Supplementary Information for

Chemically activating MoS$_2$ via spontaneous atomic palladium interfacial doping towards efficient hydrogen evolution

Luo et al.
Supplementary Figure 1 | XPS spectra for Au-MoS$_2$, Pt-MoS$_2$, MoS$_2$ and Pd-MoS$_2$. a High-resolution XPS results (Mo 3d region) of Au-MoS$_2$, Pt-MoS$_2$, MoS$_2$ and Pd-MoS$_2$. b High-resolution XPS results (Au 3d region ) of Au-MoS$_2$. c High-resolution XPS results (Pt 3d region ) of Pt-MoS$_2$. 
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In-situ heat treatment TEM coupling with EELS. a-d TEM patterns of Pd-MoS$_2$ taken at different temperatures (RT, 200°C, 500°C, 600°C), the corresponding scale bars are 100 nm. e-h EELS patterns of Pd-MoS$_2$ taken at different temperatures (RT, 200°C, 500°C, 600°C).
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![Supplementary Figure 10](image_url)
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Supplementary Figure 12| Electrochemical activity of Pd-MoS\(_2\) catalysts.

a Polarization curves of 2\%Pd-MoS\(_2\), 5\%Pd-MoS\(_2\), 10\%Pd-MoS\(_2\) and 15\%Pd-MoS\(_2\).

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Supplementary Figure 13| EIS spectrum. a-b EIS comparison for 1%Pd-MoS$_2$ and MoS$_2$ in terms of Nyquist plots. The black solid lines are experimental results, and the red dotted lines are best-fit curves. c Equivalent circuit models used for fitting the EIS response of HER, where $R_s$ is the electrolyte resistance, $R_1$ is related to the interface resistance, $R_2$ denotes the charge-transfer resistance, and CPE represents the constant phase element.
Supplementary Figure 14 | Electrochemical stability. **a** Chronoamperometry (CP) tests of 1%Pd-MoS₂ and MoS₂ at a current density of 10 mA cm⁻² (10 h). **b** CP tests of 1%Pd-MoS₂ at a current density of 10 mA cm⁻² (100 h).
**Supplementary Figure 15| XPS spectrum.** a High-resolution XPS results (Pd 3d region) of the Pd-MoS\(_2\) before electrolysis at 10 mA cm\(^{-2}\) for 100 h. b High-resolution XPS results (Pd 3d region) of the Pd-MoS\(_2\) after electrolysis at 10 mA cm\(^{-2}\) for 100 h.
Supplementary Figure 16 | Optimized atomic configurations of Pd atoms in 2H-MoS$_2$ and 1T-MoS$_2$. a The formation energy ($E_f$) of Pd atoms on hollow sites in 2H-MoS$_2$. b The formation energy ($E_f$) of Pd atoms on Mo atop sites in 2H-MoS$_2$. c The formation energy ($E_f$) of Pd atoms replace S sites in 2H-MoS$_2$. d The formation energy ($E_f$) of Pd atoms replace Mo sites in 2H-MoS$_2$. e The formation energy ($E_f$) of Pd atoms on hollow sites in 1T-MoS$_2$. f The formation energy ($E_f$) of Pd atoms on Mo atop sites in 1T-MoS$_2$. g The formation energy ($E_f$) of Pd replace S sites in 1T-MoS$_2$. h The formation energy ($E_f$) of Pd atoms replace Mo sites in 1T-MoS$_2$. 

\( E_f = 2.35 \text{ eV} \)
\( E_f = 1.75 \text{ eV} \)
\( E_f = -0.17 \text{ eV} \)
\( E_f = -2.22 \text{ eV} \)
\( E_f = 2.07 \text{ eV} \)
\( E_f = 1.75 \text{ eV} \)
\( E_f = 1.36 \text{ eV} \)
\( E_f = -1.39 \text{ eV} \)
Supplementary Figure 17| Formation energy of S-vacancy. Formation of SVs in 2H-MoS$_2$, 2H-Pd-MoS$_2$, 1T-MoS$_2$ and 1T-Pd-MoS$_2$. 
Supplementary Figure 18| H atom absorbing at Pd sites of 2H-Pd-MoS$_2$ and 1T-Pd-MoS$_2$. 
**Supplementary Figure 19| H adsorption free energy.** Adsorption positions for single H atom absorbing at basal plane of 2H-MoS\(_2\), basal plane of 1T-MoS\(_2\), Pd site of 2H-Pd-MoS\(_2\), S-vacancy of 1T-MoS\(_2\) and S atop site of 1T-Pd-MoS\(_2\), and the adsorption free energies are given.
**Supplementary Table 1.** The element stoichiometry of MoS$_2$ and 1\%Pd-MoS$_2$.

| Crystalline           | The stoichiometry of elements |
|-----------------------|-------------------------------|
| MoS$_2$               | 1:1.87 (Mo:S)                 |
| 1\%Pd-MoS$_2$         | 1:1.82:0.02 (Mo:S:Pd)         |
**Supplementary Table 2.** The solubility product constants of the different sulfides.

| Molecular formula | $K_{sp}$  | $P_{k_{sp}}$ | $(-\lg k_{sp})$ |
|-------------------|-----------|--------------|-----------------|
| $\alpha$-NiS      | $3.2\times10^{-19}$ | 18.5         |                 |
| $\beta$-NiS       | $1.0\times10^{-24}$ | 24.0         |                 |
| $\gamma$-NiS      | $2.0\times10^{-26}$ | 25.7         |                 |
| PdS               | $2.03\times10^{-58}$ | 57.69       |                 |
| FeS               | $6.3\times10^{-18}$  | 17.2         |                 |
| $\alpha$-CoS      | $5\times10^{-22}$    | 21.3         |                 |
| $\beta$-CoS       | $3\times10^{-26}$    | 25.5         |                 |
**Supplementary Table 3.** ICP-OES results of dissolved S, Mo, Pt, Au and Pd ions in solution after this redox process.

| Dissolved ions into the solution ($\mu$g mL$^{-1}$) | Mo  | S    | Pd  | Au | Pt |
|-------------------------------------------------|-----|------|-----|----|----|
| Pd-MoS$_2$                                      | 70.02 | 41.18 | 0   | -  | -  |
| MoS$_2$                                         | 0   | 0    | -   | -  | -  |
| Pt-MoS$_2$                                      | 82.17 | 0    | -   | -  | 0  |
| Au-MoS$_2$                                      | 77.63 | 0    | -   | 0  | -  |
**Supplementary Table 4.** ICP-OES results of Pd in solution and samples in MoS$_2$ (2H) after reaction with Pd (Ⅱ)

| The amount of Pd in solution or sample (μg mL$^{-1}$ or wt %) | Pd         |
|------------------------------------------------------------|------------|
| Solution before redox reaction                             | 12.12      |
| Solution after redox reaction                              | 11.87      |
| MoS$_2$ (2H) after reaction with Pd (Ⅱ)                    | Under detect limit |
**Supplementary Table 5.** Pd L-edge EXAFS curves fitting parameters.

| Sample   | Shell | $N$   | $R$(Å) | $\sigma^2$(10$^{-3}$ Å$^2$) | $\Delta E_0$(eV) | R-factor |
|----------|-------|-------|--------|----------------------------|------------------|----------|
| Pd-MoS$_2$ | Pd-S  | 4.3±0.3 | 2.33±0.01 | 3.9±0.7 | 1.3±0.8 | 0.006 |

$N$, coordination number; $R$, distance between absorber and backscatter atoms; $\sigma^2$, Debye-Waller factor; $\Delta E_0$, inner potential correction accounting for the difference in the inner potential between the sample and the reference compound.
Supplementary Table 6. The fitting results about PALS.

| Sample      | $\tau_1$(ns) | $I_1$(%) | $\tau_2$(ns) | $I_2$(%) | $\tau_3$(ns) | $I_3$(%) |
|-------------|--------------|----------|--------------|----------|--------------|----------|
| MoS$_2$     | 0.1836       | 49.1     | 0.356        | 49.2     | 2.359        | 1.683    |
| 1%Pd-MoS$_2$| 0.2062       | 57.5     | 0.385        | 40.8     | 2.309        | 1.736    |
**Supplementary Table 7.** Summary of peak area ratio, and degree of defects for 1%Pd-MoS$_2$ and MoS$_2$.

| Sample       | Peak area ratio (S:Mo) | Element (At %) | Degree of defects (%) |
|--------------|------------------------|----------------|-----------------------|
| MoS$_2$      | 1.361                  | Mo: 17.98      | S: 82.02              | 0                      |
| 1%Pd-MoS$_2$ | 1.128                  | Mo: 20.2       | S: 76.33              | Pd: 3.47               | 16.7%                 |
**Supplementary Table 8.** Comparison of HER activity for 1%Pd-MoS$_2$ with other MoS$_2$-based electrocatalysts in acidic media.

| Catalyst                  | Electrolytes          | $\eta$ (mV vs RHE) for $j = -10$ mA cm$^{-2}$ | Current density ($\mu$A cm$^{-2}$) | References                  |
|---------------------------|-----------------------|-----------------------------------------------|------------------------------------|-----------------------------|
| 1% Pd-MoS$_2$             | 0.5 M H$_2$SO$_4$     | 89                                            | 805                                | This work                   |
| 1%Pd-MoS$_2$/CP           | 0.5 M H$_2$SO$_4$     | 78                                            | -                                  |                             |
| CoMoS$_3$-PHS MS          | 0.5 M H$_2$SO$_4$     | 171                                           | 11                                 | Adv.Mater. 28, 92-97 (2016) |
| MoS$_2$ flakes            | 0.5 M H$_2$SO$_4$     | $\sim$250                                     | 3.5                                | J.Am.Chem.Soc. 138, 16632 (2016) |
| MoS$_2$ films             | 0.5 M H$_2$SO$_4$     | $\sim$175                                     | 40                                 |                             |
| P-1T-MoS$_2$              | 0.5 M H$_2$SO$_4$     | 153                                           | 15.8                               | J.Am.Chem.Soc. 138, 7965 (2016) |
| P-2H-MoS$_2$              | 0.5 M H$_2$SO$_4$     | 218                                           | 10.5                               |                             |
| P-2H-MoS$_2$+S IT-MoS$_2$ | 0.5 M H$_2$SO$_4$     | 257                                           | 7.9                                |                             |
| 2H-MoS$_2$                | 0.5 M H$_2$SO$_4$     | 203                                           | 12.6                               |                             |
|                           |                       | 343                                           | 3.2                                |                             |
| V-MoS$_2$(EC)             | 0.5 M H$_2$SO$_4$     | 320                                           | -                                  | Nat.Commun. 8, 15113 (2017)  |
| MoS$_2$-BP                | 0.5 M H$_2$SO$_4$     | 85                                            | -                                  | Nano lett. 17, 4311 (2017)  |
| MoSSe                     | 0.5 M H$_2$SO$_4$     | 300                                           | -                                  | Nano Energy 12, 72211-2855 (2016) |
| Pt-MoS$_2$                | 0.1 M H$_2$SO$_4$     | $\sim$140                                     | -                                  | Energy. Environ. Sci. 8, 1594-1601 (2015) |
| SV-MoS$_2$                | 0.5 M H$_2$SO$_4$     | 170                                           | -                                  | Nat. Mater. 15, 364 (2016)  |
| V-MoS$_2$                 | 0.5 M H$_2$SO$_4$     | 250                                           | -                                  |                             |
| Edge ox 1T MoS$_2$        | 0.5 M H$_2$SO$_4$     | $\sim$200                                     | -                                  | Nano lett. 13, 6222-7 (2013) |
| SL-MoS$_2$-CN TS          | 0.5 M H$_2$SO$_4$     | $\sim$220                                     | -                                  | RSC Advance 4, 34733 (2014)  |
| M-MoS$_2$                 | 0.5 M H$_2$SO$_4$     | 175                                           | -                                  | Nat Commun. 7, 10672 (2016) |
| MoS$_2$/CoSe$_2$          | 0.5 M H$_2$SO$_4$     | 68                                            | 73                                 | Nat Commun. 6, 5982 (2015)  |
**Supplementary Table 9.** The EIS fitting results of 1%Pd-MoS$_2$ and MoS$_2$.

| Sample       | $R_S$ (Ω cm$^2$) | $R_1$ (Ω cm$^2$) | $R_2$ (Ω cm$^2$) |
|--------------|------------------|------------------|------------------|
| MoS$_2$      | 0.51             | 18.38            | 92.89            |
| 1%Pd-MoS$_2$ | 0.18             | 1.14             | 7.5              |
**Supplementary Table 10.** The intrinsic activity of each site in 1%Pd-MoS$_2$.

| Voltage (V) | Total Current density (mA cm$^2$) | The Current density contributed by Pd doping (mA cm$^2$) | $\text{TOF (s}^{-1}\text{)}$ |
|------------|-----------------------------------|--------------------------------------------------------|-----------------|
| 0          | 0.805                             | 0.774                                                  | 0.15            |
| 0.1        | 14.756                            | 14.756                                                 | 2.77            |
| 0.15       | 41.882                            | 41.882                                                 | 7.84            |
| 0.16       | 48.622                            | 48.622                                                 | 9.10            |
| 0.2        | 89.556                            | 88.328                                                 | 16.54           |
| 0.24       | 114.33                            | 112.96                                                 | 21.15           |
**Supplementary Table 11.** The TOF of other MoS$_2$-based catalysts reported in the literature.

| Catalyst                  | TOF ($s^{-1}$) at exchange current density | Overpotential (V) | Corresponding TOF ($s^{-1}$) | Reference               |
|---------------------------|-------------------------------------------|-------------------|-------------------------------|-------------------------|
| MoS$_2$                   | 0.013                                     | -                 | -                             | *Nano lett.* 13, 1341 (2013) |
| UHV-deposited MoS$_2$     | -                                         | 0.1               | 1                             | *Science* 317, 100 (2007) |
| MoS$_2$ nanoparticles on Au(III) | -                                         | 0.16              | 10                            |                         |
| MoS$_2$ nanoparticles     | 0.02                                      | -                 | -                             |                         |
| Sub-monolayer             | [Mo$_3$S$_{13}$]$^{2-}$ HOPG              | -                 | -                             | *Nat.Chem.* 6, 248-253 (2014) |
| [Mo$_3$S$_4$]$^{4+}$ cubanes/HOPG | 0.07                                      | 0.3               | 1~5                           | *J.Phys.Chem.C.* 112, 17492 (2018) |
| Amorphous MoS$_3$-CV film |                                           | 0.22/0.24         | 0.8/2                         | *Chem.Sci.* 2, 1262 (2011) |
| MoS$_2$                   | -                                         | 0.3               | 3.83                          | *J.Am.Chem.Soc.* 139, 15479 (2017) |
| Zn-MoS$_2$                | -                                         | 0.3               | 15.44                         |                         |
| Irradiated Au-MoS$_2$     | -                                         | 0.3               | 8.76                          | *J.Am.Chem.Soc.* 137, 7365 (2015) |
| Double-gyroid MoS$_2$     | -                                         | 0.2               | 1                             | *Nat.Mater.* 11, 963 (2012) |
| MoO$_3$-MoS$_2$ nanowires | 0.272 | 4 | Nano lett. **11**, 4168 (2011) |
|---------------------------|-------|---|--------------------------------|
| Irradiated Au-MoS$_2$     | -     | 0.3 | 8.76 | J. Am. Chem. Soc. **137**, 7365 (2015) |
| Amorphous MoS$_3$         | -     | 0.2 | 0.3 | ACS Catal. **2**, 1916 (2012) |
| Defect-Rich MoS$_2$ sheets| -     | 0.3 | 0.725 | Adv.Mater. **25**, 5807 (2013) |
| V-MoS$_2$/Au              | 0.05–0.16 | - | - | Nat.Mater. **15**, 364 (2014) |
Supplementary Table 12. Comparison of HER activity for 1%Pd-MoS$_2$ with the 1T-MoS$_2$, the 2H-MoS$_2$ with S-vacancies and 1T-MoS$_2$ with S-vacancies in acidic media.

| Catalyst | Electrolytes | η (mV vs RHE) for $j = -10$ mA cm$^{-2}$ | Current density (μA cm$^{-2}$) | References |
|----------|--------------|----------------------------------------|-------------------------------|------------|
| 1% Pd-MoS$_2$ | 0.5 M H$_2$SO$_4$ | 89 | 805 | This work |
| 1%Pd-MoS$_2$/CP | | 78 | | |
| P-1T-MoS$_2$ | 0.5 M H$_2$SO$_4$ | 153 | 15.8 | J. Am. Chem. Soc. 138, 7965-72 (2016) |
| P-2H-MoS$_2$ | | 218 | 10.5 | |
| 1T-MoS$_2$ | | 203 | 12.6 | |
| 2H-MoS$_2$ with S-vacancies | 0.5 M H$_2$SO$_4$ | 320 | - | Nat. Commun. 8, 15113 (2017) |
| 1T-MoS$_2$ with edges | 0.5 M H$_2$SO$_4$ | ~200 | - | Nano lett. 13, 6222-7 (2013) |
| 1T-MoS$_2$ | 0.5 M H$_2$SO$_4$ | 175 | - | Nat Commun. 7, 10672 (2016) |
| 1T-MoS$_2$ with SVs | 0.5 M H$_2$SO$_4$ | 200 | - | Sci. Rep. 6, 31092 (2016) |
| 2H-MoS$_2$ with SVs | 0.5 M H$_2$SO$_4$ | 170 | 40 | J. Am. Chem. Soc. 138, 16632 (2016) |
| 1T-MoS$_2$ | 0.5 M H$_2$SO$_4$ | ~210 | - | J. Am. Chem. Soc. 135, 10274 (2016) |

P-1T-MoS$_2$ refers to 1T-MoS$_2$ with abundant S-vacancies and edges (the degree of defects exceeds 83.7%); P-2H-MoS$_2$ refers to 2H-MoS$_2$ with abundant S-vacancies and edges.
Supplementary Note 1: To judge the spontaneity of the chemical reaction

(1)

\[ \text{Mo}^{4+} + e^- \rightarrow \text{Mo}^{3+} \quad \phi^{0} \text{Mo}^{4+} / \text{Mo}^{3+} = -0.04 \text{ V} \]

\[ \text{Pd}^{2+} + 2e^- \rightarrow \text{Pd} \quad \phi^{0} \text{Pd}^{2+} / \text{Pd} = 0.951 \text{ V} \]

\[ 2\text{Mo}^{3+} + \text{Pd}^{2+} \rightarrow 2\text{Mo}^{4+} + \text{Pd} \]

\[ E^0 = \phi^{0} \text{Pd}^{2+} / \text{Pd} - 2\phi^{0} \text{Mo}^{4+} / \text{Mo}^{3+} = 0.951 \text{ V} - 2 \times (-0.04 \text{ V}) = 1.031 \text{ V} \]

\[ \Delta G^0 = -nE^0F = -2 \times 1.031 \times 96500 \text{ J} = -198.983 \text{ kJ} < 0 \]

(2)

\[ \text{Pd}^{2+} + 2e^- \rightarrow \text{Pd} \quad \phi^{0} \text{Pd}^{2+} / \text{Pd} = 0.951 \text{ V} \]

\[ \text{PdS} \rightarrow \text{Pd}^{2+} + \text{S}^{2-} \quad \text{ksp} = 2.03 \times 10^{-58} \]

\[ \text{Pd} + \text{S}^{2-} \rightarrow \text{Pd}^{2+} + 2e^- \quad \phi^{0} \text{PdS/Pd} \]

\[ \phi^{0} \text{PdS / Pd} = \phi^{0} \text{Pd}^{2+} / \text{Pd} - \frac{RT}{nF} \ln \left( \frac{1}{[\text{Pd}^{2+}]} \right) = 0.951 - \frac{8.314 \times 298}{2 \times 96500} \times \ln \left( \frac{1}{2.03 \times 10^{-58}} \right) = -0.754 \text{ V} \]

(3)

\[ \text{PdS} + 2e^- \rightarrow \text{Pd} + \text{S}^{2-} \quad \phi^{0} \text{PdS / Pd} = -0.754 \text{ V} \]

\[ 2\text{Mo}^{4+} + 2e^- \rightarrow 2\text{Mo}^{3+} \quad \phi^{0} \text{Mo}^{4+} / \text{Mo}^{3+} = -0.04 \text{ V} \]

\[ \text{Mo}^{4+} + \text{Pd} + \text{S}^{2-} \rightarrow \text{Mo}^{3+} + \text{PdS} \]

\[ E^0 = -0.04 \text{ V} - (-0.754 \text{ V}) = 0.75 \text{ V} \]

\[ \Delta G^0 = -nE^0F = -2 \times 0.75 \times 96500 \text{ J} = -144.75 \text{ kJ} < 0 \]
Supplementary Note 2: Verifying the reaction mechanism

We mixed the pristine MoS$_2$ sample (HM-MoS$_2$) with Pd (II), Pt (IV), and Au (III) complex solutions for reaction, respectively, and the oxidizability of Pt (IV) and Au (III) were intentionally tuned to be weaker than Pd (II) through complexation. On one hand, all of the Mo (III) was oxidized into Mo (IV), accompanied with the complete reduction of Pt (IV) and Au (III) into Pt (0) and Au (0) metallic states in the resultant Pt-MoS$_2$ and Au-MoS$_2$ hybrids. (Supplementary Fig. 1). Moreover, the leaching of Mo ions into the solution after redox reaction was measured through ICP-OES test (Supplementary Table 3), which well corresponding to what suggested from Equation (4Mo$^{3+} \rightarrow 3$Mo$^{4+}$+3e($left$) +V_{Mo}^{\text{///}}$ (one Mo left)). Furthermore, the oxidation of all Mo (III) into Mo (IV) and the leaching of Mo ions (due to principle of conservation of charge) together unambiguously demonstrate that Mo in valence (III) can act as the reducing agent towards the reduction of Pt, Au, and Pd, etc. On the other hand, Pd is expectedly accommodated into MoS$_2$ sample as Pd (II), as confirmed by binding energies peaks at only 336.7 eV (3d$_{5/2}$) and 342 eV (3d$_{3/2}$) observed, using high-resolution X-ray photoelectron spectroscopy (Fig. 1b). The final Mo exhibits mixed valence states of III/IV, corresponding to the Mo (III) oxidation followed by Mo (IV) reduction, accompanied with the incorporation of Pd. The leaching of Mo ions and S ions into the solution was also detected by ICP-OES(Supplementary Table 3), further corresponding to redox reaction (2Mo$^{4+}$ +S$^{2-}$ +2e $\rightarrow$ 2Mo$^{3+}$ +V$_S^{\text{///}}$ (one S left)). These results indicate the successful doping of Pd into MoS$_2$ backbone through spontaneous atomic Pd interfacial redox doping mechanism.
To further confirm our conclusion, we used the standard 2H MoS$_2$ sample (Mo: S=1:2, without Mo (III) species) instead of the chemically synthesized MoS$_2$ (homemade pristine MoS$_2$ with stoichiometry at 1:1.87) to react with Pd (II). As shown in Fig. 1a and Supplementary Fig. 2, the Mo L$_3$-edge XANES spectra and high-resolution XPS results (Mo 3d region) of 2H MoS$_2$ sample confirmed that all Mo atoms are present as Mo (IV). The reaction between standard 2H MoS$_2$ and Pd (OAc)$_2$ was controlled at the same condition as those illustrated in the Methods. The concentrations of Pd in the solution before and after the reaction were monitored through ICP-OES, as shown in Supplementary Table 4. Clearly, no obvious change in Pd concentration is observed. Meanwhile, the final 2H-MoS$_2$ sample after reaction with Pd was also tested through ICP-OES, where no Pd (under the detection limit) was obtained in the final sample. All these results confirm that standard 2H-MoS$_2$ is not capable of reducing Pd (II), further validating that Pd atoms are introduced through the redox mechanism.

**Supplementary Note 3: Aberration-corrected HAADF-STEM images of 1%Pd-MoS$_2$**

Due to the fact that MoS$_2$ was chemically synthesized through a hydrothermal technique, the final sample shows a flower-like two-dimensional nanosheets structure with both monolayer and multilayer flakes being observed through high-resolution TEM (HRTEM) and atomic force microscopy (AFM). The multi-dispersion nature of our catalyst makes it showing different contrast in HAADF-STEM image. The brighter regions can be ascribed to the presence of multilayer MoS$_2$. The uniformly
darker regions can be found when the electron beam exposure time was over 60 s. In order to minimize such knock-on damage, the electron beam exposure time was limited to 20 s for each region of the specimen investigated. Furthermore, we have to mention that the Pd redox doping can induce more Mo vacancies and S vacancies, which results in regions where a perfect crystalline atomic lattice is not visible. (Supplementary Fig. 9 and Supplementary Fig. 11)

**Supplementary Note 4: Pd doped configurations**

Four possible doped sites of 2H-MoS$_2$ and 1T-MoS$_2$ were taken into account, as shown in Supplementary Fig. 16. In the case of 2H-MoS$_2$, a is Pd atoms above hollow sites, b is Pd atoms above Mo atom, c is Pd atom replacing S atom, and d is Pd atom replacing Mo atom. In case of 1T-MoS$_2$, e, f are Pd atom above Mo atom, g is Pd atom replacing S atom, and h is Pd atom replacing Mo atom. The formation energy ($E_f$) for these different structures were also calculated to evaluate their structural stability by $E_f = E_{tot} - E_{0[MoS2]} - E_{Pd}$, where $E_{tot}$ is the total energy for MoS$_2$ with doped or supported metal atoms. In the cases of metal doped MoS$_2$, $E_{0[MoS2]}$ is the energy for MoS$_2$ with one Mo or S vacancy, while for the cases of metal supported on MoS$_2$, $E_{0[MoS2]}$ is the energy for perfect MoS$_2$. $E_{Pd}$ is the energy of one metal atom referred to its bulk metal. According to our calculations, when Pd atoms replace Mo atoms, the formation energy is the lowest.
Supplementary Note 5: Phase transition

Supplementary Fig. 17 shows that increasing of Pd-doping concentrations and S-vacancy concentrations both can promote phase transition of MoS$_2$. When the concentration of SVs is 1.67% and the concentrations of Pd atoms exceed 24%, 1T-MoS$_2$ becomes more stable than 2H-MoS$_2$. Moreover, when the concentration of SVs increase to 16.7% (close to the SV concentrations of experimental sample), the critical Pd-doping concentration of phase transition to reduce to 3%. According to previous reports, when the concentrations of SVs are around 15%, the catalytic activity of SVs is the highest$^2$. However, the high concentrations of SVs will greatly reduce the electrical conductivity of MoS$_2$, and affect catalytic performance. Nevertheless, the increase content of of 1T metal phase causing by a small amount of Pd-doping well compensates the conductivity reduction of MoS$_2$, and makes the active sites get electrons more easily. In addition, it is well known that the in-plane surface of 1T-MoS$_2$ is catalytically active for the HER$^3$. In literature, the traditional way to induce phase transitions is lithium insertion$^4$, and where the active sites of surface are covered by lithium and thereby results in activity loss. However, in our system, the surface of 1T-MoS$_2$ is fully exposed, with active sites of surface been fully utilized.

Supplementary Note 6: TOF calculation

The TOF was calculated according the formula:

$$\text{TOF} = \frac{\text{Total number } H_2 \text{ atoms per second}}{\text{Total number of active sites per unit area}} = \frac{j}{(2 \times q) N}$$
Where \( q = 1.6 \times 10^{-19} \text{ C} \) is the elementary charge, and 2 accounts for 2 H atoms per \( \text{H}_2 \) molecule.

The DFT calculations suggest that the S atoms near the Pd dopants in the MoS\(_2\) are the prior adsorption sites, but the sulfur vacancies also may be as catalytically active sites. In the following we use the number of the sulfur vacancies and the S atoms near the Pd dopants in the MoS\(_2\) as the number of active sites, which can be estimated from the number of Pd.

The number of the sulfur vacancies is estimated using defect reaction.

\[
N_{S\text{--vacancy}} = N_{Pd}
\]

The 1\%Pd-MoS\(_2\) loading (on a glassy carbon electrode) was 222 \( \mu \text{g} \text{ cm}^{-2} \). The MoS\(_2\) is highly dispersed as few-layer thick sheets. We assume in the following calculation that all Pd atoms are surface exposed.

From ICP the atomic percentages of Pd were determined to be 1\%. Using the deposited mass, molar masses and above atomic percentages, the number of Pd atoms, the total S vacancies, and the TOFs were calculated to be:

\[
N_{Pd} = \frac{222 \mu \text{g/cm}^2}{160.072 \text{g/mol}} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times 1\% = 8.35 \times 10^{15} \text{ cm}^{-1}
\]

\[
N_{S\text{--vacancy}+Pd--S} = 1.67 \times 10^{16} \text{ cm}^{-1}
\]

TOF at 0 V: TOF= 0.15 s\(^{-1}\) \((j=0.774 \text{ mA cm}^{-2})\)

TOF at 0.1 V: TOF= 2.77 s\(^{-1}\) \((j=14.756 \text{ mA cm}^{-2})\)

TOF at 0.15 V: TOF= 7.84 s\(^{-1}\) \((j=41.882 \text{ mA cm}^{-2})\)

TOF at 0.16 V: TOF= 9.10 s\(^{-1}\) \((j=48.622 \text{ mA cm}^{-2})\)
TOF at 0.2 V: TOF = 16.54 s$^{-1}$ ($j$=88.328 mA cm$^{-2}$)

TOF at 0.24 V: TOF = 21.15 s$^{-1}$ ($j$=112.961 mA cm$^{-2}$)

**Supplementary Note 7: Generation of intrinsically more active S atop active sites (Pd-S* sites)**

The average TOFs of 1%Pd-MoS$_2$ are 0.15 s$^{-1}$, 2.77 s$^{-1}$, 7.84 s$^{-1}$, 9.10 s$^{-1}$, 16.54 s$^{-1}$ and 21.15 s$^{-1}$ at 0 V, 0.1 V, 0.15 V, 0.16 V, 0.2 V and 0.24 V, respectively. (Supplementary Table 10). As far as we known, the highest TOF$_{S\text{-}vaca}$ ever reported for MoS$_2$ was 0.05–0.16 s$^{-1}$ at 0 V, where a well-defined monolayer MoS$_2$ was supported on Au substrate, thus making all the SVs in the catalysts available at the reaction interface.\(^2\) For all other catalysts represented multicrystalline or amorphous structures, much inferior catalytic behaviors were observed. For our 1%Pd-MoS$_2$ catalyst, it not only shows the highest TOF among all the multicrystalline or amorphous structured catalysts, but also represents TOF of 0.15 s$^{-1}$ at 0 V, on the high end of the values reported in literature. (see Supplementary Table 11 for details)

Taking into the account of the multicrystalline nature of our testing electrode, we can confirm that the much higher average TOF was obtained. Thus, the high average TOF of the 1%Pd-MoS$_2$ reflect that the increased catalytic activity is originated from both increase in active site density and the intrinsic activity of each site.

In addition, we also adopted another strategy by comparing the activity of our catalysts with the highest value reported for the 1T-MoS$_2$, the 2H-MoS$_2$ with S-vacancies and 1T-MoS$_2$ with S-vacancies. (1) The lowest overpotential reported for
1T-MoS$_2$ at 10 mA cm$^{-2}$ is $\sim$200 mV; (2) As far as we known, the best activity of 2H-MoS$_2$ with S-vacancies is reported by Linyou Cao, et al$^5$, where the catalysts with optimal S-vacancies exhibits overpotential of 170 mV at 10 mA cm$^{-2}$. The catalyst shows a maximum catalytic activity with SV densities vary between 7$\%$–15$\%$, and further increasing the SV concentration leads to performance decay.$^6$ (3) Even in the case of 1T-MoS$_2$ with abundant S-vacancies and edges (the degree of defects exceeds 83.7$\%$), the lowest overpotential ever reported is 153 mV$^5$. In our work, the 1$\%$Pd-MoS$_2$/CP exhibit very low overpotential at 10 mA cm$^{-2}$ of only 78 mV, which is 75 mV smaller than the most active MoS$_2$ catalysts reported shown above. With the Tafel slope measured at 80 mV dec$^{-1}$, the decrease in overpotential corresponds to approximately 10 times increase in actives site density, provided that the sites only exhibits the same intrinsic activity with that of the S-vacancies and edges in 1T-MoS$_2$. This is impossible as the degree of the defects in the reported sample is already very high (83.7$\%$) and the catalyst loading used for tests were similar between our tests (0.15 mg cm$^{-2}$ vs 0.22 mg cm$^{-2}$). (see Supplementary Table 1 for details) Therefore, it is actually the huge improvement in catalytic activity that leads us to look for the active sites with high intrinsic activity, where DFT calculations were adopted and the Pd adjacent S atoms were confirmed as supreme active sites towards HER. Furthermore, the effect of Pd doping can also be clearly evidenced by comparing the catalytic activity before and after Pd doping. It is noted that electron paramagnetic resonance (EPR) can be used to measure unpaired electrons on coordinatively unsaturated defective sites and reflect basal sulfur vacancies present in these layers.$^7$.
We have also compared the EPR signals before and after Pd doping. As shown in Fig. 2f, the 1%Pd-MoS$_2$ exhibits approximately 3 times as many unsaturated sites than the pristine MoS$_2$. However, the overpotential (20 mA cm$^{-2}$) was reduced by 266 mV, corresponding to an increase in active site density by 2113 times (calculated from the Tafel slope), if the increase in site density is the only reason for the catalytic performance enhancement. This huge difference unambiguously points to the generation of more active HER sites after Pd doping.

**Supplementary Methods**

**Electrical resistances measurements.** The electrical resistances of samples were determined by using a homemade button cell. The powder samples were pressed in the mold with certain pressure and time (~10 MPa, 5 min). The sample is inserted between two smooth polished steel discs. Electrochemical impedance spectroscopy (EIS) performed at high frequency using Princeton Applied Research PARATAT MC. The operating frequency range was between 10 mHz and 10 kHz, the DC potential was 0 V compared to an open circuit, and the AC amplitude was 10 mV. In this case, the phase angle between the voltage applied and the current induced is zero; the impedance of the sample as a function of frequency is present as a horizontal line. The value of resistance of sample is equal to the impedance; and the resistance can be directly read from the $|Z|$ -axis in the Bode. The electronic conductivity was calculated according the formula:

$$\sigma = \frac{I}{RS}$$
Here, the $l$ is the thickness of specimen, $R$ is electrical resistance of specimen, $S$ is the area of specimen. $l$ and $S$ can get from the mould. $R$ is obtained from Bode spectra (Bode spectra are read from the electrochemical impedance spectroscopy).

**Computational details.** The formation energy ($E_f$) for different S-vacancies were calculated to evaluate their structural stability, according to the formula $E_f = E_{SV} + E_S - E_{MoS_2}$, where $E_{SV}$ is the total energy for MoS$_2$ with S-vacancy, $E_s$ is the energy for single S atom and $E_{MoS_2}$ is the total energy for MoS$_2$ without vacancy, respectively.

The Gibbs free energy of H adsorption is calculated by $\Delta G_H = \Delta E_H + T\Delta S + \Delta E_{ZPE}$. $\Delta E_H$ is the adsorption energy of the H atom. $T\Delta S$ is the gas-phase entropy contribution of a hydrogen molecule at 298 K (It is a constant, 0.40 eV). $\Delta E_{ZPE}$ is the zero-point energy difference between the adsorbed state of the system and the gas phase state.

“Additionally, the potential dependence of hydrogen adsorption is including using the computational hydrogen electrode model$^8$, where $\Delta G_H^+(aq) + \Delta G_e^- = 1/2\Delta G_{H(aq)}$ at a potential of $U=0$ V versus RHE.

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