Electronic Supplementary Information

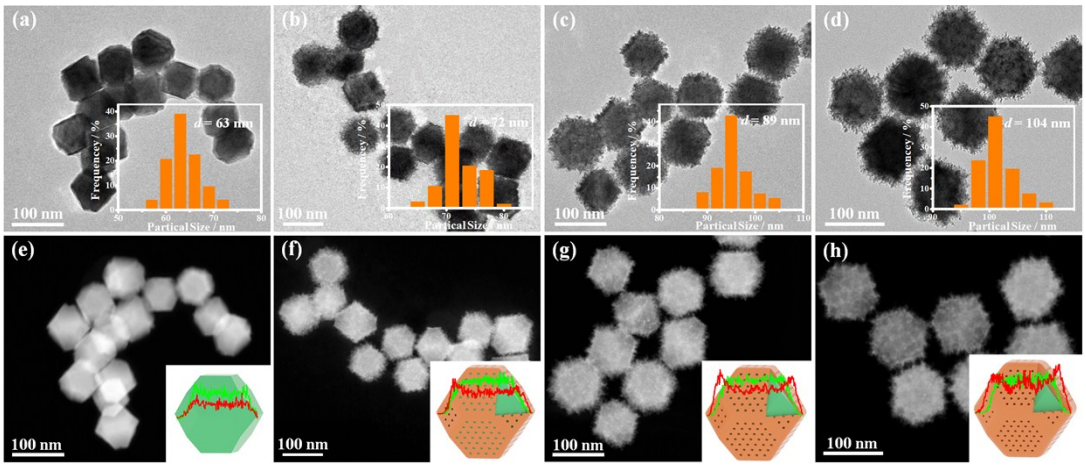

Fig. S1 TEM images of the formation process of the c-Pd@PdPt MTO at (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 4 h, respectively. Inset in is particle-size distribution histograms. HAADF-STEM and the corresponding elemental distribution images of the reaction intermediates at (e) 0.5 h, (f) 1 h, (g) 2 h and (h) 4 h, respectively.

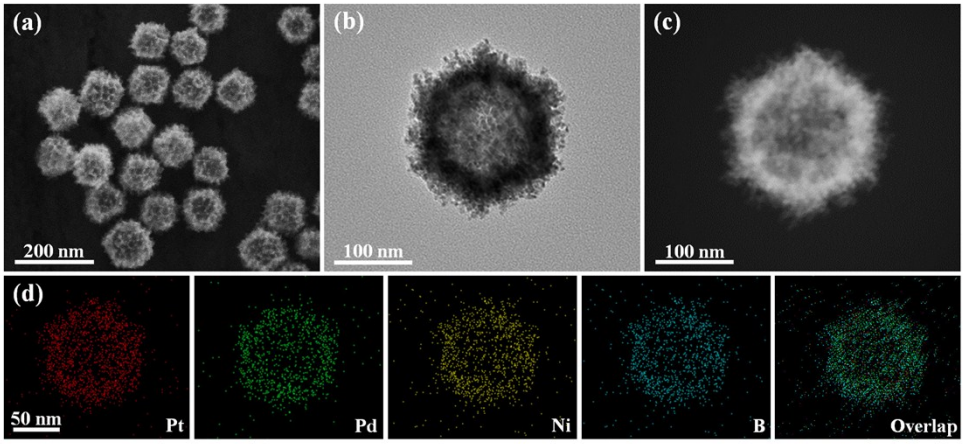

Fig. S2 (a) SEM, (b) TEM, (c) HRTEM, and (d) elemental mapping images of the PtPd-Ni-B MTONs

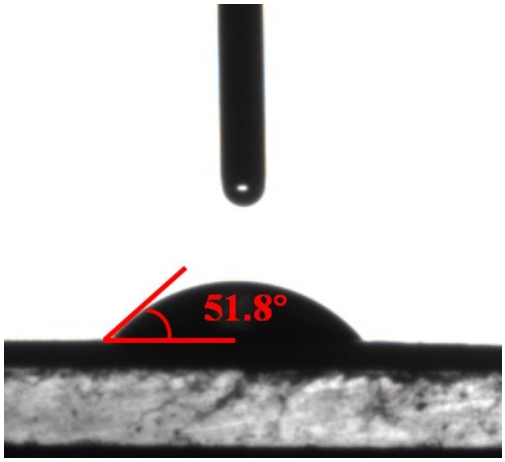

Fig. S3 Contact angles of the c-PtPd MTONs.

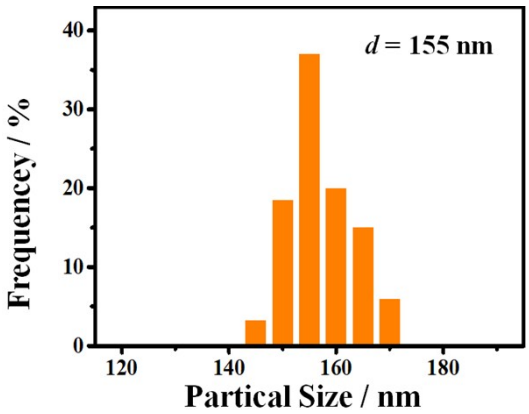

Fig. S4 Particle-size distribution histogram of the c-PtPd@a-NiB CSHs.

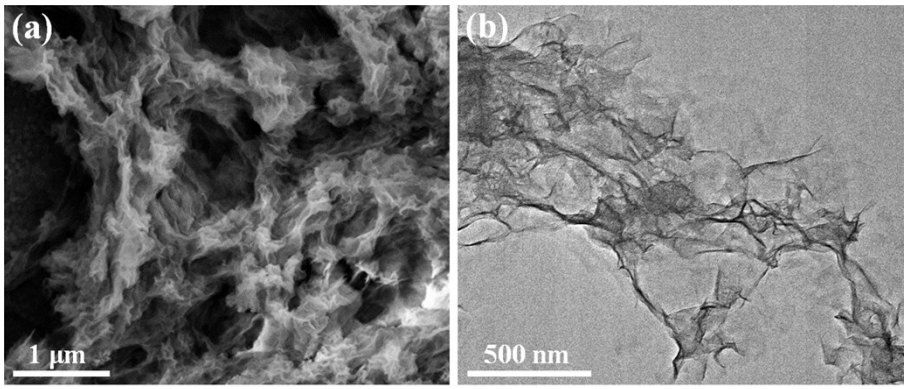

Fig. S5 (a) SEM and (b) TEM images of the a-NiB nanosheets.

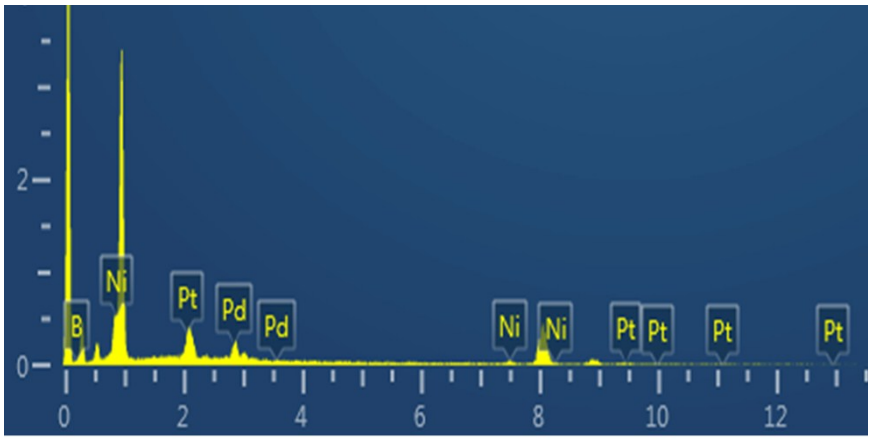

Fig. S6 EDX spectrum of the c-PtPd@a-NiB CSHs.

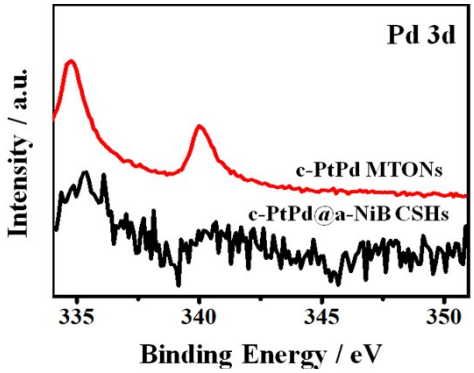

Fig. S7 XPS spectra of the Pd 3d for the c-PtPd MTONs and c-PtPd@a-NiB CSHs.

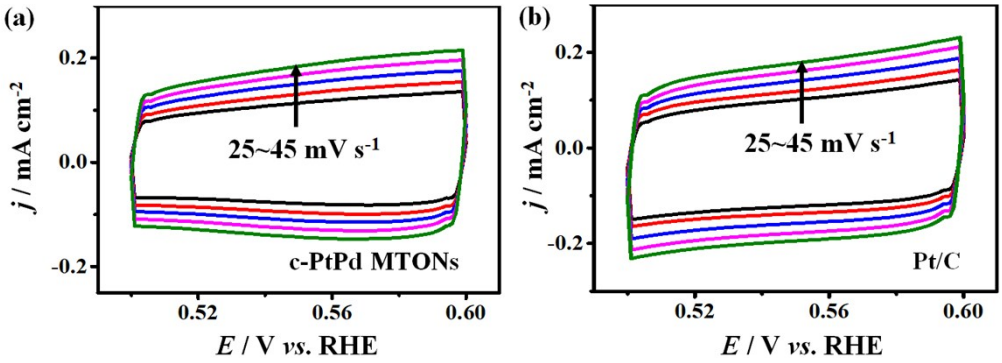

Fig. S8 (a-b) Typical cyclic voltammogram (CV) curves of the c-PtPd MTONs and Pt/C with different scan rates.

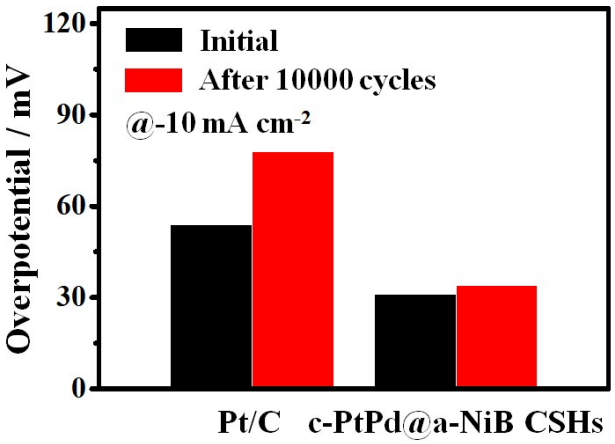

Fig. S9 Comparison of the required overpotentials at -10 mA cm^{-2} for the Pt/C and c-PtPd@a-NiB CSHs initial and after 10000 cycles stability testing.

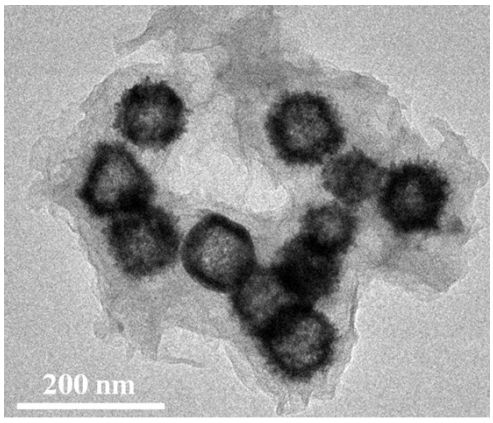

Fig. S10 TEM image of the c-PtPd@a-NiB CSHs after HER testing in 1 M KOH electrolyte.

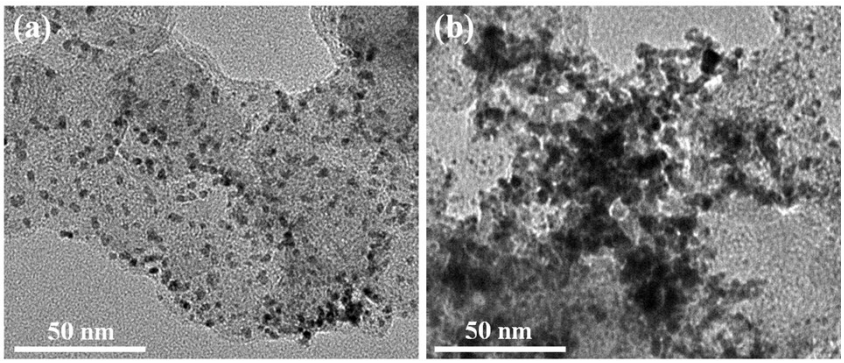

Fig. S11 TEM images of Pt/C (a) before and (b) after HER testing in 1 M KOH electrolyte.

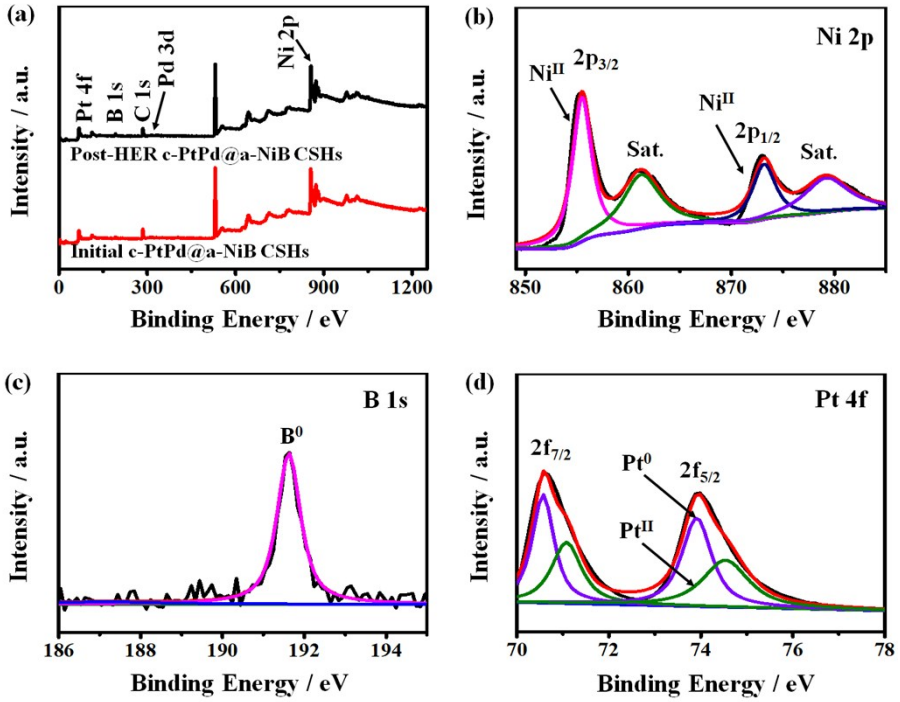

Fig. S12 (a) The XPS survey spectrum of initial and post-HER c-PtPd@a-NiB CSHs. (b) Ni 2p, (c) B 1s and (d) Pt 4f XPS spectra for the post-HER c-PtPd@a-NiB CSHs.

Table S1. Comparison of HER activities in 1 M KOH for c-PtPd@a-NiB CSHs with other reported Pt-based electrocatalysts.

Catalyst	Overpotential at 10 mA cm^{-2} (mV)	Electrolyte	Ref.
c-PtPd@a-NiB CSHs	**31**	**1 M KOH**	**This work**
Pt/h-BN	75	1 M KOH	1
Pt–Ni alloy	65	1 M KOH	2
PtNi-O nanostructure	40	1 M KOH	3
Pt–Ni nanocages	104	1 M KOH	4
Pt–Ni/NiS nanowires	42	1 M KOH	5
Pt–Ni nanowires	40	1 M KOH	6
Ni_3N/Pt	50	1 M KOH	7
Pt NWs/SL-$Ni(OH)_2$	70	1 M KOH	8
PtNi nanoparticles	82	1 M KOH	9
Pt–Ni alloy nanoparticles	72	1 M KOH	10
Pt-Ni-P nanowire	44	1 M KOH	11
D-PtNi/C	40	1 M KOH	12
Pt−$Co(OH)_2$/CC	32	1 M KOH	13
Ni-MOF@Pt	102	1 M KOH	14
PtNiP MNs/C	54	1 M KOH	15

References

1. A. Guha, T. Veettil Vineesh, A. Sekar, S. Narayanaru, M. Sahoo, S. Nayak, S. Chakraborty and T. N. Narayanan, *ACS Catal.*, 2018, **8**, 6636-6644.
2. Z. Cao, Q. Chen, J. Zhang, H. Li, Y. Jiang, S. Shen, G. Fu, B. A. Lu, Z. Xie and L. Zheng, *Nat. Commun.*, 2017, **8**, 15131.
3. Z. Zhao, H. Liu, W. Gao, W. Xue, Z. Liu, J. Huang, X. Pan and Y. Huang, *J. Am. Chem. Soc.*, 2018, **140**, 9046-9050.
4. Z. Cao, H. Li, C. Zhan, J. Zhang, W. Wang, B. Xu, F. Lu, Y. Jiang, Z. Xie and L. Zheng, *Nanoscale*, 2018, **10**, 5072-5077.
5. P. Wang, X. Zhang, J. Zhang, S. Wan, S. Guo, G. Lu, J. Yao and X. Huang, *Nat. Commun.*, 2017, **8**, 14580.
6. P. Wang, K. Jiang, G. Wang, J. Yao and X. Huang, *Angew. Chem., Int. Ed.*, 2016, **55**, 12859-12863.
7. Y. Wang, L. Chen, X. Yu, Y. Wang and G. Zheng, *Adv. Energy Mater.*, 2017, **7**, 1601390.
8. H. Yin, S. Zhao, K. Zhao, A. Muqsit, H. Tang, L. Chang, H. Zhao, Y. Gao and Z. Tang, *Nat. Commun.*, 2015, **6**, 6430.
9. J. Chen, J. Wang, J. Chen and L. Wang, *J. Mater. Sci.*, 2017, **52**, 13064-13077.
10. Z. Du, Y. Wang, J. Li and J. Liu, *J. Nanopart. Res.*, 2019, **21**.
11. P. Wang, Q. Shao, J. Guo, L. Bu and X. Huang, *Chem. Mater.*, 2020, DOI: 10.1021/acs.chemmater.0c00172.
12. H. Chen, G. Wang, T. Gao, Y. Chen, H. Liao, X. Guo, H. Li, R. Liu, M. Dou, S. Nan and Q. He, *J. Phys. Chem. C*, 2020, **124**, 5036-5045.
13. Z. Xing, C. Han, D. Wang, Q. Li and X. Yang, *ACS Catal.*, 2017, **7**, 7131-7135.
14. K. Rui, G. Zhao, M. Lao, P. Cui, X. Zheng, X. Zheng, J. Zhu, W. Huang, S. X. Dou and W. Sun, *Nano Lett*, 2019, **19**, 8447-8453.
15. C. Li, Y. Xu, D. Yang, X. Qian, X. Chai, Z. Wang, X. Li, L. Wang and H. Wang, *ACS Sustainable Chem. Eng.* , 2019, **7**, 9709-9716.