

Electronic Supplementary Information

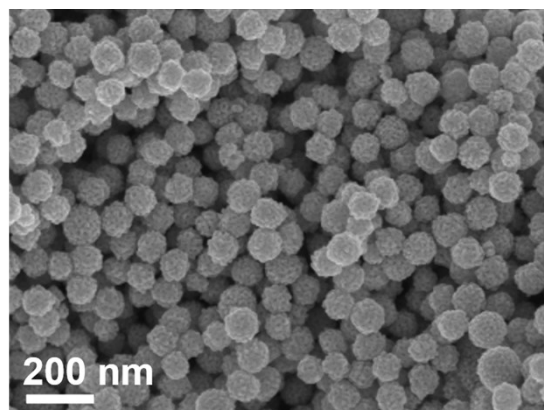


Fig. S1 SEM image of the Pd mNPs.

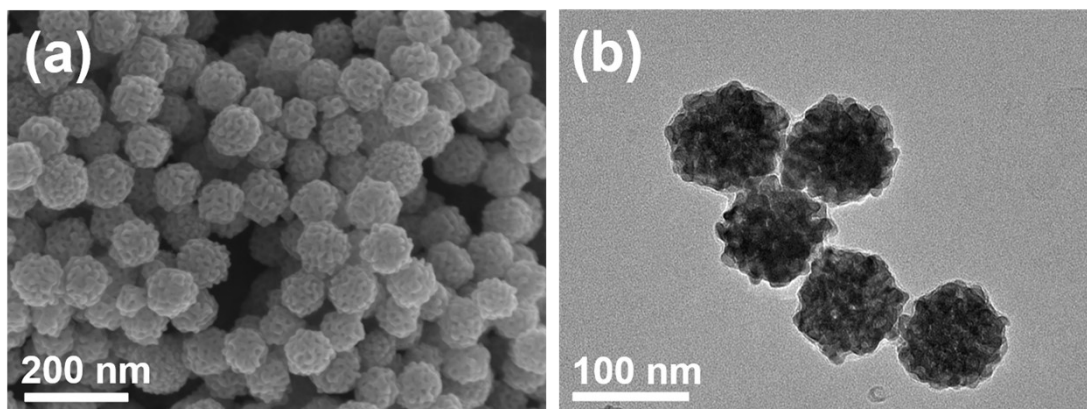


Fig. S2 (a) SEM and (b) TEM images of the Pd₂B mNPs.

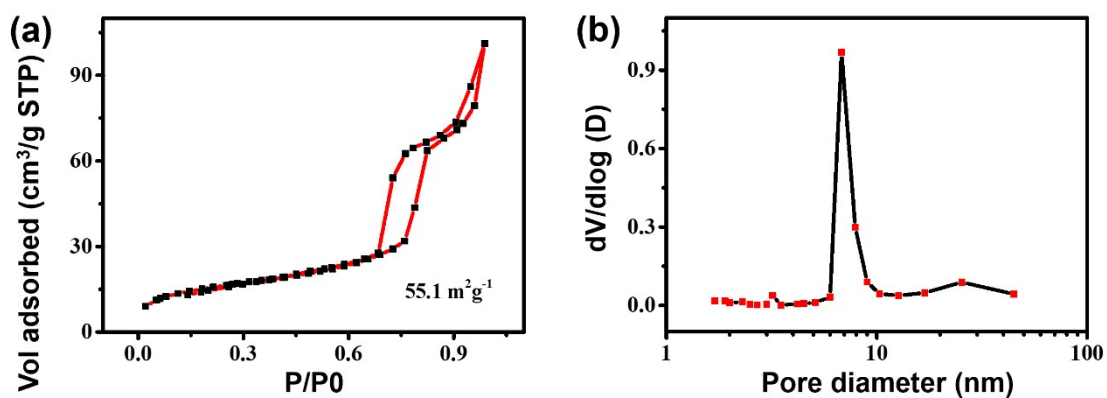


Fig. S3 (a) The N₂ adsorption-desorption isotherm along and (b) the pore size distribution curve for the Pd₂B mNPs.

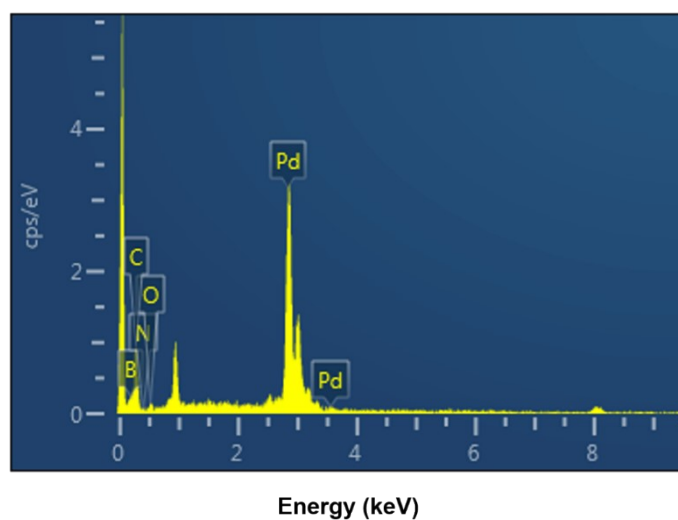


Fig. S4 EDX spectrum of the Pd₂B@PEI mNPs.

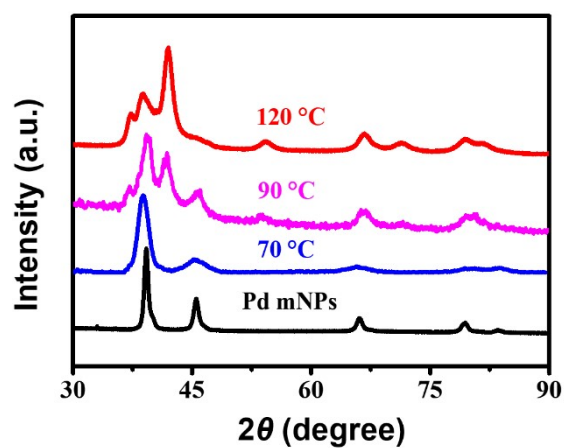


Fig. S5 The XRD patterns of phase transformation from Pd mNPs (fcc) to Pd₂B mNPs (hcp) at different reaction temperatures.

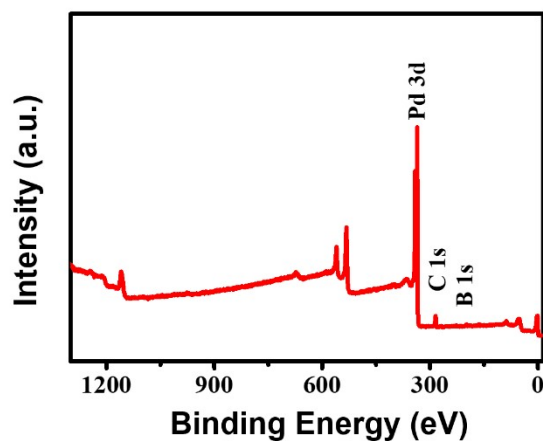


Fig. S6 The XPS survey spectrum of the Pd₂B mNPs.

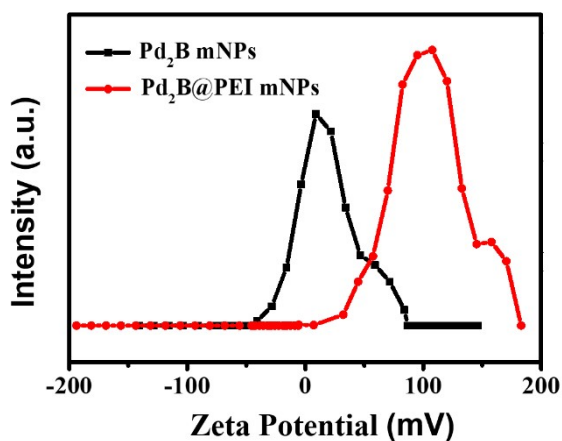


Fig. S7 Zeta potential distribution of Pd₂B mNPs and Pd₂B@PEI mNPs measured at pH=7.

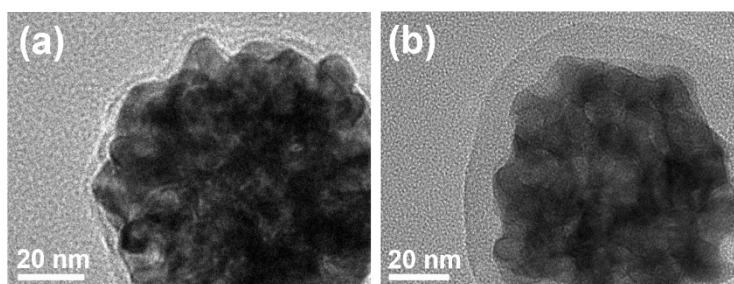


Fig. S8 TEM image of the (a) Pd₂B@PEI mNPs-0.1 and (b) Pd₂B@PEI mNPs-0.5 samples. The PEI concentrations for the synthesis of Pd₂B@PEI mNPs-0.1 and Pd₂B@PEI mNPs-0.5 are 0.1 and 0.5 mg_{PEI} mL⁻¹, respectively.

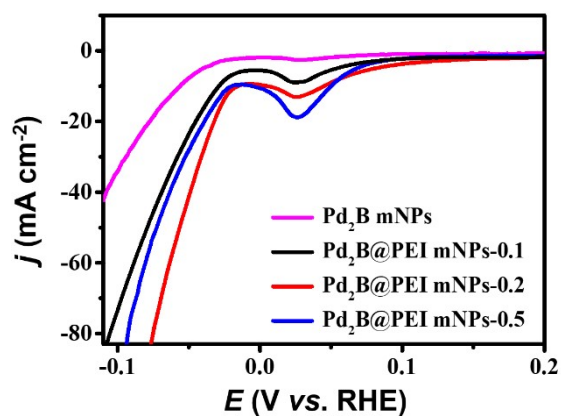


Fig. S9 LSV HER curves of various catalysts.

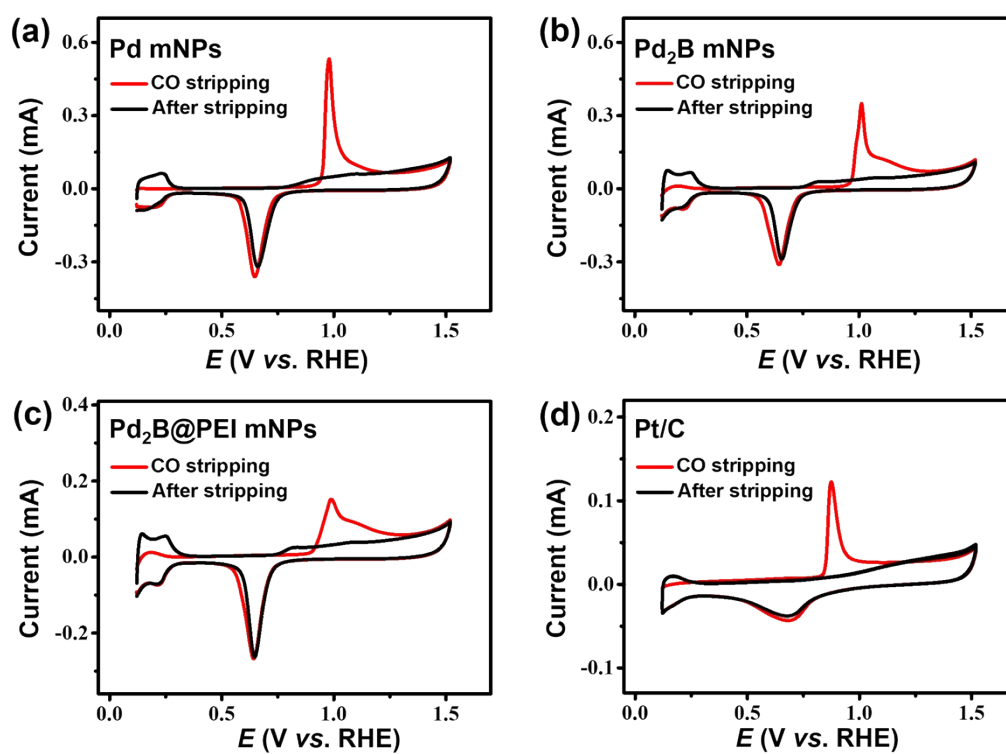


Fig. S10 CO-stripping curves of the catalysts recorded in a CO-saturated 0.5 M H₂SO₄ solution with a scan rate of 20 mV s⁻¹.

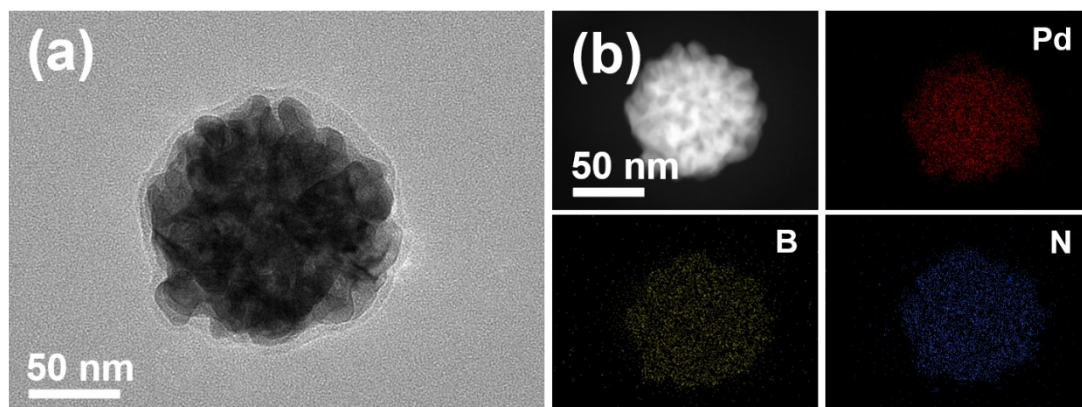


Fig. S11 (a) TEM image, (b) HAADF-STEM image and elemental mapping images of the post-HER Pd₂B@PEI mNPs.

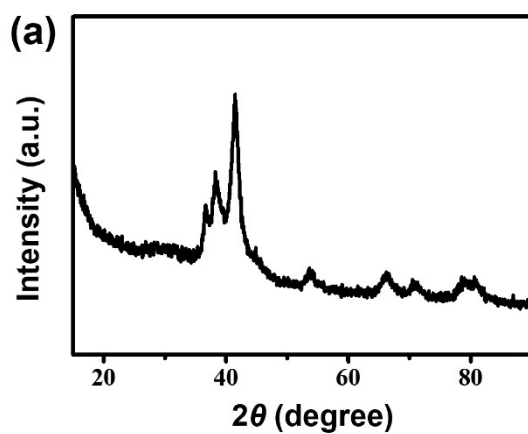


Fig. S12 The XRD pattern of the post-HER-Pd₂B@PEI mNPs.

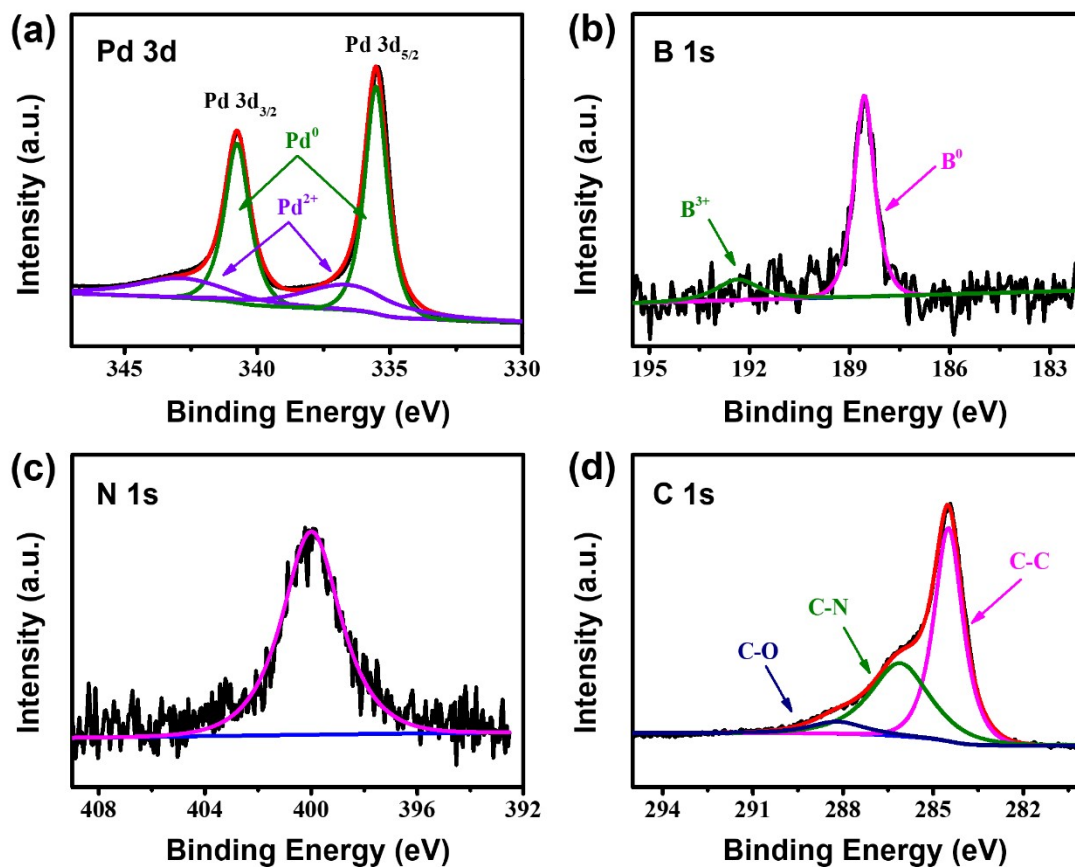


Fig. S13 High-resolution XPS spectrum of (a) Pd 3d, (b) B 1s, (c) N 1s and (d) C 1s for the post-HER $\text{Pd}_2\text{B@PEI}$ mNPs.

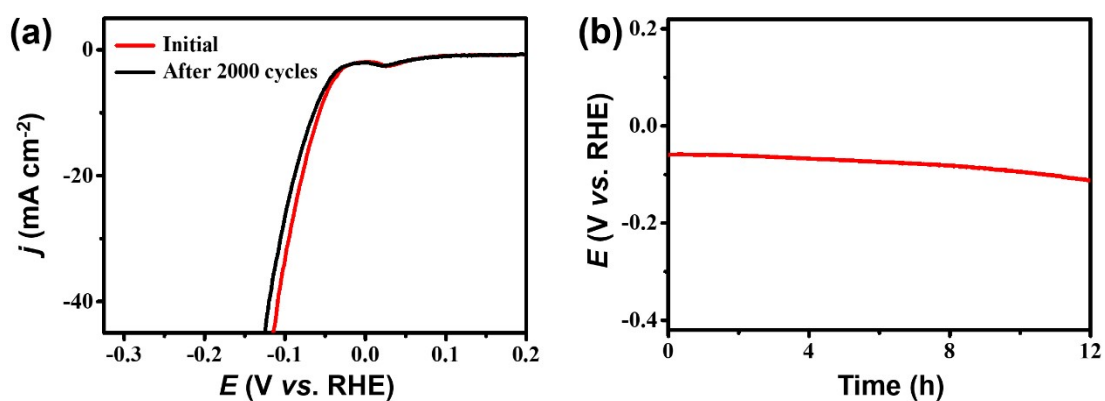


Fig. S14 (a) LSV HER curves of the Pd_2B mNPs before and after 2000 cycles. (c) V-t curve (without iR compensation) of Pd_2B mNPs at a cathodic current density of 10 mA cm^{-2} for 12 h.

Table S1. HER performance comparison between the Pd₂B@PEI mNPs and some other reported electrocatalysts.

Electrocatalysts	Electrolytes	Tafel mV dec ⁻¹	Overpotential at 10 mA cm ⁻² (mV)	Ref.
Pd₂B@PEI mNPs	0.5 M H₂SO₄	44	15	This work
PdCPC(I)	0.5 M H ₂ SO ₄	57	269	1
Mn ₃ N ₂ /PdO	0.5 M H ₂ SO ₄	49.6	44.6	2
VS ₂ -Pd	0.5 M H ₂ SO ₄	75	128	3
Pd ₃ P ₂ S ₈	0.5 M H ₂ SO ₄	29	52	4
Mo ₂ C-Pd-9%	0.5 M H ₂ SO ₄	51	28	5
Pd-Si NW-2	0.5 M H ₂ SO ₄	70	153	6
GaPd ₂	0.5 M H ₂ SO ₄	55.2	24.3	7
Pd/Bi/Cu HNAs	0.5 M H ₂ SO ₄	61	79	8
PdHx	0.5 M H ₂ SO ₄	32.5	32	9
PEI@NiP ₂ -CC	0.5 M H ₂ SO ₄	33.2	44	10

Table S2. The CO stripping tests were carried out to calculated the electrochemically active surface areas (ECSAs) for catalyst.

Catalyst	ECSA (m ² g ⁻¹)
Pd mNPs	34.2
Pd ₂ B mNPs	29.1
Pd ₂ B@PEI mNPs	20.6
Pt/C	46.9

References

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