

Supporting Information(SI):

**Mo-doped ultrafine VC nanoparticles confined in few-layer
graphitic nanocarbon for improved electrocatalytic hydrogen
evolution**

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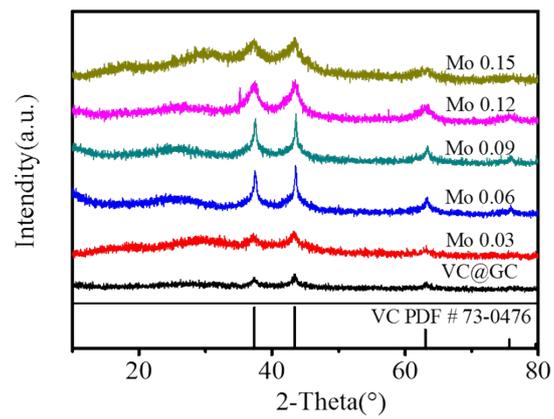


Fig. S1 XRD patterns of samples with different Mo-doping amount.

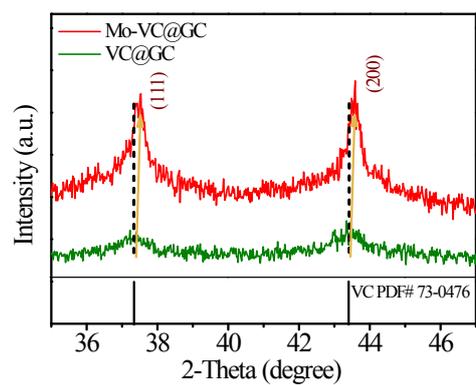


Fig. S2 XRD patterns with zoomed-in image of VC@GC and Mo-VC@GC.

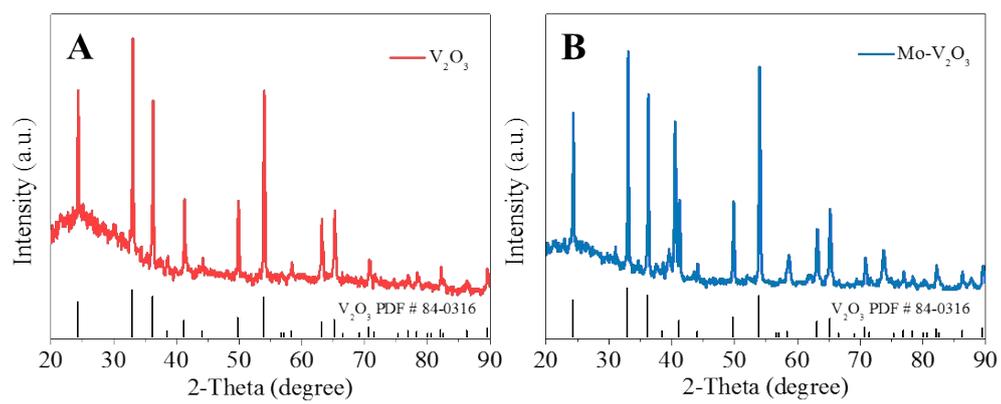


Fig. S3 XRD patterns of (A) V_2O_3 and (B) $Mo-V_2O_3$.

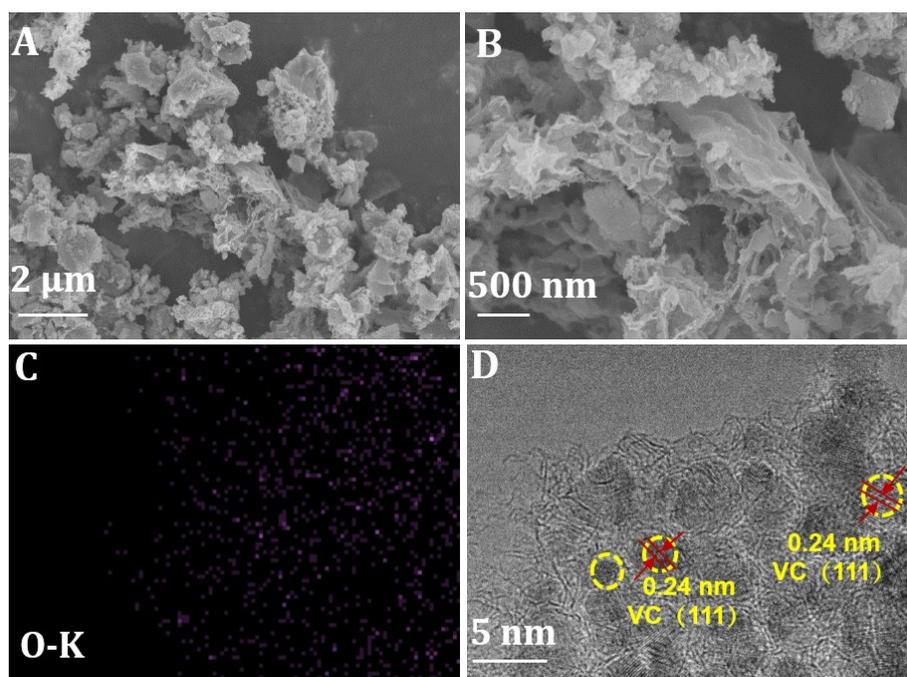


Fig. S4 (A-B) SEM images, (C) the O elemental mapping image, (D) the high-resolution TEM image of Mo-VC@GC.

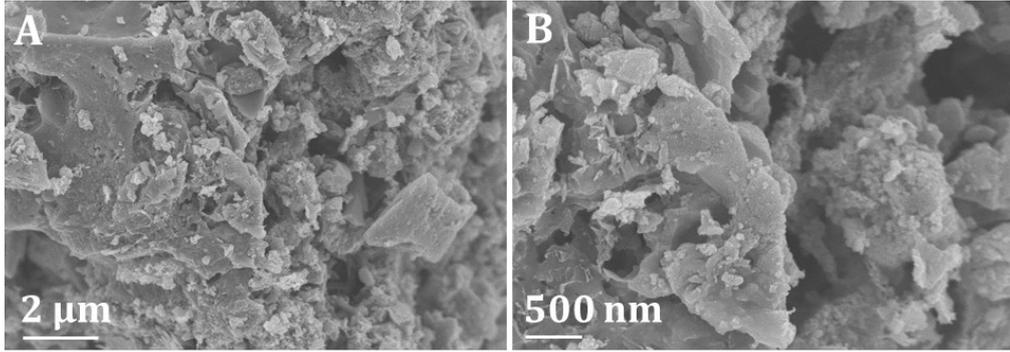


Fig. S5 (A-B) SEM images of VC@GC.

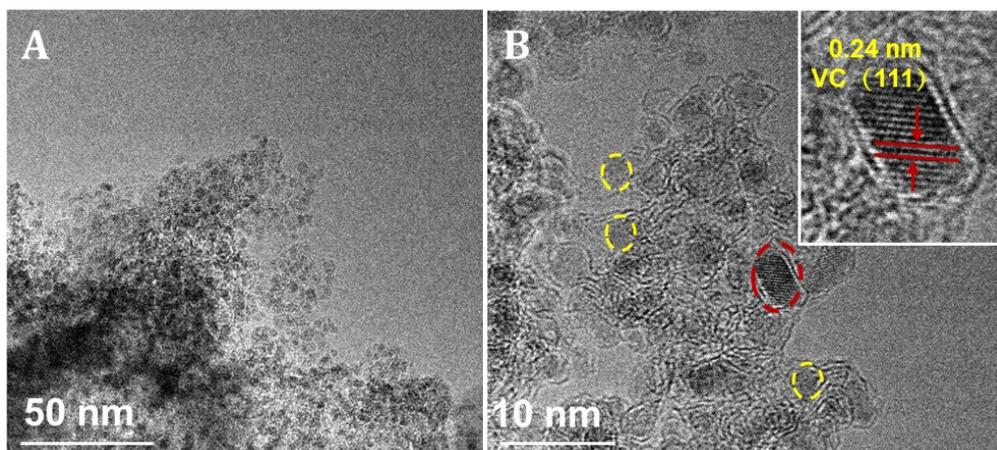
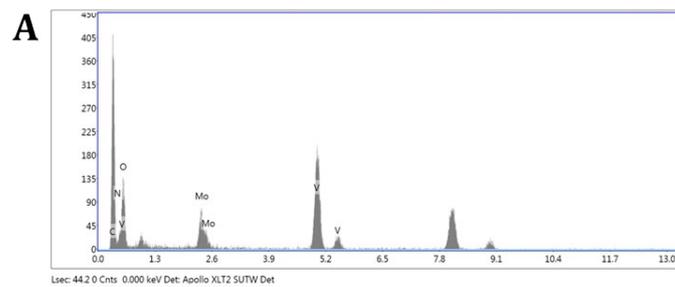


Fig. S6 (A-B) TEM and high-resolution TEM images of VC@GC.



B

Element	Weight %	Atomic %	Net Int.	Error %	Kratio
C K	13.90	16.53	37.3	6.90	0.09
N K	53.39	54.46	86.1	8.62	0.18
O K	32.39	28.92	43.7	12.06	0.04
V K	0.27	0.07	113.5	16.45	0.01
MoK	0.05	0.01	11.5	22.17	0.00

Fig. S7 EDX results of Mo-VC@GC.

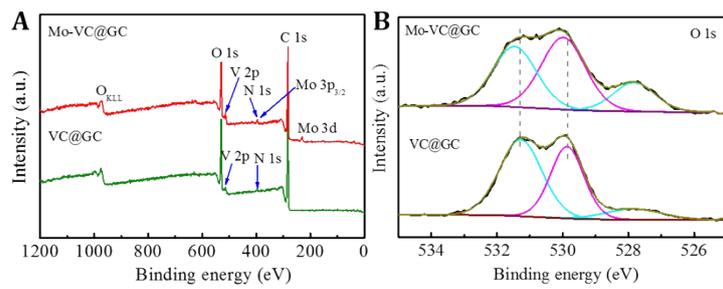


Fig. S8 (A) Survey, (B) O 1s XPS spectra of VC@GC and Mo-VC@GC.

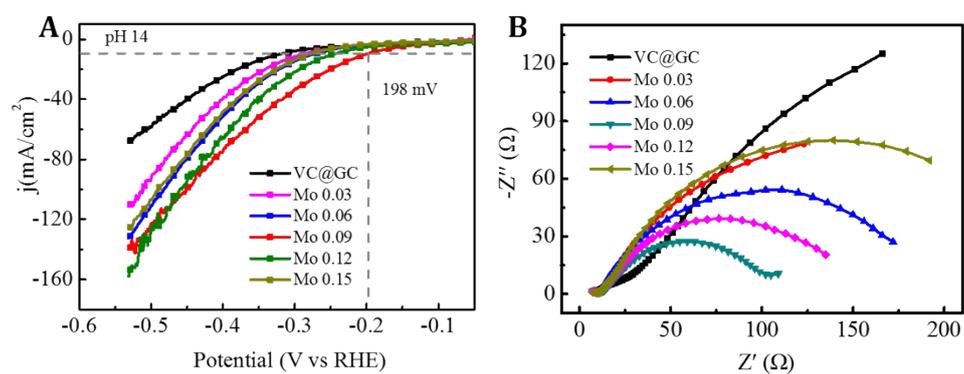


Fig. S9 (A) Polarization curves, (B) Nyquist plots obtained at the overpotential $\eta=233\text{mV}$ of samples with different Mo-doping amount at pH 14.

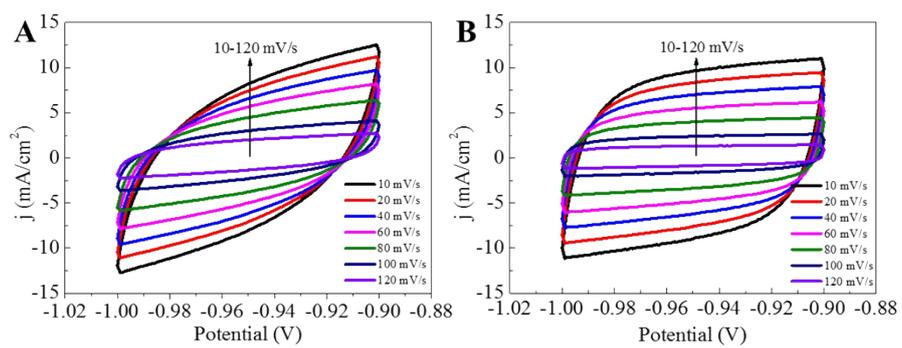


Fig. S10 CV curves of (A) VC@GC and (B) Mo-VC@GC at different scan rates.

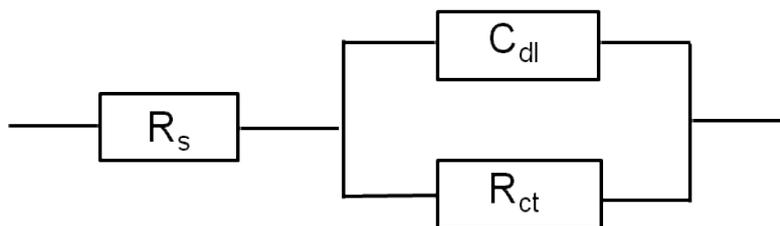


Fig. S11 Electrical equivalent circuit used to simulate the Nyquist plots in Fig. 5C, where R_s is the electrolyte resistance, R_{ct} is the charge-transfer resistance, and C_{dl} represents the double-layer capacitance.

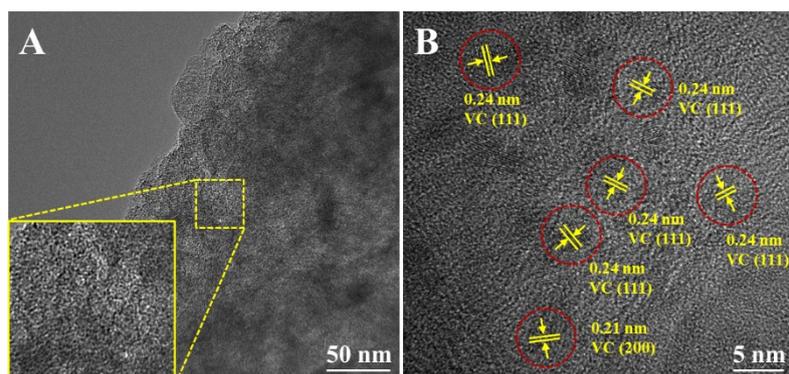


Fig. S12 (A) TEM and (B) HRTEM images of Mo-VC@GC after the stability test of i-t curve for 80h at pH 14.

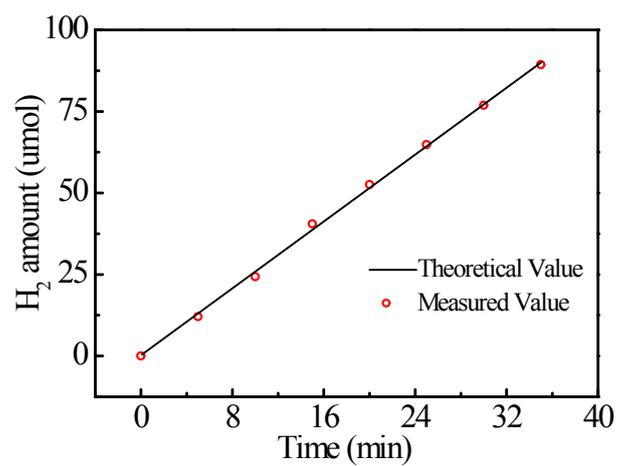


Fig. S13 Hydrogen production efficiency over Mo-VC@GC at a current density of 8.27 mA/cm², measured for 35 min.

Table S1. The mass percent of Mo and V in the Mo-VC@GC.

Elements	the mass percentage (%)
Mo	8.66
V	21.65

Table S2. Comparison of HER performance of reported TMCs electrocatalysts.

Catalyst	Electrolyte	η_{10} (mV)	Stability test	Reference
Mo-VC@GC	1 M KOH	198	80 h	This work
VC@NCNT	1 M KOH	159	100 h	<i>Nanoscale</i> 2018 , 10, 14272-14279
	0.5 M H ₂ SO ₄	161		
Ni-VC-@C/Ti	1 M KOH	146	20 h	<i>J. Mater. Chem. A</i> 2017 , 5, 23028-23034
	0.5 M H ₂ SO ₄	138		
VC-NS	0.5 M H ₂ SO ₄	98	10000 cycles	<i>Nano energy</i> 2016 , 26, 603-609
Mo ₂ C/VC	0.5 M H ₂ SO ₄	122	10000 cycles	<i>Nano Energy</i> 2019 , 60, 520-526
Mo ₂ C@GC	0.5 M H ₂ SO ₄	125	10000 s	<i>ACS Appl. Mater. Interfaces</i> 2018 , 10, 18761-18770
W ₂ C@WC	0.5 M H ₂ SO ₄	310	1000 cycles	<i>Appl. Catal. B</i> 2018 , 236, 147-153
W ₂ C@CNT-S	1 M KOH	148	30 h	<i>Nanoscale</i> 2019 , 11, 4876-4884
	0.5 M H ₂ SO ₄	176		
W ₂ C IO	0.5 M H ₂ SO ₄	146	10 h	<i>Nanoscale</i> 2019 , 11, 11505-11512
WC/W ₂ C@C NWs	1 M KOH	56	2000 cycles	<i>J. Mater. Chem. A</i> 2018 , 6, 15395-15403
	0.5 M H ₂ SO ₄	69		