire, and the reference electrode was a 3 M NaCl Ag/AgCl (RE-5B, BASi) with a Luggin capillary. The temperature of the electrochemical cell was maintained at 25 °C using a water bath. All potentials were reported versus reversible hydrogen electrode (RHE). The RHE was measured by performing hydrogen evolution and hydrogen oxidation reactions at a rotating Pt electrode (1600 rpm) in a H_2-purged electrolyte prior to each measurement. The catalyst ink was prepared by suspending the catalyst in 3.75 mL of isopropanol, 1.25 mL of deionized water, and 20 μL of 5 wt% Nafion solution. Ir loading was 2 $\mu g/cm^2$ for all cases. The catalysts were activated by performing 50 cycles of cyclic voltammetry from 0.05 V to 1.5 V in an Ar-saturated 0.05 M H_2SO_4 aqueous solution with a scan rate of 500 mV/s. Then, the electrolyte solution was changed with a fresh 0.05 M H_2SO_4 solution and the solution was thoroughly purged with Ar again. The oxygen evolution reaction (OER) was conducted from 1.35 V to 1.6 V in 100 mL of the Ar-saturated 0.05 M H_2SO_4 solution at 1600 rpm with a scan rate of 5 mV/s in a positive direction. The durability tests were performed in an Ar-saturated 0.05 M H_2SO_4 solution by chronopotentiometry at 1 mA/cm^2 current density at 1600 rpm. Faradaic efficiency was estimated by measuring the produced O_2 directly. A carbon paper (Toray) was used as a working electrode instead of glassy carbon RDE to maximize O_2 production. The catalyst ink was drop-casted on the carbon paper, and the working electrode was vertically positioned. Before the reaction, the electrochemical cell was purged with He (99.999 %, Air Liquide) sufficiently. The OER was performed at 25 °C in

0.05 M H_2SO_4 solution by conducting chronopotentiometry at 4.5 mA with magnetic stirring. The produced O_2 was measured by gas chromatography (GC, Younglin GC 6000 series) equipped with a thermal conductivity detector. The theoretically expected amount of O_2 production was calculated from the charge passed during the reaction.

Characterizations Inductively coupled plasma optical emission spectroscopy (ICP-OES 720, Agilent) was used to estimate the actual weight fractions of Ir and Ni. Inductively coupled plasma mass spectroscopy (ICP-MS 7700S, Agilent) was used to measure the amount of Ir and Ni ions in the 0.05 M H_2SO_4 electrolyte solution dissolved during the OER. The high resolution transmission electron microscopy (HR-TEM) images were obtained using a TF30 ST (Tecnai) with an accelerating voltage of 300 kV. The energy-dispersive X-ray spectroscopy (EDS) mapping data and high angle annular dark field-scanning TEM (HAADF-STEM) images were obtained using a Titan cubed G2 60-300 (FEI) with an accelerating voltage of 300 kV. X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG Scientific) was used to investigate the surface state of the catalysts. The energy scale was calibrated by adjusting the C 1s peak at 284.8 eV. X-ray absorption near-edge structure (XANES) measurements were conducted with 8C Nano XAFS beamline of the Pohang Light Source (PLS).

Additional Data;

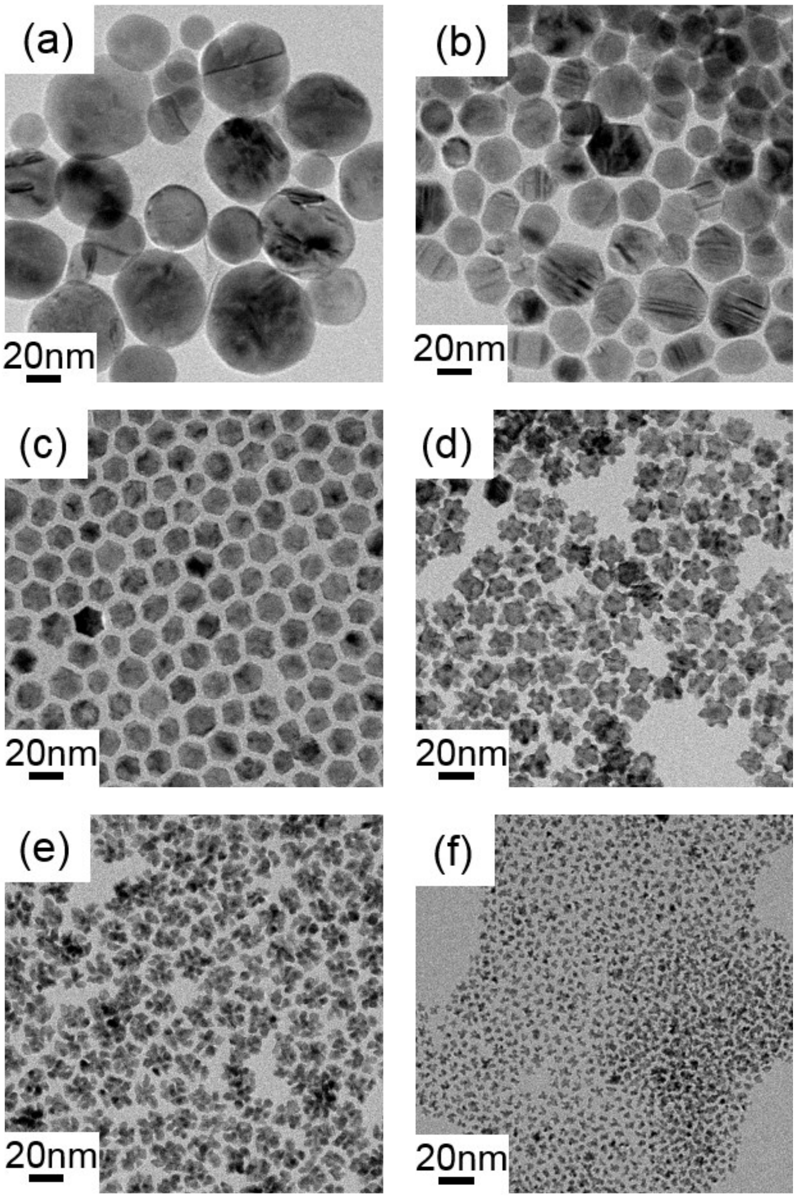

Figure S1. TEM images of Ir-Ni nanoparticles synthesized with Ir/Ni precursor atomic ratios of (a) 0, (b) 0.17, (c) 0.38, (d) 1.0, and (e) 3.0 synthesized after 5 min at 280 ˚C. (f) TEM image of Ir nanoparticles synthesized after 30 min at 280 ˚C.

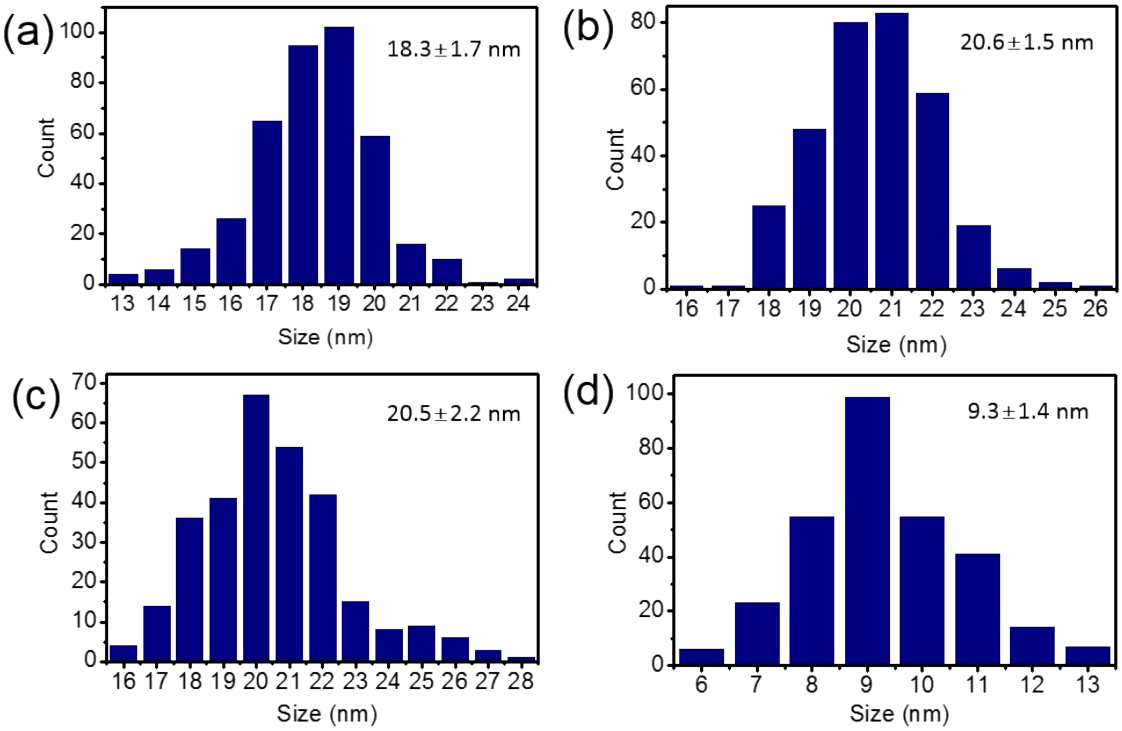

Figure S2. Histograms for nanoparticle size distribution of (a) Ir-Ni TL, (b) Ir-Ni SC, (c) Ir-Ni LP, and (d) Ir dendrites. The longest length from tip to tip was measured.

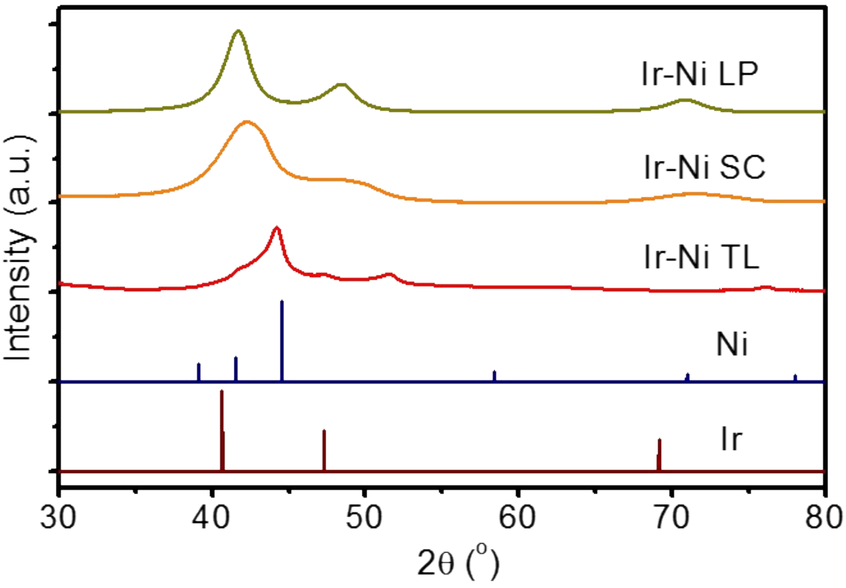

Figure S3. X-ray diffraction patterns of Ir-Ni nanoparticles. XRD peaks for metallic Ir and Ni are also shown.

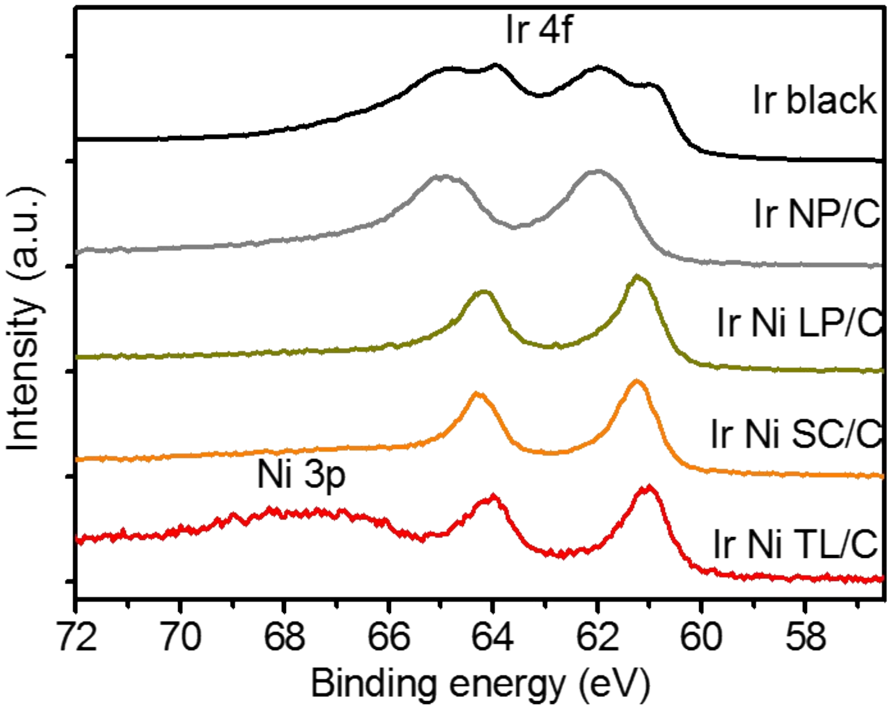

Figure S4. X-ray photoelectron spectroscopy data for Ir black, Ir nanoparticles, or Ir-Ni bimetallic nanoparticles supported on carbon black.

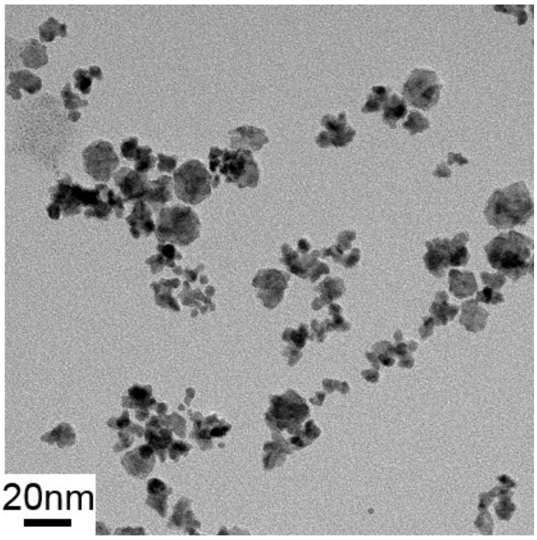

Figure S5. TEM images of Ir-Ni nanoparticles synthesized in the absence of water.

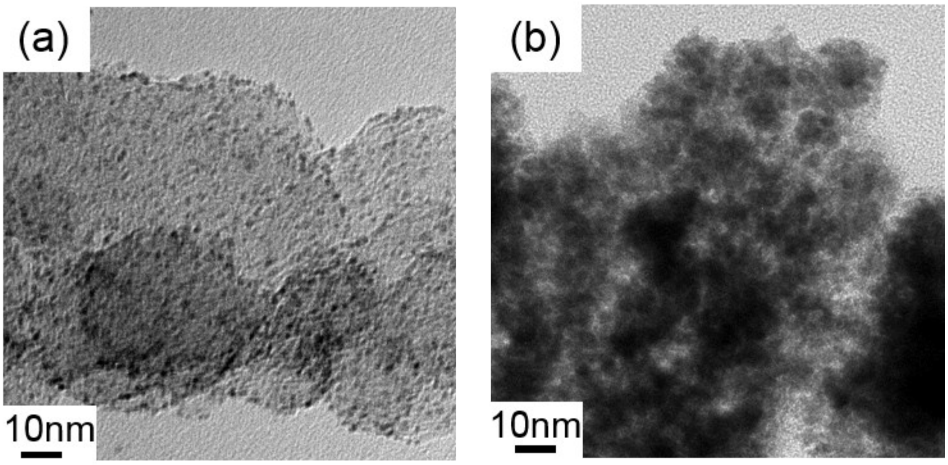

Figure S6. TEM images of (a) Ir nanoparticles supported on carbon black and (b) Ir black.

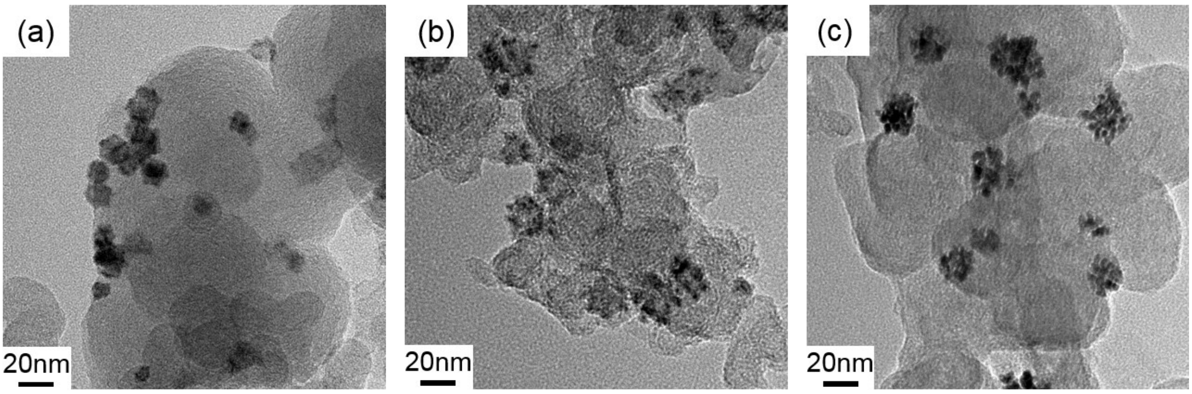

Figure S7. TEM images of (a) Ir-Ni TL/C, (b) Ir-Ni SC/C, and (c) Ir-Ni LP/C obtained after the activation procedure of repeating cyclic voltammetry (CV) in a range of 0.05 to 1.5 V (vs. RHE) with a scan rate of 500 mV/s for 50 cycles.

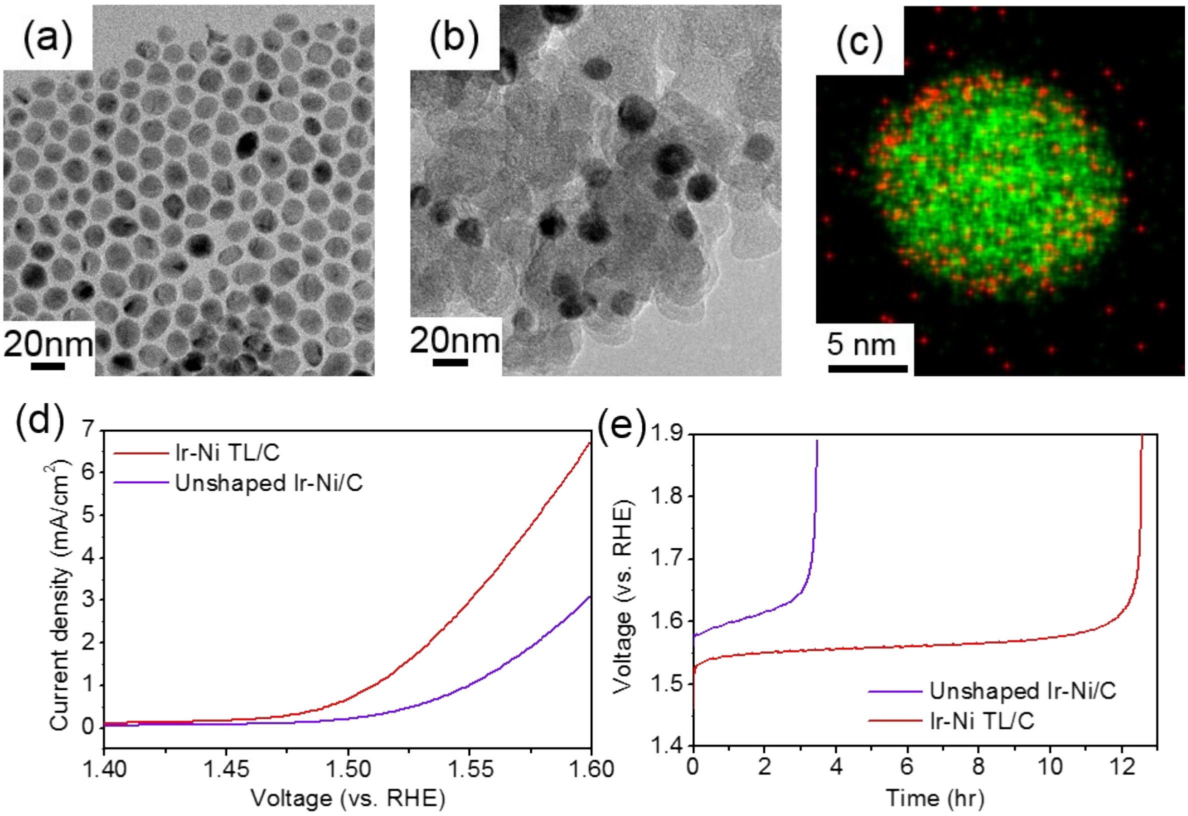

Figure S8. (a) TEM image of the unshaped Ir-Ni nanoparticles synthesized with the same Ir/Ni precursor atomic ratio of 0.38 as Ir-Ni TL nanoparticles by decreasing the dissolving time of metal precursors in deionized water to 3 hrs. (b) TEM image of the unshaped Ir-Ni nanoparticles deposited on the carbon. The weight fraction of Ir and Ni were 1.0 wt% and 12.7 wt%, respectively. (c) EDS mapping image (red: Ir, green: Ni). (d) LSV results and (e) chronopotentiometry curves at a constant current density of 1 mA/cm^2 for shaped Ir-Ni TL nanoparticles and unshaped Ir-Ni nanoparticles. Measurement conditions: 2 $\mu g_{Ir}/cm^2$, Ar-saturated 0.05 M H_2SO_4, 1600 rpm, scan rate for LSV 5 mV/s.

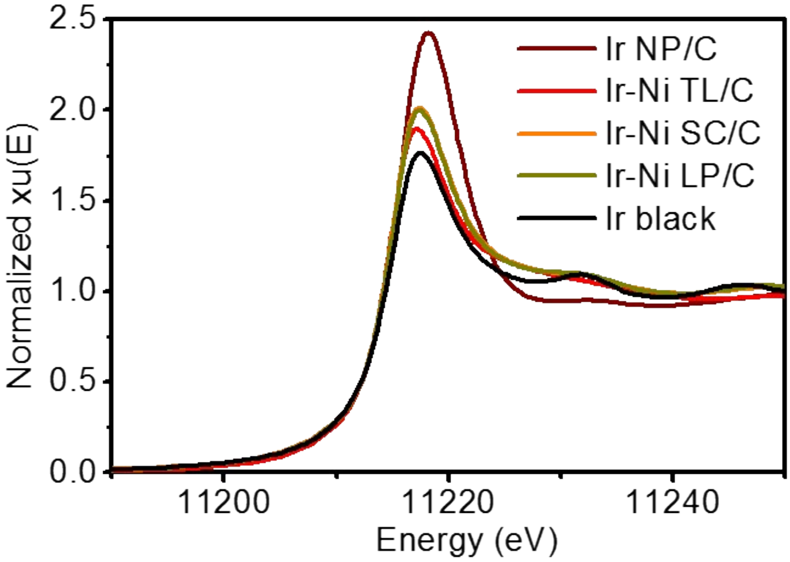

Figure S9. X-ray absorption near edge structure measurement results for Ir L3 edges.

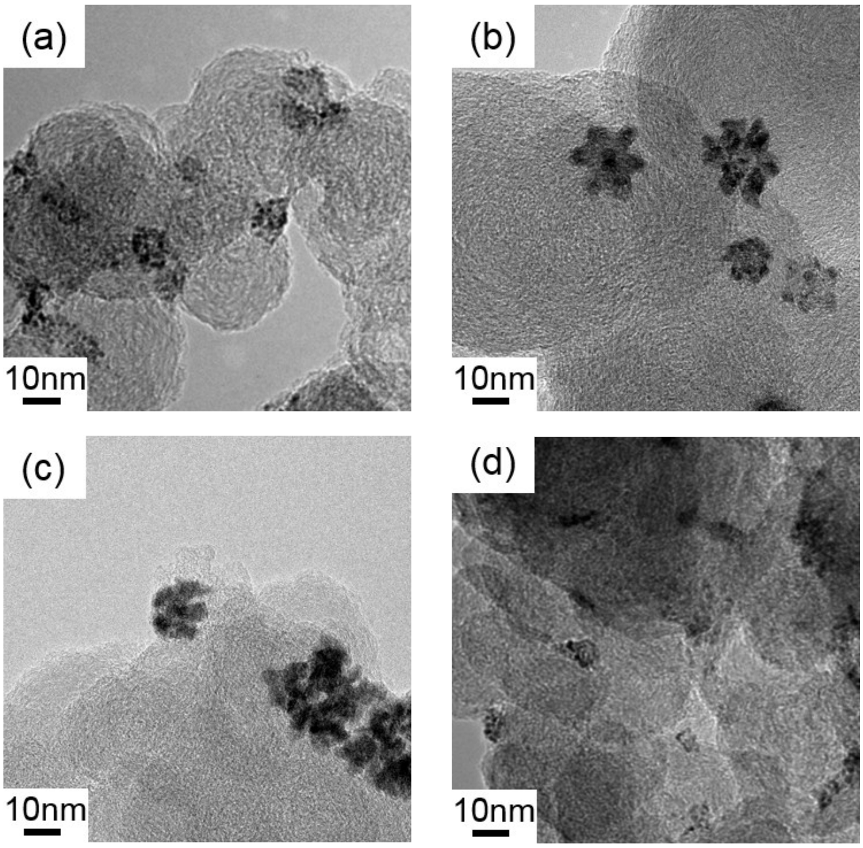

Figure S10. TEM images of (a) Ir-Ni TL/C, (b) Ir-Ni SC/C, and (c) Ir-Ni LP/C after chronopotentiometry at 1 mA/cm^2 for 1 hr. (d) TEM image of Ir-Ni TL/C after 5 hrs of chronopotentiometry at 1 mA/cm^2.

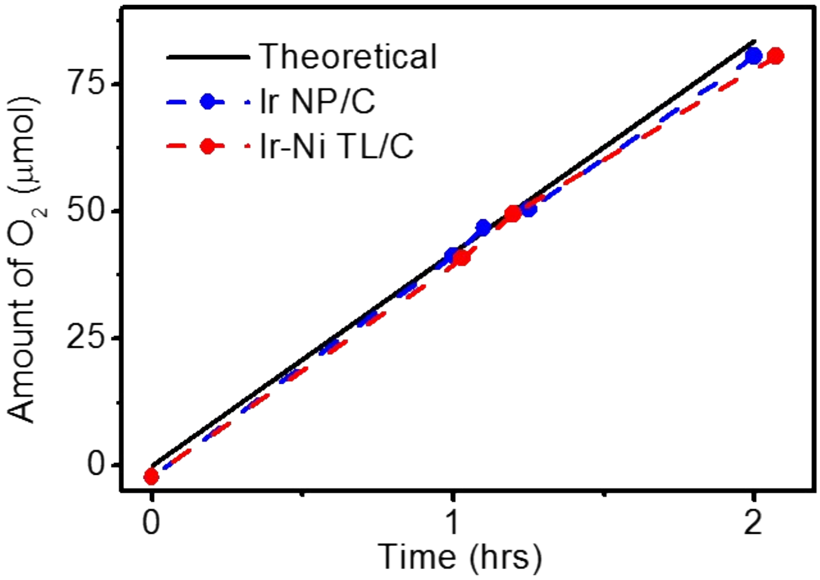

Figure S11. O_2 production expected assuming Faraday efficiency is 100% (solid line) and actual O_2 production directly measured by GC (dashed line) for Ir nanoparticles/C and Ir-Ni TL/C. Carbon paper was used as a working electrode instead of the glassy carbon RDE. The OER was performed by conducting chronopotentiometry at 4.5 mA in 0.05 M H_2SO_4 solution.

References

S1. H. N. Nong, H. S. Oh, T. Reier, E. Willinger, M. G. Willinger, V. Petkov, D. Teschner and P. Strasser, *Angew. Chem. Int. Edit.*, 2015, 54, 2975-2979.