Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

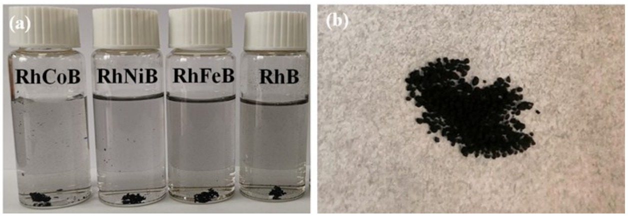

Fig. S1 (a) Photograph of the obtained aerogels in aqueous solutions. (b) Photograph of the typical RhCoB aerogel.

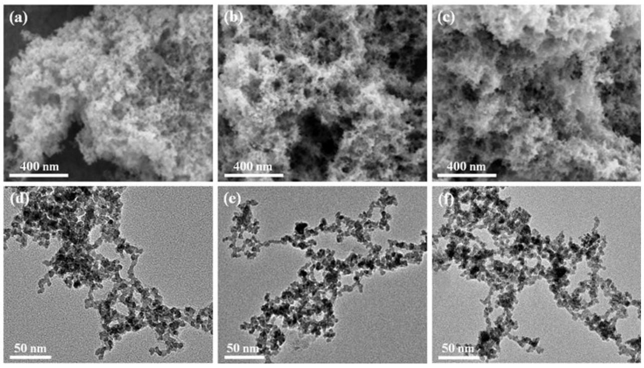

Fig. S2 (a-c) SEM and (d-f) TEM images and of various samples: (a, d) RhB, (b, e) RhNiB, and (c, f) RhFeB aerogels.

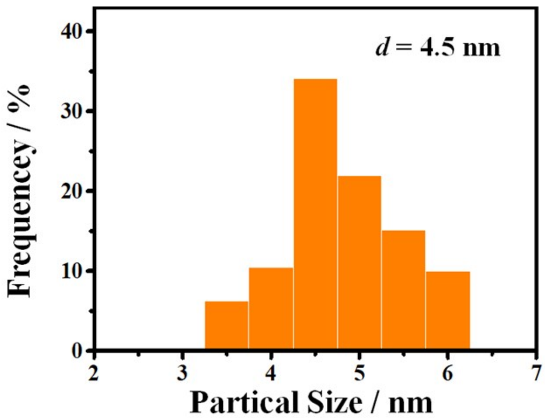

Fig. S3 Particle-size distribution histogram of the RhCoB aerogels.

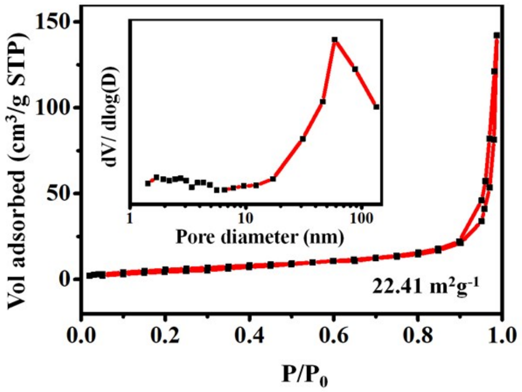

Fig. S4 N_2 adsorption-desorption isotherm for the RhCoB aerogels. The inset is the BJH pore-size distribution curve.

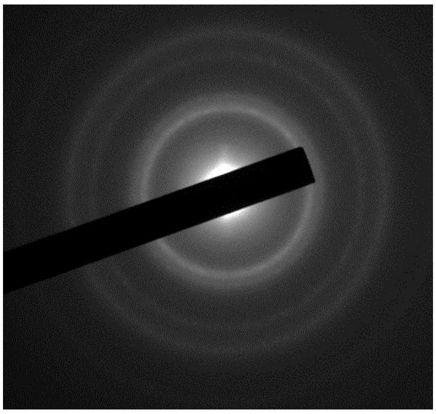

Fig. S5 the SAED pattern of the RhCoB aerogels.

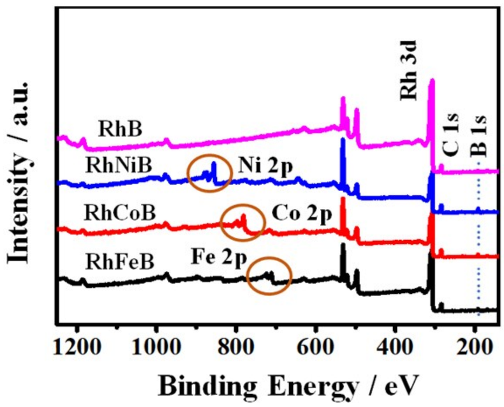

Fig. S6 XPS spectra of the RhB, RhNiB, RhCoB, and RhFeB aerogels.

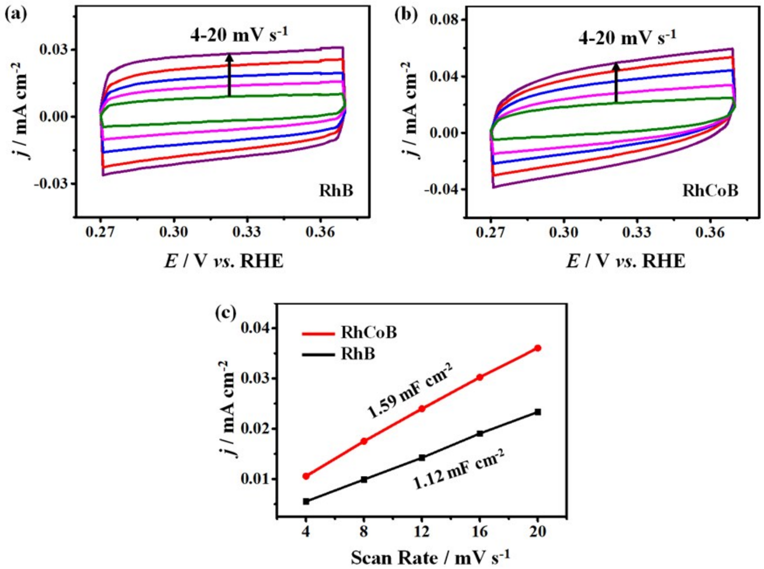

Fig. S7 (a-b) CVs and (c) the corresponding C_{dl} of RhB and RhCoB aerogels.

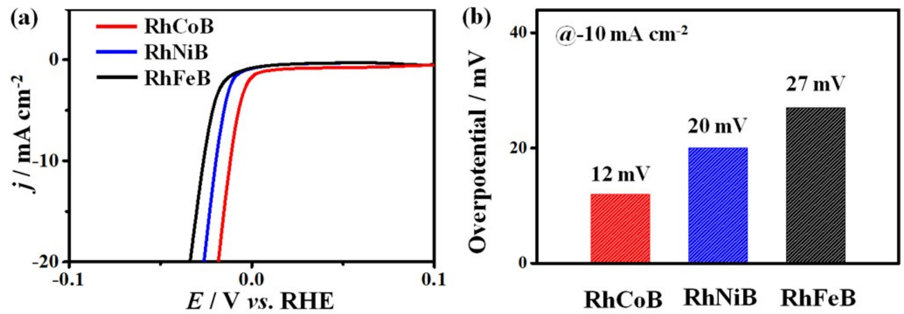

Fig. S8 (a) Polarization curves for various RhMB aerogels obtained in 0.5 M H_2SO_4 electrolyte. (b) Comparison of the overpotentials at -10 mA cm^{-2}.

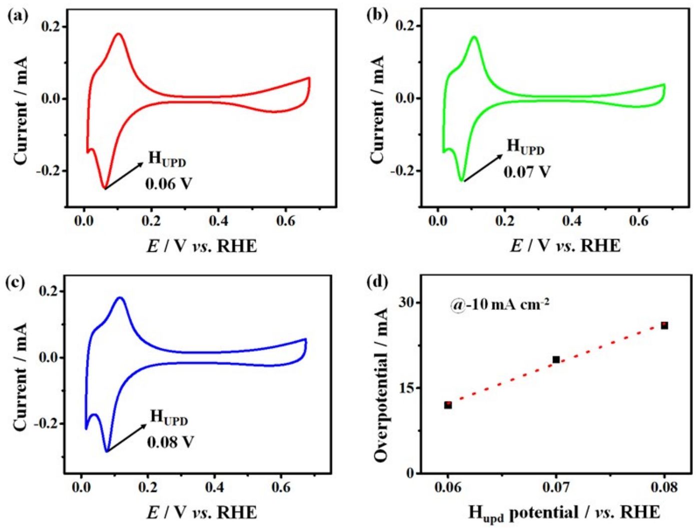

Fig. S9 H_{UPD} behavior of (a) RhCoB, (b) RhNiB and (c) RhFeB aerogels with scan rate of 50 mV s^{-1}. (d) Relationships between HER activity and H_{UPD} potential on RhCoB, RhNiB, and RhFeB aerogels. The scan rate for CV curves is 50 mV s^{-1}.

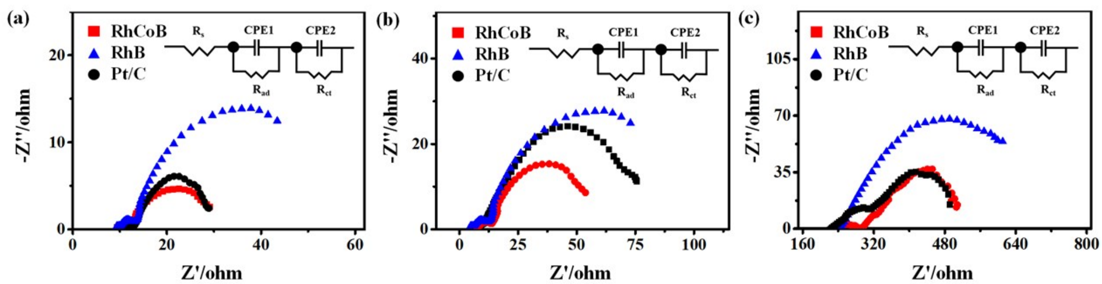

Fig. S10 Nyquist plots of RhCoB aerogels obtained in (a) 0.5 M H_2SO_4 with an overpotential of 50 mV , (b) 1 M KOH with an overpotential of 100 mV , and (c) 1 M PBS with an overpotential of 300 mV.

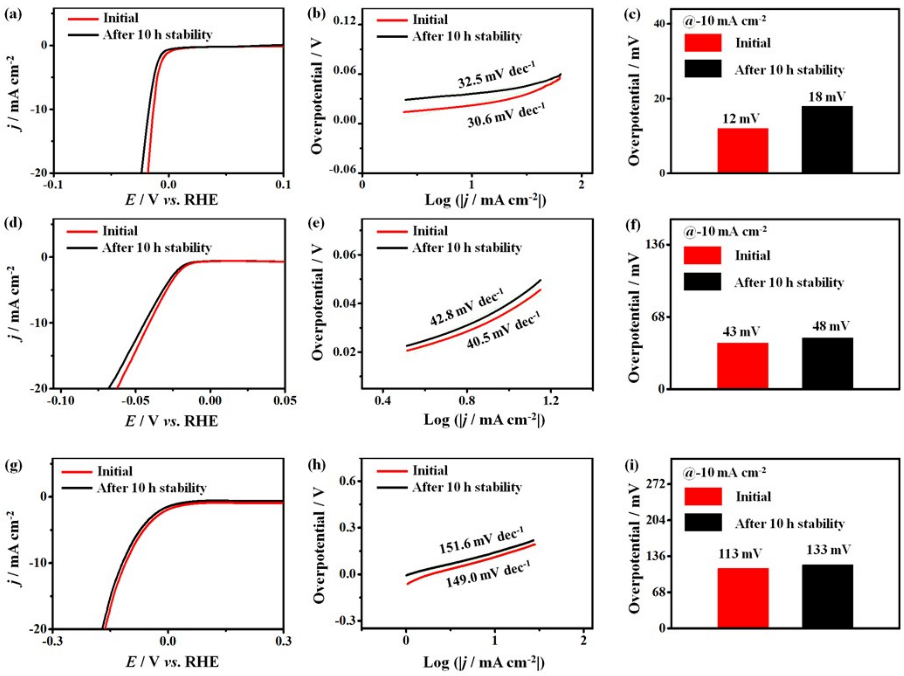

Fig. S11 (a, d, g) Polarization curves of RhCoB aerogels before and after 10 h chronopotentiometric (V-t) stability in acidic (a), alkaline (d), and neutral (g) electrolytes, respectively. (b, e, h) The corresponding Tafel slopes derived from a, d, g, respectively. (c, f, i) Comparison of the required overpotentials at -10 mA cm^{-2}.

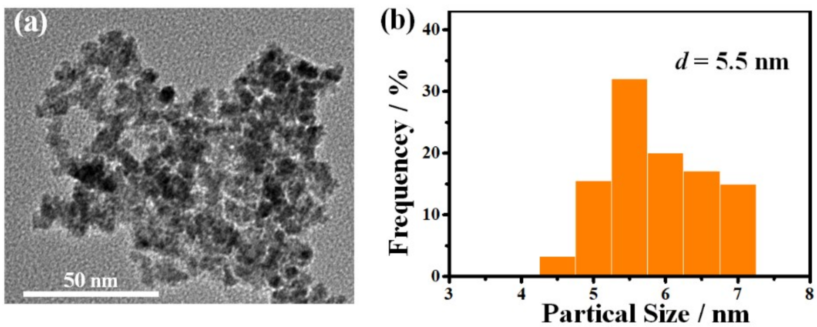

Fig. S12 (a) TEM image and (b) particle-size distribution histogram of the RhCoB aerogels after catalytic stability testing.

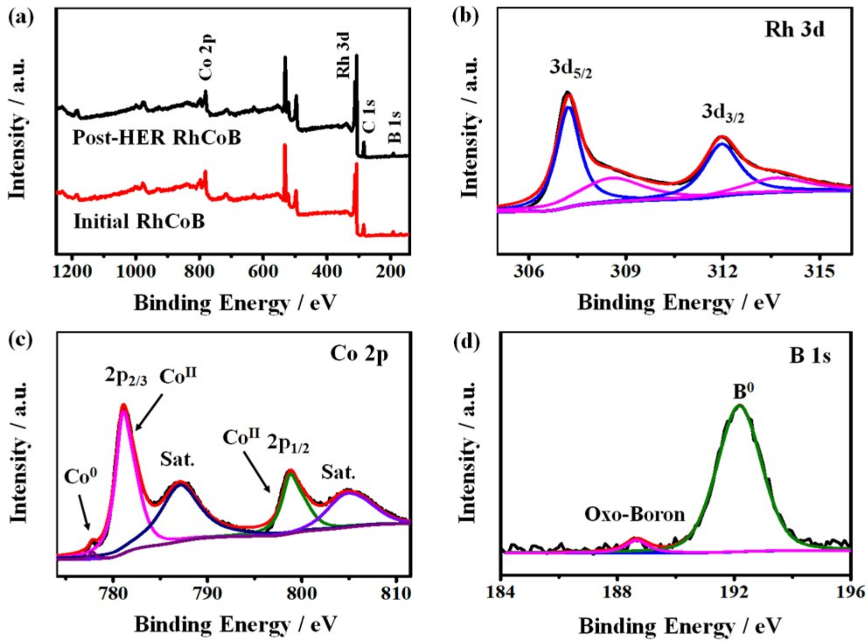

Fig. S13 (a) XPS survery spectra of inital and post-HER RhCoB catalysts. (b) Rh 3d, (c) Co 2p and (d) B 1s XPS spectra for the RhCoB catalysts after 10 h V-t stability testing in acidic electrolyte.

Table S1 Comparison of HER activities in 0.5 M H_2SO_4 for RhCoB aerogels with other reported Rh-based electrocatalysts.

Catalyst	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	Ref.
RhCoB aerogels	**12**	**30.7**	**0.5 M H_2SO_4**	**This work**
boron-doped RhFe alloy	25	32	0.5 M H_2SO_4	1
Rh_2S_3 hexagonal nanoprisms	117	44	0.5 M H_2SO_4	2
Rh_2P electrocatalyst	20	/	0.5 M H_2SO_4	3
Rh_2P-based electrocatalyst	14	31.7	0.5 M H_2SO_4	4
Rh-MoS_2 nanocomposites	47	24	0.5 M H_2SO_4	5
Rh*x*P/NPC	19	36	0.5 M H_2SO_4	6
Rh Hollow nanoparticles	28.1	24	0.5 M H_2SO_4	7
Rh-Ag-Si ternary composites	120	51	0.5 M H_2SO_4	8
Rh-Au-Si nanocomposite	60	24	0.5 M H_2SO_4	9
rGO/CoP-Rh catalysts	72	43	0.5 M H_2SO_4	10

Table S2. Comparison of HER activities in 1 M KOH for RhCoB aerogels with other reported non-Pt electrocatalysts.

Catalyst	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	Ref.
RhCoB aerogel	**43**	**32.1**	**1 M KOH**	**This work**
RuP_2@NPC	52	69	1 M KOH	11
MoS_2/Ni_3S	110	31.8	1 M KOH	12
Mo_2C@NC	60	/	1 M KOH	13
MoP_2 NS/CC	85	70	1 M KOH	14
Mn-CoP/Ti	76	52	1 M KOH	15
NiRu@N-C	50	36	1 M KOH	16
CoMoP@C	81	55	1 M KOH	17
Rh NSs	43	107	1 M KOH	18
$NiPS_3$ nanoparticles	99	/	1 M KOH	19
Mo_2C@C nanospheres	47	71	1 M KOH	20

References

1. L. Zhang, J. Lu, S. Yin, L. Luo, S. Jing, A. Brouzgou, J. Chen, P. K. Shen and P. Tsiakaras, *Appl. Catal. B: Environ.*, 2018, **230**, 58-64.
2. D. Yoon, B. Seo, J. Lee, K. S. Nam, B. Kim, S. Park, H. Baik, S. Hoon Joo and K. Lee, *Energy Environ. Sci.*, 2016, **9**, 850-856.
3. H. Duan, D. Li, Y. Tang, Y. He, S. Ji, R. Wang, H. Lv, P. P. Lopes, A. P. Paulikas, H. Li, S. X. Mao, C. Wang, N. M. Markovic, J. Li, V. R. Stamenkovic and Y. Li, *J. Am. Chem. Soc.*, 2017, **139**, 5494-5502.
4. F. Yang, Y. Zhao, Y. Du, Y. Chen, G. Cheng, S. Chen and W. Luo, *Adv. Energy Mater.*, 2018, **8**, 1703489.
5. Y. Cheng, S. Lu, F. Liao, L. Liu, Y. Li and M. Shao, *Adv. Funct. Mater.*, 2017, **27**, 1700359.
6. Q. Qin, H. Jang, L. Chen, G. Nam, X. Liu and J. Cho, *Adv. Energy Mater.*, 2018, **8**, 1801478.
7. J. Du, X. Wang, C. Li, X.-Y. Liu, L. Gu and H.-P. Liang, *Electrochim. Acta*, 2018, **282**, 853-859.
8. B. Jiang, Y. Sun, F. Liao, W. Shen, H. Lin, H. Wang and M. Shao, *J. Mater. Chem. A*, 2017, **5**, 1623-1628.
9. B. Jiang, L. Yang, F. Liao, M. Sheng, H. Zhao, H. Lin and M. Shao, *Nano Res.*, 2017, **10**, 1749-1755.
10. H. Zheng, X. Huang, H. Gao, W. Dong, G. Lu, X. Chen and G. Wang, *J. Energy Chem.*, 2019, **34**, 72-79.
11. Z. Pu, I. S. Amiinu, Z. Kou, W. Li and S. Mu, *Angew. Chem., Int. Ed.*, 2017, **56**, 11559-11564.
12. J. Zhang, T. Wang, D. Pohl, B. Rellinghaus, R. Dong, S. Liu, X. Zhuang and X. Feng, *Angew. Chem., Int. Ed.*, 2016, **55**, 6702-6707.
13. X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova and T. Asefa, *Angew. Chem., Int. Ed.*, 2014, **53**, 4372-4376.
14. W. Zhu, C. Tang, D. Liu, J. Wang, A. M. Asiri and X. Sun, *J. Mater. Chem. A*, 2016, **4**, 7169-7173.
15. T. Liu, X. Ma, D. Liu, S. Hao, G. Du, Y. Ma, A. M. Asiri, X. Sun and L. Chen, *ACS Catal.*, 2016, **7**, 98-102.
16. Y. Xu, S. Yin, C. Li, K. Deng, H. Xue, X. Li, H. Wang and L. Wang, *J. Mater. Chem. A*, 2018, **6**, 1376-1381.
17. Y.-Y. Ma, C.-X. Wu, X.-J. Feng, H.-Q. Tan, L.-K. Yan, Y. Liu, Z.-H. Kang, E.-B. Wang and Y.-G. Li, *Energy Environ. Sci.*, 2017, **10**, 788-798.
18. N. Zhang, Q. Shao, Y. Pi, J. Guo and X. Huang, *Chem. Mater.*, 2017, **29**, 5009-5015.
19. J. Zhang, R. Cui, X. a. Li, X. Liu and W. Huang, *J. Mater. Chem. A*, 2017, **5**, 23536-23542.
20. Y. Y. Chen, Y. Zhang, W. J. Jiang, X. Zhang, Z. Dai, L. J. Wan and J. S. Hu, *ACS Nano*, 2016, **10**, 8851-8860.