Site-specific electrodeposition enables self-terminating growth of atomically dispersed metal catalysts

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The growth of atomically dispersed metal catalysts (ADMCs) remains a great challenge owing to the thermodynamically driven atom aggregation. Here we report a surface-limited electrodeposition technique that uses site-specific substrates for the rapid and room-temperature synthesis of ADMCs. We obtained ADMCs by the underpotential deposition of a non-noble single-atom metal onto the chalcogen atoms of transition metal dichalcogenides and subsequent galvanic displacement with a more-noble single-atom metal. The site-specific electrodeposition enables the formation of energetically favorable metal-support bonds, and then automatically terminates the sequential formation of metallic bonding. The self-terminating effect restricts the metal deposition to the atomic scale. The modulated ADMCs exhibit remarkable activity and stability in the hydrogen evolution reaction compared to state-of-the-art single-atom electrocatalysts. We demonstrate that this methodology could be extended to the synthesis of a variety of ADMCs (Pt, Pd, Rh, Cu, Pb, Bi, and Sn), showing its general scope for functional ADMCs manufacturing in heterogeneous catalysis.
Atomically dispersed metal catalysts (ADMCs), with maximum atom efficiency and unique metal coordination environments, are considered as an important frontier in heterogeneous catalysis research. However, single-metal atoms tend to form aggregates driven by the decrease of surface free energy. In recent years, many methods based on physical and chemical approaches have emerged for the synthesis of ADMCs. Most of these methods either depend on expensive equipment and sophisticated techniques, or suffer from the harsh conditions used (high temperatures/pressures), low metal loading, and time-consuming procedures. A universal strategy for fast, mild, scalable and controllable ADMCs synthesis remains in high demand.

We considered whether we could synthesize ADMCs by simply using the room-temperature electrodeposition (ED) method. Owing to its facile operation, mildness, large scalability, low cost, and precision, ED has been extensively used for the fabrication of nanomaterials and industrial applications (e.g., electroplating). However, this process leads to the inevitable formation of multilayer bulk structures with nonuniform coverage. To circumvent this difficulty, surface-limited techniques—typically underpotential deposition (UPD), a process by which monolayers form at potentials above the thermodynamic value—have been used to afford single-layer coverage. Examples of the successful use of this method include the syntheses of a two-dimensional (2D) Pt layer on a Au electrode by the quenching effect of underpotential-deposited hydrogen by the Moffat group.

We reasoned that the single-atom layer could potentially be upgraded to single atoms deposited site-specifically on a supporting substrate for UPD (Fig. 1(iii) and Supplementary Fig. 1c). If the substrate consists of isolated active sites owing to the nonuniform work function (Supplementary Note 1), Transition metal dichalcogenides (TMDs) possessing isolated and nonuniformly distributed chalcogen sites (e.g., S, Se, and Te)—elements that have Lewis base character with lone pair electrons and suitable electronegativity—can potentially interact with, and hence stabilize single-metal atoms. Owing to the strong coordination and electronic interaction between the depositing metal and the chalcogen sites on the substrate, the metal–support interaction is energetically favorable compared to the metal–metal interaction in the crystal lattice of the bare metal during the UPD process. After the formation of a metal–support bond, the sequential deposition of metal–metal bonds is forbidden at the UPD potential (Fig. 1(iii)). Growth from a single atom would be self-terminated and would be automatically and strictly controlled. Site-specific UPD provides the activation energy and fast kinetics for the formation of thermodynamically favored metal–support bonds and atomic dispersion. The self-termination enables the synthesis of single atoms preferentially constrained at these specific sites under the UPD process on a

**Fig. 1 Methodological development of ADMC preparation by electrodeposition.** The blue wedge structure represents the downsizing of electrodeposition on nanomaterials from a multilayer (i) to a single layer (ii) and further to single atoms (iii). Representative examples of each electrochemical method are shown: (i) Electrically conductive substrates with high surface areas (e.g., graphene or carbon nanotubes) are often used to electrodeposited metal nanoparticles or metallic thin films. However, this process typically leads to the formation of a multilayered bulk phase (represented by the blue or pink ball constructed nanostructures in the figure). (ii) Conventional underpotential deposition (UPD), typically of a metal cation (e.g., Cu²⁺, Ag⁺, Bi³⁺, or Pb²⁺) deposited onto uniform metal support (e.g., Au, Pd, or Pt) at a potential more positive than its equilibrium potential (the potential at which it deposits onto itself), has been widely investigated for the growth of a 2D single layer. (iii) Inspired by these findings, we proposed that the synthesis of ADMCs might be realized through site-specific electrodeposition on transition metal dichalcogenides (e.g., MoS₂) with isolated active sites for UPD. The site-specific UPD enables the energetically favorable deposition of single-atom metal on the chalcogen sites, and then automatically terminates the sequential aggregation of metal atoms.
timescale of minutes. This site-specific ED (SED) method represents a major breakthrough with respect to other extremely time-consuming and procedurally demanding strategies.

**Results**

**Synthesis and structural characterization of ADMCs.** We approached the fabrication of ADMCs by first exploring the UPD of Cu atoms on chemically exfoliated molybdenum disulfide (ce-MoS2), which was used as a prototypical TMD substrate to demonstrate the feasibility of a site-specific UPD strategy for fabricating ADMCs. Chemical exfoliation by lithium intercalation (Supplementary Fig. 2) gives rise to a deformed crystal phase with disparate electronic properties in the ultrathin nanosheets of MoS2 (Supplementary Fig. 3)16–18. We chose to utilize the metallic ce-MoS2 material for its high conductivity, which potentially realized the charge transfer at the interface between MoS2 support and electrode during ED process. The decreased deposition potential between two notable cathodic peaks (Supplementary Fig. 4) demonstrates the capability of ce-MoS2 to deposit Cu at potentials more positive than the equilibrium potential of ECu2+/Cu2+ (Supplementary Table 1). During the UPD of Cu atoms on ce-MoS2, the cathodic current signal decreases rapidly and reaches a saturated plateau, where the growth of Cu atoms on the surface terminates automatically (Supplementary Fig. 4f, product termed Cu-SAs/MoS2). No obvious nanoparticles or clusters were discernable in Cu-SAs/MoS2, whereas elemental Cu was detected by X-ray photoelectron spectroscopy (XPS; Supplementary Fig. 4g–i), indicating the successful growth of a single atom on MoS2 by using UPD (Supplementary Note 2)19.

To deposit single-atom Pt on ce-MoS2, PtCl2− ions were introduced into the Cu-SAs/MoS2 system for the galvanic exchange of Cu atoms by Pt(II) (Supplementary Fig. 5). The open-circuit potential was measured to monitor the potential response during the replacement step (Cu2+/Cu2+ − Pt2+ → Cu2+/Cu2+ + Pt, Supplementary Fig. 5). Under these conditions, Pt was atomically dispersed on the ce-MoS2 nanosheets (Pt-SAs/MoS2). After functionalization, the coordination structures of Pt species in Pt-SAs/MoS2 were further confirmed by X-ray absorption spectroscopy, along with the Pt foil and PtO2 as a comparison. The Pt L3-edge X-ray absorption near-edge structure (XANES) analysis showed that the white line intensity for Pt-SAs/MoS2 was obviously higher than that for the Pt foil (Fig. 2h), indicating that the Pt species in Pt-SAs/MoS2 were partially oxidized. The positive oxidation state (1.7, inset of Fig. 2h) could be ascribed to the formation of Pt—S bond, resulting in the electron transfer from Pt to S. The extended X-ray absorption fine structure (EXAFS) spectra showed that no appreciable Pt—Pt bond (2.76 Å) was detected in Pt-SAs/MoS2 (Fig. 2l), confirming that no Pt nanoparticles or clusters existed. A dominant peak in Pt-SAs/MoS2 was observed at 2.26 Å, which corresponds to the Pt—S bond with a coordination number of 3.2 (Supplementary Fig. 6, and Supplementary Table 5)22. The theoretical Pt—S distance (2.218, 2.218, and 2.467 Å) derived from the optimized Pt—Mo atop model fits well with our EXAFS data (mean bond length 2.26 Å). No first shell of Pt—Mo interaction excludes the possibility of covalent attachment of Pt atoms on S vacancies or Mo edge sites, in agreement with the magnified HAADF-STEM image (Fig. 2c). The strong bonding interaction between Pt atoms and neighboring S atoms in the support not only protects the single atoms from aggregation but also helps to regulate the electronic structure of single-atom metals.

**Generality of the SSED technique.** To demonstrate the versatility of the SSED method, we used various supporting TMD substrates, as well as precursor metals of interest, to construct a library of single-atom catalysts (Fig. 3a). We observed that Cu adatoms can be underpotentially deposited on different TMD substrates (ce-WS2, ce-MoSe2, ce-WSe2, and ce-MoTe2; Fig. 3b). The HAADF-STEM images of Pt-SAs/WS2, Pt-SAs/MoSe2, and Pt-SAs/WSe2 confirm the predominance of single Pt atoms on the supports (Fig. 3c and Supplementary Fig. 7). We also extended the SSED method to the fabrication of other single-atom metals (Pd, Rh, Pb, Sn, and Bi; Fig. 3b and Supplementary Figs. 8–10), implying the broad applicability of this methodology and great potential for various heterogenous catalytic applications.

Bridging the gap between laboratory studies and industrial applications of materials remains challenging. To fulfill the requirements for large-scale industrial settings, we attempted to design a model experimental apparatus for producing Pt-SAs/MoS2 in excellent yield (Supplementary Fig. 11). In addition, the loading of the single-atom metal can be precisely adjusted by controlling the time of Cu UPD or the number of active sites in the support (Supplementary Fig. 12); the precise and controlled loading of the single-atom metal can be achieved within minutes.

**Mechanism of single-atom immobilization.** To better understand the process of site-specific UPD on the TMD materials, we tried to correlate the underpotential shift (ΔU) with physical parameters pertinent to the system, which might semiquantitatively explain the energy gain for the energetically favored UPD compared to bulk deposition (Supplementary Note 4). We note that ΔU is linearly proportional to the absolute value of single-atom–support bonding (ΔGbp) in Supplementary Tables 6 and 7; Supplementary Figs. 13–15). We reason that the binding interaction arising from the specific affinity of metal adatoms to the substrate atoms is responsible for the energetically favored single-atom deposition of a metal on TMD materials (Fig. 3e). An explanation of the UPD on TMDs is therefore provided, which emphasizes the fact that this phenomenon is also general, where...
the binding energy of the adsorbed atoms on the substrate exceeds that in the respective bulk crystal.

In the self-terminating process of Cu UPD on the ce-MoS2 nanosheets, the single-atom deposition reached saturation rapidly and was not dependent on the concentration of metal precursor (Supplementary Fig. 16). Moreover, the excessively high concentration of metal precursor did not lead to the formation of single-atom aggregation or nanoparticles (Supplementary Table 8). These results highlight the intelligence of SSED for single-atom synthesis, which is capable of finding the termination point of the deposition reaction.

To further interpret the changes in electron state and electron–phonon interactions during the process of Cu UPD on ce-MoS2, we used operando Raman spectroscopy and electrochemical techniques to monitor the in situ growth of single-atom Cu (Supplementary Fig. 17). The notable change in the intensity and position of J3 peak suggests perturbation of the 1T vibration modes, particularly the vibration from the S atoms induced by the covalent attachment of Cu adatoms. We then conducted an additional control experiment to confirm that immobilization is not mediated by the weak noncovalent interactions of physisorption (Supplementary Fig. 18). We also proposed using Lewis acid-base chemistry to elucidate the plausible coordinative interaction between Cu2+ ions and S atoms prior to single-atom immobilization (Supplementary Note 5 and Supplementary Fig. 19).

All of these experiments demonstrate the critical role of the applied potential and S atoms for effective single-atom dispersion and stabilization. During the process of site-specific UPD, these two important factors provide energetically favored metal–support bonds and activation energy, respectively, for the self-terminating growth of atomically dispersed metal in terms of both thermodynamics and kinetics (Fig. 3e).

**Electrochemical HER study.** Encouraged by the successful fabrication of Pt-SAs/MoS2, we selected the hydrogen evolution reaction (HER) as a model reaction for evaluating the electrocatalytic activity of single Pt atoms. Compared to ce-MoS2, Pt-SAs/MoS2 showed exceptional electrocatalytic activity in the HER.
with negligible overpotential (Fig. 4a). Specifically, the overpotential required to achieve a current density of 10 mA cm$^{-2}$ for Pt-SAs/MoS$_2$ was only ~59 mV, which remarkably surpasses most of the state-of-the-art single-atom electrocatalysts (Supplementary Table 9). Pt-SAs/MoS$_2$ shows strikingly higher electrocatalytic HER activity than commercial Pt/C (Fig. 4a), a bulk Pt electrode, and aggregated Pt nanoparticles (Pt-NPs/MoS$_2$; Supplementary Fig. 20). For instance, as normalized to the loading amount of Pt, the mass activity of Pt-SAs/MoS$_2$ at an overpotential of 0.05 V was 17.14 A mg$^{-1}$, exceeding that of commercial Pt/C by a factor of 114 (inset of Fig. 4a). The catalytic production of H$_2$ by Pt-SAs/MoS$_2$ was further verified by gas chromatography analysis (Supplementary Fig. 21). Electrochemical impedance spectroscopy (EIS) further explains the superior HER kinetics for Pt-SAs/MoS$_2$ compared to pure ce-MoS$_2$, which implies a much faster Faradaic process originating from the introduction of single-atom Pt (Supplementary Fig. 21).

To investigate the mechanistic insights into the outstanding electrocatalytic activity of Pt-SAs/MoS$_2$ in the HER, we evaluated the catalysis kinetics from Tafel plots (Fig. 4b)$^{28}$. Pt-SAs/MoS$_2$ exhibits a Tafel slope of 31 mV dec$^{-1}$, whereas ce-MoS$_2$ exhibits a much larger Tafel slope of 91 mV dec$^{-1}$, implying faster kinetics owing to single-atom Pt decoration. The Tafel slope demonstrates that the HER on Pt-SAs/MoS$_2$ undergoes a Volmer–Tafel
pathway and that the Tafel recombination process is the dominant rate-limiting step (Supplementary Note 6, and Supplementary Fig. 22)\textsuperscript{29}. The Pt-SAs/MoS\textsubscript{2} catalyst delivers an extremely high exchange current density of 2.24 mA cm\textsuperscript{−2}, which is largely increased by a factor of 1.6 compared to commercial Pt/C (Supplementary Fig. 21). With the introduction of thiocyanate ion (SCN\textsuperscript{−}), the HER activity on Pt-SAs/MoS\textsubscript{2} was dramatically decreased due to blocking of the active Pt sites (Supplementary Fig. 21), suggesting that the activity indeed stems from the Pt single atoms. The turnover frequency (TOF) value of
these active Pt sites on Pt-SAs/MoS₂ is 47.3 s⁻¹ (100 mV), which is considerably higher than those of reported single-atom electrocatalysts (Fig. 4c, Supplementary Note 7, and Supplementary Table 9).

The electrocatalytic durability of Pt-SAs/MoS₂ was evaluated by an accelerated degradation test. Performance similar to that of the initial measurement for Pt-SAs/MoS₂ after 1000 cycles or 2 h demonstrates the high long-term stability of Pt-SAs/MoS₂ (Fig. 4d), much better than that of commercial Pt/C (Supplementary Fig. 23). The recycled Pt-SAs/MoS₂ that underwent the accelerated degradation test bore no signs of aggregated Pt atoms or Pt-containing crystalline phases, demonstrating the high stability of the single-atom Pt attached to the ce-MoS₂ nanosheets (Supplementary Fig. 23).

Similarly, compared to state-of-the-art single-atom electrocatalysts, exceptional electrocatalytic activities in the HER were also measured for Pt-SAs/WS₂, Pt-SAs/MoSe₂, and Pd-SAs/MoS₂ (Supplementary Fig. 24). It should also be noted that this methodology for the deposition of single-atom metal on TMDs is highly repeatable, and six independent batches of materials displayed consistent HER performance. The results further indicated the synthetic stability and repeatability of the SSED method.

We performed first-principles calculations to gain deeper atom-level insight into the electronic interactions between Pt and MoS₂ and the catalytic contribution of single-atom Pt immobilization on Pt-SAs/MoS₂ for HER. The difference in charge density (Fig. 4e, Supplementary Fig. 25) reveals a redistribution of the electronic structure. Approximately 0.09 electrons are transferred from the Pt atom to MoS₂ through the formation of a Pt–S bond based on Bader charge calculation. As illustrated by the projected density of states (PDOS, Fig. 4f), the hybridization between Pt (5d orbitals) and the neighboring S atoms effectively improves the dominance of d-electron orbitals near the Fermi level (Supplementary Fig. 26), leading to enhanced catalytic activity. Pt-SAs/MoS₂, with a higher Fermi level and lower work function, shows higher electronic energy levels and enhanced capability to provide electrons (Supplementary Fig. 27), and hence enables better conductivity (also evidenced by the experimental EIS results). We also calculated the free energy (ΔG₂H°) for hydrogen adsorption to further elucidate the thermodynamic improvement of HER after immobilization of single-atom Pt (Fig. 4g and Supplementary Fig. 28). Compared to that of pure MoS₂ (0.160 eV), the calculated ΔG₂H° for the Pt-SAs/MoS₂ is approximately −0.067 eV, representing more favorable HER behavior than the commercial Pt catalyst (−0.139 eV).

From the apparent Tafel slope value obtained in the electrochemical HER study, the electrocatalytic pathway at atomic Pt in Pt-SAs/MoS₂ resembles that of conventional metal nanocrystals. However, our XANES, XPS, and Bader charge analysis experimentally and theoretically show that the single Pt atoms are positively charged, leading to a much higher total unoccupied density of Pt 5d states. We reason that the atomic-scale tailoring should conventionally modulate the adsorption state of hydrogen atoms on the Pt atom of Pt-SAs/MoS₂ owing to the unoccupied Pt 5d orbitals combined with H 1s orbital (Supplementary Fig. 29). We conclude that the maximum number of adsorbed H atoms in Pt-SAs/MoS₂ is six per Pt atom. Overall, the strengths of hydrogen adsorption decrease with an increase in the number of adsorbed H atoms, resulting in a minimum value if six H atoms are adsorbed (Supplementary Note 8). Compared to Pt nanocrystal, the increased number of catalytic Pt sites for H adsorption, as well as the lower adsorption energy of the product H₂, decrease the effective barrier in the overall kinetics, which explains the fast HER kinetics and high TOF that were experimentally observed.

Discussion

ED methods have been widely used for single-atom synthesis in recent years. However, these processes are usually either completed within hours (at least 10 h) or less controllable, which result in the formation of nanoclusters/nanoparticles at longer cycling time or higher metal precursor concentration33–35 (detailed comparison shown in Supplementary Fig. 30, Supplementary Note 9, and Supplementary Table 10). In this work, we report a self-terminating ED method to enable the growth of single-atom metals. The applied potential is a critical parameter, which distinguishes ED from other deposition techniques. Controlling the potential restricted to UPD region—at which metal–support bonding predominates over metallic bonding—can lead to the adsorbed single-metal atoms on the isolated chalcogen atoms with inherent nucleophilicity. Once the surface-limited reaction (UPD) reaches saturation, the self-termination stops the continuous atom growth regardless of the metal precursor concentration or deposition time, which reinforces the only formation of single-atom metals. The electrochemical synthesis directly provides the electrons for reducing single-metal ions into their elemental states. The fast kinetics accelerates the single-atom dispersion process and hence gives a much higher efficiency compared to some time-consuming and procedurally demanding methods (Supplementary Table 3). In addition, many conventional synthetic methods have been used under high temperature and pressure, which results in safety concerns and much energy consumption on an industrial scale. On the contrary, our electrochemical system is energy-efficient and green because it operates under mild conditions.

TMDs materials (e.g., MoS₂, WS₂, MoSe₂) have recently emerged as promising and efficient electrocatalysts for HER36–38. With a properly designed system, these TMDs materials show excellent HER activities, largely narrowing the gap with commercial Pt. A general consensus has been reached that the activity of pristine TMDs originates from their coordinatively unsaturated chalcogen atoms along the edges, while the basal planes are inert. Here, we fully harnessed the chalcogen atoms to construct single-atom Pt, which holds great promise as an efficient strategy to activate and optimize the inert basal plane of pristine TMDs materials.

Although UPD phenomena on some other metal chalcogenides (e.g., CdS, CdSe, Pd₃P₂S₈) or thiol-reagent modified electrodes have been previously reported, they were used to estimate the number of catalytic active sites, probe the energy states of the semiconductors, or detect the metal ions of interest, respectively. Thus, apart from the supporting substrates (MoS₂, WS₂, MoSe₂, WSe₂) used in our work, we hypothesize that these reported substrates might be potentially used as the site-specific substrates for the synthesis of ADMCs. With the N, P, O, or halogen atoms also possessing lone pair electrons and high affinities for metals, some metal nitrides, metal phosphides, MXenes, layered double hydroxides might serve as the candidate substrates for site-specific UPD of single-atom metals. We reasoned that more functional ADMCs could be obtained by UPD of a single-atom nonnoble metal (for example, Ag, Cd, and Hg) onto the site-specific substrates and subsequent galvanic displacement with a more-noble single-atom metal (for example, Ir, Ru, and Au) (Fig. 3a). Considering that the formed Pt SA might be further utilized as the nucleation site for the secondary UPD of single-atom nonnoble metal, we also propose that the SSED technology might also be generally applied to the bottom-up precise synthesis of bi- and multimetallic single-metal-site or cluster catalysts for series of domino and tandem reactions.

Methods

Materials. Molybdenum(IV) sulfide (MoS₂) powder, molybdenum(IV) selenide (MoSe₂) powder, tungsten(IV) sulfide (WS₂) powder, n-butyl lithium in hexane
of (2.5 M), rhodium(III) chloride (RhCl₃), potassium tetrachloroplatinate(II) (K₂PtCl₄), and Nafion perfluorinated resin solution (5 wt% in a mixture of low aliphatic (isobutanol and water, containing 45% water) were purchased from Sigma–Aldrich (St. Louis, MO); aluminum oxide powder (0.05 CR) was purchased from BAIKOWSKI (USA); NaBH₄ and SnO were purchased from the First Reagent Factory (China); potassium tetrachloroplatinate(II) (K₂PtCl₄) and Pt/C (5 wt%) were purchased from Macklin (China); acetonitrile, polyvinylpyrrolidone (PVP), CuSO₄·5H₂O, and Bi(NO₃)₃·5H₂O, were purchased from Nanjing Chemical Reagent (China); iodine and tungsten(IV) sesilene (WS₂) powder were purchased from Aladdin Industrial Corporation (China). All aqueous solutions were prepared with Millipore water (18.2 MΩ cm resistivity).

Synthesis of Pt-SAs/MoS₂. Chemically exfoliated transition metal dichalcogenides (ce-TMDs) were synthesized by lithium intercalation method[40] (details in Supplementary Methods). For the synthesis of Pt-SAs/MoS₂, a glassy carbon electrode was first polished with aluminum oxide powder, followed by ultrasonic cleaning in water and drying at room temperature. A working electrode was made by drop-casting 5 μL of the ce-MoS₂ suspension to cover a glassy carbon electrode (3-mm diameter). Cu atoms were first underpotentially deposited on the ce-MoS₂ nanosheets by controlling the potential at +0.10 V vs Ag/AgCl at which only the UPD process occurs, in an Ar-saturated solution of 0.1 M H₂SO₄ containing 2 mM K₂PtCl₄. The electrode was left in this solution using the Athena and Artimas software (0.9.25 version)[42]. Raman spectra were collected on a LabRAM Aramis Raman spectrometer (HORIBA, Ltd., Japan). The turnover frequency (TOF) of the catalyst was calculated according to the following equation:

\[
\text{TOF} = I/(2F \times n),
\]

where \(I\) is the measured current during the linear sweep measurement, \(F\) is the Faraday constant (96,500 C mol⁻¹) and \(n\) is the molar amount of active Pt sites. The factor 0.125 represents two electrons required to form one molecule of hydrogen (\(2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\)). Detailed calculations are shown in Supplementary Note 7.

DFT calculations. We performed first-principle calculations by using the Vienna ab initio simulation package (VASP 5.4.4) with the Perdew–Burke–Ernzerhof generalized gradient approximation for the exchange-correlation functional and the projector augmented wave method. The DFT-D2 method was adopted to describe the van der Waals interactions between the adsorbed atoms and the support. We used a 2 × 3 × 1 supercell of MX₂ (X = S, Se; M = Mo, W) and a vacuum region of 18 Å to eliminate interactions between the neighboring cells of slab models for all calculations. The plane-wave cutoff energy was set as 400 eV for all calculations; 3 × 3 × 1 and 5 × 5 × 1 1–centered k points were adopted for geometry optimization and self-consistent electronic calculation, respectively. All atoms were relaxed until the residual force was <0.01 eV/Å and the self-consistent field tolerance level was 1.0 × 10⁻⁵ a.u. for the geometry optimizations.

For the geometry optimizations of Cu-SAs/MoS₂, we chose a 2 × 3 × 1 supercell of MoS₂ and then placed one Cu atom on four inequivalent adsorption sites (Mo1, Mo2, S1, and S2). The formation energy of the Cu adsorption was calculated as follows:

\[
E = E_{\text{Cu} \cdot \text{MoS}_2} - E_{\text{MoS}_2} - E_{\text{Cu}}.
\]

We found that the structure in which Cu is adsorbed on the Mo1 site was the most stable with the lowest energy of formation. Similar phenomena were observed for Cu-SAs/MoS₂ and Cu-SAs/WS₂ with the Mo1 site being the most stable adsorption site. Subsequently, we substituted the Cu atoms with Pt and found that structures having a Pt atom bounded at the Mo1 site were still the most stable for Pt-SAs/MoS₂, Pt-SAs/WS₂, and Pt-SAs/MoS₂.

The differential charge density (Fig. 4e) was plotted according to the charge density distributions of Mo₂S₆ and Pt₂S₆ (Supplementary Fig. 25) as follows:

\[
\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^\text{H₂O} + \Delta G_{\text{ads}}^\text{TAS}.
\]

where \(\Delta G_{\text{ads}}\) is the energy of hydrogen adsorption; \(\Delta G_{\text{ads}}^\text{H₂O}\) is the difference in zero-point energy between the adsorbed states and the gas phase. The hydrogen adsorption site was confirmed by comparing the energy of hydrogen adsorption at different positions on the catalyst surface after free geometry optimization with an optimization tolerance level of 2.0 × 10⁻⁵ a.u. (Supplementary Fig. 28). The van der Waals correction was taken into consideration in all these calculations.

Data availability. All data are available from the authors, please refer to author contributions for specific data sets. Source data are provided as a Source Data file. Source data are provided with this paper.

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