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Supplementary Information

Reduction tuning of ultrathin carbon shell armour covering IrP_2 for accelerated hydrogen evolution kinetics with Pt-like performance

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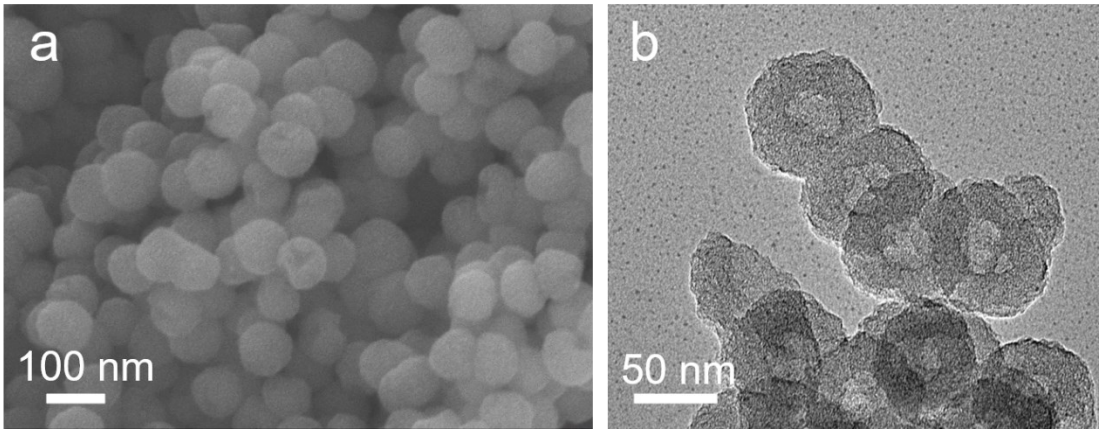

Fig. S1 (a) SEM and (b) TEM image of NC.

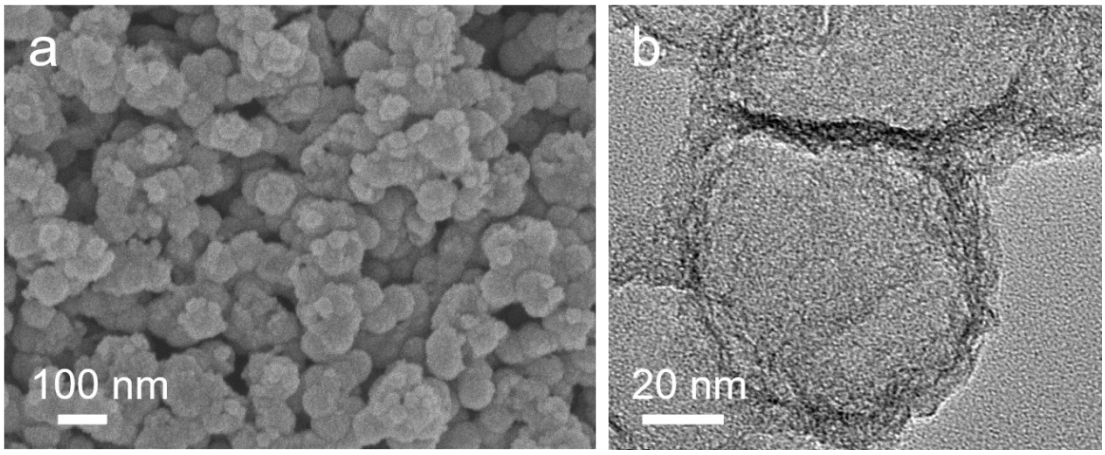

Fig. S2 (a) SEM and (b) TEM image of NPC.

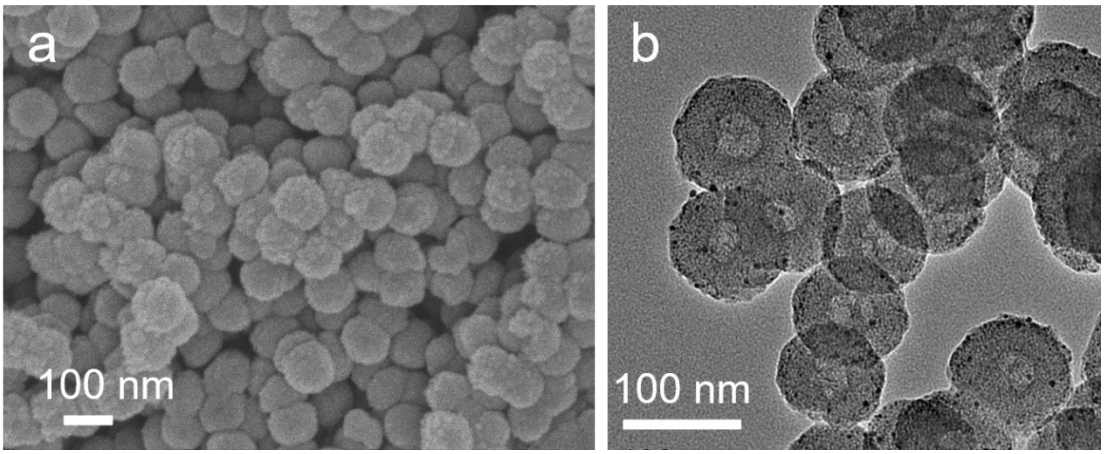

Fig. S3 (a) SEM and (b) TEM image of Ir@NC.

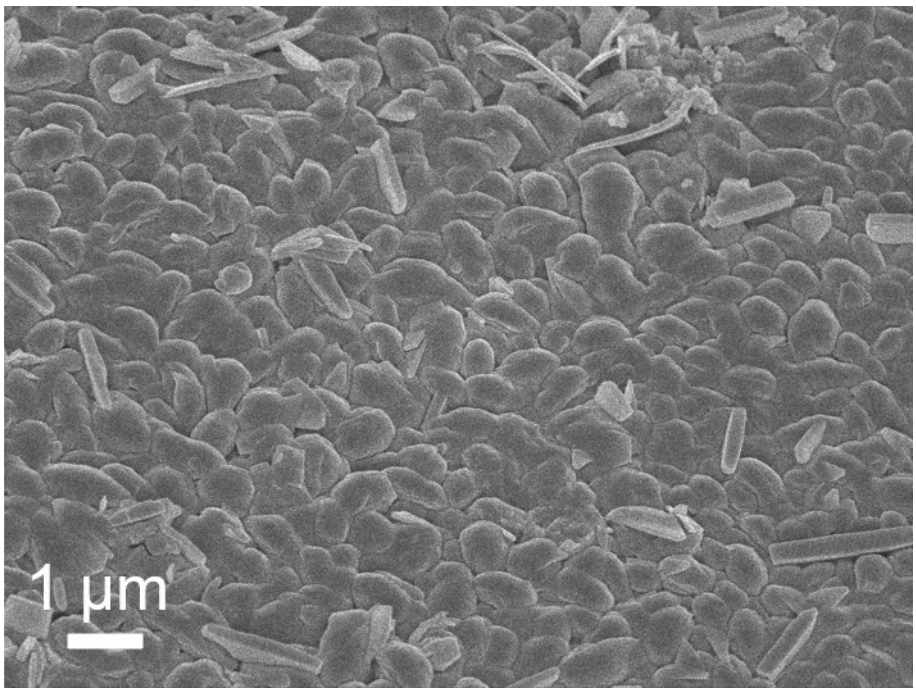

Fig. S4 SEM image of IrP_2 NPs.

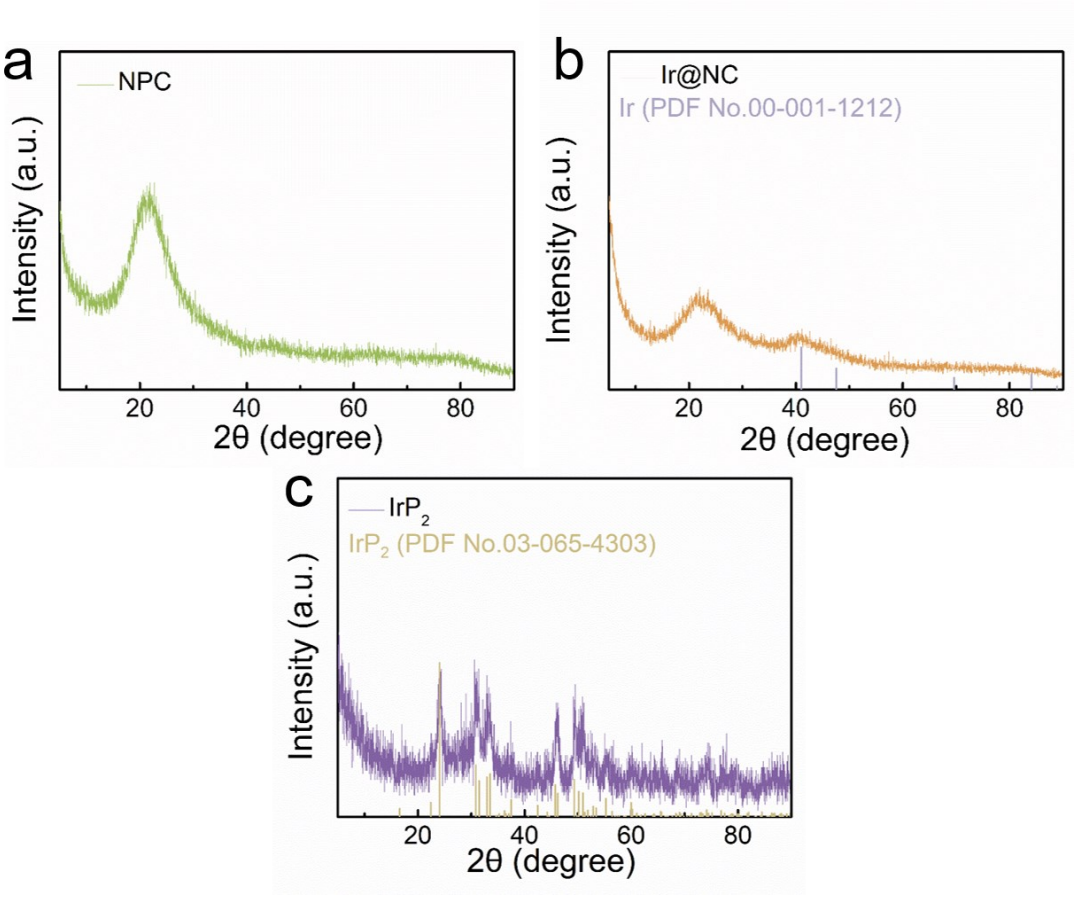

Fig. S5 XRD patterns of (a) NPC, (b) Ir@NC, and (c) IrP_2 NPs.

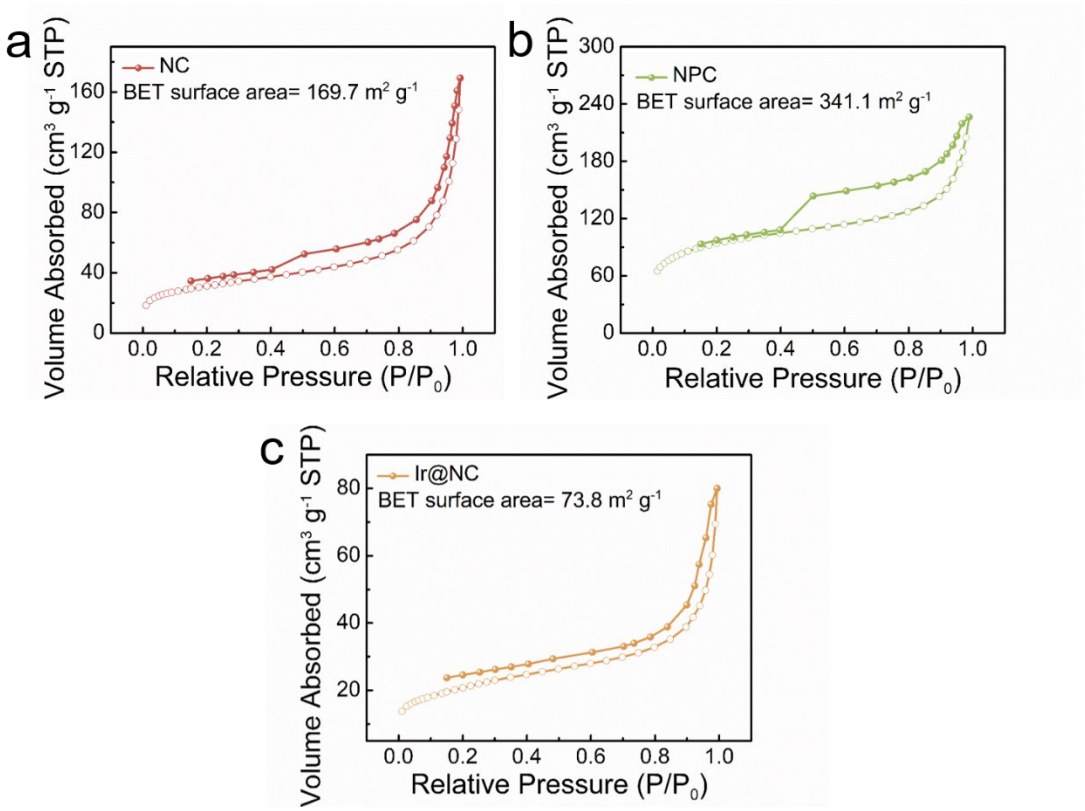

Fig. S6 N_2 sorption isotherm and pore size distribution of (a) NC, (b) NPC, and (c) Ir@NC.

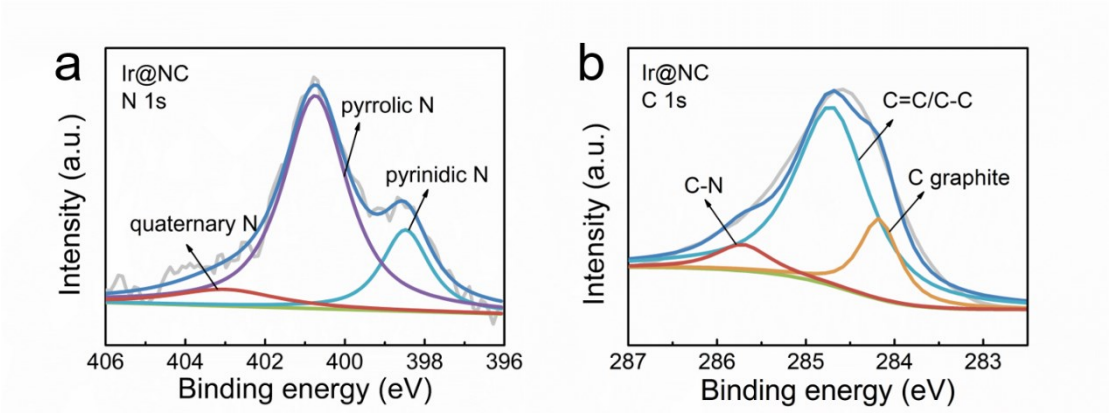

Fig. S7 (a) N 1s and (b) C 1s XPS spectrum of Ir@NC.

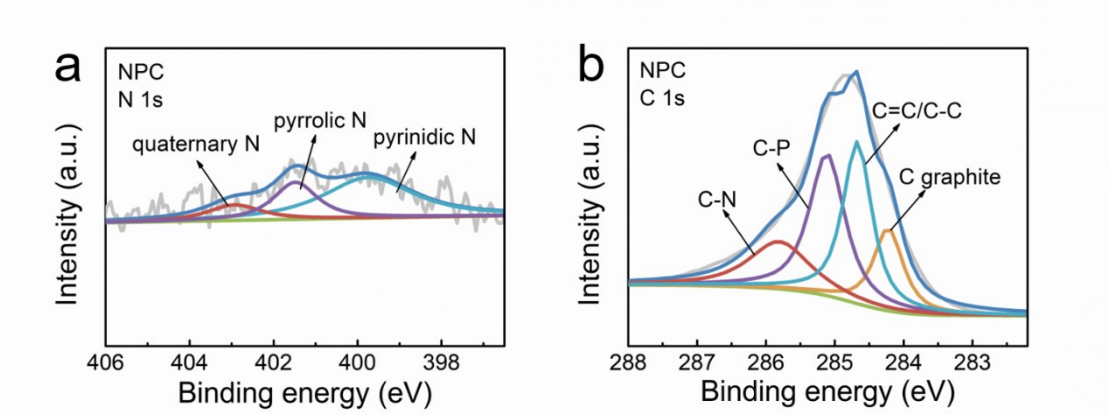

Fig. S8 (a) N 1s and (b) C 1s XPS spectrum of NPC.

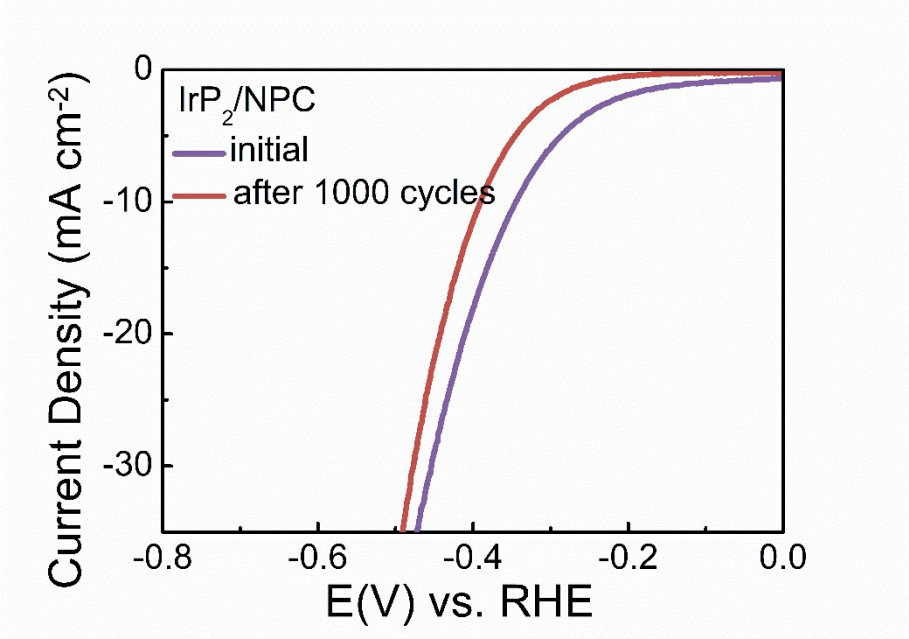

Fig. S9 HER polarization curves of IrP_2/NPC before and after 1000 CV cycles from -0.2 to 0.1 V (vs. RHE) in 0.5 M H_2SO_4.

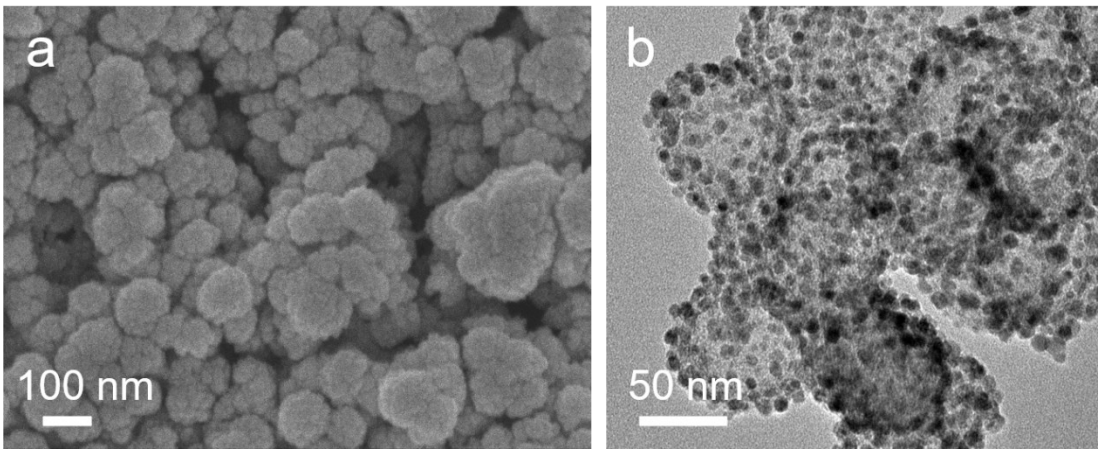

Fig. S10 (a) SEM and (b) TEM images of IrP_2@NPC after stability test in 0.5 M H_2SO_4.

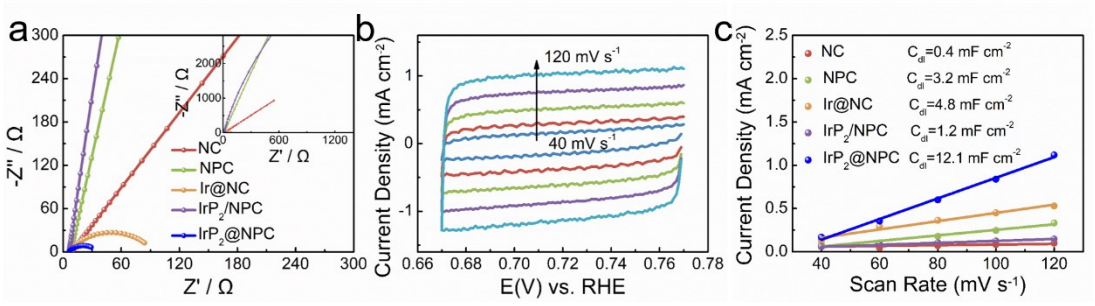

Fig. S11 (a) Nyquist plots of NC, NPC, Ir@NC, IrP_2/NPC, and IrP_2@NPC nanoshells. (b) CV scans of double-layer capacitance measurement of IrP_2@NPC nanoshells at different scanning rates in 1.0 M KOH. (c) Double-layer capacitances of these catalysts.

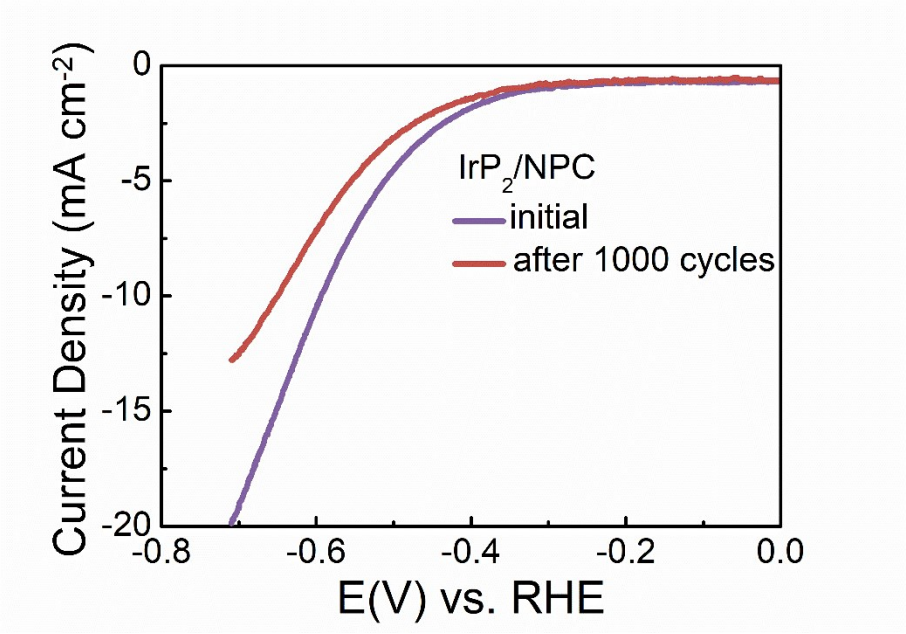

Fig. S12 HER polarization curves of IrP_2/NPC before and after 1000 CV cycles from -0.2 to 0.1 V (vs. RHE) in 1.0 M KOH.

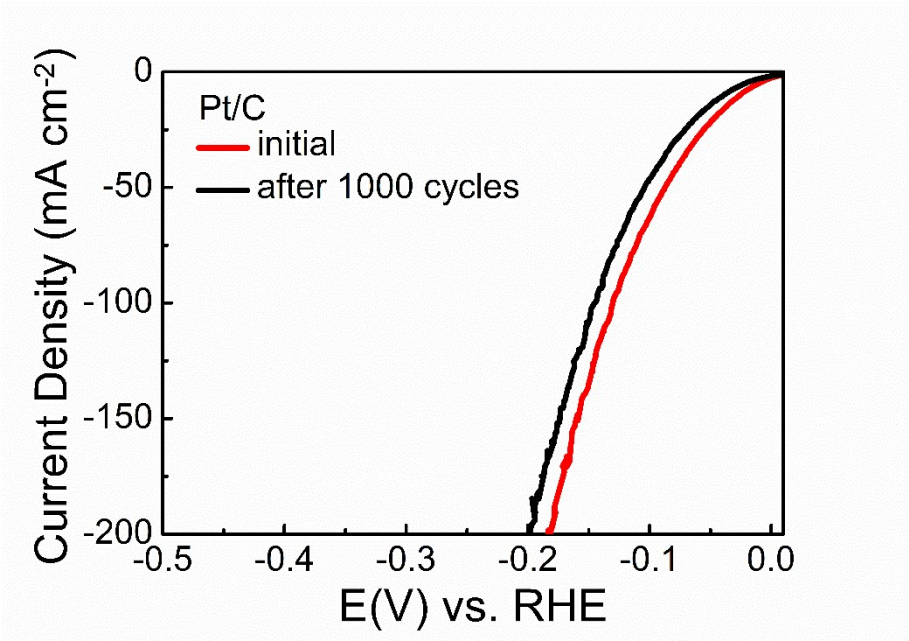

Fig. S13 HER polarization curves of Pt/C before and after 1000 CV cycles from -0.2 to 0.1 V (vs. RHE) in 1.0 M KOH.

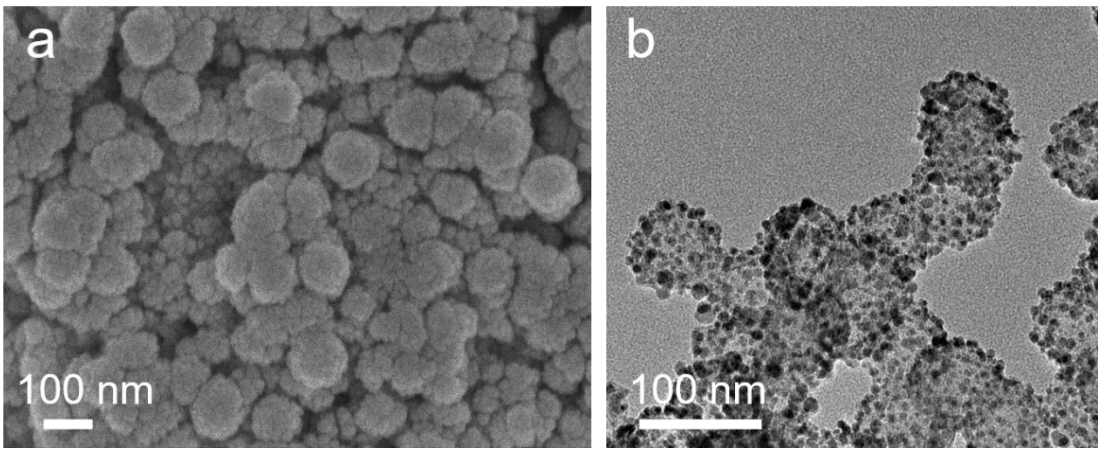

Fig. S14 (a) SEM and (b) TEM images of IrP_2@NPC after stability test in 1.0 M KOH.

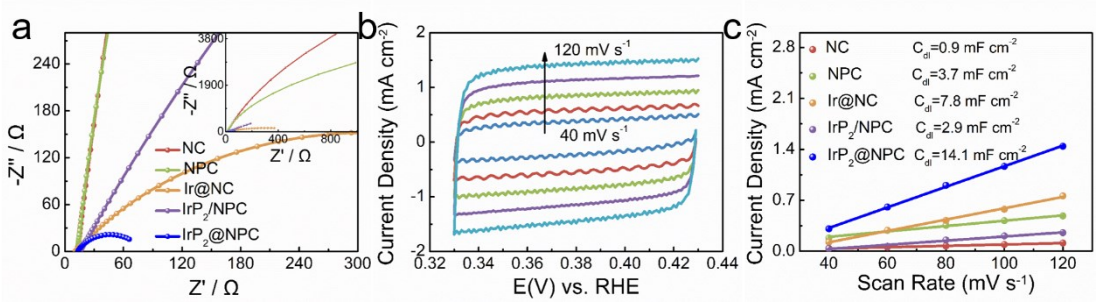

Fig. S15 (a) Nyquist plots of NC, NPC, Ir@NC, IrP_2/NPC, and IrP_2@NPC nanoshells. (b) CV scans of double-layer capacitance measurement of IrP_2@NPC nanoshells at different scanning rates in 1.0 M PBS. (c) Double-layer capacitances of these catalysts.

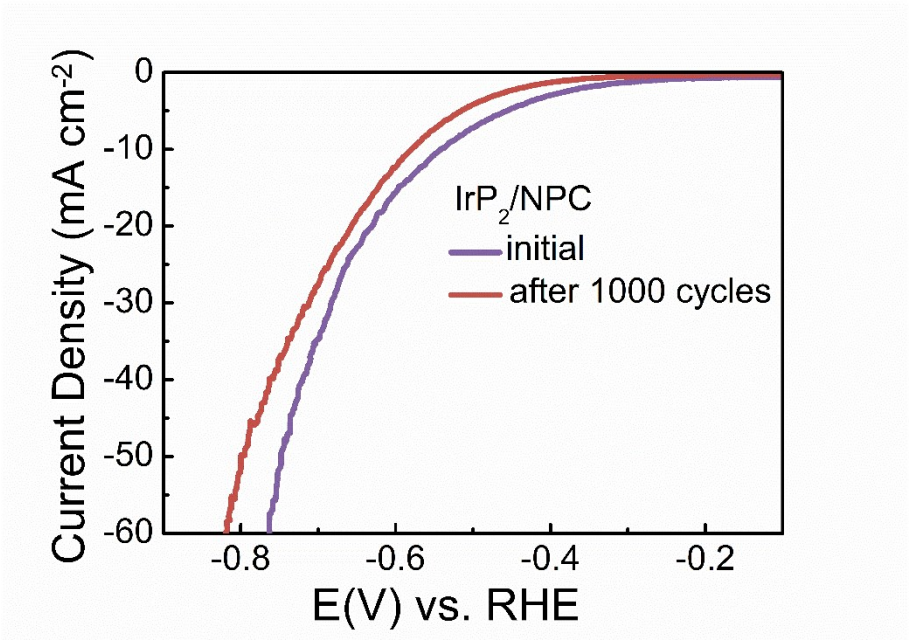

Fig. S16 HER polarization curves of Pt/C before and after 1000 CV cycles from -0.2 to 0.1 V (vs. RHE) in 1.0 M PBS.

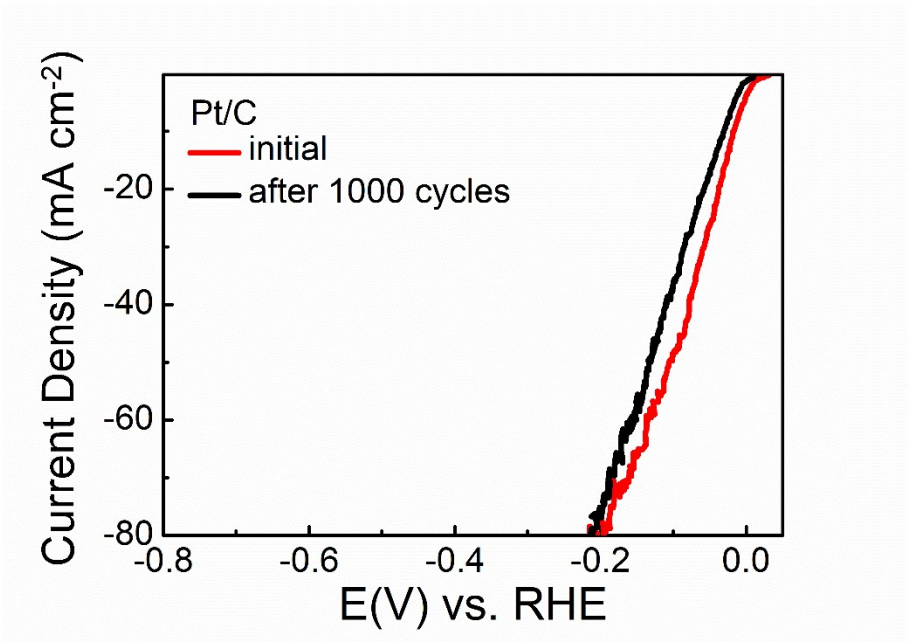

Fig. S17 HER polarization curves of IrP_2/NPC before and after 1000 CV cycles from -0.2 to 0.1 V (vs. RHE) in 1.0 M PBS.

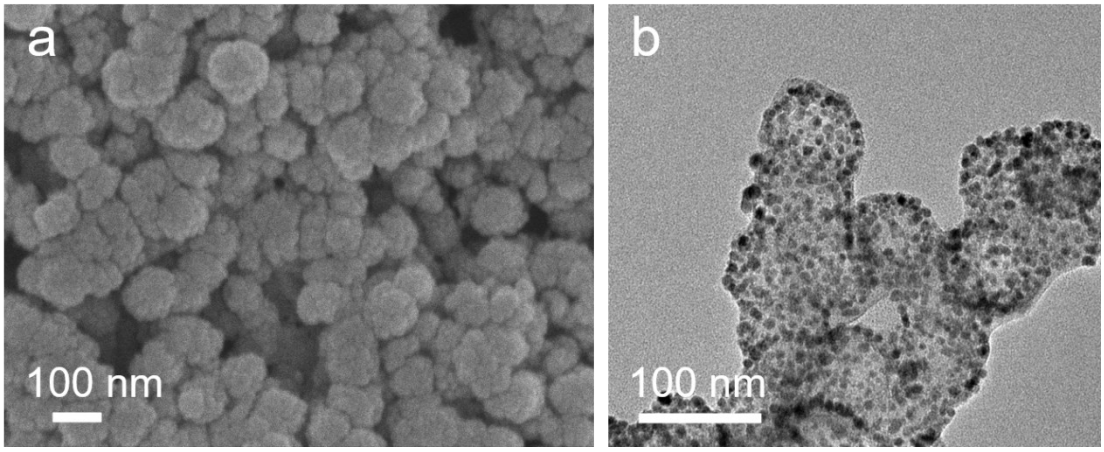

Fig. S18 (a) SEM and (b) TEM images of IrP_2@NPC after stability test in 1.0 M PBS.

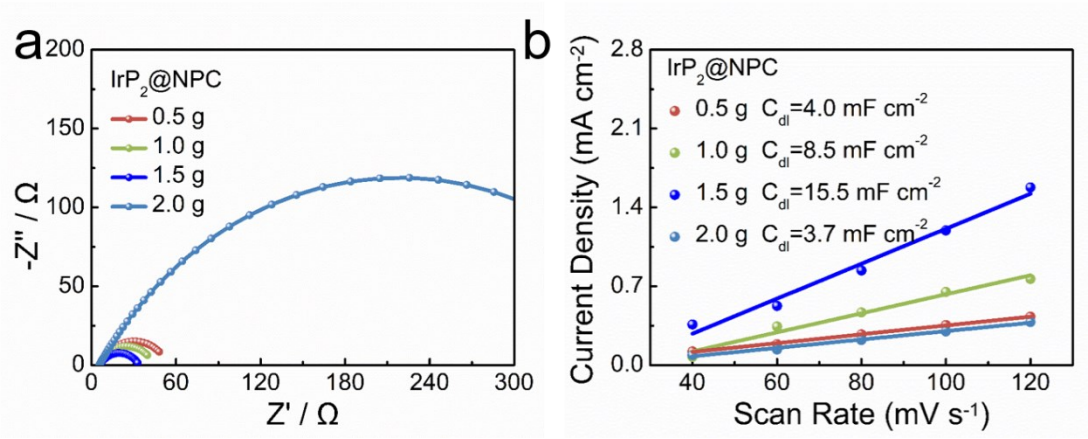

Fig. S19 (a) Nyquist plots and (b) C_{dl} of IrP_2@NPC series samples in 0.5 M H_2SO_4.

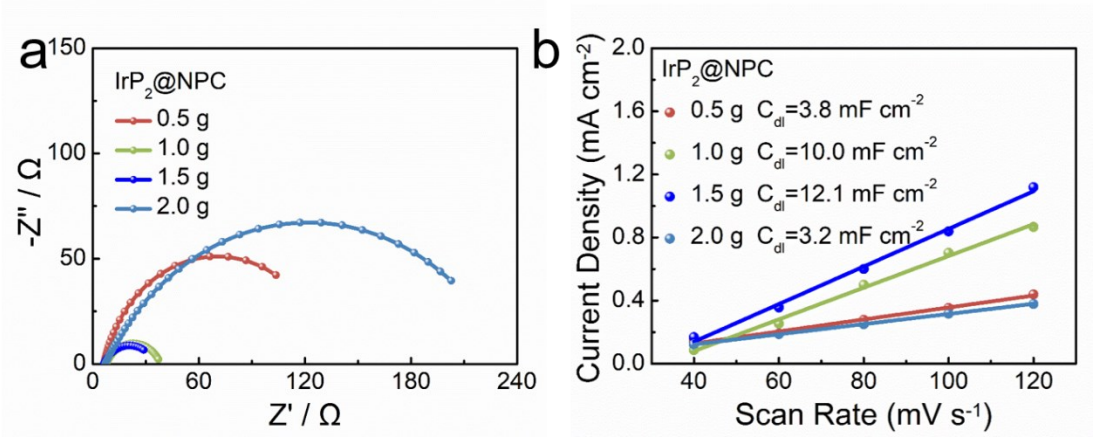

Fig. S20 (a) Nyquist plots and (b) C_{dl} of IrP_2@NPC series samples in 1.0 M KOH.

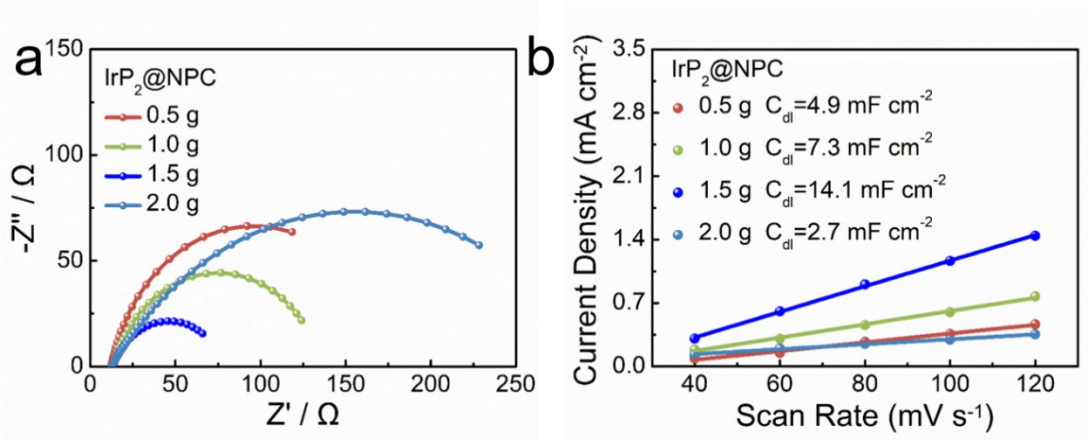

Fig. S21 (a) Nyquist plots and (b) C_{dl} of IrP_2@NPC series samples in 1.0 M PBS.

Table S1. Atomic content of Ir, P, C, N, and O estimated by EDX measurements for IrP_2@NPC with varied P content.

Samples	Atomic content (at. %)				
	Ir	P	C	N	O
IrP_2@NPC (0.5 g)	1.27	7.05	71.1	2.89	17.69
IrP_2@NPC (1.0 g)	1.70	10.86	69.92	2.53	14.99
IrP_2@NPC (1.5 g)	1.65	13.41	59.67	2.34	22.93
IrP_2@NPC (2.0 g)	1.12	14.97	61.82	2.19	19.90

Table S2. Comparison of HER activity between IrP_2@NPC and recently reported transition metal phosphides electrocatalysts in a wide pH range.

Electrocatalysts	j (mA cm^{-2})	η (mV)	b (mV dec^{-1})	Electrolyte solution	Refs.
	10	32	37	0.5 M H_2SO_4	
IrP_2@NPC	10	42	56	1.0 M KOH	This work
	10	90	87	1.0 M PBS	
	10	38	38	0.5 M H_2SO_4	
RuP_2@NPC	10	52	69	1.0 M KOH	1
	10	57	87	1.0 M PBS	
	10	51	46	0.5 M H_2SO_4	
RuP_x@NPC	10	74	70	1.0 M KOH	2
	10	110	59	1.0 M PBS	
	10	19	37	0.5 M H_2SO_4	
RuP(L-RP)	10	18	34	1.0 M KOH	3
	10	95	54	1.0 M PBS	
IrP_2@NC	10	8	28	0.5 M H_2SO_4	4
	10	28	50	1.0 M KOH	
	10	130	69	0.5 M H_2SO_4	
WP NAs/CC	10	150	102	1.0 M KOH	5
	10	200	125	1.0 M PBS	
WP_2 NPs/W	10	143	66	0.5 M H_2SO_4	6

	10	214	92	1.0 M KOH	
	10	201	95	1.0 M PBS	
	10	58	63.6	0.5 M H_2SO_4	
MoP_2 NS/CC	10	67	70	1.0 M KOH	7
	10	85	98.3	1.0 M PBS	
	10	124	58	0.5 M H_2SO_4	
MoP NA/CC	10	80	83	1.0 M KOH	8
	10	187	94	1.0 M PBS	
	10	115	65	0.5 M H_2SO_4	
MoP NPs@NC	10	80	59	1.0 M KOH	9
	10	136	71	1.0 M PBS	
	10	67	51	0.5 M H_2SO_4	
CoP/CC	10	209	129	1.0 M KOH	10
	2	65	93	1.0 M PBS	
	20	95	65	0.5 M H_2SO_4	
np-CoP NWs/Ti	20	150	71	1.0 M KOH	11
	10	178	125	1.0 M PBS	
	10	87	46	0.5 M H_2SO_4	
CoP@BCN	10	215	52	1.0 M KOH	12
	10	122	59	1.0 M PBS	

Table S3 Elemental values of fitted equivalent circuit resistances of NC, NPC, Ir@NC, IrP_2/NPC, and IrP_2@NPC in 0.5 M H_2SO_4, 1.0 M KOH, and 1.0 M PBS.

Samples	0.5 M H_2SO_4		1.0 M KOH		1.0 M PBS	
	R_s/Ω	R_{ct}/Ω	R_s/Ω	R_{ct}/Ω	R_s/Ω	R_{ct}/Ω
NC	6.05	195380	8.5	942570	12.67	39147
NPC	7.4	27519	7.794	605480	12.75	12238
Ir@NC	5.48	34.16	6.6	86.34	10.46	600.7
IrP_2/NPC	6.92	13872	6.238	37529	15.47	5528
IrP_2@NPC	5.79	30	6.19	28.5	13.15	56.5

Table S4 Elemental values of fitted equivalent circuit resistances of IrP_2@NPC with various P amount in 0.5 M H_2SO_4, 1.0 M KOH, and 1.0 M PBS.

Samples	0.5 M H_2SO_4		1.0 M KOH		1.0 M PBS	
	R_s/Ω	R_{ct}/Ω	R_s/Ω	R_{ct}/Ω	R_s/Ω	R_{ct}/Ω
IrP_2@NPC (0.5 g)	6.5	42.93	6.4	129.4	12.27	167.8
IrP_2@NPC (1.0 g)	5.8	38.71	7.63	30.69	13.33	123.3
IrP_2@NPC (1.5 g)	5.79	30	6.19	28.5	13.15	56.5
IrP_2@NPC (2.0 g)	5.46	426.7	6.9	229.8	12.35	285.8

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