Electronic Supplementary Information for

Anodic hydrazine oxidation assisted hydrogen evolution over bimetallic RhIr mesoporous nanospheres

Mei Zhang, Ziqiang Wang*, Zhongyao Duan, Shengqi Wang, You Xu, Xiaonian Li,

Liang Wang* and Hongjing Wang*

State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

*Corresponding authors: Ziqiang Wang; Liang Wang; Hongjing Wang

E-mails: zqwang@zjut.edu.cn; wangliang@zjut.edu.cn; hjw@zjut.edu.cn

Electrochemical measurements: The electrochemical experiments were performed in a standard three-electrode system. Graphite rod and Hg/HgO electrode were used as the counter electrode and reference electrode in alkaline solution, respectively. For the fabrication of working electrodes, catalysts (2 mg) was dispersed in 1 mL of mixed solution containing 800 μL isopropanol, 200 μL H_2O to form a homogeneous catalyst ink. After sonication for 1 h, 5 μL of catalyst inks were loaded onto a glassy carbon electrode (GCE) with 3 mm in diameter and dried at room temperature, further coating 3 μL of Nafion (0.5 wt %). The electrochemical tests for the overall hydrazine electrolysis were performed in 1.0 M KOH as the cathode electrolyte and 1.0 M KOH/0.5 M N_2H_4 as the anode electrolyte. Before electrocatalytic experiments, the electrolyte was bubbled by N_2 gas for 30 min. The polarization curves were recorded by linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} with *iR* compensation. For *iR* compensation, the uncompensated ohmic resistance value for each electrode in the electrolyte solution was measured. The potential was based on *iR* correction using the equation: $E(iR\text{-corrected}) = E–iR$, where i is the current and R is the uncompensated electrolyte ohmic resistance measured by electrochemical impedance spectroscopy. All potentials were recorded with respect to RHE. The double layer capacitance (C_{dl}) was acquired from the cyclic voltammetry (CV) at different scan rates from 20 to 120 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) investigations were recorded in the frequency range from 100 kHz to 0.1 Hz at -0.8 V. Faradaic efficiency (FE) for the HER was determined using $FE = n/(Q/2F)$,[1] where F is the Faraday constant, n is the total amount of H_2, and Q is the total amount of charge obtained by the *i–t* curve at voltage of 0.6 V.

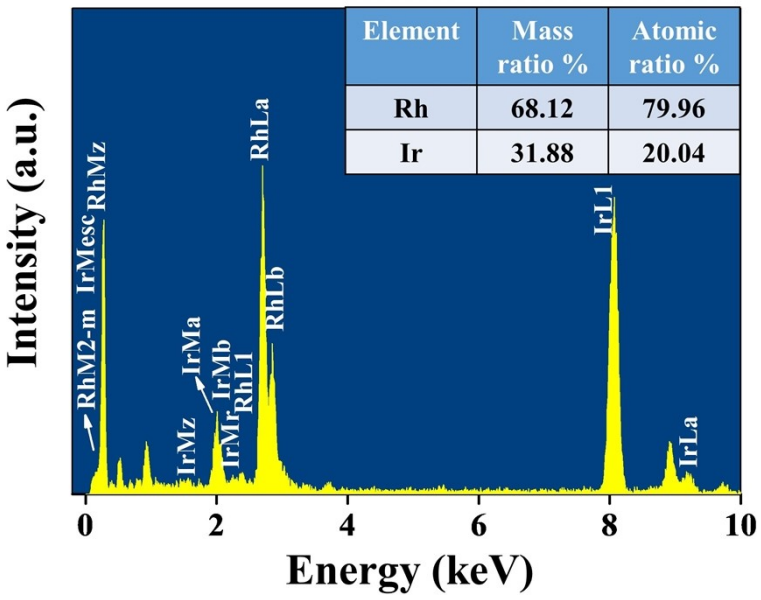

Fig. S1 EDX spectrum of RhIr MNs.

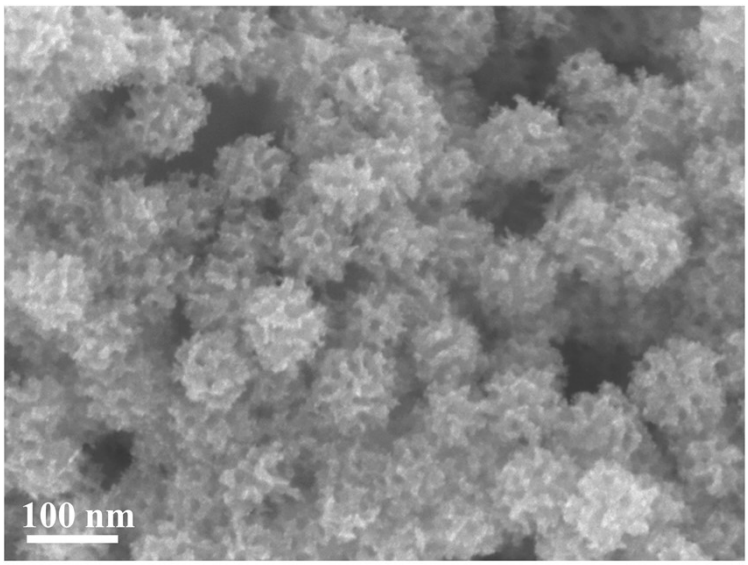

Fig. S2 SEM image of Rh MNs.

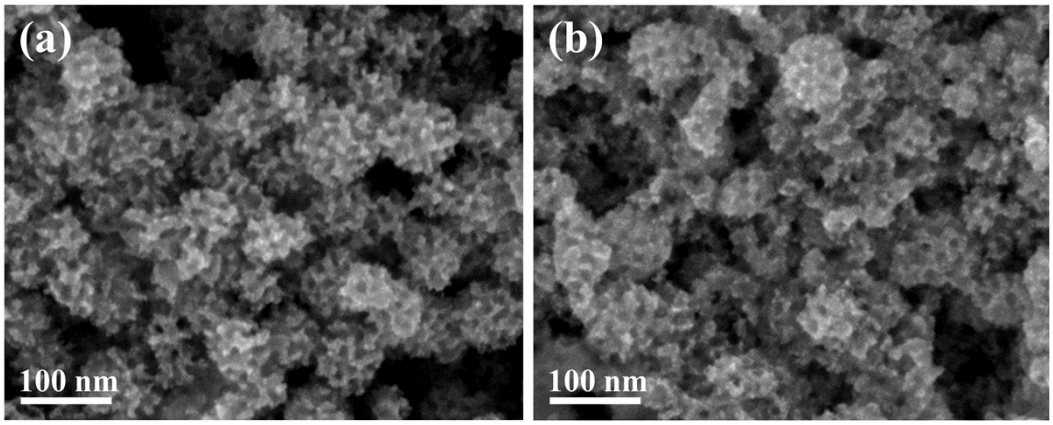

Fig. S3 SEM images for the samples with different precursor solutions: (a) K_3RhCl_6 : $IrCl_3$ = 3:1 and (b) K_3RhCl_6 : $IrCl_3$ = 1:3.

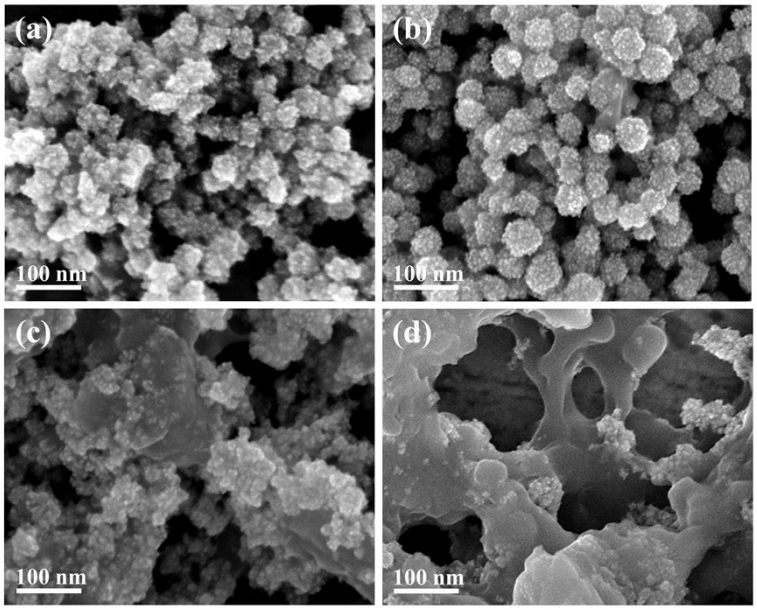

Fig. S4 SEM images of the samples obtained from different surfactants: (a) F127, (b) Brij 58, (c) CTAC, and (d) PVP.

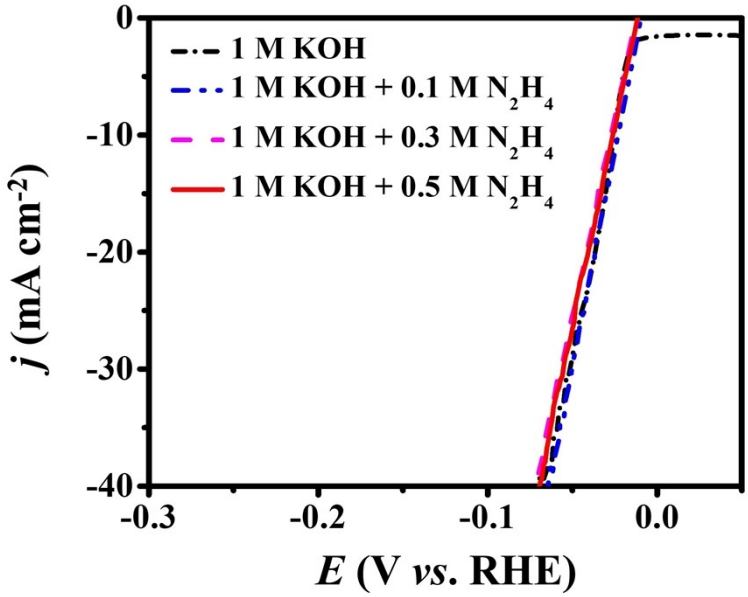

Fig. S5 HER polarization curves of RhIr MNs in 1.0 M KOH with different concentrations of N_2H_4.

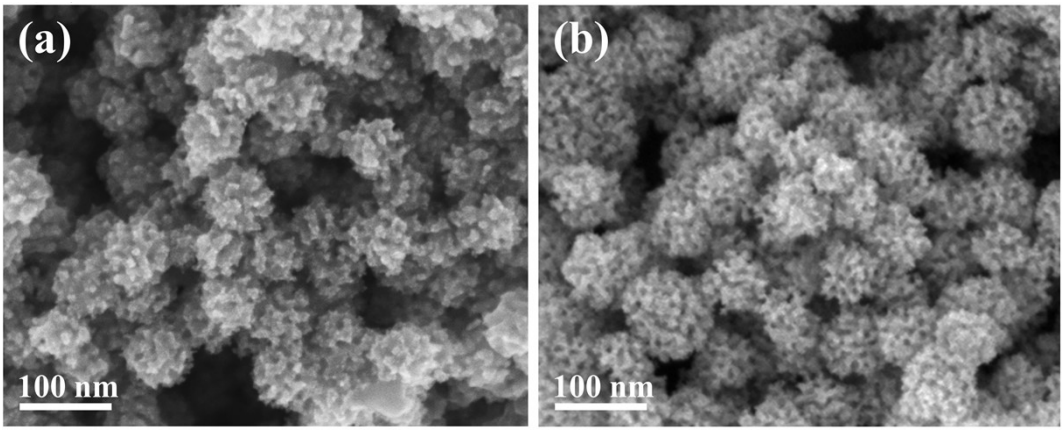

Fig. S6 SEM images of RhIr MNs after durability tests in (a) 1.0 M KOH and (b) 1.0 M KOH/0.5 M N_2H_4.

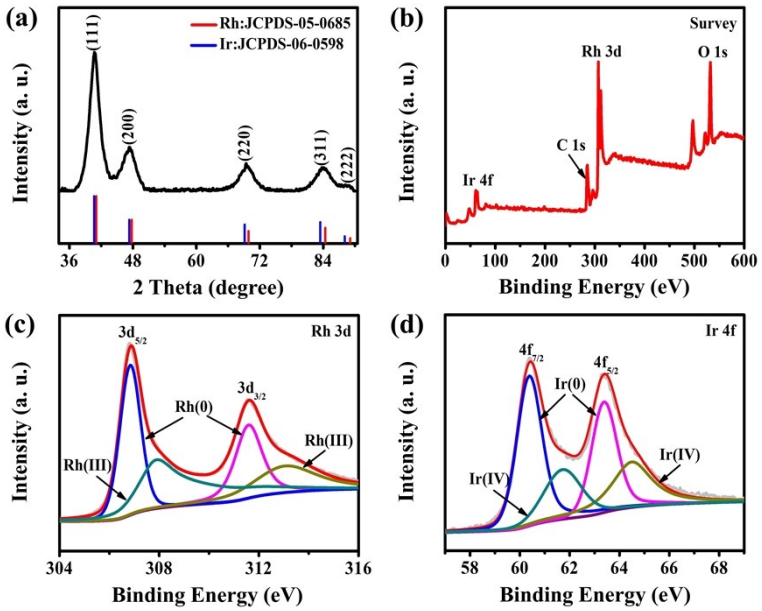

Fig. S7 Characterizations of post-HER RhIr MNs after durability test in 1.0 M KOH. (a) XRD pattern, (b) XPS survey spectrum, and high-solution XPS spectrum of (c) Rh 3d and (d) Ir 4f.

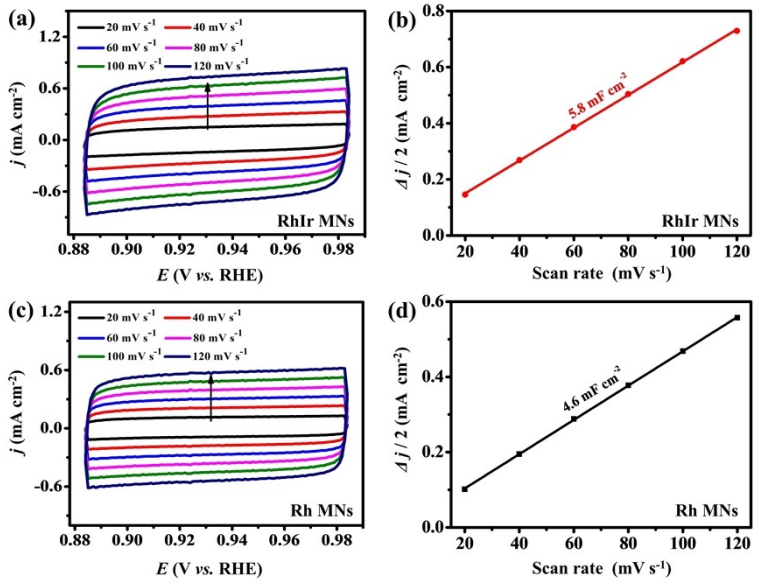

Fig. S8 CV curves of (a) RhIr MNs and (c) Rh MNs at various scan rates from 0.884 to 0.984 V (*vs.* RHE) and capacitive current densities of (b) RhIr MNs and (d) Rh MNs in 1.0 M KOH solution.

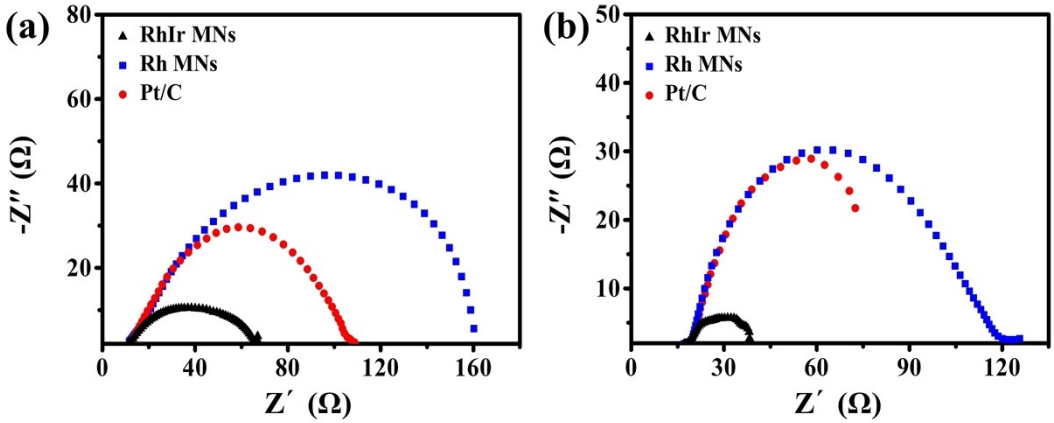

Fig. S9 EIS spectra of various catalysts for (a) HER in 1.0 M KOH at -0.02 V (*vs*. RHE) and (b) HzOR in 1.0 M KOH/0.5 M N_2H_4 at 0.05 V (*vs*. RHE).

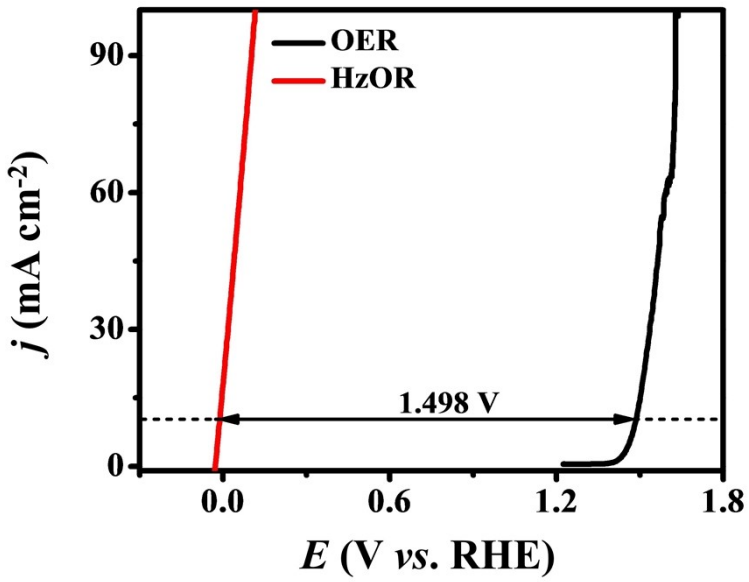

Fig. S10 Polarization curves of RhIr MNs for OER in 1.0 M KOH and HzOR in 1.0 M KOH/0.5 M N_2H_4.

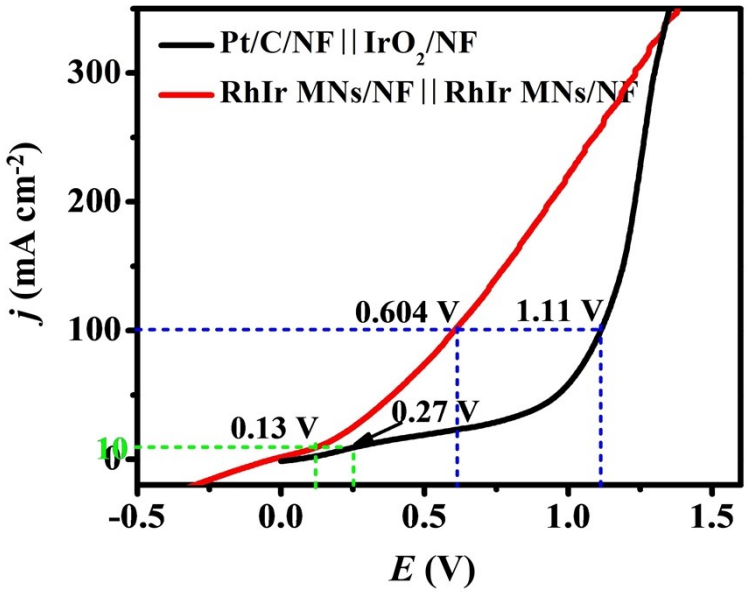

Fig. S11 Polarization curves for RhIr MNs/NF‖RhIr MNs/NF and Pt/C/NF‖IrO_2/NF in overall hydrazine electrolysis.

Table S1. HER performance comparison between RhIr MNs and other reported electrocatalysts.

Electrocatalysts	Electrolytes	Overpotential (mV) at 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Ref.
RhIr MNs	**1 M KOH**	**20**	**30.7**	**This work**
$CoSe_2/MoSe_2$	1 M KOH	168	106.4	1
RhCo-ANAs	1 M KOH	32.4	31.9	2
RhCoB	1 M KOH	43	32.1	3
Rh/Rh_2P-NFAs.	1 M KOH	19.5	50	4
$Rh\text{-}Rh_2P@C$	1 M KOH	37	32	5
w-Rh_2P NS/C	1 M KOH	18.3	61.5	6
$RhP_x@NPC$	1 M KOH	69	80	7
Rh_2P	1 M KOH	30	50	8
Rh NSs	1 M KOH	43	107	9
Rh/N-CBs	1 M KOH	77	74.16	10
$Ru\text{-}Ru_2P@NPC$	1 M KOH	46	39.75	11
$Ni_3N\text{-}Co_3N$	1 M KOH	43	35.1	12
PW-Co_3N	1 M KOH	41	40	13
Rh_2S_3/NC	1 M KOH	38	41	14
Ni NCNA	1 M KOH	47	41	15

Table S2. HzOR performance comparison between RhIr MNs and other reported electrocatalysts.

Electrocatalysts	Electrolytes	Potential (V) at 10 mA cm^{-2}	Tafel slope ($mV\ dec^{-1}$)	Ref.
RhIr MNs	**1.0 M KOH+ 0.5 M hydrazine**	**-0.012**	**30**	**This work**
$CoSe_2/MoSe_2$	1.0 M KOH+ 0.5 M hydrazine	-	142	1
Ni_3N-Co_3N	1.0 M KOH+ 0.5 M hydrazine	−0.088	−	12
PW-Co_3N	1.0 M KOH+ 0.1 M hydrazine	−0.055	−	13
Rh_2S_3/NC	1.0 M KOH+ 0.1 M hydrazine	0.095	46	14
Ni NCNA	1.0 M KOH+ 0.3 M hydrazine	−0.026	32.6	15
Cu_1Ni_2-N	1.0 M KOH+ 0.5 M hydrazine	0.5	44.1	16
Ni (Cu)@NiFeP /NM	1.0 M KOH+ 0.5 M hydrazine	~0.117	147	17
$CoSe_2$	1.0 M KOH+ 0.5 M hydrazine	−0.017	−	18
Ni_2P	1.0 M KOH+ 0.5 M hydrazine	~−0.065	55	19
$NiFe(OH)_2$-SD/NF	1.0 M KOH+ 0.5 M hydrazine	0.06	62	20

Table S3. The overall hydrazine splitting performance comparison between RhIr MNs and other reported electrocatalysts.

Electrocatalysts	Electrolytes	substrate	Voltage (V) at 10 mA cm^{-2}	Ref.
RhIr MNs	**1.0 M KOH+ 0.5 M hydrazine**	**NF**	**0.13**	**This work**
$CoSe_2/MoSe_2$	1.0 M KOH+ 0.5 M hydrazine	CC	0.85	1
Ni_3N-Co_3N	1.0 M KOH+ 0.5 M hydrazine	NF	0.071	12
PW-Co_3N	1.0 M KOH+ 0.1 M hydrazine	NF	0.025	13
Rh_2S_3/NC	1.0 M KOH+ 0.5 M hydrazine	CP	0.108	14
Ni NCNA	1.0 M KOH+ 0.3 M hydrazine	NF	0.023	15
Cu_1Ni_2-N	1.0 M KOH+ 0.5 M hydrazine	CC	0.24	16
Ni(Cu)@NiFeP /NM	1.0 M KOH+ 0.5 M hydrazine	NF	0.147	17
$CoSe_2$	1.0 M KOH+ 0.5 M hydrazine	NF	0.164	18
Ni_2P	1.0 M KOH+ 0.5 M hydrazine	NF	~0.12	19

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