Supporting Information

Ultra-high electrocatalytic activity of VS₂ nanoflowers for efficient

hydrogen evolution reaction

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-	s			24) 24.			Map Sum Spectrum		
		10		An Ens		Element	wt%	wt% Sigma	
20-			212	ALC: NO		С	17.36	0.71	
s/eV		A	ALC: NO			0	7.38	0.60	
- b	V	20	<u>A</u>			Na	0.36	0.06	
10- - 0	1 T		1			S	36.93	0.42	
- M		_ 223	Tr end	25 µm		V	37.96	0.44	
CNa		V				Total	100		
0-11111	• • • • • •	1 1 1 1							
0 2					12	14	16	18	ke\

Fig. S1 EDX spectrum and elements ratio of VS_2 nanoflowers.



Fig. S2 XPS wide survey of VS_2 nanoflowers.



Fig. S3 N_2 adsorption-desorption isotherms of (a) VS_2 nanoflowers and (b) VS_2 nanosheets with insets of their morphologies, respectively.



Fig. S4 SEM figures of VS_2 nanostructures prepared at (a) 12 hours and (b) 36 hours with their (c) polarization curves.



Fig. S5 SEM figures of samples prepared with ratios (orthovanadate : TAA) of (a) 6vs16 and (b) 6vs48 mmol, along with their (c) polarization curves.



Fig. S6 Galvanostatic test of VS_2 nanoflowers at a constant cathodic current density of 10 mA/cm^2 in 0.5M H₂SO₄ solution.



Fig. S7 (a) & (b) SEM images of VS₂-NF after 8000 cycles of LSV test.



Fig. S8 Illustration of top & front views of 1T-VS₂ nanoribbon with full hydrogenation at the top edge. The orange dot line indicates the direction of the increment of hydrogenation.



Fig. S9 The calculated ΔG_H of 1T-VS₂ edge as a function of hydrogen coverages: (a) individual ΔG_H and (b) average ΔG_H .

Catalyst	Onset potential (mV vs. RHE)	η (mV) at 10 mA/cm ²	Tafel slope (mV/dec)	$\begin{bmatrix} J_0 \\ (mA/cm^2) \end{bmatrix}$	Loading (mg/cm ²)	Ref.
VS ₂ -NF	32	58	34	0.074	0.33	This Work
VS ₂ -CP	ca. 40	ca. 70 (42 IR-corrected)	36 (IR- corrected)	0.955	1.6	1
VS ₂ -CVD	ca. 30	68 (IR-corrected)	34 (IR- corrected)	_	0.010	2
Edge- enriched MoS ₂ -CVD	ca. 300	ca. 470	98	0.023	_	3
1T-MoS ₂ -NS	ca. 115	175	41	0.1	43	4
MoSe ₂ -NS- on-CC	ca. 170	ca. 190	69	0.021	_	5
WS ₂ -NS	ca. 110	150	72	0.0025	0.285	6
1T-WS ₂ - strained	80~100	220	60	0.02	0.0002~0.0065	7
WSe ₂ -NS	ca. 150	ca. 280	78	_	1.06	8
MoP	ca. 50	140	54	0.0034	0.860	9
Ni ₅ P ₄ -Ni ₂ P- NS	Ca. 110	120	79.1	0.116	68.2	10

Table S1 Comparison of HER performance of VS_2 nanoflowers with other reported TMDs electrocatalysts in acid media.

References

- 1. H. F. Liang, H. H. Shi, D. F. Zhang, F. W. Ming, R. R. Wang, J. Q. Zhuo and Z. C. Wang, *Chem. Mater.*, 2016, **28**, 5587-5591.
- J. T. Yuan, J. J. Wu, W. J. Hardy, P. Loya, M. Lou, Y. C. Yang, S. Najmaei, M. L. Jiang, F. Qin, K. Keyshar, H. Ji, W. L. Gao, J. M. Bao, J. Kono, D. Natelson, P. M. Ajayan and J. Lou, *Adv. Mater.*, 2015, 27, 5605-5609.
- S. Li, S. S. Wang, M. M. Salamone, A. W. Robertson, S. Nayak, H. Kim, S. C. E. Tsang, M. Pasta and J. H. Warner, ACS Catal., 2017, 7, 877-886.
- 4. X. M. Geng, W. W. Sun, W. Wu, B. Chen, A. Al-Hilo, M. Benamara, H. L. Zhu, F. Watanabe, J. B. Cui and T. P. Chen, *Nat. Commun.*, 2016, 7.
- 5. B. Qu, X. B. Yu, Y. J. Chen, C. L. Zhu, C. Y. Li, Z. X. Yin and X. T. Zhang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 14170-14175.
- 6. Z. Z. Wu, B. Z. Fang, A. Bonakdarpour, A. K. Sun, D. P. Wilkinson and D. Z. Wang, *Appl. Catal. B-Environ.*, 2012, **125**, 59-66.
- 7. D. Voiry, H. Yamaguchi, J. W. Li, R. Silva, D. C. B. Alves, T. Fujita, M. W. Chen, T. Asefa, V. B. Shenoy, G. Eda and M. Chhowalla, *Nat. Mater.*, 2013, **12**, 850-855.
- X. Q. Wang, Y. F. Chen, B. J. Zheng, F. Qi, J. R. He, Q. A. Li, P. J. Li and W. L. Zhang, J. Alloy Compd., 2017, 691, 698-704.
- 9. P. Xiao, M. A. Sk, L. Thia, X. M. Ge, R. J. Lim, J. Y. Wang, K. H. Lim and X. Wang, *Energ Environ. Sci.*, 2014, 7, 2624-2629.
- 10. X. G. Wang, Y. V. Kolen'ko, X. Q. Bao, K. Kovnir and L. F. Liu, *Angew. Chem. Int. Edit.*, 2015, **54**, 8188-8192.