Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

In-situ Phase Transition Induced TM-MoC/Mo_2C (TM= Fe, Co, Ni, and Cu) Heterostructure Catalysts for Efficient Hydrogen Evolution

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#These two authors contributed equally to this work.

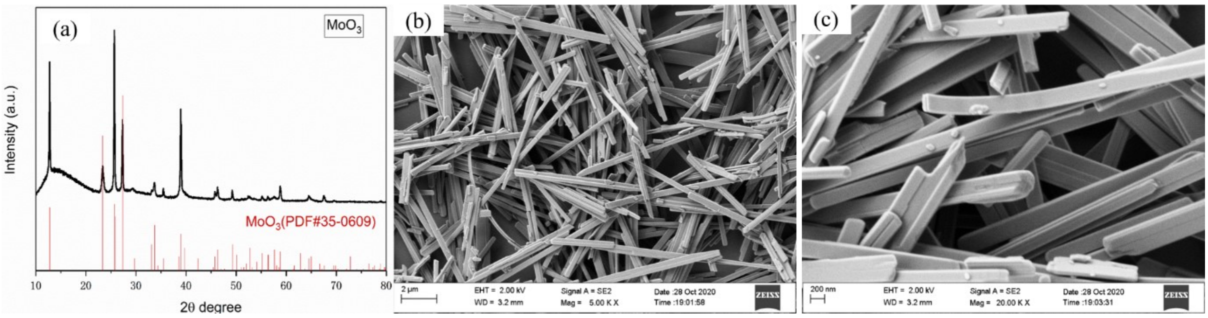
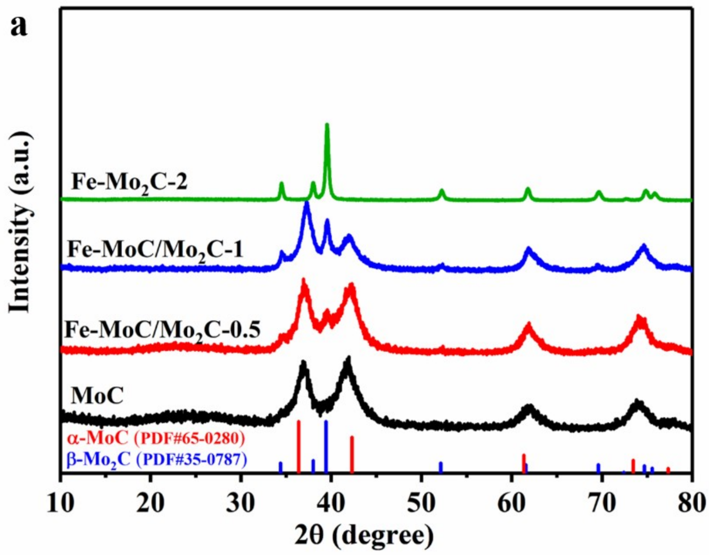
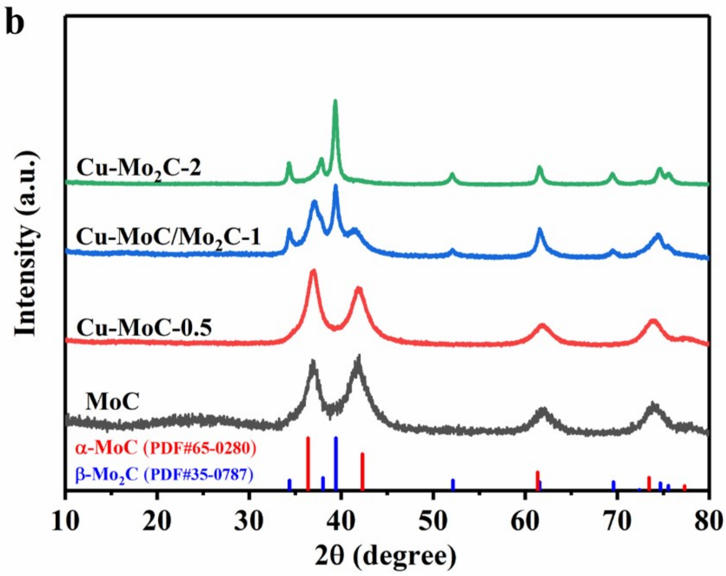


Figure S1 (a)XRD pattern and (b,c)SEM images of Co-MoO$_3$





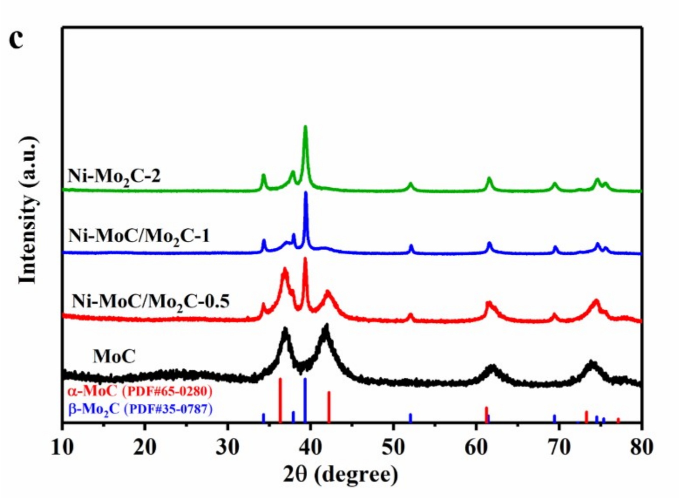


Figure S2 XRD patterns of (a)Fe, (b)Cu, (c)Ni coupled samples.

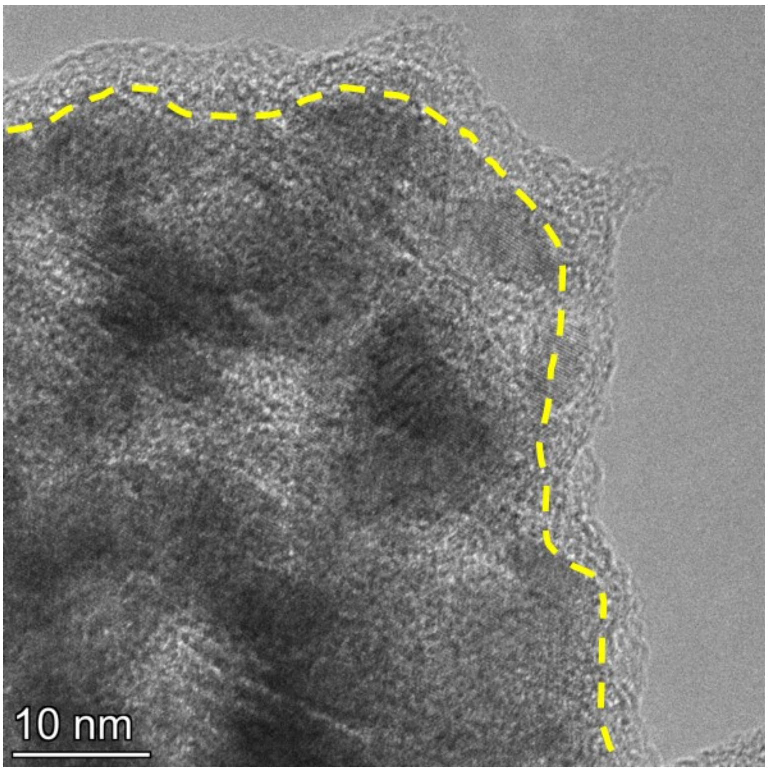


Figure S3 Carbon layer around the Co-MoC/Mo_2C-0.5

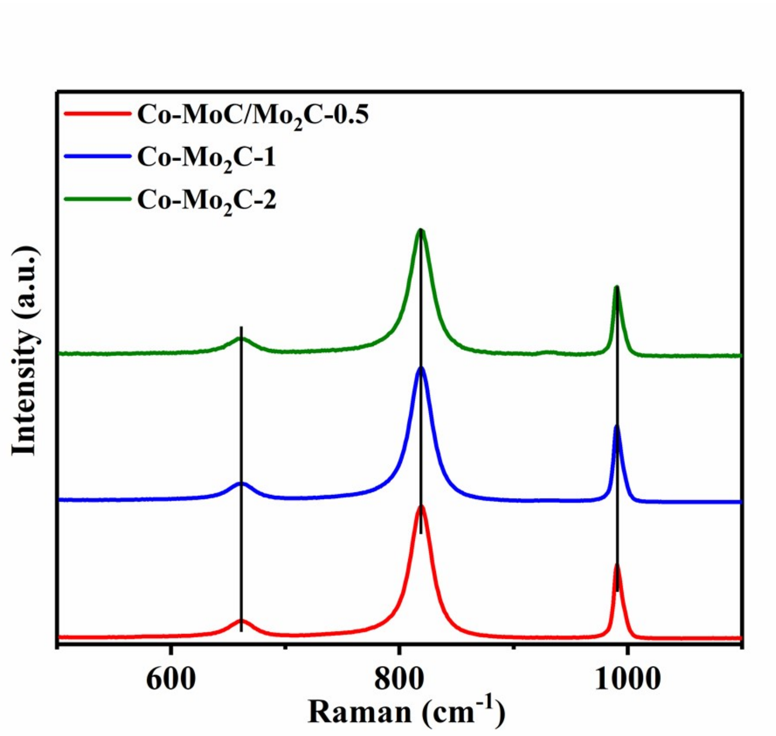


Figure S4 Low-wave Raman patterns of Co-MoC/Mo_2C-0.5, Co-Mo_2C-1 and Co-Mo_2C-2

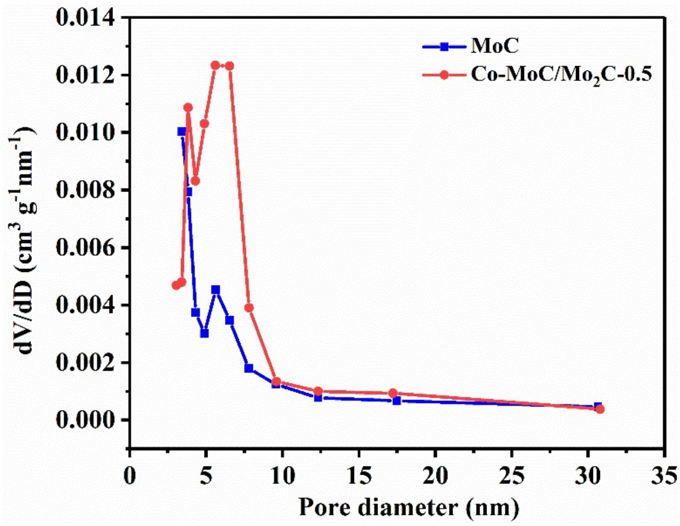


Figure S5 Pore size distribution plots of pure MoC and Co-MoC/Mo_2C.

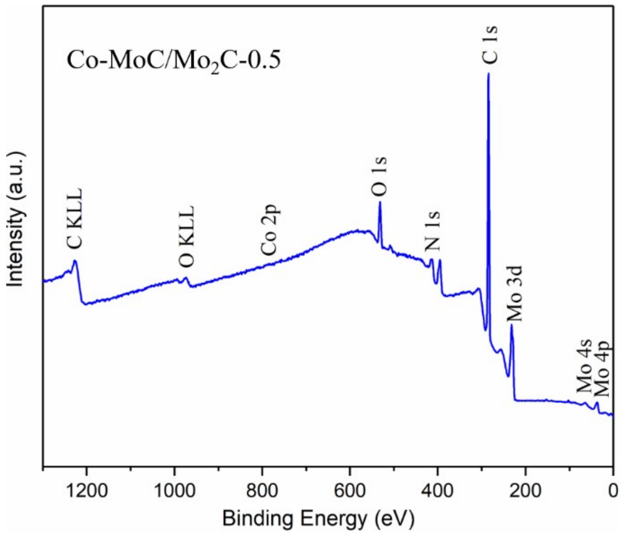


Figure S6 XPS survey spectrum of Co-MoC/Mo_2C-0.5

Table S1 Fitting parameters (peak position, peak area, and species percentage) for Mo 3d spectra taken on the Co-Mo_xC catalysts

catalysts	Species	peaks $3d_{5/2}$	peaks $3d_{3/2}$	Area $3d_{5/2}$	Area $3d_{3/2}$	Mo^{2+} and Mo^{3+}
MoC	Mo^{3+}	228.7	231.8	46849	33463	34.5
	Mo^{4+}	229.9	234.1	22031	16947	
	Mo^{6+}	232.7	235.8	67968	45312	
Co-MoC/Mo_2C-0.5	Mo^{2+}	228.2	231.5	13145	8648	56.1
	Mo^{3+}	229.1	232.1	7764	11413	
	Mo^{4+}	229.8	233.4	7681	5155	
	Mo^{6+}	232.8	236.2	11236	8025	

	Mo^{2+}	228.1	231.4	31542	21028	
Co- Mo_2C-1	Mo^{4+}	229.5	234.6	18945	1739	31.4
	Mo^{6+}	233	236.2	62616	31308	

Table S2 Fitting parameters of peak position for Mo^{2+} and Mo^{3+} spectra taken on the Co-MoC/Mo_2C-0.5, Ni-MoC/Mo_2C-0.5, Fe-MoC/Mo_2C-0.5, and Cu-MoC/Mo_2C-0.5 catalysts.

Catalysts	Species	Peaks	
		$3d_{5/2}$	$3d_{3/2}$
Co-MoC/Mo_2C-0.5	Mo^{2+}	228.2	231.5
	Mo^{3+}	229.1	232.1
Ni-MoC/Mo_2C-0.5	Mo^{2+}	228.3	231.3
	Mo^{3+}	228.7	231.6
Fe-MoC/Mo_2C-0.5	Mo^{2+}	228.9	232.1
	Mo^{3+}	229.5	232.4
Cu-MoC/Mo_2C-0.5	Mo^{2+}	229.1	232.4
	Mo^{3+}	229.5	233.1

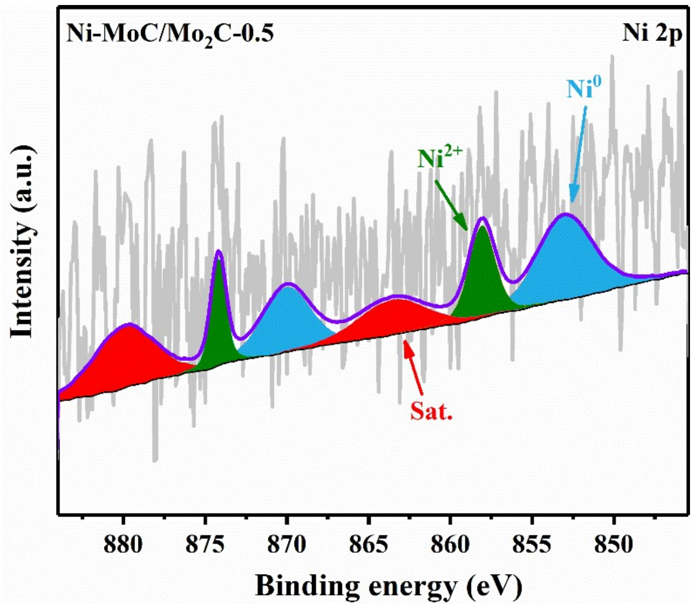


Figure S7: Ni 2p spectra of Ni-MoC/Mo_2C-0.5

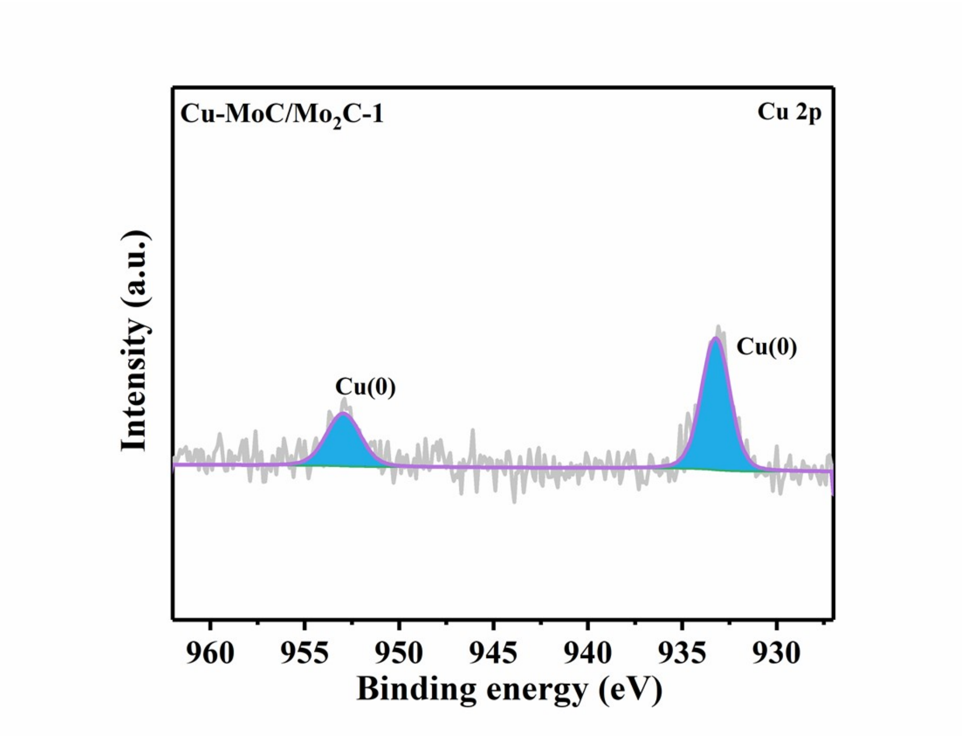


Figure S8. Cu 2p spectra of Cu-MoC/Mo_2C-1

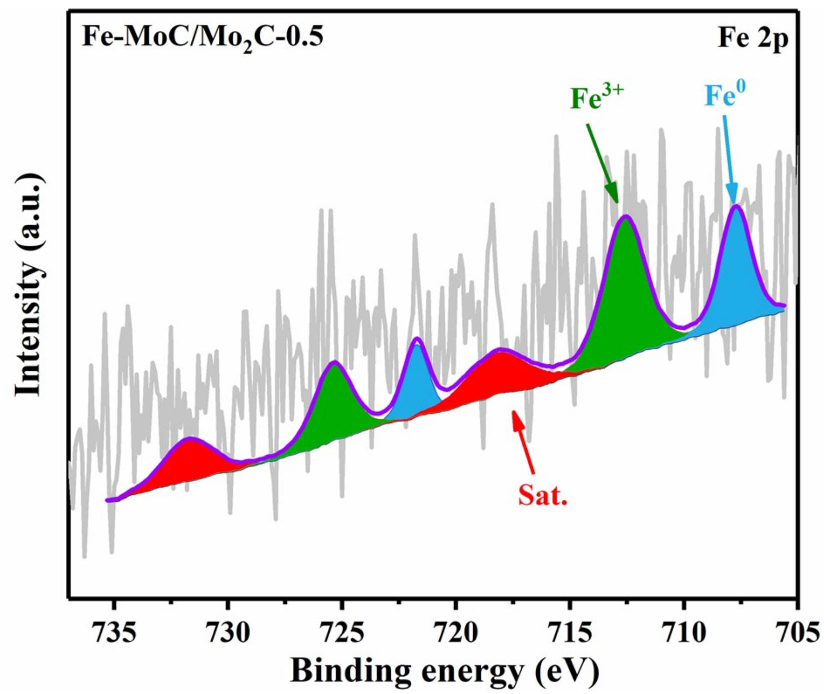


Figure S9. Fe 2p spectra of Fe-MoC/Mo_2C-0.5

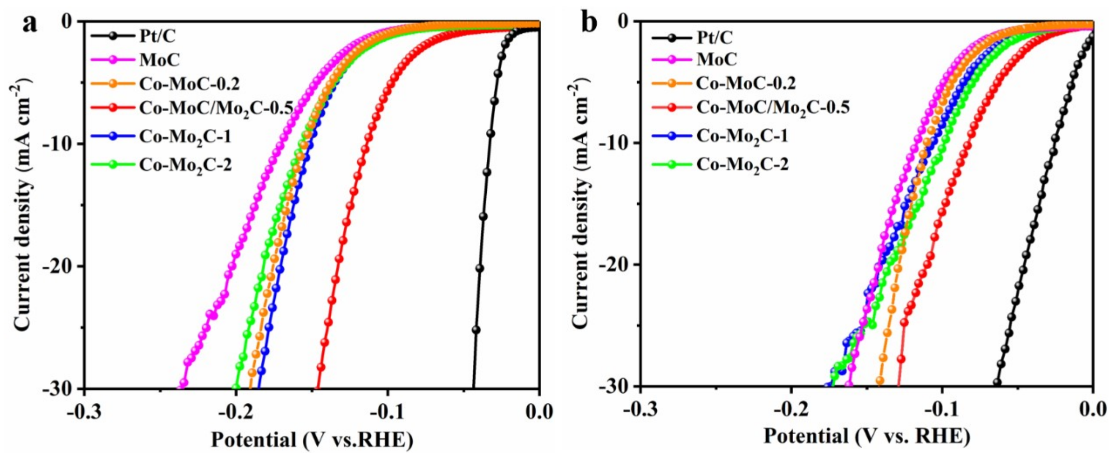


Figure S10. LSV of Co doped samples in (a) 0.5 M H_2SO_4 and (b)1 M KOH

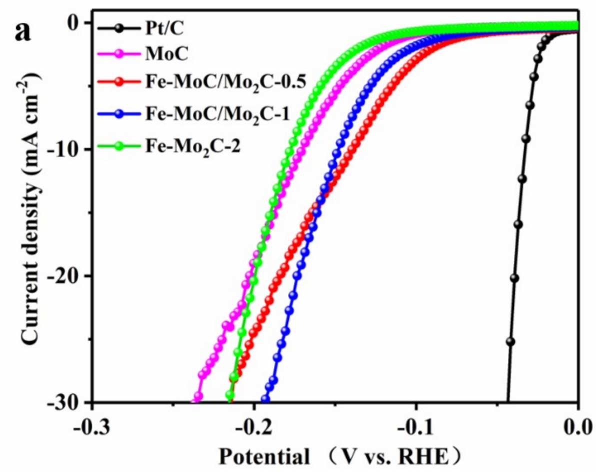


Figure S11 LSV of Fe doped samples in (a) 0.5 M H_2SO_4 and (b)1 M KOH

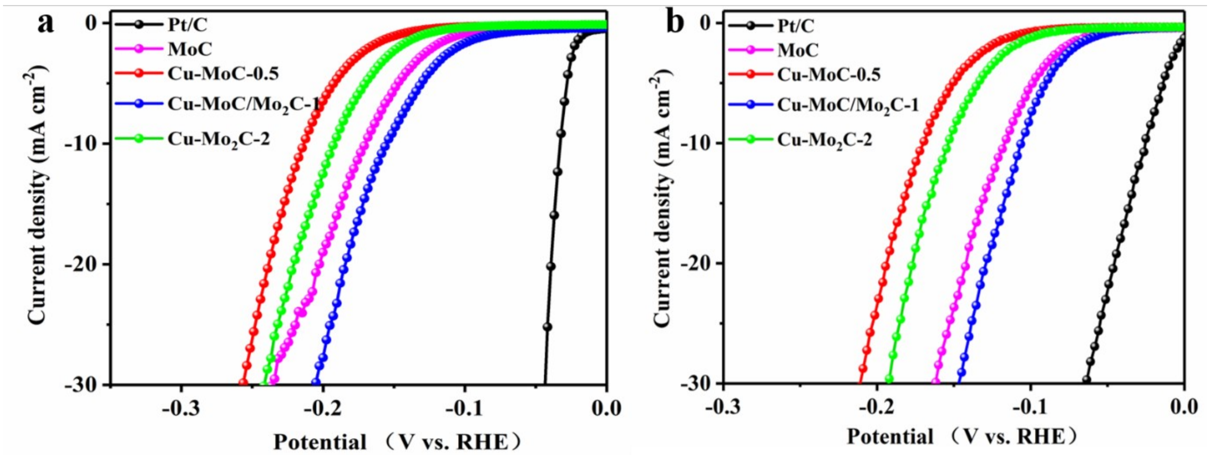


Figure S12 LSV of Cu doped samples in (a) 0.5 M H_2SO_4 and (b)1 M KOH

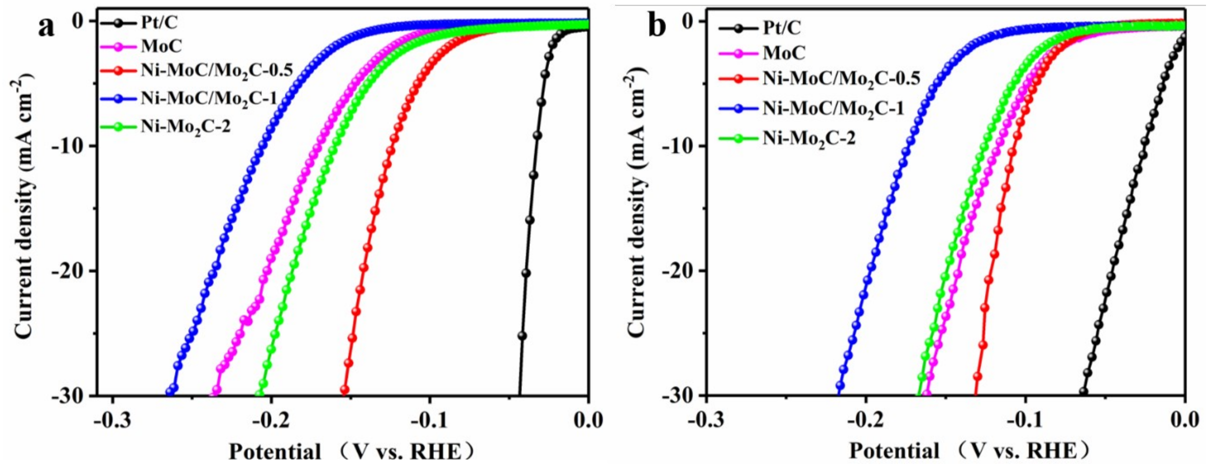


Figure S13 LSV of Ni doped samples in (a) 0.5 M H_2SO_4 and (b)1 M KOH

Table S3 HER activity comparison of recently published Mo-based catalysts in 0.5 M H_2SO_4

Catalyst	η_{10}	Tafel slope	reference
Ni/Mo_2C (1:2)-NCNFs	143	57.8	[1]
MoC–Mo_2C-31.4	126	43	[2]
Mo_2C-carbon sphere	164	85	[3]
Mo_xC-0.4	155	53	[4]
Mo_2N–Mo_2C/HGr-3	157	55	[5]
Co-NC@Mo_2C	143	60	[6]
MoCx/C	135	62	[7]
Mo_2C–GNR	152	65	[8]
Mo_2C@SNC	146	83	[9]

Table S4 Comparison of Catalytic Performance of Different HER Electrocatalysts in 0.5 M H_2SO_4

Electrocatalyst	η_{10} (mV)	Tafel slpoe (mV dec^{-1})	j_0 (mA cm^{-2})	C_{dl} (mF cm^{-2})
MoC	171	77	0.14	3.1
Co-MoC/Mo_2C-0.5	114	54	0.22	17.9
Fe-MoC/Mo_2C-0.5	138	80	0.2	8.9
Cu-MoC/Mo_2C-1	156	78	0.16	4.4
Ni-MoC/Mo_2C-0.5	124	53	0.18	9.1

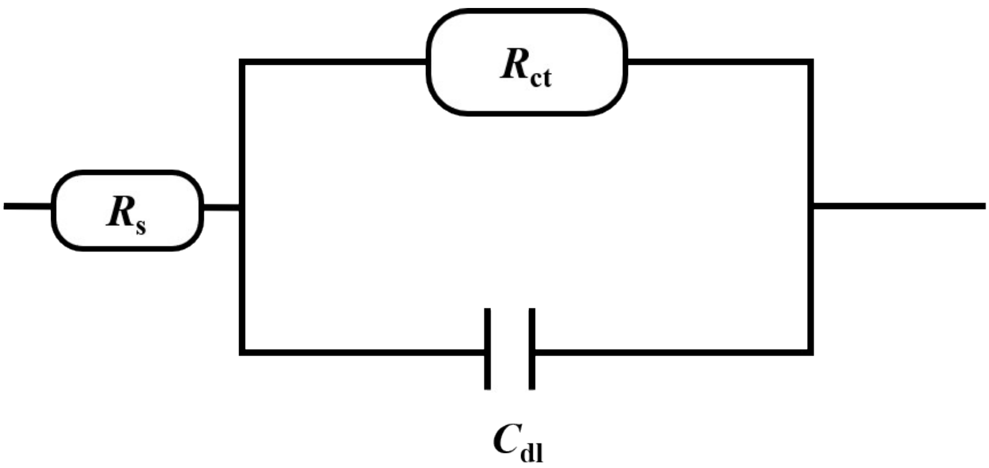


Figure S14 Equivalent circuit model of the TM-MoC/Mo_2C heterostructure catalysts in 0.5 M H_2SO_4. R_s: the electrolyte resistance, C_{dl}: double layer capacitance, R_{ct}: charge transfer resistance.

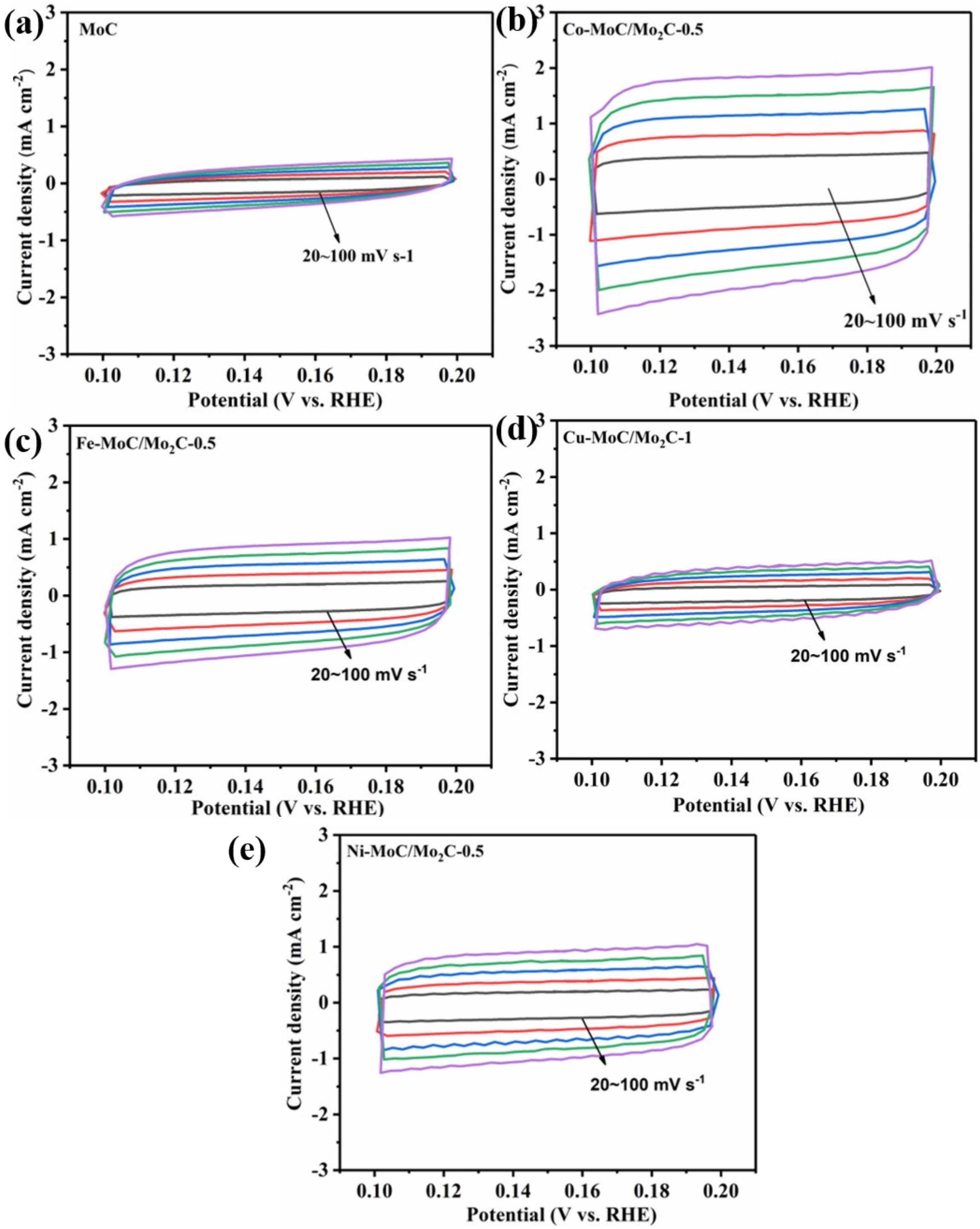


Figure S15 Cyclic voltammetry curves in a non-faradaic potential region under different scan rates of (a) MoC, (b) Co-MoC/Mo_2C-0.5, (c) Fe-MoC/Mo_2C-0.5, (d) Cu-MoC/Mo_2C-1, (e) Ni-MoC/Mo_2C-0.5

Table S5 Comparison of Catalytic Performance of Different HER Electrocatalysts in 1 M KOH

Electrocatalyst	η_{10} (mV)	Tafel slpoe (mV dec^{-1})	j_0 (mA cm^{-2})	C_{dl} (mF cm^{-2})
MoC	120	63	0.20	5.5
Co-MoC/Mo_2C-0.5	82	53	0.44	15.2
Fe-MoC/Mo_2C-0.5	97	56	0.29	8.1
Cu-MoC/Mo_2C-1	106	50	0.21	9.9
Ni-MoC/Mo_2C-0.5	107	40	0.14	7.2

Table S6 HER activity comparison of recently published Mo-based catalysts in 1 M KOH

Catalyst	η_{10}	Tafel slope	Reference
Mo_2N–Mo_2C/HGr-3	154	68	[5]
Co-NC@Mo_2C	99	66	[6]
MoC_x/C	150	99	[7]
Mo_2C–GNR	121	54	[8]
Co/β-Mo_2C@N-CNTs	170	92	[10]
h-Mo_2C/MoO_2	92	56.6	[11]

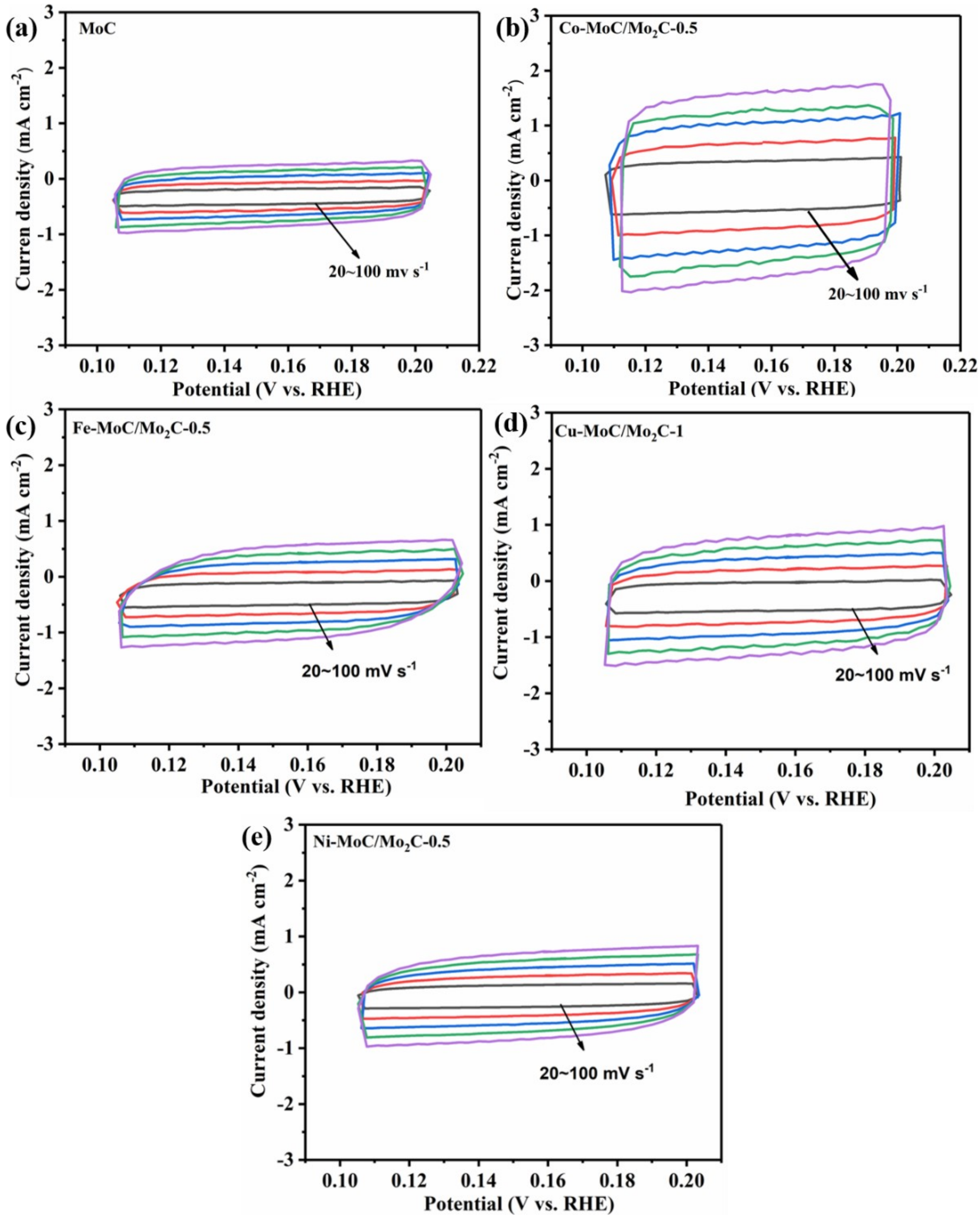


Figure S16 Cyclic voltammetry curves in a non-faradaic potential region under different scan rates of (a) MoC, (b) Co-MoC/Mo_2C-0.5, (c) Fe-MoC/Mo_2C-0.5, (d) Cu-MoC/Mo_2C-1, (e) Ni-MoC/Mo_2C-0.5

Figure S17 Equivalent circuit model of the TM-MoC/Mo_2C heterostructure catalysts in 1 M KOH. R_s: the electrolyte resistance, C_{dl}: double layer capacitance, R_{ct}: charge transfer resistance.

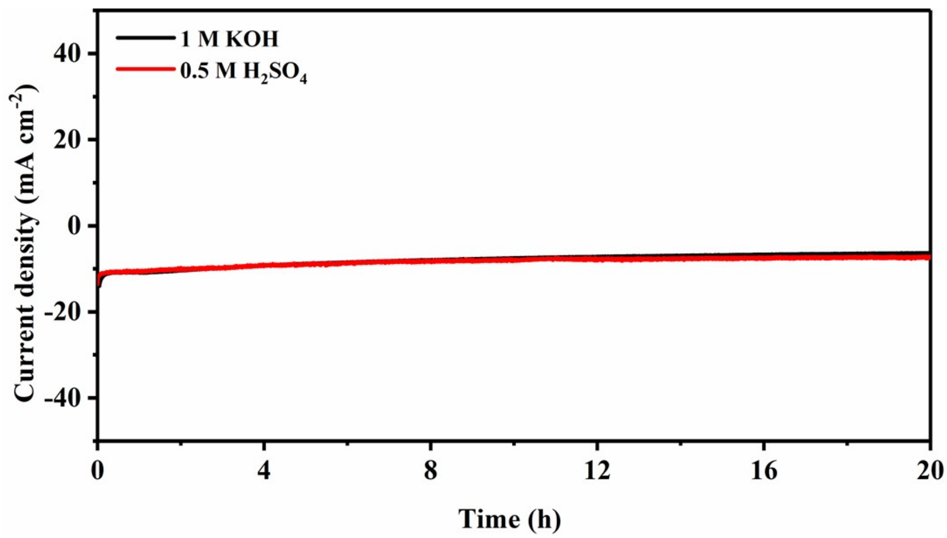


Figure S18 I–t curve at the current density of Co-MoC/Mo_2C-0.5 in both 0.5 M H_2SO_4 and 1 M KOH.

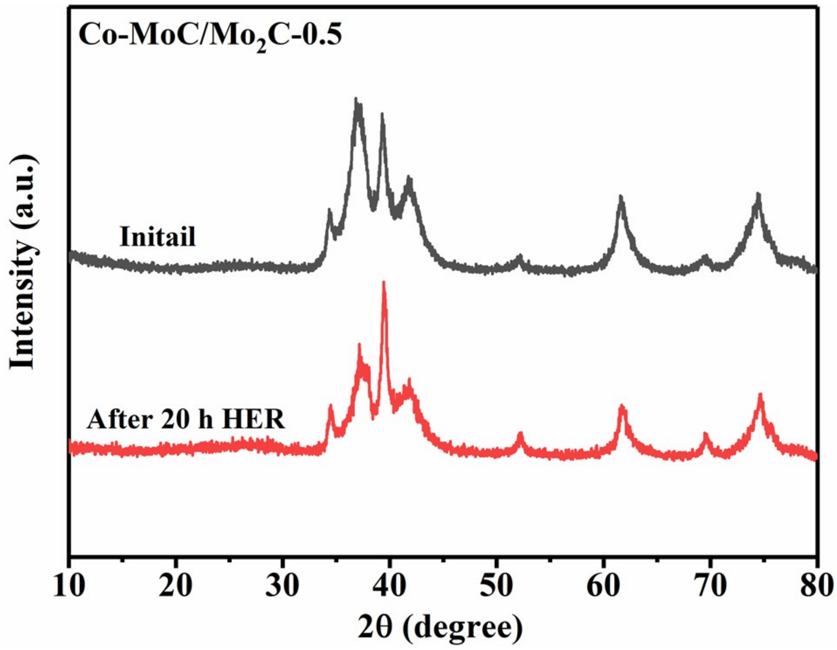


Figure S19 XRD patterns of the Co-MoC/Mo_2C-0.5 catalyst before and after 20 h durability test. The results show that the Co-MoC/Mo_2C-0.5 catalyst has a highly stability.

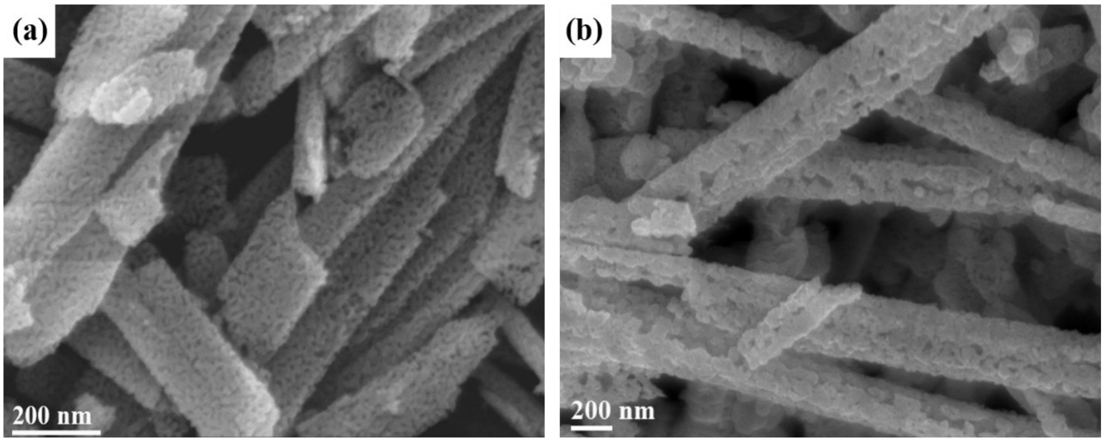


Figure S20 SEM images of Co-MoC/Mo_2C-0.5 catalyst (a) before and (b) after 20 h durability test.

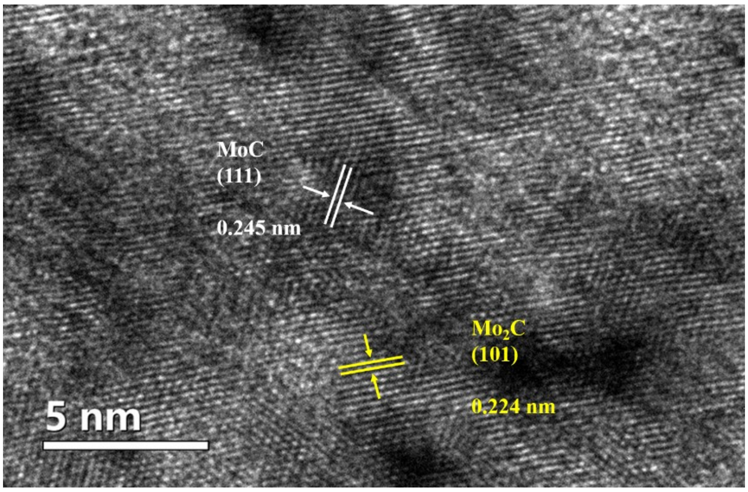


Figure S21 TEM images of Co-MoC/Mo_2C-0.5 catalyst after 20 h durability test. The almost unchanged TEM images of the Co-MoC/Mo_2C-0.5 electrode before and after the stability test shows that the catalyst has super stability.

Reference:

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