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

Supporting Information

Cost Effective Mo Rich Mo_2C Electrocatalysts for Hydrogen Evolution Reaction

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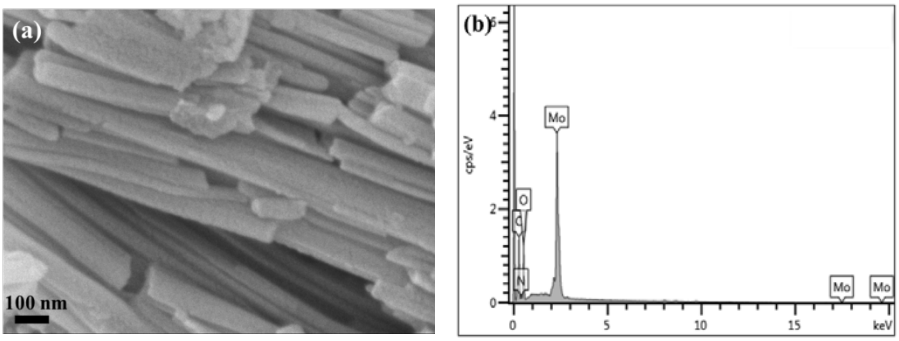

Fig. S1. (a) SEM image and (b) EDS of $Mo_3O_{10}(C_6H_8N)_2 \cdot 2H_2O$.

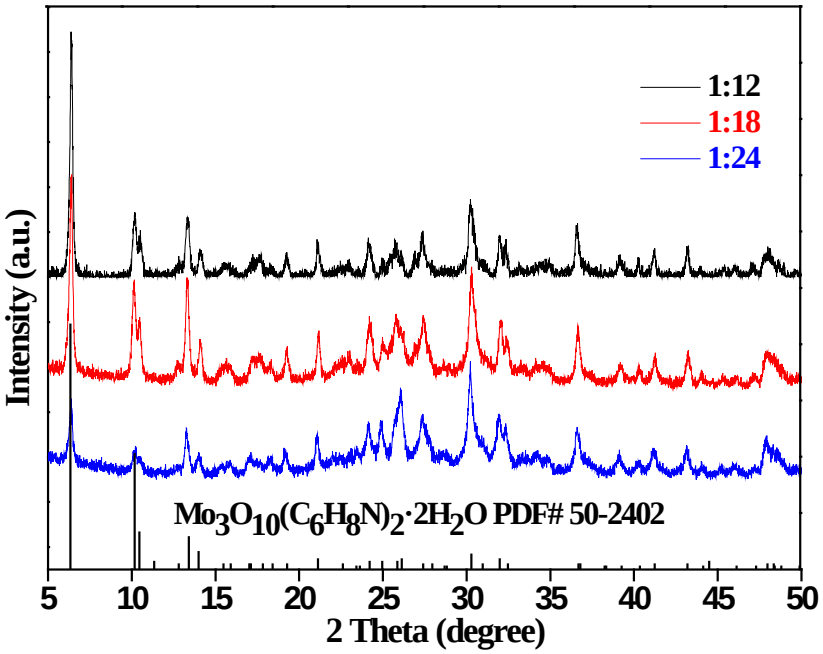

Fig. S2. XRD patterns of $Mo_3O_{10}(C_6H_8N)_2 \cdot 2H_2O$ and prepared Mo-Mo_2C-n precursor samples with ammonium heptamolybdate to aniline molar ratio of 1:12, 1:18 and 1:24.

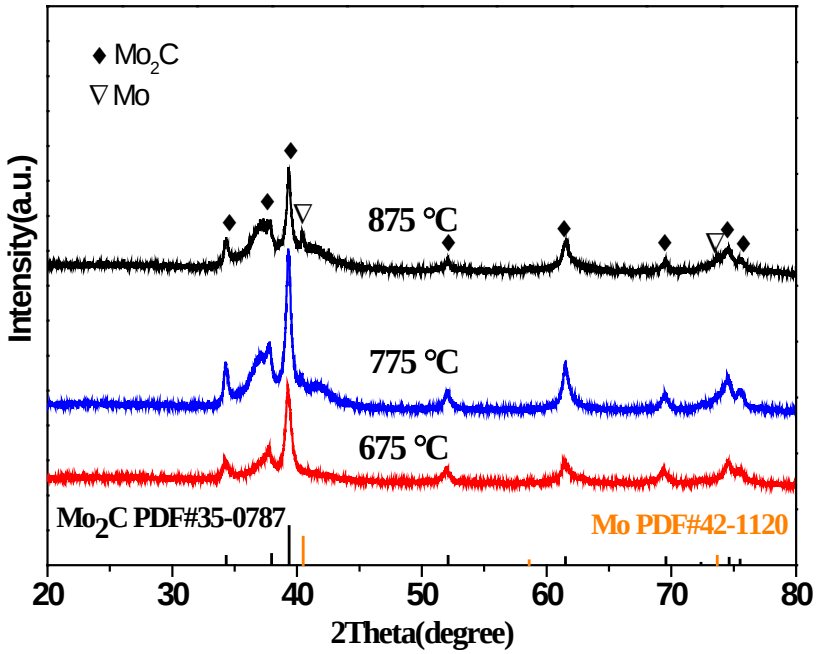

Fig. S3. XRD patterns of molybdenum carbides synthesized at 675, 775 and 875 ℃.

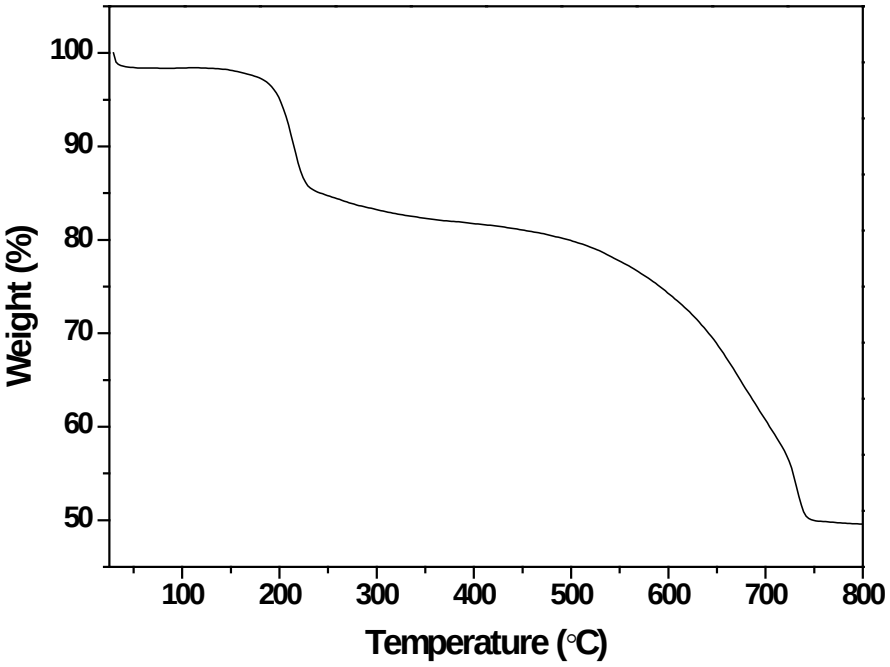

Fig. S4. TGA curve of the prepared $Mo_3O_{10}(C_6H_8N)_2 \cdot 2H_2O$ at heating rate of 5 ℃ min^{-1} under nitrogen gas from room temperature to 800 ℃.

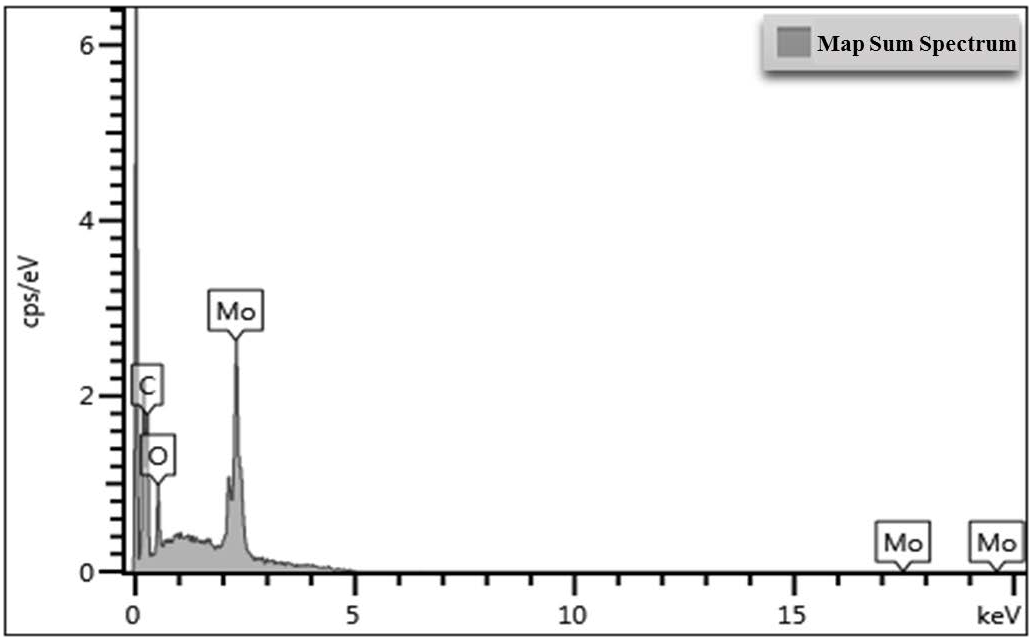

Fig. S5. EDS spectra of Mo-Mo_2C-0.077

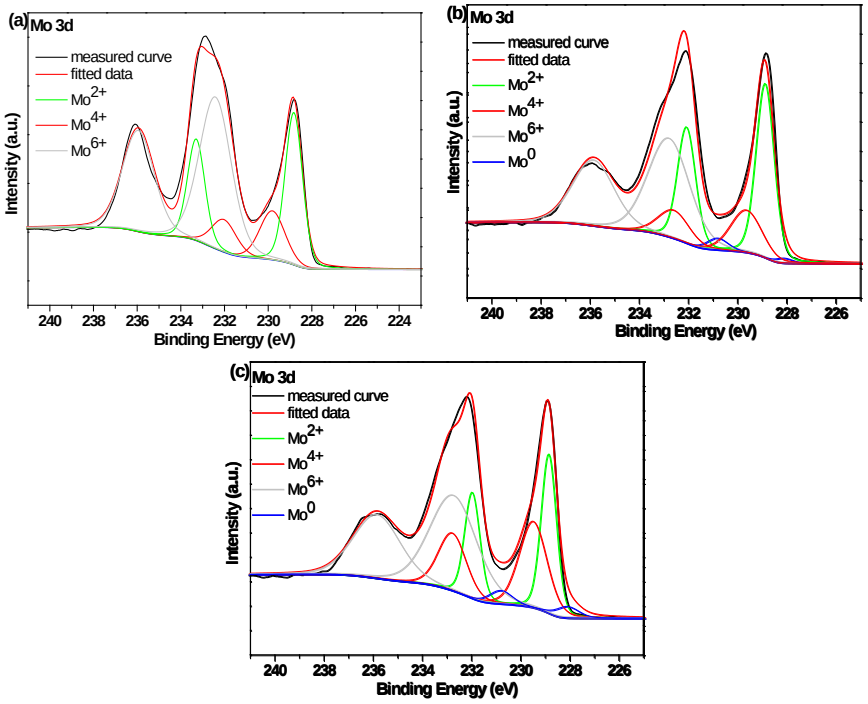

Fig. S6. (a) XPS Mo 3d spectra of Mo_2C; (b) Mo-Mo_2C-0.055 and; (c)Mo-Mo_2C-0.082 catalyst samples.

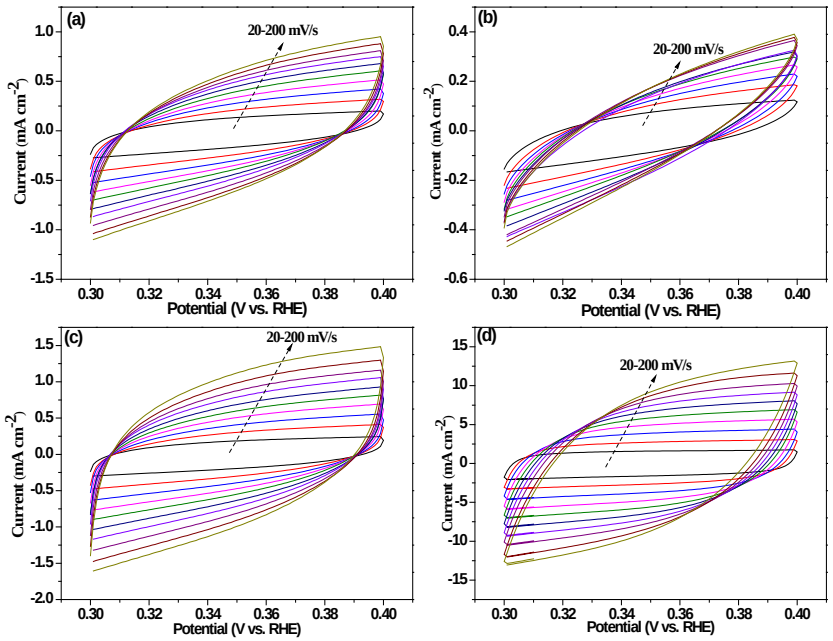

Fig. S7. Cyclic voltammograms of (a)Mo_2C; (b)Mo-Mo_2C-0.055; (c) Mo-Mo_2C-0.077 and; (d) Mo-Mo_2C-0.082 with scanning rates from 20 to 200 mV s^{-1} and the potential range from 0.30 - 0.40 V vs RHE in a 0.5 M H_2SO_4 solution.

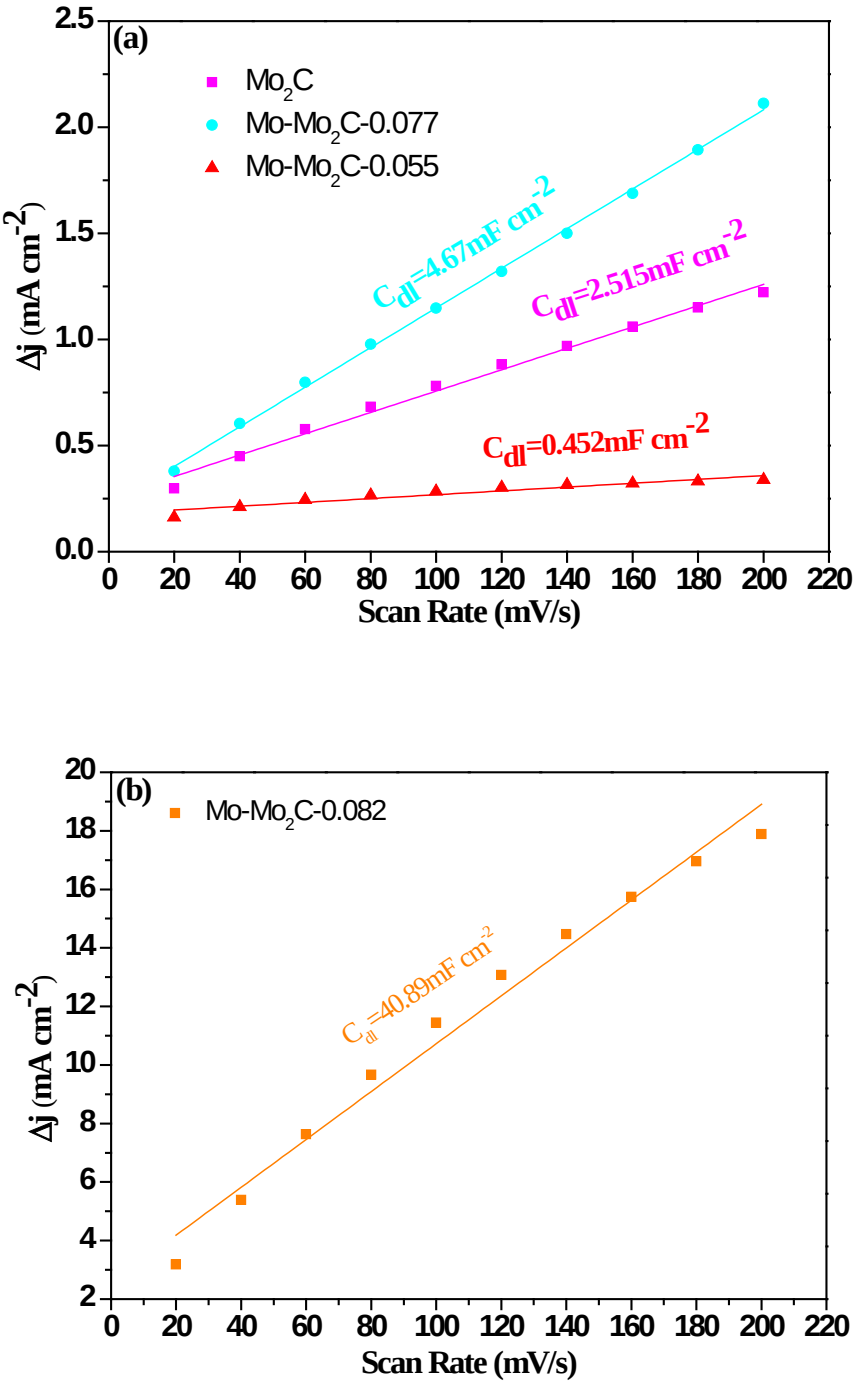

Fig. S8. Estimated the double-layer capacitances (C_{dl}) by plotting the current density variation against scan rate to fit a linear regression. $\Delta j = (j_a - j_c)/2$ was obtained at 350 mV vs. RHE the CV in Fig. S5 in the Supporting Information.

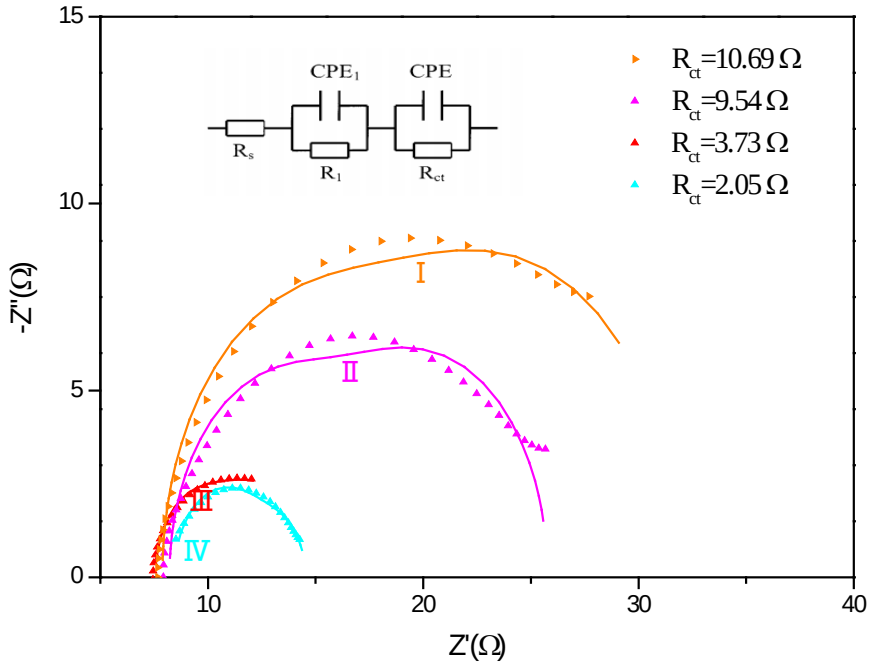

Fig. S9. Nyquist plots from a 0.5 M H_2SO_4 solution on the modified GCEs comprised of (Ⅰ) Mo-Mo_2C-0.082, (Ⅱ) Mo_2C, (Ⅲ) Mo-Mo_2C-0.055, (Ⅳ) Mo-Mo_2C-0.077, and (Ⅴ) commercial Pt/C electrocatalysts at 180 mV in 0.5M H_2SO_4. The inset is an equivalent circuit model for electrochemical impedance tests. R_s, R_1 and R_{ct} represent the resistances of the electrolyte, electrode porosity and charge-transfer, respectively. The constant phase angle element (CPE) represents the double layer capacitance of a solid electrode in the real-world situation.

Table S1. Controlled Mo-Mo_2C-n synthesis conditions

Electrocatalyst	AH/An*	Temperature (℃)	Heating rate (℃/min)	Ar flow rate (ml/min)
Mo_2C**	1:18	675	2	125
Mo-Mo_2C-0.055***	1:12	775	2	125
Mo-Mo_2C-0.077	1:18	775	2	125
Mo-Mo_2C-0.082	1:24	775	2	125

*Ammonium Heptamolybdate tetrahydrate/Aniline molar ratio for the synthesis of Mo-Mo_2C-n. **Although at the same AH/An molar ratio of 1:18, only Mo_2C is formed due to the sample annealing temperature (675 ºC).

***This number presents the Mo content.

Table S2 Summary of the Elemental contents of Mo-Mo_2C-n catalysts

Electrocatalyst	C content (wt.%)[a]	O content (wt.%)[a]	Mo content (wt.%)[b]
Mo-Mo_2C-0.055	5.8	-	94.2
Mo-Mo_2C-0.077	8.6	-	91.4
Mo-Mo_2C-0.082	22.8	2.9	74.3

[a] Data are determined by CHNS/O elemental analysis;

[b] Data are calculated according to the results of a.

Table S3 Summary of component content of Mo-Mo_2C-n

Electrocatalyst	Mo_2C content (wt.%)*	Mo metallic content (wt.%)*
Mo-Mo_2C-0.055	94.5	5.5
Mo-Mo_2C-0.077	92.3	7.7
Mo-Mo_2C-0.082	91.8	8.2

* Data are obtained using Jade 6.0 software.

Table S4 Comparison of the HER activities of Mo-Mo_2C-0.077 with reported Mo_xC electrocatalysts in a 0.5 M H_2SO_4 electrolyte.

Electrocatalyst	Loading (mg cm^{-2})	η_{Onset} (mV)	η_{10}[a] (mV)	Tafel slope (mV dec^{-1})	j_0[b] (mA cm^{-2})	Counter electrode	Ref.
Mo-Mo_2C-0.077	0.38	67	150	55	0.019	Graphite rod	This work
Mo_2C/G	-	87	236	76	-	Pt foil	1
Mo_2C	0.102	-	198	56	-	Graphite rod	2
Mo_2C/MoP@NPC	-	-	160	75	-	Carbon rod	3
MoO_2/α-Mo_2C	0.68	-	152	65	-	Pt foil	4
MoO_2/MoC@C	0.57	-	133(η_{20}[c])	77.3	0.371	Graphite rod	5
Mo_2C/CLCN	0.357	85	145	48.2	0.062	Carbon rod	6
Mo_2C@NPC-4	0.265	~44	144	52.5	-	Pt wire	7
MoC/C	0.57	-	144(η_{20})	63.6	0.104	Graphite rod	8
MoC@C			157(η_{20})	93.3	0.390		
Mo_2C-QDs/NG	0.28	-	146	60	0.05	Carbon rod	9
c-α-MoC_{1-X}@BCN	0.7-0.8	20	124	47	0.124	Graphite rod	10
h-β-Mo_2C@BCN		20	140	103	0.392		
o-β-Mo_2C@BCN		48	168	80	0.109		
o-α-Mo_2C@BCN		40	195	73	0.011		
h-η-MoC@BCN		45	182	67	0.006		
BCF/Mo_2C	10.7	-	115(η_{20})	84.8	-	Graphite rod	11
MoC@NC nanoribbon	0.385	24	~150	54	0.007	Graphite rod	12
Mo_2C nanoribbon/ N-G film	-	84	162	57	-	Carbon rod	13
MoCat catalyst	0.4	44	96	37	0.018	Carbon electrode	14
MoO_2/C	0.84	-	246	107.1	0.05	Carbon rod	15
MoC/C			179	91.1	0.13		
Mo_2C/C			135	75.1	0.36		
3DHP-Mo_2C	-	75	166	75	0.287	Graphite rod	16
NiMo_2C@C	0.15	65	169	100	0.22	Graphite rod	17
50R@MS	0.362	20	112	65	0.44	Graphite rod	18
Mo_2C-RGO	0.285	70	130	57.3	-	Pt mesh	19
MoC_X nano-octahedrons	0.8	25	142	53	0.023	Graphite rod	20

[a] η_{10}: Overpotential required for an electrode to produce a current density of 10 mA cm^{-2}.

[b] j_0: Exchange current density (mA cm^{-2}).

[c] η_{20}: Overpotential required to produce a current density of 20 mA cm^{-2}.

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