## **Electronic Supplementary Information**

Phosphine Vapor-assisted Construction of Heterostructured  $Ni_2P/NiTe_2$  Catalysts for Efficient Hydrogen Evolution

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**Fig. S1.** (a)  $Ni_2P/NiTe_2$  electrode in 0.5 M  $H_2SO_4$  without applying a cathodic potential. (b) The stability of the  $Ni_2P/NiTe_2$  electrode at a current density of -50 mA cm<sup>-2</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



Fig. S2. Digital image of the prepared NiTe and  $Ni_2P/NiTe_2$  electrodes.



Fig. S3. SEM images of (a) NiTe and (b)  $Ni_2P/NiTe_2$  nanosheets prepared with 12 mmol  $NaH_2PO_2$ .



Fig. S4. The side view and top view of the (011) and (101) planes of the NiTe hexagonal structure.

It should be noted that in hexagonal structure of the same material, (101) and (011) are crystallographically equivalent, because they are in the same family of planes of NiTe (Hexagonal,  $a=b\neq c$ ,  $\alpha=\beta=90^{\circ}$ ,  $\gamma=120^{\circ}$ ), by extension, {011} family. Fig. S4 also demonstrates the same structure of (101) and (011) of NiTe. Therefore, these two planes have the same surface structure and same *d* spacing of 2.9 Å. Thus, both of descriptions in the present work and literatures are valid and either one can be used.



Fig. S5. XRD patterns of NiTe before and after annealing in Ar.



Fig. S6. XRD patterns of NiTe, Ni2P and NiTe annealed with red phosphorous (P-NiTe)inAr.



Fig. S7. High-resolution XPS spectra on P2p of Ni<sub>2</sub>P/NiTe<sub>2</sub>.



**Fig. S8.** High resolution XPS spectra of (a) Ni2p, (b) Te3d and (c) P2p of different amount NaH<sub>2</sub>PO<sub>2</sub> (0 mmol, 6 mmol, 12 mmol and 18 mmol) treated NiTe catalysts.

To investigate the electronic interaction between Ni<sub>2</sub>P and NiTe<sub>2</sub>, the XPS spectra for all the prepared samples with different molar concentration of P precursors (from 0 mmol NaH<sub>2</sub>PO<sub>2</sub> to 18 mmol NaH<sub>2</sub>PO<sub>2</sub>) were carried out. In Fig. S8a for Ni2p XPS, the peaks at around 856.3 eV and 874.0 eV can be assigned to Ni<sup>2+</sup> 2p3/2 and Ni<sup>2+</sup> 2p1/2 of Ni<sub>2</sub>P/NiTe<sub>2</sub> or Ni<sub>2</sub>P/NiTe, respectively. The other two peaks at about 853.2 eV and 871.7 eV belong to Ni<sup>0</sup> derived from nickel foam. For Te3d XPS in Fig. S8b, the peaks at 572.9 eV and 583.3 eV correspond to Te<sup>2-</sup> 3d5/2 and Te<sup>2-</sup> 3d3/2 of NiTe<sub>2</sub> and NiTe in Ni<sub>2</sub>P/NiTe<sub>2</sub> or Ni<sub>2</sub>P/NiTe, respectively. For P2p, the XPS peaks at 129.7 eV and 134.0 eV corresponds to metal phosphide and phosphate, respectively. As seen from Fig. S8a-c, there is no obvious XPS peaks shift for the prepared samples, which indicates the electronic interaction between Ni<sub>2</sub>P and NiTe<sub>2</sub> are not the reason for the enhanced HER activity.

Additionally, we have measured metal phosphide/phosphate peak data ratio from XPS. As shown in Fig. S8c, the XPS peaks data ratios for metal phosphide/phosphate are 8.9%, 12.3% and 16.2%, respectively, with the increment of the amount of  $NaH_2PO_2$  from 6 mmol to 18 mmol, indicating a higher degree of metal phosphide formed at high  $NaH_2PO_2$  concentration.



Fig. S9. The HER polarization curves of NiTe and pure nickel foam.



Fig. S10. The HER polarization curves of  $Ni_2P/NiTe_2$  prepared with different amount of  $NaH_2PO_2$  precursor.



Fig. S11. XRD patterns of  $Ni_2P/NiTe_2$  prepared with different amount of  $NaH_2PO_2$  precursor.



Fig. S12. SEM image of  $Ni_2P/NiTe_2$  on NF (a) and its magnified morphology (b, c)preparedwith18mmol $NaH_2PO_2$ precursor.



Fig. S13. AFM topographic images with height profiles of NiTe nanosheets.



Fig. S14. AFM topographic images with height profiles of  $Ni_2P/NiTe_2$  nanosheets prepared with 12 mmol  $NaH_2PO_2$  as  $PH_3$  precursor.



Fig. S15. AFM topographic images with height profiles of  $Ni_2P/NiTe_2$  nanosheets prepared with 18 mmol  $NaH_2PO_2$  as  $PH_3$  precursor.



Fig. S16. Tafel plots of NiTe,  $Ni_2P$  and  $Ni_2P/NiTe_2$  to calculate the exchange current density.



**Fig. S17.** Time-dependent potential curves of the  $Ni_2P/NiTe_2$  electrode under a static current density of -50 mA cm<sup>-2</sup> without iR correction for 50 h.



Fig. S18. XRD patterns of Ni<sub>2</sub>P/NiTe<sub>2</sub> before and after HER stability test.



Fig. S19. TEM-EDS mapping of Ni<sub>2</sub>P/NiTe<sub>2</sub> after HER stability test.



Fig. S20. XPS of Ni<sub>2</sub>P/NiTe<sub>2</sub> before and after HER stability test.

We have compared the XPS spectra of the Ni<sub>2</sub>P/NiTe<sub>2</sub> catalyst before and after HER stability. As shown in Fig. S20a, the peaks at around 852.8 eV and 871.7 eV are attributed to Ni<sup>0</sup> from the nickel foam substrate, which can also be observed before the stability test. The existence of Ni2p3/2 and Ni2p1/2 peaks can be assigned to Ni<sup>2+</sup> oxidation state in the Ni<sub>2</sub>P/NiTe<sub>2</sub> composite. In addition, by comparing the XPS spectra before and after stability, we have not observed clear shift of binding energies at Ni2p. However, a positive binding energy shift were observed at the Te3d and P2p XPS spectra after HER, which can be attributed to the oxidation when the sample was exposed to air or the oxidation of the element by the dissolved oxygen in the electrolyte. For the valence state of Te, the peaks at Te3d5/2 and Te3d3/2 correspond to  $Te^{2-}$  in the Ni<sub>2</sub>P/NiTe<sub>2</sub> catalyst (Fig. S20b), while the corresponding satellite peaks result from the oxidation of Te on the surface. For P2p in Fig. S20c, both metal phosphide and phosphate were observed before and after HER, however, different from the slightly positive shifted metal phosphate peak, the metal phosphide peak shows less change, demonstrating the formed Ni<sub>2</sub>P are stable during long-term water electrolysis.



**Fig. S21.** Theoretical *vs.* experimental amounts of  $H_2$  during bulk water electrolysis. The electrolysis was carried out in a two compartment gastight H-cell at a potential of -1.2 V (*vs.* SCE) and the generated  $H_2$  is detected online by a gas chromatograph system at the electrolysis time of 8 min, 16 min and 24 min, respectively.

The plot of the theoretical and experimental amounts of  $H_2$  against time is shown in Fig. S21. The electrolysis was carried out in a two compartment gastight H-cell at a potential of -1.2 V (*vs.* SCE) and the generated  $H_2$  is detected online by a gas chromatograph system, respectively. The Faradaic efficiency (FE) was calculated to be 99.2 ± 1% by using the following equation.

$$FE = \frac{2FV\upsilon p_0}{RT_0 I} \times 100\%$$
$$FE = \frac{2 \times 96,485 \times V\upsilon \times 1.01 \times 10^5}{8.314 \times 298.15 \times I} \times 100\% = \frac{0.315 \times V \times \upsilon}{I} \times 100\%$$

FE = Faradaic efficiency; v = volume concentration of H<sub>2</sub> in the exhaust gas from the cell; V = Ar flow rate (20 mL min<sup>-1</sup>).



Fig. S22. CV charging current measured in a non-Faradaic potential range at differentscanratesforthepreparedelectrodes.



Fig. S23. ECSA-normalized HER polarization curves of the fabricated electrodes.



**Fig. S24.** EIS Nyquist plots of different electrode at overpotential ( $\eta$ ) = 200 mV.



**Fig. S25.** The top (up) and side (down) views of theoretical model structures of (a)  $Ni_2P(111)$ , (b)  $NiTe_2(011)$ , (c) NiTe(011), (d)  $Ni_2P/NiTe_2(011)$ , and (e)  $Ni_2P/NiTe(011)$ . The steel blue, dark orange and magenta balls represent Ni, Te and P atoms, respectively.



**Fig. S26.** The calculated reaction energy diagram of water dissociation on NiTe<sub>2</sub>(011), NiTe(011), Ni<sub>2</sub>P/NiTe<sub>2</sub>(011) and Ni<sub>2</sub>P/NiTe(011).

For alkaline HER, the water dissociation reaction is considered as a key rate determining step. Fig. S26 shows the calculated reaction energy diagram of water dissociation on NiTe<sub>2</sub>(011), NiTe(011), Ni<sub>2</sub>P/NiTe<sub>2</sub>(011) and Ni<sub>2</sub>P/NiTe(011). The energy barriers for water dissociation are 1.85 eV and 1.78 eV on NiTe(011) and NiTe<sub>2</sub>(011), respectively, and such high energy barriers clearly hinders the dissociation of water on NiTe(011) and NiTe<sub>2</sub>(011). However, the water dissociation barrier is reduced to 1.45 eV on Ni<sub>2</sub>P/NiTe<sub>2</sub>(011) surface, which indicate Ni<sub>2</sub>P/NiTe<sub>2</sub>(011) surface can promote water dissociation substantially and increase the rate of H\* formation.



**Fig. S27.** The top (up) and side (down) views of the optimized structures of  $H^*$  adsorbed on (a) Ni<sub>2</sub>P(111), (b) NiTe<sub>2</sub>(011), and (c) NiTe(011). The steel blue, dark orange, magenta and white balls represent Ni, Te, P and H atoms, respectively.



Fig. S28. The top (up) and side (down) views of the optimized structures of (a) NiTe (101) and (b) Ni<sub>2</sub>P/NiTe(101). The top (up) and side (down) views of the optimized structures of H\* adsorbed on (c) NiTe(101) and Ni<sub>2</sub>P/NiTe(101). The calculated  $\Delta G_{H^*}$  are listed below.

To further elucidate the NiTe (011) plane is the same as NiTe (101) plane that widely used in the literatures, we have calculated the free energy of H\*  $\begin{pmatrix} \Delta G \\ H^* \end{pmatrix}$  at NiTe(101) and Ni<sub>2</sub>P/NiTe(101) as well. The calculation results show that they have the same value of 0.54 eV and 0.16 eV, respectively, as that calculated on NiTe(011) and Ni<sub>2</sub>P/NiTe(011), because they are in the same family of planes of NiTe, that is the {011} family.



Fig. S29. XRD patterns of  $Ni_3S_2$  and  $Ni_2P/NiS_2$ .



**Fig. S30.** (a) TEM and (b-d) the corresponding elemental mapping images for Ni, S, P and (e) the overlapping of S and P elements in  $Ni_2P/NiS_2$  nanosheets.



Fig. S31. CV charging current measured in a non-Faradaic potential range at differentscanratesforthepreparedsamples.



Fig. S32. Extraction of the  $C_{dl}$  from  $Ni_3S_2$  and  $Ni_2P/NiS_2$  electrodes.



Table S	1. Compa	rison	of the N	i <sub>2</sub> P/NiT	e <sub>2</sub> electrode	HER ca	atalytic	ac	tivity	with
recently	reported	HER	catalysts	from	non-precious	materi	als in	1	М	KOH.

Catalysts	η (mV) at 10	Catalyst	Reference			
	mA cm <sup>-2</sup>	loading				
		[mg cm <sup>-2</sup> ]				
Ni <sub>2</sub> P/NiTe <sub>2</sub> /NF	62	1.4	This work			
Ni <sub>3</sub> N-VN/NF	64	1.5	<i>Adv. Mater</i> , <b>2019</b> , 31, 1901174.			
Co-NiS <sub>2</sub> /NF	80	1.02	<i>Angew. Chem. Int. Ed</i> , <b>2019</b> , 58, 18676.			
NiCo <sub>2</sub> S <sub>4</sub> /NF	110	N/A	<i>Adv. Funct. Mater</i> , <b>2019</b> , 29, 1807031.			
CoP/NPC/TF	80	1.5	<i>Adv. Energy Mater</i> , <b>2019</b> , 9, 1803970.			
Ni <sub>11</sub> (HPO <sub>3</sub> ) <sub>8</sub> (OH) <sub>6</sub> /NF	121	3	<i>Energy Environ. Sci</i> , <b>2018</b> , 11, 1287.			
Se-(NiCo)Sx/(OH)/NF	103	N/A	<i>Adv. Mater</i> , <b>2018</b> , 30, 1705538.			
Co-MoS <sub>2</sub> /CFP	48	2	<i>Adv. Mater</i> , <b>2018</b> , 30, 1801450.			
Mo-Ni <sub>2</sub> P/NF	78	1.13	Nanoscale, 2017, 9 16674.			
h-niSx/NF	60	142.2	<i>Adv. Energy Mater</i> , <b>2016</b> , 6, 1502333.			
NiSe/NF	96	2.8	<i>Angew. Chem. Int. Ed</i> , <b>2015</b> , 54, 9351.			
MoSe <sub>2</sub> /Ni <sub>0.85</sub> Se/NF	117	6.48	ACS Cent. Sci, <b>2017</b> , 4, 112.			
NiFe LDH@NiCoP/NF	120	2	<i>Adv. Funct. Mater</i> , <b>2018</b> , 28, 1706847			
CeO <sub>2</sub> /Cu <sub>3</sub> P/NF	148 @ -20 mA cm <sup>-2</sup>	N/A	<i>Nanoscale</i> , <b>2018</b> , 10, 2213			
Co/Co <sub>3</sub> O <sub>4</sub> /NF	90	N/A	<i>Nano Lett.</i> <b>2015</b> , 15, 6015			
NiCo <sub>2</sub> S <sub>4</sub> /Ni <sub>3</sub> S <sub>2</sub> /NF	119	N/A	ACS Appl. Mater. Interfaces, <b>2018</b> , 13, 10890.			
Ni(OH) <sub>2</sub> /MoS <sub>2</sub> /CC	80	N/A	<i>Nano Energy</i> , <b>2017</b> , 37, 74.			
MoS <sub>2</sub> /NiCo-LDH/CFP	78	N/A	Joule, <b>2017</b> , 1, 383.			
Ni/CeO <sub>2</sub> -CNT/NF	90	0.8	<i>Nano Lett</i> , <b>2015</b> , 15, 7704.			

Sample	Charge state on Ni			
Ni <sub>2</sub> P(111)	0.13			
NiTe(011)	0.01			
NiTe <sub>2</sub> (011)	-0.02			
Ni <sub>2</sub> P(111)/NiTe(011)	0.04			
Ni <sub>2</sub> P(111)/NiTe <sub>2</sub> (011)	0.03			

**Table S2.** DFT calculated charge state on Ni at different samples.