Supporting information

Engineering ultrafine PtIr alloy nanoparticles into porous nanobowls *via* a reactive template-engaged assembly strategy toward high-performance electrocatalytic hydrogen production

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Experimental section

Reagents and Chemicals. *N*, *N*′-methylenebisacrylamide (MBAA) was purchased from Alfa Aesar Co., Ltd. Hexachloroplatinic (IV) acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), iridous chloride ($IrCl_3$), formaldehyde (HCHO), and sulfuric acid (H_2SO_4) were obtained from Sinopharm Chemical Reagent Co., Ltd. Commercial Pt black catalyst was supplied by Johnson Matthey Corporation. All these reagents were of analytical reagent grade and used without further purification.

Preparation of Pt_7Ir nanobowls. For a typical synthesis of Pt_7Ir NBs, 50 mg of MBAA was initially dissolved into 7.0 mL of distilled water. Then, 0.75 mL of 0.05 M H_2PtCl_6 solution and 0.25 mL of 0.05 M $IrCl_3$ solution were successively added into the above solution under the constant stirring for 5 min. After that, 1.5 mL of HCHO solution was introduced to the mixed solution. After stirring for 10 min, the resultant solution was transferred into a 25 mL stainless-steel autoclave, which was heated to 100 °C in an oven and maintained for 4 h. After cooling down to room temperature, the obtained products were separated by centrifugation, further washed by ethanol aqueous solution (1:1) for several times, and then followed by freeze-drying. As a contrast, Pt_4Ir and Pt_2Ir samples were also prepared through the same synthetic condition except changing the feeding ratio of H_2PtCl_6 and $IrCl_3$ to 1:1 and 1:3, respectively.

Materials Characterization. The morphology of the samples was measured by the SEM (Hitachi S5500), TEM, HRTEM (JEOL JEM-2100F, 200 kV), and AC

HAADF-STEM (JEOL JEM-ARM 200F). XRD patterns were obtained on a Model D/max-rC X-ray diffractometer using Cu Kα radiation source (λ = 1.5406 Å). EDS spectra were performed on a scanning electron microscope of Hitachi S5500. XPS analyses were carried out on a Thermo VG Scientific ESCALAB 250 spectrometer with a monochromatic Al Kα X-ray source.

Electrochemical Measurements. All the electrochemical tests were carried out on a CHI 760E electrochemical workstation using a standard three-electrode system at room temperature. The detailed configuration of the three-electrode system is listed as follows. The catalyst-modified glassy carbon electrode, a platinum wire and a saturated calomel electrode were used as the working electrode, the auxiliary electrode, and the reference electrode, respectively. The catalyst ink was prepared by dispersing 2 mg of catalyst into 1 mL deionized water with the sonication treatment for 20 min. After that, 8 μL of the above suspension and 3 μL of Nafion solution (5 wt%) were dropped onto the surface of glassy carbon electrode. The HER measurement was conducted in N_2-saturated 0.5 M H_2SO_4 solution. The linear sweep voltammetry (LSV) curves were performed at a sweep rate of 5 mV s^{-1}.

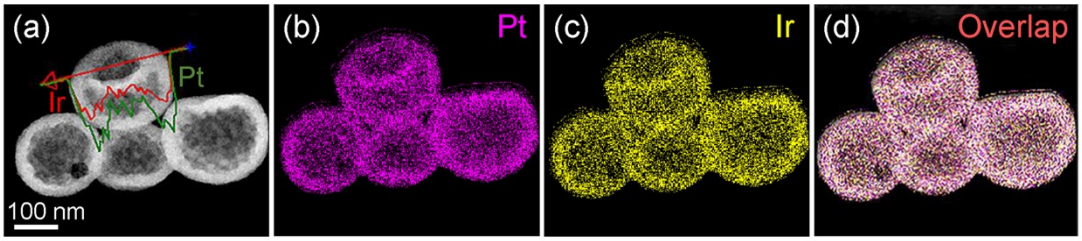

Fig. S1. (a) EDX line scanning profiles and (b-d) elemental mapping images of Pt_7Ir NBs.

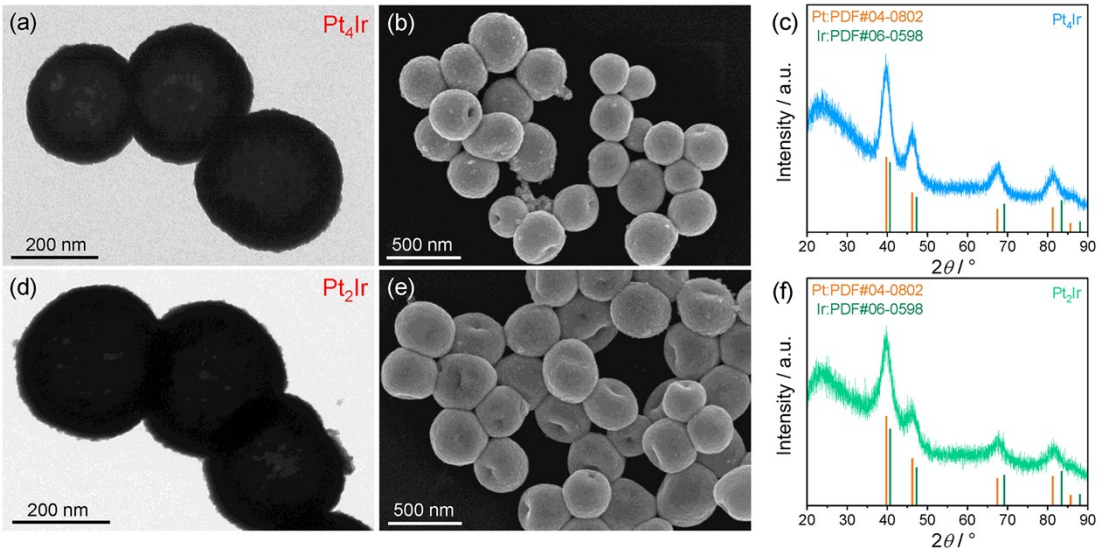

Fig. S2. TEM images, SEM images and XRD patterns of (a-c) Pt_4Ir NBs and (d-f) Pt_2Ir NBs.

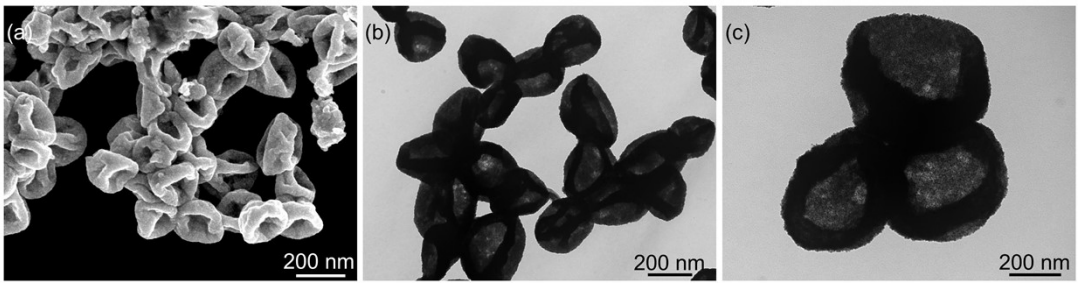

Fig. S3 SEM (a) and TEM (b-c) images of pure Pt nanobowls.

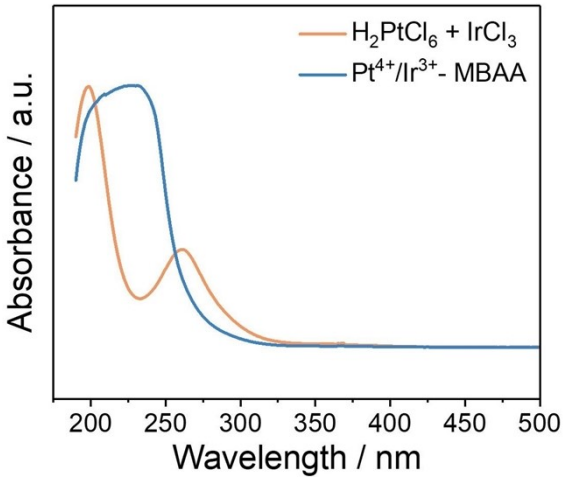

Fig. S4 UV/Vis absorption spectra of H_2PtCl_6 + $IrCl_3$ solution, and the mixture solution of H_2PtCl_6, $IrCl_3$ and MBAA.

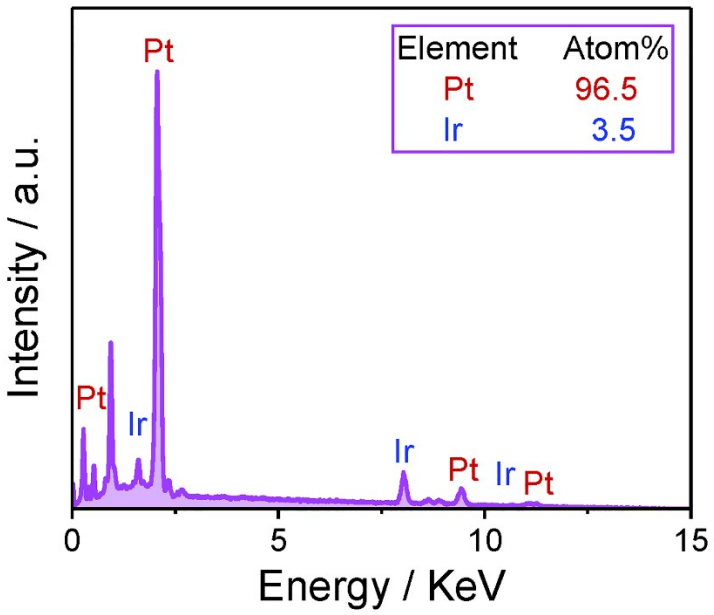

Fig. S5. EDS spectrum of the intermediate sample harvested at 30 min.

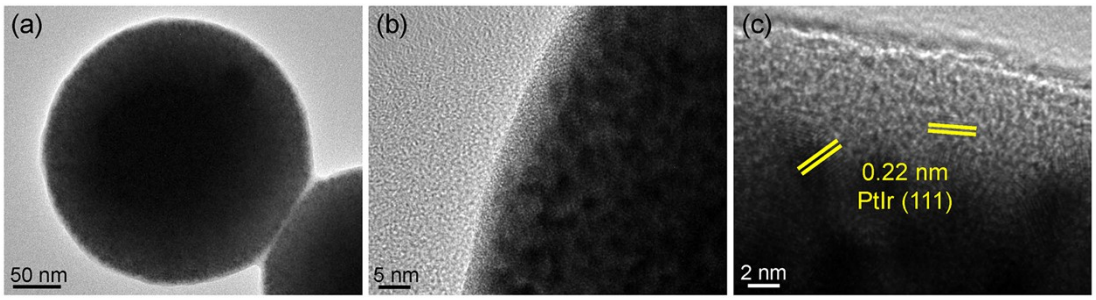

Fig. S6. TEM and HRTEM images of the intermediate sample collected at 1 h.

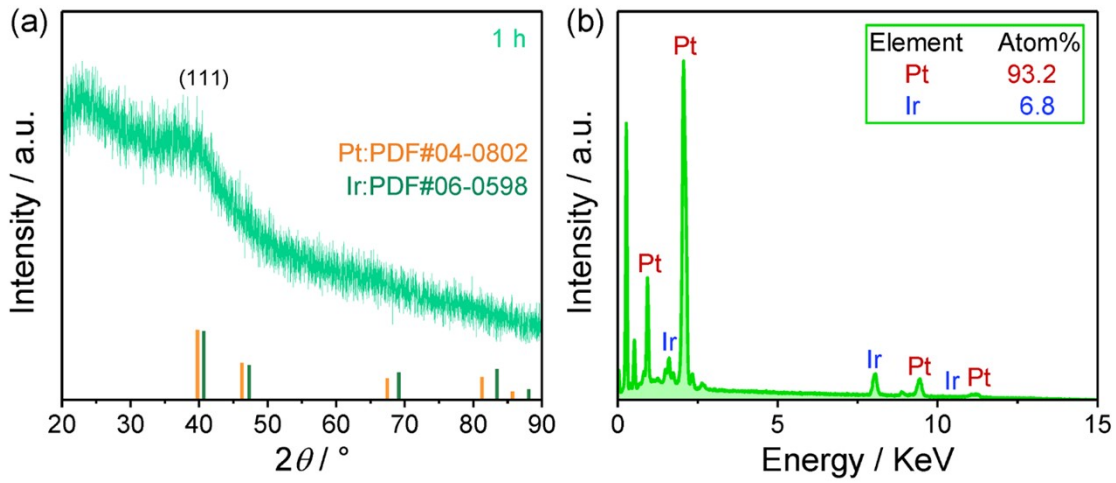

Fig. S7. (a) XRD pattern and (b) EDS spectrum of the intermediate sample obtained at 1 h.

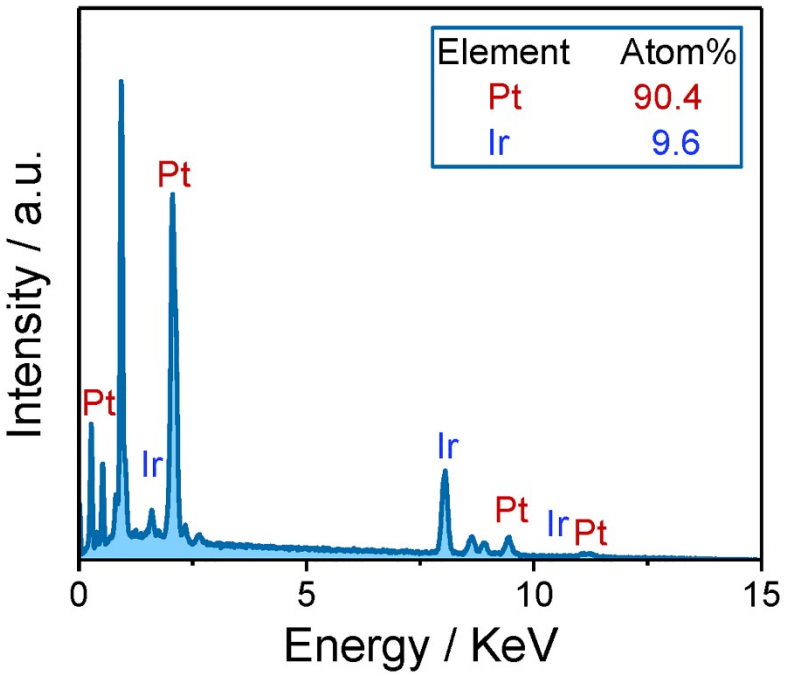

Fig. S8 EDS spectrum of the intermediate product obtained at 2 h.

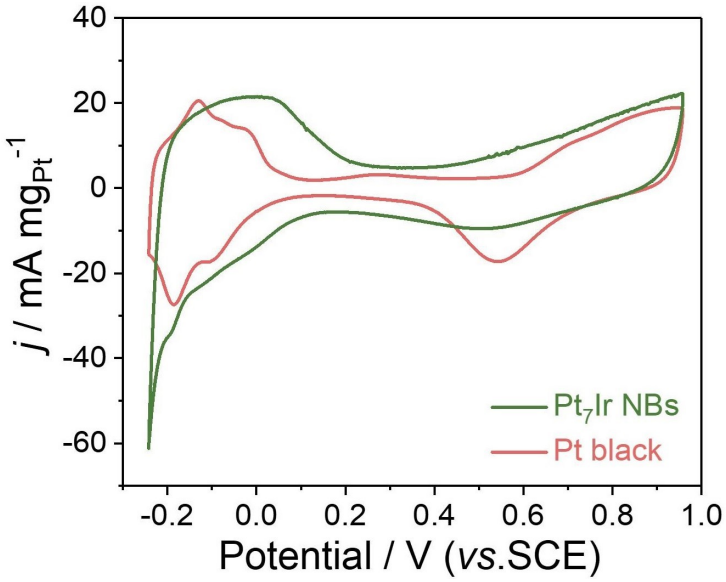

Fig. S9 CVs of Pt_7Ir NBs and Pt black in H_2SO_4 solution.

Table S1. HER activity comparisons of Pt_7Ir NBs with previously reported catalysts.

Sample	η_{10} (mV)	Tafel slope (mV dec^{-1})	Reference
Pt_7Ir NBs	20	12.5	This work
np-$Pd_{50}Ir_{50}$	21	24	*J. Mater. Chem. A*. 2023, 11, 11526
PtW_6O_{24}/C	22	29.8	*Nat Commun*. 2020, 11, 490
Pd/Cu-Pt NRs	22.8	25	*Angew. Chem. Int. Ed*. 2017, 56, 16047
Pt_2Pd_1 NC	25	32	*ACS Appl. Energy Mater*. 2020, 3, 11142
IrNi NFs	25	29.7	*Small Methods*. 2020, 4, 1900129
Pt_2Sr/NC	27	26	*J Energy Chem.* 2022, 64, 315
PtSb NPs	27	50.45	*J. Colloid Interface Sci.* 2021, 584, 729
PtCu DNFs	27	34	*ACS Appl. Energy Mater.* 2018, 1, 5054
PdCuIr/C	27	NA	*Angew. Chem. Int. Ed.* 2021, 60, 8243
PtAg NCs	36	40	*J. Colloid Interface Sci.* 2017, 494, 15
Ir-Au-Si-2	38.2	24	*ChemCatChem.* 2019, 11, 2126
PtCu/WO_3@CF	41	45.9	*Adv. Funct. Mater*. 2022, 32, 2112207
H-AgPt NCs	51	40	*J. Colloid Interface Sci.* 2017, 505, 307

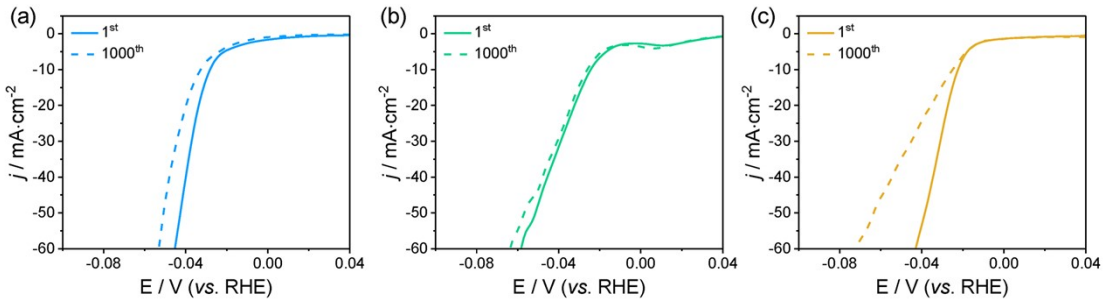

Fig. S10. LSV curves before and after 1000 cycles of (a) Pt_4Ir NBs, (b) Pt_2Ir NBs and (c) Pt black.

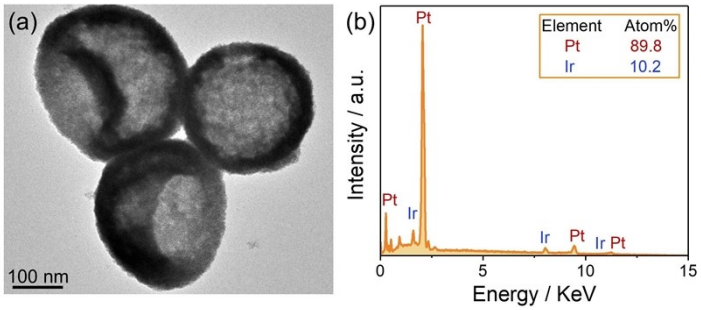

Fig. S11. (a) TEM image and (b) EDS spectrum of Pt_7Ir NBs after 1000 cycles.