

## Supporting Information

### Construction of efficient bismuth/boron-based flexible electrode in organic media toward neutral hydrogen evolution

Jinli Fan<sup>†a</sup>, Weiju Hao<sup>†a\*</sup>, Chengyu Fu<sup>a</sup>, Ziliang Chen<sup>b</sup>, Rikai Liang<sup>a</sup>, Cheng Lian<sup>c</sup>, Qiang Zhang<sup>a\*</sup>,  
Guisheng Li<sup>a</sup>

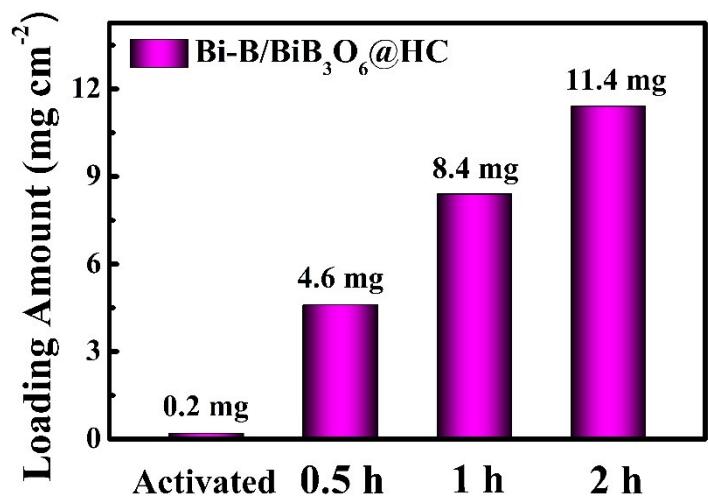
<sup>a</sup> University of Shanghai for Science and Technology, Shanghai 200093, PR China.

<sup>b</sup> Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University,  
Suzhou 215123, PR China.

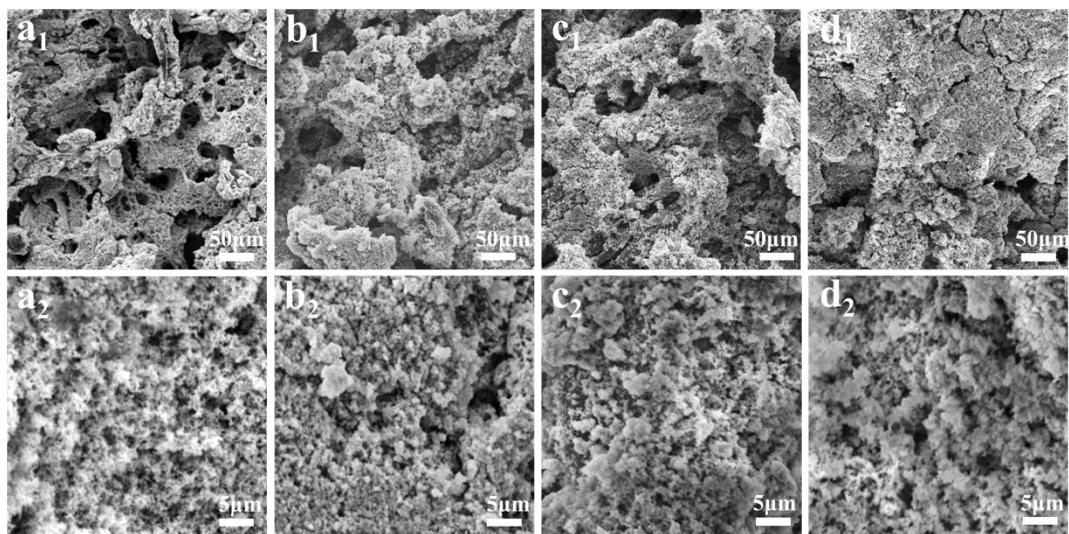
<sup>c</sup> State Key Laboratory of Chemical Engineering, Shanghai Engineering Research  
Center of Hierarchical Nanomaterials, School of Chemistry and Molecular  
Engineering, East China University of Science and Technology, Shanghai 200237, PR  
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\* Corresponding author: Weiju Hao. Qiang Zhang

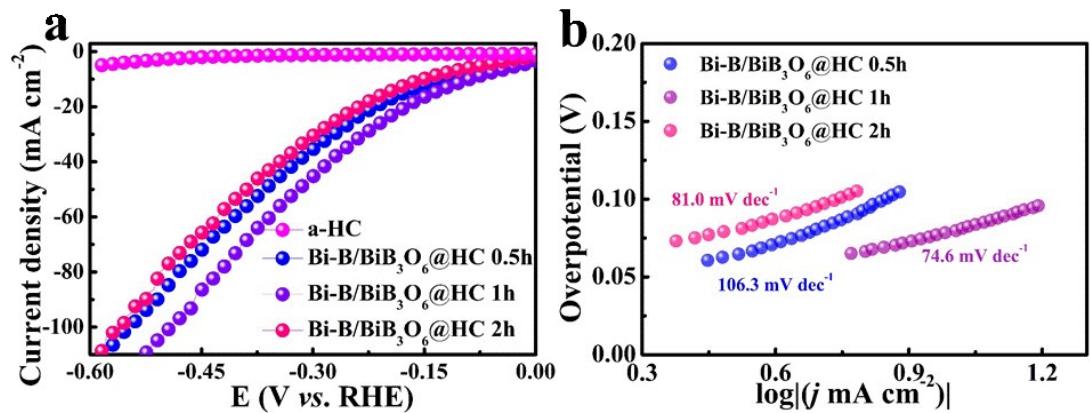
E-mail: [wjhao@usst.edu.cn](mailto:wjhao@usst.edu.cn) [qiangzhang@usst.edu.cn](mailto:qiangzhang@usst.edu.cn)



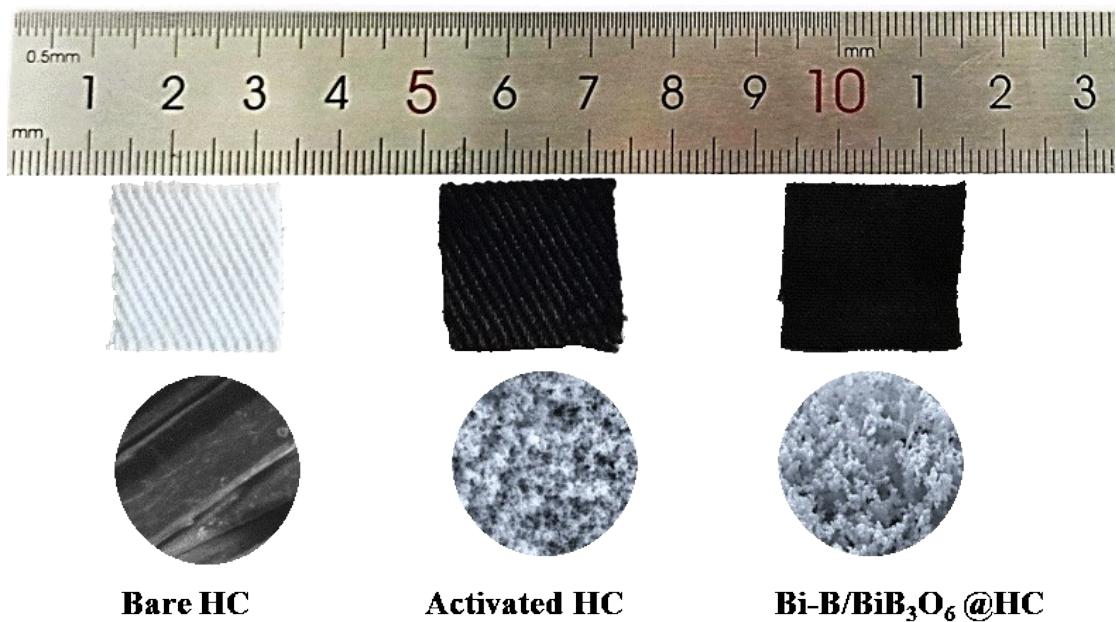
**Fig. S1.** Loading amount of activated Bi-B/BiB<sub>3</sub>O<sub>6</sub> on the HC substrate at different plating time (0.5 h, 1 h and 2 h).



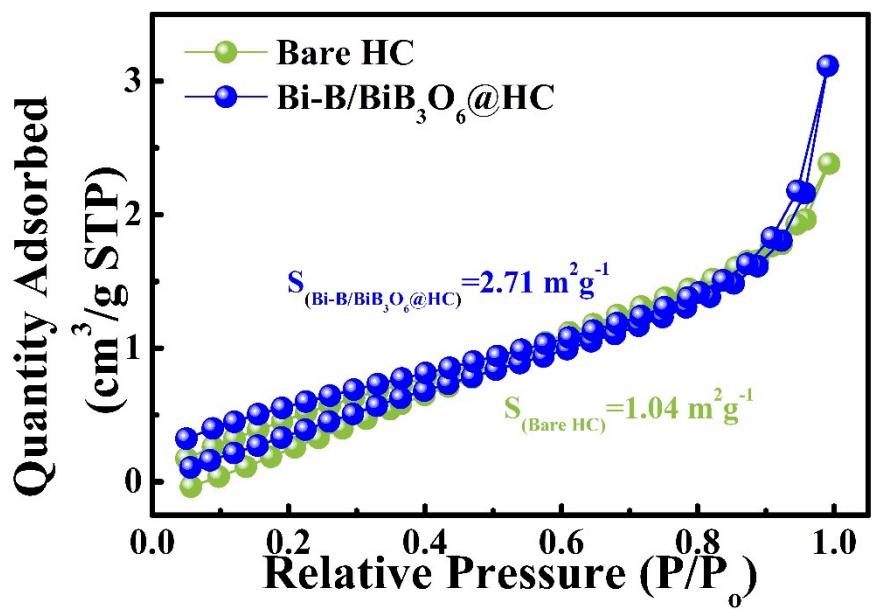
**Fig. S2.** SEM images of Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC electrode during HER process at 25°C. (a<sub>1</sub>), (a<sub>2</sub>): activated HC; (b<sub>1</sub>), (b<sub>2</sub>): 0.5 h; (c<sub>1</sub>), (c<sub>2</sub>): 1 h; (d<sub>1</sub>), (d<sub>2</sub>): 2 h.



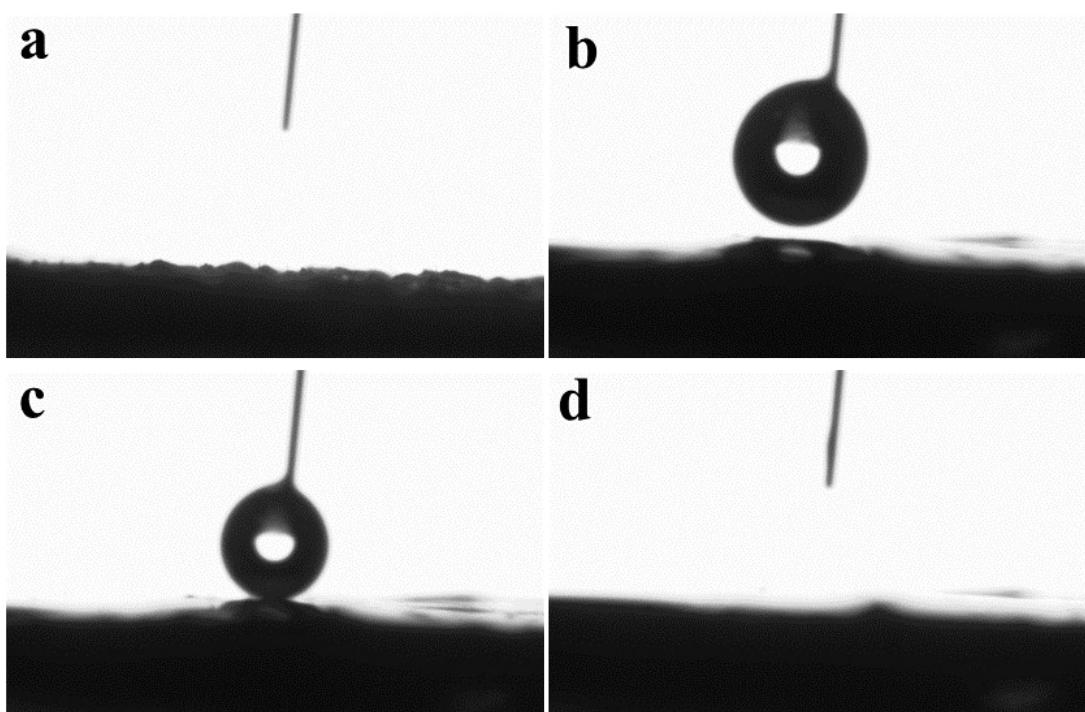
**Fig. S3.** (a) LSV curves; (b) Tafel slopes of Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC electrode at different electroless plating time without *iR*-correction in 1.0 M PBS.



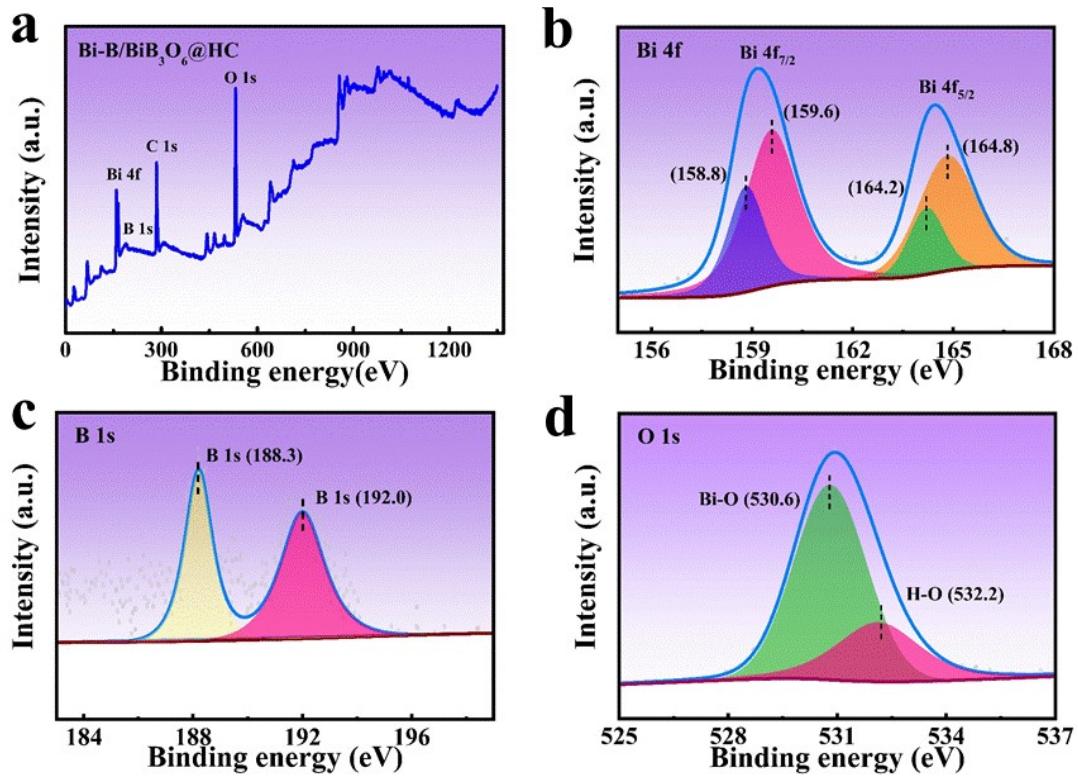
**Fig. S4.** Photograph and SEM images of bare HC, activated HC and Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC electrodes.



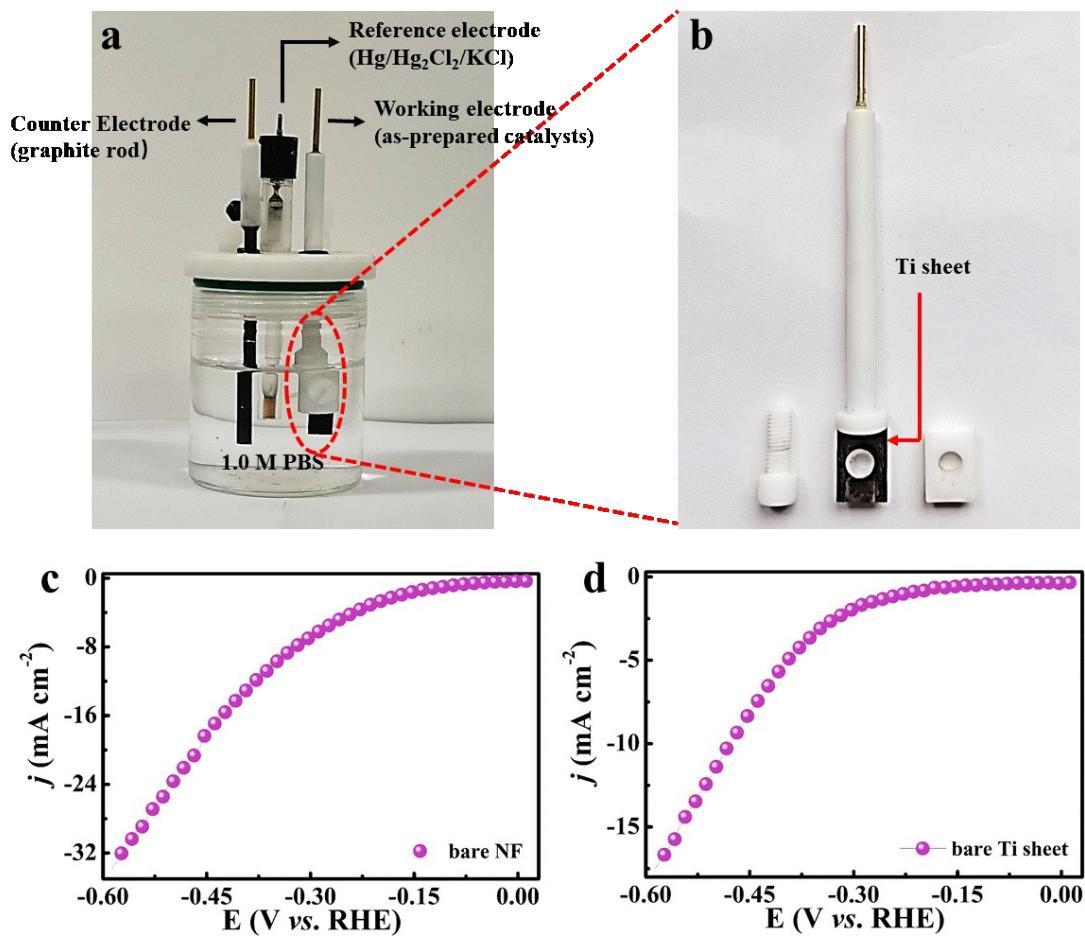
**Fig. S5.** Nitrogen adsorption-desorption isotherm curves of bare HC and Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC electrodes.



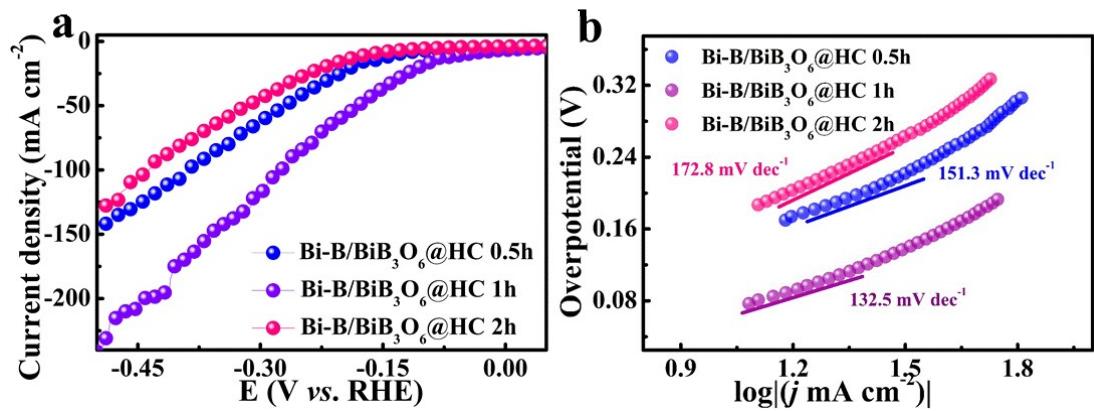
**Fig. S6.** Contact angle measurements of Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC electrode.



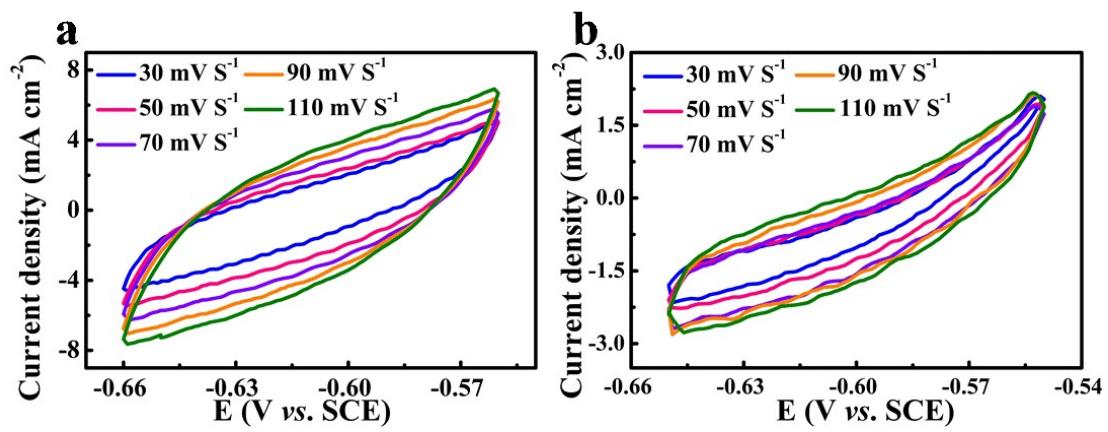
**Fig. S7.** (a) Full XPS patterns of Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC electrode and the corresponding high-resolution. (b) Bi 4f. (c) B 1s. (d) O 1s.



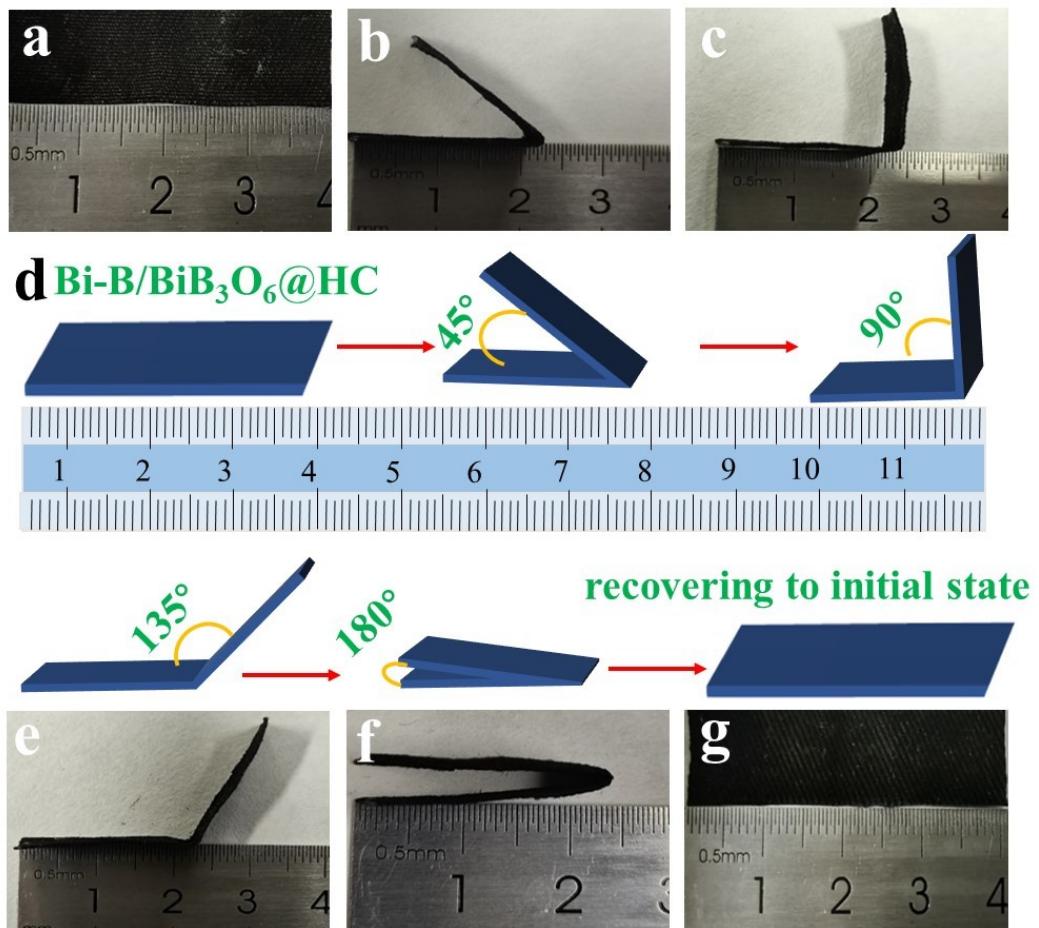
**Fig. S8.** (a) Photograph of the three-electrode cell for neutral water splitting HER measurements; (b) photograph of working electrode; (c) LSV curve of bare NF; (d) LSV curve of bare Ti sheet.



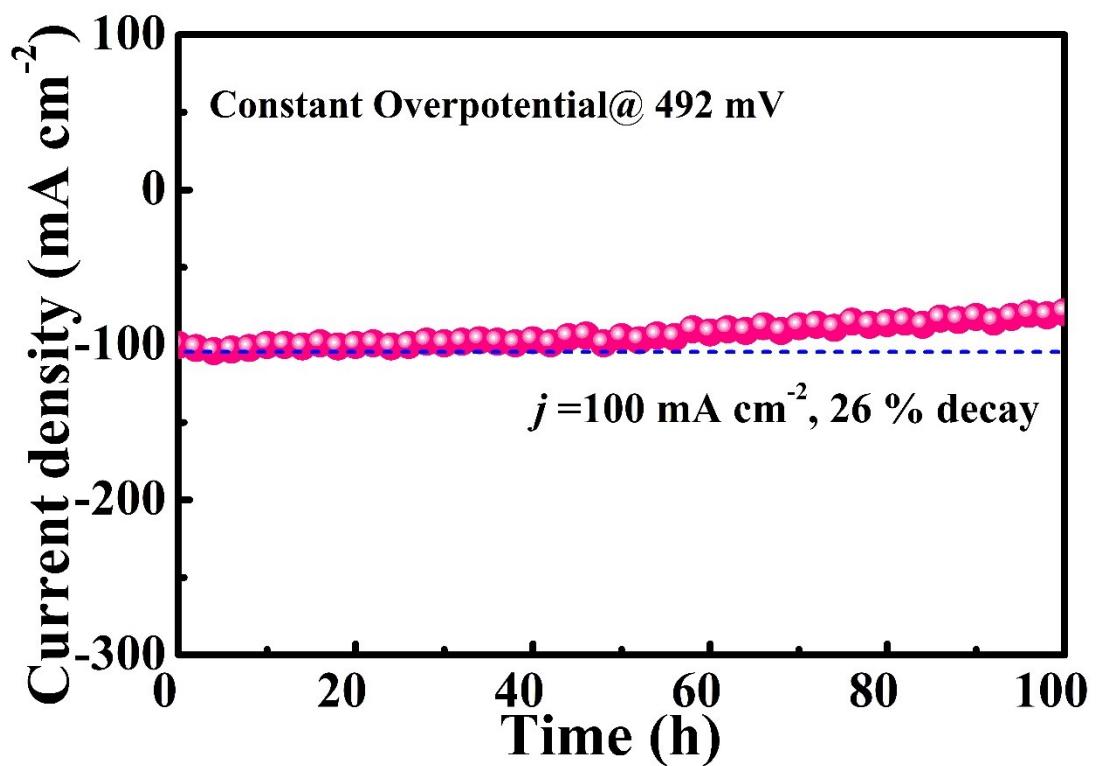
**Fig. S9.** (a) LSV curves; (b) Tafel slopes of  $\text{Bi-B/BiB}_3\text{O}_6@\text{HC}$  electrode at different electroless plating time without  $iR$ -correction in 1.0 M KOH + 0.5 M NaCl.



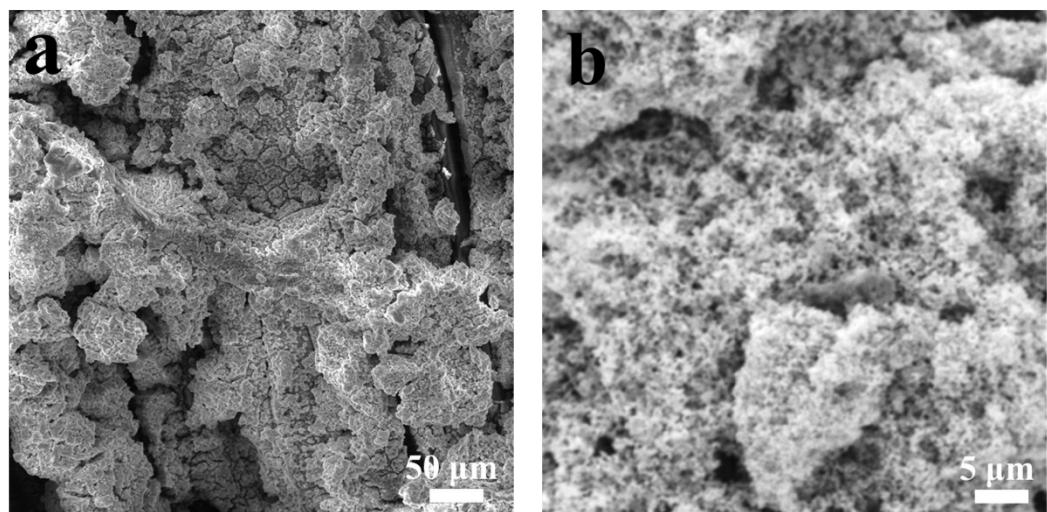
**Fig. S10.** Cyclic voltage (CV) measurements of (a) Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC and (b) Bi-B/BiB<sub>3</sub>O<sub>6</sub>@NF in the non-Faradaic current range at scan rates of 30, 50, 70 ,90 and 110  $\text{mV S}^{-1}$ .



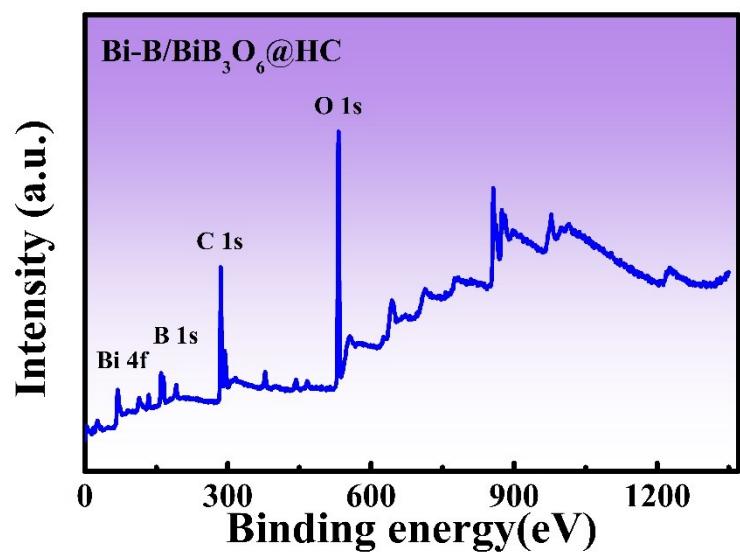
**Fig. S11.** Photograph of folding scheme of Bi-B/Bi<sub>3</sub>O<sub>6</sub>@HC flexible electrode.



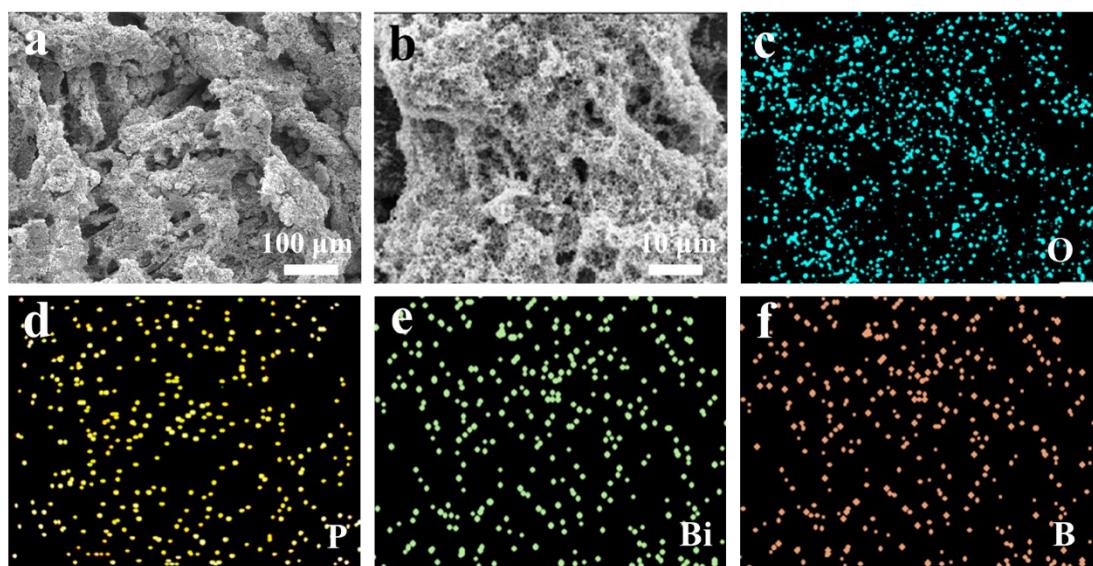
**Fig. S12.** Chronopotentiometric measurements of stability of Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC electrode at the current density of 100 mA cm<sup>-2</sup> for 100 h.



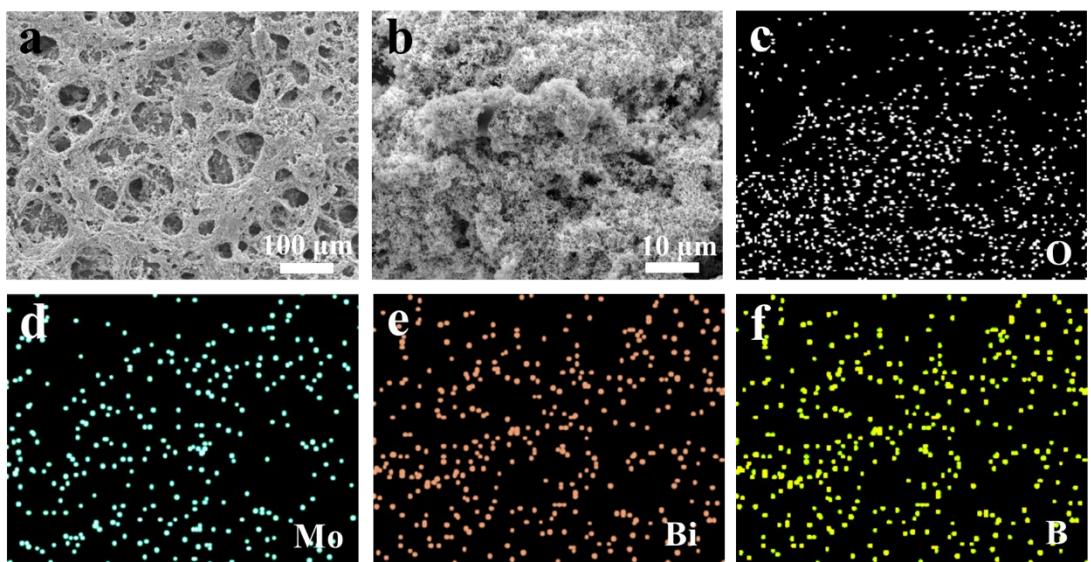
**Fig. S13.** SEM images of chronoamperometric measurements of stability of Bi-BiB<sub>3</sub>O<sub>6</sub>@HC electrode at the current density of 100 mA cm<sup>-2</sup> after 36 h.



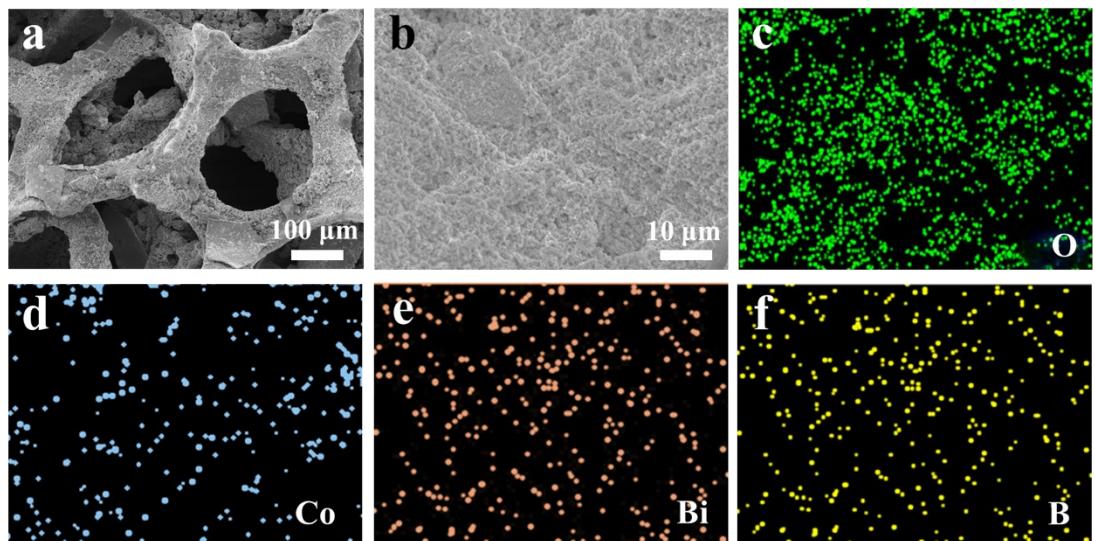
**Fig. S14.** XPS pattern of HER-cycled Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC electrode.



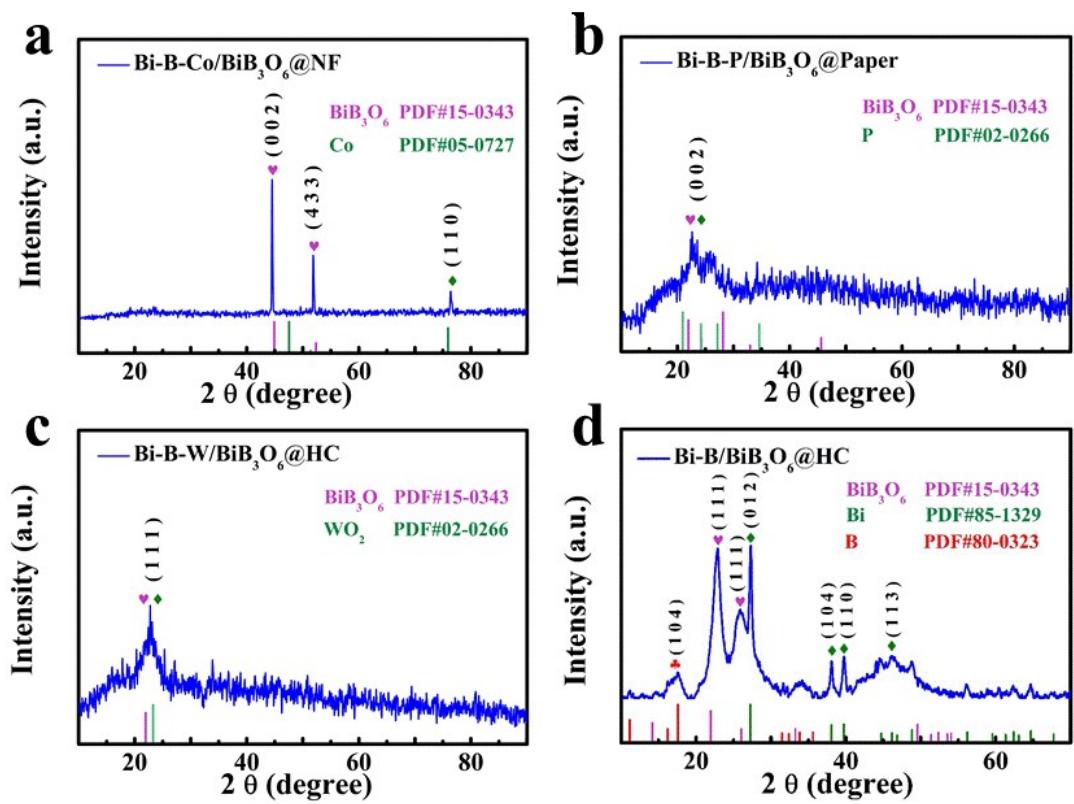
**Fig. S15.** (a-b) SEM images of Bi-B-P/BiB<sub>3</sub>O<sub>6</sub>@HC at different magnification, and corresponding elemental mapping of (c) O element; (d) P element; (e) Bi element; and (f) B element.



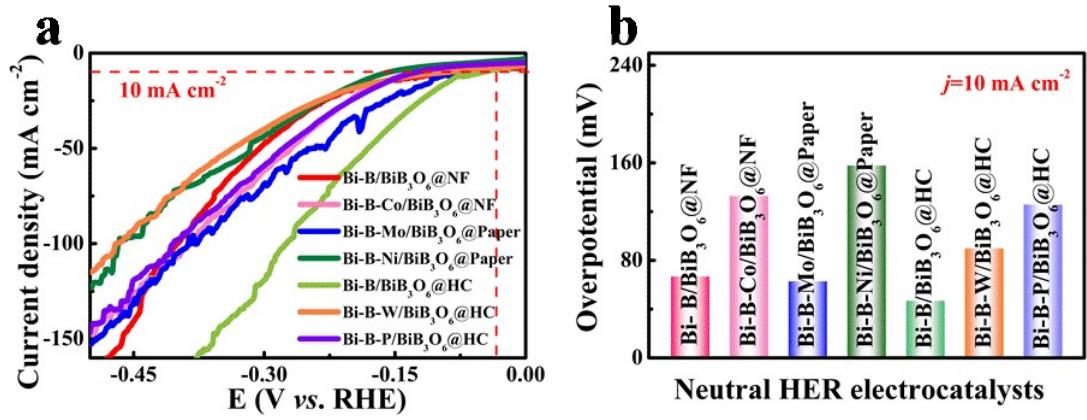
**Fig. S16.** (a-b) SEM images of Bi-B-Mo/BiB<sub>3</sub>O<sub>6</sub>@Paper at different magnification, and corresponding elemental mapping of (c) O element; (d) Mo element; (e) Bi element; and (f) B element.



**Fig. S17.** (a-b) SEM images of Bi-B-Co/BiB<sub>3</sub>O<sub>6</sub>@NF at different magnification, and corresponding elemental mapping of (c) O element; (d) Co element; (e) Bi element; and (f) B element.



**Fig. S18.** XRD patterns of (a) Bi-B-Co/BiB<sub>3</sub>O<sub>6</sub>@NF; (b) Bi-B-P/BiB<sub>3</sub>O<sub>6</sub>@Paper; (c) Bi-B-W/BiB<sub>3</sub>O<sub>6</sub>@HC; and (d) Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC.

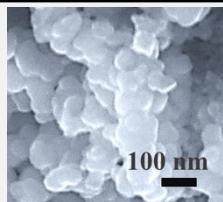
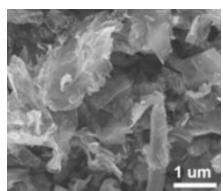
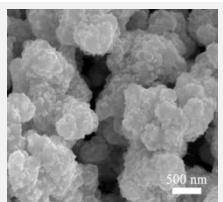
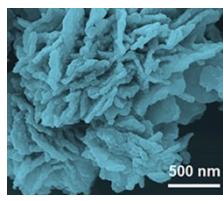
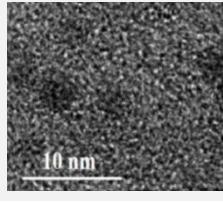
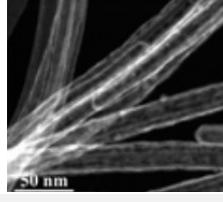
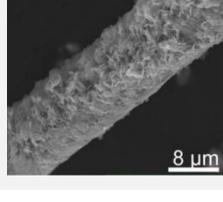


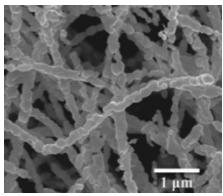
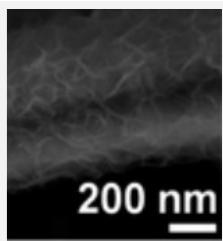
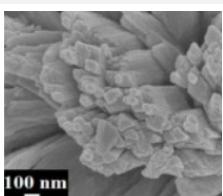
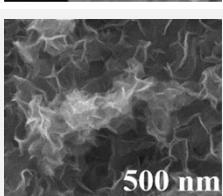
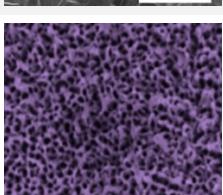
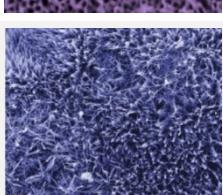
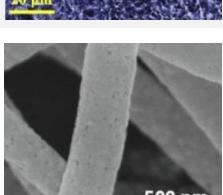
**Fig. S19.** (a) LSV curves and (b) histogram at  $10 \text{ mA cm}^{-2}$  of Bi-B/BiB<sub>3</sub>O<sub>6</sub>@NF, Bi-B-Co/BiB<sub>3</sub>O<sub>6</sub>@NF, Bi-B-Mo/BiB<sub>3</sub>O<sub>6</sub>@Paper, Bi-B-Ni/BiB<sub>3</sub>O<sub>6</sub>@Paper, Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC, Bi-B-W/BiB<sub>3</sub>O<sub>6</sub>@HC and Bi-B-P/BiB<sub>3</sub>O<sub>6</sub>@HC in 1.0 M KOH + 0.5 M NaCl.

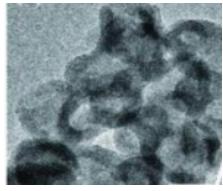
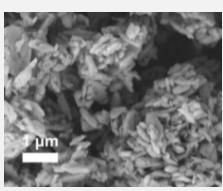
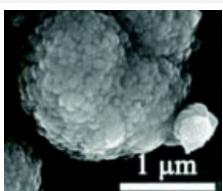
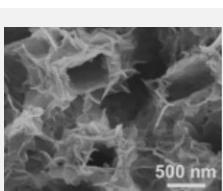
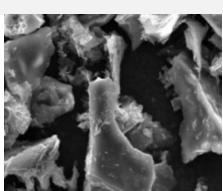
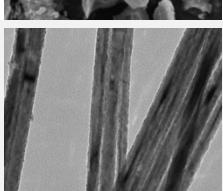
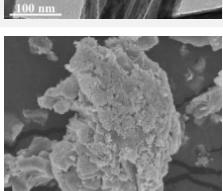
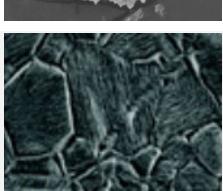
**Table S1.** ICP-AES analysis results of Bi-B based catalytic electrodes.

	B	Bi	Ni	W	Mo	P	Co	Atomic ratio
Bi-B/BiB <sub>3</sub> O <sub>6</sub> @HC	4.52	1.38	-	-	-	-	-	3.28:1
Bi-B/BiB <sub>3</sub> O <sub>6</sub> @HC Post-HER	3.63	1.19	-	-	-	-	-	3.05:1
Bi-B/BiB <sub>3</sub> O <sub>6</sub> @NF	3.5	1.09	-	-	-	-	-	3.21:1
Bi-B-W/BiB <sub>3</sub> O <sub>6</sub> @HC	2.47	0.92	-	0.17	-	-	-	14.52:5.41:1
Bi-B-Ni/BiB <sub>3</sub> O <sub>6</sub> @Paper	3.07	1.03	0.21	-	-	-	-	14.61:4.9:1
Bi-B-Mo/BiB <sub>3</sub> O <sub>6</sub> @Paper	4.10	1.59	-	-	0.272	-	-	15:5.84:1
Bi-B-P/BiB <sub>3</sub> O <sub>6</sub> @HC	4.14	1.34	-	-	-	0.24	-	17.25:5.58:1
Bi-B-Co/BiB <sub>3</sub> O <sub>6</sub> @NF	3.36	1.08	-	-	-	-	0.22	15.27:4.9:1

**Table S2.** Comparison of the HER performance of Bi-B/BiB<sub>3</sub>O<sub>6</sub>@HC with other electrocatalysts in PBS according to Figure 2h.

Catalysts	Electrolyte	$\eta_{10}$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	Morphology	Reference
Bi-B/BiB <sub>3</sub> O <sub>6</sub> @HC	1.0 M PBS	88.5	74.6		This work
MoS <sub>2</sub> /NLG-3	1.0 M PBS	142	72.9		1
Co-Ni-P/NF	1.0 M PBS	95	151		2
pFe/FeP	1.0 M PBS	125	66		3
Ru/GC	1.0 M PBS	115	173.7		4
RhCu NWs- 2	0.1 M PBS	165	211		5
NSOC/CS	1.0 M PBS	103	113.7		6

NiRh <sub>2</sub> O <sub>4</sub>	1.0 M PBS	156	224.4		7
CoMoNiS-NF-31	1.0 M PBS	117	56		8
Fe-CoP	1.0 M PBS	134	50.1		9
MoS <sub>2</sub> /NVO	1.0 M PBS	96	70		10
S-MoP	1.0 M PBS	140	98		11
Cu@WC	1.0 M PBS	173	119		12
Co, Mo <sub>2</sub> C-CNF	1.0 M PBS	206	92.8		13
CoSAs-MoS <sub>2</sub> /TiN NRs	1.0 M PBS	203	82.7		14

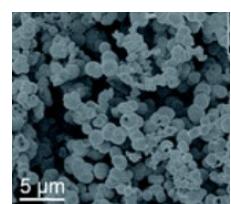
WS <sub>2</sub> /CoS <sub>2</sub> /CC	1.0 M PBS	175	81		15
TM-Mo <sub>2</sub> C@NCF	1.0 M PBS	109	110		16
Cu-Ni <sub>3</sub> S <sub>2</sub>	1.0 M PBS	128	151.0		17
Mo-CoP/NC/TF	1.0 M PBS	130	84.1		18
K-G <sub>4.0</sub> T <sub>2.0</sub> Mo <sub>1.0</sub>	pH=7	150	197.2		19
RuCu NWs	0.01 M PBS	190	314		20
Co <sub>9</sub> S <sub>8</sub> /NF	1.0 M PBS	193.9	168.3		21
Karst NF	1.0 M PBS	110	99		22

$\text{NiS}_{2(1-x)}\text{Se}_{2x}$

1.0 M PBS

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