Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Experimental Section

Materials Preparation:

A one-step hydrothermal method was used to synthesize Fe-MoS_2 NSs. First, a piece of nickel foam was sonicated in 5M HCl solution to remove the oxide layer on the surface and rinsed subsequently with water and ethanol, then dried in a vacuum oven. After that, an aqueous solution was prepared by mixing ammonium tetrathiomolybdate (80 μmol, $H_8N_2MoS_4$) and iron (II) chloride tetrahydrate (2.5 μmol, 5 μmol, 10 μmol $FeCl_2{\cdot}4H_2O$). After thirty minutes of stirring, the final brown solution was transferred into a Teflon-lined stainless steel autoclave with a piece of clean nickel foam (2.5 cm × 2.5 cm) at the bottom and maintained at 200 °C for 18 h. The Fe-MoS_2 NSs were washed with absolute ethanol and water for several times to remove possible residues.

Materials Characterization:

The morphology and structure of the prepared samples was examined by SEM (SEM, Zeiss SUPRA40) and TEM (JEOL 2000FX). Chemical composition of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220i-XL) using a monochromatic Al K_α source at the pass energy of 10 eV. The crystal structures of the samples were performed on a BRUKER AXS X-ray diffractometer (XRD) using Cu K_α radiation at 40 kV and 40 mA. Raman Spectroscopy was collected on Horiba Scientific LabRAM HR Evolution system using 532 nm laser source. The Raman band of silicon wafer at 520.7 cm^{-1} was used for calibration.

Electrochemical Measurements:

All electrochemical measurements were carried out on an electrochemical workstation (Bio-logic Inc) at room temperature using 1M KOH as the electrolyte. Pt plate and Hg/HgO (1M KOH) were used as counter electrode and reference electrode, respectively. The MoS_2 NSs grown on nickel foam were directly used as the working electrode. An extremely low scan rate of 0.5 mV s^{-1} was applied for all linear sweep voltammetry measurements (LSV) to eliminate effect of the faradic current. The long-term stability of the electrodes was measured by chronopotentiometry. Impedance spectra of the electrodes were recorded at potential of 1.52 V (vs. RHE) in a frequency range of 100 mHz to 100 KHz at amplitude of 10 mV. All potentials had been calibrated with the respect to the reversible hydrogen electrode (RHE) via the equation: $E_{vsRHE} = E_{vsHg/HgO} + 0.059 \times PH + 0.098$, where the $E_{vsHg/HgO}$ was the potential measured against the Hg/HgO electrode. The potentials were corrected by 85% iR-compensation.

Computational method:

All calculations were carried out using the density functional theory (DFT) with the generalized Perdew-Burke-Ernzerhof (PBE),[1] and the projector augmented-wave (PAW) pseudopotential planewave method as implemented in the VASP code.[2,3] For the PAW pseudopotential, we included $4d^54s^1$, $3d^74s^1$, $3s^23p^4$, $2s^22p^4$ and $1s^1$ were treated as valence electrons for Mo, Fe, S, O and H atoms, respectively. A 12×12×10 Monkhorst-Pack (MP) k-point grid was used for MoS_2 unitcell geometry optimization calculations. Good convergence was obtained with these parameters, and the total energy was converged to 1×10^{-6} eV per atom. Energy convergence with respect to the plane wave cutoff was tested by varying setting between 300 and 600 eV considering the electron spinpolarization. Convergence to within 10 meV was achieved with a cutoff energy of 500 eV for all calculations. We chose monolayer MoS_2 with a vacuum thickness of 25 Å to represent the slab to calculate intermediates adsorptions. In this study, we systematically explored the adsorption of O, OH and OOH on Fe doped monolayer MoS_2 for OER studies, and the OER on active sites were studied in detail in the following four electron reaction paths:

$$H_2O(l) + * \rightarrow OH^* + (H^+ + e^-) \tag{1}$$

$$OH^* \rightarrow O^* + (H^+ + e^-) \tag{2}$$

$$O^* + H_2O(l) \rightarrow OOH^* + (H^+ + e^-) \tag{3}$$

$$OOH^* \rightarrow * + O_2(g) + (H^+ + e^-) \tag{4}$$

where * stands for an active site on the surface of Fe doped monolayer MoS_2, (l) and (g) denote liquid and gas phases, respectively. O^*, OH^* and OOH^* are adsorbed intermediates. It was reported that the potential-determining step could either be the formation of O^* from OH^* (step 2) or the transformation of O^* to OOH^* (step 3), and the overpotential of OER process could be calculated by examining the reaction free energies of different elementary steps using reported methods. [4]

To obtain the rate-limiting step of OER on Fe doped MoS_2, we calculated the adsorption energy of O^*, OH^* and OOH^*. The adsorption energies were calculated from DFT simulations based on:

$$\Delta E_{OH^*} = E(OH^*) - E(*) - (E_{H_2O} - {}^{1}\!/_{2}E_{H_2}) \tag{5}$$

$$\Delta E_{OOH^*} = E(OOH^*) - E(*) - (2E_{H_2O} - {}^{3}\!/_{2}E_{H_2}) \tag{6}$$

$$\Delta E_{O^*} = E(O^*) - E(*) - (E_{H_2O} - E_{H_2}) \tag{7}$$

here, $E(OH^*)$, $E(OOH^*)$, $E(O^*)$ and $E(^*)$ are the ground state energies of models with the adsorbed intermediates of OH^*, OOH^*, O^* and Fe doped 4×4×1 MoS_2 supercell obtained from DFT calculations, respectively. E_{H_2O} and E_{H_2} are the computed DFT energies of H_2O and H_2 molecules in the gas phase. For adsorption energy calculations, corrects resulted from the zero points energy (ZPE) and entropy are considered in our study. Therefore, we can calculate reaction free energies based on the calculated adsorption energies by the following equation:[4]

$$\Delta G_{ads} = \Delta E + \Delta ZPE - T\Delta S \tag{8}$$

where T is the temperature and ΔS is the entropy change. It should be noted that we only considered the standard molar vibrational entropy here based on the reported method.[5] In this study, we ignore the solvent correction to the adsorbed intermediates. For each step, the reaction free energy is defined as the difference between free energies of without and with adsorbed intermediates.[4]

The first step is to split water molecule on the active site and to release a proton and an electron (Eq. 1):

$$\Delta G_1 = E\left(OH^*\right) - E(*) - \left(E_{H_2O} - {}^1\!/_2 E_{H_2}\right) + (\Delta ZPE - T\Delta S) + k_b T \ln a_{H^+} - eU \tag{9}$$

The second step is oxidation of OH* species to O* with release of a proton and of an electron (Eq. 2):

$$\Delta G_2 = E\left(O^*\right) - E\left(OH^*\right) + {}^1\!/_2 E_{H_2} + (\Delta ZPE - T\Delta S) + k_b T \ln a_{H^+} - eU \tag{10}$$

The third step is to split water molecule on top of oxygen and to release a proton and an electron (Eq. 3):

$$\Delta G_3 = E\left(OOH^*\right) - E\left(O^*\right) - \left(E_{H_2O} - {}^1\!/_2 E_{H_2}\right) + (\Delta ZPE - T\Delta S) + k_B T \ln a_{H^+} - eU \tag{11}$$

The fourth step is the evolution of oxygen (Eq. 4):

$$\Delta G_4 = 4.92 - (\Delta G_1 + \Delta G_2 + \Delta G_3) \tag{12}$$

Here, k_B is Boltzmann constant, a_{H^+} represents the activity of protons. U is the potential at the electrode and e is the charge transferred. For an ideal catalyst, all four steps have the same reaction free energy of 1.23 eV at zero potential (4.92 eV divide by 4), and the reaction free energy would reduce to zero at equilibrium potential of U=1.23 V. For simplicity, in this study we restricted pH=0. It should be noted that we used 4×4×1 supercell and only consider one intermediate, such as O*, in our model, and we did not explore the coverage effect on the binding energy in this study. The calculated free energy based on equations (9)-(12) can be used to estimate the overpotential η^{OER} based on the following equation:

$$\eta^{OER} = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}/e - 1.23 \tag{13}$$

and the optimized overpotential can be calculated using

$$\eta^{OER}_{opt} = (\Delta G_2 + \Delta G_3)/2e - 1.23 \tag{14}$$

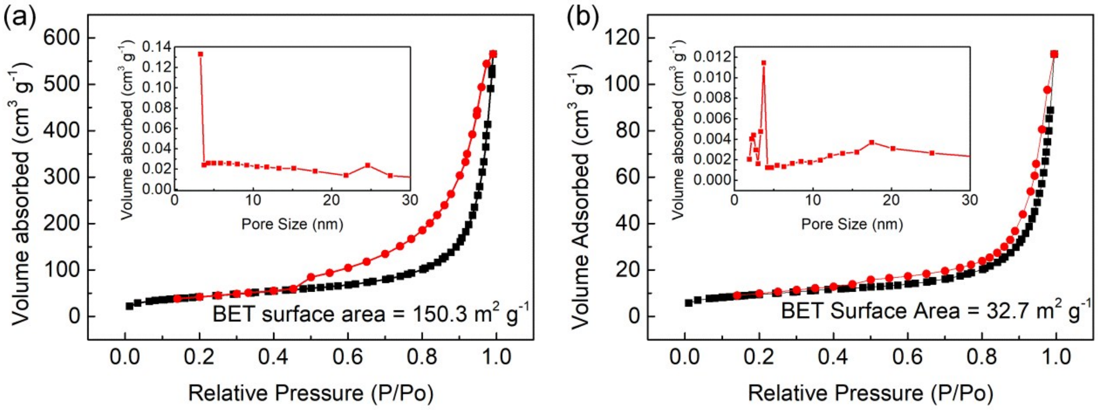


Fig. S1 Nitrogen adsorption-desorption isotherms of (a) Fe-MoS_2 and (b) MoS_2. Black, adsorption isotherms; red, desorption isotherms. The insets are the corresponding pore size distributions. The Brunauer-Emmett-Teller (BET) specific areas of Fe-MoS_2 and MoS_2 were determined by nitrogen gas sorption to be 150.3 m^2 g^{-1} and 32.7 m^2 g^{-1}, respectively.

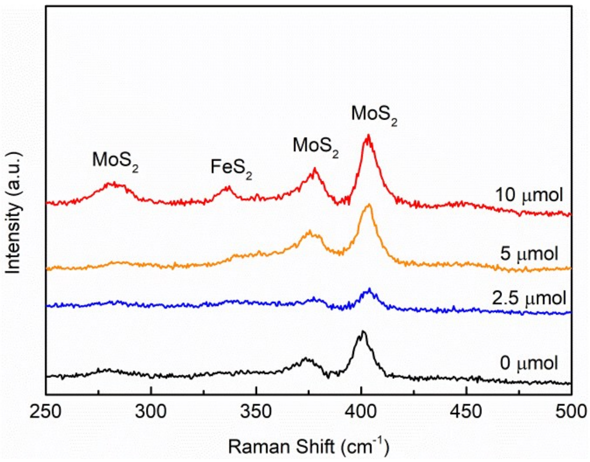


Fig. S2 Raman spectra of MoS_2 with the addition of different amount of Fe.

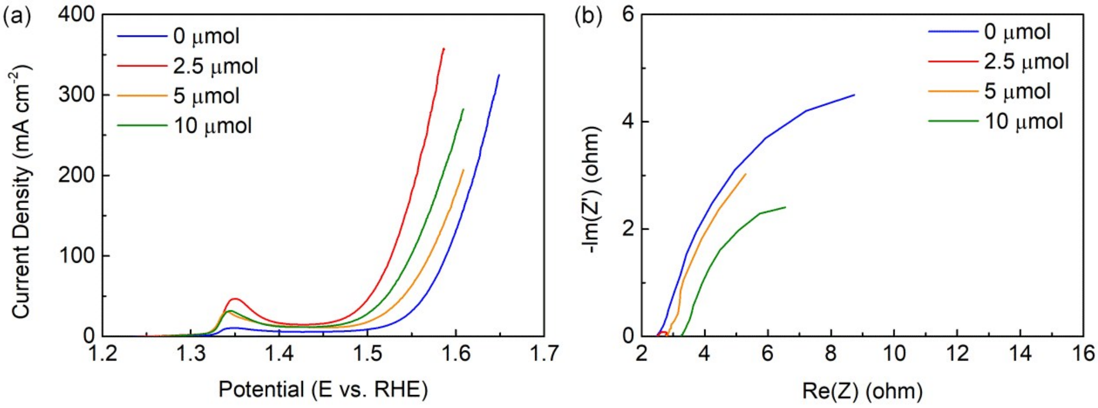


Fig. S3 The relationship between the amount of Fe and the OER performance. (a) LSV polarization curves and corresponding EIS curves.

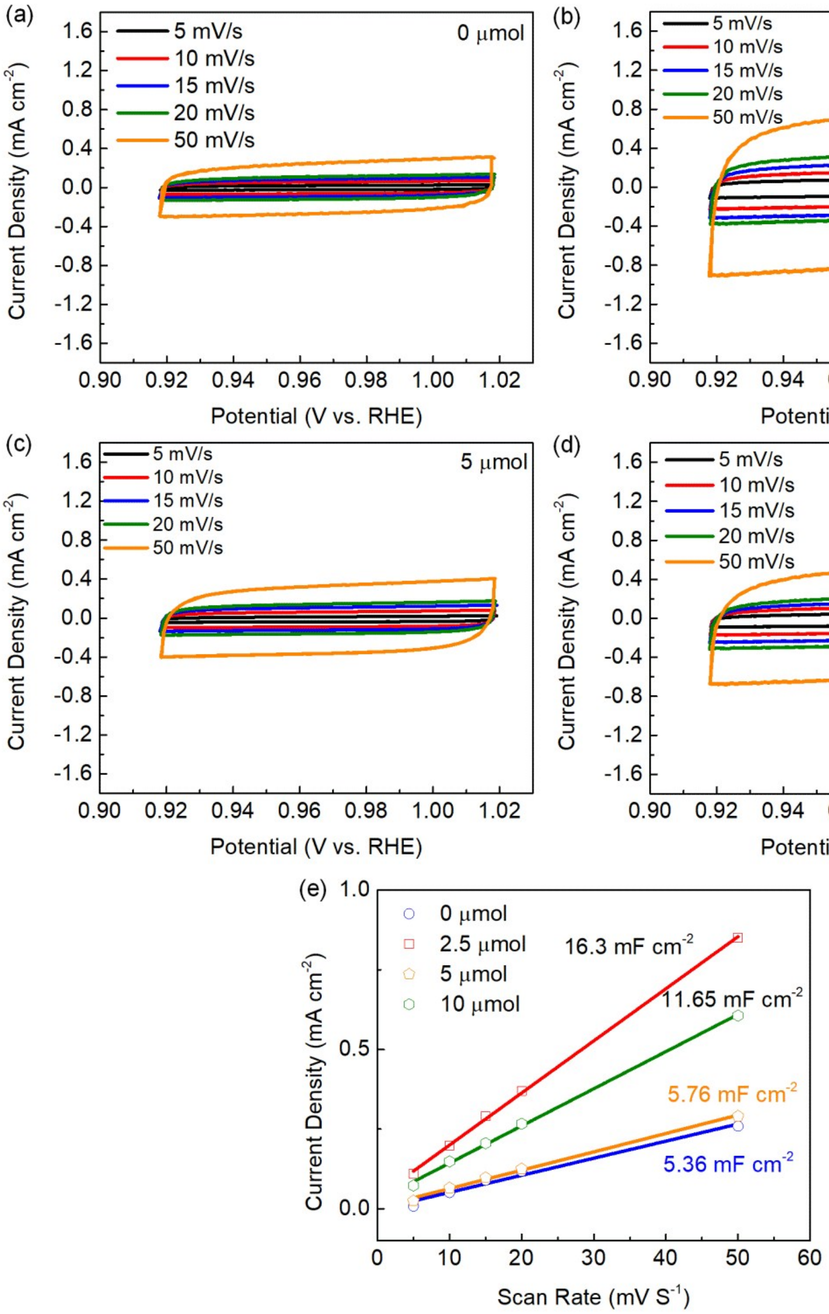


Fig. S4 CVs of Fe-MoS_2 with different amount of Fe. (a) 0 μmol, (b) 2.5 μmol, (c) 5 μmol and (d) 10 μmol at different scan rates: 5, 10, 15, 20 and 50 mV s^{-1} in 1.0 M KOH. (e) Corresponding capacitive currents at 0.98 V vs. RHE as a function of scan rates.

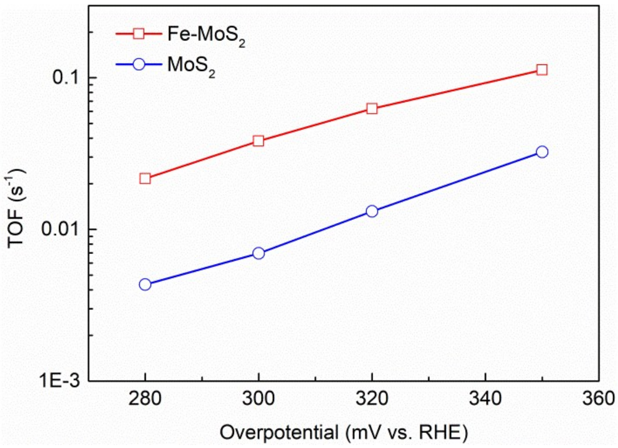
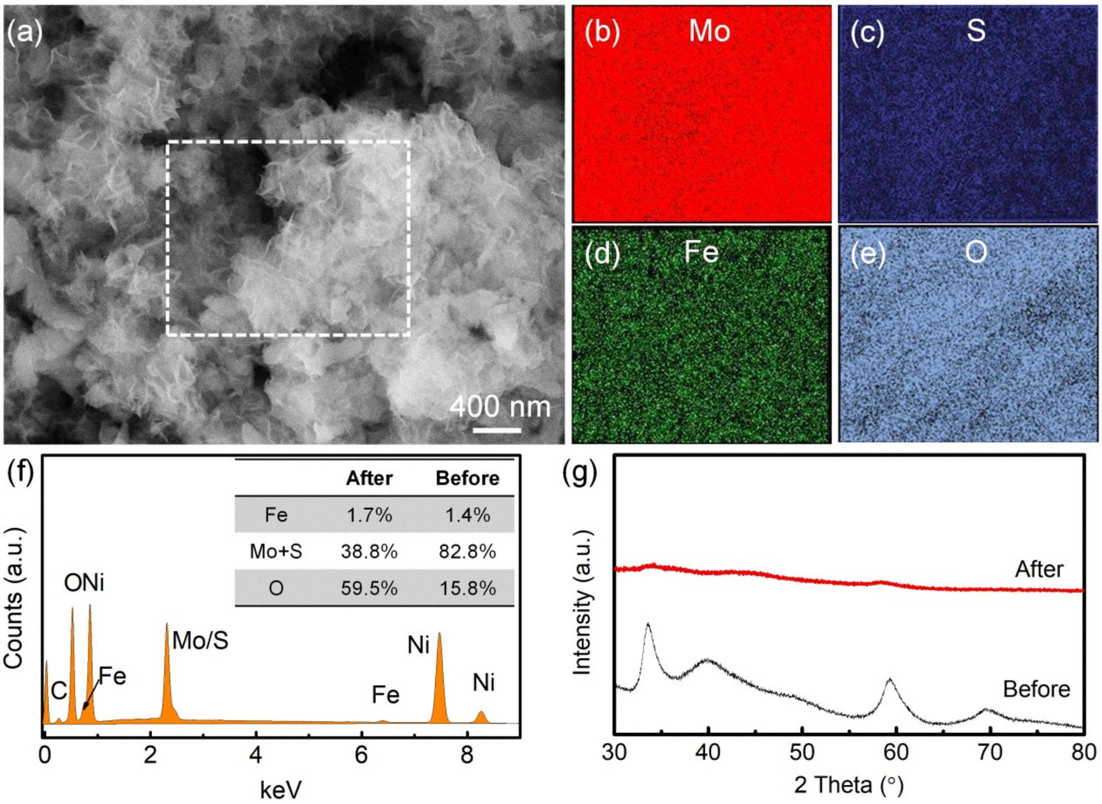


Fig. S5 Average TOF values of MoS_2 and Fe-MoS_2 at different overpotentials.



	After	Before
Fe	1.7%	1.4%
Mo+S	38.8%	82.8%
O	59.5%	15.8%

Fig. S6 (a) SEM image, (b-e) elemental mapping and (f) corresponding EDS spectrum of Fe-MoS_2 after stability test. The inset in (f) shows the comparison of elemental contents of Fe-MoS_2 before and after stability test. (g) XRD diffraction comparison of Fe-MoS_2 before and after stability testing.

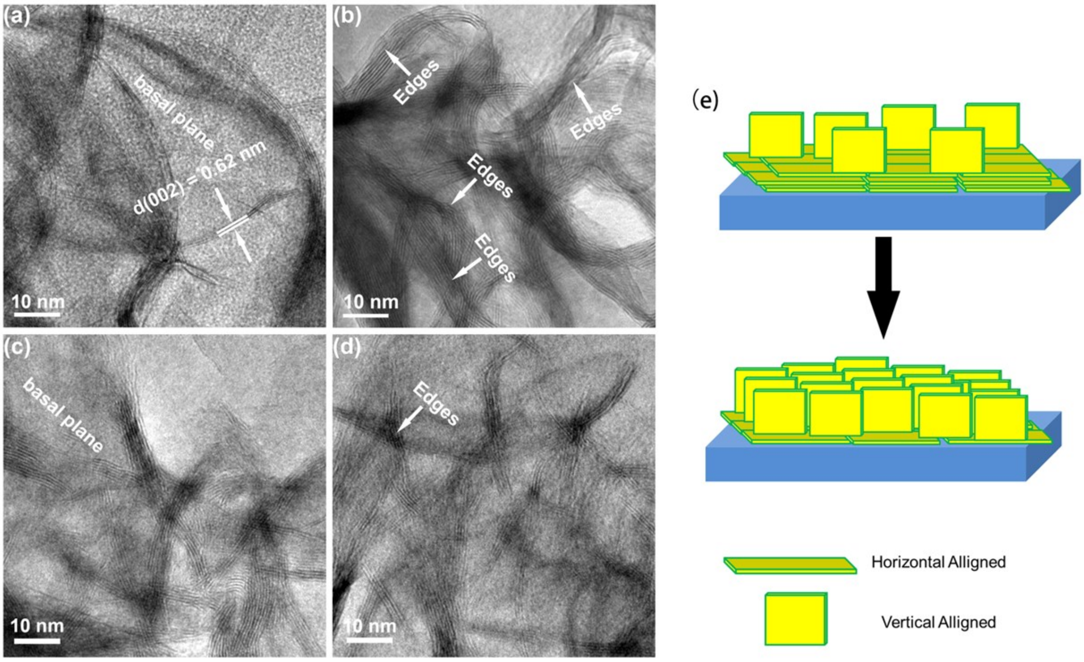


Fig. S7 TEM images of Fe-MoS_2 with different amount of Fe. (a) 0 μmol, (b) 2.5 μmol, (c) 5 μmol and (d) 10 μmol. Note that the strippled lines in the TEM images are the vertically aligned layers. (e) Schematic diagram depicts the different layer alignment: horizontally aligned and vertically aligned.

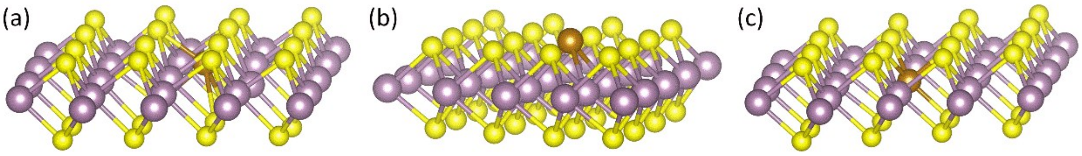


Fig. S8 Atomic configurations of the possible Fe doping sites in MoS_2. (a) Interstitial Fe with calculated formation energy of 4.52 eV. (b) Substitutional Fe at S site with formation energy of 3.26 eV. (c) Substitutional Fe at Mo site with formation energy of 2.54 eV. The yellow, brown and gray balls represent S, Fe and Mo atoms, respectively.

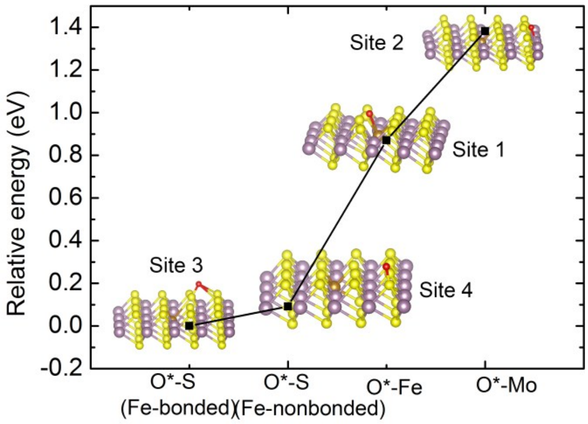


Fig. S9 The calculated relative energies of intermediate of O* at the possible sites in Fe-doped MoS_2, namely, Fe (Site 1), Mo (Site 2), Fe-bonded S atoms (Site 3) and S atoms far away from Fe (Site 4). The red, yellow, brown and gray balls represent O, S, Fe and Mo atoms, respectively. Here, we consider the adsorption site with the lowest ground states energy as a common reference. It shows that O bonded with Fe-bonded S atoms (Site 3) has the lowest relative energy, which proves that O prefers to bond with Fe-bonded S atoms.

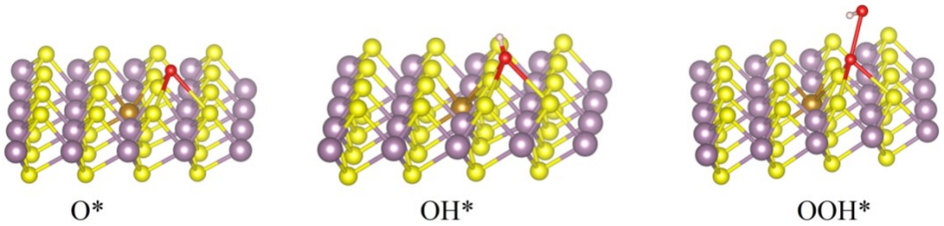

O* OH* OOH*

Fig. S10 Atomic configurations of three intermediates adsorption in Fe-doped MoS_2. The red, yellow, brown and gray balls represent O, S, Fe and Mo atoms, respectively.

References

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2. P. Blöchl, *Phys. Rev. B,* 1994, **50**, 17953.
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4. I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov and J. Rossmeisl, *ChemCatChem,* 2011, **3**, 1159-1165.
5. X. M. Cao, R. Burch, C. Hardacre and P. Hu, *Catal. Today, 2011,* **165**, 71-79.