Atomic-scale evidence for highly selective electrocatalytic N–N coupling on metallic MoS₂

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Molybdenum sulfide (MoS₂) is the most widely studied transition-metal dichalcogenide (TMD) and phase engineering can markedly improve its electrocatalytic activity. However, the selectivity toward desired products remains poorly explored, limiting its application in complex chemical reactions. Here we report how phase engineering of MoS₂ significantly improves the selectivity for nitrite reduction to nitrous oxide, a critical process in biological denitriﬁcation, using continuous-wave and pulsed electron paramagnetic resonance spectroscopy. We reveal that metallic 1T-MoS₂ has a protonation site with a pKₐ of ~5.5, where the proton is located ~3.26 Å from redox-active Mo site. This protonation site is unique to 1T-MoS₂ and induces sequential proton–electron transfer which inhibits ammonium formation while promoting nitrous oxide production, as conﬁrmed by the pH-dependent selectivity and deuterium kinetic isotope effect. This is atomic-scale evidence of phase-dependent selectivity on MoS₂, expanding the application of TMDs to selective electrocatalysis.

Significance

Molybdenum sulfide (MoS₂) is the most studied two-dimensional (2D) material bar graphene. Current research on crystal-phase engineering focuses almost exclusively on the improvement of catalytic activity. However, the potential advantages of phase engineering toward regulation of selectivity control during multistep catalytic processes remain unexplored. Here, we report atomic-scale evidence on how metallic MoS₂ shows significantly higher selectivity compared to the semiconducting phase during multielectron reduction of nitrite to nitrous oxide. Namely, a reaction intermediate speciﬁc to metallic MoS₂ increases the selectivity by decoupling the proton and electron transfer steps. This has previously been shown to be a universal mechanism to enhance selectivity, and therefore, our work opens directions of the application of 2D materials toward selective electrocatalysis.

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double-resonance (ENDOR) spectroscopy. Specifically, a proton located at the first coordination sphere (~3.26 Å) of a redox-active Mo center was found to have a pK_a value matching that involved in the pH-dependent electrocatalytic selectivity and H/D kinetic isotope effect (KIE). The observed pH-dependent behavior is specific to 1T-MoS_2 as oxo-MoS_x was assigned to the 1T phase using high-resolution transmission electron microscopy (HRTEM), Raman- and X-ray photoelectron spectroscopy (XPS). These results not only provide atomic-scale evidence of SPET in heterogeneous catalysis, but also demonstrate how the phase engineering of TMDs can be used to enhance their electrocatalytic selectivity.

Results and Discussion

Synthesis and Characterization of MoS_2. oxo-MoS_x was synthesized hydrothermally according to a previously reported procedure (35, 36). Briefly, equimolar amounts of molybdate and L-cysteine were mixed and heated inside a Teflon-lined autoclave at 200 °C for 24 h.

An HRTEM image of the as-synthesized material is shown in Fig. 2A. Comparison of the obtained HRTEM image with that of commercial 2H-MoS_2 (Fig. 2D) revealed differences in the atomic arrangement along the basal plane. This difference was quantified using intensity profiles generated along the colored lines indicated in the HRTEM images (Fig. 2A and D). In the case of oxo-MoS_x, only the peaks derived from Mo were observed in the intensity profile (Fig. 2B). This finding is consistent with the coordination of S atoms in an octahedron, as found in 1T-MoS_2 (Fig. 2G) (37, 38). In contrast, 2H-MoS_2 showed alternating Mo–S peaks (Fig. 2E) due to the overlapping of two sulfur atoms along the direction of the electron beam (Fig. 2G).

To quantify the percentage of the 1T phase in the synthesized oxo-MoS_x, XPS measurements were performed (Fig. 2C and F and SI Appendix, Fig. S1 and Table S1). The binding energy of the Mo 3d peaks in 1T-MoS_2 (Fig. 2C) was ~1 eV lower than that in 2H-MoS_2 (Fig. 2F), which is consistent with the previously reported binding energy of Li-intercalated 1T-MoS_2 (39, 40).

The 1T phase percentage was determined to be ~55% from the deconvolution of the Mo 3d spectra and is close to the phase purity previously achieved using hydrothermal synthesis (37, 41–47). The ratio of Mo:S in oxo-MoS_x was determined to be 1:1.9, which is consistent with the composition of MoS_2, and hence, the as-synthesized oxo-MoS_x is hereafter denoted as 1T-MoS_2. The structures of 1T-MoS_2 and 2H-MoS_2 were also analyzed by Raman (Fig. 2H) and ultraviolet-visible (UV-vis) spectroscopy (Fig. 2J). The Raman peaks at 150 (I_1), 239 (I_2), and 337 cm⁻¹ (I_3) (11, 48–50), and the monotonic change of the UV-vis spectrum (41, 51) are also consistent with the formation of the metallic 1T phase (for more details, see SI Appendix, Figs. S2 and S3).

pH-dependent NO_2⁻ Reduction on MoS_2. The selectivity of 1T-MoS_2 and 2H-MoS_2 toward electrochemical NO_2⁻ reduction was investigated in a three-electrode H-type cell. The reduction of NO_2⁻ to N_2O (2NO_2⁻ + 4e⁻ + 6H⁺ → N_2O + 3H_2O) is a four-electron, six-proton multistep reaction and the N–N coupling from NO to N_2O (equation 2 in Fig. 3) is a critical step to detoxify NO_2⁻ to harmless dinitrogen (Fig. 3, bold red lines). The catalysts to convert nitrite to dinitrogen is of considerable practical importance, as nitrate and nitrite are ubiquitous as environmental pollutants (25). However, the N–N coupling in this reaction strongly competes with NH_4⁺ production (NO_2⁻ + 8H⁺ + 6e⁻ → NH_4⁺ + 2H_2O) at pH < 3 (Fig. 3; bold blue lines). The selectivity and reaction rate of N_2O production on 1T-MoS_2 and 2H-MoS_2 at 0.1 V versus a reversible hydrogen electrode (RHE) is shown in Fig. 4A and B (SI Appendix, Fig. S4). For 1T-MoS_2 (red symbols), the Faradaic efficiency (FE) toward N_2O exhibited a clear volcano-type pH dependence with a local maximum at pH 5, providing the maximum FE to date of 42% at near-neutral pH. The formation rate of N_2O also exhibited a maximum at pH 5. Meanwhile, the formation of the NH_4⁺ byproduct was effectively suppressed at pH 5 (SI Appendix, Fig. S5). The conversion ratio of NO to N_2O reaches 93% based on the reaction rate of N_2O and NH_4⁺ (equations 2 and 4 in Fig. 3) at pH 5. In the case of 2H-MoS_2, however, the FE and formation rate of N_2O were pH-independent (Fig. 4A and B, blue symbols). The FE of N_2O for 2H-MoS_2 is lower than 5%, and NH_4⁺ dominated the products in the entire pH range investigated (Faradic efficiency > 70%, SI Appendix, Fig. S5).

pH-dependent KIE. To evaluate the role of protons in the selectivity of denitrification, the KIE of NO_2⁻ reduction was evaluated in a deuterated solution by measuring the amount of N_2O generated after 4 h (Fig. 4C). In the case of 2H-MoS_2, the KIE is ≥ 1.2 at pH 4.5 and 5, indicating that proton transfer is involved in the rate-limiting step of N_2O formation. In the case of 1T-MoS_2, the KIE was constant at ~1.0 below pH 5.5, but gradually decreased at
higher pH, demonstrating the presence of two distinct pH regions. Namely, proton transfer is not involved in the rate-limiting step of N₂O formation below pH 5.5, but is involved at pH ≥ 6. The border between the two pH regions is pH 5.5, a value that coincides with the optimal pH of electrochemical N₂O production (Fig. 4A and B).

The observed difference in the pH dependence of selectivity and the KIE can be explained by considering that an electron and a proton are transferred simultaneously (CPET) during the rate-limiting step of 2H-MoS₂, whereas they are decoupled (SPET) in the case of 1T-MoS₂ (Fig. 4A). Although SPET has traditionally been considered to be less desirable for electrocatalysis due to the generation of high-energy intermediates (53–55), the theoretical model proposed by Koper suggests that SPET may have unique advantages, such as the pH-dependent suppression of side reactions (33, 34, 56). Fig. 1B shows the energy landscape of SPET pathway at equilibrium. When the pH is lower than the pKₐ of the reaction intermediate, proton transfer is thermodynamically favored, and the rate-limiting step
is electron transfer. On the other hand, at pH values higher than the \( pK_a \) of the intermediate, proton transfer becomes thermodynamically uphill and rate-limiting. Thus, the reaction rates exhibit a pH dependence that reaches a maximum at a pH value close to the \( pK_a \) of the reaction intermediate (Fig. 1C) (34) and results in a KIE of 1 at pH below the \( pK_a \) and a deviation at higher pHs. These predictions are consistent with the results obtained here for 1T-MoS\(_2\) (Fig. 4). In the case of CPET, however, protons and electrons are transferred simultaneously, meaning that only the total driving force (electrode potential vs. RHE) influences the reaction rate. The pH has no effect on the reaction rate if the total driving force is maintained constant as in our experiments (54, 55). The difference in selectivity between the two crystal phases can be explained by hypothesizing that 2H-MoS\(_2\) induces CPET, whereas 1T-MoS\(_2\) induces SPET. Support for this hypothesis can be obtained if a reaction intermediate with a \( pK_a \) close to the optimal pH of \( \text{N}_2\text{O} \) production (pH 5) is generated by 1T-MoS\(_2\).

**EPR Detection of Active Species in 1T-MoS\(_2\).** To directly confirm the existence of an intermediate that satisfies the \( pK_a \) requirement, CW-EPR spectroscopy was performed at pH values ranging from 4 ~ 7. At all examined pHs, 20 mM of dithionite was used as a reductant to activate the catalyst, as described previously (35). The electrochemical potential generated upon adding dithionite was +50 mV vs. RHE, which is close to the electrochemical conditions used for evaluating the pH dependence of selectivity (Fig. 4). The CW-EPR experiments were performed at 30 K, where peak splitting was clearly observed (SI Appendix, Fig. S6).

The addition of dithionite increased the X-band (9.64 GHz) CW-EPR signals in the range of 350 ~ 370 mT between pH 4 and 7 (Fig. 5, black lines). These signals were assigned to Mo\(^V\) species with oxo ligands based on the similarity of the spectral shape and g values with those previously reported for Mo\(^V\) oxo species (57–60). As these signals were detected only in the presence of dithionite (SI Appendix, Fig. S7), the Mo\(^V\) species are predicted to be formed in situ. However, the obtained EPR spectra were clearly influenced by the pH, indicating that the detected Mo\(^V\) species are also in a different electronic state. Specifically, the EPR signal with \( g = [1.966, 1.940, 1.910] \) at pH \( \leq 5.5 \) is anisotropic, but at pH \( \geq 6 \), the signal becomes isotropic (\( g = 1.928 \)). This finding further suggests the existence of a protonation site within 1T-MoS\(_2\) with a \( pK_a \) of \( \sim 5.5 \). In other words, the detected intermediate has a \( pK_a \) value that is consistent with the SPET behavior suggested from the pH dependence of the Faradaic efficiency (Fig. 4A), reaction rate (Fig. 4B), and KIE (Fig. 4C).

Simulations of the CW-EPR spectra (Fig. 5, red lines) for 1T-MoS\(_2\) also show a clear transition from anisotropic to isotropic structures at higher pH values, as the rhombic signal with \( g = [1.966, 1.940, 1.910] \) obtained at pH 5.5 shifted to an isotropic one (\( g = 1.928 \)) at pH 6. The maximum concentration of the Mo\(^V\) intermediate at pH 5.5 is estimated to be 0.053 mol % based on the EPR calibration (SI Appendix, Fig. S8). Further details on the satellite peaks caused by the hyperfine coupling of \(^{16}\text{O}\) (\( I = 5/2 \)), as well as the Q-band pulsed electron spin-echo–EPR spectra measured at 34 GHz are presented in SI Appendix, Figs. S9 and S10. In contrast to 1T-MoS\(_2\), no changes in the EPR spectra of 2H-MoS\(_2\) were observed by changing the pH (SI Appendix, Fig. S11), indicating that the Mo\(^V\) intermediate is specific to 1T-MoS\(_2\).

**ENDOR Detection of Protons.** To directly confirm the location of the proton with respect to the electrochemically active Mo\(^V\) species of 1T-MoS\(_2\), \(^1\)H Davies ENDOR spectroscopy, which is ideal for the detection of strongly coupled nuclei (61–63), was performed. We could examine the presence of the exchangeable proton(s) by subtracting the \(^1\)H ENDOR spectrum obtained in D\(_2\)O solution from that obtained in H\(_2\)O. In the pH region from 4.0 to 5.5, the subtracted \(^1\)H Davies ENDOR spectra of 1T-MoS\(_2\) contained a signal with a hyperfine coupling value of 3.9 MHz at
Field-dependent ENDOR and corresponding simulations revealed $^1$H ENDOR signals with a hyperfine coupling tensor for the exchangeable proton of $A = [-3.4, 4.5, 2.5]$ MHz, which corresponds to an isotropic hyperfine coupling value ($A_{iso}$) of 1.2 MHz and anisotropic hyperfine coupling value ($A_{dip}$) of $[-4.6, 3.3, 1.3]$ MHz. To confirm the $^1$H ENDOR results, $^2$H ENDOR measurements were also conducted in D$_2$O solution. The $^2$H Mims ENDOR spectra (Fig. 6B), which are sensitive for the detection of weakly coupled nuclei, also contain the corresponding signal (hyperfine coupling value of 0.6 MHz at $g = 1.966$) with a magnetogyric ratio of $^1$H/$^2$H $\sim 6.5$, confirming that the observed proton is labile. From the $A_{dip}$ values obtained from the simulation, the distance of the proton and the Mo$\text{V}$ center and the angle of O–Mo–H was estimated to be $\sim 3.26$ Å and $\sim 115^\circ$, respectively, which is reasonable considering the bond lengths of Mo–S ($\sim 2.41$ Å) and

g = 1.966 (Fig. 6A and SI Appendix, Fig. S12), which was assigned to a proton coupled to a Mo center. Field-dependent ENDOR and corresponding simulations revealed $^1$H ENDOR signals with a hyperfine coupling tensor for the exchangeable proton of $A = $

![Fig. 4. Electroreduction of NO$_2$ to N$_2$O on MoS$_2$. (A) Faradaic efficiency, (B) reaction rate, and (C) KIE of N$_2$O production via NO$_2$ reduction (0.1 M) by 1T-MoS$_2$ and 2H-MoS$_2$ as a function of pH at 0.1 V vs. RHE for 4 h. Error bars correspond to the average taken over three independent experiments.](image-url)

![Fig. 5. EPR spectra of 1T-MoS$_2$. X-band CW-EPR spectra of 1T-MoS$_2$ generated after reduction by 20 mM dithionite at the indicated pH values (black lines) and the corresponding simulations (red lines). The simulations were performed using the following parameters: $g = [1.966, 1.940, 1.910]$, $A = [130, < 50, 175]$ MHz for pH 4–5.5; $g = 1.928$ for pH 6–7. Experimental conditions: microwave frequency, 9.46 GHz; microwave power, 1 mW; modulation frequency, 100 kHz; modulation amplitude, 1.0 mT; time constant, 40.96 ms; conversion time, 48.00 ms; sweep time, 96 s; four scans; temperature 30 K.](image-url)
S–H (~1.35 Å) (48, 64). The location of the labile proton with respect to the MoV site, characterized at the atomic scale in this study, is shown schematically in Fig. 6C.

Confirmation of the Involvement of 1T Phase. CW-EPR and pulsed ENDOR spectroscopy revealed that SPET is induced by a protonation site with a pKₐ of ~5.5, where the proton is located ~3.26 Å from redox-active Mo site. Finally, to ensure that all these spectroscopic observations are indeed specific to metallic 1T phase, we collected Raman spectra under the same conditions used for CW-EPR and ENDOR analysis. Even in the presence of the reductant, the J₁ peak, which is characteristic of the 1T phase, was observed at 155 cm⁻¹ in all pH regions examined (Fig. 7A, red lines). The J₁ band at 155 cm⁻¹ was blue-shifted compared to the dried 1T-MoS₂ sample (J₁ at 150 cm⁻¹, Fig. 2H), and the peak intensity exhibited the same pH dependence as that observed in the CW-EPR spectra of distorted MoV oxo species (Fig. 5). As the blue shift in the J₁ band is consistent with the distortion of the octahedral coordination of the 1T phase (48, 65), the consistency of the pH dependence in the Raman and CW-EPR spectra, as well as the ENDOR detection of protons, corroborate the formation of distorted/anisotropic MoV species as a consequence of the SPET reaction. The formation of distorted coordination is also supported by the pH-dependent peak intensity of E₂g¹ (48). The pH dependence of J₁ and E₂g¹ is summarized in Fig. 7B. In contrast to 1T-MoS₂, the 2H-MoS₂ showed no clear changes in the Raman spectra (E₂g¹ and A₁g), in agreement with the negligible effect of the pH on the selectivity of 2H-MoS₂. In addition, the 1T phase content was determined to be ~57% from the deconvolution of the Mo 3d spectra after NO₂⁻ reduction (SI Appendix, Fig. S13), which is close to that before reaction (~55%). Furthermore, we also exclude the possibilities of impurities like MoOₓ (66) from XPS data (Fig. 2C) and amorphous MoSₓ from Raman and electrocatalytic performance (SI Appendix, Fig. S14). Thus, we conclude that the SPET behavior, which is the origin for the highly selective N–N coupling, is unique to the atomic arrangement of MoS₂ in the 1T phase.

Conclusions

In summary, we have identified the atomic-scale origin of the phase-dependent selectivity of MoS₂ toward N–N coupling during nitrite reduction, a practically important reaction to restore the balance of the nitrogen cycle. The 1T-MoS₂ can...
generate N₂O with an FE of up to 42%, which is far superior to 2H-MoS₂ (FE of N₂O < 5%, FE of NH₄⁺ > 70%). The pH-dependent CW-EPR and Raman spectra obtained from 1T-MoS₂ provide evidence for a MoV intermediate with a p₃ coordination at a pH of ~5.5, which is consistent with the SPET behavior suggested from the pH dependence of the FE, reaction rate, and KIE. This intermediate is absent in the case of 2H-MoS₂, which exhibits potential independent selectivity. Taken together, these results unambiguously confirm that a MoV intermediate unique to 1T-MoS₂ is responsible for inducing the SPET pathway that promotes N—N coupling in a highly selective manner. Simulations based on the ENDOR spectra indicate that the labile proton is located ~3.26 Å from the redox-active MoV center, providing atomic-scale insight into the SPET mechanism to promote the selectivity of complex multistep reactions. This, in turn, demonstrates how the electrocatalytic selectivity of TMDs can be markedly improved by phase engineering, which may further expand their prospects as next-generation materials.

**Materials and Methods**

**Synthesis of 1T-MoS₂.** The 1T-MoS₂ was synthesized using the same method as described in our previous report (3b). Briefly, 3 mmol of sodium molybdate (Na₂MoO₄, Sigma-Aldrich) and 3 mmol of L-cysteine (C₅H₇NO₃S, Wako) were dissolved in 60 mL of ultrapure water (18.2 MΩ, Millipore Ltd.). The solution was stirred for 20 min and subsequently transferred to a Teflon-lined, 100-mL stainless steel autoclave reactor. After hydrothermal treatment at 200 °C for 24 h, the reactor was allowed to cool down naturally to room temperature. The formed black precipitates were collected by filtration, washed with ultrapure water and ethanol alternatively three times. The as-obtained black powder was dried under vacuum (4 Pa) at 60 °C for 12 h.

**Crystalline 2H-MoS₂.** The 2H-MoS₂ (Molybdenum(IV) Sulfide, Cat. No.: 139–13272) was purchased from Wako Pure Chemical Corporation.

**Characterizations.** Raman spectra were collected on a Bruker Raman microscopy system (Senterra) using a 532-nm excitation laser. The coadditions of 20 spectra were recorded with an integration time of 10 s. The UV-vis spectra of powder samples were recorded in diffuse transmission mode using a spectrometer (UV-2550, Shimadzu) equipped with a multipurpose large-sample compartment and a built-in integrating sphere (MPC-2200, Shimadzu). X-ray photoelectron spectroscopy (XPS) measurements were performed using a photoelectron spectrometer (AXIS Ultra DLD, Kratos Analytical, Ltd.) with Al Kα radiation. The binding energy was calibrated by setting the C 1s peak to 284.6 eV.

**Preparation of Working Electrodes.** A diluted Nafion solution (0.13 wt %) was prepared by dissolving 50 μL of 10 wt % Nafion solution (Sigma-Aldrich) into a solution containing 3 mL of H₂O and 1 mL of ethanol. The synthesized powder samples (3 mg) were dispersed in 200 μL of the diluted Nafion solution and the mixture was sonicated for about 10 min to generate a homogenous ink. The ink suspension was transferred onto a carbon paper (EC-TP1, TOYO Corporation) with a geometrical area of 1.5 cm² and dried naturally at room temperature before electrochemistry experiments.

**Electrolysis Experiments and Product Analysis.** For electrochemical nitrite reduction under potentiostatic conditions, a two-compartment cell separated by a cation-exchange membrane (Nafion 117, Sigma-Aldrich) was used. A Ag/AgCl (in a saturated KCl solution) and platinum wire were employed as the reference- and counter electrodes, respectively. The electrolyte consisted of 0.1 M nitrite in either 0.2 M citric acid (at pH 4, 4.5, 5, 5.5) or 0.2 M phosphate buffer (at pH 6, 6.5, 7) solutions. The volume of the electrolyte in the working and counter compartments was 28 and 20 mL, respectively. Prior to electrolysis, the solution in both chambers was bubbled with argon (99.999%) for 30 min to remove dissolved oxygen. All of the potentials were converted to the RHE scale by the equation: 

\[ U_{RHE} = U_{AgCl/Ag}(KCl \text{ sat}) + 0.197 + 0.059 \times \text{pH} \]

During electrolysis, the solution was stirred using a stirring bar at a rate of 500 rpm. After 4 h of electrolysis, the amount of N₂O generated was analyzed by gas chromatography (GC) equipped with a thermal conductivity detector (GC–BAP, Shimadzu). Argon (99.99%) was used as the carrier gas. Ammonia was detected and quantified using commercially available colorimetric titration kits (HACH). The concentration–absorbance calibration curves were obtained using standard ammonia hydrocarbonate solutions, which contained the same concentrations of the buffer used in the electrolysis experiments. The Faraday efficiency is calculated as follows: Faraday efficiency = zn(Q/E), where z is the stoichiometric number of electrons consumed for generating 1 mole of product. For nitrite reduction to N₂O and NH₄⁺,

\[ 2\text{NO}_2^- + 6\text{H}^+ + 4e^- \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O} (z = 4) \]

\[ \text{NO}_2^- + 8\text{H}^+ + 6e^- \rightarrow \text{NH}_4^+ + 2\text{H}_2\text{O} (z = 6) \]

n is the molar amount of the products determined by gas chromatography, Q is the total charge that passed through the electrochemical cell, and F is the Faraday constant (96,485 C mol⁻¹).

**CW-EPR Spectroscopy.** X-band (9.64 GHz) CW-EPR spectra were acquired on a Bruker EMX/Plus 6/1 spectrometer equipped with a liquid helium quartz cryostat (Oxford Instruments ESR900) using a temperature and gas flow controller (Oxford Instruments ITC503). The preparation procedures of CW-EPR samples are as follows: 3 mg of catalyst powder was added into 200 μL of a buffer solution (Buffer solution was prepared using either 0.2 M citric acid (Wako, Japan) for pH 4, 5, and 5.5, or 0.2 M phosphate [Wako] for pH 6 and 7, respectively) and the mixture was sonicated for 5 min to generate a homogeneous suspension. After purging the suspension with N₂ to remove the dissolved oxygen, 8.3 μL of a 0.5 M dithionite (Sigma-Aldrich) solution was added under N₂ bubbling to reduce the catalyst. After 5 min, 20 μL of glycerol (Sigma-Aldrich) was added and 200 μL of the suspension was transferred to a CW-EPR tube and frozen in liquid nitrogen immediately. The CW-EPR spectra were collected under the following experimental conditions: microwave frequency, 9.64 GHz; microwave power, 1 mW; modulation frequency, 100 kHz; modulation amplitude, 1.0 mT; time constant, 40.96 ms; conversion time, 48.00 ms; sweep time, 96 s; four scans; temperature 30 K.

**ENDOR Spectroscopy.** Q-band (34 GHz) ENDOR measurement was performed on a Bruker Elexsys E580 spectrometer with a cryostat (Oxford CF-935) and an Oxford ITC temperature controller. The data were obtained by an EN5107D2 resonator at 30 K. The 1H Davies ENDOR spectra were obtained using \( T = T_2 = T_1 \equiv T_\tau \equiv T_{\text{echo}} \equiv T_{\text{chirp}} \equiv T_{\text{pulse}} \equiv T_{\text{mod}} \equiv T_{\text{interpulse}} \equiv T_{\text{time}} = 400 \text{ ms} \). The radio-frequency pulse length (7) was 20 μs. The 1H Mims ENDOR spectroscopy was carried out by a sequence of \( n_2 T_2 = n_2 T_1 \equiv n_2 T_\tau \equiv n_2 T_{\text{echo}} \equiv n_2 T_{\text{chirp}} \equiv n_2 T_{\text{pulse}} \equiv n_2 T_{\text{mod}} \equiv n_2 T_{\text{interpulse}} \equiv n_2 T_{\text{time}} = 32 \text{ ms} \) and an interpulse time of \( n_2 T_{\text{interpulse}} = 400 \text{ ms} \). All ENDOR spectra were collected by stochastic sampling for a better baseline of the spectra. All of the simulations (CW-EPR, ENDOR) were performed using EasySpin (67).

**In Situ Raman Spectroscopy.** Raman spectra of MoS₂ were collected on a Bruker Raman microspectroscopy system (Senterra) using a 532-nm excitation laser. For in situ measurements, the surface of a MoS₂ electrode was immersed in a degassed buffer solution with 20 mM dithionite under N₂ atmosphere. The coadditions of 20 spectra were recorded with an integration time of 10 s.

**Data Availability.** All study data are included in the article and SI Appendix.

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