

Supplementary Information

Solvent evaporation plus hydrogen reduction method to synthesize IrNi/C catalysts for hydrogen oxidation

*Weiwei Zhang, Wei Ding, Siguo Chen, Li Li, Hongmin Wang and Zidong Wei **

The State Key Laboratory of Power Transmission Equipment & System Security and New
Technology, College of Chemistry and Chemical Engineering, Chongqing University, Chongqing,
400044, P. R. China.

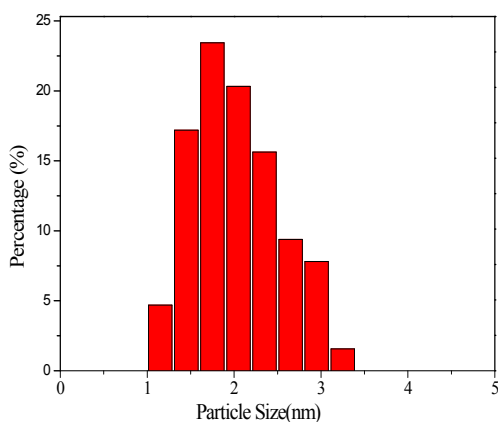


Fig. S1 Histogram of particle size distributions of the IrNi NPs.

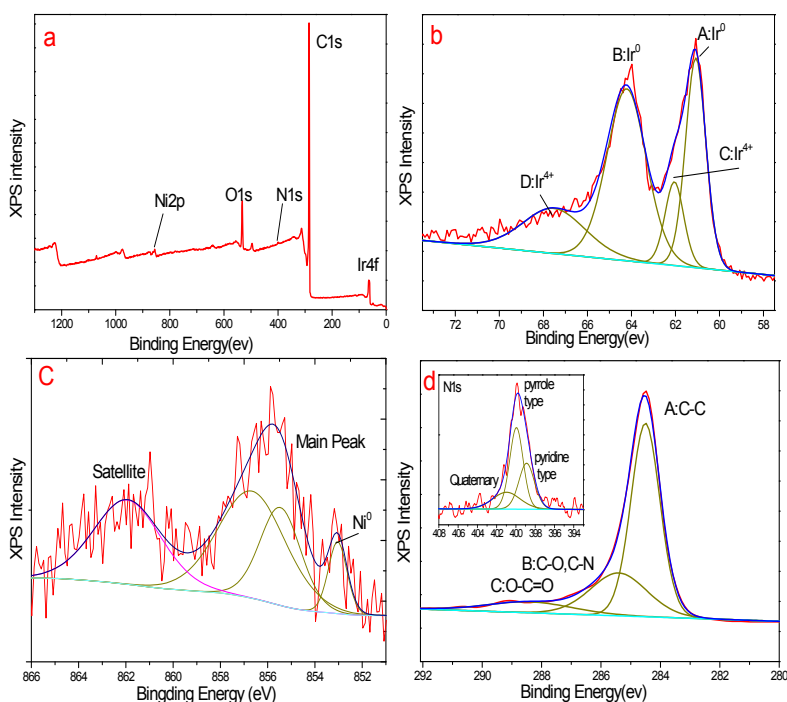


Fig. S2 XPS patterns for IrNi/C-NH₃-500. (a) full XPS spectrum. (b) Ir 4f spectrum. (c) Ni 2p spectrum. (d) C 1s spectrum and the inset is N 1s spectrum.

Fig. S2a gives the full XPS spectrum of the IrNi/C-NH₃-500. The surface atomic ratio of Ir/Ni is 2/1, fairly in line with the mol ratio in the bulk from the EDS data. Fig. S2b and S2c illustrate the XPS spectra for Ir 4f and Ni 2p core-level regions of the catalyst. Deconvolution of the Ir 4f region shows the presence of 2 pairs of doublets. The most intense doublet with binding energies of 61.08 (Ir 4f_{7/2}) and 64.22 eV (Ir 4f_{5/2}) is attributed to metallic Ir. Another doublet at 62.05 and 67.52 eV could be assigned to the Ir⁴⁺ in IrO₂. The XPS results suggest that 72% of the Ir is present in a metallic state and 28% is present in IrO₂. The Ni 2p_{3/2} spectra are characterized by a main peak (852-858eV) with a satellite at higher BE(860-865eV).^{1,2,3} Deconvolution of the main peak shows the presence of Ni⁰ and Ni^{x+}. Combining XPS spectra with the XRD results, it's verified that the contraction in

Ir-Ir bond is a consequence of Ni diffusing into the Ir cluster. The existence of oxidized Ni is attributed to surface-oxidation of the external surface Ni after long time ambient exposure. Fig. S2d gives the XPS spectra of C 1s and N 1s. C 1s spectrum shows three peak components at 284.5, 285.4 and 288.39 eV, which are assigned to the carbon component in C-C, C-O/C-N and O=C-O, respectively. As seen in the inset of Fig. S2d, the peaks at 398.9, 400, 401 eV of N can be attributed to pyridinic-like, quaternary and pyrrolic-like N, respectively, indicating the incorporation of N into the carbon support with a surface content of 0.63 at%.

Table S1 The structural parameters from XRD patterns and mass activities of the catalysts.

Catalyst	Ir(111) peak position(°)	d-spacing of 111(Å)	Lattice parameter a_{fcc} (Å)	Particle size (nm)	Mass activity ($A \cdot g_{IrNi}^{-1}$)
IrNi/C-NH ₃ -500	41.88	2.155	3.7325	2.7	453.4
IrNi/C-NaOH-500	42.10	2.142	3.7099	3.8	356.1
IrNi/C-500	42.51	2.124	3.6788	3.0	342.4
Ir/C-NH ₃ -500	40.66	2.218	3.8416	3.7	331.9
Ir ₂ Ni/C-NH ₃ -500	41.70	2.166	3.7515	2.6	407.5
IrNi ₂ /C-NH ₃ -500	42.69	2.116	3.6649	2.2	305.1
IrNi/C-NH ₃ -300	41.42	2.178	3.7723	1.3	366.4
IrNi/C-NH ₃ -400	41.62	2.170	3.7584	1.6	379.6
IrNi/C-NH ₃ -600	41.72	2.164	3.7480	4.8	283.1

References:

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- 3 M. V. Landau, M. Herskowitz, T. Hoffman, D. Fuks, E. Liverts, D. Vingurt and N. Froumin, *Ind. Eng. Chem. Res.*, 2009, **48**, 5239–5249.