available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Communication (Special Issue of Photocatalysis for Solar Fuels)

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

Yamei Li ^{a,*}, Ryuhei Nakamura ^{a,b}^a Biofunctional Catalyst Research Team, RIKEN Center for Sustainable Resource Science (CSRS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan^b Earth-Life Science Institute (ELSI), Tokyo Institute of Technology, 2-12-1-I7E Ookayama, Meguro-ku, Tokyo 152-8550, Japan

ARTICLE INFO

Article history:

Received 27 September 2017

Accepted 26 October 2017

Published 5 March 2018

Keywords:

Hydrogen evolution reaction

Molybdenum sulfide

Electrocatalyst

In-situ Raman spectroscopy

Artificial photosynthesis

Clean energy

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 H₂ 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, Mo₃–μ₃S, 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 Mo₃–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.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

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 under-

lying 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 MoS₂ crystals, whereas the basal plane is inactive [2,4,7,8,11,19]. Several [MoS₂]-bearing compounds that mimic the edge sites, including [Mo₃S₁₃]²⁻ and [(PY₅Me₂)MoS₂]²⁺ [2,9,20,21], exhibit superior HER activities. For amorphous MoS_x, in situ spectroscopic analyses combined

* Corresponding author. Tel: +81-48-467-9372; Fax: +81-48-462-4639; E-mail: yamei.li@riken.jp, yamei.li@elsi.jp

This work was supported by a JSPS Grant-in-Aid for Scientific Research (26288092).

DOI: 10.1016/S1872-2067(17)62945-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 3, March 2018

with density functional theory (DFT) calculations indicate that terminal di-sulfur species $(\text{S-S})_{\text{terminal}}$ are critical for efficient HER [16–18]. During the HER, this $(\text{S-S})_{\text{terminal}}$ species is converted into unsaturated -S sites, on which the hydrogen atom adsorption is thermoneutral ($\Delta G_{\text{H}^0} \approx 0$), 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 $(\text{S-S})_{\text{terminal}}$ 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 3d 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(a) shows the j - U curves of the syn- MoS_x and c- MoS_2

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 Na₂SO₄ 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.

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 ($\text{H}_2\text{O} + \text{H}_{\text{ads}} + \text{e}^- = \text{H}_2 + \text{OH}^-$ [Heyrovsky reaction]) or a recombination step ($\text{H}_{\text{ads}} + \text{H}_{\text{ads}} = \text{H}_2$ [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-

Fig. 2. In situ Raman spectra of syn-MoS₂ obtained under electrocatalytic conditions at potentials (U vs. RHE) stepped in the negative (a) and positive (b) directions, as shown by arrows. The assignment of peaks are depicted, and the bands with shifted peaks are denoted in shadow. Each spectrum was collected from samples in phosphate buffered solution (pH = 7) after poisoning the potential until a steady-state current was reached. All spectra were normalized by the peak at 406 cm⁻¹, which can be attributed to the bulk signal of A_{1g} vibration in hexagonal MoS₂. The spectra are offset vertically for clarity.

trode potential. Meanwhile, other bands assigned to the stretching vibrations for Mo-Mo (236 cm⁻¹), coupled Mo-S (368 cm⁻¹), Mo₃-μ₃S (464 cm⁻¹), and terminal S-S (500 cm⁻¹) [29–31] show clear potential dependence (Fig. 2(a)). The existence of a bridging S-S species at 550 cm⁻¹ was also confirmed by XPS (Fig. S2).

In contrast to previous Raman studies that focused on the Mo-S, S-S, and S-H regions [8,18], here we investigate the interplay among Mo-Mo, Mo-S, S-S, and S-H species by monitoring synchronized changes of their corresponding Raman bands. In situ Raman spectra of syn-MoS_x were collected under potentiostatic conditions at stepped potential values from 600 to -150 mV. The band at ~236 cm⁻¹, assigned to a Mo-Mo bond [30,31], gave a markedly decreased intensity when the potential was shifted towards negative values (Fig. 2(a)). Furthermore, along with the decrease in Mo-Mo band intensity, its peak frequency gradually shifted from 236 to ~224 cm⁻¹ when the potential was decreased from +400 to -150 mV. As this band is ascribed to the stretching vibration of the Mo-Mo bond, the lowered frequency of the band suggests that the Mo-Mo bond was weakened during the course of negative potential scanning.

In addition to the Mo-Mo vibrational bands, we also monitored the potential dependent behavior of the terminal S₂²⁻ ligands. Over the potential range 600–400 mV, no terminal S₂²⁻ species located at 500 cm⁻¹ were observed. Upon changing the

potential towards negative values, the terminal S₂²⁻ species at 500 cm⁻¹ appeared from 300 mV (Fig. 2(a), right). By plotting the peak intensity of the terminal S₂²⁻ Raman bands ($I_{\nu(\text{S-S})\text{terminal}}$) and that of the Mo-Mo vibration ($I_{\nu(\text{Mo-Mo})}$) as a function of potential (Fig. 3(a)), the development of the terminal S₂²⁻ band and the decrease in the intensity of the Mo-Mo band were clearly synchronized. This synchronized behavior is further confirmed by reversing the applied potential towards positive values (Fig. 2(b)). After re-poising the potential at positive values of 400 and 600 mV (Fig. 2(b)), it was observed that the Raman feature of the Mo-Mo vibration was recovered in both frequency and intensity, at the expense of disappeared terminal S-S ligands. These findings indicate that the generation of terminal S-S ligands is associated with the weakening of the Mo-Mo bond, and the synchronized structural changes proceed in a reversible manner that depends on the applied potential.

Since the structural changes, including both Mo-Mo bond weakening and the emergence of terminal S₂²⁻ species, occur mainly prior to the HER in syn-MoS_x (Fig. 3(a) and (c)), it can be considered as an activation process. The intensity of the Mo-Mo band at 224 cm⁻¹ further decreased during the HER (-100 to -150 mV), suggesting that the activated species is involved in the reaction. The importance of the activation process for facilitating the HER is demonstrated by comparison with c-MoS₂. No similar structural changes were observed when c-MoS₂ was

Fig. 3. Plots of the Raman intensity of the stretching vibrations of the Mo–Mo and terminal S–S species (a), plot of the peak frequency of the Mo–Mo, $\text{Mo}_3\text{-}\mu_3\text{S}$ and $(\text{Mo-S})_{\text{coupled}}$ Raman bands (b), and the current density (c) as a function of applied potential ranging from 600 to –150 mV vs. RHE. (c) is the same as the red line in Fig. 1(a).

used as a catalyst, which inefficiently catalyzes the HER (Fig. 1). As shown in the potential dependent Raman spectra of c- MoS_2 (Fig. S4), a species at 239 cm^{-1} showed a decreased intensity; however, there was no accompanying frequency change, and neither terminal S–S ligands at 500 cm^{-1} nor bridging S–S ligands at 550 cm^{-1} were detected across the entire potential region.

The chemical origin of the above structural changes were further analyzed based on the synchronized changes in the vibrational feature of two other bands at 464 and 368 cm^{-1} , which were assigned to $\text{Mo}_3\text{-}\mu_3\text{S}$ and coupled Mo–S vibrations, respectively [29–31]. The former of these, which exists in syn- MoS_x at 600 mV, showed a reduced peak frequency to 457 cm^{-1} along with a decreasing potential from 600 to –150 mV (Fig. 2, right panel and Fig. 3(b)). The potential dependence of the peak shift in the 464 cm^{-1} band showed a similar trend to that for the Mo–Mo band; namely, the shifts of both two bands appeared at the same potential of ~300 mV (Fig. 3(b)) and were reversible by controlling potential (Fig. 2). The frequency change of the $\text{Mo}_3\text{-}\mu_3\text{S}$ band from 464 to 457 cm^{-1} that is caused by the emergence of terminal S–S ligands is in harmony with the theoretical calculations for $[\text{Mo}_3\text{S}_{12}]^{2-}$ clusters [30], in which the band at 462 cm^{-1} is mainly derived from the $\text{Mo}_3\text{-}\mu_3\text{S}$ vibration, but also contains a minor contribution from terminal S–S species. Additionally, the band at 368 cm^{-1} , assignable to a coupled Mo–S stretching vibration (including $\text{Mo}_3\text{-}\mu_3\text{S}$ and $\text{Mo-}\mu_2\text{S}_2\text{-Mo}$ components), was observed to emerge as a high frequency shoulder at 383 cm^{-1} from an applied potential of ~300 mV accompanied with a peak shift (Fig. 2(a), right panel and Fig. 3(b)), and this change was reversibly controlled by the potential (Fig. 2(b), right panel).

The synchronized behavior in the frequency shifts of the $\text{Mo}_3\text{-}\mu_3\text{S}$, Mo–Mo, and coupled Mo–S Raman bands, together with the emergence of terminal S–S ligands (Figs. 2 and 3), support the assumption that trinuclear Mo_3 -thio species are the chemical species involved in the process of generating functional species for the HER in syn- MoS_x . As further support, for the less-efficient c- MoS_2 catalyst, disregarding the potential-independent Mo–Mo band and the absence of terminal S–S species as discussed earlier, the $\text{Mo}_3\text{-}\mu_3\text{S}$ species at 453 and 465 cm^{-1} did not show any frequency change, and the band assignable to the coupled Mo–S vibration at 368 cm^{-1} was not observed (Fig. S4).

Based on analysis of the Raman features as a function of potential, scanned in both positive and negative directions, together with the comparison between syn- MoS_x and c- MoS_2 , we herein propose a model that the reversible structural change of trinuclear Mo_3 -thio species in syn- MoS_x serves as an activation mechanism for facilitating the HER at neutral pH. Upon decreasing the potential, the internal reorganization of the trinuclear Mo centers induce the formation of terminal S–S ligands ligated at the Mo sites, coupled with weakening of the Mo–Mo bond. Indeed, multinuclear Mo–thio complexes are known to undergo intramolecular redox processes and structural rearrangements [30–33]. A proposed transformation of trinuclear Mo_3 -thio species in syn- MoS_x is illustrated in Scheme 1, with the changes in the Raman features of the corresponding moieties depicted.

At neutral pH, Raman spectroscopy on another well-known HER catalyst, amorphous MoS_x (a- MoS_x) [8], showed that a trinuclear Mo_3 -thio species with both terminal and bridging S–S ligands was present in the as-prepared state; the structure of the trinuclear Mo_3 -thio species was maintained at positive potential to –130 mV vs. RHE. In our case, the generation of a trinuclear Mo_3 -thio species in syn- MoS_x requires an internal reorganization on a crystalline support. Despite the necessity for an activation process to generate the functional Mo_3 -thio species in syn- MoS_x , the similarity in the Raman features with that of a- MoS_x in the $\text{Mo}_3\text{-}\mu_3\text{S}$ (450–457 cm^{-1}), S–S (terminal) (500–525 cm^{-1}), and S–S (bridging) (550–555 cm^{-1}) vibrational bands implied that both of these two catalysts share similar functional species on the surface, which has been found to be

Scheme 1. Proposed structural change of Mo_3 -thio species as a function of potential, involving the synchronized weakening of the Mo–Mo bond and the emergence of terminal S–S species in a trinuclear Mo_3 -thio species. Based on the frequency decrease in the Mo–Mo band from 236 to 224 cm^{-1} , along with the emergence of terminal S–S species located at 500 cm^{-1} at the same potential of 300 mV. The resulting species serves to initiate the HER at a potential lower than –94 mV.

involved in the HER [8,16,18].

One possible source of the terminal S–S ligand is the bridging S–S species, and no other oxidative S species (valence state higher than –1) were identified by XPS and Raman analysis. No S–H species located in the frequency range 2480–2562 cm^{-1} [18] could be identified across the whole potential region (Fig. S5). The conversion of a bidentate S–S ligand from a bridging to terminal mode, accompanied by the cleavage of $\text{Mo}-\mu_2\text{S}_2-\text{Mo}$ bond (Scheme 1), is predicted to weaken the Mo–Mo bond similar to that reported in multinuclear Mo–thio molecules [29,31]. The fact that c-MoS₂, which does not contain bridging S–S ligands, cannot generate terminal S–S ligands also favors this assumption (Fig. S4). It is noted that the Raman bands of the bridging S–S species maintained a similar intensity when the potential was decreased (Fig. 2), implying that most of the bridging S–S ligands remained in the structure. As the chemical structure of Mo₃-thio drastically changed during activation, the Raman cross-section of $\nu(\text{S}-\text{S})_{\text{bridging}}$ might vary accordingly because of the change in polarizability of a newly-established bonding structure. This might induce an offset effect against the consumption of $(\text{S}-\text{S})_{\text{bridging}}$ for maintaining the intensity of $\nu(\text{S}-\text{S})_{\text{bridging}}$.

In summary, in situ electrochemical spectroscopic results obtained for syn-MoS_x indicate that both the trinuclear Mo₃ centers and terminal S–S ligands synergistically facilitate the HER. The critical role of internal reorganization within trinuclear Mo₃-thio species for generating terminal S–S ligands was supported by the observed synchronized frequency changes in

Mo–Mo, Mo₃–S, and $(\text{Mo}-\text{S})_{\text{coupled}}$ vibrations initiated at the same potential (300 mV) at which terminal S–S species emerged. The inability of c-MoS₂ to mediate such internal reorganization further supports the validity of this model. Therefore, these results show that a synergistic relationship exists between the generation of terminal S–S species and the weakening of Mo–Mo bonds, with the metal center and sulfur ligands functioning as a whole, rather than independently, to facilitate an efficient HER at neutral pH.

References

- [1] Y. F. Wang, S. R. Narayanan, W. Wu, *ACS Nano*, **2017**, 11, 8421–8428.
- [2] H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science*, **2012**, 335, 698–702.
- [3] T. Y. Wang, J. Q. Zhuo, K. Z. Du, B. B. Chen, Z. W. Zhu, Y. H. Shao, M. X. Li, *Adv. Mater.*, **2014**, 26, 3761–3766.
- [4] T. F. Jaramillo, K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Hørch, I. Chorkendorff, *Science*, **2007**, 317, 100–102.
- [5] H. Vrubel, D. Merki, X. L. Hu, *Energy Environ. Sci.*, **2012**, 5, 6136–6144.
- [6] D. Merki, S. Fierro, H. Vrubel, X. Hu, *Chem. Sci.*, **2011**, 2, 1262–1267.
- [7] B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jorgensen, J. H. Nielsen, S. Hørch, I. Chorkendorff, J. K. Nørskov, *J. Am. Chem. Soc.*, **2005**, 127, 5308–5309.
- [8] P. D. Tran, T. V. Tran, M. Orio, S. Torelli, Q. D. Truong, K. Nayuki, Y. Sasaki, S. Y. Chiam, R. Yi, I. Honma, J. Barber, V. Artero, *Nat. Mater.*,

Graphical Abstract

Chin. J. Catal., 2018, 39: 401–406 doi: 10.1016/S1872-2067(17)62945-0

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

Yamei Li *, Ryuhei Nakamura

RIKEN Center for Sustainable Resource Science (CSRS), Japan; Tokyo Institute of Technology, Japan

Synergy between trinuclear Mo centers and di-sulfur ligands for facilitating electrocatalytic hydrogen evolution was revealed using in situ Raman spectroscopy at neutral pH, providing important insights into the nature of metal-ligand interactions in the hydrogen evolution.

- 2016, 15, 640–646.
- [9] J. Kibsgaard, T. F. Jaramillo, F. Besenbacher, *Nat. Chem.*, **2014**, 6, 248–253.
- [10] M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li, S. Jin, *J. Am. Chem. Soc.*, **2013**, 135, 10274–10277.
- [11] J. F. Xie, H. Zhang, S. Li, R. X. Wang, X. Sun, M. Zhou, J. F. Zhou, X. W. Lou, Y. Xie, *Adv. Mater.*, **2013**, 25, 5807–5820.
- [12] C. Tsai, K. Chan, J. K. Nørskov, F. Abild-Pedersen, *Catal. Sci. Technol.*, **2015**, 5, 246–253.
- [13] J. F. Xie, J. J. Zhang, S. Li, F. Grote, X. P. Zhang, H. Zhang, R. X. Wang, *J. Am. Chem. Soc.*, **2013**, 135, 17881–17888.
- [14] H. Tang, K. P. Dou, C. C. Kaun, Q. Kuang, S. H. Yang, *J. Mater. Chem. A*, **2014**, 2, 360–364.
- [15] D. J. Li, U. N. Maiti, J. Lim, D. S. Choi, W. J. Lee, Y. Oh, G. Y. Lee, S. O. Kim, *Nano Lett.*, **2014**, 14, 1228–1233.
- [16] B. Lassalle-kaiser, D. Merki, H. Vrubel, S. Gul, V. K. Yachandra, X. L. Hu, J. Yano, *J. Am. Chem. Soc.*, **2015**, 137, 314–321.
- [17] H. G. S. Casalongue, J. D. Benck, C. Tsai, R. K. B. Karlsson, S. Kaya, M. L. Ng, L. G. M. Pettersson, F. Abild-Pedersen, J. K. Nørskov, H. Ogasawara, T. F. Jaramillo, A. Nilsson, *J. Phys. Chem. C*, **2014**, 118, 29252–29259.
- [18] Y. L. Deng, L. R. L. Ting, P. H. L. Neo, Y. J. Zhang, A. A. Peterson, B. S. Yeo, *ACS Catal.*, **2016**, 6, 7790–7798.
- [19] L. R. L. Ting, Y. L. Deng, L. Ma, Y. J. Zhang, A. A. Peterson, B. S. Yeo, *ACS Catal.*, **2016**, 6, 861–867.
- [20] A. Hijazi, J. C. Kemmagne-Mbougouen, S. Floquet, J. Marrot, J. Fize, V. Artero, O. David, E. Magnier, B. Pegot, E. Cadot, *Dalton Trans.*, **2013**, 42, 4848–4858.
- [21] T. F. Jaramillo, J. Bonde, J. D. Zhang, B. L. Ooi, K. Andersson, J. Ulstrup, I. Chorkendorff, *J. Phys. Chem. C*, **2008**, 112, 17492–17498.
- [22] C. A. Kumar, A. Saha, K. Raghavachari, *J. Phys. Chem. A*, **2017**, 121, 1760–1767.
- [23] N. Kornienko, J. Resasco, N. Becknell, C. M. Jiang, Y. S. Liu, K. Q. Nie, X. H. Sun, J. H. Guo, S. R. Leone, P. D. Yang, *J. Am. Chem. Soc.*, **2015**, 137, 7448–7455.
- [24] L. Xiao, S. Zhang, J. Pan, C. X. Yang, M. L. He, L. Zhuang, J. T. Lu, *Energy Environ. Sci.*, **2012**, 5, 7869–7871.
- [25] B. E. Conway, B. V. Tilak, *Electrochim. Acta*, **2002**, 47, 3571–3594.
- [26] P. D. Tran, M. Nguyen, S. S. Pramana, A. Bhattacharjee, S. Y. Chiam, J. Fize, M. J. Field, V. Artero, L. H. Wong, J. Loo, J. Barber, *Energy Environ. Sci.*, **2012**, 5, 8912–8916.
- [27] S. M. Tan, A. Ambrosi, Z. Sofer, Š. Huber, D. Sedmidubský, M. Pumera, *Chem. Eur. J.*, **2015**, 21, 7170–7178.
- [28] T. J. Wieting, J. L. Verble, *Phys. Rev. B*, **1971**, 3, 4286–4292.
- [29] A. Müller, W. Jaegermann, J. H. Enemark, *Coord. Chem. Rev.*, **1982**, 46, 245–280.
- [30] A. Müller, R. Jostes, W. Jaegermann, R. Bhattacharyya, *Inorg. Chim. Acta*, **1980**, 41, 259–263.
- [31] A. Müller, R. Jostes, W. Eltzner, C. S. Nie, E. Diemann, H. Bogge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, *Inorg. Chem.*, **1985**, 24, 2872–2884.
- [32] V. P. Fedin, M. N. Sokolov, Y. V. Mironov, B. A. Kolesov, S. V. Tkachev, V. Y. Fedorov, *Inorg. Chim. Acta*, **1990**, 167, 39–45.
- [33] V. P. Fedin, B. A. Kolesov, Y. V. Mironov, V. Y. Fedorov, *Polyhedron*, **1989**, 8, 2419–2423.

原位Raman光谱揭示中性条件下硫化钼结构变化对其电催化析氢反应的促进作用

Yamei Li ^{a,*}, Ryuhei Nakamura ^{a,b}

^a理化学研究所可持续资源科学中心, 生物功能催化剂研究组(CSRS), 广泽2-1, 和光, 埼玉351-0198, 日本

^b东京工业大学地球生命科学研究(ELSI), 大冈山2-12-1-I7E, 目黑区, 东京152-8550, 日本

摘要: 硫化钼是析氢反应(HER)有前途的电催化剂。S-或Mo物种均被认为是形成吸附氢触发HER反应的活性位, 但Mo中心和S配体间相互作用的本质仍不清楚。另外, 采用中性的水作为质子源用于产氢, 来开发低成本的水裂解催化剂体系为研究者高度关注, 但人们很少研究中性水条件下HER反应的机理。本文采用原位电化学Raman光谱对所合成的硫化钼中Mo-Mo和S-S物种在中性条件下的结构变化进行了监测。结果显示, 归属于端位S-S物种的谱带随着Mo-Mo, Mo₃-μ₃S和Mo-S振动谱带频率而同步变化, 表明Mo-Mo键与端位S-S键起着协同作用, 从而有利于氢气的生成。这可能是通过三核Mo₃-μ₃S物种的内部重组而确认的。本文所揭示的HER反应中金属-配体相互作用的本质与作用表明了一个不同的反应机理, 而以往的机理认为, S或Mo活性位独立起作用而促进HER反应的进行。

关键词: 产氢反应; 硫化钼; 电催化剂; 原位拉曼光谱; 人工光合成; 清洁能源

收稿日期: 2017-09-27. 接受日期: 2017-10-26. 出版日期: 2018-03-05.

*通讯联系人. 电话: +81-48-467-9372, 传真: +81-48-462-4639; 电子信箱: yamei.li@riken.jp, yamei.li@elsi.jp

基金来源: 日本学术振兴会(26288092).

本文的全文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).