Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Construction of stable Mo_xS_y/CeO_2 heterostructures for electrocatalytic hydrogen evolution reaction

Hongxian Liu[a], Pai Wang[a], Jinxiu Jiang[a], Gang Cheng[b], Tongwei Wu[a] and Yanning Zhang[a*]

[a] Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, Sichuan, China.

[b] Institute of Energy Research, Jiangxi Academy of Sciences, Nanchang, P. R. China

Table S1. The calculated cohesive energy and binding energy.

	E_b (eV/atom)	E_c (eV/atom)
2H-MoS_2	0.51	-5.10
Mo_3S_4	-0.69	-4.24
Mo_4S_3	-1.45	-4.00
Mo_4S_4	-0.91	-4.28
Mo_6S_8	-0.08	-4.85

The calculated binding energy per atom (E_b) and cohesive energy per atom (E_c) are defined as

$$E_b = (xE_{Mo} + yE_S - E_{MoxSy})/(x+y) \quad (1)$$

$$E_c = (E_{MoxSy} - xE_{Mo} - yE_S)/(x+y) \quad (2)$$

where x and y are the numbers of Mo and S atoms. Please note that the E_{Mo} and E_S of Equ. (1) are the energy of Mo and S atoms in their most stable states.[1, 2] Unlike the Equ. (1), E_{Mo} and E_S in Equ. (2) are the energy of isolated Mo and S atoms, respectively.[3] The energy of isolated Mo/S atoms are calculated by a symmetry broken spin polarized method in a slightly non-cubic cells, 12 Å ×13 Å ×14 Å.

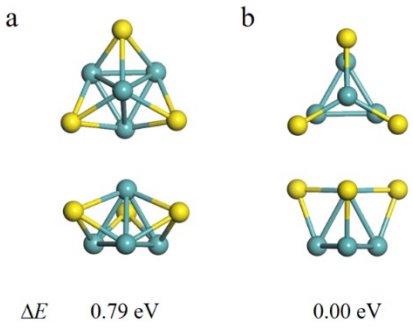

Fig. S1 The optimized and relative energy of free-standing Mo_4S_3 structures, (a) $Mo_4(\mu_3\text{-}S)_3$, (b) $Mo_4(\mu_2\text{-}S)_3$. The Mo and S atoms are denoted by cyan and yellow, respectively.

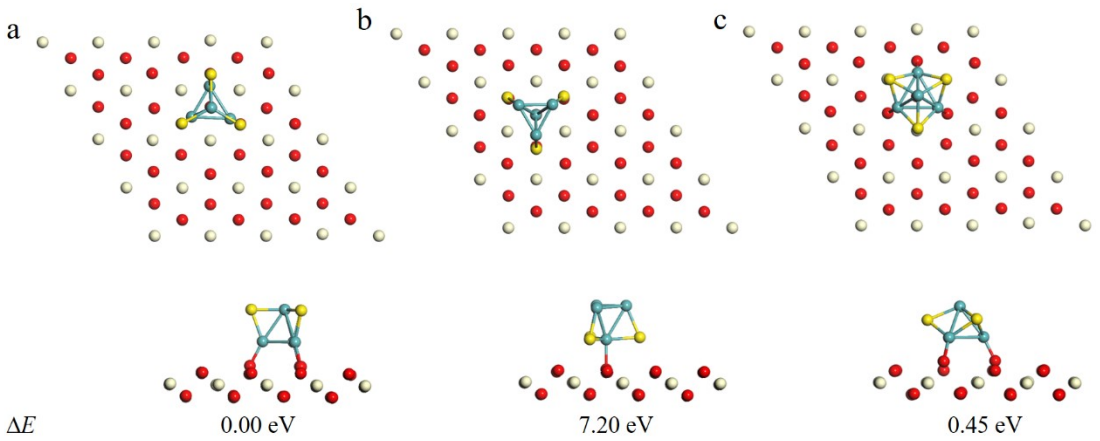

Fig. S2 The relative energy of Mo_4S_3/CeO_2 structures, (a) $Mo_4(\mu_2\text{-}S)_3$-config. 1, (b) $Mo_4(\mu_2\text{-}S)_3$-config. 2, (c) $Mo_4(\mu_3\text{-}S)_3$. The Mo and S atoms are denoted by cyan and yellow, respectively.

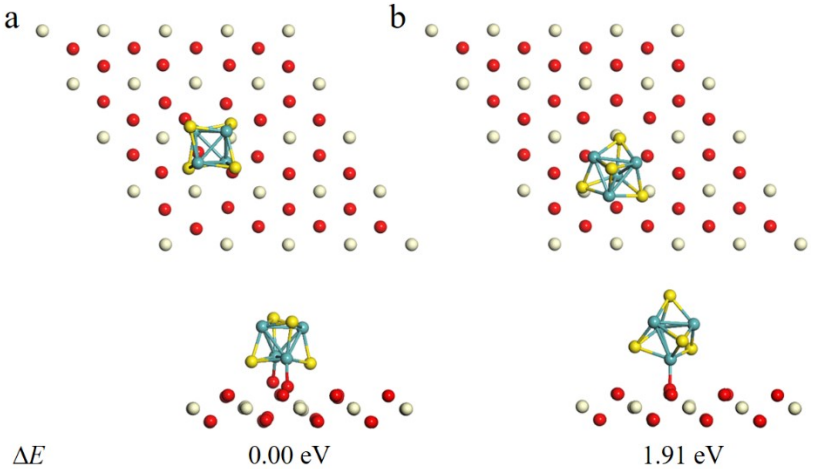

Fig. S3 The relative energy of Mo_4S_4/CeO_2 structures, (a) Mo_4S_4-config.1, (b) Mo_4S_4-config. 2. The Mo, S atoms are denoted by cyan and yellow, respectively.

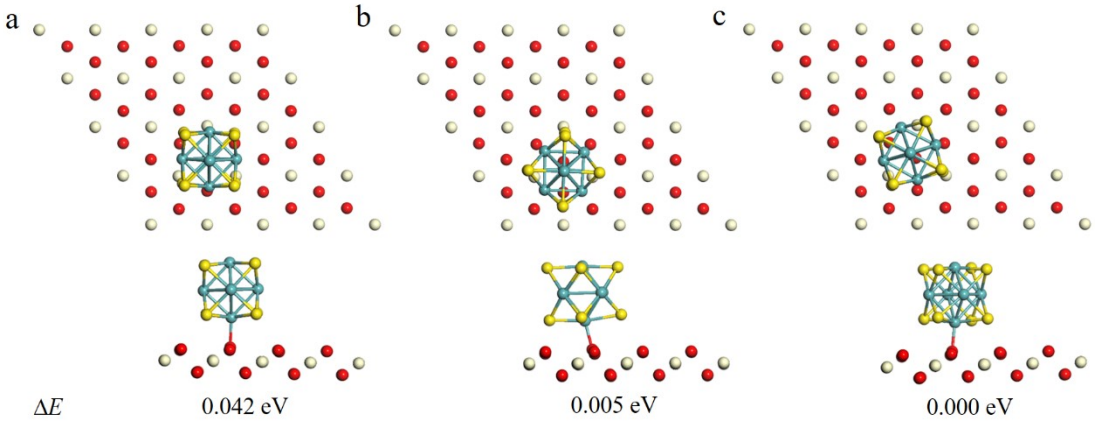

Fig. S4 The relative energy of Mo_6S_8/CeO_2 structures, (a) Mo_6S_8-config. 1, (b) Mo_6S_8-config. 2, (c) Mo_6S_8-config. 3. The Mo and S atoms are denoted by cyan and yellow, respectively.

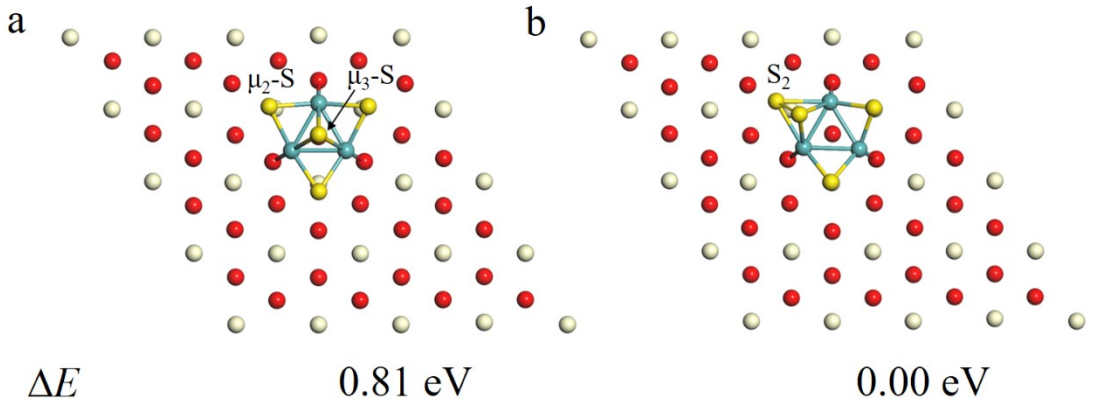

Fig. S5 The relative energy of Mo_3S_4/CeO_2 structures, (a) initial structure, (b) AIMD reconstructed structure.

Table S2. The Bader charge and magnetic moment of inner-layer Ce^{4+} and reduced Ce^{3+} on Mo_xS_y/CeO_2.

		Inner-layer Ce^{4+}	Reduced Ce^{3+}		
Mo_3S_4/CeO_2	Bader charge (e)	9.60	9.92	9.93	9.90
	Magnetic moment (μ_B)	0.00	0.95	0.95	0.95
Mo_4S_3/CeO_2	Bader charge (e)	9.60	9.93	9.93	9.93
	Magnetic moment (μ_B)	0.00	0.94	0.95	0.95
Mo_4S_4/CeO_2	Bader charge (e)	9.60	9.89	9.86	
	Magnetic moment (μ_B)	0.00	0.95	0.95	

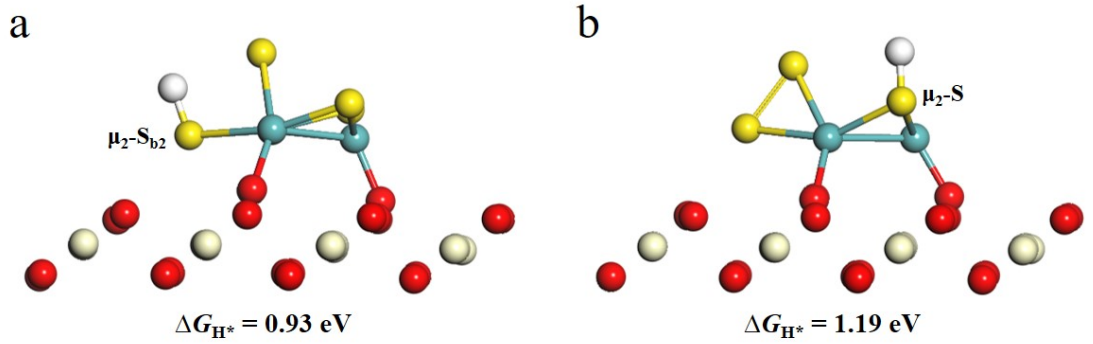

Fig. S6 The optimized structures of Mo_3S_4/CeO_2 for hydrogen adsorption, (a) μ_2-S_{b2}, (b) μ_2-S.

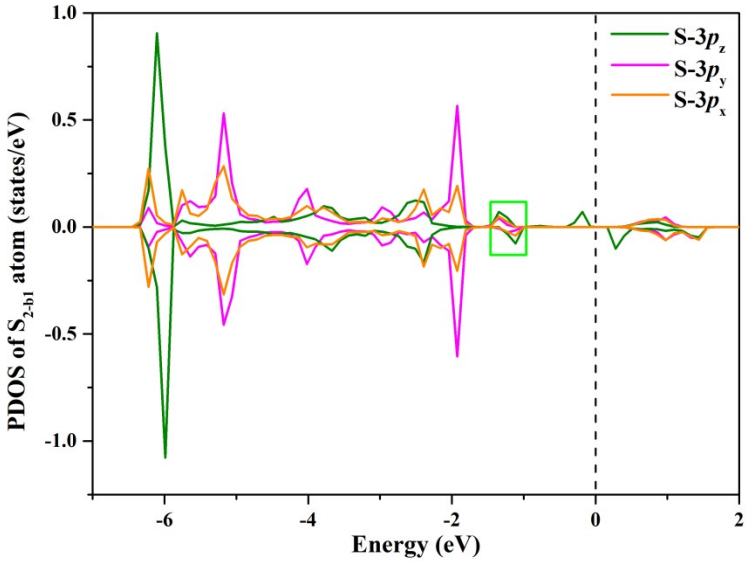

Fig. S7 The PDOS of S_{b1} atom on Mo_3S_4/CeO_2.

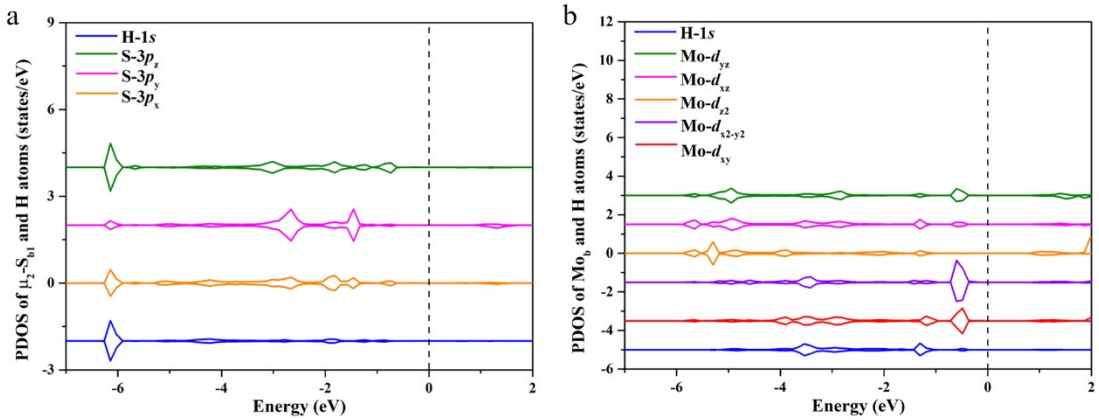

Fig. S8 The PDOS of S_{b1} and Mo_b atoms when interact with the H atoms on Mo_3S_4/CeO_2.

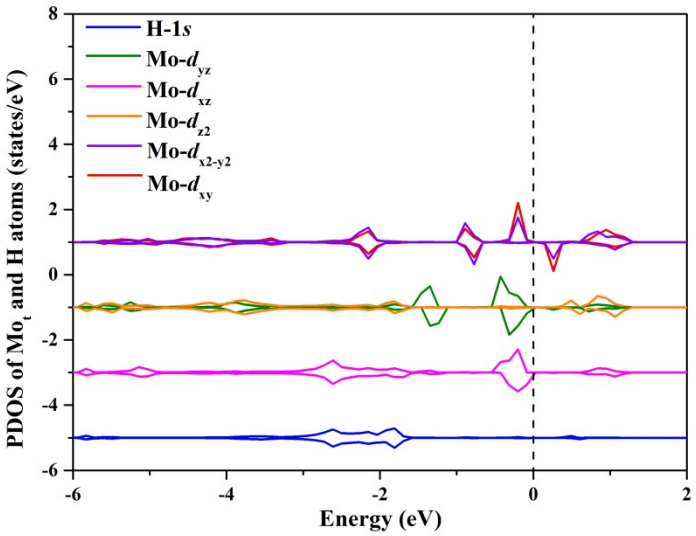

Fig. S9 The PDOS of Mo_b atom when interacts with the H atoms on Mo_4S_4/CeO_2.

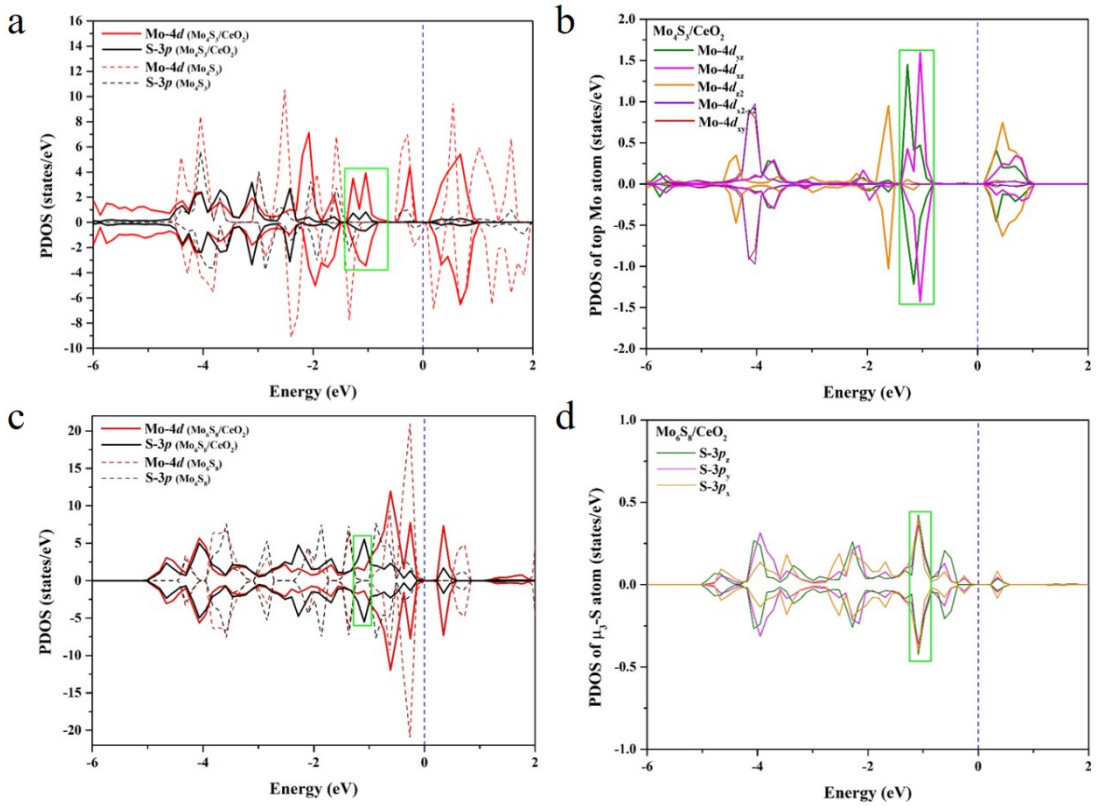

Fig. S10 The PDOS of (a) Mo_4S_3, (b) Mo_b atom on Mo_4S_3/CeO_2, (c) Mo_6S_8, (d) μ_3-S atom on Mo_6S_8/CeO_2. The solid lines represent the PDOS of absorbed Mo_xS_y clusters, and the dotted lines represent the PDOS of free-standing Mo_xS_y clusters.

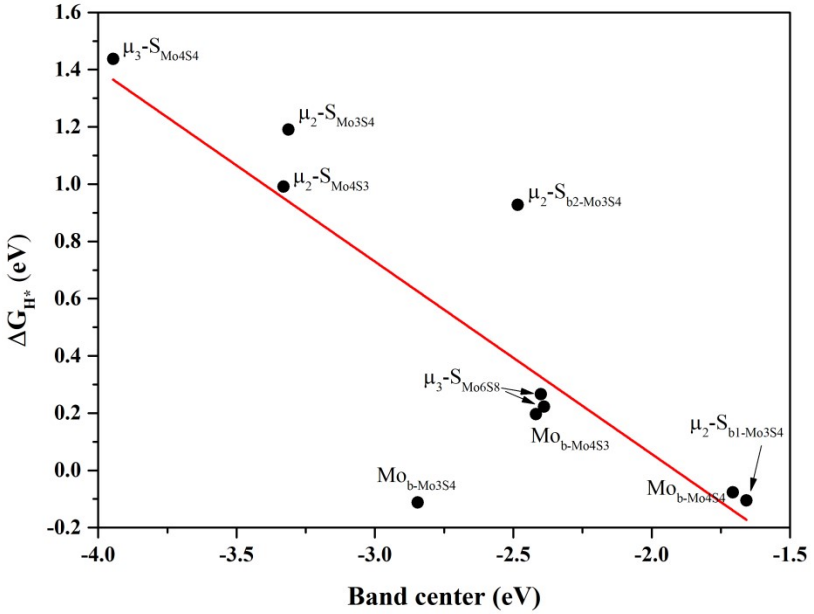

Fig. S11 The relation between ΔG_{H^*} and the *p*/*d* band center of Mo_xS_y/CeO_2. The *p* band center of μ_2-$S_{b1\text{-}Mo3S4}$ and μ_2-$S_{b2\text{-}Mo3S4}$ were calculated by performing single-point self-consistent calculations.

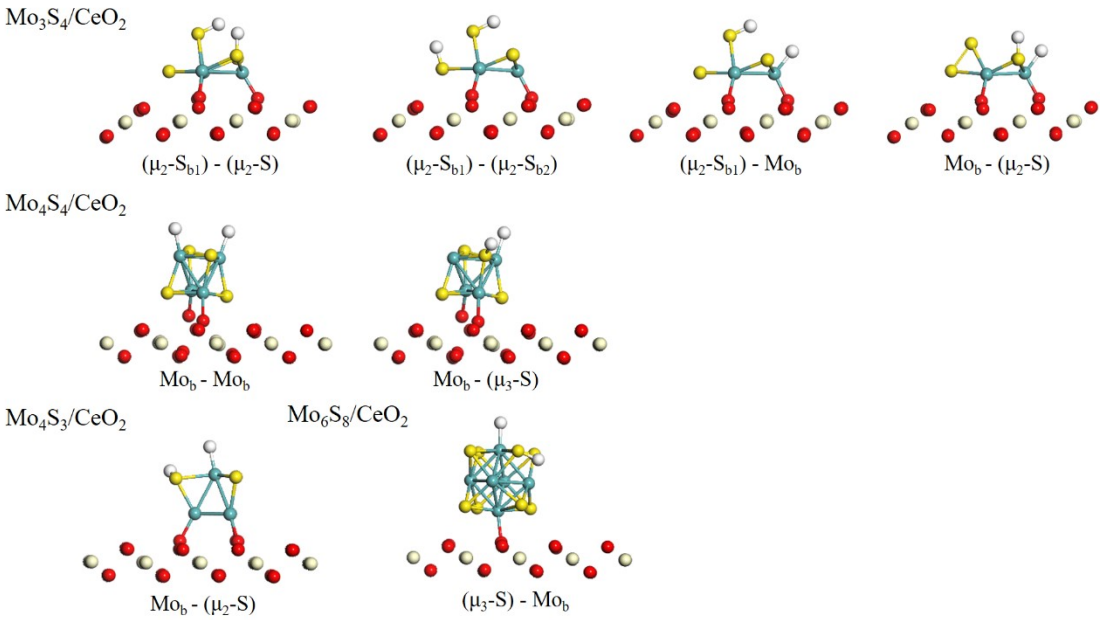

Fig. S12 The optimized structures of Mo_xS_y/CeO_2 with two H atoms absorption.

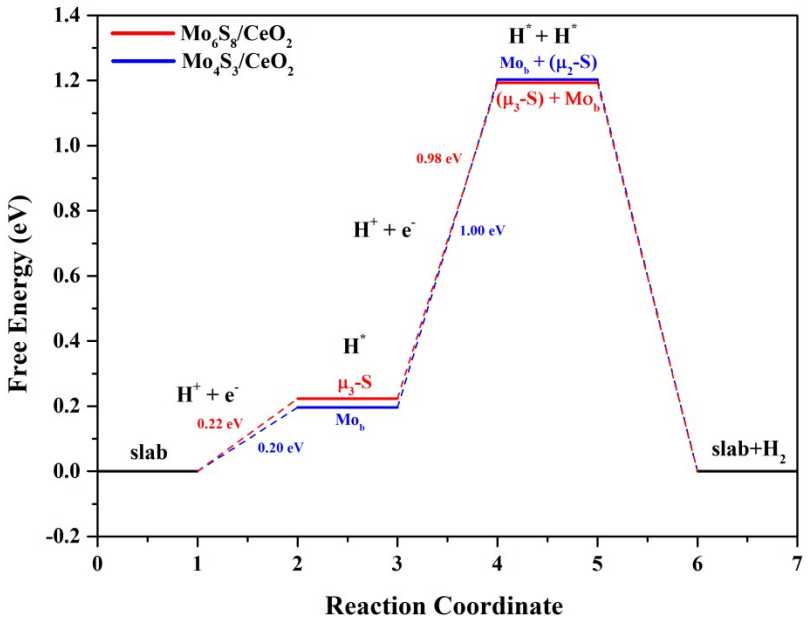

Fig. S13 The calculated reaction pathways with Volmer-Tafel reaction mechanisms of Mo_4S_3/CeO_2 and Mo_6S_8/CeO_2.

References

1. A. Arab and M. Habibzadeh, *Journal of Nanostructure in Chemistry*, 2016, **6**, 111-119.
2. K. Gao, X.-R. Zhang, Z.-C. Yu and P.-Y. Huo, *Computational and Theoretical Chemistry*, 2018, **1138**, 168-175.
3. D. W. Zhou, J. S. Liu, S. H. Xu and P. Peng, *Physica B: Condensed Matter*, 2010, **405**, 2863-2868.