Supporting Information:

2D-Heterogeneous Vanadium Compound Interfacial Modulation Enhanced Synergistic Catalytic Hydrogen Evolution for Full pH Range Seawater Splitting

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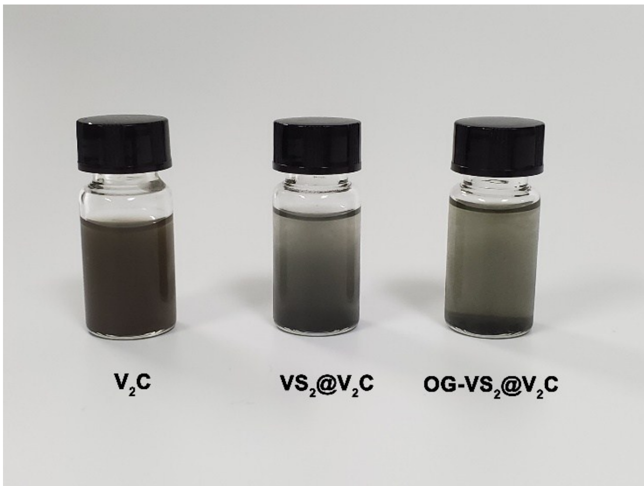

Fig. S1 Colloidal solutions of three catalytic materials.

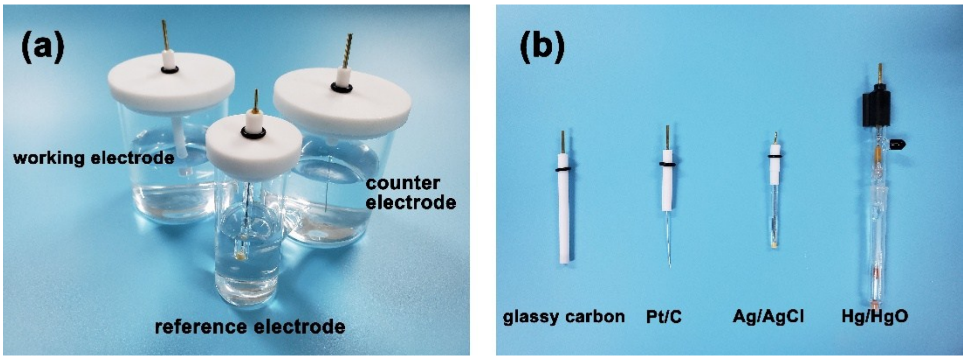

Fig. S2 Equipment used in electrocatalytic testing: (a) three-electrode electrolytic cell (b) various electrodes.

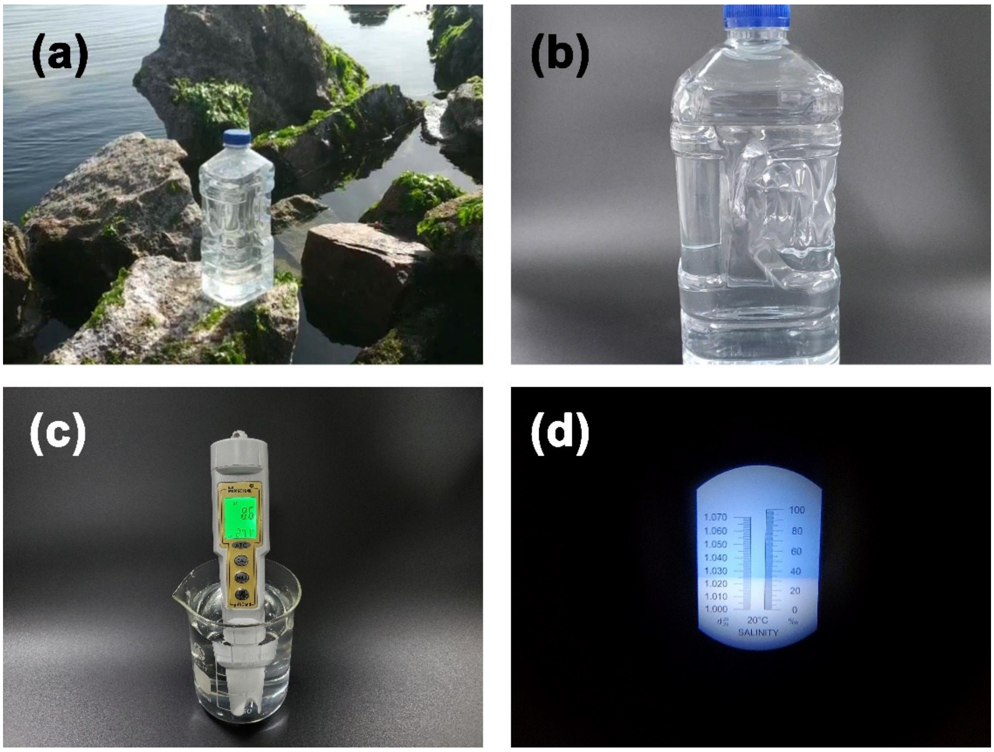

Fig. S3 (a) and (b) The seawater collection and purification. (c) The PH test of seawater. (d) The salinity test of seawater.

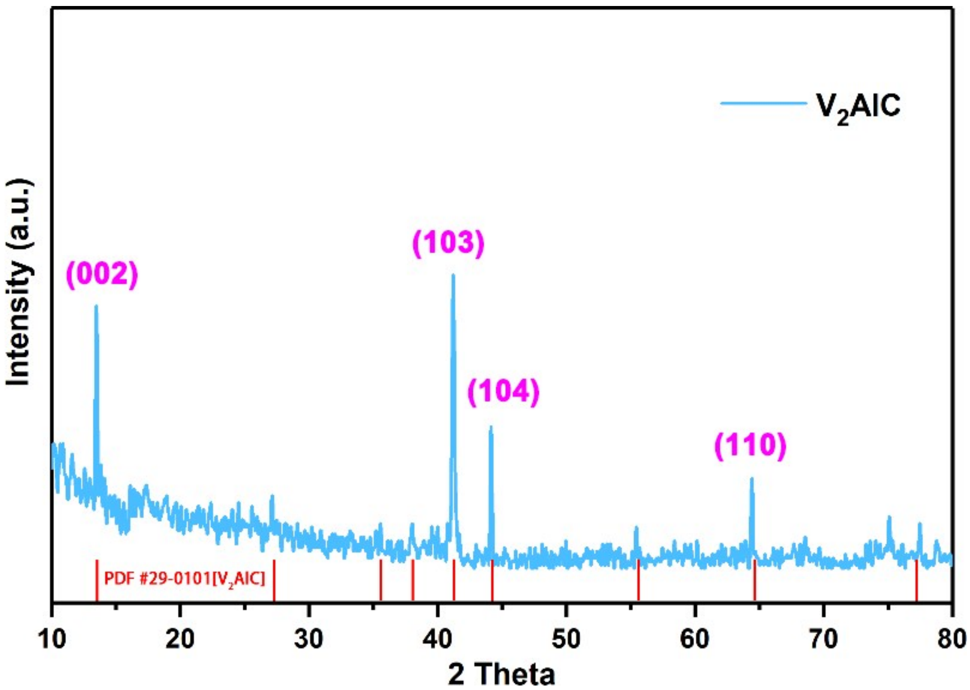

Fig. S4 XRD pattern of V_2AlC precursor.

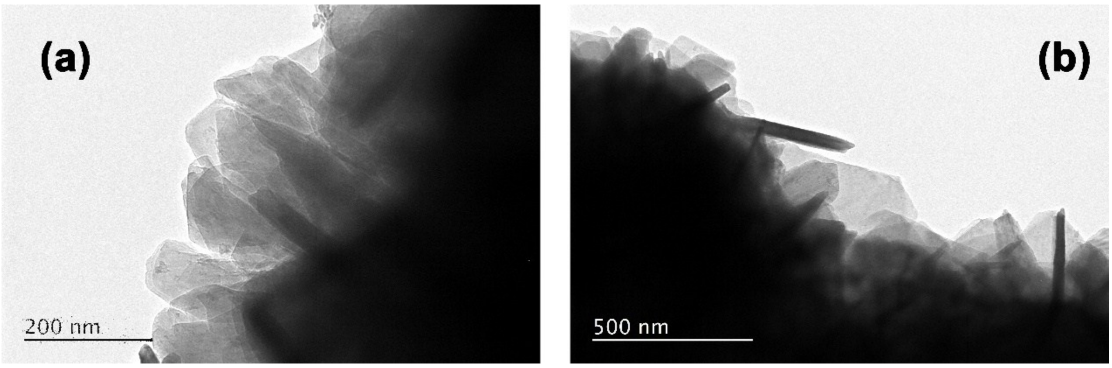

Fig. S5 Electron microscope pictures of different positions of $VS_2@V_2C$ catalyst.

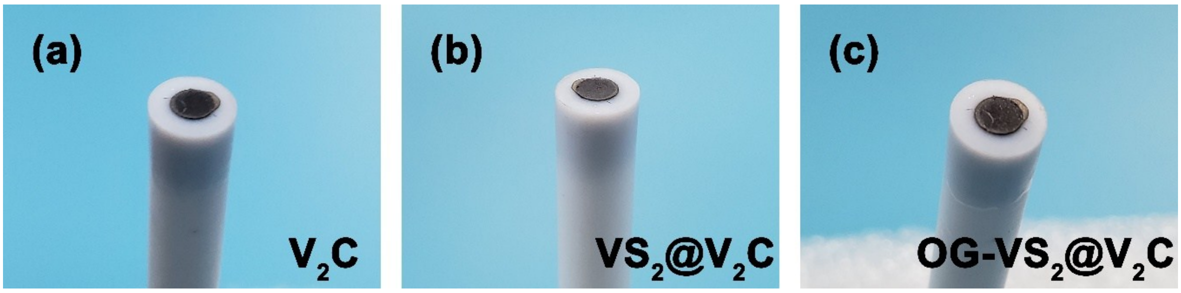

Fig. S6 Three kinds of catalytic material freshly prepared working electrode. (a) V_2C. (b) VS_2@V_2C. (c) OG-VS_2@V_2C.

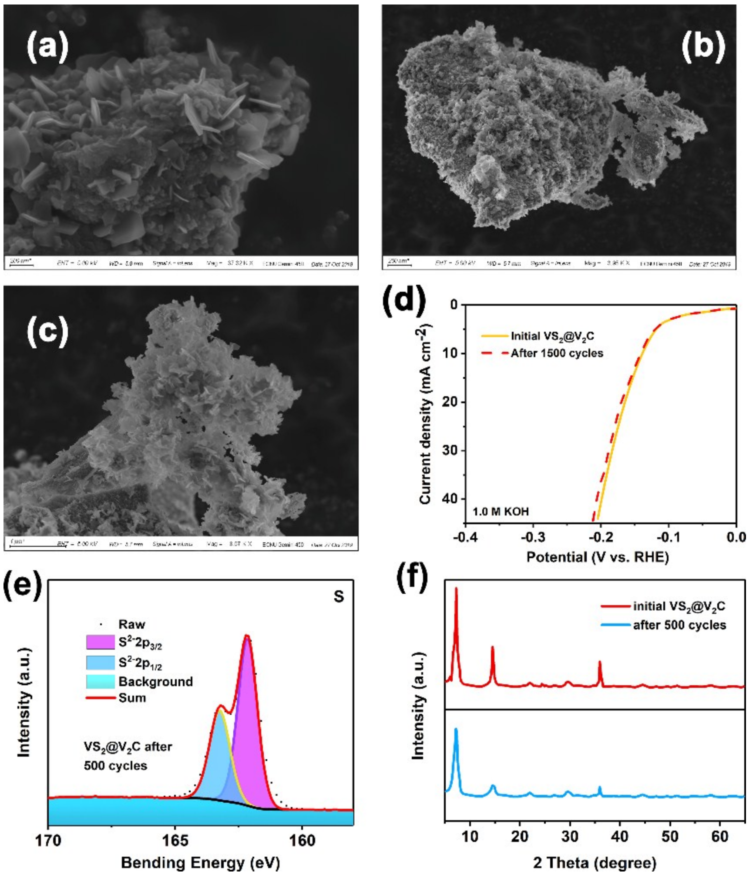

Fig. S7 (a)-(c) Different magnification electron microscope pictures of $VS_2@V_2C$ catalyst after a long cycle. (d) Test results of hydrogen evolution stability of the composite material. (e) XPS pattern of $VS_2@V_2C$ catalyst after a long cycle. (f) XRD patterns of initial $VS_2@V_2C$ and catalyst after a long cycle.

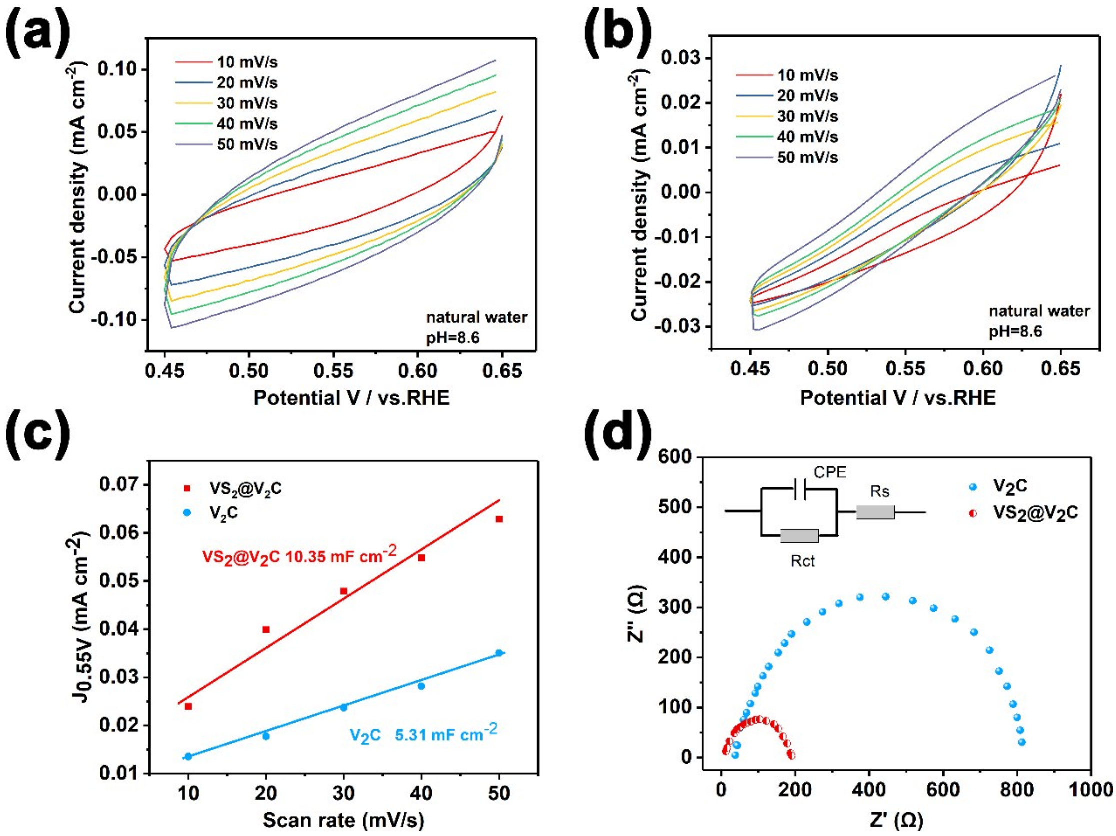

Fig. S8 (a)-(b) Cyclic voltammetry tests of VS_2@V_2C and V_2C. (c) Double-layer capacitor performance results of VS_2@V_2C and V_2C. (d) EIS AC impedance spectrum of VS_2@V_2C and V_2C. The illustration shows the equivalent circuit.

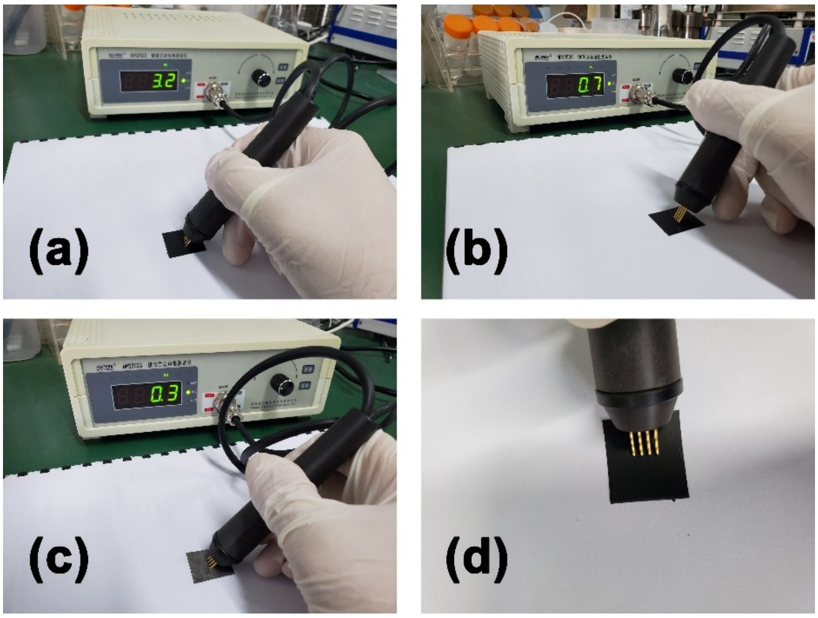

Fig. S9 The square resistance test results of (a) V_2C-3.2Ω·cm (b) OG-VS_2@V_2C-0.7Ω·cm (c) VS_2@V_2C-0.3Ω·cm. (d) Composite material film and four-probe tester.

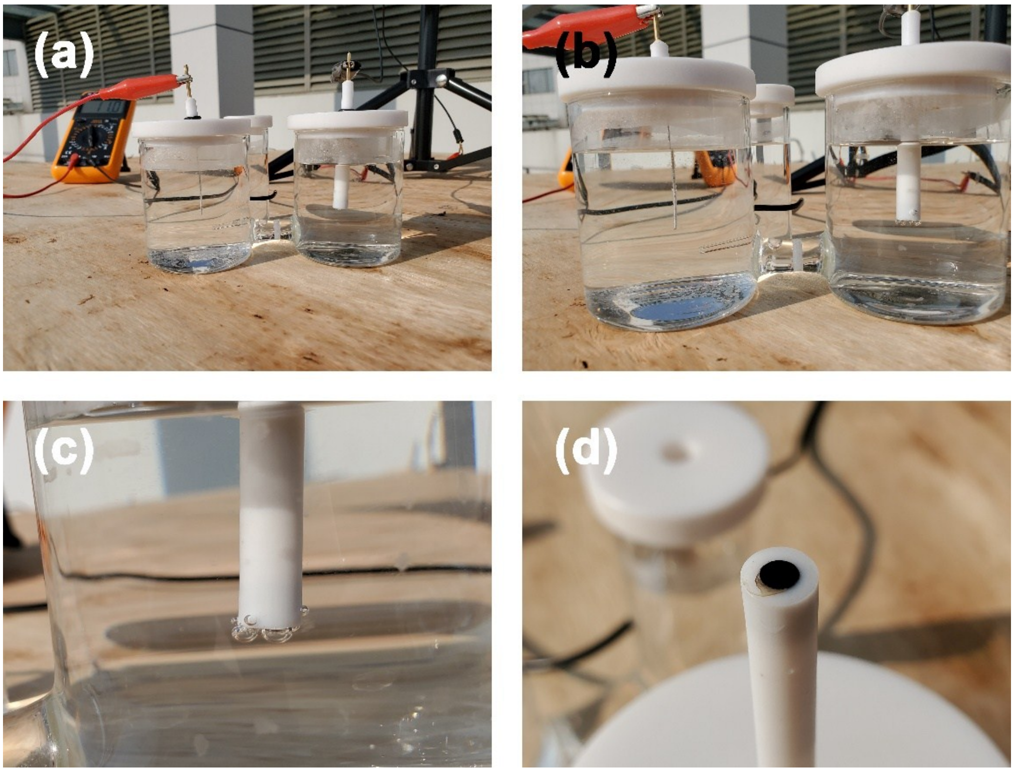

Fig. S10 Electrohydrogen evolution system powered by solar photovoltaic cells.

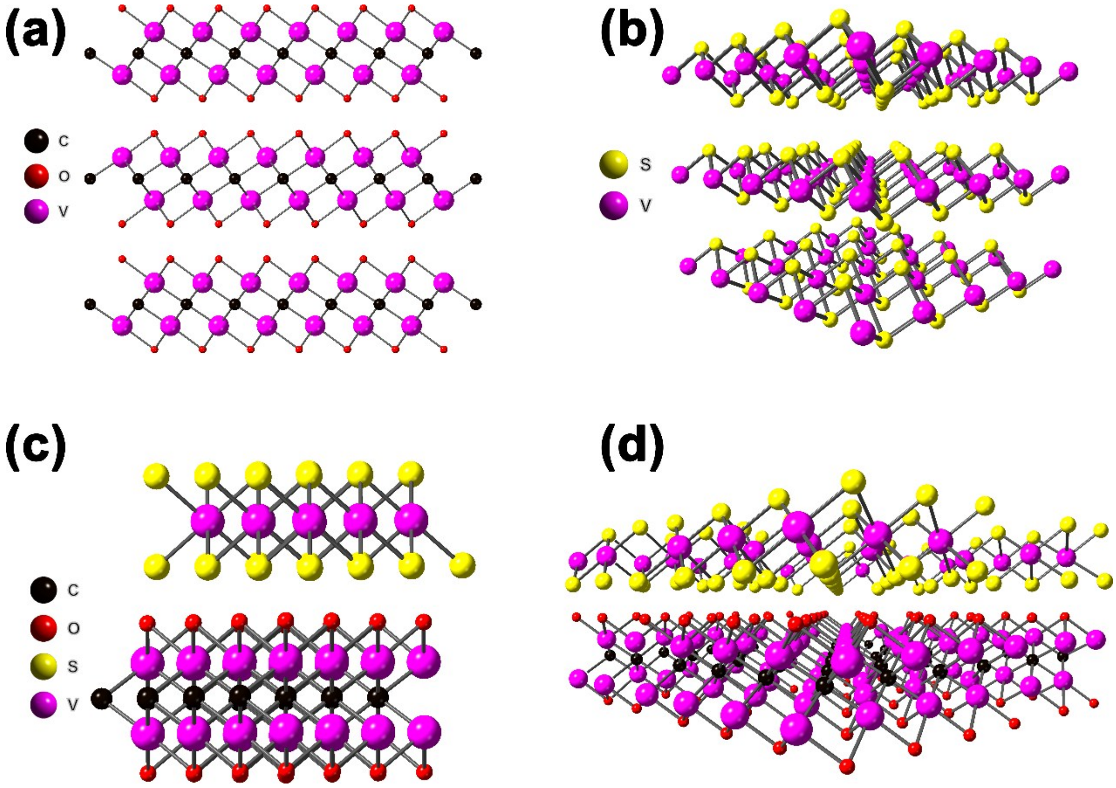

Fig. S11 The optimized crystal structure model of (a) V_2CO_2 (b) MoS_2 (c)-(d)VS_2@V_2C.

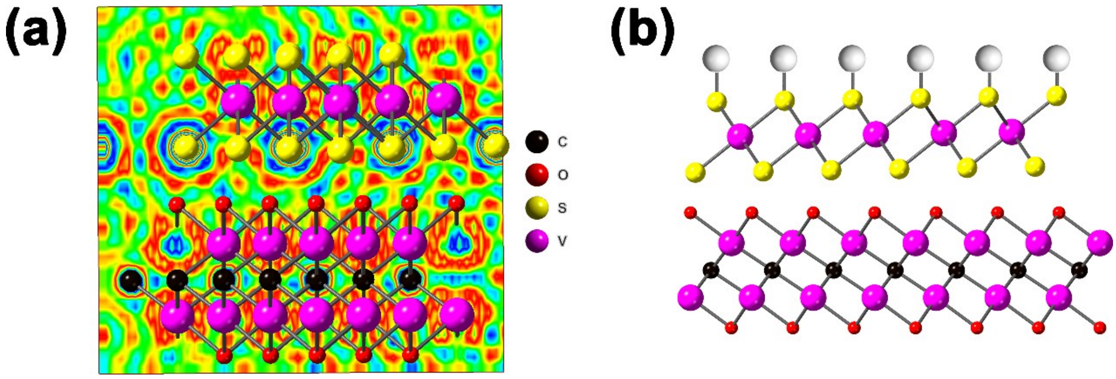

Fig. S12 (a) Charge density difference graph on VS_2@V_2C (110) crystal plane. (b) Composite material hydrogen adsorption model.

Table S1 Variation of hydrogen evolution overpotential of each catalytic material with pH at the current density of 20 mA cm^{-2} (mV).

Catalyst\pH	0	2.0	4.0	7.0	8.6	10.0	12.0	13.8
V_2C	526	748	931	-	-	-	-	572
OG-VS_2@V_2C	273	402	549	724	634	573	455	304
VS_2@V_2C	148	271	387	527	444	396	320	164
Pt/C	86	176	281	489	428	367	246	91

Table S2 Variation of Tafel slope of each catalytic material with pH at the current density of 20 mA cm^{-2} (mV/dec).

Catalyst\pH	0	2.0	4.0	7.0	8.6	10.0	12.0	13.8
OG-VS_2@V_2C	54	93	146	193	174	158	121	85
VS_2@V_2C	37	81	124	171	160	149	105	48
Pt/C	28	76	103	155	143	132	99	32

Table S3 recent advance of HER performance of VS_2-based catalysts.

Morphology	η (mV) at 10 mA cm^{-2}	Tafel slope	Electrolyte	Year	Ref.
VS_2@V_2C	94	37	0.5 M H_2SO_4	-	This work
	137	58	1.0 M KOH	-	
VS_2/rGO	350	150	1.0 M KOH	2015	1
MoS_2 nanodots/VS_2 nanosheets	291	58.1	1.0 M KOH	2018	2
N-doped Ni_3S_2 nanosheets	151	107.5	1.0 M KOH	2018	3
VSSe nanoplates	180	87	1.0 M KOH	2019	4
VS_4/rGO	210	73	1.0 M KOH	2018	5
VS_2@MoS_2 nanocomposites	177	54.9	1.0 M KOH	2017	6

VSe nanosheets	**206**	**88**	**1.0 M KOH**	**2016**	**7**
VS_2 nanoflowers	**400**	**170**	**0.5 M H_2SO_4**	**2018**	**8**
Bulk VS_2	**120**	**70**	**0.5 M H_2SO_4**	**2019**	**9**
VS_2 nanosheets	**450**	**201**	**0.5 M H_2SO_4**	**2015**	**1**
CVD grown VS_2 nanosheets	**68**	**34**	**0.5 M H_2SO_4**	**2015**	**10**
$V_{0.09}Mo_{0.91}S_2$	**240**	**69**	**0.5 M H_2SO_4**	**2014**	**11**

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