Molybdenum compound MoP as an efficient

electrocatalyst for hydrogen evolution reaction

Experimental Section

Materials synthesis and methods

Ammonium molybdate tetrahydrate, ((NH₄)₆Mo₇O₂₄•4H₂O, Sigma-Aldrich, Bioultra, >99.0%), Ammonium hydrogen phosphate ((NH₄)₂HPO₄, Sigma-Aldrich, regent grade, \geq 98.0%) and citric acid (C₆H₈O₇, Sigma-Aldrich, ACS reagent, \geq 99.5%) are used as received and no further purification experiments are conducted. In a typical procedure, Stoichiometric (NH₄)₆Mo₇O₂₄•4H₂O and (NH₄)₂HPO₄ (*i.e.* 1:1 for MoP and 3:1 Mo₃P in molar ratio) were dissolved in DI-water. Citric acid was added in a molar ratio of 2 (citric acid): 1 (Mo). After evaporation of water, the obtained brown slurry was dried, grinded and sintered at 500 °C for 5 h to prepare the precursor of catalyst. Catalysts MoP, Mo₃P can be synthesized in H₂ at 650, in Ar at 800 °C for 2 h, respectively. Note that the as-synthesized MoP and Mo₃P should be deactivated in 2 vol.% O₂/Ar for 2 h, after which they could be handled in ambient air. Metal Mo is obtained by reducing commercial MoO₃ by H₂ at elevated temperature (850 °C).

Materials characterization

Crystal structures of the as-synthesized Mo, Mo₃P and MoP were examined by an X-Ray diffraction (XRD) using a Cu K α radiation source (Bruker, D2 Phaser). For Morphology, a field emission scanning electron microscope (FE-SEM, JEOL, JSM6701F, Japan) coupled with Energy dispersive X-ray spectroscope (EDS), transmission electron microscopy (TEM, Philips CM300) were employed. To probe the composition, X-ray photoelectron spectroscopy (XPS) experiments were performed on a VG Escalab 200i-XL spectrometer equipped with a monochromatic Al $K\alpha$ (1486.6 eV) X-ray source.

Electrode preparation and electrochemical measurements

Polarization curves of the HER were collected by an Autolab PGSTAT302/FRA system (Eco Chemie, Netherland) in a three-electrode configuration at room temperature, where Pt foil and Saturated Calomel Electrode (SCE) were used as the auxiliary electrode and the reference electrode, respectively. All the potentials were recorded with respect to the reversible hydrogen electrode (RHE). Catalyst ink was typically made by dispersing 7 mg of catalyst in 2 ml ethanol. After adding 0.5 ml of 0.05 wt.% of Nafion solution (Gashub, Singapore) and ultrasonication, an aliquot of 5 μ L was pipetted onto the glassy carbon electrode (0.1963 cm²) to reach the catalyst loading of 0.86 mg cm⁻². Current density was normalized to the geometrical area of the working electrode under 2000 rpm. Especially, to circumvent the charge effect, the data for Tafel plot is collected under a staircase mode (with a step size of 5 mV). Electrochemical impedance spectroscopy (EIS) for the polarization of HER was carried out in a potentiostatic mode in the frequency range of 10⁵ Hz to 0.01 Hz under the amplitude of 10 mV. At different overpotentials (η =0 ~ 100 mV), EIS curves were recorded.

Computational Methods and Models

All the calculation were performed using density-functional theory (DFT) method as implemented in a Vienna *ab initio* simulation package (VASP) ¹⁻³ by using generalized gradient approximation Perdew-Burke-Eznerhof (GGA-PBE) method ⁴. Projector augmented wave method (PAW) ^{5, 6} was used to describe the interaction between the atomic cores and electrons. Based on experimental data for bulk Mo (a = b = c = 3.147 Å, space group: Im-3m) and MoP (a = b = 3.231 Å, c = 3.207 Å, $\gamma = 120^{\circ}$ and space group: P-6m2), we optimized all the structural parameters of bulk Mo amd MoP by using 5 x 5 x 5 Monkhorst-Pack k-point and an energy cut-off of 400 eV until the forces acting on each atom become less than 0.01 eV/Å. The calculated lattice parameters of Mo (a = b = c = 3.152 Å) and MoP (a = b = 3.229Å and c = 3.209 Å) are in good agreement with experimental data. We adopted a catalytic model that is similar to a previous report ⁷ for Mo and MoP. The surfaces of Mo (110) and MoP (001) are chosen for the consideration of the dominating planes based on experimental observation. The 2 \times 2 (110) Mo and (001) MoP surfaces were constructed by cleaving optimized bulk Mo and MoP in a six-atom-layer-thick slab. A $5 \times 5 \times 1$ Monkhorst-Pack kpoint was employed accordingly. Since the cleaving of MoP will result in two different (001) surfaces, one with Mo as top surface (Mo-terminated) and other with P as top surface (Pterminated), we considered both the surfaces for the calculation.

Adsorption of H atom(s) on (110)-Mo and (001)-MoP surfaces

The differential adsorption energy of H adsorption is chosen to describe the stability of hydrogen according to the literature ⁷ and the equation is given below:

$$\Delta E_{\rm H} = E({\rm MoP} + {\rm nH}) - E({\rm MoP} + ({\rm n-1}) {\rm H}) - 1/2 E({\rm H}_2)$$
(1)

Where E(MoP + nH) is the total energy of MoP with the n hydrogen atoms adsorbed on surface, E(MoP + (n-1)H) is the total energy of MoP with (n-1) hydrogen atoms adsorbed on surface and $E(H_2)$ is the total energy of hydrogen molecule in gas phase. The equation (1) gives the binding energy of single H atom adsorption when n is equal to 1. The calculated binding energy of single H atom on (110)-Mo and (001)-MoP, Mo terminated surface is listed in Table S1. The data shows that the 3-coordinated hollow site is preferable for H adsorption on (110)-Mo

 Table S1. Calculated binding energy (eV) of single H atom on (110)-Mo and (001)-MoP

 surfaces

Binding site	Binding energy (eV)			
	(110)-Mo	(001) MoP, Mo terminated		
Тор	-0.01	-0.11		
Bridge	-0.63	_b		
Hollow $(H1)^a$	-0.77	-0.87		
Hollow $(H2)^a$	-0.77	-0.64		

^{*a*} For definition see Figure S1, for (110)-Mo both the H1 and H2 site are same. ^{*b*} The adsorption on bridge site is unstable and the H atom moves to hollow site



Figure S1. Top view of (a) (110)-Mo and (b) (001)-MoP, Mo terminated surfaces; It shows the binding sites for H adsorption (only the first two atomic layers are shown. Mo – cyan sphere, P – magenta sphere).

For adsorption of H atom on (001)-MoP, Mo terminated surface we also consider top (T), bridge (B) and 3-coordinated hollow (see Figure S1b). The surface of (001)-MoP, Mo terminated surface has two hollow sites H1 and H2 (for definition see Figure S1b). The results show that H1 site is favorable for H adsorption. In contrast, for (001)-MoP, P terminated surface, the favorable binding site is the top side (see Figure S2).

Based on the results of single H atom adsorption on the surface, we select the hollow site for adsorption of the second and more H atoms on (110)-Mo and (001)-MoP, Mo terminated surfaces while the top sites is chosen for (001)-MoP, P terminated surface. The calculated differential binding energy of H atom on (110)-Mo, (001)-MoP, Mo terminated and (001)-MoP, P terminated surfaces is listed in Table S2. Since top surface of our surface models has four Mo or P atoms, adsorption of one, two, three and four H atom is considered as 1/4, 2/4, 3/4 and 4/4 monolayer (ML) coverage, respectively.

Catalytic activity of Mo and MoP

To compare the catalytic activity of Mo and MoP, we calculated the Gibbs free energy of hydrogen adsorption following the equation below:

$$\Delta G^{\circ}_{\rm H} = \Delta E_{\rm H} + \Delta E_{\rm ZPE} - T \Delta S_{\rm H} \tag{2}$$

Where ΔE_{ZPE} is the difference in zero point energy between the adsorbed state and the gas phase, ΔS_{H} is the entropy difference between the adsorbed state and the gas phase. The gas phase entropy of H is taken from ref.⁸. The calculated $\Delta G^{\circ}_{\text{H}}$ values for H adsorption on (110)-Mo, (001)-MoP, Mo and P terminated surfaces are listed in Table S2. It will be a good catalyst for hydrogen evolution if the free energy of adsorbed H is close to that of the reactant or product (*i.e.*, $\Delta G^{\circ}_{\text{H}} \cong 0$).

H Coverage	(110)-Mo		(001) MoP, Mo terminated		(001) MoP, P terminated	
	$\Delta E_{\rm H} ({\rm eV})$	$\Delta G^{\circ}_{\mathrm{H}}(\mathrm{eV})$	$\Delta E_{\rm H} ({\rm eV})$	$\Delta G^{\circ}_{\mathrm{H}}(\mathrm{eV})$	$\Delta E_{\rm H} ({\rm eV})$	$\Delta G^{\circ}_{\mathrm{H}}(\mathrm{eV})$
1/4 ML	-0.77	-0.53	-0.87	-0.63	-0.64	-0.36
2/4 ML	-0.71	-0.47	-0.84	-0.60	-0.29	-0.03
3/4 ML	-0.70	-0.46	-0.82	-0.59	0.08	0.34
4/4 ML	-	-	-	-	0.28	0.54

Table S2 Calculated binding energy and Gibbs free energy of H adsorption on (110) Moand (001) MoP, Mo and P terminated surfaces



Figure S2. Top view of H adsorbed (110)-Mo, (001)-MoP, Mo and P terminated surfaces. Only first two atomic layers are shown.

H Coverage	$\Delta E_{\rm H} ({\rm eV})$
1/4 ML	0.20
2/4 ML	0.14

Table S3 Calculated binding energy and Gibbs free energy of H adsorption on (001) Mo₃P, P terminated.



Top view of H adsorbed (001)-Mo₃P surface. Only first two atomic layers are shown. Similar to MoP, the cleaving of Mo₃P will results in two different (001) surfaces, one with Mo as top surface (Mo-terminated) and other with P as top surface (P-terminated). As the (001) MoP, P-terminated surface is identified as the active sites for adsorption/desorption of H, we studied the H adsorption on (001) Mo₃P, P-terminated surface. The calculated binding energy of first and second H atom on (001) Mo₃P, P-terminated surface is 0.20 and 0.14 eV, respectively (see Table S3). The results indicate that the H adsorption on (001) Mo₃P, Pterminated surface is unfavorable, not rendering Mo₃P as a potential catalyst for HER.



Figure S3 bulk Mo_3P materials synthesized at 800 °C under Ar.



Figure S4 EDS of as-synthesized (a) MoP and (b) Mo_3P . The calculated atomic ratios of Mo: P from EDS are 0.645/0.657 and 0.69/0.21.



Figure S5 XRD pattern of aged MoP



Figure S6 MoP after electrochemical test (c) Mo 3 d and (d) P 2p.



Figure S7 Bode plot of MoP: (a) in 0.5 M H_2SO_4 ; (b) 1 M KOH.

Table S4 Fitting data of EIS of MoP in 0.5 M H_2SO_4 and 1 M KOH

			СРЕ		
	K _s (22)	$K_{\rm ct}$ (22)	$Q(10^{-2}S s^n)$	n	
$0.5 \text{ M H}_2 \text{SO}_4$ $\eta = 50 \text{ mV}$	5.2	423.0	1.66	0.89	
0.5 M H₂SO₄ $\eta = 100 \ mV$	6.0	40.0	1.31	0.86	
$1 \text{ M KOH} \eta = 50 \text{ mV}$	5.4	195.0	0.80	0.89	
1 M KOH $\eta = 100 mV$	5.1	30.9	0.90	0.78	

 $Z_{CPE} = Q^{-1}(j \ \omega)^{-n}$



Figure S8 SEM graphs of the sample before/after the stability test.

Reference

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