

Electronic Supplementary Information

Figure S1.XRD patterns for Fe₃Mo₃C and Mo₆Ni₆C.

40-	Mo Lα1		Element	Atomic percentage
			С	20.42
<u> </u>			Ν	2.99
			Co	42.06
ζ - ζ 20 - Co Lα1 2			Ni	1.61
			Мо	32.91
N Ka1 2			Total:	100.00
С Ка 2			Co Kα1 Νi Kα1 Ν	іі КВ1
<u></u>	Trouteerleer	. [] .		
0 1		5 6		9 keV

Figure S2.EDX of (Ni_{0.2}Co_{0.8})₆Mo₆C₂.



Figure S3.Polarization curves of $Co_6Mo_6C_2$, $(Ni_{0.1}Co_{0.9})_6Mo_6C_2$, $(Ni_{0.2}Co_{0.8})_6Mo_6C_2$ and $(Ni_{0.3}Co_{0.7})_6Mo_6C_2$ on an L-shaped glassy carbon electrode in 1 M KOH.



Figure S4.Electrochemical cyclic voltammetry curves of (a) DCA-Co, (b) DCA-Mo,(c) $Co_6Mo_6C_2$, (d) $(Ni_{0.2}Co_{0.8})_6Mo_6C_2$ in 1 M KOH. The different scan rates are 10, 20, 30, 50, 70 and 100mV s⁻¹, respectively.



Figure S5.Polarization curves of Ni-Co carbide and Ni-Mo carbide at the scan rate of 2 mV s⁻¹ in

1.0 M KOH.



Fig. S6 HRTEM images of the catalyst after stability process. The TEM images of the sample after the HER stability test demonstrated that the ultra-small $(Ni_{0.2}Co_{0.8})_6Mo_6C_2$ nanoparticles are still evenly embedded into the N-doped carbon matrix, without obvious change. As shown in the HRTEM image, the continue lattice fringe with a plane distance of 0.22 nm is similar with that observed in the sample before HER process, indicating the crystal structure of these particles is not changed.



Fig. S7 (a) XPS spectrum of $(Ni_{0.2}Co_{0.8})_6Mo_6C_2$ after stability process, high resolution XPS spectra and the fitted data of Co2p (b), Mo3d (c), Ni2p (d), C1s (e) and N1s (f) of (Ni_{0.2}Co_{0.8})₆Mo₆C₂. The full survey spectrum of (Ni_{0.2}Co_{0.8})₆Mo₆C₂ confirms the existence of Ni 2p, Co 2p, Mo 3d, O 1s, N 1s, and C 1s (Fig. S7a). For the Co 2p XPS spectra (Fig. S7b), the binding energy peaks of Co $2p_{3/2}$ and Co $2p_{1/2}$ appears at 781.5 eV and 797.4 eV, respectively. The binding energy peaks at 786.3 eV and 803.4 eV are their corresponding satellite structures (S1 and S2), respectively. The spectrum of Mo 3d (Fig. S7c) implies three valence states (+2, +4, +6) for the catalyst. After a curve deconvolution, the doublets of 232.0 eV/231.2 eV and 235.3 eV/234.7 eV can be attributed to $3d_{3/2}/3d_{5/2}$ of Mo^{4+} and $3d_{3/2}/3d_{5/2}$ of Mo^{6+} , which likely stem from the MoO₂ and MoO₃ species on (Ni_{0.2}Co_{0.8})₆Mo₆C₂nanoframes surface. The peaks located at 227.6 eV for Mo $3d_{5/2}$ can be ascribed to Mo²⁺ species, which is assigned to Mo-C bond. For the Ni 2p spectrum (Fig. S7d), the peak located at 855.9 eV with satellite peaks can be assigned to Ni²⁺ 2p_{3/2} from (Ni_{0.2}Co_{0.8})₆Mo₆C₂. The details of C1s XPS spectra are shown in Figure S7e. The main peak at 283.7 eV is corresponding to the sp² bonded graphite-like carbon, and the peak (284.4 eV) corresponded to sp³ bonded carbon is also observed. It should be noted that there is only a tiny peak at 286.3 eV

which is ascribed to C=O/C-OH groups, indicating that most oxygen containing functional groups of DCA are eliminated during the high temperature treatment and a significant increase in structure ordering of the carbon matrix has been achieved. The N1s spectrum (Figure S7f) confirmed the N doping in the carbon matrix including the existence of the pyridinic N (398.0 eV) and pyrrolic N (400.4 eV). In comparison to the XPS data of the sample before HER processing, all the XPS information of the elements in the sample after HER test is not significantly changed, indicating the high stability of the as-prepared (Ni_{0.2}Co_{0.8})₆Mo₆C₂ catalyst.