Electronic Supplementary Information (ESI)

Core-Shell, Hollow-Structured Iridium–Nickel Nitride Nanoparticles for the Hydrogen Evolution Reaction

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Experimental Procedures

Synthesis. The carbon supported Iridium (Ir) and Nickel (Ni) electrocatalyst was prepared by mixing $(NH_4)_2IrCl_6$, $Ni(HCO_2)2H_2O$ salts with high area Vulcan XC72R carbon black to obtain a Ir:Ni molecular ratio of 1:3 respectively. The total metal content was around 20%. The mixture was dissolved in Millipore water and purged with Ar in an ultrasonic bath for an hour. The salts were then reduced by adding $NaBH_4$ while simultaneously purging the mixture with Ar. The mixture obtained was washed and rinsed with Millipore water, and then dried. The sample was annealed at 250°C in N_2 stream followed by NH_3 gas at 510°C for 2 hours in a tube furnace.

Catalyst inks of nanoparticles were prepared by mixing 5 mg of each catalysts with 5 mL of 18 MΩ water. The solution was ultrasonicated until a dark, uniform ink was achieved. Thin-film electrodes with nanoparticles were prepared by placing 15 µl of nanoparticle suspension onto a flat glassy carbon electrode (5 mm diameter, Pine Instrument). After drying in vacuum, the electrode was covered with 10 µl of a dilute Nafion solution (2 µg/5 µl) and dried again. All the potentials are given with respect to a reversible hydrogen electrode (RHE). A platinum wire

served as the counter electrode while Ag/AgCl reference electrode was used. The electrolytes were prepared from perchloric acid (Fisher) and MilliQ UV-plus water.

Characterization. XRD measurements were taken with a Phillips 3100 diffractometer using Cu Kα radiation (1.54056 Å). Samples for analysis were obtained by loading the slurries onto a glass slide, followed by drying them in air. The diffraction patterns were collected from 20° to 80° at a scanning rate of 0.6° per minute, with a step size of 0.02°.

In situ synchrotron XRD measurements were performed at the X7B beamline at NSLS to detail the formation of Ni nitride during annealing. The instrument parameters (Thompson-Cox-Hastings profile coefficients) were derived from the fit of a LaB_6 reference pattern. Approximately 5 mg of the carbon-supported $IrNi_3$ nanoparticles, which were reduced only by $NaBH_4$, were loaded in a 1 mm quartz reactor that was attached to a flow system, and annealed at 250°C in N_2 stream followed by NH_3 gas up to 510°C at a heating rate of 4.8 °C/min. A small resistance heater was wrapped around the reactor capillary, and the temperature was monitored with a thin chromel-alumel thermocouple placed inside the capillary near the sample. The wavelength of X-ray used was 0.3184 Å. XRD patterns were recorded on a Mar345 image plate detector during annealing; the recording time for a spectrum is *ca* 2.6 min. Details of the synchrotron XRD experiment were described earlier.[1, 2]

The as synthesized electrocatalyst were characterized by Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C) at the Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory (BNL). A 1.4Å electron probe with probe current ~50 pA was used in this study. The microscope was equipped with a cold field emission electron source with energy resolution 0.35 eV. The carbon supported nanoparticles

were dispersed in water and one drop of the slurry was deposited on a carbon covered copper grid (EMS, Hatfield, PA).

The study of HER on the carbon-supported IrNiN, Ir, Ni and Pt nanoparticles was carried out by means of slow potential sweeps (1 mV s^{-1}) in a 0.1 M $HClO_4$ solution at 2500 rpm. HER can be described using the Tafel equation, $\eta = a + b \log j + jR_s$, where η denotes the applied overpotential, j the current density, b the Tafel slope, a the intercept relative to the exchange current density j_0, and R_s (Ωcm^{-2}) the total area-specific uncompensated resistance of the system. The Tafel slope was calculated from the linear portion of the plot in the low overpotential region.

Supporting Figures

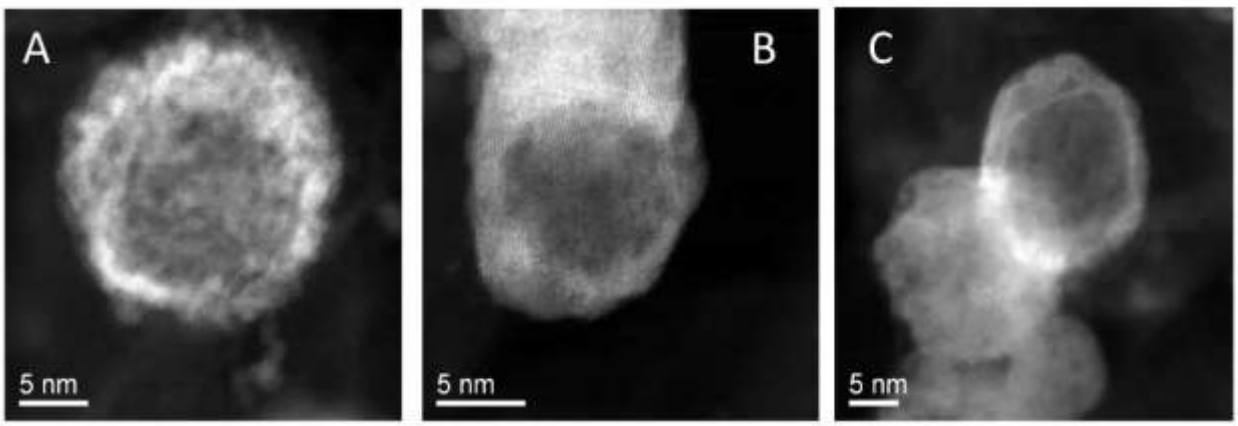

Fig. S1 HAADF-STEM images of hollow IrNiN nanoparticles.

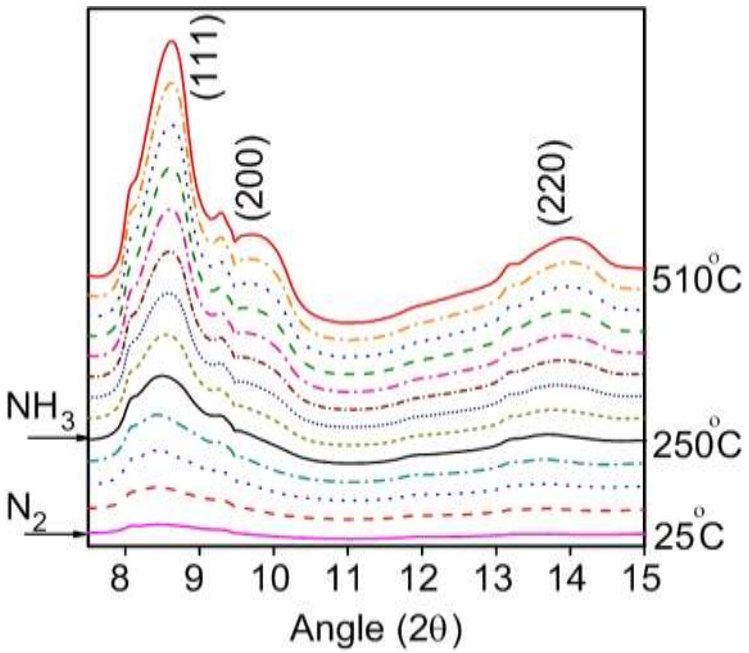

Fig. S2 *In situ* synchrotron XRD patterns (the wavelength: 0.3184 Å) obtained from the $IrNi_3$ nanoparticles during reduction in N_2 and NH_3 flow at increasing temperatures.

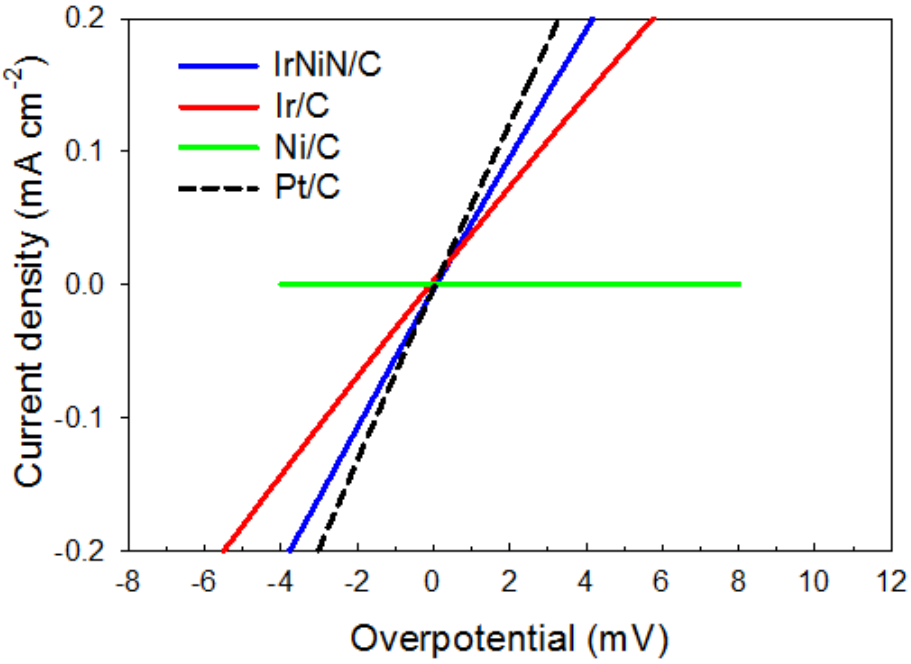

Fig. S3 The *i-η* plot at small *η* showing that the net current is linearly related to overpotential.

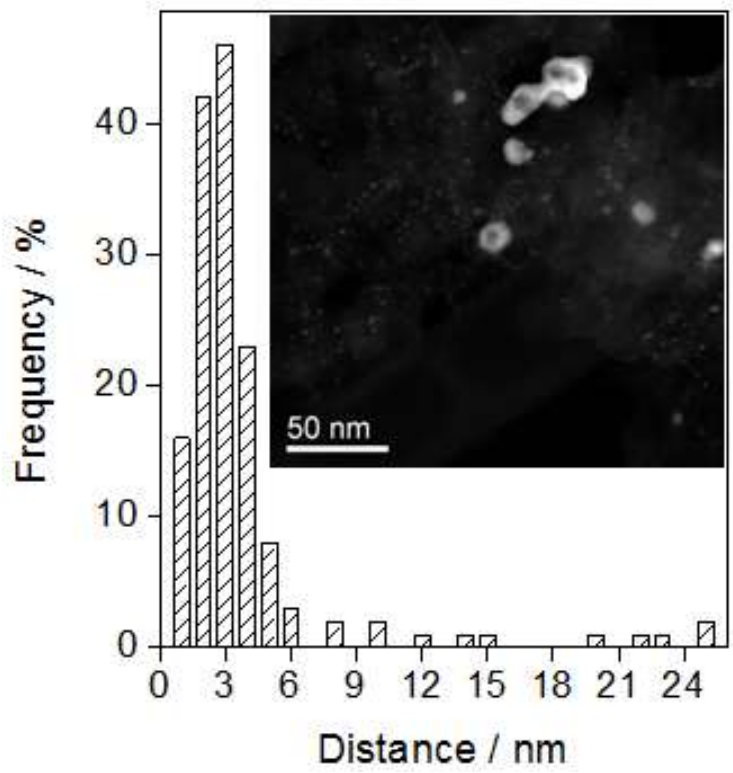

Fig. S4 Particle size distribution of IrNiN core-shell nanoparticles (sample size=150).

Catalyst	Specific mass activity @ η = 0.1V (mA cm^{-2} μg_{metal}^{-1})	Tafel slope (mV dec^{-1})	Exchange current density, j_0 (mA cm^{-2})
Pt/C	3.58[a]	30.4	0.784
IrNiN/C	2.96[b]	36.0	0.613
Ir/C	1.15[b]	59.0	0.452
Ni/C	0.0196[c]	168.3	3.52×10^{-4}

[a] based on per μg of Pt. [b] per μg of Ir. [c] per μg of Ni.

Table S1. HER specific mass activity, the Tafel slope and the exchange current density of various catalysts obtained in 0.1 M $HClO_4$.

References

1. J. A. Rodriguez, J. C. Hanson, W. Wen, X. Q. Wang, J. L. Brito, A. Martinez-Arias and M. Fernandez-Garcia, *Catal Today*, 2009, **145**, 188-194.
2. L. Barrio, A. Kubacka, G. Zhou, M. Estrella, A. Martinez-Arias, J. C. Hanson, M. Fernandez-Garcia and J. A. Rodriguez, *J Phys Chem C*, 2010, **114**, 12689-12697.