

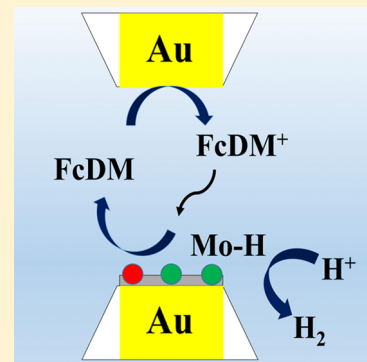
Electrochemical Surface Interrogation of a MoS₂ Hydrogen-Evolving Catalyst: In Situ Determination of the Surface Hydride Coverage and the Hydrogen Evolution Kinetics

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Supporting Information

ABSTRACT: The hydrogen evolution reaction (HER) on an electrodeposited *a*-MoS₂ electrode was investigated by a surface-selective electrochemical titration technique by application of surface interrogation scanning electrochemical microscopy. In a mildly acidic (pH 4.6) environment, the saturated surface hydride coverage of MoS₂ was determined to be 31%, much higher than that expected for a crystalline nanoparticle. The HER rate constant of a surface molybdenum atom was measured for the first time in situ to be 3.8 s⁻¹ at a 600 mV overpotential. At high Mo–H coverages, a change in the nature of the active sites was observed upon consumption of Mo–H by HER.



Much effort has been focused on developing earth-abundant alternative catalysts for the hydrogen evolution reaction (HER) to replace the current benchmark platinum.^{1,2} Molybdenum disulfide has been proposed as a candidate for replacing platinum as the HER catalyst because its hydrogen adsorption energy is similar to that of platinum.^{3,4} Many theoretical and experimental works suggest that the HER activity of MoS₂ would resemble that of a platinum surface.^{3–7} MoS₂ has a layered structure, and the HER active sites on a MoS₂ surface are known to be molybdenum-terminated edge sites, and the activity of such sites has been characterized by bulk electrochemical measurements.^{3,8} Recently, efforts to enhance the HER catalytic activity of MoS₂ have led to the development of electrodeposited MoS₂ catalysts,^{9–11} the selective exposure of the edge active sites,¹² and the activation of the inactive atoms on the MoS₂ basal planes.¹³ Despite these experimental research efforts and many theoretical calculations,^{14–17} mechanistic study of the HER by MoS₂ remains predominantly based on Tafel plot analysis;^{8,18} the chemical activity and surface density of the proposed intermediate, molybdenum hydride, have not yet been measured experimentally. In the present Letter, we report a surface-selective electrochemical titration of an electrodeposited *a*-MoS₂ HER catalyst electrode, quantifying the surface molybdenum hydride coverage and the reactivity of the intermediate hydrides.

Surface-selective redox titration of the electrodeposited (nanocrystalline, unannealed) *a*-MoS₂ electrode was made possible by the implementation of surface interrogation scanning electrochemical microscopy (SI-SECM).^{19,20} This technique involves a redox messenger molecule (mediator) in solution, rendering it exclusively selective to surface atoms in direct contact with the solution.²⁰ SI-SECM has been employed

recently in evaluating the surfaces of catalysts such as the CoP_i and nickel–iron oxyhydroxide oxygen-evolving catalysts.^{21–23}

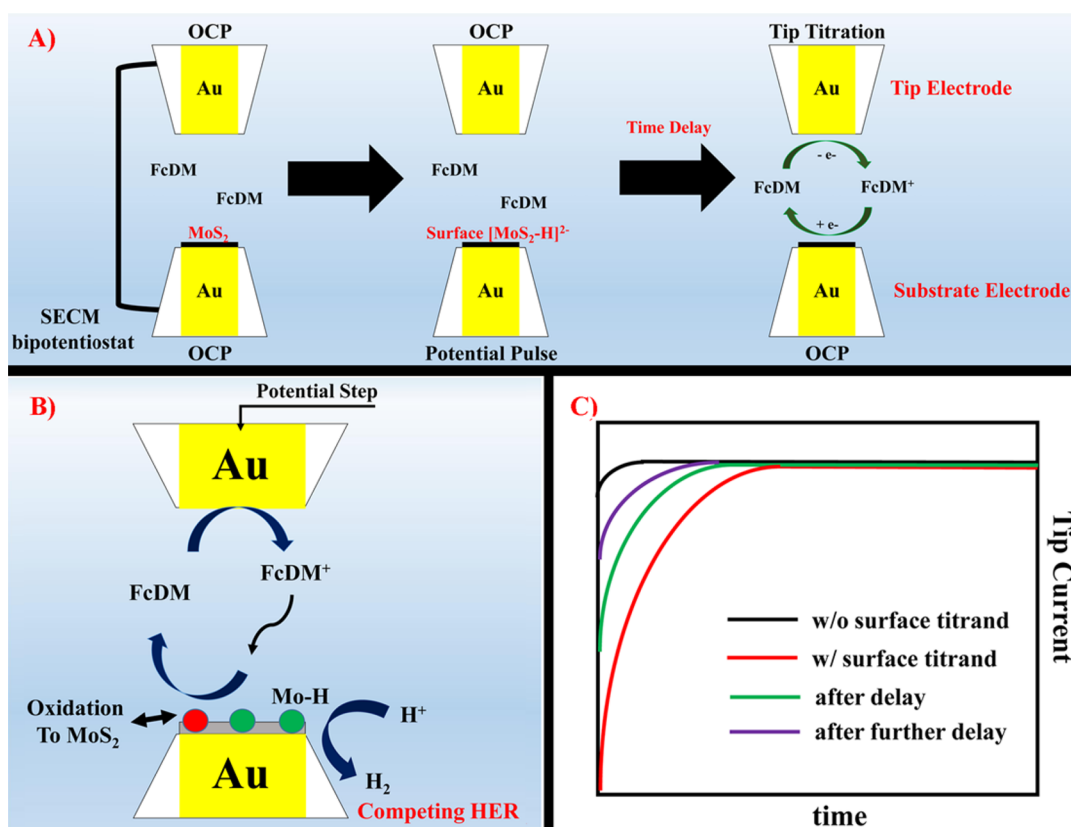
The experimental setup is depicted in Scheme 1. In a SI-SECM experiment, two ultramicroelectrodes (UMEs, 12.5 μm radius Au disk, tip, and substrate) are placed in close proximity (2.4 μm) facing one another such that a species generated at the tip electrode (top, facing down) is quantitatively detected at the substrate (bottom, facing up; for setup details, refer to the Supporting Information). In this Letter, a 1.6 mM redox mediator (1,1'-ferrocenedimethanol; FcDM) in 0.1 M potassium phosphate buffer (pH 4.6) was used to titrate reduced intermediates on the substrate. The electrodeposited *a*-MoS₂ HER catalyst film (of thickness ca. 100 nm) was prepared onto the substrate electrode by published methods (see the Supporting Information and Figure S2 for details).^{9,24,25}

At the beginning of the SI-SECM experiments, the system is at the resting state with the molybdenums in the *a*-MoS₂ in their Mo⁴⁺ oxidation states and the FcDM in solution in its reduced form; therefore, no reaction occurs (Scheme 1A, left). The titrands (redox species of interest Mo–H, [MoS₂–H]²⁻) are generated by a reducing potential pulse to the substrate electrode (Scheme 1A, center), and the titration begins by generation of the titrant (FcDM⁺) at the tip electrode by an oxidizing potential step (Scheme 1A, right). The reaction between FcDM⁺ and the Mo–H will deliver a feedback current (until full consumption of the titrand) that is monitored at the tip electrode (Scheme 1C), integration over time of which

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Scheme 1. (A) Titration Sequence,^a (B) Reactions Occurring at the Tip–Substrate Gap during Titration,^b and (C) Expected Titration Chronoamperograms in the Absence (black) and the Presence (red) of Surface Titrands^c



^aResting at OCP (left), titrand generation by a reductive substrate pulse (center), and titration at the tip electrode (right). ^bTip generation of titrands, consumption of titrands (Mo–H) by titrands, and HER by Mo–H in the absence of titrands. ^cDelayed titration responses are displayed in green and purple. The reduction of titration currents is due to the consumption of surface titrands by the HER.

should yield the surface density of Mo–H. Delaying a controlled amount of time (t_{delay}) between titrand generation and titration will let protons in solution consume the Mo–H ($[\text{MoS}_2\text{-H}]^{2-}$) by HER during t_{delay} , leading to decreased feedback current as a function of t_{delay} (Scheme 1C). Analyzing the integrated charge as a function of t_{delay} should yield the HER rate constant of Mo–H with protons. It is worth noting that the hydride formation on the surface of *a*-MoS₂ is assumed based on a recent theoretical study.¹⁴

The redox titration chronoamperograms (CA) at the tip electrode are displayed in Figure 1. The feedback current increases as a function of applied potential to the substrate electrode, indicating that more active species were generated at further reducing potentials (investigation conducted in pH 4.6 phosphate-buffered water). The integrated charge densities arising from the CAs can be plotted as a function of the substrate potential to yield the redox titration curve shown in Figure 1; all potentials hereon are reported referenced to a 1 M Ag/AgCl electrode, and the E° for HER is -0.51 V on this scale. It is worth noting that in the *a*-MoS₂ film employed in this work, a small fraction of MoS₃ (or MoS_{2+x}, $x < 1$) may be present. A small amount of charge from -0.65 to -0.8 V is attributed to the reduction of residual MoS₃ in the film (see Figures 1 and S6).⁹ The titration curve reveals one redox event starting out at -0.82 V and plateauing between -1.02 and -1.12 V. This event is attributed to the formation of Mo–H (2 e⁻ reduction of a MoS₂ unit forming $[\text{MoS}_2\text{-H}]^{2-}$), which is usually thought to be the intermediate in the MoS₂ HER.¹⁴

Molybdenum disulfide was first made popular for its use in hydrodesulfurization,²⁶ and much theoretical and experimental work has followed studying the dissociative adsorption properties of H₂ on MoS₂.^{27,28} A common model is direct formation of Mo–H and S–H or formation of two S–H and then a reductive proton migration to a neighboring Mo, again yielding Mo–H and S–H.^{27,28} Molybdenum hydride is therefore an important intermediate in MoS₂ HER because hydrogen evolution is the microscopic reverse of the H₂ dissociative adsorption. The Mo–H is also highlighted as an intermediate in a recent theoretical paper, and the calculated Pourbaix diagram suggests that it would be present in the reaction conditions employed in this Letter.¹⁴ Following the formation of Mo–H, both theory and Tafel analysis predict a coupling of Mo–H with a water-stabilized proton to expel H₂.^{8,9,14,18}

The reduction event occurring from -0.82 to -1.12 V is therefore treated as a two-electron event, reducing MoS₂ to $[\text{MoS}_2\text{-H}]^{2-}$. The quantification of the hydride coverage on *a*-MoS₂ is more complicated than cases of quantitative one-electron events such as Co^{III/II} and Ni^{III/II}.^{21–23} Therefore, in order to quantify the Mo–H density, a similar catalyst surface was adopted as a benchmark. The CoP_i catalyst (nanocrystalline cobalt oxide) was evaluated at $270 \mu\text{C}/\text{cm}^2$.^{21,29} This charge density figure was used as that for full coverage of the Mo sites in MoS₂. Taking into account the differences in the roughness factor between CoP_i and *a*-MoS₂ (2.3 and 6, respectively),²⁹ the Mo–H coverages at -0.92 V (400 mV

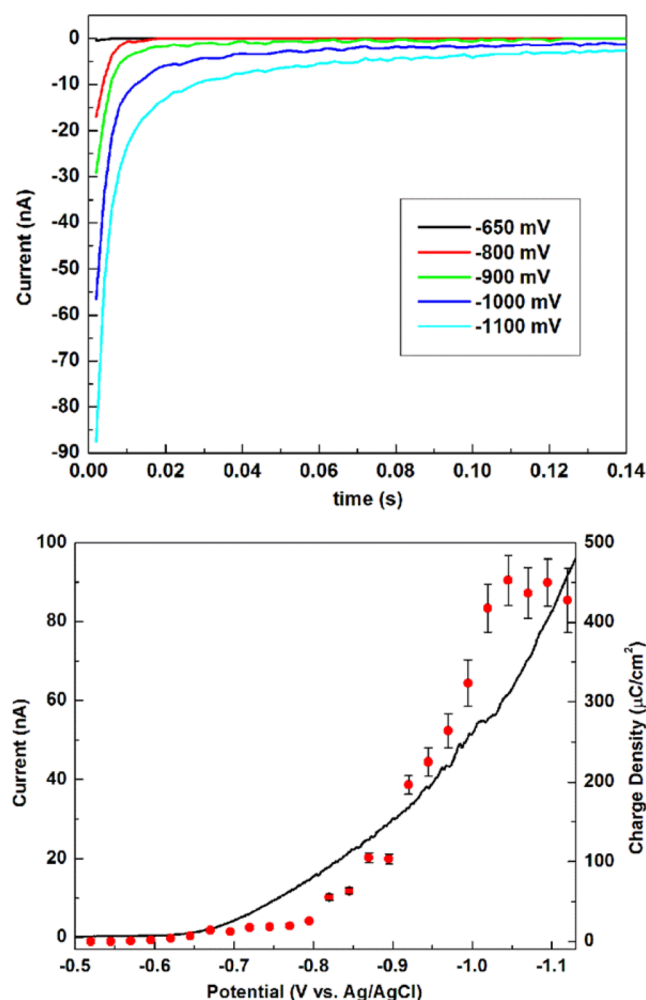


Figure 1. Redox titration CAs recorded at the tip electrode as the feedback responses arising from the reaction of Mo–H and FcDM⁺ (top frame; substrate potentials displayed in the inset). The redox titration curve obtained from charge integration of the CAs is displayed in the bottom panel in red dots (right y-axis; see also Figure S6). The black line in the bottom panel (left y-axis) is a linear sweep voltammogram of the MoS₂ electrode in its HER (scan rate was 10 mV/s). All experiments were performed in 0.1 M pH 4.6 potassium phosphate buffered water. The redox mediator employed here was 1.6 mM FcDM, and the E° for HER on this potential scale is -0.51 V vs Ag/AgCl.

overpotential) and -1.12 V (600 mV overpotential) were 14 ± 1 and $31 \pm 4\%$, respectively (see the Supporting Information for detailed calculations). The saturated hydride coverage of 31% at high overpotentials is surprisingly high for MoS₂ because even for small nanoparticles (of size 25 nm), the molybdenum-terminated edge sites are estimated to be about 8% for crystalline MoS₂;³⁰ such a low active site density is said to be the main reason that MoS₂ falls short of platinum.⁸ Moreover, hydride coverage of the 8% edge sites is known to be between 25 and 50%.^{3,8} Perhaps the enhanced HER catalysis by the electrodeposited (nanocrystalline, unannealed) material is due to an increased number of hydride-forming redox active sites.^{9,10}

The Mo–H sites in the nanocrystalline electrodeposited α -MoS₂ were indeed active for HER in pH 4.6 water, as evidenced by kinetic studies varying the t_{delay} in titration systematically (Figures 2 and S7). As seen in Figure 2, the

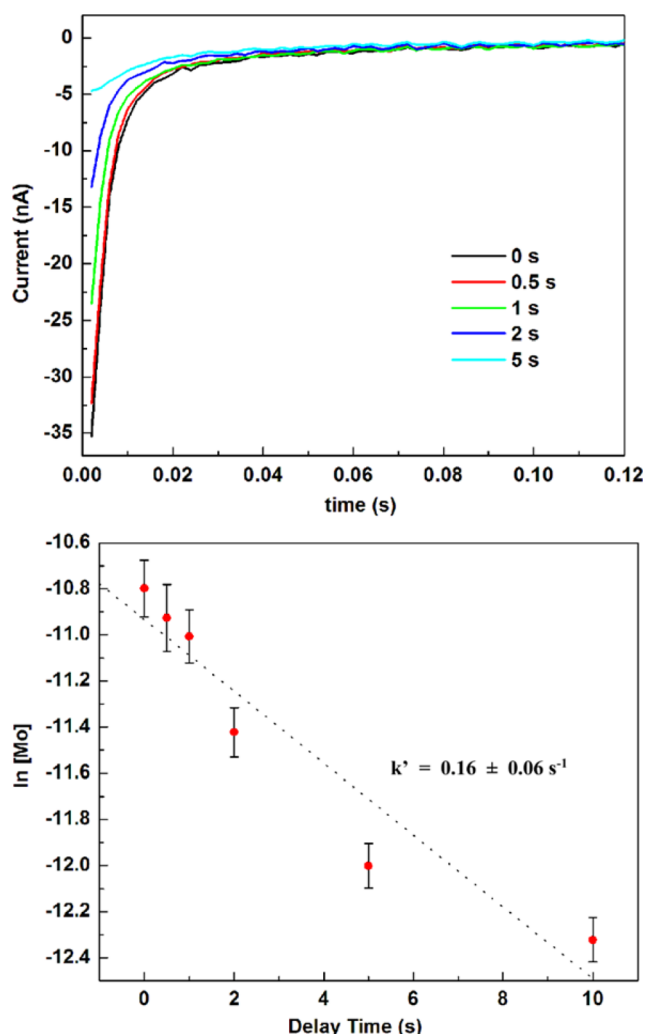


Figure 2. Redox titration CAs at -0.92 V with varying time delays between titrand generation and titration (top frame; t_{delay} shown in the inset). A systematic decrease in the feedback current as a function of t_{delay} was observed as the titrands were consumed by HER during t_{delay} in the absence of titrants. A first-order kinetic analysis was performed for Mo–H in the HER (bottom frame; see also the Supporting Information). The slope of the $\ln[\text{Mo}]$ vs t_{delay} plot (k') represents the HER rate constant of a Mo atom on the MoS₂ surface.

titration feedback current arising from the reaction between the Mo–H and the FcDM⁺ redox messenger molecules decreased with increasing t_{delay} . Because the proton is in excess in the buffered solution (0.1 M in strength), a pseudo-first-order kinetic model can be applied (see the Supporting Information for detailed calculations). When the natural log of the Mo–H surface concentration was plotted against the decay time (Figure 2), the slope of the best-fit line was the kinetic rate constant for Mo–H in the HER. At -0.92 V, at which the Mo–H coverage is 14%, the HER rate constant k' (equivalent to the turnover frequency; TOF) was 0.16 s⁻¹. This TOF for a α -MoS₂ active site is similar to that estimated from the exchange current at pH 0 (at E° , or zero overpotential);⁸ however, a direct measurement of the redox decay kinetics in situ is being reported for the first time here. Also, when H₂ evolution was measured as a function of t_{delay} , the amount of evolved H₂ agreed with the consumed amount of surface Mo–H, further reinforcing the mechanism involving Mo–H as an intermediate (see the Supporting Information and Figure S8 for details).

Observing H₂ evolution at open circuit as Mo–H was consumed seems to suggest some charge-storing ability of *a*-MoS₂ (Figure S8) because H₂ would not have been detected at open circuit if Mo–H behaved similar to an adsorbed hydrogen atom on a platinum surface. Stored charge in the *a*-MoS₂ delivered to the surface Mo–H presumably leads to H₂ evolution even at open circuit for a brief duration (until discharge, ca. 1 s).

A similar kinetic analysis was also performed at a higher overpotential at which the surface hydride coverage was 31%. The time dependence of the titration currents at –1.12 V is displayed in Figures 3 and S7. Unlike the behavior observed at

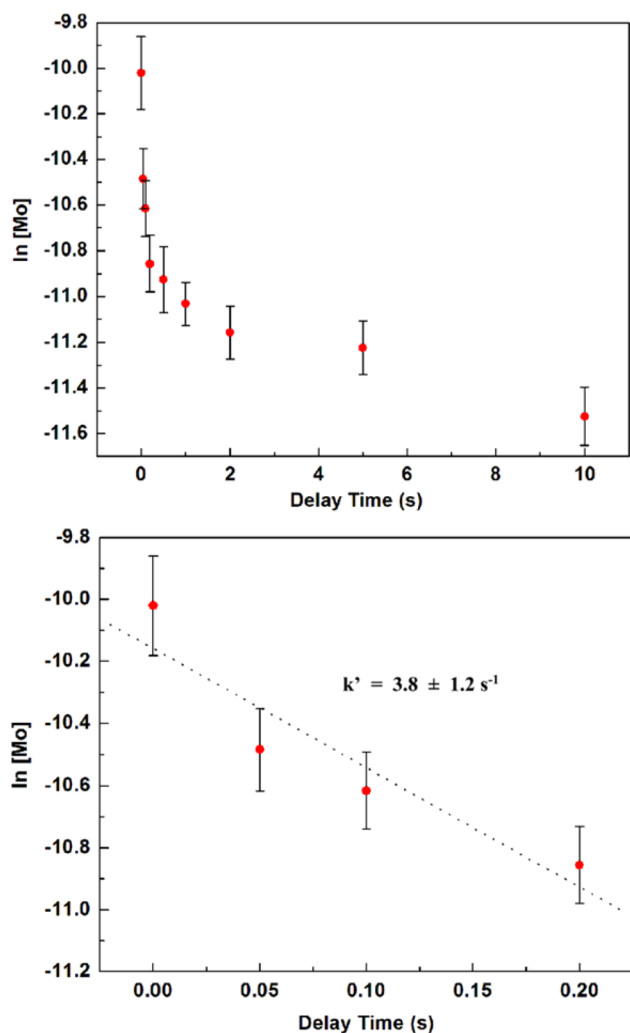


Figure 3. A $\ln[\text{Mo}]$ vs t_{delay} plot at a –1.12 V substrate potential is shown in the top panel. Two linear regions were identified; the first of the two (up to about one half-life) is displayed in the bottom panel. The HER rate constant for a surface Mo atom at –1.12 V (600 mV overpotential, 31% hydride coverage) was measured at $\sim 3.8 \text{ s}^{-1}$.

–0.92 V, pseudo-first-order kinetics with one slope for greater than two half-lives ($t_{1/2} = 4.3 \text{ s}$ for $k' = 0.16$, linear decay for 10 s; Figure 2), the $\ln[\text{Mo}]$ vs t_{delay} plot at –1.12 V exhibited two linear regions with distinct k' values; the first region spans from 0 s to approximately one half-life (0.18 s; Figure 3) with a k' of 3.8 ± 1.2 , and the second region is beyond the first half-life with a k' of 0.06 ± 0.10 (Figure S9). Because the data do not fit second-order kinetics (Figure S10); theory also predicts Mo–H

homocoupling to be unfavorable),¹⁴ it is logical to model this behavior as having a change in the active site after approximately one half-life. After approximately $55 \pm 13\%$ (uncertainty arising from the noncontinuous sampling of data; see Figure 3, t_{delay} set at 0, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 10 s) loss of the Mo–H, the *a*-MoS₂ surface becomes much less potent of a HER catalyst. This model is also convincing because k' at $t > 0.2 \text{ s}$ at –1.12 V is similar to that at –0.92 V; with one-half of the Mo–H lost from the 31% at –1.12 V, the hydride coverage should be similar to that at –0.92 V, 14%. In a practical operating situation where the electrode is constantly biased at the negative potential, the reaction rate will be similar to the initial k' measured here (Figure 3), about four turnovers per atom per second.

In this work, we have studied the HER on an electrodeposited *a*-MoS₂ surface in a mildly acidic medium (pH 4.6). The saturated surface hydride coverage was determined to be 31%, much higher than that expected for a crystalline MoS₂ nanoparticle. The HER rate constant of a surface molybdenum atom was measured for the first time in situ, 0.16 and 3.8 s^{-1} , respectively, at –0.92 V (400 mV overpotential, 14% Mo–H coverage) and –1.12 V (600 mV overpotential, 31% Mo–H coverage). Some charge storage capability of *a*-MoS₂ was observed, as evidenced by H₂ evolution by Mo–H at open circuit until discharge.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.6b01276.

Electrode alignment and approach data, MoS₂ film deposition voltammogram, and capacitance measurement data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Bard, A. J.; Fox, M. A. Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen. *Acc. Chem. Res.* **1995**, *28*, 141–145.
- (2) Gray, H. B. Powering the Planet with Solar Fuel. *Nat. Chem.* **2009**, *1*, 7.
- (3) Hinnemann, B.; Moses, P. G.; Bonde, J.; Jørgensen, K. P.; Nielsen, J. H.; Hørch, S.; Chorkendorff, I.; Nørskov, J. K. Biomimetic Hydrogen Evolution: MoS₂ Nanoparticles as Catalysts for Hydrogen Evolution. *J. Am. Chem. Soc.* **2005**, *127*, 5308–5309.
- (4) Travert, A.; Nakamura, H.; van Santen, R. A.; Cristol, S.; Paul, J.-F.; Payen, E. Hydrogen Activation on Mo-Based Sulfide Catalysts, a Periodic DFT Study. *J. Am. Chem. Soc.* **2002**, *124*, 7084–7095.
- (5) Schweiger, H.; Raybaud, P.; Kresse, G.; Toulhoat, H. Shape and Edge Sites Modifications of MoS₂ Catalytic Nanoparticles Induced by Working Conditions: A Theoretical Study. *J. Catal.* **2002**, *207*, 76–87.
- (6) Lauritsen, J. V.; Nyberg, M.; Vang, R. T.; Bollinger, M. V.; Clausen, B. S.; Topsøe, H.; Jacobsen, K. W.; Lægsgaard, E.; Nørskov, J. K.; Besenbacher, F. Chemistry of One-Dimensional Metallic Edge States in MoS₂ Nanoclusters. *Nanotechnology* **2003**, *14*, 385–389.

- (7) Sun, M.; Adjaye, J.; Nelson, A. E. Theoretical Investigations of the Structures and Properties of Molybdenum-Based Sulfide Catalysts. *Appl. Catal., A* **2004**, *263*, 131–143.
- (8) Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. Identification of Active Edge Sites for Electrochemical H₂ Evolution from MoS₂ Nanocatalysts. *Science* **2007**, *317*, 100–102.
- (9) Merki, D.; Fierro, S.; Vrubel, H.; Hu, X. Amorphous Molybdenum Sulfide Films as Catalysts for Electrochemical Hydrogen Production in Water. *Chem. Sci.* **2011**, *2*, 1262–1267.
- (10) Vrubel, H.; Merki, D.; Hu, X. Hydrogen Evolution Catalyzed by MoS₃ and MoS₂ Particles. *Energy Environ. Sci.* **2012**, *5*, 6136–6144.
- (11) Morales-Guio, C. G.; Hu, X. Amorphous Molybdenum Sulfides as Hydrogen Evolution Catalysts. *Acc. Chem. Res.* **2014**, *47*, 2671–2681.
- (12) Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. Engineering the Surface Structure of MoS₂ to Preferentially Expose Active Edge Sites for Electrocatalysis. *Nat. Mater.* **2012**, *11*, 963–969.
- (13) Li, H.; Tsai, C.; Koh, A. L.; Cai, L.; Contryman, A. W.; Fragapane, A. H.; Zhao, J.; Han, H. S.; Manoharan, H. C.; Abild-Pedersen, F.; et al. Activating and Optimizing MoS₂ Basal Planes for Hydrogen Evolution Through the Formation of Strained Sulphur Vacancies. *Nat. Mater.* **2015**, *15*, 48–53.
- (14) Huang, Y.; Nielsen, R. J.; Goddard, W. A., III; Soriaga, M. P. The Reaction Mechanism with Free Energy Barriers for Electrochemical Dihydrogen Evolution on MoS₂. *J. Am. Chem. Soc.* **2015**, *137*, 6692–6698.
- (15) Helveg, S.; Lauritsen, J. V.; Lægsgaard, E.; Stensgaard, I.; Nørskov, J. K.; Clausen, B. S.; Topsøe, H.; Besenbacher, F. Atomic-Scale Structure of Single-Layer MoS₂ Nanoclusters. *Phys. Rev. Lett.* **2000**, *84*, 951–954.
- (16) Lukowski, M. A.; Daniel, A. S.; Meng, F.; Forticaux, A.; Li, L.; Jin, S. Enhanced Hydrogen Evolution Catalysis from Chemically Exfoliated Metallic MoS₂ Nanosheets. *J. Am. Chem. Soc.* **2013**, *135*, 10274–10277.
- (17) Xie, J.; Zhang, H.; Li, S.; Wang, R.; Sun, X.; Zhou, M.; Zhou, J.; Lou, X. W.; Xie, Y. Defect-Rich MoS₂ Ultrathin Nanosheets with Additional Active Edge Sites for Enhanced Electrocatalytic Hydrogen Evolution. *Adv. Mater.* **2013**, *25*, 5807–5813.
- (18) Li, Y.; Wang, H.; Xie, L.; Liang, Y.; Hong, G.; Dai, H. MoS₂ Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2011**, *133*, 7296–7299.
- (19) Bard, A. J.; Mirkin, M. V. *Scanning Electrochemical Microscopy*, 2 ed.; CRC Press: Boca Raton, FL, 2012.
- (20) Rodríguez-López, J.; Alpuche-Avilés, M. A.; Bard, A. J. Interrogation of Surfaces for the Quantification of Adsorbed Species on Electrodes: Oxygen on Gold and Platinum in Neutral Media. *J. Am. Chem. Soc.* **2008**, *130*, 16985–16995.
- (21) Ahn, H. S.; Bard, A. J. Surface Interrogation of CoP₁ Water Oxidation Catalyst by Scanning Electrochemical Microscopy. *J. Am. Chem. Soc.* **2015**, *137*, 612–615.
- (22) Ahn, H. S.; Bard, A. J. Switching Transient Generation in Surface Interrogation Scanning Electrochemical Microscopy and Time-of-Flight Techniques. *Anal. Chem.* **2015**, *87*, 12276–12280.
- (23) Ahn, H. S.; Bard, A. J. Surface Interrogation Scanning Electrochemical Microscopy of Ni_{1-x}Fe_xOOH (0 < x < 0.27) Oxygen Evolving Catalyst: Kinetics of the “fast” Iron Sites. *J. Am. Chem. Soc.* **2016**, *138*, 313–318.
- (24) Ponomarev, E. A.; Neumann-Spallart, M.; Hodes, G.; Lévy-Clément, C. Electrochemical Deposition of MoS₂ Thin Films by Reduction of Tetrathiomolybdate. *Thin Solid Films* **1996**, *280*, 86–89.
- (25) Murugesan, S.; Akkineni, A.; Chou, B. P.; Glaz, M. S.; Vanden Bout, D. A.; Stevenson, K. J. Room Temperature Electrodeposition of Molybdenum Sulfide for Catalytic and Photoluminescence Applications. *ACS Nano* **2013**, *7*, 8199–8205.
- (26) Pecoraro, T. A.; Chianelli, R. R. Hydrodesulfurization Catalysis by Transition Metal Sulfides. *J. Catal.* **1981**, *67*, 430–445.
- (27) Cristol, S.; Paul, J. F.; Payen, E.; Bougeard, D.; Clémendot, S.; Hutschka, F. Theoretical Study of the MoS₂ (100) Surface: A Chemical Potential Analysis of Sulfur and Hydrogen Coverage. *J. Phys. Chem. B* **2000**, *104*, 11220–11229.
- (28) Cristol, S.; Paul, J. F.; Payen, E.; Bougeard, D.; Clémendot, S.; Hutschka, F. Theoretical Study of the MoS₂ (100) Surface: A Chemical Potential Analysis of Sulfur and Hydrogen Coverage. 2. Effect of the Total Pressure on Surface Stability. *J. Phys. Chem. B* **2002**, *106*, 5659–5667.
- (29) Ahn, H. S.; Tilley, T. D. Electrocatalytic Water Oxidation at Neutral pH by a Nanostructured Co(PO₃)₂ Anode. *Adv. Funct. Mater.* **2013**, *23*, 227–233.
- (30) Bonde, J.; Moses, P. G.; Jaramillo, T. F.; Nørskov, J. K.; Chorkendorff, I. Hydrogen Evolution on Nano-Particulate Transition Metal Sulfides. *Faraday Discuss.* **2009**, *140*, 219–231.