## **Electronic Supplementary Information**

## Nanodots of transition metal (Mo, W) disulfides grown on NiNi prussian blue analogue nanoplates as an electrocatalyst for efficient hydrogen evolution

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## **Experimental Section**

*Reagents:* Nickel chloride hexahydrate was purchased from Aladdin Reagent Co., China. Sodium citrate was obtained from Tianjin Ruijinte Chemical Co., Ltd., China. Potassium tetracyanidonickelate(II) was purchased from J&K Chemical Co., Ltd., China. *N,N*-Dimethylformamide (DMF) was provided by Kelong Group Chemical Reagent Co., Ltd., China. 20 wt% Pt/C was purchased from Johnson Matthey Co., United Kingdom. Ammonium thiomolybdate ((NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub>) and ammonium tetrathiotungstate ((NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub>) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd., United States. Nafion (D-520 dispersion, 5 w/w in water and 1propanol,  $\geq$ 1.00 meq g<sup>-1</sup> exchange capacity) was from Alfa Aesar Chemical Co., Ltd., United States. All chemicals were analytical reagent grade and used without further purification. Ultrapure water (18.2 M $\Omega$  cm) was employed throughout the whole study for preparing a series of solutions.

*Synthesis of NiNi PBA nanoplates:* The NiNi PBA nanoplates were synthesized by a simple precipitation method.<sup>1</sup> In a typical procedure, solution A was prepared by dispersing 0.4 mmol of nickel chloride hexahydrate and 0.3 mmol of sodium citrate into 20 mL of ultrapure water. Meanwhile, solution B was prepared by dispersing 0.4 mmol of potassium tetracyanidonickelate(II) into 20 mL of ultrapure water. Next, at room temperature, solution A was quickly added to solution B, and then the mixture was mixed for 5 min under magnetic stirring. The mixture solution was sealed and transferred to a water bath at 25 °C and atmospheric pressure and maintained static settlement for 12 h. The product was pretreated by centrifuging and washing with

ethanol and water. The blue substance was dried at 50 °C overnight in vacuum drying oven. Thus, the NiNi PBA nanoplates were prepared.

*Synthesis of MoS*<sub>2</sub>-*NiNi PBA and WS*<sub>2</sub>-*NiNi PBA nanoplates:* To obtain MoS<sub>2</sub>-NiNi PBA nanoplates, 10 mg of  $(NH_4)_2MoS_4$  and 30 mg of the above as-prepared NiNi PBA nanoplates were added to 30 mL of DMF with the assistance of ultrasonication for 15 min. The mixture was then transferred into a Teflon-lined autoclave (100 mL) to react at 200 °C for 10 h. The final products were centrifuged and washed with ethanol and ultrapure water for several times after cooled to room temperature. At last the products were vacuum-dried at 55 °C overnight. According to the above process, the WS<sub>2</sub>-NiNi PBA nanoplates were prepared, the only difference is  $(NH_4)_2MoS_4$  instead of  $(NH_4)_2WS_4$ .

*Synthesis of MoS*<sub>2</sub> *and WS*<sub>2</sub>: To obtain MoS<sub>2</sub>, 10 mg of  $(NH_4)_2MoS_4$  was added to 30 mL of DMF with the assistance of ultrasonication for 15 min. The mixture was then transferred into a Teflon-lined autoclave (100 mL) to react at 200 °C for 10 h. The final products were centrifuged and washed with ethanol and ultrapure water for several times after cooled to room temperature. At last the products were vacuum-dried at 55 °C overnight. According to the above process, the WS<sub>2</sub> was prepared, and the only difference is  $(NH_4)_2MoS_4$  instead of  $(NH_4)_2WS_4$ .

*Materials characterization:* The morphology of the samples was examined by a scanning electron microscope (SEM, S-4800, Japan) and transmission electron microscope (TEM, JEM-2100, Japan). An X-ray photoelectron spectrometer (XPS, Thermo ESCALAB 250Xi, United States) was used for the analysis of the

composition of the as-synthesized samples. The Raman spectra (Renishaw Raman microscopy, United Kingdom) were recorded over the frequency range of 200-500 cm<sup>-1</sup> using a 633 nm laser and the laser power is 0.85 mW with an Invia Reflex under ambient conditions.

Electrochemical measurements: Electrochemical measurements were accomplished with a CHI 660E (CHEN HUA Instruments Co., Shanghai, China) at room temperature. The typical three-electrode cell was employed, including a saturated calomel electrode (SCE), a Pt wire, and a glassy carbon electrode (GCE), which were used as the reference electrode, the counter electrode, and the working electrode with a diameter of 3 mm, respectively. The catalyst suspension was prepared by dispersing 6 mg of the catalyst into a mixed solution of 0.5 mL of ethanol, 0.48 mL of ultrapure water, and 20 µL of Nafion solution under ultrasonication for 20 min. The catalyst suspension (6 µL) was pipetted on to the GCE surface using a micropipette and then dried at room temperature. The catalyst loading amount is 0.5096 mg cm<sup>-2</sup> on the GCE. The SCE was placed into the electrolytic bridge, which can protect the SCE from being destroyed.<sup>2</sup> The electrolytic bridge was a glass tube filled with a solidified mixture of KCl and agar. The polarization curves were recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> with a scan rate of 10 mV s<sup>-1</sup> at room temperature. The current density was normalized by the geometric electrode area  $(0.07065 \text{ cm}^2)$ . After every measurement, the surface of GCE was polished with 500 and 50 nm Al<sub>2</sub>O<sub>3</sub> powder and washed with water and ethanol. The onset potential for the LSV curve was the overpotential when the current density was 1 mA cm<sup>-2,3,4</sup> Potentials were referenced to a reversible hydrogen

electrode (RHE): in 0.5 M H<sub>2</sub>SO<sub>4</sub>,  $E_{RHE} = E_{SCE} + (0.241 + 0.059 \text{ pH})$ . All the data presented were corrected for iR losses and background current. iR drop was compensated at 100 % through the positive feedback using the CHI660E electrochemistry workstation. Electrochemical impedance spectroscopy (EIS) measurement was executed at an overpotential of 150 mV (*vs.* RHE) in 0.5 M H<sub>2</sub>SO<sub>4</sub> with frequency from 0.01 Hz to 1000 kHz and an amplitude of 5 mV. The electrochemical stability of the catalyst was conducted by cycling the potential between 0 and -0.5 V at the scan rate of 100 mV s<sup>-1</sup>. Chronoamperometric response record from MoS<sub>2</sub>-NiNi PBA nanoplates and WS<sub>2</sub>-NiNi PBA nanoplates was tested at the constant overpotential of 144.0 and 163.0 mV (*vs.* RHE) in 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively.



**Fig. S1.** (a, b) SEM, (c) TEM and (d) HETEM images of NiNi PBA nanoplates. Inset: corresponding SAED pattern taken from a single NiNi PBA nanoplate, and lattice fringe with interplanar spacing taken from the edge of a single NiNi PBA nanoplate.



Fig. S2. (a) SEM and (b) TEM images of  $MoS_2$  nanoflowers.



Fig. S3 (a) TEM and (b) HRTEM images of  $WS_2$ -NiNi PBA nanoplates. (c) Size distribution of the  $WS_2$  nanodots. High-resolution XPS spectra of  $WS_2$ -NiNi PBA nanoplates: (d) Ni 2p, (e) W 4f, and (f) S 2p.



**Fig. S4.** Equivalent circuit of MoS<sub>2</sub>-NiNi PBA nanoplates, WS<sub>2</sub>-NiNi PBA nanoplates and NiNi PBA nanoplates.



**Fig. S5.** Cycling stability of (a) MoS<sub>2</sub>-NiNi PBA and (b) WS<sub>2</sub>-NiNi PBA nanoplates. Chronoamperometric response record from (c) MoS<sub>2</sub>-NiNi PBA nanoplates and (d) WS<sub>2</sub>-NiNi PBA nanoplates at the constant overpotential of 144.0 and 163.0 mV (*vs.* RHE) in 0.5 M H<sub>2</sub>SO<sub>4</sub>, respectively. Insets: photographs of H<sub>2</sub> evolution.

Catalyst	Total	Max.	Min.	Mean	SD
	number	(nm)	(nm)	(nm)	
MoS <sub>2</sub> -NiNi <sup>a</sup>	32	2.47	1.35	1.89	0.2920
WS <sub>2</sub> -NiNi	32	1.87	0.8	1.31	0.2425

**Table S1.** Size distribution about the 0D  $MoS_2$  and 0D  $WS_2$  nanodots obtained from Fig. 1b and Fig. S3b, respectively.

<sup>a</sup> NiNi PBA nanoplates

**Table S2.** Comparison of the electrocatalytic activity of  $WS_2$ -NiNi PBA and  $MoS_2$ -NiNi PBA nanoplates *vs.* the reported  $WS_2$ -based and  $MoS_2$ -based solid-state catalysts for HER in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Catalyst	Onset potential	Tafel slope	Reference
	(mV vs. RHE)	(mV dec <sup>-1</sup> )	
WS <sub>2</sub> -NiNi PBAs	111.0	37.0	This work
W <sub>18</sub> O <sub>49</sub> @WS <sub>2</sub> NRs	170.0	86.0	5
WS <sub>2</sub> nanodots	90	51.0	6
WC <sub>x</sub> @WS <sub>2</sub>	70.3	61.0	7
N doped WS <sub>2</sub> NSs	86.0	69.9	8
MoS <sub>2</sub> -NiNi PBAs	82.0	39.5	This work
$MoS_2/MoO_2$	104.0	76.1	9
C/MoS <sub>2</sub> /G	160.0	46.0	10
$MoS_2$ quantum dot	190.0	74.0	11
MWCNTs@Cu@MoS2	146.0	62.0	12
O doped MoS <sub>2</sub>	120.0	55.0	13
Se-doped MoS <sub>2</sub>	140.0	55.0	14
MoS <sub>2</sub> nanosheets	120.0	50.0	15
MoS <sub>2</sub> /CNF	120.0	44.0	16
MoS <sub>2</sub> /SWNT	92.0	41.0	17
IE-MoS <sub>2</sub> NSs	87.0	41.0	18
MoS <sub>2</sub> /rGO	170.0	59.8	19

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