

Supplementary Information

Ultra-highly active Ir-Ru-B/CeO₂ catalyst for hydrogen generation from hydrazine monohydrate

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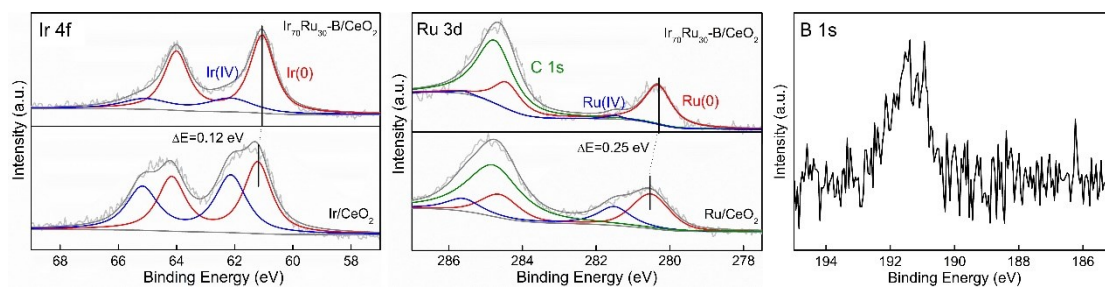


Figure S1. A comparison of XPS spectra of the $\text{Ir}_{70}\text{Ru}_{30}\text{-B/CeO}_2$ catalyst and the relevant Ir/CeO_2 and Ru/CeO_2 reference samples in the Ir 4f, Ru 3d and B 1s regions.

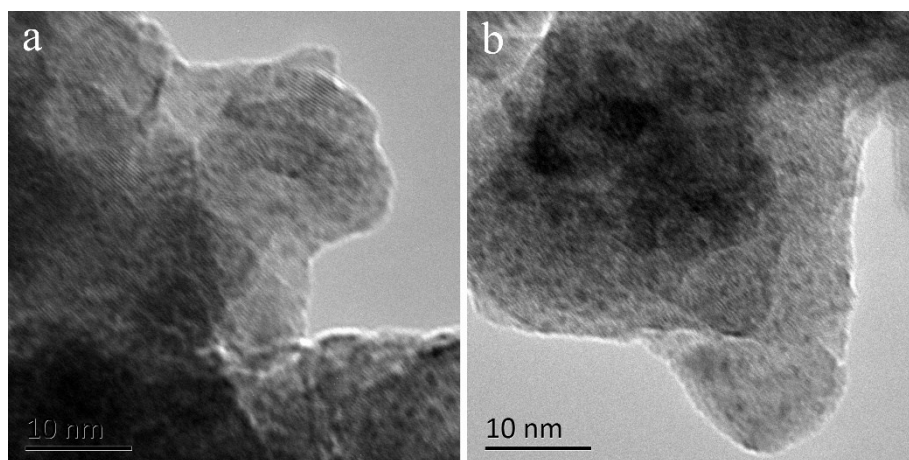


Figure S2. Representative TEM images of the $\text{Ir}_{70}\text{Ru}_{30}\text{-B/CeO}_2$ sample at different states: (a) as-prepared; (b) post-annealed at 600 °C.

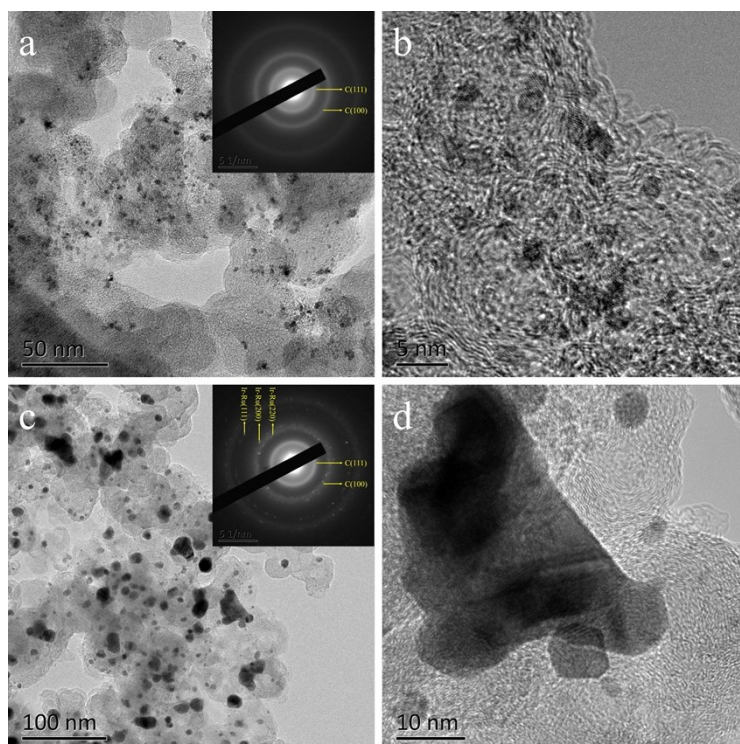


Figure S3. Representative TEM images of the Ir₇₀Ru₃₀-B/C sample at different states: (a, b) as-prepared; (c, d) post-annealed at 600 °C. The insets in (a) and (c) show the corresponding SAED patterns, respectively. The loading amount of metal was 30.0 wt% with a comparable loading density to that of Ir₇₀Ru₃₀-B/CeO₂ sample.

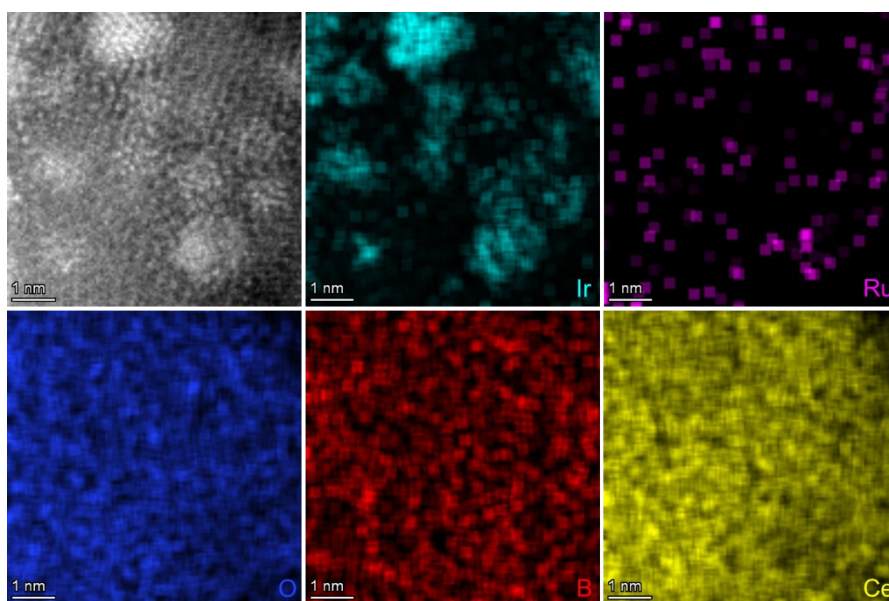


Figure S4. Atomic resolution HAADF-STEM image and corresponding EDS elemental mapping results of the as-prepared Ir₇₀Ru₃₀-B/CeO₂ catalyst.

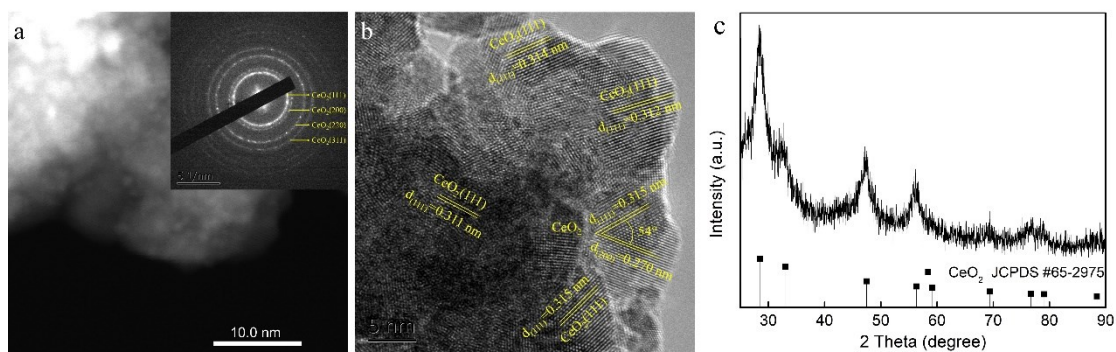


Figure S5. (a) HAADF-STEM image, (b) HRTEM image and (c) XRD pattern of the post-used Ir₇₀Ru₃₀-B/CeO₂ catalyst after ten cyclic usage. The inset in (a) shows the SAED pattern.

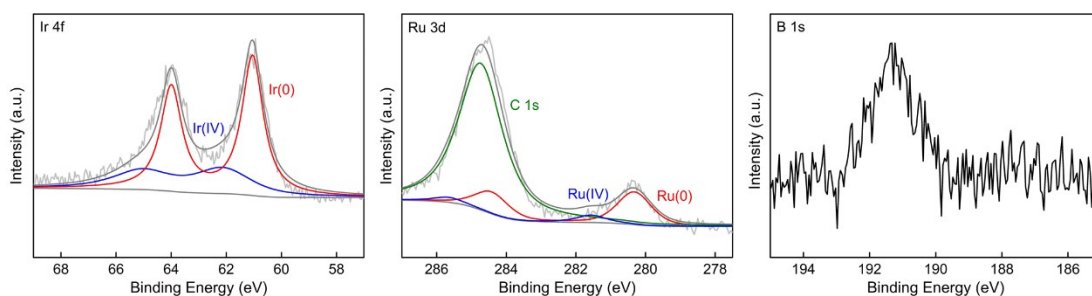


Figure S6. XPS spectra of post-used Ir₇₀Ru₃₀-B/CeO₂ catalyst after ten cyclic usage in the Ir 4f, Ru 3d and B 1s regions.

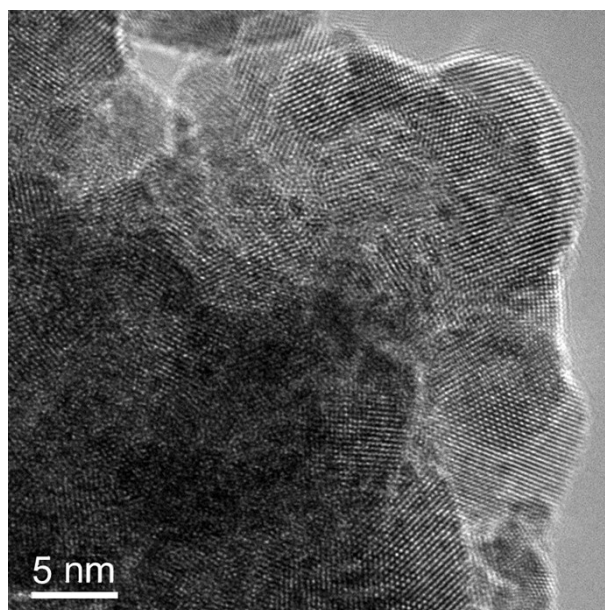


Figure S7. A representative TEM image of the Ir₇₀Ru₃₀/CeO₂ reference sample.

Table S1. A comparison of catalytic performance of the 600 °C-annealed Ir₇₀Ru₃₀-B/CeO₂ and representative N₂H₄·H₂O decomposition catalysts from open literatures.

Catalyst	Temperature (°C)	Reaction rate (h ⁻¹)	H ₂ selectivity (%)	NaOH concentration (M)	E _a (kJ mol ⁻¹)	Ref.
Rh _{0.8} Ni _{0.2} /MIL-101	50	428.6	100	0.5	49.8	1
Ni ₆₀ Pt ₄₀ /NC	50	1602	100	2.0	48.3	2
NiPt _{0.057} /Al ₂ O ₃	30	16.5	97	0	34.0	3
CoPt/La(OH) ₃	50	2400	100	3.5	45.2	4
Rh ₄₇ Ni ₁₈ P ₃₅ @MOF-74	50	715.4	100	2	49.39	5
Ni _{0.6} Pt _{0.4} /g-C ₃ N ₄	50	2194	100	0.75	35.9	6
Pt _{0.5} Ni _{0.5} /NGNs-850	50	2116	100	1	32.28	7
Rh ₅₈ Ni ₄₂ @MIL-101	50	344	100	0.5	33	8
NiFe/CeZrO ₂	70	119.2	100	2.5	50.4	9
Ni ₁₀ Mo/Ni-Mo-O	50	54.5	100	2	55	10
Ni-CeO ₂ @SiO ₂	70	219.5	100	2	59.26	11
Ni _{0.75} Ir _{0.25} /La ₂ O ₂ CO ₃	50	330	100	1.2	65.5	12
Ir ₇₀ Ru ₃₀ -B/CeO ₂	50	11510	86	2	41.2	This work

Table S2. Surface Ir/Ru atomic ratio of the Ir₇₀Ru₃₀-B/CeO₂ catalysts as determined by XPS analyses.

Sample	Ir/Ru ratio
Ir ₇₀ Ru ₃₀ -B/CeO ₂ (as-prepared)	2.58
Ir ₇₀ Ru ₃₀ -B/CeO ₂ (post-annealed at 600 °C)	2.60
Ir ₇₀ Ru ₃₀ -B/CeO ₂ (post-used)	2.63

References

1. Z. Zhang, S. Zhang, Q. Yao, G. Feng, M. Zhu, Z.H. Lu, Metal-organic framework immobilized RhNi alloy nanoparticles for complete H₂ evolution from hydrazine borane and hydrous hydrazine, *Inorg. Chem. Front.* 5(2018) 370–377.
2. Y.P. Qiu, Q. Shi, L.L. Zhou, M.H. Chen, C. Chen, P.P. Tang, G.S. Walker, P. Wang, NiPt nanoparticles anchored onto hierarchical nanoporous N-doped carbon as an efficient catalyst for hydrogen generation from hydrazine monohydrate, *ACS Appl. Mater. Interfaces* 12(2020) 18617–18624.
3. L. He, Y. Huang, A. Wang, Y. Liu, X. Liu, X. Chen, J.J. Delgado, X. Wang, T. Zhang, Surface modification of Ni/Al₂O₃ with Pt: highly efficient catalysts for H₂ generation via selective decomposition of hydrous hydrazine, *J. Catal.* 298(2013) 1–9.
4. K. Wang, Q. Yao, S. Qing, Z.H. Lu, La(OH)₃ nanosheet supported CoPt nanoparticles: a highly efficient and magnetically recyclable catalyst for hydrogen

- production from hydrazine in aqueous solution, *J. Mater. Chem. A* 7(2019) 9903–9911.
5. R. Jiang, X. Qu, F. Zeng, Q. Li, X. Zheng, Z. Xu, J. Peng, MOF-74-immobilized ternary Rh-Ni-P nanoparticles as highly efficient hydrous hydrazine dehydrogenation catalysts in alkaline solutions, *Int. J. Hydrogen Energy* 44(2019) 6383–6391.
 6. C. Wan, L. Sun, L. Xu, D.G. Cheng, F. Chen, X. Zhan, Y. Yang, Novel NiPt alloy nanoparticle decorated 2D layered g-C₃N₄ nanosheets: a highly efficient catalyst for hydrogen generation from hydrous hydrazine, *J. Mater. Chem. A* 7(2019) 8798–8804.
 7. A. Kumar, X. Yang, Q. Xu, Ultrafine bimetallic Pt-Ni nanoparticles immobilized on 3-dimensional N-doped graphene networks: a highly efficient catalyst for dehydrogenation of hydrous hydrazine, *J. Mater. Chem. A* 7(2019) 112–115.
 8. P. Zhao, N. Cao, W. Luo, G. Cheng, Nanoscale MIL-101 supported RhNi nanoparticles: an efficient catalyst for hydrogen generation from hydrous hydrazine, *J. Mater. Chem. A* 3(2015) 12468–12475.
 9. H. Zou, Q. Yao, M. Huang, M. Zhu, F. Zhang, Z. H. Lu, Noble-metal-free NiFe nanoparticles immobilized on nano CeZrO₂ solid solutions for highly efficient hydrogen production from hydrous hydrazine, *Sustain. Energy Fuels* 3(2019) 3071–3077.
 10. Y.P. Qiu, G.X. Cao, H. Wen, Q. Shi, H. Dai, P. Wang, High-capacity hydrogen generation from hydrazine monohydrate using a noble-metal-free Ni₁₀Mo/Ni-Mo-O nanocatalyst, *Int. J. Hydrogen Energy* 44(2019) 15110–15117.
 11. M.L. Huang, Q.L. Yao, G. Feng, H.T. Zou, Z.H. Lu, Nickel-ceria nanowires embedded in microporous silica: controllable synthesis, formation mechanism, and catalytic applications, *Inorg. Chem.* 59(2020) 5781–5790.
 12. X.L. Hong, Q.L. Yao, M.L. Huang, H.X. Du, Z.H. Lu, Bimetallic NiIr nanoparticles supported on lanthanum oxy-carbonate as highly efficient catalysts for hydrogen evolution from hydrazine borane and hydrazine, *Inorg. Chem. Front.* 6(2019) 2271–2278.