**Electronic Supplementary Information (ESI)** 

## Metallic 1T-VS<sub>2</sub> nanosheets featuring V<sup>2+</sup> self-doping and mesopores towards efficient hydrogen evolution reaction

Jun Xu,\*a Yuan Zhu,a Bansui Yu,a Changji Fanga and Junjun Zhang\*b

<sup>a</sup>School of Electronic Science & Applied Physics, Hefei University of Technology, Hefei 230009, P.R. China, E-mail: <u>apjunxu@hfut.edu.cn</u> (J. Xu)
<sup>b</sup>School of Physics and Materials Engineering, Hefei Normal University, Hefei 230601, P.R. China. E-mail: <u>cnjjzhang@gmail.com</u> (J. Zhang)



Fig. S1 (a,b) XRD patterns (a) and Raman spectra (b) of the V<sup>2+</sup>-doped VS<sub>2</sub> mesoporous nanosheets before (i) and after (ii) annealing at 350 °C in N<sub>2</sub> atmosphere, showing outstanding thermal stability. (c,d) HRTEM image (c) and SAED pattern (d) of the annealed VS<sub>2</sub> nanosheets.



Fig. S2 SEM image of the  $VS_2 \cdot NH_3$  precursor.



Fig. S3 (a) SEM image of the V<sup>2+</sup>-doped VS<sub>2</sub> electrocatalyst after stability measurement. Surface of the V<sup>2+</sup>-doped VS<sub>2</sub> electrocatalyst was slightly contaminated with the binder (Nafion). (b) XRD patterns of the V<sup>2+</sup>-doped VS<sub>2</sub> electrocatalyst: (i) after and (ii) before stability measurement, indicating the electrocatalyst after stability measurement shows decreased crystallinity. (c) Raman spectrum of the V<sup>2+</sup>-doped VS<sub>2</sub> electrocatalyst after stability measurement, indicating the well-reserved 1T nature. (d-f) XPS spectra of the V<sup>2+</sup>-doped VS<sub>2</sub> electrocatalyst after stability measurement, revealing good stability of the surface.

Morphology	$\eta$ (mV) at	Tafel slope	Stability test	Counter	Ref.
	$-10 \text{ mA cm}^{-2}$	$(mV dec^{-1})$	(hours)	electrode	
$V^{2+}$ -doped $VS_2$	59	38		Graphite rod Pt wire	Our work
nanosheets	43	38	70		
Array of VS <sub>2</sub>					Chem Mater 2016
nanoplates on carbon	42	36	12	Graphite rod	28 5587-5591
cloth				20, 3307 3331.	
VS <sub>2</sub> /MWCNTs	123	40	10	Carbon rod	<i>Int. J. Hydrogen</i> <i>Energy</i> , <b>2018</b> , 43, 22949-22954.
VS <sub>2</sub> nanoflowers	400	170	/		
$C/V_{1.11}S_2$ nanosheets	$\approx 50$	51	20		Electrochimica.
bulk VS <sub>2</sub>	≈ 120	70	/	Graphite rod	<i>Acta.</i> , <b>2019</b> , 300, 208-216.
VS <sub>2</sub> /rGO	350	150	/	Graphite rod	J. Solid State Chem., 2015 224 82-87
nanosheets	550	150			
VS <sub>2</sub> nanosheets	450	201			2013, 224, 02 07.
MoS <sub>2</sub> nanodots/VS <sub>2</sub> nanosheets	291	58.1	16	Graphite rod	ACS Sustainable
					Chem. Eng., 2018,
					6, 15471–15479.
N-doped Ni <sub>3</sub> S <sub>2</sub> /VS <sub>2</sub> nanosheets	151	107.5	20	Graphite rod	Electrochimica.
					Acta., <b>2018</b> , 269,
					55-61.
VSSe nanoplates	180	87	20	Graphite rod	J. Mater. Chem. A,
					2019, /, 15/14-
CVD grown VS					13721 Adv. Maton 2015
nanosheets	68	34	/	Pt foil	27 5605-5609
					27, 5005-5009.
VS <sub>2</sub> nanoflowers	58	34	12	Pt plate	<b>2017</b> 5 15080-
					15086.
Interlayer-expanded	43	36	60	Pt wire	Small. 2018. 170.
VS <sub>2</sub> nanosheets					3098-3107.
VS <sub>2</sub> nanosheets	41	36	10		Dalton Trans., 2018,
VS <sub>4</sub> /rGO	210	73	/	Pt wire	47, 13792-13799.
VS <sub>2</sub> @MoS <sub>2</sub> nanocomposites	177	54.9	20	Pt wire	ACS Appl. Mater.
					Interfaces., 2017, 9,
					29942–29949.

Table S1. Recent advance of HER performance of various  $VS_2$ -based catalysts.