Electronic Supplementary Information (ESI) for

S-edge-riched MoxSy Arrays Vertically Grown on Carbon Aerogels As Superior Bifunctional HER/OER Electrocatalysts

Yu Cheng,^a Pengfei Yuan,^b Xiaohui Xu,^a Sijie Guo,^c Kanglei Pang,^{ad} Haoran Guo,^a Zhiguo Zhang,^a Xiao Wu,^fLirong Zheng,^e and Rui Song^{*a}

^aSchool of Chemical Sciences, University of Chinese Academy of Sciences, 19 Yuquan Road, Shijingshan District, Beijing, 100049, PR China

^bInternational Joint Research Laboratory for Quantum Functional Materials of Henan Province, and School of Physics and Engineering, Zhengzhou University, Zhengzhou 450001, PR China

^cInstitute of Chemistry, Chinese Academy of Sciences (CAS), 2 Zhongguancun North Road, Haidian District, Beijing, 100190, PR China

^dSino-Danish College (SDC), University of Chinese Academy of Sciences, 19 Yuquan Road, Shijingshan District, Beijing, 100049, PR China

^eBeijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, PR China

^fResearch Institute of Aerospace Special Materials and Processing Technology, Beijing 100074, P. R. China

*Email: rsong@ucas.ac.cn

1. Experimental section

1.1 Materials.

Guar gum was supplied from Anhui biotechnology Factory. Thiourea (CH₄N₂S, 99.8% metals basis) and sodium borate (Na₂B₄O₇·10H₂O) were purchased from Aladdin Reagent Ltd. Ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O (99.8% metals basis), Sigma-Aldrich. Sulfuric acid (H₂SO₄, 98.0%), Guangzhou Chemical Reagent Factory. Potassium hydroxide (KOH), Shanghai Macklin Biochemical Co. Ltd. All solutions were prepared using deionized water (18.2 MΩ) and all materials were used without further purification.

1.2 Preparation of guar gum carbon aerogels (GCA).

The GCA was prepared through a typical freeze drying and pyrolysis processes. First, dissolving 0.7 g guar gum was dissolved into 200 g deionized water at 35 °C, then the solution was set statically for 3 h at room temperature to make guar gum fully swelling. Afterwards, 2 g sodium borate aqueous solution with 3 wt % mass fraction was added into the above solution, forming guar gum hydrogels with sodium borate as the crosslinking agent. Then, the obtained guar gum hydrogels were prepared into guar gum aerogels by freeze drying (-58 °C, model LGJ-10) for 48 h. Finally, the resultant guar gum aerogels were carbonized under N₂ atmosphere at 800 °C for 2 h with a temperature ramping rate of 5 °C min⁻¹, which led to the guar gum carbon aerogels (GCA).

1.3 Preparation of vertical Mo_xS_y nanoflake arrays on guar gum carbon aerogels ($Mo_xS_y@GCA$).

The preparation of $Mo_xS_y@GCA$ is schematically shown in **Fig. 1**. In a typical hydrothermal method with different mass ratios of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and CH_4N_2S . $Mo_4S_{16}@GCA$, for example, 0.57 mmol $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 16.00 mmol CH_4N_2S were dissolved in 50 mL of H₂O, firstly. Subsequently, 0.06 g GCA was added

to the above solution and reacted at 35 °C for 12 h under magnetic stirring. And then the obtained dispersion was transferred into a 50 mL Teflon stainless-steel reactor and kept at 180 °C for 24 h. The precipitates were obtained through centrifugation at 12000 rpm for 10 min, and then were washed with deionized water and ethanol for several times, prior to being dried under vacuum at 60 °C for 24 h. For comparison, bulk MoS_2 and GCA were prepared under the same conditions.

In order to investigate the effect of loading ratio of Mo and S atoms on HER performance, $Mo_xS_y@GCA$ samples with different ratio of Mo and S were prepared by controlling the stoichiometric ratio of the precursor, *x* and *y* represent the atomic% of Mo and S, respectively, measured by XPS and ICP. Meanwhile, to further probe into the growth mechanism of molybdenum sulfide, the optimal $Mo_4S_{16}@GCA$ samples with different hydrothermal reaction time (4 h, 8 h, 12 h, 16 h, 20 h and 24 h) were synthesized, and the resulants were subjected to related measurements, respectively (**Fig. S1, S2, S3**). Obviously, when the hydrothermal reaction time reaches 24 h, the electrochemical performance and physicochemical properties remain constant, indicating the completion of Mo_4S_{16} growth. Therefore, the hydrothermal time of the sample in this case is fixed at 24 h. In addition, we choose different loads of catalysts to test the electrochemical performance, and ultimately determine the optimal load of 0.28 mg/cm²(**Fig. S4**).

1.4 Characterizations.

The morphology and structure were examined by field-emission transmission electron microscopy (TEM, JEM-2100Plus, JEOL Ltd.), scanning electron microscopy (SEM, SU8010, Hitachi Ltd.), and energy-dispersive X-ray spectroscopies (EDS) attached to the TEM and SEM instruments, respectively. Raman spectra were collected through a Renishaw Invia Raman spectrometer (with the 532 nm laser source). The crystallinities of samples were characterized by powder X-ray diffraction (XRD) on

Rigaku Smartlab diffractometer (with Cu K α 1 radiation, $\lambda = 1.5406$ Å). X-ray photoelectron spectra (XPS) were obtained using Thermo Scientific ESCA Lab 250Xi X-ray photoelectron spectrometer (equipped with Al K α X-ray radiation). The elemental analysis were collected on an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES PQ9000, Analytik Jena). Nitrogen absorption/desorption isotherms were measured on a Micromeritics ASAP2460 instrument and after the samples were degassed about 4 h at 100 °C. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, while the pore size distribution was calculated from the absorption branch *via* the DFT methods. The X-ray absorption find structure spectra (Mo K-edge) were collected at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF). The storage rings of BSRF was operated at 2.5 GeV with a maximum current of 250 mA. Using Si (111) double-crystal monochromator, the data collection were carried out in transmission mode using ionization chamber. All spectra were collected in ambient conditions.

1.5 Electrochemical and measurements.

The catalytic electrochemical measurements were carried out in a standard threeelectrode setup using a CHI 660E electrochemical analyzer (Chenhua Instruments, Shanghai) at room temperature. The electrocatalyst were dispersed onto a carbon paper and used as a working electrode, while a saturated silver chloride electrode and a graphite rod acted as the reference and counter electrodes, respectively. And 0.5 M H₂SO₄ and 1 M KOH served as electrolyte. To successfully modify the working electrode, 5 mg of the catalyst and 80 μ L of 5 wt% Nafion solution were dispersed in 920 μ L isopropyl alcohol by the further 30 min sonication. And then, the homogeneous suspension was loaded onto the 1 cm² carbon paper with the mass loading was 0.28 mg cm⁻². The commercial Pt/C (20 wt%) and IrO₂ electrode was prepared using the same procedure, and current is normalized to the geometric area of the electrodes. And all tests carried out in this study were performed without compensating the iR drop. Linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were then conducted, LSV was performed at a scan rate of 2.0 mV s⁻¹ after the CV test became stable. Electrochemical impedance spectroscopy (EIS) was conducted with the frequency from 100.0 kHz to 0.1 Hz. The electrochemical double layered capacitance (C_{dl}) was estimated by cyclic voltammetry (CV) sweeping between 0 and 0.3 V from 10 to 250 mV s⁻¹. The long-term stability was tested by chronoamperometry and chronopotentiometry measurements. Unless otherwise specified, all the potentials reported in our work were calibrated with a reversible hydrogen electrode (RHE), according to the equation $E_{RHE} = E_{Ag/AgCl} +$ (0.197+0.059pH).

1.6 Operando Raman spectroscopy measurements.

The *operando* electrochemical/Raman system used in this case consists of three components: an electrochemical/Raman cell, an electrochemical analyzer (CHI 660E) and a Renishaw Invia Raman spectrometer. The electrochemical/Raman cell is made of a Teflon wall, a facing upward working electrode and a quartz window (ca. 1.0 mm in thickness). In this configuration, a thin layer of electrolyte (ca. 0.20 mm) and air was between the working electrode and the microscope objective.

2. Calculation of ECSA

Based on the linear fitting of Fig. 4f, we can derive its specific capacitance as follows:

 $c = \frac{k}{2} \times \frac{1}{m} = \frac{35.90 \text{ } mF/cm2}{2} \times \frac{1}{0.28 \text{ } mg/cm2} = 64.11 \text{ } F/g \quad \text{(equation S1)}$ where C is the specific capacitance of B5/GCS, m is the catalyst areal loading, k is

the fitting slope.

Then, we can calculate its ECSA by assuming a standard value of 60 μ F/cm²: $ECSA = \frac{c}{60uF/cm^2} = \frac{64.11F/g}{60uF/cm^2} = 106.84m^2/g$ (equation S2)

3. DFT calculation

Computational methods

First-Principles calculations were carried out within the density functional theory framework.¹ The projector-augmented wave (PAW) method^{2,3} and the generalized gradient approximation (GGA)⁴ for the exchange-correlation energy functional, as implemented in the Vienna ab initio simulation package (VASP)⁵⁻⁷ were used. The GGA calculation was performed with the Perdew-Burke-Ernzerhof (PBE)⁸ exchange-correlation potential. A plane-wave cutoff energy of 400 eV was used. All atoms were fully relaxed with a tolerance in total energy of 0.1 meV, and the forces on each atom were less than 0.02 eV/Å. The van der Walls interactions were included by DFT-D2⁹ method.

For HER, Gibbs free energy is calculated as ^{10,11} :

$$\Delta G_{ads} = \Delta E_{ads} + 0.24 eV$$

Where ΔE_{ads} is defined as follows:

$$\Delta E_{ads} = \Delta E_{H}/_{sup} - (E_{sup} + 1/2E_{H2})$$

Where the $\Delta E_{H/sup}$ is the total energy of H atom on the support and E_{H2} is the total energy of the gas H_2 ^{10,11} calculated by setting the isolated H_2 in a box of 9.0 Å×10.0 Å×11.0Å. The Gibbs free energy for the well-known highly efficient Pt catalyst is near-zero as $|\Delta G_{ads}| \approx 0.09$ eV ¹².

For OER, the Gibbs free energy is calculated by the generally reported four electrons process:

- (1) $OH^- + * \Rightarrow OH^* + e^-$
- (2) $OH^- + OH^* \implies O^* + H_2O(l) + e^-$
- (3) $O^* + OH^- \Rightarrow OOH^* + e^-$

(4) OOH* + OH⁻ \Rightarrow O₂* + H₂O (l) +e⁻

(5)
$$O_2^* \Rightarrow O_2 + *$$

The change in free energy (ΔG) of per reaction step is calculated as ¹³:

$$\Delta G = \Delta E + \Delta ZPE - T \cdot \Delta S + \Delta G_{U} + \Delta G_{pH}$$

Where ΔE is the change of the total reaction energy obtained from DFT calculation, ΔZPE is the change of the zero-point energy, T is the temperature (300K), and ΔS is the change of the entropy. $\Delta G_U = -eU$, here U is the potential at the electrode and e is the transferred charge. $\Delta G_{pH} = k_B \cdot T \times \ln 10 \times pH$ where k_B is the Boltzmann constant and T =300 K. In this work, the influence of PH was neglected. The free energy of O₂ is obtained from the reaction O₂+2H₂ \rightarrow 2H₂O, which is 4.92 eV at 300K and pressure of 0.035 bar. The free energy of OH⁻ is defined as G(H₂O) - G(H⁺), and the free energy of H⁺ is equal to 1/2H₂. The entropies of molecules (including O₂, H₂ and H₂O, etc.) in the gas (or liquid) phase are taken from the "CRC Handbook of Chemistry and Physics" ¹⁴.

4. XAFS Analysis and Results.

The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages. The k³-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, k³-weighted $\chi(k)$ data of Mo K-edge were Fourier transformed to real (R) space using a hanning windows (dk=1.0 Å-1) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of IFEFFIT software packages.¹⁵⁻¹⁷



Fig. S1. XRD patterns of Mo_4S_{16} @GCA with different growth time.



Fig. S2. SEM images of Mo_4S_{16} @GCA with different growth time. Obviously, with

the prolongation of the reaction time, the distribution of the Mo_4S_{16} nanoflakes becomes denser and more uniform.



Fig. S3. (a) LSV curves of Mo_4S_{16} @GCA with different growth time for HER. (b) LSV curves of Mo_4S_{16} @GCA with different growth time for OER. (c) Nyquist plots of different samples over the frequency range from 100.0 kHz to 0.1 Hz at the potential of - 150 mV vs. RHE. Obviously, when the reaction time reaches 24h, the electrochemical properties remain basically constant.



Fig. S4. LSV curves of Mo₄S₁₆@GCA with different loading.



Fig. S5. SEM graphs of $MoS_2@GCA$, $Mo_2S_6@GCA$, $Mo_4S_{16}@GCA$ and $Mo_6S_{16}@GCA$.



Fig. S6. (a) Nitrogen adsorption-desorption isotherms of GCA. (b) Pore size distribution of GCA.



Fig. S7. (a) SEM images of GCA. (b) TEM images of GCA.



Fig. S8. XPS survey spectra of Mo_4S_{16} @GCA and MoS_2 @GCA, respectively. (a) C1s. (b) O1s. (c) N1s.



Fig. S9. SEM images of bulk MoS_2 , distinctly, bulk MoS_2 is aggregated seriously.



Fig. S10. (a) TEM images of bulk MoS_2 . (b) HRTEM images of bulk MoS_2 . The inherent aggregation and multi-layers of bulk MoS_2 exposes less active sites.



Fig. S11. Fourier transform k^3 -weighted EXAFS spectra and corresponding fitting curves of Mo_xS_y@GCA.



Fig. S12. LSV polarization curves of carbon paper in 0.5 M H₂SO₄, 1 M KOH and 1 M

PBS. Obviously, carbon paper has no electrocatalytic activity.



Fig. S13. Nyquist plots of $MoS_2@GCA$, $Mo_2S_6@GCA$, $Mo_4S_{16}@GCA$ and $Mo_6S_{16}@GCA$ over the frequency range from 100.0 kHz to 0.1Hz at the open-circuit voltage with an AC voltage of -350 mV.



Fig. S14. Long-time stability for 64h of Mo₄S₁₆@GCA on 100mA cm⁻².



Fig. S15. SEM graphs of Mo_4S_{16} @GCA before and after chronopotentiometry measurement for 64h.



Fig. S16. CV curves of (a) $MoS_2@GCA$, (b) $Mo_2S_6@GCA$, (c) $Mo_4S_{16}@GCA$ and (d) $Mo_6S_{16}@GCA$.



Fig. S17. Nitrogen adsorption-desorption isotherms. (a) $MoS_2@GCA$, (b) $Mo_2S_6@GCA$, (c) $Mo_4S_{16}@GCA$ and (d) $Mo_6S_{16}@GCA$. The reason that the specific surface area of $Mo_xS_y@GCA$ is much smaller than that of GCA is that Mo_xS_y occupies much pores of GCA. Meanwhile, GCA will play a confinement effect on the growth of Mo_xS_y .



Fig. S18. ECSA of $Mo_xS_y@GCA$.



Fig. S19. LSV curve of bulk MoS_2 for OER in 1M KOH.



Fig. S20. (a) LSV polarization curves of Mo_4S_{16} @GCA in 1 M KOH. The inset shows the in-situ experimental observation in LSV test, where a lot of bubbles are observed. (b) Long-term stability of Mo_4S_{16} @GCA during overwater splitting with voltage of 1.8 V.

Sample	Shell	N a	R (Å) ^b	$\frac{\sigma^2}{(\text{\AA}^2 \cdot 10^3)^{c}}$	$\Delta E0$ (eV) ^d	R factor (%)
Mas	Mo-Mo	3.5	3.16	4.3	2.9	0.2
M052	Mo-S	4.8	2.41	2.8	3.9	0.3
MoSz@GCA	Mo-C	1.9	1.75	5.5	8.0	0.0
M052@GCA	Mo-S	3.3	2.39	7.1	-0.6	0.9
Mo ₂ S ₆ @GCA	Mo-C	1.8	1.72	4.4	3.1	1.0
	Mo-S	3.6	2.39	7.8	-1.1	1.0
Mo ₄ S ₁₆ @GCA	Mo-C	1.4	1.69	3.8	6.9	1.2
	Mo-S	4.2	2.40	8.7	0.8	1.2
Mo ₆ S ₁₆ @GCA	Мо-С	1.6	1.75	1.5	9.2	0.0
	Mo-S	4.9	2.39	9.3	-0.6	0.9

Table S1. EXAFS fitting parameters at the Mo K-edge for various samples

^{*a*} N: coordination numbers; ^{*b*} R: bond distance; ^{*c*} σ^2 : Debye-Waller factors; ^{*d*} ΔE_0 : the inner potential correction. *R* factor: goodness of fit. S_0^2 were set as 0.75/0.885/0.95 respectively for Mo-C/Mo-S/Mo-Mo, was obtained from the experimental EXAFS fit of Mo₂C/MoS₂ reference by fixing CN as the known crystallographic value and was fixed to all the samples.

	onset potential (mV)	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	References
MoS ₂	180	220	53	ACS Appl. Mater. Interfaces. 2015, 7, 23741- 23749.
1 T-MoS ₂	40	108	36	<i>Chem. Mater.</i> 2017, 29, 4738-4744.
MoS ₂ @GQD	95	120	40	ACS Appl. Mater. Interfaces. 2017, 9, 3653- 3660.
NCF-Mo ₂ C	40	144	55	ACS Nano. 2016, 10, 11337-11343.
MoS ₂ /Graphene	30	110	67	<i>Chem. Mater.</i> 2016, 28, 5733-5742
MoS ₂ /N-RGO	5	56	41	Adv. Energy Mater. 2016, 6, 1600116.
MoS ₂ - Co(dmgBF ₂) ₂	41	103	45	J. Mater. Chem. A. 2018, 6, 138–144.
PVP- MoS ₂ -RGO		66	38	Small 2018, 180336.
Co-ExMoS ₂		89	53	ACS Nano 2018, 12, 4565-4573.
(MoS ₂) _x (SnO ₂) ₁₋ _x /rGO		263	50	ACS Appl. Mater. Interfaces 2017, 9, 8065- 8074.
1T-2H MoS ₂		126	35	J. Phys. Chem. C. 2017, 121, 15071-15077.
pBC-N/MoS ₂	108		61	ACS Appl. Mater. Interfaces. 2016, 8, 3558- 3566.
MoS ₂ /CA	140	_	59	ACS Sustainable Chem. Eng. 2015, 3, 3140-3148.
Mo-N/C@MoS ₂		117	64	Adv. Funct. Mater. 2017, 27, 1702300.
Graphene /2H- MoS ₂ -QD		136	141	<i>Chem. Mater.</i> 2017, 29, 5782-5786.

Table S2. Comparison of the HER activity of $Mo_xS_y@GCA$ and other MoS_2 based electrocatalysts reported in literature

MoS ₂ ultrathin nanosheets	120		55	J. Am. Chem. Soc. 2013, 135, 17881-17888.
1T-Phase MoS ₂	120	220	61	ACS Appl. Mater. Interfaces. 2017, 9, 25291- 25297.
Mo_2B_4	270 (3.5m v)			J. Am. Chem. Soc. 2017, 139, 12915-12918.
Edge-exposed MoS ₂	54		100	Nanoscale. 2014, 6, 2131–2136.
1T MoS ₂	113	156	43	<i>Catal. Sci. Technol.</i> 2017, 7, 718–724.
Mo ₄ S ₁₆ @GCA	24	54	56	This work

Table S3. The free energy of different configurations is calculated according to the traditional four-electron process. Green, red, blue and brown spheres represents B, O, N and C atoms

System		Η adsorption ΔG _H (eV)	H adsorption site	
	Perfect	-1.86	S	
	S vacancy	-1.03	Мо	
	Mo vacancy	-0.22	S	
MoS doul vacancies	MoS double vacancies	-0.08	S	
	O substitute S	-0.25	О	
		0.94	S	
	N substitute S	-0.86	N	
		1.38	S	
	Perfect	2.22	S	
2H basal plane	S vacancy	-0.12	Мо	
	Mo vacancy	-0.31	S	
	MoS double	-0.19	S	

	vacancies		
	O substitute S	1.36	О
		2.16	S
	N substitute S	-1.34	N
		0.88	S
1T double	d=6.073	-0.52	S
layers (AA)	d=5.827	-0.16	S
2H double layers (AA)	d=7.270	2.68	S
	d=6.758	2.63	S
	d=6.278	2.98	S
	pristine	-2.23	Мо
1T edge		-1.40	S
	S rich	-0.57	S
2H edge	Pristine	-0.82	Мо
		-0.78	S
	50% S	-0.74	S

87.5% 8	0.11	S
100% S	0.18	S

	ΟER η ₁₀ (mV)	electrolyt e	Mass loading	References
NiC/NiD-PCC	360	1 M KOH	8.00 mg/cm ²	<i>Energy Environ. Sci.</i> 2016, 9, 3411-3416.
P _{8.6} -Co ₃ O ₄ /NF	235	1 М КОН	10.60 mg/cm ²	ACS Catal. 2018, 8, 2236- 2241
Ni-Co-P HNBs	270	1 M KOH	2.00 mg/cm ²	Energy Environ. Sci. 2018, 11, 872-880.
NiS/Ni ₂ P/CC	255	1 М КОН	_	ACS Appl. Mater. Interfaces 2018, 10, 4689-4696.
PA-NiO	245	1 М КОН	-	ACS Energy Lett. 2018, 3, 892–898.
MoS ₂ -Ni ₃ S ₂ HNRs/NF	249	1 М КОН	16.00 mg/cm ²	ACS Catal. 2017, 7, 2357–2366.
NiSe ₂	235	1 M KOH	_	ACS Sustainable Chem. Eng. 2018, 6, 2231–2239.
Ni ₂ P/Ni/NF	200	1 М КОН	_	ACS Catal. 2016, 6, 714–721.
CoP/Ni ₅ P ₄ /CoP		0.5 M H ₂ SO ₄	250.00 mg/ml	Energy Environ. Sci., 2018, 11, 22462252
NF/NiMoO-H ₂ /Ar	140	1 М КОН	6.00 mg/ml	Energy Environ. Sci., 2018, 11, 18901897
(Ni _{0.33} Co _{0.67})S ₂ NWs/CC	216	1 M KOH	_	DOI: 10.1021/acsami.8b04386
Mo ₄ S ₁₆ @GCA	370	1 М КОН	0.28 mg/ml	This work

Table S4. Comparison of the OER activity of $Mo_xS_y@GCA$ and other MoS_2 based electrocatalysts reported in literature

s	ystem	Support (eV)	*OH (eV)	*O (eV)	*00H (eV)	Overpotential (V)	Active site
1T basal plane	Pristine	-344.744	-357.038	-353.376		> 1.85	S
2H basal plane	Pristine	-358.244	-366.75	-363.886	-372.611	1.42	S
	Pristine	-342.939	-354.189	-350.225	-358.407	1.69	Мо
			-353.376	-349.881	-356.332	1.78	S
1T edge	S rich	-270.127	-281.985	-276.462	-285.552	0.78	S in S rich site
			-281.079	-276.3	-285.193	0.98	S
			-281.441	-277.755	-285.796	1.84	Мо
2Н	pristine	-338.403	-348.987	-344.489	-353.021	1.37	S
edge			-350.867	-347.69		> 2.77	Мо

Table S5. The calculated free energy of different configurations

87.5% OH covered	-410.128	-420.372	-416.139	-424.306	0.83	S
50% S	-362.441	369.303	-373.483		> 1.00	S
100% S	-382.198	-392.251	-388.134		> 0.43	S

*No numerical value indicates that the OOH structure is automatically decomposed into O and OH structures during the optimization process.

System	ZPE-TS (T=300K) (eV)
О-Н	0.317
S-H	0.198
Мо-Н	-0.023
*ОН	0.297
*0	-0.017
*OOH	0.240

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