Electronic Supplementary Information

Experimental section

Materials: Sodium molybdate dihydrated ($Na_2MoO_4 \cdot 2H_2O$, ≧99%) was purchased from Aladdin Ltd. (Shanghai, China). Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, A.R.) purchased from Chengdu Kelong Chemical Reagent Factory. Citric acid ($C_6H_7O_8 \cdot H_2O$, A.R.) was provided by Beijing Chemical Works. Sodium borate ($Na_2B_4O_7 \cdot 10H_2O$, A.R.) were purchased from Tianjin Chemical Corporation. Pt/C (10 wt% Pt) was provided by Alfa Aesar (China) Chemicals Co. Ltd. Titanium mesh was provided by Phychemi Hong Kong Company Limited. All chemical regents were used as received without further purification. Deionized water was made by the Millipore system and used in all experimental process.

Preparation of Co-Mo-B/Ti and Co-B/Ti: Firstly, $CoCl_2 \cdot 6H_2O$ (2.38 g), $Na_2MoO_4 \cdot 2H_2O$ (0.73 g), $C_6H_8O_7 \cdot H_2O$ (2.10 g) and $Na_2B_4O_7 \cdot 10H_2O$ (4.77 g) were dissolved in 50 mL deionized water under vigorous stirring for 30 min. Then one piece of the pretreated titanium mesh was vertically immersed into the aqueous solution. After that, Co-Mo-B film deposition was carried out in a three-electrode system. Saturated calomel electrode and Pt wire were served as reference electrode and counter electrode, respectively. Ti mesh was served as the working electrode for the deposition process under -1.1 V for 60 min. Finally, the prepared product Co-Mo-B/Ti was rinsed with deionized water and ethanol several times and dried at 60 °C under vacuum for 2 h. For further comparison, Co-B/Ti was also prepared under identical synthesis conditions, but without adding $Na_2MoO_4 \cdot 2H_2O$ into the electrolytes.

Characterizations: The samples were characterized by different analytic techniques. X-ray powder diffraction (XRD) pattern was obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm. Scanning electron microscopy (SEM) measurements was performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV.

The X-ray photoelectron spectrometer (XPS) measurements were carried out on an ESCALABMK II X-ray photoelectron spectrometer equipped with Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) at room temperature. In a typical three-electrode system, the Co-Mo-B/Ti or Co-B/Ti was used as the working electrode, graphite rod as the counter electrode and Hg/HgO electrode as the reference electrode. LSV was performed at a scan rate of 2 mV s^{-1} in 1.0 M KOH solution. The potentials were referenced to that of reversible hydrogen electrode (RHE) and iR correction was applied to all original data unless special illustration, using the following equation: E (RHE) = E (Hg/HgO) + (0.098 + 0.059 pH) -iR V, R was determined through fitting of AC impedance data to a modified Randles circuit at open circuit potential.

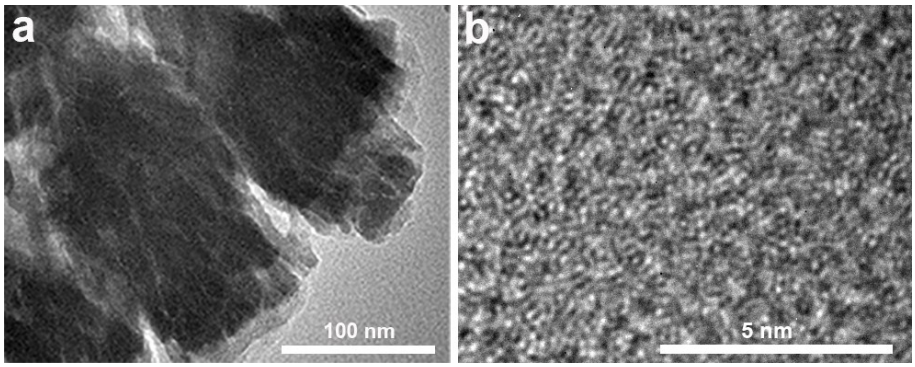


Fig. S1 TEM and HRTEM images of Co-Mo-B.

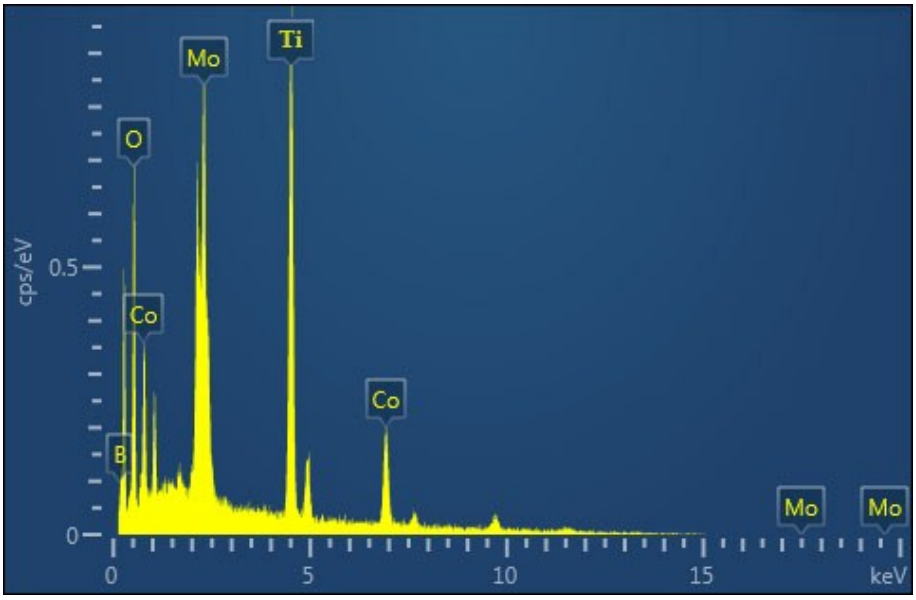


Fig. S2 EDX spectrum of Co-Mo-B/Ti.

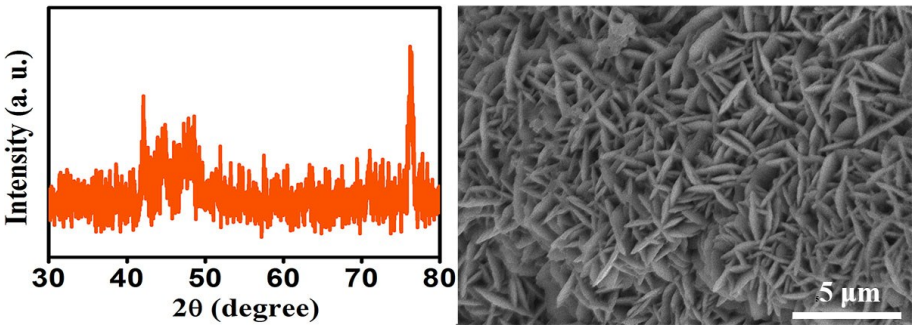
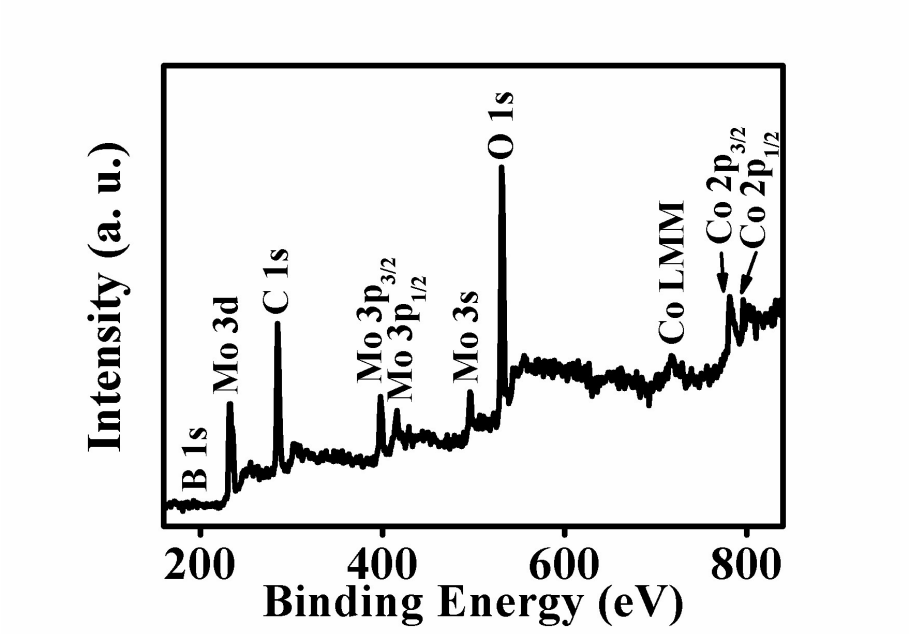


Fig. S3 XRD pattern and SEM image of Co-B.

Fig. S4 XPS



survey spectrum of Co-Mo-B.

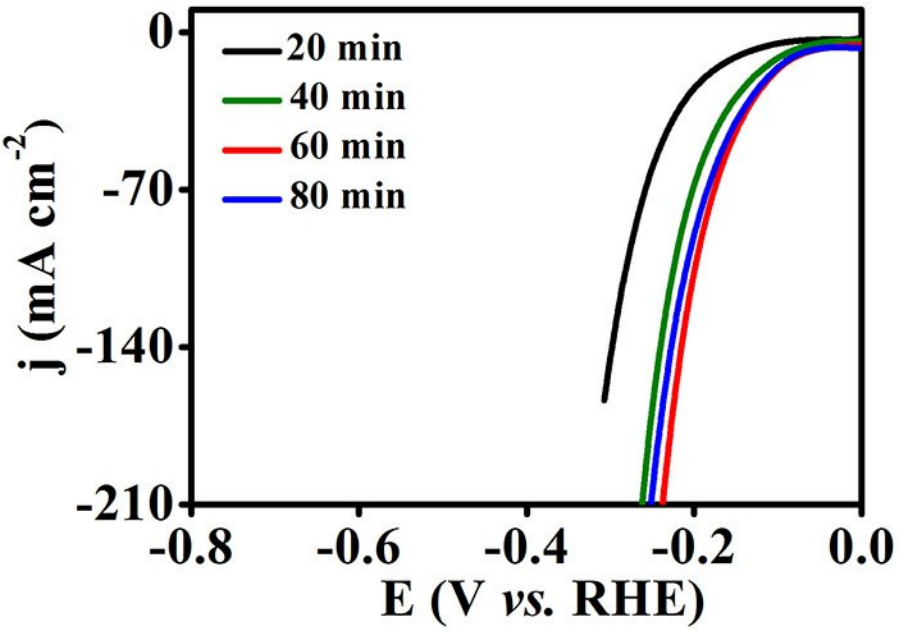


Fig. S5 LSV curves of Co-Mo-B/Ti with different deposition time.

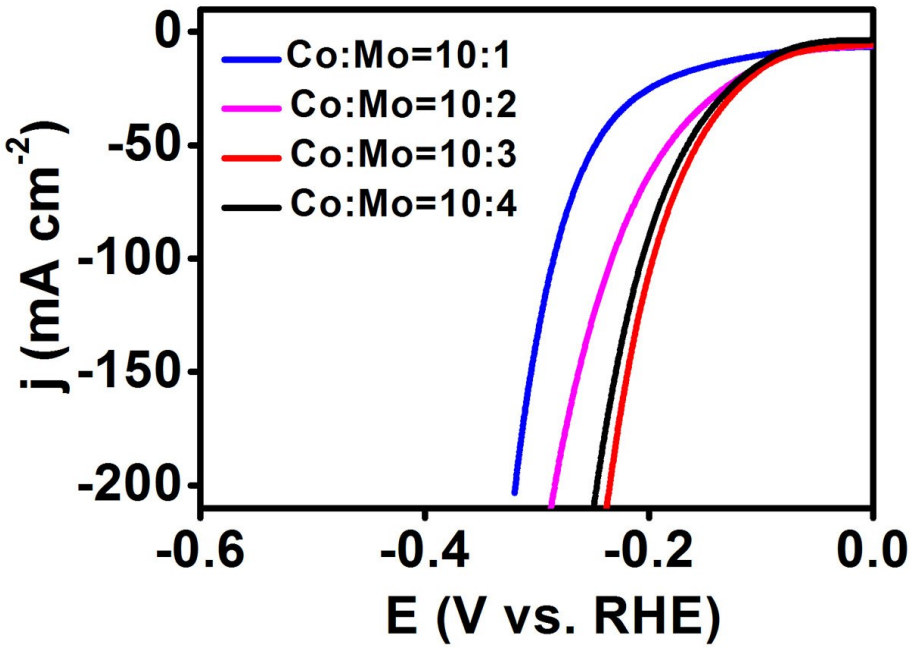


Fig. S6 LSV curves of Co-Mo-B/Ti with different atomic ratios of Co/Mo.

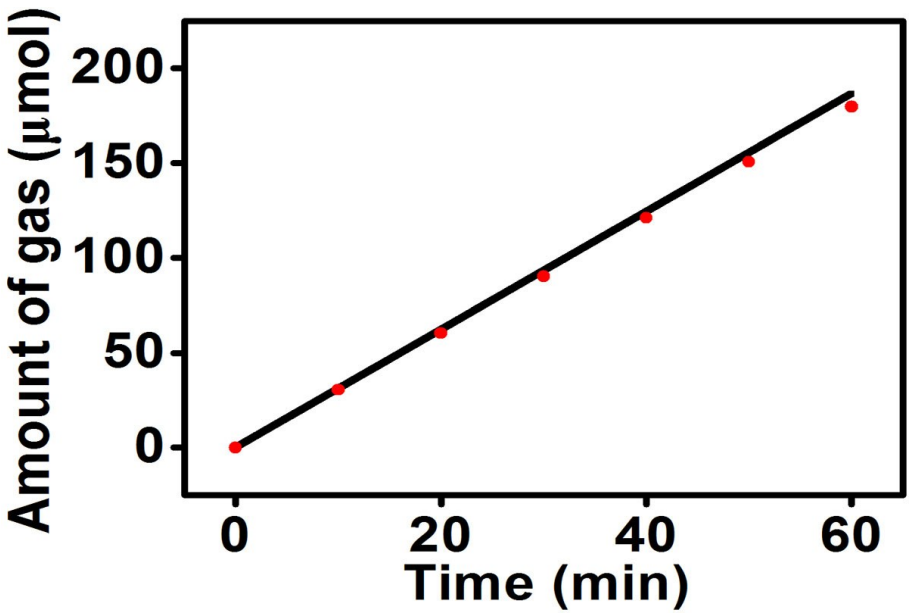


Fig. S7 The measured H_2 quantity (red) compared with theoretically calculated H_2 (black) quantity vs. time for Co-Mo-B/Ti.

Table S1 Comparison of HER performance of Co-Mo-B/Ti with other reported non-noble-metal electrocatalysts under alkaline conditions.

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	Ref.
Co–Mo–B film/Ti	20	110	1.0 M KOH	This work
Co–B film/Ti		300		
Co–Ni–B/GC	10	133	1.0 M NaOH	1
MoB/CP	5	250	1.0 M KOH	2
Co-3Mo-B/GC	20	~100	1.0 M NaOH	3
Co-W-B/NF	20	~160	1.0 M KOH	4
Co_2B-500/NG/GC	10	127	1.0 M KOH	5
Ni-Mo2C/CMF	20	~125	1.0 M KOH	6

Ni-Mo$_2$C/CMF Ni-Mo$_2$C/C				

MF Ni-Mo$_2$ C/C MF Ni-Mo$_2$				

C/C MF Ni-Mo_2C/C MF				
MoS_2|NiS|MoO_3/Ti foil	20	~110	1.0 M KOH	7
CoO/MoO_x/NF	10	163	1.0 M KOH	8
$CoMoS_4$/CC	10	143	1.0 M KOH	9
Mo_2C/C	20	~120	1.0 M KOH	10
Co_9S_8-Ni_xS_y/Ni	10	163	1.0 M KOH	11
$CoNi_2S_4$-220/GC	32	400	1.0 M KOH	12
NiS_2/MoS_2/GC	10	204	1.0 M KOH	13
NiMoN films/CC	20	~135	1.0 M KOH	14

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