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Structural change of molybdenum sulfide facilitates the electrocatalytic hydrogen evolution reaction at neutral pH as revealed by in situ Raman spectroscopy

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ABSTRACT

Molybdenum sulfides are promising electrocatalysts for the hydrogen evolution reaction (HER). S- and Mo-related species have been proposed as the active site for forming adsorbed hydrogen to initiate the HER; however, the nature of the interaction between Mo centers and S ligands is unclear. Further, the development of cost-effective water-splitting systems using neutral water as a proton source for H_2 evolution is highly desirable, whereas the mechanism of the HER at neutral pH is rarely discussed. Here, the structural change in the Mo–Mo and S–S species in a synthesized molybdenum sulfide was monitored at neutral pH using in situ electrochemical Raman spectroscopy. Analysis of the potential dependent Raman spectra revealed that the band assigned to a terminal S–S species emerged along with synchronized changes in the frequency of the Mo–Mo, Mo_3–μ_3S, and Mo–S vibrational bands. This indicates that Mo–Mo bonds and terminal S–S ligands play synergistic roles in facilitating hydrogen evolution, likely via the internal reorganization of trinuclear Mo_3–thio species. The nature and role of metal-ligand interactions in the HER revealed in this study demonstrated a mechanism that is distinct from those reported previously in which the S or Mo sites function independently.

To generate hydrogen as a clean energy carrier through water-splitting in (photo)electrochemical or polymer electrolyte membrane (PEM) systems, scalable electrocatalysts constructed from earth-abundant elements are desirable for catalyzing the hydrogen evolution reaction (HER). Molybdenum sulfides are promising HER catalysts because of their low overpotential, robustness, and scalability [1–9]. The laminated lattice structure of molybdenum sulfide materials is highly amenable to electronic and structural modification, such as defect engineering [10,11], doping [12,13] and hybridization [3,14,15]. However, maximizing the potential of this catalyst for the HER requires molecular level understanding of the underlying reaction mechanism.

To identify the active species responsible for hydrogen evolution, in situ and ex situ X-ray absorption [16], X-ray photoelectron spectroscopy (XPS) [17], EPR [8] and Raman [8,18] spectroscopic analyses were performed for both crystalline and amorphous molybdenum sulfide materials. It is generally considered that catalytically competent active species are located at the edge of hexagonal MoS_2 crystals, whereas the basal plane is inactive [2,4,7,8,11,19]. Several [MoS_2]-bearing compounds that mimic the edge sites, including [Mo_3S_{13}]$^{2-}$ and [(PY5Me$_2$)MoS$_2$]$^{2+}$ [2,9,20,21], exhibit superior HER activities. For amorphous MoS_x, in situ spectroscopic analyses combined

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with density functional theory (DFT) calculations indicate that terminal di-sulfur species $(S–S)_{terminal}$ are critical for efficient HER [16–18]. During the HER, this $(S–S)_{terminal}$ species is converted into unsaturated -S sites, on which the hydrogen atom adsorption is thermoneutral ($\Delta G_H^0 \cong 0$), thereby contributing to the superior catalytic activity [7,17]. Alternatively, Tran et al. [8] recently proposed that, based on the detection of a high-*g* value EPR signal under HER conditions, a molybdenum hydride moiety (Mo–H) is the active species in amorphous MoS_x. A similar mechanism for Mo–H as the active species was also proposed for $Mo_3S_4^-$ by Kumar et al. [22] based on DFT calculations.

Despite intensive spectroscopic and theoretical studies, the nature of the interactions between Mo centers and S ligands in the active species for the HER remains ambiguous, particularly at neutral pH [8]. Although a number of studies have examined the HER at acidic pH [16–18,23], the development of cost-effective water-splitting systems using neutral water as a proton source for H_2 evolution is highly desirable because it is abundant and safe for handling [1,24]. Previous spectroscopic measurements of molybdenum sulfides have demonstrated that either $(S–S)_{terminal}$ species or molybdenum hydride moieties play an important role in the HER; however, the possibility that Mo- and S-related species synergistically function to facilitate the HER, rather than independently, has not been considered. Herein, in situ Raman spectroscopic analysis of a low-crystallinity molybdenum sulfide catalyst under electrochemical conditions revealed for the first time that both Mo-Mo and S–S species play synergistic roles in facilitating the HER.

A molybdenum sulfide electrocatalyst was synthesized using a hydrothermal approach with molybdate and L-cysteine as Mo and S sources, respectively, at a Mo:S atomic ratio of 2 (see Supplementary Information). The synthesized MoS_x (syn-MoS_x) had markedly higher HER activity than commercially available hexagonal MoS_2 (c-MoS_2), although, based on their X-ray diffraction (XRD) patterns (see Fig. S1 in Supporting Information, (SI)), both materials have hexagonal crystal structures. With respect to c-MoS_2, the syn-MoS_x exhibited broadening of the diffraction peaks with a much lower intensity, indicating that it possesses a lower crystallinity of the two. The Mo 3*d* XPS spectrum indicated that the Mo ions in syn-MoS_x are in a +4 oxidation state, with a Mo $3d_{5/2}$ binding energy of 229.1 eV (Fig. S2(a)). In addition, the S $2p_{3/2}$ spectrum (Fig. S2(b)) showed two components with binding energies of 161.8 and 163.3 eV, attributed to the lattice S^{2-} and bridging S_2^{2-}/apical S^{2-} ligands, respectively [3,17]. Based on quantitative analysis by XPS, the S:Mo ratio (x) is about 1.68, and the deviation from the ideal stoichiometry of MoS_2 may correlate with the low crystallinity (as revealed by XRD), as well as the presence of bridging S_2^{2-} ligands. This is supported by the identification of a Raman band at 550 cm^{-1} assignable to a bridging S_2^{2-} species which is not present in c-MoS_2 (as will be discussed later). SEM images (Fig. S3) show that syn-MoS_x has a spherical morphology with an average diameter of ~300 nm assembled by nanosheets, while c-MoS_2 has a sheet-like morphology with a lateral length of 1–3 μm.

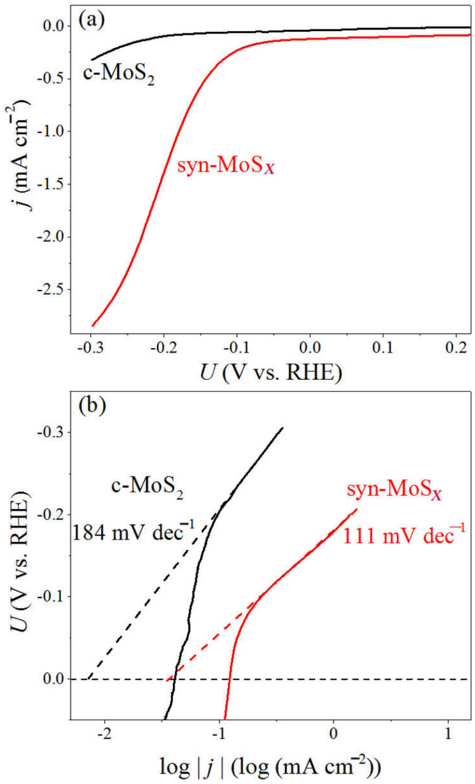

Fig. 1. *J*-*U* curves (a) and Tafel plots (b) of syn-MoS_x and c-MoS_2 electrocatalysts for hydrogen evolution at pH = 7. Scanning rate: 2 mV s^{-1}. Catalyst loading amount: 0.523 mg cm^{-2}. Supporting electrolyte: 0.2 mol L^{-1} Na_2SO_4 and 50 mmol L^{-1} phosphate buffer. Onset potential was read from the knee point of the Tafel plot in b where the curve starts to deviate from linear [26]. Exchange current density values were derived by extrapolating the Tafel plots shown in b to 0 V vs. RHE.

Fig. 1(a) shows the *j*-*U* curves of the syn-MoS_x and c-MoS_2 electrocatalysts at pH = 7, from which the Tafel plots (log|*j*|–*U*) were derived and illustrated in Fig. 1(b). All potential (*U*) values were reported versus a reversible hydrogen electrode (RHE). From these plots, it can be seen that compared to c-MoS_2 the syn-MoS_x catalyst clearly possesses the higher HER activity, as indicated by the more positive onset potential (−94 mV), lower Tafel slope (111 mV dec^{-1}), and higher exchange current density (0.034 mA cm^{-2}). The Tafel slope close to 120 mV dec^{-1} is an indication that the one electron transfer step from the electrode to either H_2O or H_3O^+ ([Volmer reaction]) is the rate-determining step of the HER catalyzed by syn-MoS_x [6,25]. This is because other mechanisms, such as either an electrochemical desorption step ($H_2O + H_{ads} + e^- = H_2 + OH^-$ [Heyrovsky reaction]) or a recombination step ($H_{ads} + H_{ads} = H_2$ [Tafel reaction]), would result in Tafel slopes of 40 and 30 mV dec^{-1}, respectively.

To monitor the structural change of the syn-MoS_x catalyst that occurred during the HER, Raman spectroscopy was performed under in situ electrochemical conditions (Fig. 2). As shown by the black line in Fig. 2(a), prior to initiating the HER (at 600 mV), several intense peaks were observed at 149, 190, 236, 368, 406, 464, and 550 cm^{-1}. The band at 406 cm^{-1} can be assigned to the A_{1g} vibration mode in hexagonal MoS_2 [27,28] and its intensity and peak position are independent of the elec-