Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Arousing the electrocatalytic hydrogen evolution activity of inert two-dimensional MoS_2 surface via single-atom metal doping

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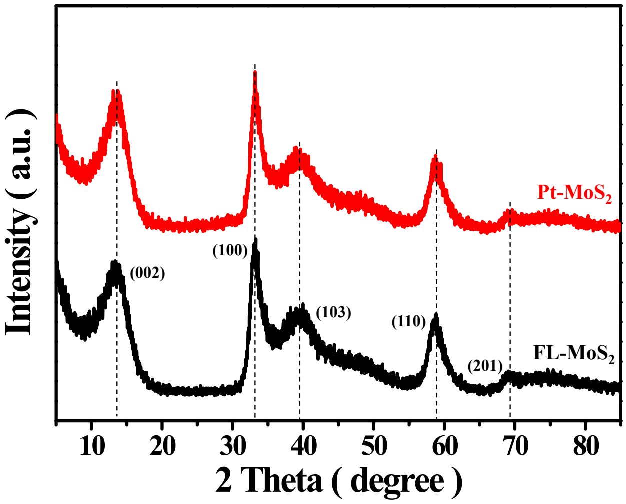

Figure S1. XRD patterns of Pt-MoS$_2$ in comparison to pure few-layer MoS$_2$ nanosheets (FL-MoS$_2$). The result showed no Pt-containing crystal phases involved in the Pt-MoS$_2$ samples.

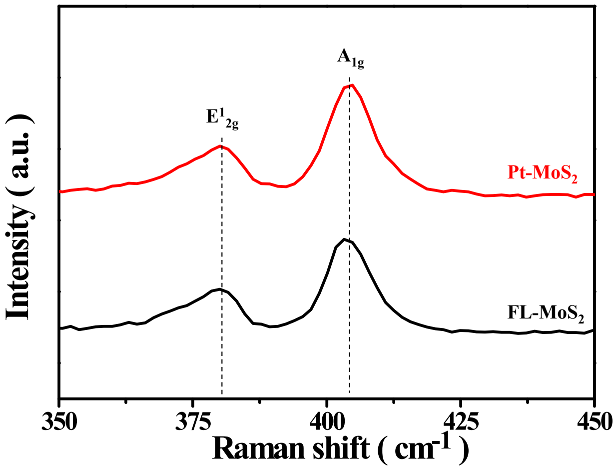

Figure S2. Raman spectra of Pt-MoS$_2$ in comparison to pure few-layer MoS$_2$ nanosheets (FL-MoS$_2$).

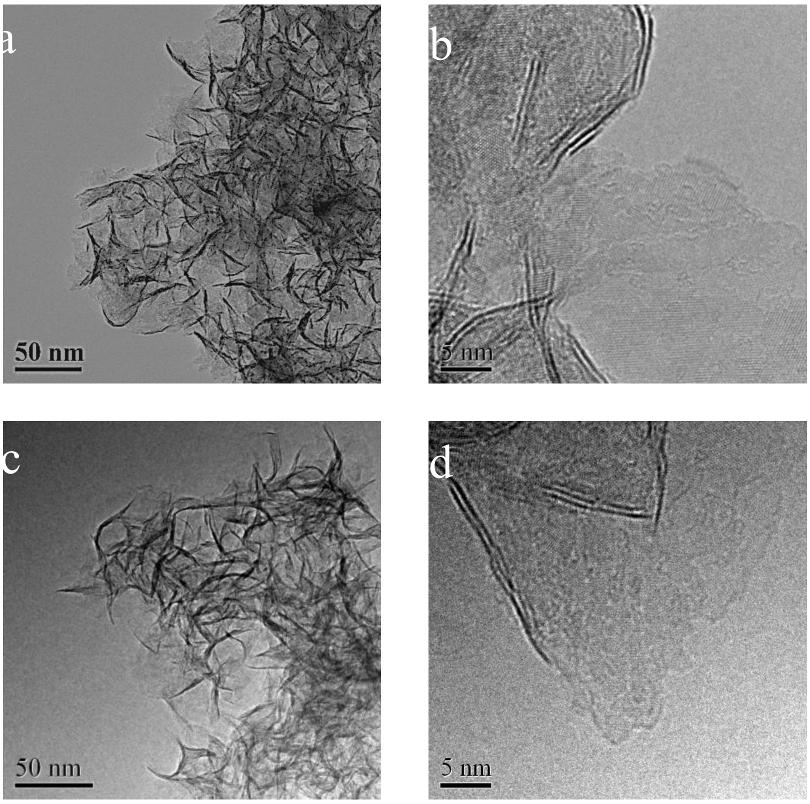

Figure S3. (a-b) TEM images of pure few-layer MoS_2 nanosheets (FL-MoS_2). (c-d) TEM images of Pt-MoS_2.

In order to confirm the doping and adsorption configuration for metal atoms doped MoS_2, periodically repeated single trilayer MoS_2 crystal models have been used. The Pt atom doping is adopted as an example and four possible cases have been taken into account, as shown in Fig. S4 for the optimized results. a-d are the substitutional doping cases: a-b are Pt atoms replacing Mo atoms, while c-d are Pt atoms replacing S atoms. e-h are the supported cases: e-f are corresponding to Pt atoms above Mo atoms, while g-h are Pt atoms above hollow sites. The formation energy (E_f) for these different structures has also been calculated to evaluate their structural stability, which is calculated as: $E_f = E_{tot} – E_0[MoS_2] – E_i$, where E_{tot} is the total energy for MoS_2 with doped or supported metal atoms. In the cases of metal doped MoS_2, $E_0[MoS_2]$ is the energy for MoS_2 with one Mo or S vacancy, while for the cases of metal supported on MoS_2, $E_0[MoS_2]$ is the energy for perfect MoS_2. E_i is the energy of one metal atom referred to its bulk metal.

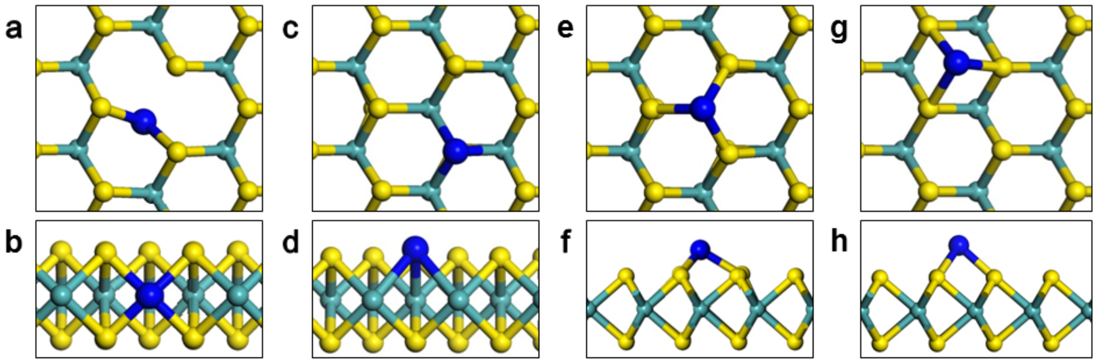

Figure S4. Optimized atomic configurations of Pt atoms in MoS_2 two-dimensional structures: top view and side view of Pt atom doping into the Mo site (a-b); top view and side view of Pt atom doping into the S site (c-d); top view and side view of Pt atom supported just above the Mo atom (e-f); top view and side view of Pt atom supported above the hollow site (g-h).

According to the calculated results, when Pt atoms replace Mo atoms or S atoms, the E_f are -2.22 eV and 0.42 eV, while the E_f are 2.82 eV and 3.41 eV for Pt atoms supported above Mo atoms or hollow sites, respectively. One can see that the case in Fig. S4a-b is the most likely doping configuration, while the case in Fig. S4e-f shows the best supporting configuration but Pt atoms are easy to agglomerate when they just monodisperse on MoS_2. Thus, the doping configurations are more likely to form with respect to the supported configurations.

The descriptor of HER activity, adsorption free energy of H* ($\Delta G_H{}^o$), can be obtained by correcting the adsorption energy of H*. The differential binding energy is often used to describe the stability of H atoms, which is defined by: $\Delta E_H = E(MoS_2 + H) - E(MoS_2) - 1/2E(H_2)$, where $E(MoS_2 + H)$ is the total energy for the metal atoms doped or supported MoS_2 catalysts with one absorbed H atom, $E(MoS_2)$ represents the total energy for the catalyst without H atoms, and $E(H_2)$ is the energy of a gas phase hydrogen molecule. For metal catalysts, $\Delta G_H{}^o$ has used to be roughly calculated as: $\Delta G_H{}^o = \Delta E_H + 0.24$ eV[1], which is taken for the following calculations.

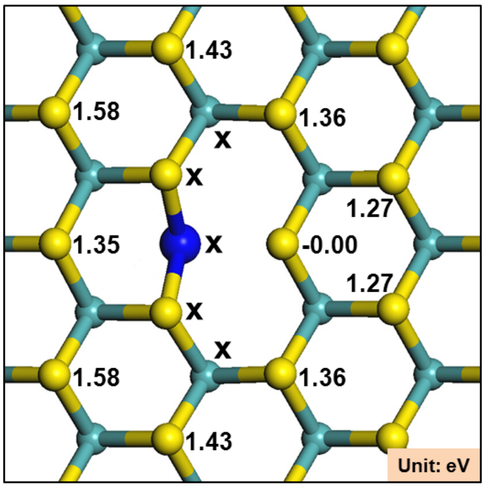

Figure S5. Calculated adsorption free energy of H* ($\Delta G_H{}^o$) on S and Pt atoms of different sites (in units of eV). The sites marked with ‘x’ indicate that H atoms cannot adsorb on them. The green, yellow, blue spheres represent Mo, S, Pt atoms, respectively.

As shown in Fig. S5, Pt atom doping can affect the adsorption free energy of H* ($\Delta G_H{}^o$) on its surrounding S atoms. For the coordinatively unsaturated S atom neighboring to the Pt atom, the free energy is around 0 eV, while for other S atoms around, the free energy is still higher than +1.0 eV. Moreover, H atoms cannot adsorb on the doped Pt atom. Thus, it indicates that the active sites are not the doped Pt atoms, but the coordinatively unsaturated S atoms neighboring to them, resulting in the prior adsorption sites for H atoms.

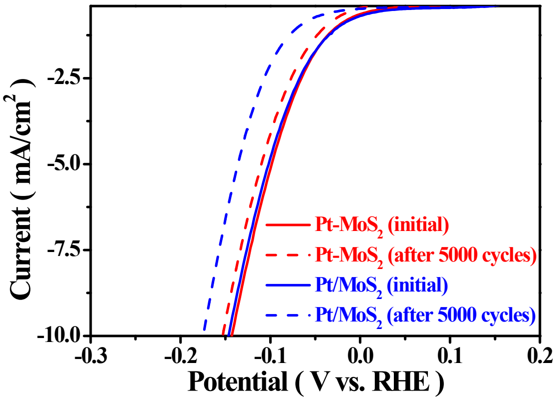

Figure S6. HER polarization curves of Pt-MoS$_2$ recorded initially and after 5000 CV sweeps between -0.13 V and +0.57 V (vs. RHE) in comparison with that of Pt/MoS$_2$.

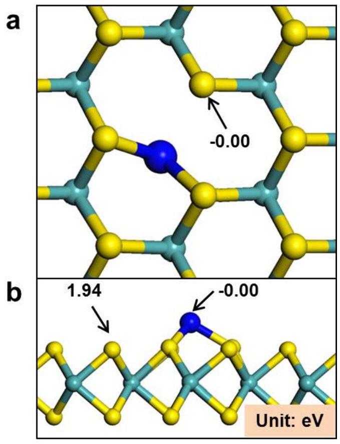

Figure S7. Calculated adsorption free energy of H* ($\Delta G_H{}^o$) on S and Pt atoms for Pt doped MoS_2 (a) and Pt supported on MoS_2 (b). The green, yellow, blue spheres represent Mo, S, and Pt atoms, respectively.

It can be seen that in the doped case, owing to the steric hindrance, the H atom cannot adsorb on the doped Pt atom, while the prior adsorption site is the neighboring unsaturated S atom with $\Delta G_H{}^o$ of about 0 eV. In the supported case, the prior adsorption site is the Pt atom with $\Delta G_H{}^o$ of also about 0 eV. These results indicate that H atom would own the similar adsorption ability in both the doped and supported cases, resulting in a similar HER activity.

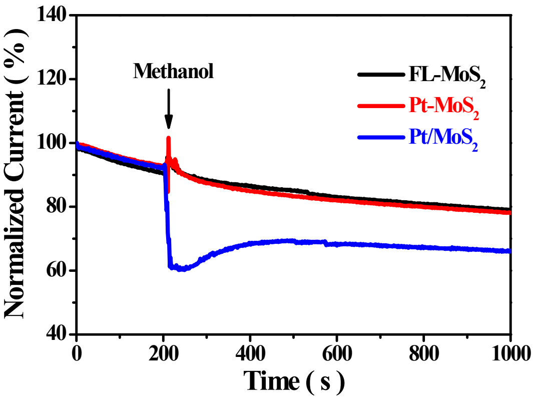

Figure S8. Chronoamperometric responses in the O_2-saturated 1 M NaOH at -0.25 V (vs. Hg/HgO) for FL-MoS_2, Pt-MoS_2 and Pt/MoS_2. 10% (v/v) methanol was injected into the electrolyte solution at 200 s.

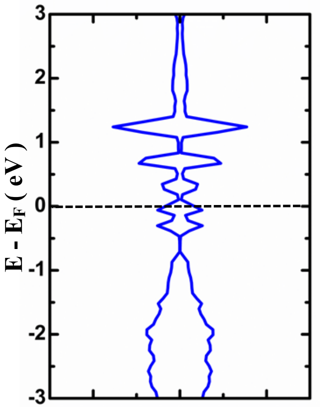

Figure S9. Projected density of states (PDOS) for the doped Pt atoms of the Pt-MoS_2. The position of the Fermi level is as shown in dashed lines.

It can be obviously seen that there are some hybridized electronic states from both Pt and S (as shown in Fig. 3) around the Fermi level of doped Pt atoms. Therefore, the stimulating activity of Pt-MoS_2 can be attributed to the hybridized Pt and S electronic states of the Pt-MoS_2.

Table S1. Formation energy (E_f) and adsorption free energy of H* (ΔG_H^o) for varied metal atoms doped MoS_2.

Metal	E_f (eV)	ΔG_H^o (eV)
Pt	-2.22	-0.00
Co	-3.17	-0.07
Ni	-2.42	-0.28
Mo	—	1.83

References

1. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and J. K. Nørskov, *J. Electrochem. Soc.*, 2005, **152**, J23-J26.