# **Supporting Information**

# NiCoP/CoP nanoparticles supported on Ti<sub>4</sub>O<sub>7</sub> as the electrocatalyst possessing an excellent catalytic performance towards hydrogen evolution reaction

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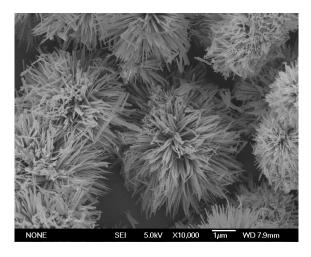
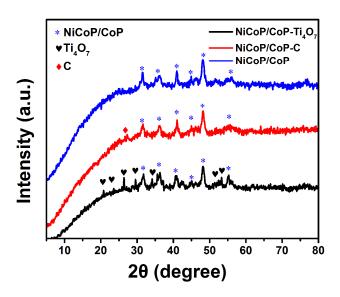
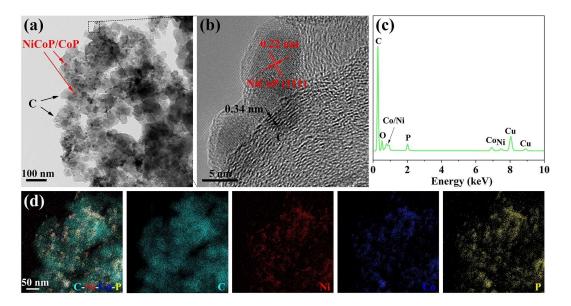


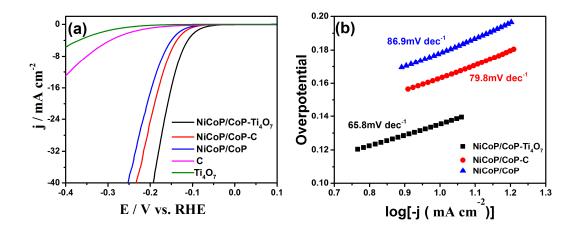
Figure S1. SEM image of NiCo<sub>2</sub>O<sub>4</sub>.



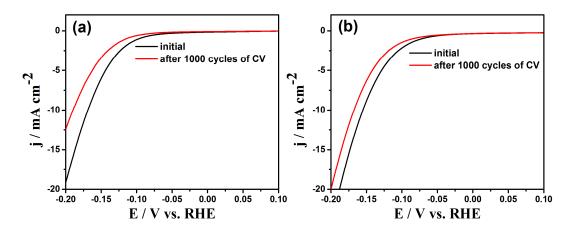
**Figure S2.** XRD patterns of NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>, NiCoP/CoP-C and NiCoP/CoP.



**Figure S3.** (a) TEM image, (b) HRTEM image, (c) EDX spectra and (d) EDX elemental mapping images of NiCoP/CoP-C.



**Figure S4.** (a) LSV curves, (b) Tafel plots of NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>, NiCoP/CoP-C and NiCoP/CoP (using carbon rod as the counter electrode).



**Figure S5.** LSV curve comparison before and after 1000 cycles of CV for (a) NiCoP/CoP and (b) NiCoP/CoP-C.

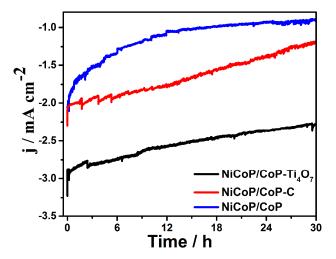


Figure S6. I-t curves of NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>, NiCoP/CoP-C and NiCoP/CoP.

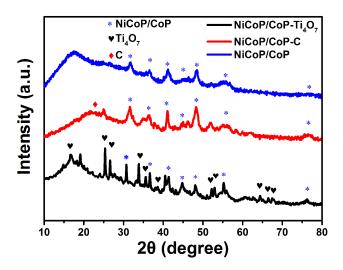
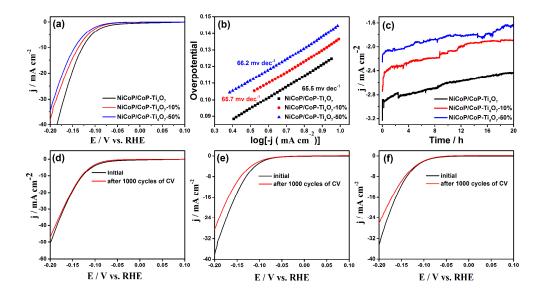
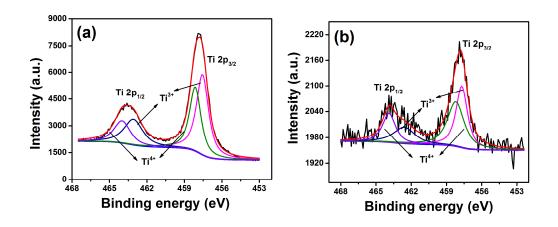


Figure S7. XRD patterns of NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>, NiCoP/CoP-C and NiCoP/CoP after 30 h of I-t measurements.



**Figure S8.** (a) LSV curves, (b) Tafel plots, (c) I-t curves of NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>, NiCoP/CoP-10% and NiCoP/CoP-50%, LSV curve comparison before and after 1000 cycles of CV for (d) NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>, (e) NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>-10% and (f) NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>-50%.



**Figure S9.** (a-b) XPS spectra of Ti (2p) for Ti<sub>4</sub>O<sub>7</sub> and NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>, respectively.

**Table S1.** The catalytic performance of NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>, NiCoP/CoP-C, NiCoP/CoP and other reported electrocatalysts towards HER in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

	Loading mass	E <sub>onset</sub>	E <sub>10mA cm-2</sub>	Tafel slope	Ref.
	(mg cm <sup>-2</sup> )	(mV)	(mV)	(mV dec <sup>-1</sup> )	
NiCoP/CoP-Ti <sub>4</sub> O <sub>7</sub>	0.199	48	128	65.5	
NiCoP/CoP-C	0.199	75	156	79.3	this work
NiCoP/CoP	0.199	92	171	86.3	
CoS <sub>2</sub> film	/	/	190	51.4	
CoS <sub>2</sub> MW	25	/	158	58	(S1)
CoS <sub>2</sub> NW	1.7	/	145	51.6	
MoS <sub>2</sub> /CNFs	/	64	190	110	(S2)
WS <sub>2(1-x)</sub> Se <sub>2x</sub> -CFs	0.21	190	250	105	(S3)
MoS <sub>2</sub> /CoS <sub>2</sub>	18.6	/	87	73.4	(S4)

# Synthesis of NiCo<sub>2</sub>O<sub>4</sub>-Ti<sub>4</sub>O<sub>7</sub>-10% and NiCo<sub>2</sub>O<sub>4</sub>-Ti<sub>4</sub>O<sub>7</sub>-50%

NiCo<sub>2</sub>O<sub>4</sub> nanowires were synthesized by the hydrothermal method and calcination. First of all, 291 mg of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 145 mg of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 300 mg of urea were dissolved in 35 mL deionized water and stirred for 30 min to form a homogeneous solution. After that, 13.7 or 123 mg of Ti<sub>4</sub>O<sub>7</sub> was uniformly dispersed in the solution and sonicated for 30 min. Next, the as-prepared compounds were transferred into a 50 mL Teflon-lined stainless autoclave and heated at 120 °C for 6 h. Afterward, the autoclave was naturally cooled down to room temperature. The black

precipitate was washed four to five times with deionized water and ethanol, respectively, and then dried in a vacuum oven at 60 °C for 8 h. Finally, it was annealed at 250 °C in  $N_2$  for 2 h with a heating rate of 2 °C min<sup>-1</sup>. The obtained materials were denoted as  $NiCoP/CoP-Ti_4O_7-10\%$  and  $NiCoP/CoP-Ti_4O_7-50\%$ , respectively.

# Synthesis of NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>-10% and NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>-50%

100 mg of NiCo<sub>2</sub>O<sub>4</sub>-Ti<sub>4</sub>O<sub>7</sub>-10% and NiCo<sub>2</sub>O<sub>4</sub>-Ti<sub>4</sub>O<sub>7</sub>-50% were mixed with 500 mg sodium hypophosphite using a mortar to grind into powder, respectively. Subsequently, the samples were heated at 300 °C for 120 min under N<sub>2</sub> atmosphere. The obtained catalysts were denoted as NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>-10% and NiCoP/CoP-Ti<sub>4</sub>O<sub>7</sub>-50%, respectively.

# References

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