

*Electronic Supplementary Information*

**Constructing Urchin-Like Ni<sub>3</sub>S<sub>2</sub>@Ni<sub>3</sub>B on Ni Plate as a Highly Efficient Bifunctional Electrocatalyst for Water Splitting Reaction**

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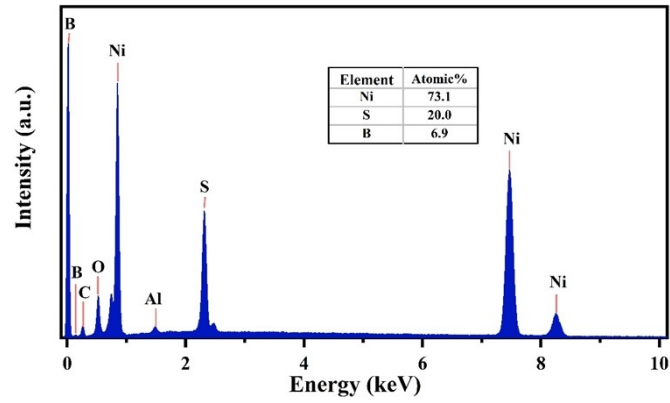
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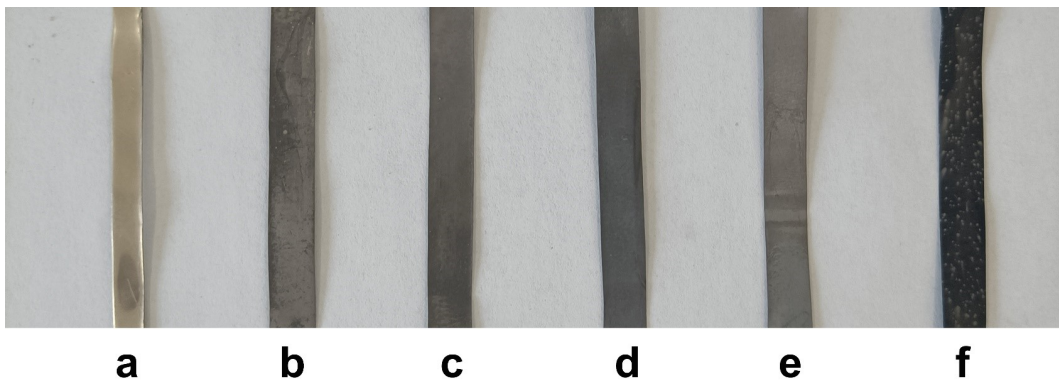
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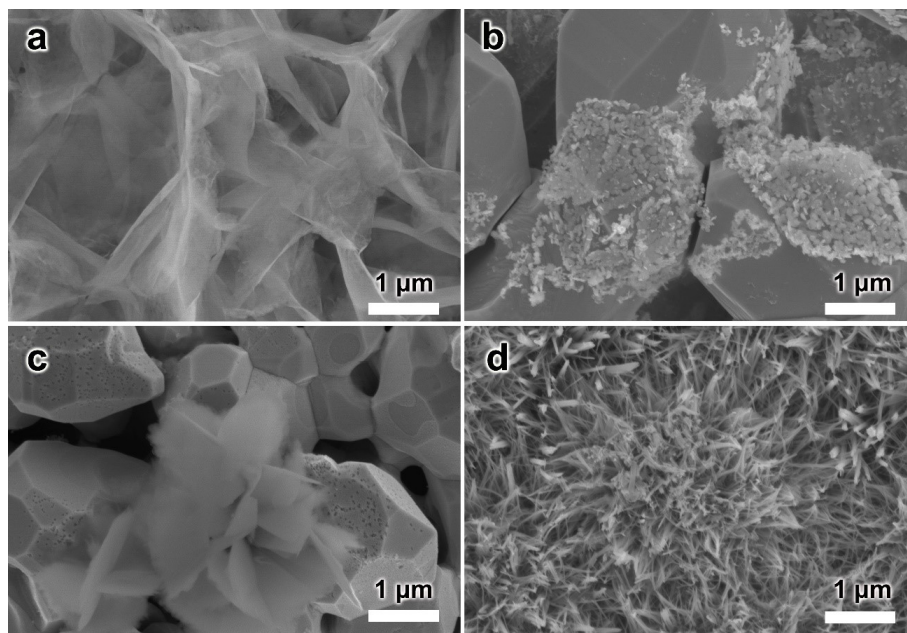
**Fig. S1.** the EDS spectrum and corresponding element contents of  $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{B}$



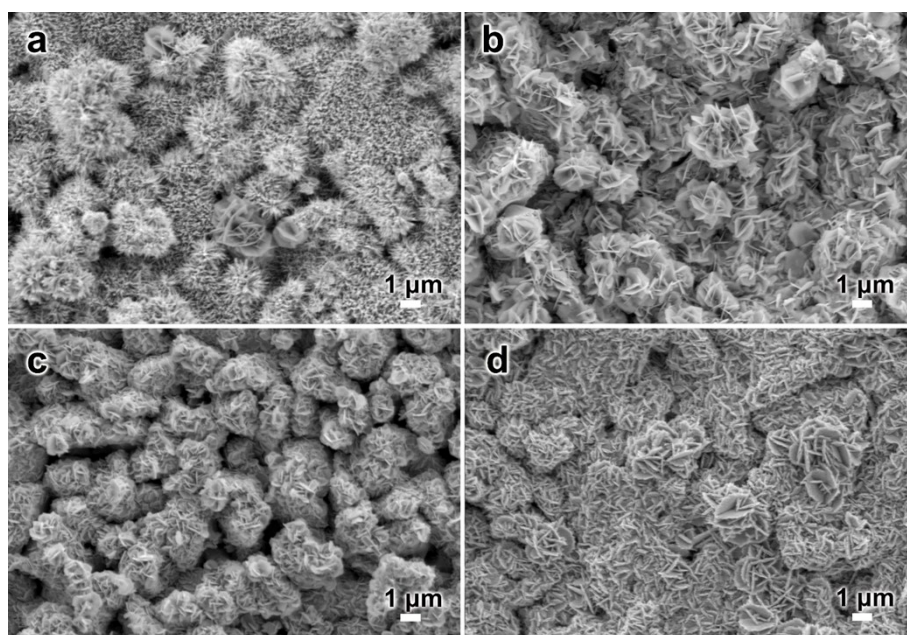
**Fig. S2.** Photograph of (a) Ni plates, (b)  $\text{Ni}_3\text{B}/\text{NP}$ , (c)  $\text{Ni}_3\text{B}/\text{NP}-1$ , (d)  $\text{Ni}_3\text{B}/\text{NP}-2$ , (e)  $\text{Ni}_3\text{B}/\text{NP}-3$  and (f)  $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{B}/\text{NP}$ .

**Table S1.** Comparison of the pH of solutions containing different components.

Solution composition	pH
$\text{CO}(\text{NH}_2)_2$	9.25
$\text{NH}_4\text{F}$	6.56
$\text{CO}(\text{NH}_2)_2 + \text{NH}_4\text{F}$	8.68
$\text{CO}(\text{NH}_2)_2 + \text{NH}_4\text{F} + \text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	8.75



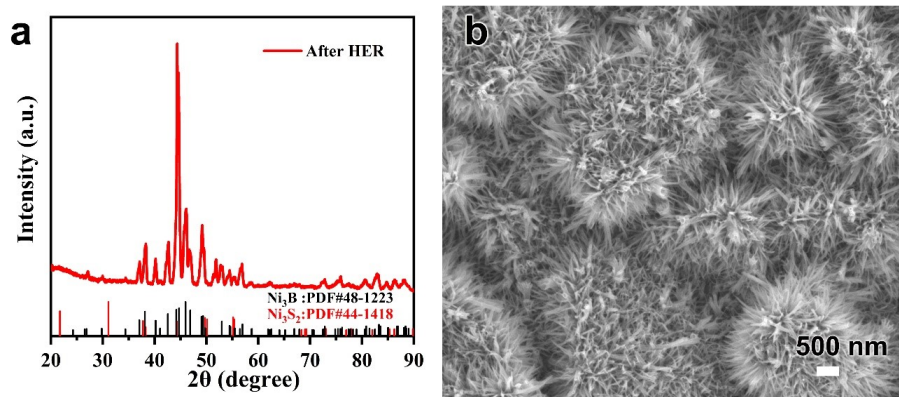
**Fig. S3.** SEM images of (a)  $\text{Ni}_3\text{B/NP-1}$ , (b)  $\text{Ni}_3\text{B/NP-2}$ , (c)  $\text{Ni}_3\text{B/NP-3}$  and (d)  $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{B/NP}$ .



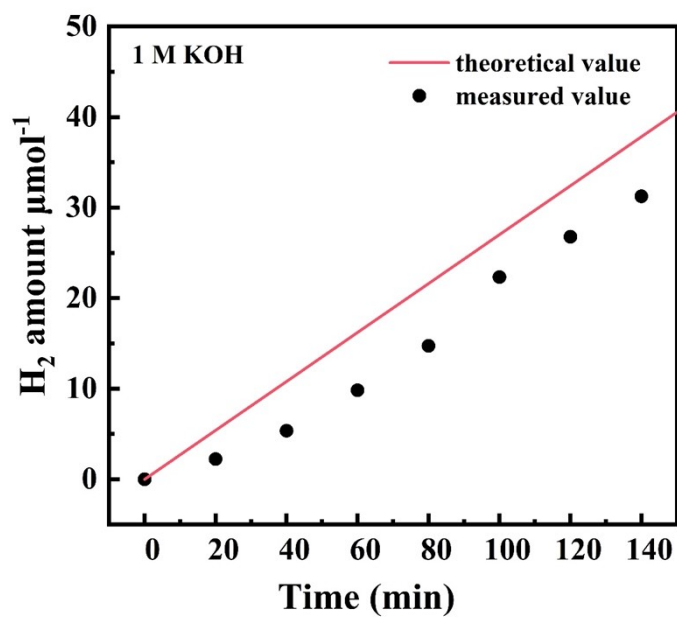
**Fig. S4.** SEM images of different sulfur ion concentrations (a) 80 mL, (b) 120 mL, (c) 160 mL and (d) 200 mL for sulfide reactions.

**Table S2.** The simulated series resistance ( $R_s$ ) and charge transfer resistance ( $R_{ct}$ ) based on the Nyquist plots (Figure 4a) in the presence of  $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{B}/\text{NP}$ ,  $\text{Ni}_3\text{S}_2/\text{NP}$  and  $\text{Ni}_3\text{B}/\text{NP}$ .

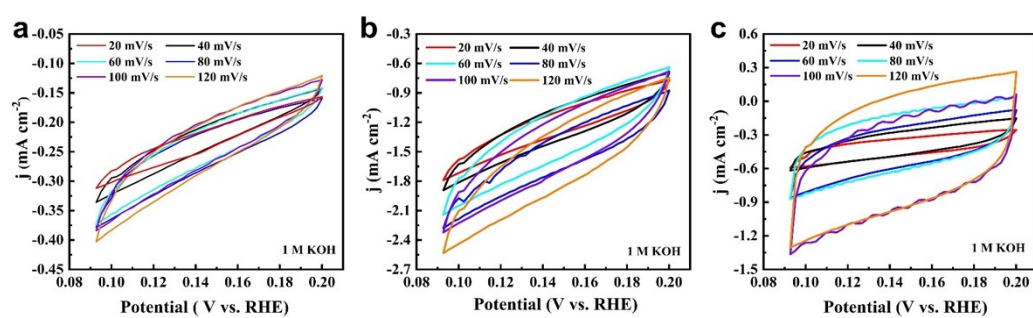
Sample	$R_s$ ( $\Omega \text{ cm}^2$ )	$R_{ct}$ ( $\Omega \text{ cm}^2$ )
$\text{Ni}_3\text{S}_2@\text{Ni}_3\text{B}/\text{NP}$	0.44	4.83
$\text{Ni}_3\text{B}/\text{NP}$	0.28	12.41
$\text{Ni}_3\text{S}_2/\text{NP}$	0.59	9.95



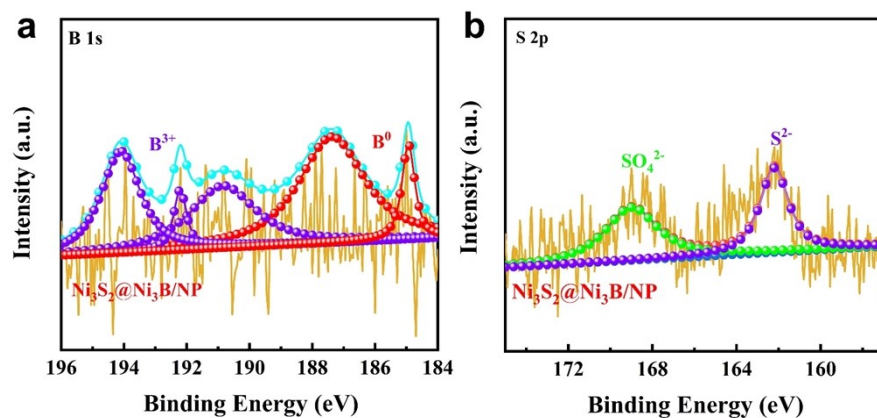
**Fig. S5.** (a) XRD pattern and (b) SEM image of  $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{B}/\text{NP}$  after HER.



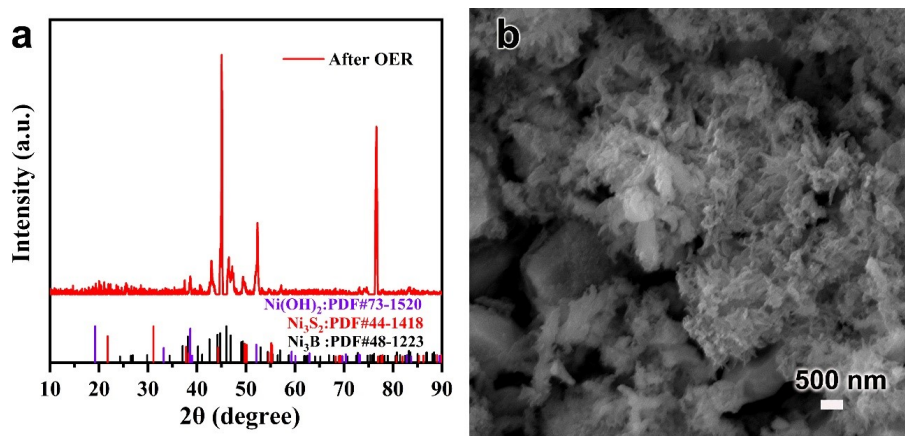
**Fig. S6.** Faradaic efficiency of Ni<sub>3</sub>S<sub>2</sub>@Ni<sub>3</sub>B/NP for HER.



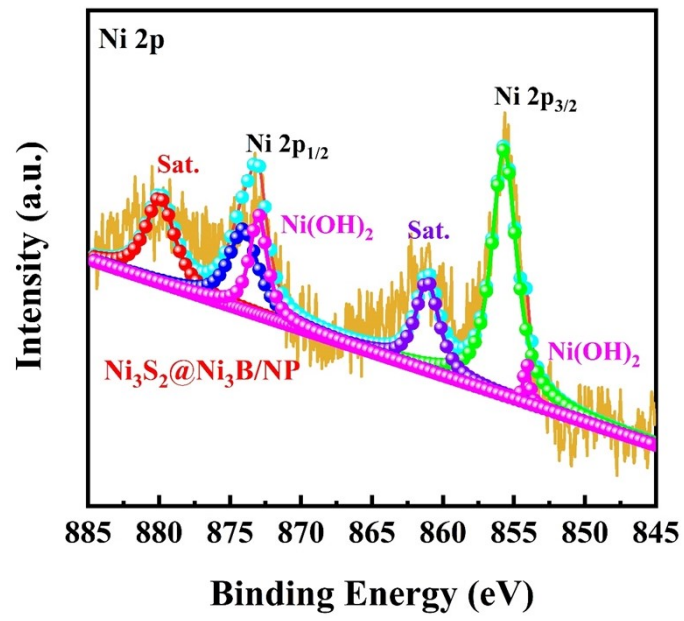
**Fig. S7.** Cyclic Voltammetry curves of (a) Ni<sub>3</sub>B, (b) Ni<sub>3</sub>S<sub>2</sub> and (c) Ni<sub>3</sub>S<sub>2</sub>@Ni<sub>3</sub>B/NP.



**Fig. S8.** High-resolution XPS spectra of (a) B 1s and (b) S 2p in Ni<sub>3</sub>S<sub>2</sub>@Ni<sub>3</sub>B/NP.



**Fig. S9.** (a) XRD pattern and (b) SEM images of Ni<sub>3</sub>S<sub>2</sub>@Ni<sub>3</sub>B/NP after OER.



**Fig. S10.** High-resolution XPS spectra of  $\text{Ni}_3\text{S}_2@\text{Ni}_3\text{B}/\text{NP}$  after OER.

**Table S3.** Comparison of the electrocatalytic performance of Ni<sub>3</sub>S<sub>2</sub>@Ni<sub>3</sub>B/NP with some representative electrocatalysts reported recently for HER and OER.

Catalyst	Electrolyte solution	HER/OER	Current density (j)	Overpotential ( $\eta$ )	Stability test	Reference
Ni <sub>3</sub> S <sub>2</sub> @Ni <sub>3</sub> B/NP	1 M KOH	HER	10 mA cm <sup>-2</sup> 100 mA cm <sup>-2</sup> 1000 mA cm <sup>-2</sup>	182 mV 304 mV 517 mV	100 h	This work
		OER	10 mA cm <sup>-2</sup> 100 mA cm <sup>-2</sup> 1000 mA cm <sup>-2</sup>	288 mV 383 mV 632 mV		
Ni <sub>3</sub> B/NP	1 M KOH	OER	10 mA cm <sup>-2</sup>	300 mV	1500 h	J. Mater. Chem. A, 2019, 7, 5288.
Ni-Fe-OH@Ni <sub>3</sub> S <sub>2</sub> /NF	1 M KOH	OER	100 mA cm <sup>-2</sup>	300 mV	50 h	Adv. Mater., 2017, 29, 1606200.
Ni <sub>3</sub> S <sub>2</sub> /NF	1 M KOH	HER	10 mA cm <sup>-2</sup>	223 mV	200 h	J. Am. Chem. Soc. 2015, 137, 14023.
		OER		260 mV		
boronized NiFe	1 M KOH	OER	10 mA cm <sup>-2</sup>	309 mV	3000 h	Energy Environ. Sci., 2019, 12, 684.
Zr <sub>0.8</sub> Ni <sub>0.2</sub> B <sub>2</sub>	1 M KOH	OER	10 mA cm <sup>-2</sup>	350 mV	12 h	Electrochim. Acta, 2021, 389, 138789.
Zr <sub>0.8</sub> Co <sub>0.2</sub> B <sub>2</sub>		HER		420 mV	12 h	
Co-B@Co-Bi	1 M KOH	OER	10 mA cm <sup>-2</sup>	291 mV	25 h	ACS Sustainable Chem. Eng., 2019, 7, 5620.
Ni <sub>1</sub> Co <sub>3</sub> @BC	1 M KOH	OER	10 mA cm <sup>-2</sup>	309 mV	20 h	Appl. Surf. Sci., 2020, 532, 147381.
Cu(OH) <sub>2</sub> NRs@Ni(OH) <sub>2</sub> NSs	1 M KOH	HER	10 mA cm <sup>-2</sup>	200 mV	20 h	ChemistrySelect, 2021, 6, 4129.
Ni <sub>3</sub> S <sub>2</sub> /NF	1 M KOH	HER	10 mA cm <sup>-2</sup>	189 mV	50 h	J. Mater. Chem. A, 2019 7, 18003.
		OER	10 mA cm <sup>-2</sup>	296 mV	5000 s	
Ni <sub>3</sub> S <sub>2</sub> @Co(OH) <sub>2</sub>	1 M KOH	OER	10 mA cm <sup>-2</sup>	290 mV	40 h	Int. J. Hydrogen Energ., 2019, 44, 22955.