Electronic Supplementary Material (ESI) for Energy & Environmental Science

Elecronic Supplementary Information:

Highly Active and Durable Nanostructured Molybdenum Carbide Electrocatalysts for Hydrogen Production

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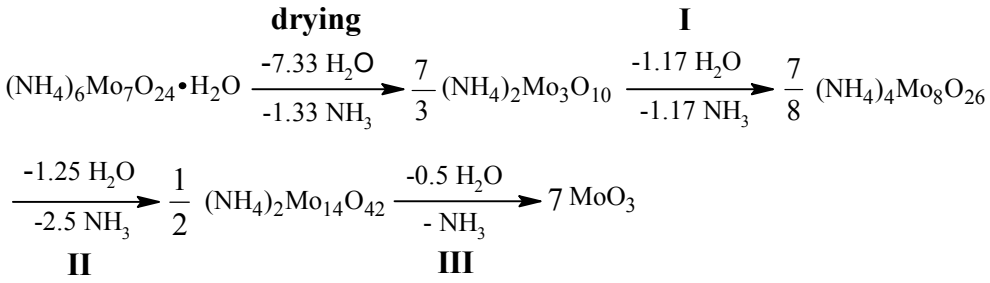
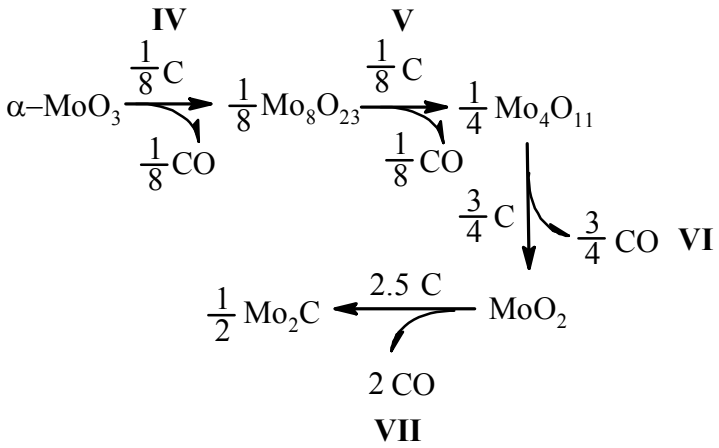


Scheme S1. Decomposition mechanism of ammonium molybdate.



Scheme S2. The formation of β-Mo_2C by carburization of α-MoO_3 and carbon.

Table S1 Tafel slopes different catalysts collected in a H_2-saturated 0.1 M $HClO_4$ solution.

Catalyst	b_R (mV dec^{-1})[a]	b_{Tafel} (mV dec^{-1})[b]
Mo_2C/CNT	55.2	65.3±3.1
Mo_2C/XC	59.4	67.7±3.5
Mo_2C	87.6	83.9±5.2
Bulk Mo	83.8	85.6 ±4.8
Pt/C	--	30.2±1.7

[a] Slopes obtained from the plot of $\log(R_{ct}^{-1})$ versus overpotential in Figure 7. [b] Average slopes with errors obtained from semi-log polarization curves.

Table S2 Comparison of mass activity of different molybdenum carbide and molybdenum sulfide catalysts.

Catalysts	j@η=150mV (mA cm^{-2}) [a]	Loading (mg cm^{-2})	Mass activity@η=150mV (mA mg^{-1})
Mo_2C/CNT	9.8	2	4.9
Mo_2C/XC	3.2	2	1.6
bulk Mo_2C	0.21	2	0.1
Mo_2C in ref 25	1	1.4	0.7
MoS_3 in ref 40	0.35	0.032	10.9
MoS_3/CNT in ref 40	0.50	0.021	23.8
MoS_2/RGO in ref 41	c.a. 8.0	1	8.0
$CuMoS_4$ in ref 12	0.5	0.0416	12.0

[a] The reported current densities were collected in different conditions.

Table S2 displays the mass activity at η = 150 mV among various Mo-based catalysts. It should be noted that the scan rates, electrolytes, pH and types of electrode used for the referenced catalysts were different. Generally speaking, the MoS_x catalysts have higher mass activities than the Mo_2C catalysts. Amon these catalysts, the MoS_3/CNT performes the best.

Table S3 Exchange current densities based on specific surface area of different catalysts.

Catalysts	$j_{0,R}$ (mA cm^{-2}) [a]	Loading (mg cm^{-2})	Specific surface area (cm^2 mg^{-1})	j_0'' (mA cm^{-2}) [b]
Mo_2C/CNT	1.4×10^{-2}	2	150.5	4.6×10^{-5}
Mo_2C in ref 25	4.4×10^{-5}	1.4	36.6	2.5×10^{-5}

[a] The exchange current density calculated by the charge-transfer resistance at zero overpotential.
[b] The exchange surrent density calculated based on specific surface area.

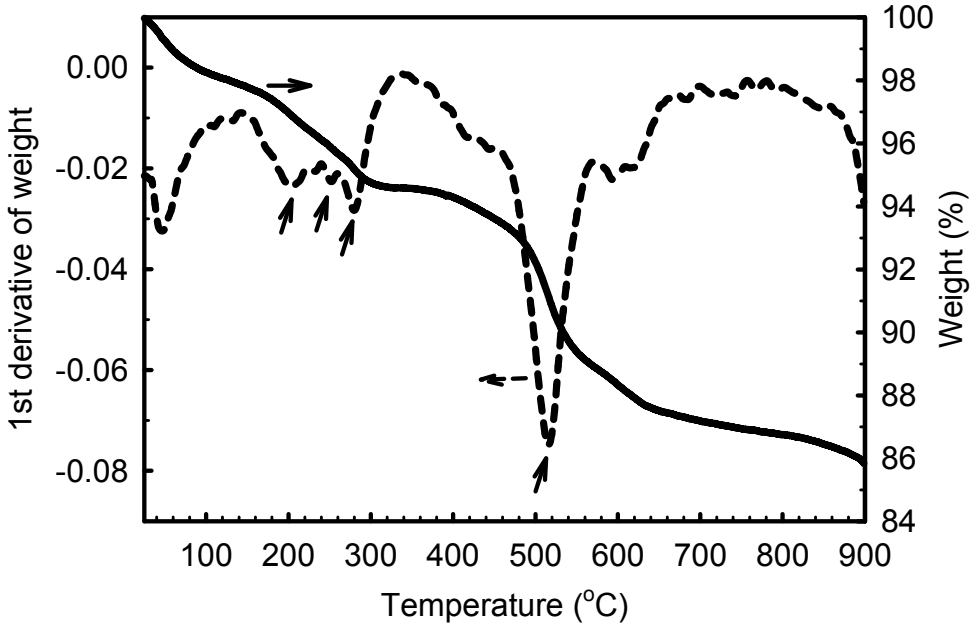


Fig. S1 TG trace (solid curve) and its first derivative (dash curve) of the carbon-supported ammonium molybdate under Au atmosphere.

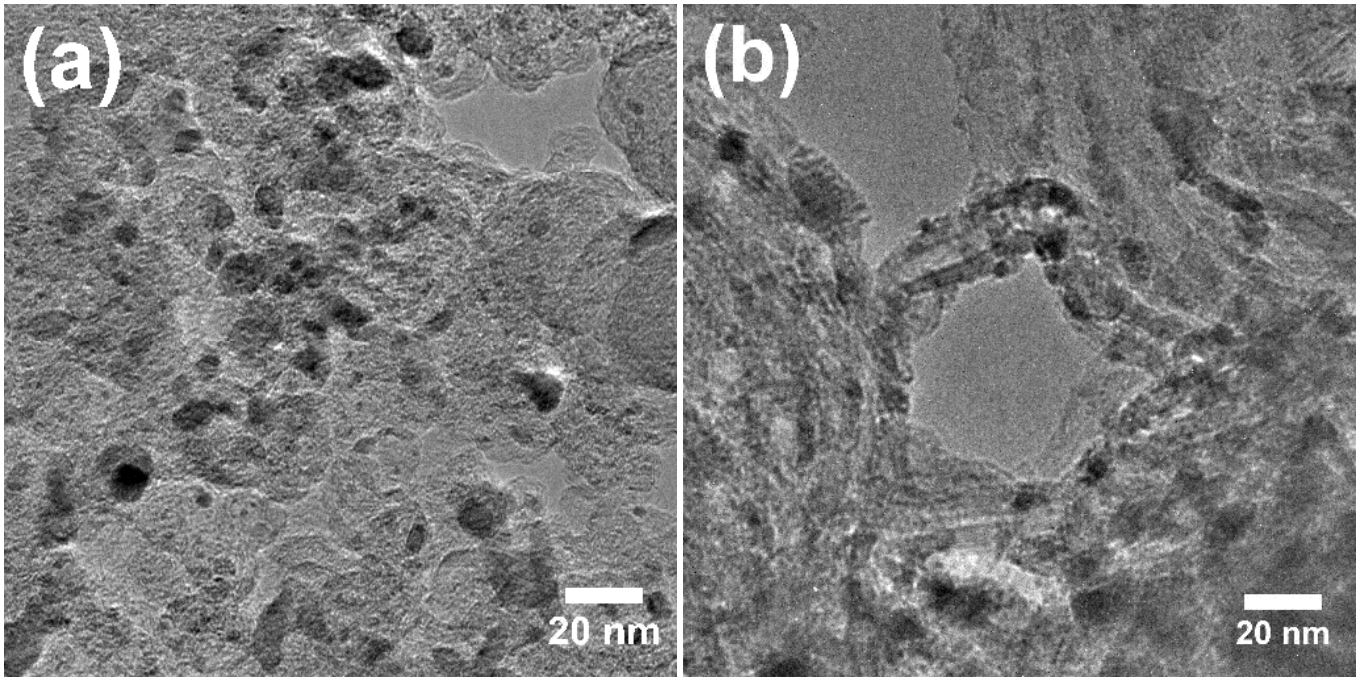


Fig. S2 Magnified TEM images in Fig 3.

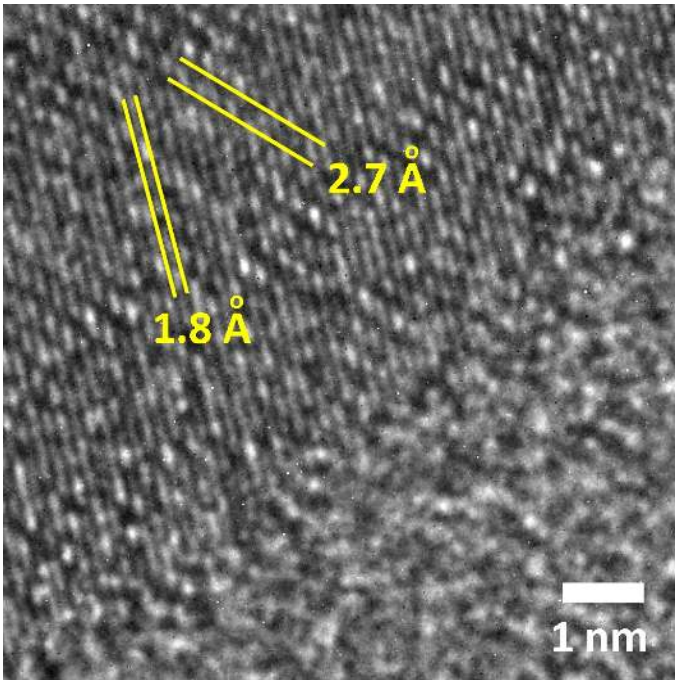


Fig. S3 A HRTEM image showing the orthorhombic β-Mo_2C strucutre of a XC72 carbon black-supported Mo_2C nanoparticle.

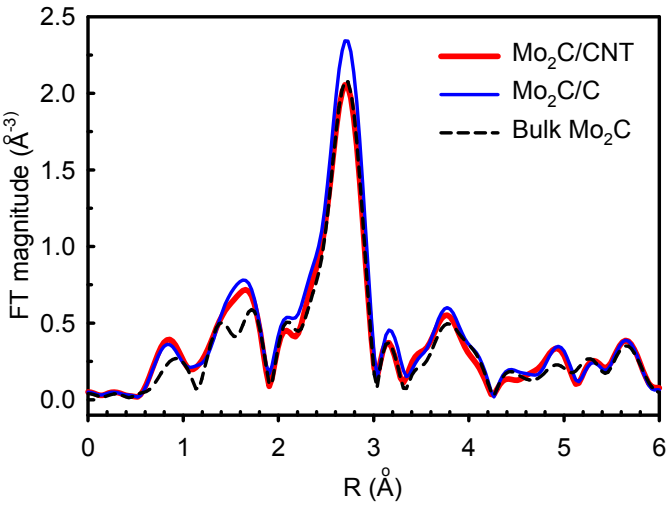


Fig. S4 k^2-weighted EXAFS Fourier transform magnitudes at Mo K edge from CNT-supported Mo_2C, XC-72-supported Mo_2C and bulk unsupported Mo_2C.

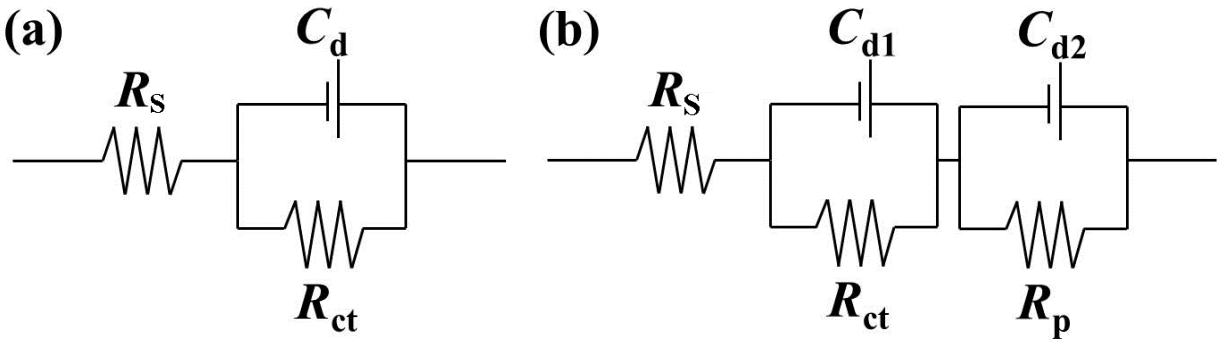


Fig. S5 Electrical Equivalent circuit models for fitting the EIS response of hydrogen evolution reaction on Mo_2C-based electrodes: (a) one-time constant model and (b) two-time constant model, where R_s is the series resistance, R_{ct} denotes the charge transfer resistance, R_p related to is the porosity the electrode surface, and the double layer capacitance is represented by the elements C_d, C_{d1} and C_{d2}.

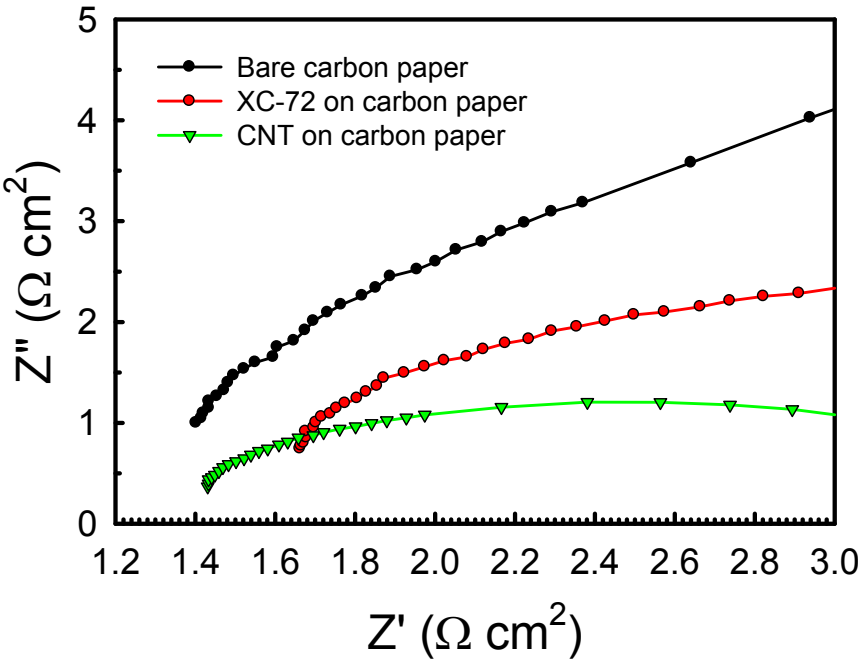


Fig. S6 Nyquist plots of bare carbon paper, XC-72 on carbon paper, and CNT on carbon paper performed at η = 0 V vs RHE from 10^6 Hz to 100 Hz, using amplitudes of 5 mV.

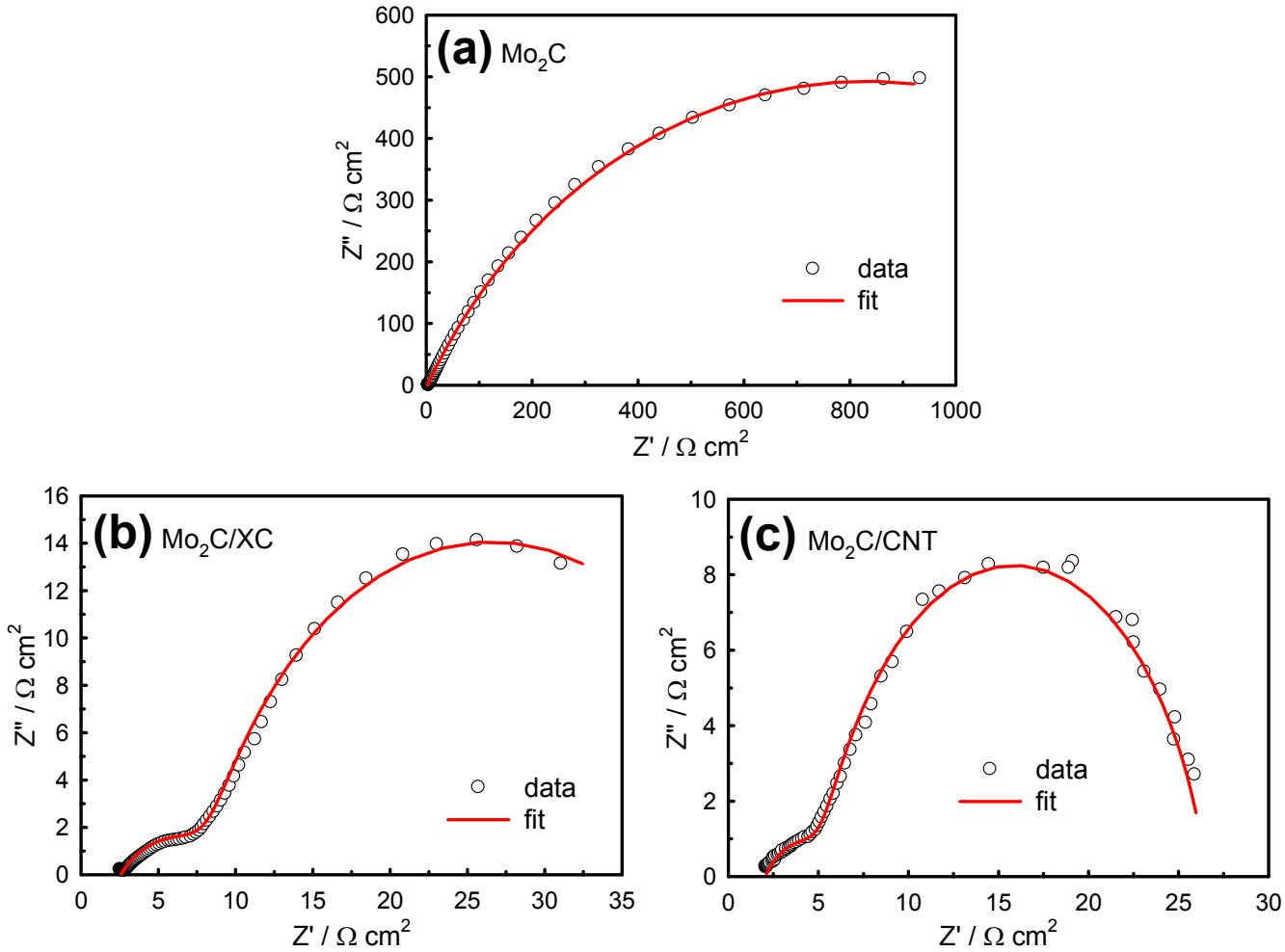


Fig. S7 Nyquist plots of experimental and simulated data for bulk Mo_2C (a) simulated by the one-time constant model and both Mo_2C/XC (b) and Mo_2C/CNT (c) by the two-time constant model.

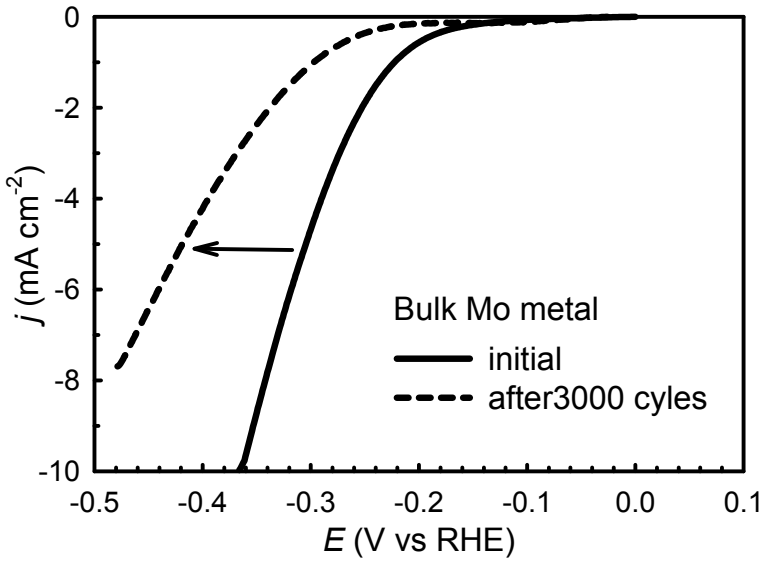


Fig. S8 The polarization curves of bulk Mo metal before and after potential sweeps (-0.3~+0.63 V vs RHE) for 3000 cycles in 0.1 M $HClO_4$ solution.

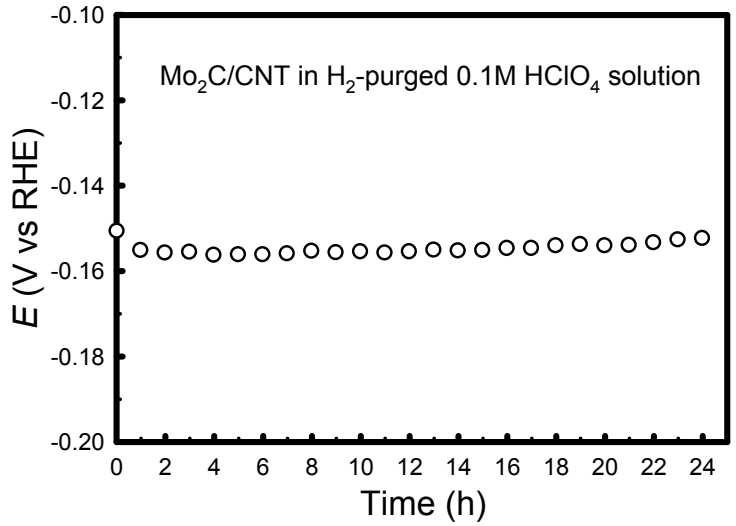


Fig. S9 Long term durability test of the Mo_2C/CNT catalyst for 24 hr in H_2-purged 0.1M $HClO_4$ solution. The overpotential was recorded for driving the HER at a current density of 10 mA cm^{-2} as a function of time.

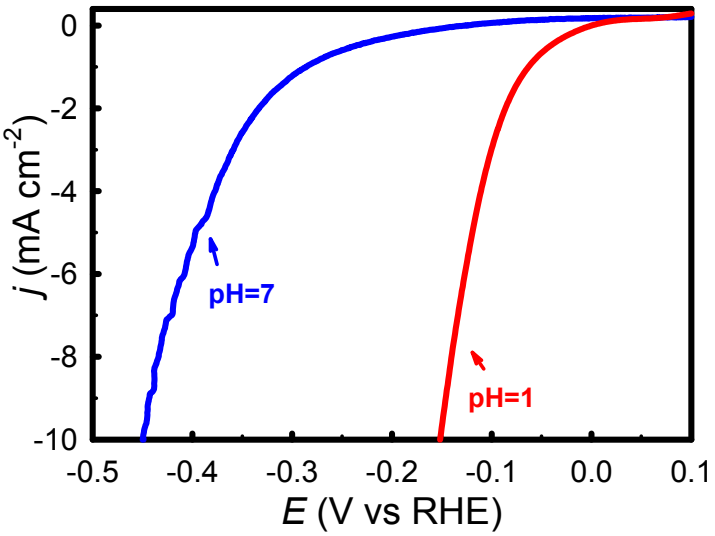


Fig. S10 The polarization curves of Mo2C/CNT in phosphate buffer solution (pH = 7) and 0.1 M HClO4 solution (pH = 1), respectively.