Supporting Information (SI):

Molybdenum and cobalt co-doped VC nanoparticles encapsulated in nanocarbon as efficient electrocatalysts for hydrogen evolution reaction

Xiaoyi Li[a], Jianfeng Huang[*a], Liangliang Feng[*a], Danyang He[a], Zixuan Liu[b], Guodong Li[c], Ning Zhang[a], Yongqiang Feng[a], Liyun Cao[*a]

a School of Material Science and Engineering, International S&T Cooperation Foundation of Shaanxi Province，Xi'an Key Laboratory of Green Manufacture of Ceramic Materials, Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an 710021, P. R. China.

b Faculty of Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK

c State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.

* Corresponding authors

E-mail: huangjf@sust.edu.cn; fengll@sust.edu.cn; 2644245930@qq.com

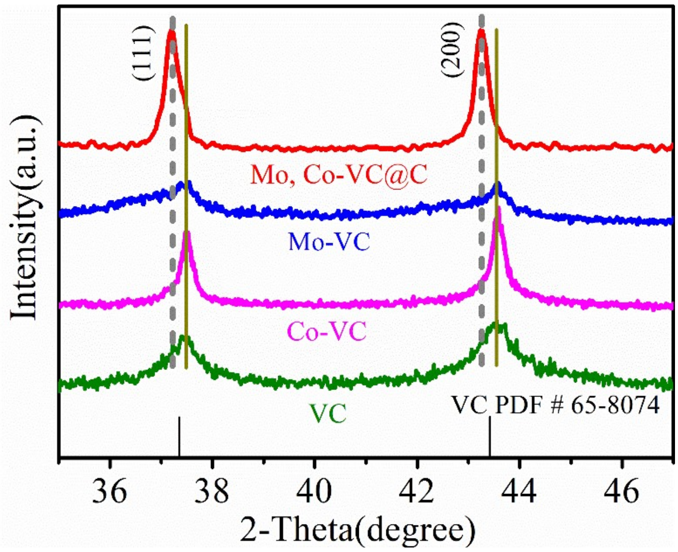

Fig. S1 XRD patterns with zoomed-in image of VC, Mo-VC, Co-VC and Mo, Co-VC@C.

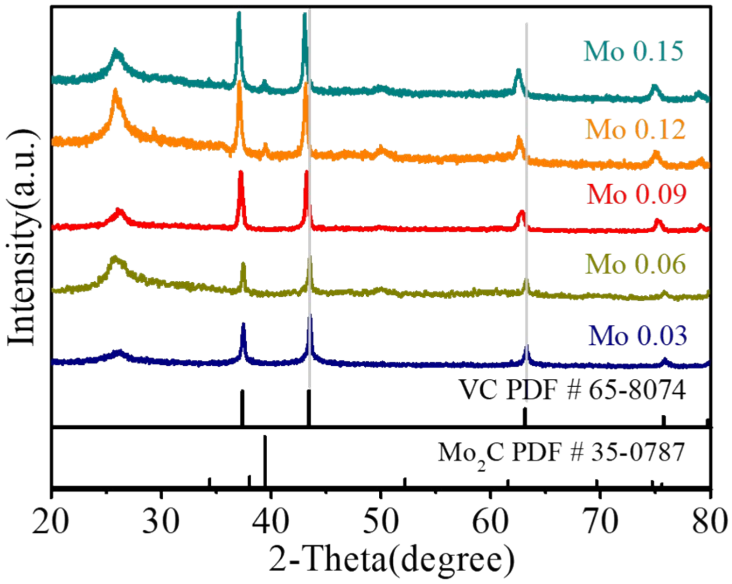

Fig. S2 XRD patterns of samples with different Mo-doping amounts.

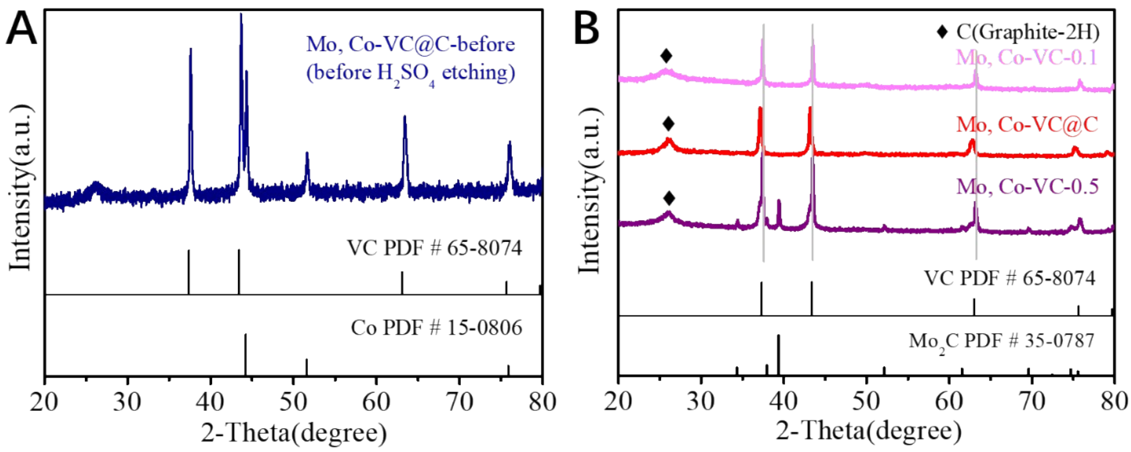

Fig. S3 XRD patterns of (A) Mo, Co-VC@C-before (before H_2SO_4 etching); (B) Mo, Co-VC-0.1 (Co 0.1g), Mo, Co-VC@C (Co 0.3 g) and Mo, Co-VC-0.5 (Co 0.5g).

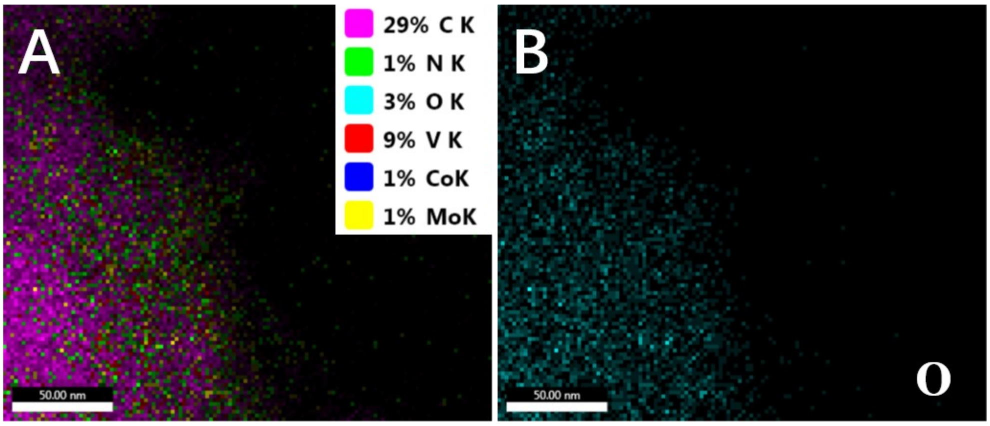

Fig. S4 (A-B) The elemental mapping images of Mo, Co-VC@C.

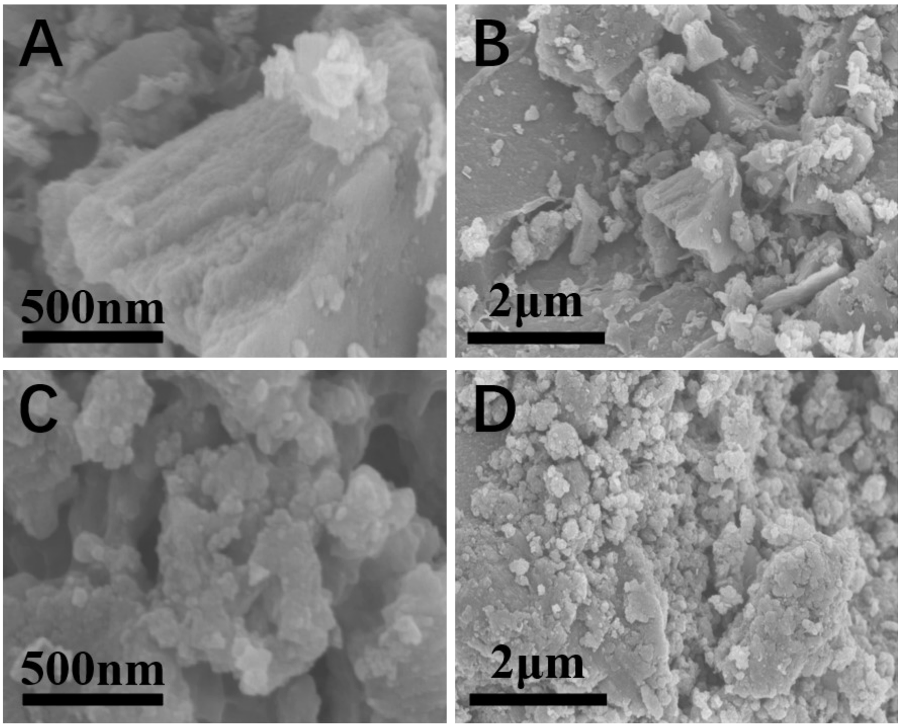

Fig. S5 (A-B) SEM images of VC; (C-D) SEM images of Mo, Co-VC@C.

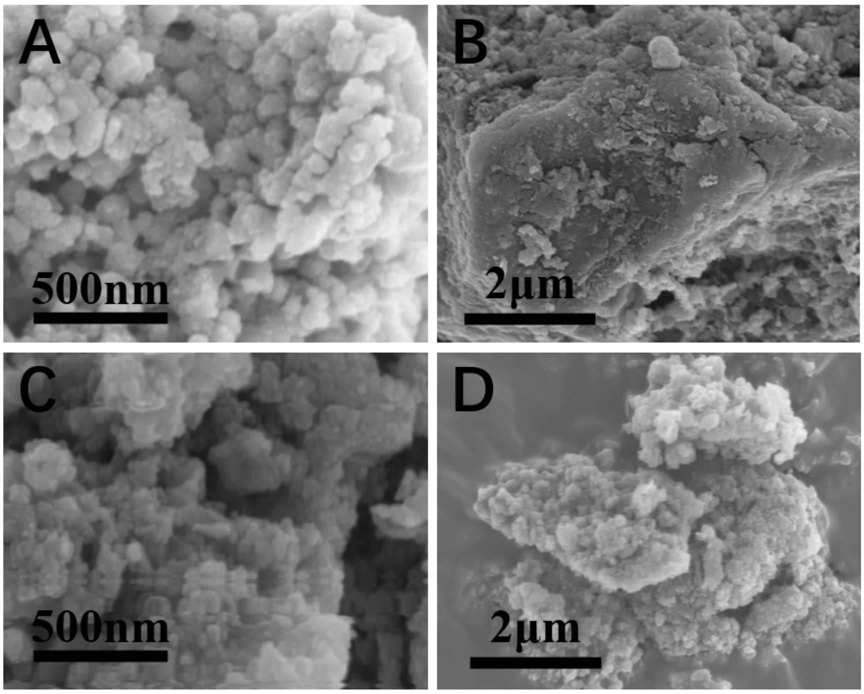

Fig. S6 (A-B) SEM images of Mo, Co-VC-0.1 (Co 0.1g); (C-D) SEM images of Mo, Co-VC-0.5 (Co 0.5g).

Table S1. Peak properties of Mo, Co-VC@C and VC.

Samples	Peaks	Position, 2 theta (°)	FWHM (radians)	Calculated crystallite size (D, nm)	Calculated average crystallite size (D', nm)
Mo, Co-VC@C	Peak1	26.09294	5.8079	1.40408514	**2.798167747**
	Peak2	37.22031	17.15777	0.488559966	
	Peak3	43.32616	0.75475	11.32564561	
	Peak4	62.80551	52.57823	0.177024122	
	Peak5	75.21084	10.25644	0.977700988	
	Peak6	79.14802	4.26596	2.415990661	
VC	Peak1	26.30134	4.80451	1.698037387	**3.510623493**
	Peak2	37.44705	0.98751	8.494298705	
	Peak3	43.57816	1.51291	5.655012455	
	Peak4	63.33178	2.06729	4.515032725	
	Peak5	78.75982	29.14271	0.352671431	
	Peak6	78.85275	29.49526	0.348688253	

Table S2. ICP data of Mo, Co-VC@C.

Elements	The mass percentage (%)
Mo	3.205
Co	0.017
V	15.020

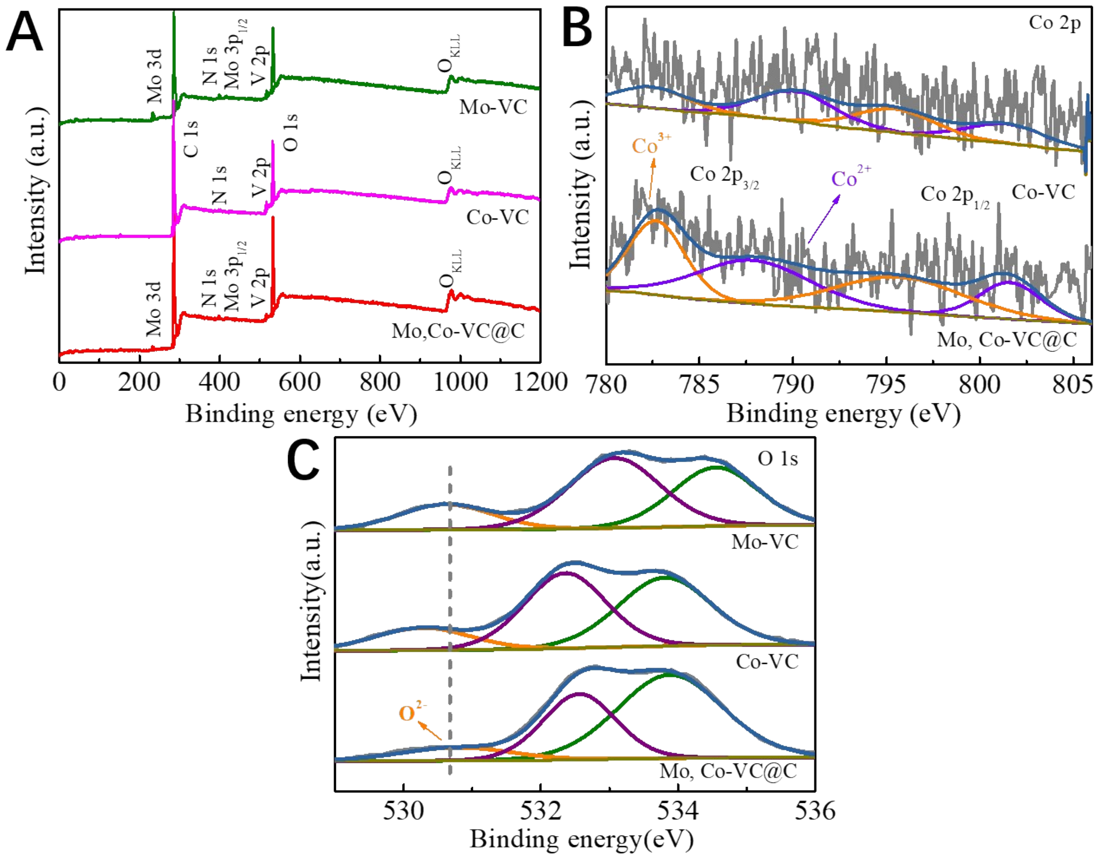

Fig. S7 (A) XPS survey spectra of Mo-VC, Co-VC and Mo, Co-VC@C; (B) Co 2p XPS spectrum of Co-VC and Mo, Co-VC@C; and (C) O 1s XPS spectrum of Mo-VC, Co-VC and Mo, Co-VC@C.

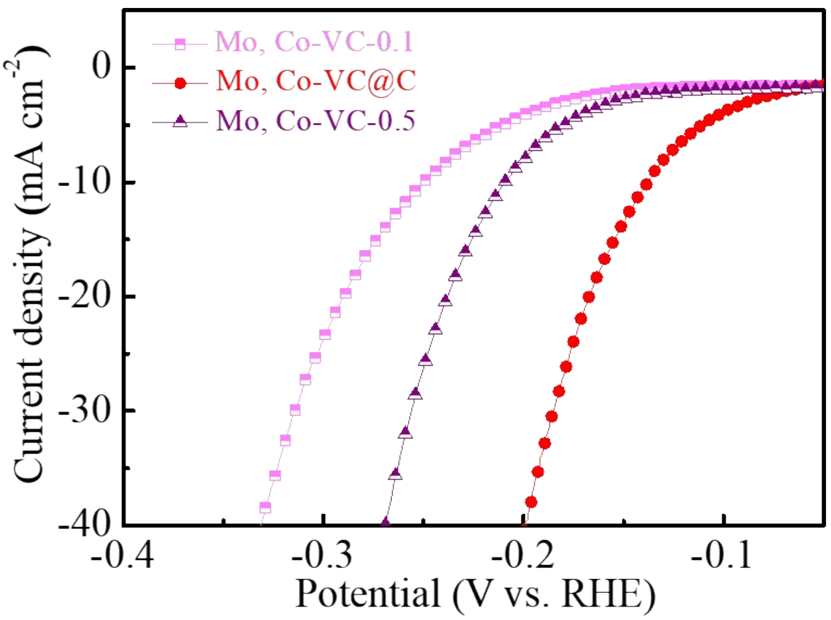

Fig. S8 HER Polarization curves of Mo, Co-VC-0.1 (Co 0.1g), Mo, Co-VC@C (Co 0.3 g) and Mo, Co-VC-0.5 (Co 0.5g).

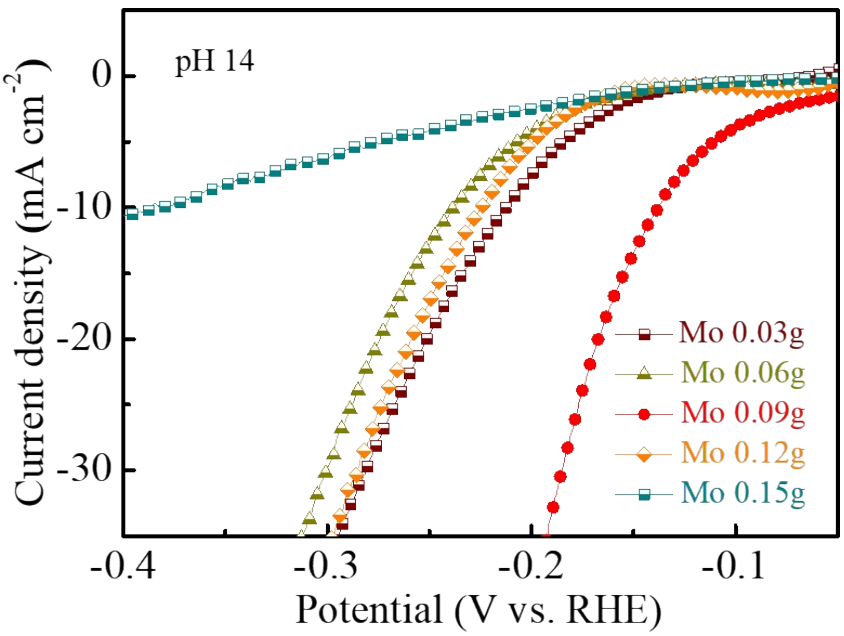

Fig. S9 Polarization curves of samples with different Mo-doping amount.

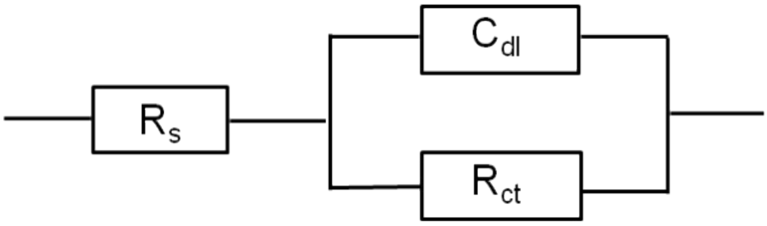

Fig. S10 Electrical equivalent circuit used to simulate the Nyquist plots in Fig. 5C, where R_s is the electrolyte resistance, R_{ct} is the charge-transfer resistance, and C_{dl} represents the double-layer capacitance.

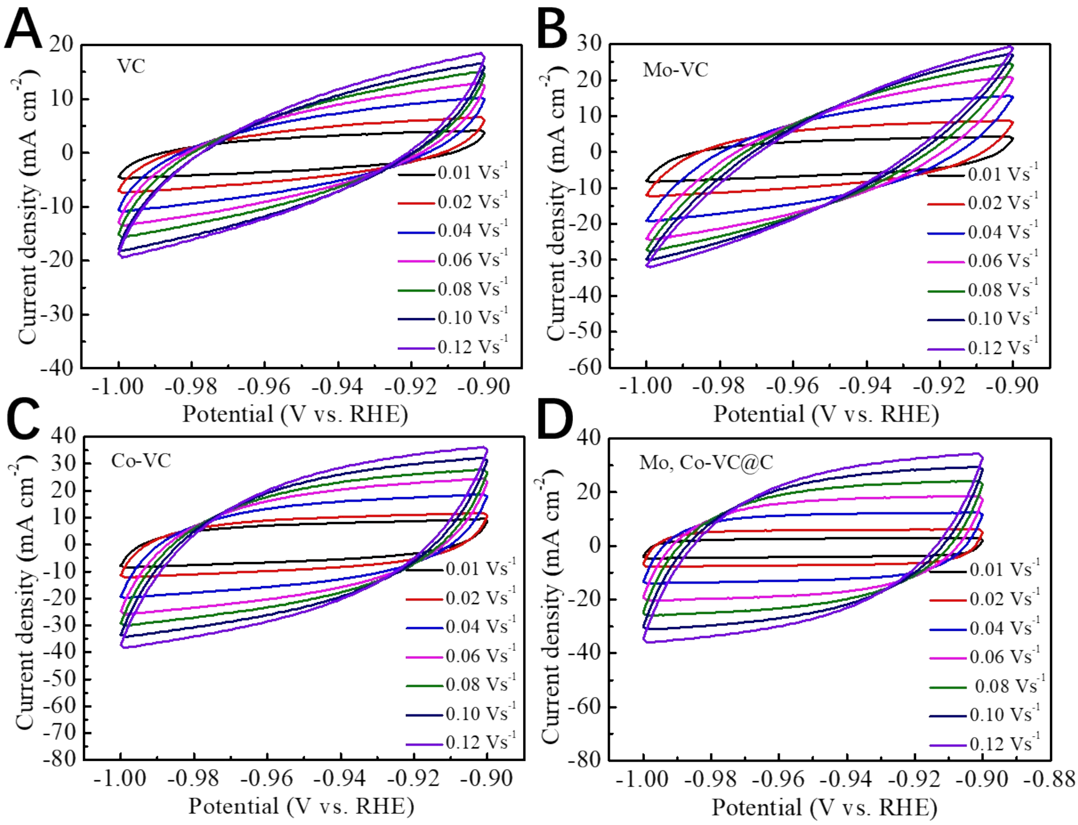

Fig. S11 CV curves of (A) VC, (B) Mo-VC, (C) Co-VC and (D) Mo, Co-VC@C at different scan rates from 10 to 120 mV/s in 1 M KOH.

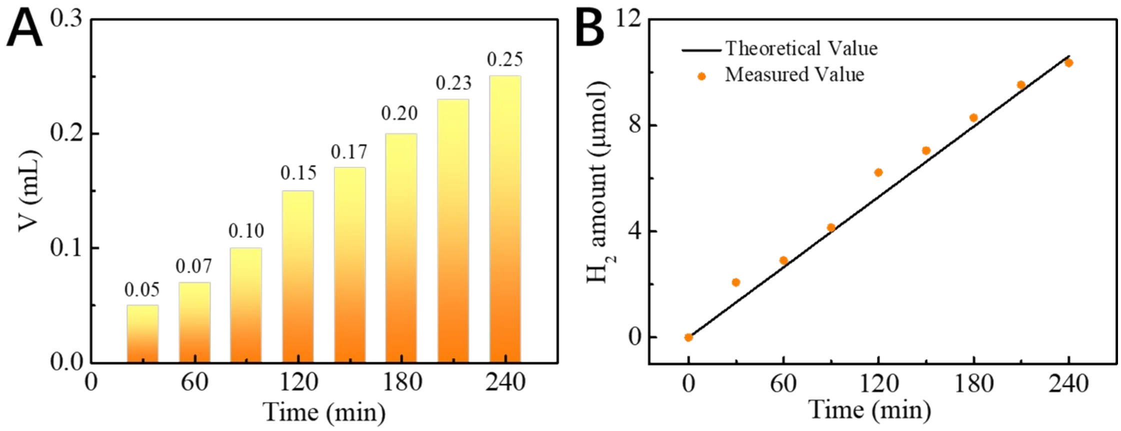

Fig. S12 (A) The volume of the hydrogen-produced gas from the HER of Mo, Co-VC@C was recorded every 30 minutes; (B) Hydrogen production efficiency for HER under potentiostatic electrolysis with Mo, Co-VC@C at overpotential η_{10} = 233 mV at pH 14.

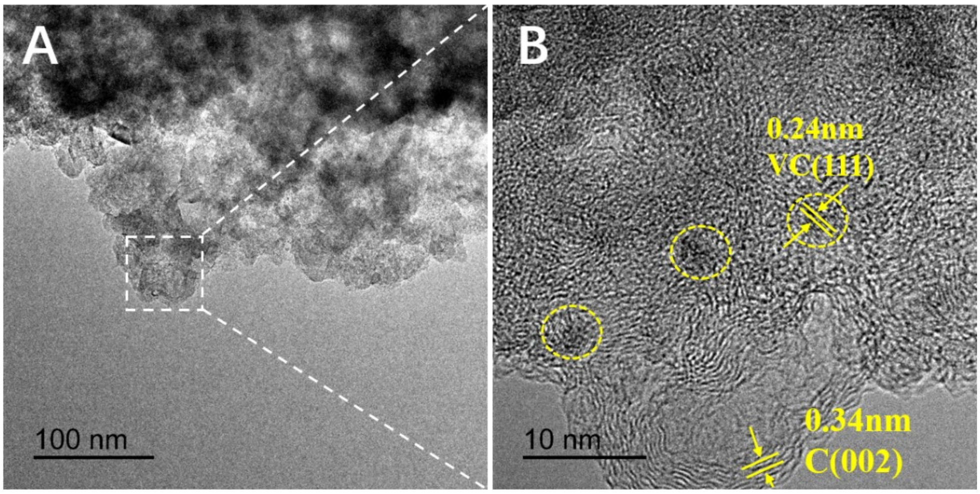

Fig. S13 (A-B): TEM and HRTEM images of Mo, Co-VC@C after the stability test of I-t curve for 110 h at pH 14.

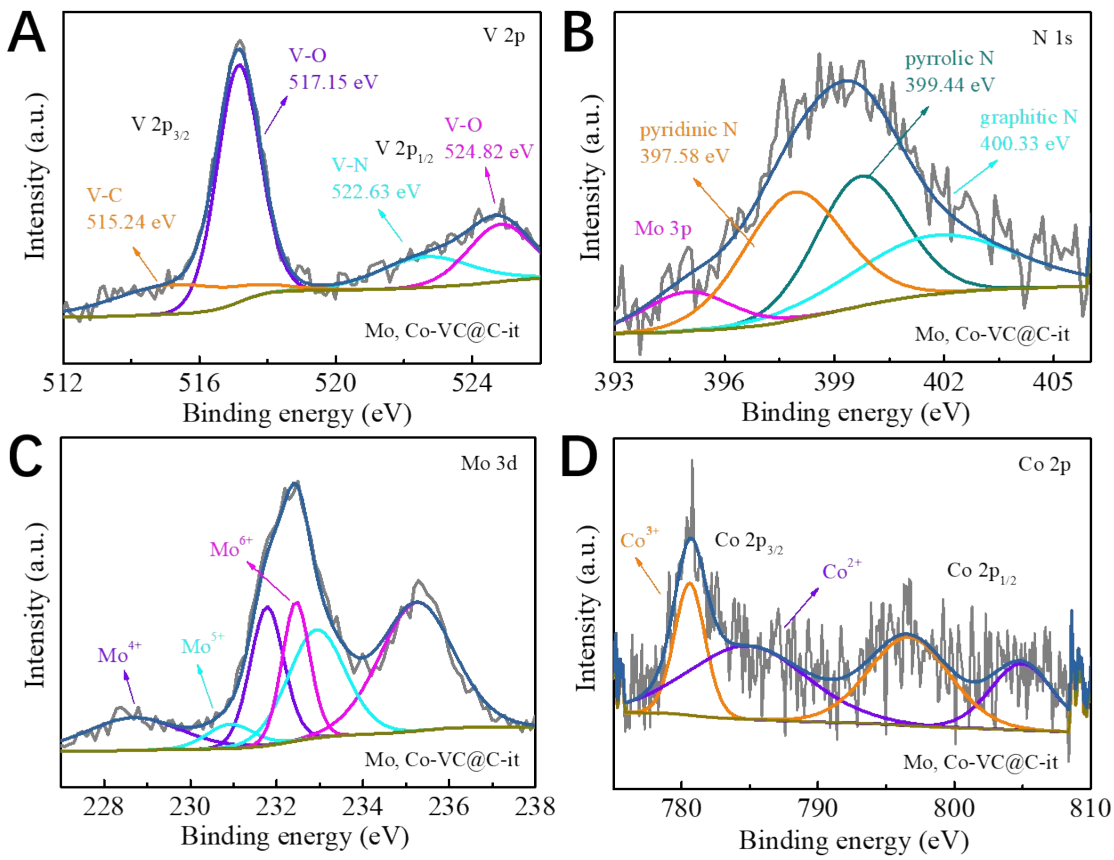

Fig. S14 The XPS spectrum of Mo, Co-VC@C after HER durability test at pH 14: (A) V 2p, (B) N 1s, (C) Mo 3d, (D) Co 2p.

Table S3. Comparison of HER performance of reported TMCs electrocatalysts.

Catalyst	Electrolyte	Current density(*j*)	Overpotential at the corresponding *j*	Reference
Mo, Co-VC@C	1 M KOH	10 mA/cm^2	137 mV	This work
VC/NC	1 M KOH 0.5 M H_2SO_4	10 mA/cm^2 10 mA/cm^2	142 mV 76 mV	*J. Power Sources* **2021**, 490, 229551
VC@NC/CC	1 M KOH 0.5 M H_2SO_4	100 mA/cm^2 100 mA/cm^2	238 mV 461 mV	*ChemSusChem* **2020**, 13, 3671-3678
VC@NCNT	1 M KOH 0.5 M H_2SO_4	10 mA/cm^2 10 mA/cm^2	159 mV 161 mV	*Nanoscale* **2018**, 10, 14272-14279
Mo_2C/VC @C	0.5 M H_2SO_4	10 mA/cm^2	122 mV	*Nano Energy* **2019**, 60, 520-526
Mo_2C/C	1 M KOH 0.5 M H_2SO_4	10 mA/cm^2 10 mA/cm^2	125 mV 180 mV	*ACS Appl. Mater. Inter.* **2017**, 9, 41314-41322
Mo_2C/KB	0.5 M H_2SO_4	10 mA/cm^2	180 mV	*ACS Sustainable Chem. Eng.* **2018**, 6, 983−990
MoC/NPC @CNTs	0.5 M H_2SO_4	10 mA/cm^2	175 mV	*Sustain. Energy Fuels* **2020**, 4, 407
Co_3Mo_3C	1 M KOH	1 mA/cm^2 10 mA/cm^2	72 mV 169 mV	*Inorg. Chem. Front.* **2019**,6, 940-947
Co/Mo_2C	1 M KOH	10 mA/cm^2	157 mV	*Int. J. Hydrogen Energy* **2020**, 45, 21221-21231
Ni-Mo/WC	1 M KOH	10 mA/cm^2	134 mV	*Int. J. Hydrogen Energy* **2021**, 46, 22813-22831
W_2C-HS	0.5 M H_2SO_4	10 mA/cm^2 100 mA/cm^2	153 mV 264 mV	*ACS Omega* **2019**, 4, 4185−4191