Supporting Information

Acid-Directed Morphology Control of Molybdenum Carbide Embedded in Nitrogen Doped Carbon Matrix for Enhanced Electrocatalytic Hydrogen Evolution

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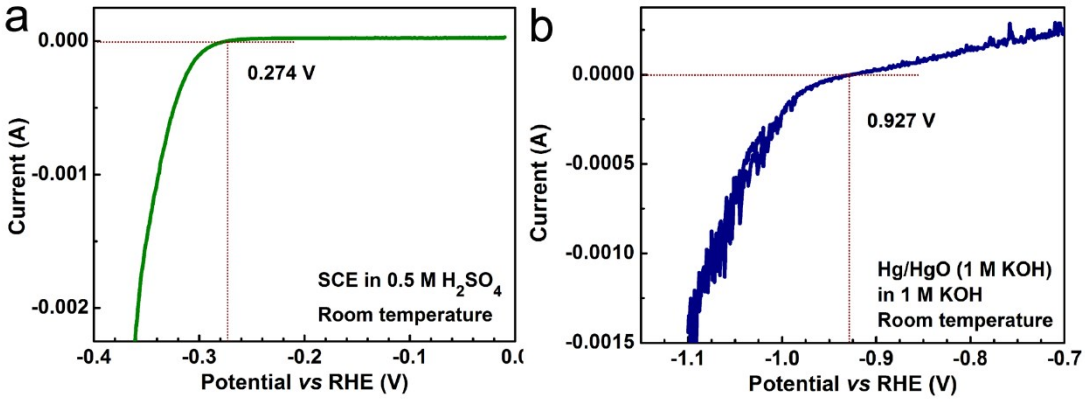

Fig. S1 Calibration curves of reference electrodes. (a) saturated calomel electrode (SCE) in 0.5 M H_2SO_4 solution and (b) Hg/HgO (1.0 M KOH) electrode in 1.0 M KOH at room temperature.

Before electrochemical measurement, all the reference electrodes should to be calibrated to guarantee the veracity and reliability of test results [S1]. In the calibration process, Pt sheet (purchased from Aldrich) were used as working and counter electrodes, SCE and Hg/HgO (1.0 M KOH) electrode were applied as reference electrodes in 0.5 M H_2SO_4 solution and 1.0 M KOH, respectively. Before calibration, H_2 was led continuously into the solution for 30 min to saturate the solution with hydrogen. Then, calibration curves in 0.5 M H_2SO_4 and 1.0 M KOH were obtained with a scan rate of 1 mV/s at room temperature, as shown in Figure S1. The corrected potentials of SCE and Hg/HgO electrode are 0.274 V and 0.927 V *vs* RHE, respectively.

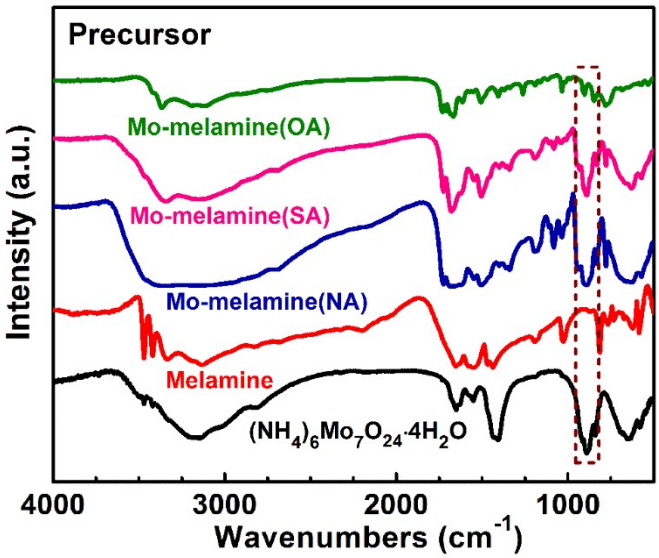

Fig. S2 FTIR spectra of as-prepared Mo-melamine(OA), Mo- melamine (SA), Mo-melamine (NA) precursors.

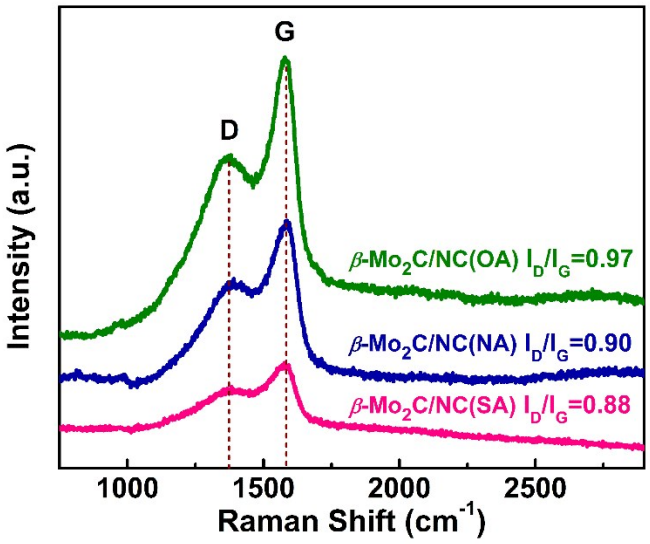

Fig. S3 Raman spectra for as-prepared β-Mo_2C/NC(OA), β-Mo_2C/NC(SA), β-Mo_2C/NC(NA).

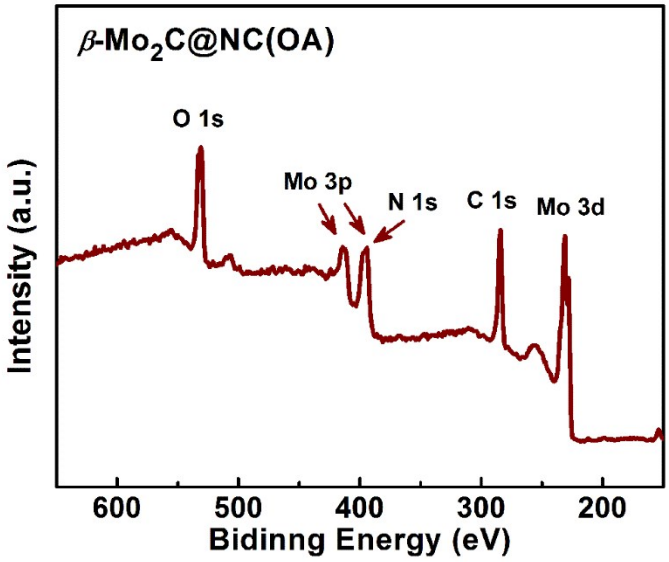

Fig. S4 Survey XPS spectrum of β-Mo_2C/NC(OA).

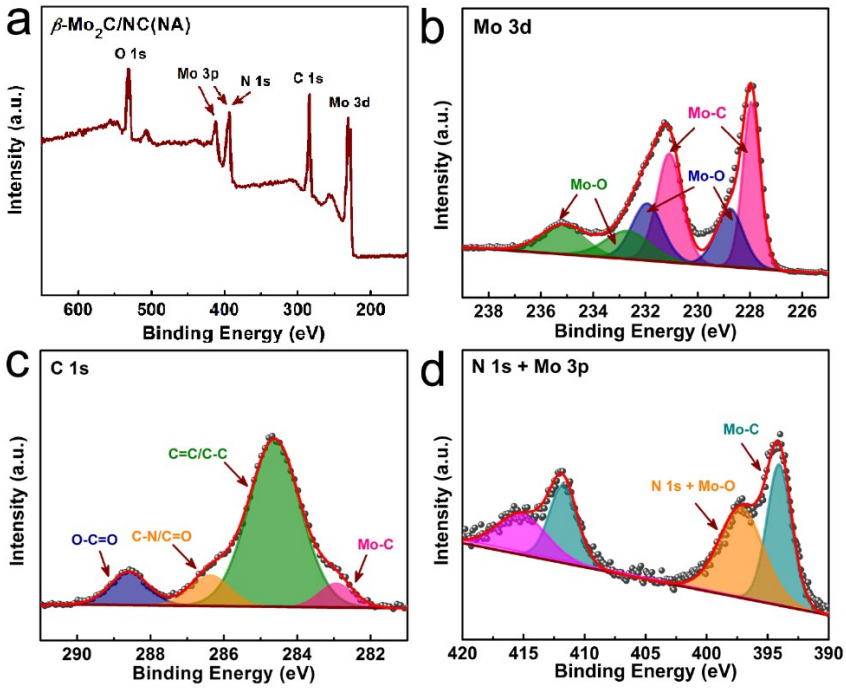

Fig. S5 (a) Survey XPS spectrum of β-Mo_2C/NC(NA); High-resolution XPS spectra of (b) Mo 3d, (c) C 1s and (d) N 1s - Mo 3p of β-Mo_2C/NC(NA).

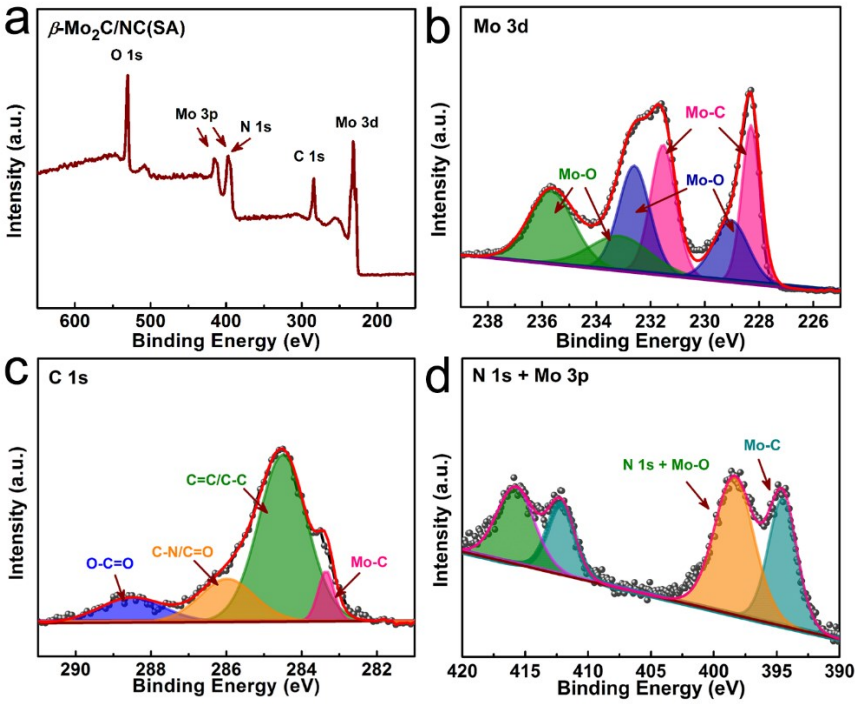

Fig. S6 (a) Survey XPS spectrum of β-Mo_2C/NC(SA); High-resolution XPS spectra of (b) Mo 3d, (c) C 1s and (d) N 1s-Mo 3p of β-Mo_2C/NC(SA).

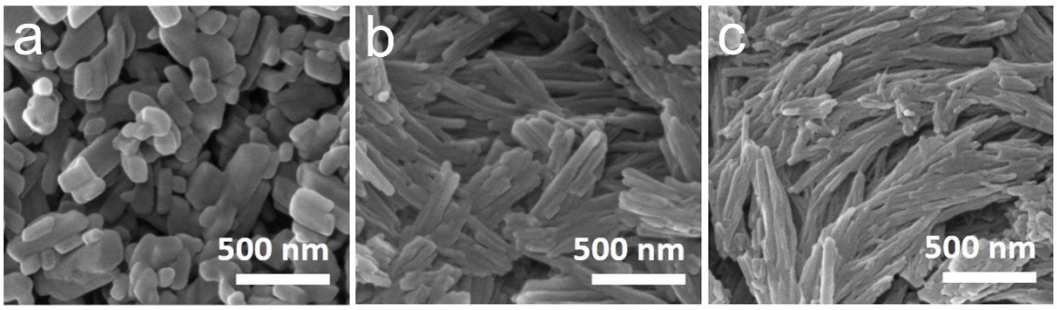

Fig. S7 SEM images of precursor for (a) β-Mo_2C/NC(OA), (b) β-Mo_2C/NC(NA) and (c) β-Mo_2C/S-NC(SA)

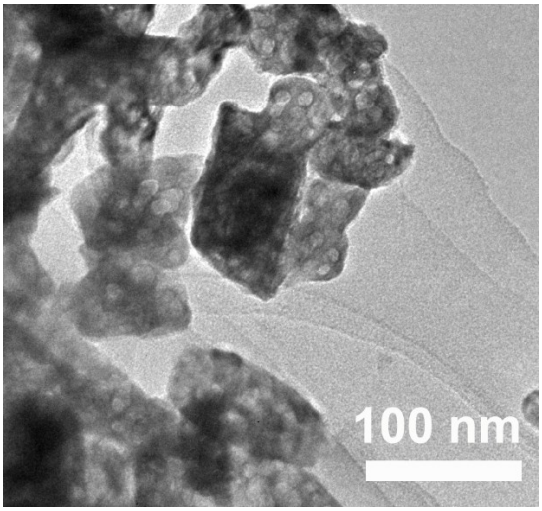

Fig. S8 High-magnifed TEM images of β-Mo_2C/NC(OA).

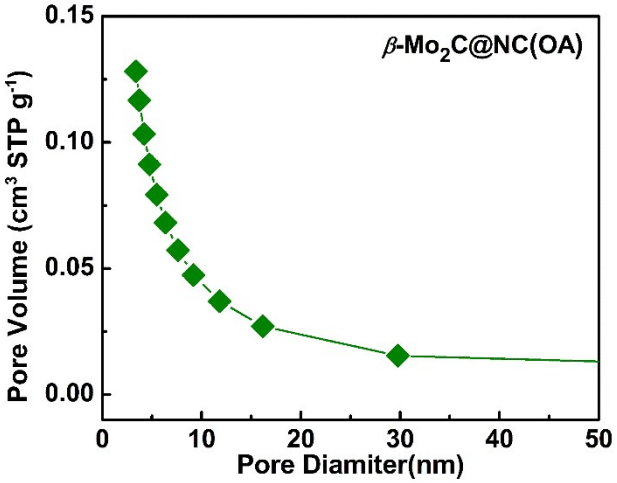

Fig. S9 Pore size distribution diagram of as-prepared β-Mo_2C/NC(OA).

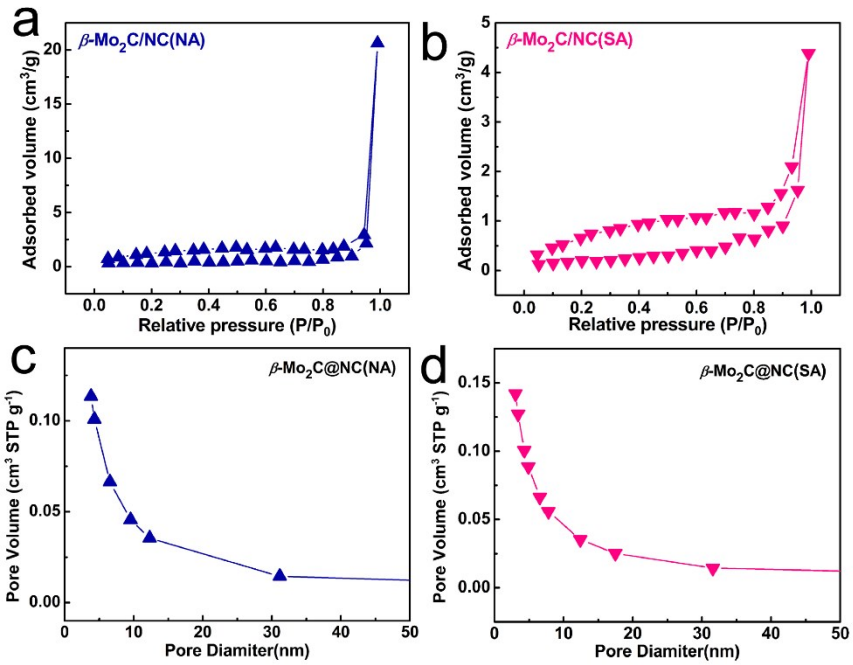

Fig. S10 (a, b) Nitrogen absorption and desorption diagrams and (c, d) pore size distribution diagrams of as-prepared β-Mo_2C/NC(NA), β-Mo_2C/NC(SA).

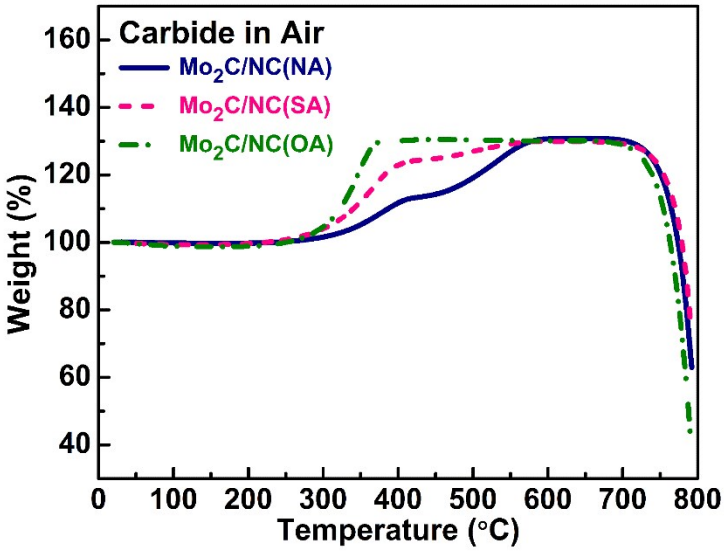

Fig. S11 TGA curves for carbide of Mo_2C/NC(OA), Mo_2C/NC(SA), Mo_2C/NC(NA).

As shown in Figure S10, Mo_2C nanoparticles were oxidized to MoO_3 during the TGA measurement in oxygen atmosphere, followed by the consumption of carbon and dopants. When the temperature rises to 600ºC, all the substances convert to only MoO_3. The weight percent of Mo_2C in as-prepared samples is estimated according to the following equation:

$$m\%\ (Mo_2C) = \text{residual mass} * M(Mo_2C)/2M(MoO_3)$$

$$= 130.8\ \text{wt.\%} * 204/(2*144) = 92.6\ \text{wt.\%}$$

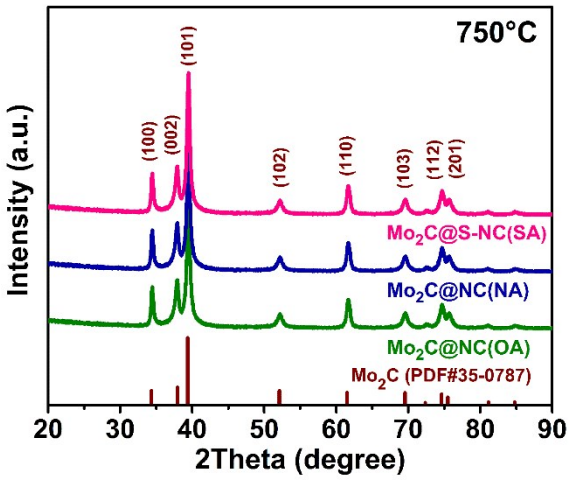

Fig. S12 XRD patterns of β-Mo_2C/NC(OA), β-Mo_2C/NC(NA) and β-Mo_2C/NC(SA) samples

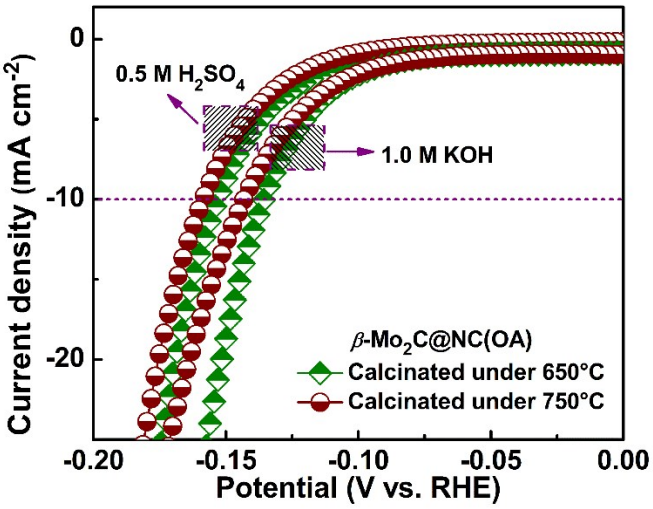

Fig. S13 Polarization curves after *i*R correction in 0.5 M H_2SO_4 (a) and 1.0 M KOH (b) for Mo_2C/NC(OA) obtained at 650ºC and 750ºC.

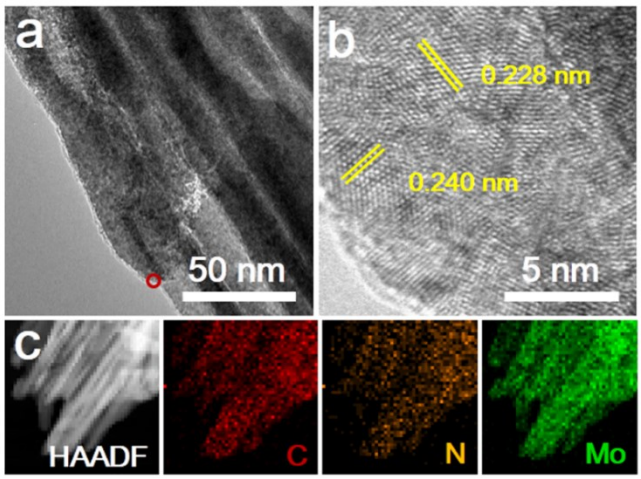

Fig. S14 (a) TEM images, (b) HRTEM images, (c) HAADF and corresponding element mapping of β-Mo_2C/NC(NA).

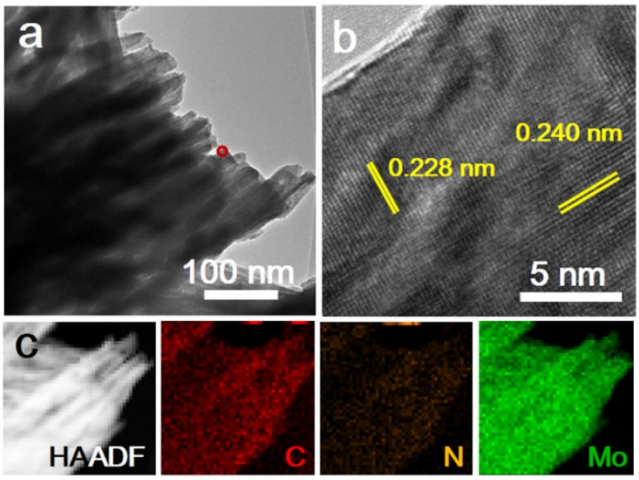

Fig. S15 (a) TEM images, (b) HRTEM images, (c) HAADF and corresponding element mapping of β-Mo_2C/NC(SA).

Table S1. Overpotential and Tafel slope of previously reported Mo_2C-based electrocatalysts in acidic and alkaline condition.

Samples	Synthesize method	Mass loading (mg cm^{-2})	Overpotential(mV) (-10 mA cm^{-2})		Tafel slope (mV dec^{-1})		Ref.
			0.5 M	1.0 M	0.5 M	1.0 M	

			H_2SO_4	KOH	H_2SO_4	KOH	
β-Mo_2C-NC	Acid-Assisted	0.19	152	135	58	52	This work
Mo_2C/NCF	Dopamine-polymerized	0.28	144	100	55	65	S2
Mo_2C nanobelts	Two-step	0.50	140	110	51.3	49.7	S3
Co_4Mo_2@NC	Physical mixing	0.35	-	218	-	73.5	S4
Pure β-Mo_2C	impregnation	1.0	-	130	-	66.5	S5
MoC-Mo_2C/PNCDs	MOF-derived	0.40	-	121	-	60	S6
Mo/Co@N–C	MOF-derived	0.70	187	157	82	148	S7
NP-Mo_2C	carburization	0.21	210	-	64	-	S8
Ni/Mo_2C-NCNFs	electrospinning	1.4	195	143	77.4	57.8	S9
MoC–Mo_2C	molybdate reacting with aniline	0.14	126	120	43	42	S10

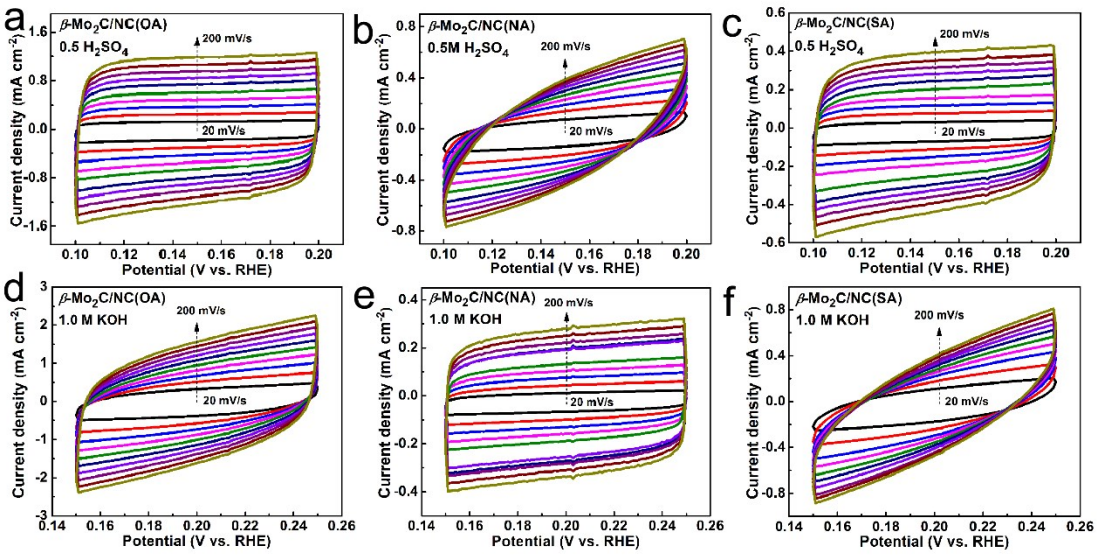

Fig. S16 Cyclic voltammetry curves of β-Mo_2C/NC(OA), β-Mo_2C/NC(SA), β-Mo_2C/NC(NA) under different scan rate. These data were used to generate the plots showing the extraction of the C_{dl} for different samples shown in Figure 4 and Figure 5 in the main text.

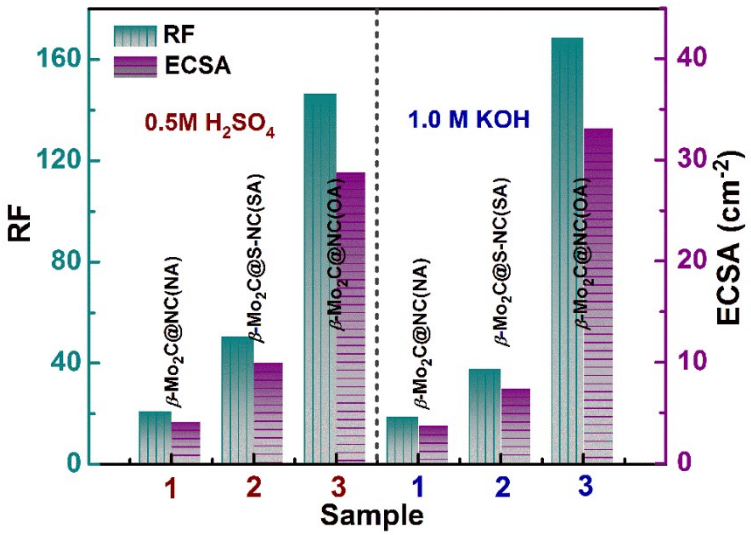

Fig. S17 Comparison of the ECSA and RF for as-prepared catalysts

ECSA calculation:

ECSA=C_{dl}/C_s, in which C_s is the specific capacitance, which is equal to 0.040 mF/cm^2 for a smooth electrode surface. Then the roughness factors (RF) were obtained by dividing the ECSA by the geometric area of the GCE.

Table S2. The fitting data of R_s and R_{ct} for as-prepared catalysts

Catalysts	0.5 M H_2SO_4		1.0 M KOH	
	R_s (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{ct} (Ω)
β-Mo_2C/NC(OA)	5.44	0.45	5.87	0.38
β-Mo_2C/NC(SA)	7.43	1.86	6.32	1.87
β-Mo_2C/NC(NA)	5.14	3.07	5.56	1.55

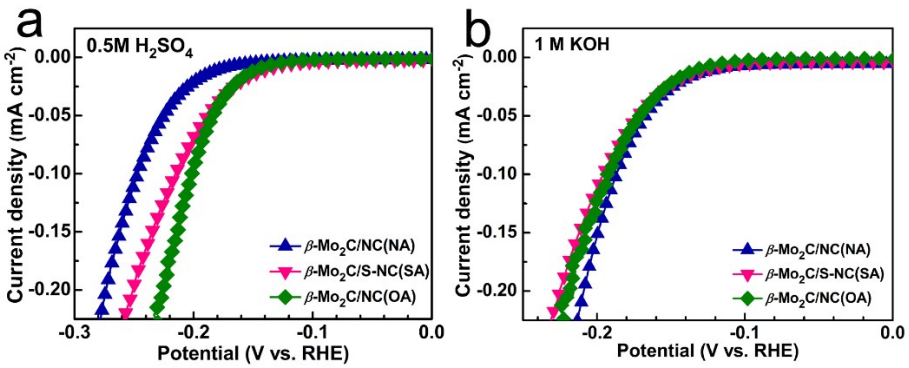

Fig. S18 ECSA-calibrated LSV curves for as-prepared catalysts.

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