Amorphous Molybdenum Sulfides as Hydrogen Evolution Catalysts

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CONCEPTUS:

Providing energy for a population projected to reach 9 billion people within the middle of this century is one of the most pressing societal issues. Burning fossil fuels at a rate and scale that satisfy our near-term demand will irreversibly damage the living environment. Among the various sources of alternative and CO₂-emission free energies, the sun is the only source that is capable of providing enough energy for the whole world. Sunlight energy, however, is intermittent and requires an efficient storage mechanism. Sunlight-driven water splitting to make hydrogen is widely considered as one of the most attractive methods for solar energy storage. Water splitting needs a hydrogen evolution catalyst to accelerate the rate of hydrogen production and to lower the energy loss in this process. Precious metals such as Pt are superior catalysts, but they are too expensive and scarce for large scale applications.

In this account, we summarize our recent research in the preparation, characterization, and application of amorphous molybdenum sulfide catalysts for the hydrogen evolution reaction. The catalysts can be synthesized by electrochemical deposition under ambient conditions from readily available and inexpensive precursors. The catalytic activity is among the highest for non-precious catalysts. For example, at a loading of 0.2 mg/cm², the optimal catalyst delivers a current density of 10 mA/cm² at an overpotential of 160 mV. The growth mechanism of the electrochemically deposited film catalysts is revealed by an electrochemical quartz microcrystal balance study. While different electrochemical deposition methods produce films with different initial compositions, the active catalysts are the same and are identified as a "MoS₂⁺" species. The activity of the film catalysts can be further promoted by divalent Fe, Co, and Ni ions, and the origins of the promotional effects have been probed. Highly active amorphous molybdenum sulfide particles are also prepared from simple wet chemical routes. Electron transport is sometimes slow in the particle catalysts, and an impedance model has been established to identify this slow electron transport. Finally, the amorphous molybdenum sulfide film catalyst has been integrated onto copper(I) oxide photocathode for photoelectrochemical hydrogen evolution. The conformal catalyst extracts efficiently the excited electrons to give an impressive photocurrent density of -5.7 mA/cm² at 0 V vs. RHE. The catalyst also confers good stability.

INTRODUCTION

Solar irradiation reaching the surface of the Earth in a period of one hour is sufficient to satisfy the world's energy demand for one whole year at the current consumption rate. However, solar energy harvesting is often separated in time and location from consumption, demanding efficient energy storage and distribution systems at a scale commensurate with our energy demand. Electrochemical and photoelectrochemical production of hydrogen from water has long been considered as an attractive method for solar energy storage. Hydrogen is a clean energy vector that can be stored, distributed, and used on demand generating clean water as exhaust. Pt-group metals are the most efficient electrocatalysts for the hydrogen evolution reaction (HER; 2H⁺ + 2e⁻ → H₂). Unfortunately, these metals are among the rarest and most expensive elements on earth, making them unsuitable for energy storage at a global scale. Therefore, it is imperative to replace Pt-group metals with materials made entirely of earth-abundant elements for HER. In addition, techno-economic analyses have suggested that a life-time of 15 or better 20 years for a solar hydrogen production device is required in order to achieve economically competitive H₂ production. This requirement further limits the HER catalysts to only those of superior stability, simple maintenance, and minimum environmental impact during operation and at the end of the use-life.
Hinnemann et al. identified the edge site of MoS$_2$ as a promising hydrogen evolution catalyst in 2005. In principle, when the free energy of adsorbed atomic hydrogen is close to that of the reactant or product (i.e., $\Delta G_0^\text{H} \sim 0$), a material is potentially a good HER catalyst. They showed by DFT calculations that this holds for the active sites of hydrogen evolving enzymes such as nitrogenase and hydrogenase, and the edge site of MoS$_2$. Subsequent experiments by Jaramillo et al. using MoS$_2$ nano-crystals showed that the HER activity is indeed directly proportional to the edge length of the crystals but not to the surface area. Preferential exposure of edge sites has resulted in more active MoS$_2$ electrocatalysts. Since the original studies of Hinnemann et al. and Jaramillo et al., exten-
sive efforts have been devoted to the preparation of nanosstruc-
tured crystalline molybdenum sulfide materials for HER; these
efforts have been reviewed by us and others. This account
summarizes our work, from the first report in 2011 until a recent
application in photoelectrochemical hydrogen production.

DISCOVERY OF AMORPHOUS MOLYBDENUM
SULFIDE FILMS AS HER CATALYSTS

Sometime in 2009, we considered [MoS$_4$]$_2^-$ and its transition
metal complexes [M(MoS$_4$)$_2$]$^{2-}$ as potential homogeneous HER
catalysts. Quickly we found that hydrogen evolution occurred
from solutions containing these compounds. But more thorough
investigations revealed that the molecular complexes decomposed
under electrolysis conditions to yield active heterogeneous catalysts
on the electrodes. This initiated our research in the preparation
and application of these catalysts, later identified as amorphous
molybdenum sulfides.

Amorphous molybdenum sulfides prove to be highly active
and versatile catalysts for HER in acidic solutions. Amorphous
materials are generally prepared at milder temperatures and
with faster solidification processes than crystalline materials.
Although amorphous molybdenum sulfides lack a long range
order, they have short-range atomic arrangements that give rise
to interesting catalytic properties. Our group discovered
that amorphous molybdenum sulfides, known already since
1825, are a highly active catalyst for HER. The simple and
mild preparation methods along with the low cost of the pre-
cursor materials make this class of catalysts very attractive for
the development of cost-effective electrochemical and photo-
electrochemical hydrogen production devices. This account
summarizes our work, from the first report in 2011 until a recent
application in photoelectrochemical hydrogen production.

Figure 1. (a) Cyclic voltammograms during the deposition of a molybdenum sulfide film by cyclic voltammetry (25 cycles). Conditions:
glassy carbon substrate, NaClO$_4$ electrolyte (0.1 M), 2 mM (NH$_4$)$_2$[MoS$_4$], scan rate 50 mV/s. Inset: digital image of an amorphous molyb-
denum sulfide film on ITO during hydrogen evolution. (b) Thickness of MoS$_3$-CV films as a function of scanning cycles. Inset: SEM
image of a MoS$_2$-CV film on ITO. The size bar corresponds to 50 nm. (c) Polarization curves (at pH = 0) of MoS$_3$-CV films made from
different numbers of scanning cycles. The films were deposited on a rotating glassy carbon electrode. (d) Polarization curves of a MoS$_3$-
CV film on a rotating glassy carbon disk electrode recorded at different pHs. Adapted with permission from ref 18. Copyright 2011 Royal
Society of Chemistry.
The HER catalytic activity of these molybdenum sulfide films, initially labeled as MoS2-CV, was first studied by linear sweep voltammetry. Figure 1d shows the polarization curves of MoS2-CV on a rotating glassy carbon disc electrode. The MoS2-CV films displayed high catalytic activity for hydrogen evolution; the activity is higher at more acidic solutions. A typical film (made by 25 scanning cycles) on a glassy carbon disk gave current densities of 14 and 160 mA/cm2 at a overpotential; the activity is higher at more acidic solutions. A Quartz Crystal Microbalance (EQCM).21 EQCM is a powerful tool to study electron transfer processes coupled to small changes of mass on an electrode. By setting a high gain on the frequency-to-voltage converter of the EQCM, it was possible to investigate in detail the mass changes during a single cycle of deposition. The deposition potential window was kept from 0.7 to -0.4 V vs RHE while the starting point was chosen at 0.3 V since initial experiments showed no change of mass at this potential. Starting from 0.3 V, the potential was first polarized positively to 0.7 V, reversed from 0.7 to -0.4 V, and then reversed again to 0.3 V. The mass change during the sixth deposition cycle is represented in Figure 2a. The mass of the film increased in the potential region of 0.3 to 0.7 V, decreased in the region of 0.2 to -0.2 V, and increased again from -0.25 to -0.4 V. Based on previous studies of the electrochemistry of [MoS4]2-22,23 the oxidative deposition process was attributed to the oxidation of [MoS4]2- according to eq 1 in Figure 2a. This oxidation produced not only MoS2 but also elemental S. The reductive corrosion from 0.2 to -0.3 V consumed 70% of the newly deposited mass. Reduction of MoS3 to MoS2 would not amount to this weight loss. The reaction was assigned to the reverse reaction of eq 1, i.e., eq 2 in Figure 2a. Following this corrosion, a new reductive deposition took place between -0.25 V and -0.4 V. This reaction was assigned to a reduction of [MoS4]2- to form amorphous MoS2, SH, and OH (eq 3, Figure 2a). The repetitive deposition and corrosion sequence during an individual scanning cycle resulted in a staircase growth of the film, as shown in Figure 3a (black trace).

EQCM was then applied to monitor film growth under various deposition conditions.24 It was found that higher concentration of [MoS4]2- in the deposition bath resulted in faster depositions. The potential window, especially the negative potential limit, also had an influence on the film growth. This influence was due to the potential dependent corrosion of MoS3 according to eq 2 at the cathodic potentials.

According to eqs 1-3, potential cycling would always produce a molybdenum sulfide film that is a mixture of amorphous MoS2, MoS3, and other sulfur species. On the other hand, electrolysis at a constant positive or negative potential would yield a "pure" amorphous MoS2 or MoS3 film. EQCM was used to monitor the film growth at 0.7 V and -0.4 V, respectively. Indeed, with constant potential electrolysis, only constant film growth, but no corrosion, was observed (Figure 3a). Oxidative deposition at 0.7 V is the fastest method to grow a film, followed by potential cycling between 0.7 and -0.4 V. Reductive electrolysis at -0.4 V is the slowest method to deposit a film. The activity of three films, grown by oxidative electrolysis, potential cycling, and reductive electrolysis was compared. For films of the same mass (15 µg/cm2), the activity was roughly the same. This was an indication that the three different films might be transformed to the same active species during catalysis.

Amorphous MoS3 films grown by oxidative electrolysis were then used for the benchmarking of the catalytic activity of this class of catalysts. Figure 3b shows the activity of films at different loadings. Within the range of 26 to 198 µg/cm2, the activity increased with an increase in loading while the Tafel slopes remained at about 40 mV/dec. At a loading of about 200 µg/cm2, which is the conventional loading of Pt in fuel cells, the catalyst gave a current density of 10 mA/cm2 at an overpotential of 160 mV (see Table 1 below for comparison of the electrochemical HER performance parameters for the different amorphous catalysts presented in this account).
As different deposition methods yielded molybdenum sulfide films of different compositions, these films were analyzed by X-ray photoelectron spectroscopy (XPS) together with MoS2 microcrystals.21 For MoS2 crystals, the Mo 3d spectrum is dominated by a doublet with a Mo 3d5/2 binding energy of 229.5 eV (Figure 3b). This doublet is attributed to the MoVI ion in MoS2. A small doublet with a Mo 3d3/2 peak at 232.7 eV is also visible. This binding energy corresponds to that of MoIV ion, as in Mo3. An S 2s peak of 226.7 eV is also visible in the Mo region. The S 2p spectrum shows one doublet with S 2p3/2 binding energy of 162.4 eV, corresponding to the sulfur states were used to fit the S 2s and S 2p spectra. 21 The S 2p3/2 doublet with a Mo 3d5/2 peak at 229.8 eV is dominated by the Mo IV ion in MoS3. Three different sulfur states were used to fit the S 2s and S 2p spectra. 21 The S 2p3/2 doublet with a Mo 3d 5/2 binding energy of 229.5 eV (Figure 3b). This doublet is attributed to the Mo IV ligand in MoS2. The Mo:S ratio is 1:1.9; the MoVI ion contributes to 4% of the total Mo ions at the surface.

Potentiostatic anodic electrophoration (AE) at 0.7 V vs. RHE yielded amorphous MoS1 films plus some elemental sulfur according to eq 1. The XPS spectra of this film (Figure 2c) show one Molybdenum doublet with a 3d5/2 binding energy of 229.8 eV corresponding to MoIV in MoS3. Three different sulfur states were used to fit the S 2s and S 2p spectra. The S 2p3/2 doublet with a Mo 3d5/2 peak at 229.5 eV (Figure 3b). This doublet is attributed to the Mo IV ligand in MoS2. The Mo:S ratio is 1:1.9; the MoVI ion contributes to 4% of the total Mo ions at the surface.

Chemical reactions related to film growth and corrosion:

1) Oxidative deposition of MoS3 from [MoS4]2–:

\[
[MoS_4]^{2-} \rightarrow MoS_3 + \frac{1}{8} S_8 + 2e^- 
\]

2) Reductive corrosion by reverse reaction:

\[
MoS_3 + \frac{1}{8} S_8 + 2e^- \rightarrow [MoS_4]^{2-} 
\]

3) Reductive deposition of MoS2 from [MoS4]2–:

\[
[MoS_4]^{2-} + 2H_2O + 2e^- \rightarrow MoS_2 + 2HS^- + 2H^+ 
\]

Figure 2. (a) Top: The evolution of current (red line) and film mass (black line) during a potential scanning cycle for the electrochemical deposition of a molybdenum sulfide film. Arrows and numbers indicated the direction of potential scanning. Conditions: Au substrate, NaClO4 electrolyte (0.1 M), 2 mM (NH4)2[MoS4], scan rate 50 mV/s. Bottom: Chemical reactions related to film growth and corrosion. (b) XPS spectra of MoS2 microcrystals. Left: Mo 3d and S 2s region, experimental data (·), fitting envelope (·), MoS2 (·), MoO3 (·). Right: S 2p region, experimental data (·), fitting envelope (·), MoS2 (·), MoO3 (·). (c) XPS spectra of a MoS2-AE film growth by potentiostatic anodic electrophoration at 0.7 V vs. RHE. Left: Mo 3d and S 2s region, experimental data (·), fitting envelope (·), MoS2 (·), S2– 2s (·), S2– 2s (·), S2– 2s (·). Right: S 2p region, experimental data (·), fitting envelope (·), S2– 2s (·), S2– 2s (·), S2– 2s (·). (d) XPS spectra for MoS2-AE after activation for HER. Left: Mo 3d region, experimental data (·), fitting envelope (·), MoS2 (·), MoO2S(–) (·), MoO(–) (·), S2– 2s (·), S2– 2s (·). Right: S 2p region, experimental data (·), fitting envelope (·), S2– 2s (·), S2– 2s (·). Adapted with permission from ref 21. Copyright 2013 American Chemical Society.
The activation of the MoS$_2$-AE film was followed by XPS and EQCM. Immersing the as-prepared film in 1.0 M H$_2$SO$_4$ seemed to remove most of the residual elemental S, indicated by a decrease of the Mo:S ratio to 1:3.2 and a mass loss of 7%.\textsuperscript{21} The acid washed MoS$_2$ film was then transformed to the active catalyst by a linear potential sweep. A mass decrease of 17% was observed at potentials just positive of the onset potential for HER (Figure 4). This mass decrease is consistent with the removal of slightly less than one equivalent of S from MoS$_2$. Figure 2d shows the XPS spectra for the activated catalyst. The Mo 3d spectrum contains small peaks due to Mo IV in Mo oxysulfide and Mo VI in MoO$_3$ besides a dominant catalyst. The Mo 3d spectrum contains small peaks due to close to 1:2, and the relative intensity of S 2- and S$_2$ (vide supra). While metallic edge sites are the active sites for structure (amorphous versus crystalline) and XPS properties that of crystalline MoS$_2$ and that indicates both S 2- and S$_2$ ratio close to 2 but a S 2p XPS spectrum that is distinct from shows two doublets due to S 2- and S$_2$.

The amorphous MoS$_2$ catalyst should be distinguished then from the ubiquitous MoS$_2$ nanocrystals by its different structure (amorphous versus crystalline) and XPS properties (vide supra). While metallic edge sites are the active sites for HER catalyzed by MoS$_2$ nanoparticles, there is no defined edges in amorphous MoS$_2$, films. However, chemically speaking, the edge sites in MoS$_2$ crystals can be considered as Mo and S sites that are coordinatively unsaturated. These unsaturated sites can adsorb hydrogen and mediate HER. In the MoS$_2$ films, there shall be plenty of such unsaturated, "defect" Mo and S sites due to its amorphous nature. As a consequence, these amorphous films exhibit remarkable high HER activity.

**PROMOTION OF THE HER ACTIVITY OF AMORPHOUS MOLYBDENUM SULFIDE FILMS BY FIRST-ROW TRANSITION METAL IONS**

Thin films active for HER were also deposited from aqueous solution of (NH$_4$)$_2$[Co(MoS$_4$)$_2$] by cyclic voltammetry. The optimized deposition conditions were analogous to those for the deposition of amorphous molybdenum sulfide films. Similar films could be made from solutions containing a mixture of CoCl$_2$ and (NH$_4$)$_2$[MoS$_4$]. Presumably, (NH$_4$)$_2$[Co(MoS$_4$)$_2$] formed in this mixture was the precursor for the films. Deposition from solutions of CoCl$_2$ and (NH$_4$)$_2$[MoS$_4$] allowed the variance of the Co to Mo ratio in the deposition bath. XPS analysis of the films revealed the presence of Mo, Co and S. The Co-Mo-S films are active for HER; in fact, their activity is higher than the MoS$_2$ catalyst.\textsuperscript{24} The addition of cobalt and nickel to MoS$_2$ nanocrystals was known to enhance their catalytic activity for the hydrodesulfurization reaction.\textsuperscript{26} Bonde et al. also showed that Co$_{2+}$ promoted MoS$_2$ and WS$_2$ nanocrystals for HER.\textsuperscript{27} This prompted us to investigate the promotion of the HER activity of MoS$_2$, by Co and several other first-row transition metals ions. The ions were in the oxidation state of +2.

Figure 5 shows the catalytic activity of the ternary M-MoS$_2$, films (M = Mn, Fe, Co, Ni, Cu, and Zn) at pH 7 and 0.\textsuperscript{26} Fe, Co and Ni ions are effective promoters, while Mn, Cu and Zn ions give no or only a small promotion. At pH = 7, the best promoter is Co$_{2+}$, which gives MoS$_2$, a 5 times increase in current density at $\eta = 200$ mV. At pH = 0, the best promoter is Fe$_{2+}$, which gives MoS$_2$, a two-fold increase in current density at both $\eta = 200$ mV and $\eta = 150$ mV. In general, the promotion by the same ion is stronger at pH = 7 than at pH = 0.

**Figure 3.** (a) The time-dependent growth of molybdenum sulfide films deposited by three different deposition methods: anodic electrolysis at 0.7 V (AE), cathodic electrolysis (CE) at -0.4 V, and cyclic voltammetry (CV) between 0.7 and -0.4 V. (b) Stable ($10^6$) polarization curves in 1.0 M H$_2$SO$_4$ for MoS$_2$ films at different loadings. Conditions: Au substrate; scan rate, 5 mV/s. Adapted with permission from ref 21. Copyright 2013 American Chemical Society.

**Figure 4.** Mass change during the activation of a MoS$_2$ film in the first linear sweep scan. Conditions: Au substrate, H$_2$SO$_4$ electrolyte (1M), scan rate 5 mV/s. Adapted with permission from ref 21. Copyright 2013 American Chemical Society.
The origin of the promotional effects of Fe, Co, and Ni ions was probed. The morphology and thickness of the MoS$_{2+x}$ and M-MoS$_{2+x}$ films were studied by SEM. Incorporation of Fe, Co or Ni ions resulted in appreciable increase in the porosity of the film. The thickness of the film also increases considerably after the incorporation of Fe, Co or Ni ions. The un-promoted MoS$_{2+x}$ film had a maximum thickness of 150 nm, while the Fe, Co, and Ni-promoted films were up to 500 nm in thickness under the same deposition conditions. The compositions of the films were determined by XPS and inductively coupled plasma atomic emission spectroscopy (ICP-AES). It was shown that only a low amount of Mn, Cu, or Zn ions (1-5%) could be incorporated to the MoS$_{2+x}$ films, which was the reason for their lack of promotion in the activity of these films. On the other hand, a significant amount of Fe, Co, and Ni ions could be incorporated. From a deposition bath containing a 1:3 ratio of MCl$_2$ (M = Fe, Co, Ni) to (NH$_4$)$_2$[MoS$_4$], M-MoS$_{2+x}$ films with a M:Mo ratio between 1:3 and 1:4 could be deposited. In addition, the M-MoS$_{2+x}$ films (M = Fe, Co, Ni) had a Mo content that was about 3 times that of unpromoted MoS$_{2+x}$ film grown under analogous conditions. This indicates that Fe, Co, and Ni ions promoted the growth of the MoS$_{2+x}$ films. The relative electrochemical surface areas of the unpromoted and Fe, Co, and Ni-promoted MoS$_{2+x}$ films were compared using their double layer capacitance. The capacitance could be determined by cyclic voltammetry. The Fe, Co, and Ni-promoted MoS$_{2+x}$ films had surface areas that were 1.4 to 3.3 times of that of the unpromoted MoS$_{2+x}$ film.

The above data indicate that Fe, Co, and Ni ions promote the growth of the MoS$_{2+x}$ film, increasing its thickness, loading, porosity, and surface area. This increase is on the order of 3 fold as well. Therefore, the promotion at pH = 0 is mostly associated with film growth. At pH = 7, however, the promoted films are 5-12 times more active. Clearly at higher pHs, Fe, Co, and Ni ions seem to increase the intrinsic activity of MoS$_{2+x}$ for HER. It is hypothesized that these ions modify the absorption energy of hydrogen at the unsaturated Mo and S sites which are the active sites for HER. Similar promotional effects are known for the hydrodesulfurization reaction of natural gas and refined petroleum products and the HER, where transition metal ions such as Co$^{2+}$ significantly enhance the activity of MoS$_{2}$ nanoparticles. DFT calculations suggest that Co ions bind to inactive sulfur edge sites, making them catalytically active.

CHEMICALLY SYNTHESIZED AMORPHOUS MOLYBDENUM SULFIDE PARTICLES

While highly active amorphous molybdenum sulfide films could be prepared by electrodeposition as described in the previous sections, the preparation of similarly active nanoparticles through chemical synthesis is also desirable. Chemical synthesis tends to be more scalable and can allow the deposition of catalyst films without using electrochemistry which might be unsuitable for certain substrates. As our earlier work showed that amorphous MoS$_{3}$ film could be activated to form the active MoS$_{2+x}$ catalyst, we thought amorphous MoS$_{3}$ particles might have the same property. Amorphous MoS$_{3}$ particles are normally prepared by acidification of tetrathiomolybdate solutions. We found that similar particles could be obtained by acidification of a solution of MoO$_{3}$ and Na$_2$S, making the synthesis more economical. XPS spectra of the resulting MoS$_{3}$ particles resembles those of known MoS$_{3}$ samples. The Mo to S ratio is 1 to 3. Figure 5a shows the TEM image of the
particles. Electron diffraction study confirmed the amorphous nature of the particles.

The chemically synthesized amorphous MoS$_3$ particles were deposited on various electrodes by drop-casting and spray-casting methods. The resulting electrodes had rather good activity for HER at pH = 0. For example, at a loading of 32 $\mu$g/cm$^2$, a MoS$_3$-modified glassy carbon electrode gave a current density of 2.3 mA/cm$^2$ at $\eta$ = 200 mV. This activity is comparable to that of many nanostructured and crystalline MoS$_2$ particles, although it is only 1/8 of that of an amorphous MoS$_{2+x}$ film at a similar loading. Importantly, the amorphous MoS$_3$ particles also underwent an activation process to form an active species that has similar XPS spectra as the MoS$_{2+x}$ species formed from amorphous MoS$_2$ films. This indicates that the active species from chemically synthesized MoS$_3$ particles is also MoS$_{2+x}$.

Annealing of amorphous MoS$_3$ particles resulted in significant change in composition and crystallinity. When annealed at 350 $^\circ$C for 1 h, the particle size increased from below 100 nm to about 1 $\mu$m (compare Figure 6a and 6b), and the particles became polycrystalline. The composition remained close to MoS$_2$. When further annealed at 650 $^\circ$C for 30 min, the particles became single crystalline MoS$_2$ of 100 nm in width and several $\mu$m in length. Even larger microcrystals of MoS$_2$ could be purchased from Aldrich. The activity of various molybdenum sulfide particles was measured using a carbon paste electrode as the substrate (Figure 6c). The amorphous MoS$_3$ particles had the highest activity, followed by polycrystalline MoS$_3$ (annealed at 350 $^\circ$C, labeled as MoS$_3$-350), and then the small MoS$_2$ single crystal particles (annealed at 650 $^\circ$C, labeled as MoS$_2$-650). The larger MoS$_2$ microcrystals had the lowest activity. The activity trend is consistent with our hypothesis for the high activity of amorphous molybdenum sulfide catalysts. In the amorphous MoS$_3$ particles, there are a large number of unsaturated Mo and S sites that might catalyze HER. When annealed at high temperatures, the particles become more crystalline so that there are fewer such "defect" sites. Finally, the largest crystals have the least amount of defect sites.

The Tafel slope of chemically synthesized amorphous MoS$_3$ particles was larger than those of electrochemically deposited MoS$_{2+x}$ films. The latter are constantly about 40 mV/dec while the former are as high as 63 mV/dec. Moreover, a higher loading of MoS$_3$ particles led to a higher Tafel slope. This is illustrated in Figure 7a. At a loading of 28 $\mu$g/cm$^2$, a glassy carbon electrode modified by MoS$_3$ particles gave a Tafel slope of 47 mV/dec at a loading of 282 $\mu$g/cm$^2$, an analogous electrode gave a Tafel slope of 63 mV/dec. We thought the higher Tafel slopes observed for MoS$_3$ particles, especially at higher loadings, might be due to slow electron transport in this type of materials that have modest electronic
conductivity. This was confirmed by electrochemical impedance spectroscopy. The equivalent circuit that fits the impedance data is shown in Figure 7b. This is a transmission line model that have been previously used to model porous materials with intermediate resistivity, e.g., TiO2 films in Grätzel cells. The porous and resistive nature of MoS2 particles is accounted for by repeating units of R in series with R where R represents a non-negligible electronic resistance of MoS2, and R represents the charge transfer resistance due to HER. Figure 7c shows the fitting of the Nyquist plot for the HER by MoS2 particles at the loading of 282 µg/cm². A notable feature is the 45° line observed in the high frequency region which originates from the slow electron transport process. Consequently, this feature was designated as a fingerprint for slow electron transport in an electrocatalytic process. The fitting of impedance data also yielded charge transfer resistance, R, which is inversely proportional to HER rate. The linear fitting of the plot of log R vs. overpotential gives the charge transfer Tafel slope. It was found that the slopes were about 40 mV for MoS2 particles at both low and high loadings. Thus, the higher apparent Tafel slopes obtained from voltammetric data reflected not only the electrode kinetics but also the slow electron transport process in the catalyst. Adding carbon black particles (Vulcan3) to amorphous MoS2 particles improved the conductivity of the system, resulting in a lower Tafel slope and an absence of the 45° line in the Nyquist impedance plot. Alternatively, more conductive amorphous molybdenum sulfide particles could be prepared by chemical reduction of [MoS4]2− with NaBH4. The resulting particles have XPS spectra similar to MoS2+x and have an apparent Tafel slope of less than 40 mV/dec at both low and high loadings (Table 1).

PHOTOELECTROCHEMICAL HYDROGEN EVOLUTION FROM COPPER(I) OXIDE COATED WITH AN AMORPHOUS MOLYBDENUM SULFIDE CATALYST

The amorphous molybdenum sulfide catalysts, especially the electrodeposited films, exhibit many features that are attractive for photoelectrochemical hydrogen evolution: they can be deposited under ambient conditions using readily available and inexpensive precursors, they have high HER activity and stability, and they are optically rather transparent. Therefore, we collaborated with the Grätzel group in our institute to apply the MoS2+x catalyst to promote the photoelectrochemical hydrogen evolution on Cu2O. Surface-protected cuprous oxide is arguably the state-of-the-art p-type oxide for photoelectrochemical hydrogen evolution. It has a direct band gap of 2 eV and can produce a maximum photocurrent of 14.7 mA/cm² and maximum solar to hydrogen efficiency of 18% under 1 sun irradiation. Pt34 and RuO235 had been used as the HER catalysts for Cu2O in earlier studies.

The deposition of molybdenum sulfide catalyst was achieved by photoelectrochemistry utilizing unfiltered irradiation from a Xe lamp. Under illumination, photons with energy greater than the band gap of Cu2O are absorbed to generate electron-hole pairs in the metal oxide photocathode. Engineering of a p-n junction between the p-type cuprous oxide and a thin layer of n-type Al-doped ZnO (AZO) reduces electron-hole recombination and facilitates the extraction of electrons from the photocathode. Excited electrons are driven through the TiO2 protective layer and into the semiconductor/electrolyte interface. Excited electrons reaching the electrolyte solution have enough chemical potential to drive the oxidative deposition of MoS2 (eq 3 in Figure 2). The unfiltered irradiation has a small fraction of photons with enough energy to create holes in the TiO2 that under the applied bias drives the oxidative deposition of MoS2 (eq 1 in Figure 2). Overall,
the photoelectrochemical deposition of the MoS$_{2+x}$ catalyst is analogous to the electrochemical deposition of the same catalyst in the dark. Figure 8a shows the surface protected Cu$_2$O before and after the deposition of 100 nm thick catalyst.

The MoS$_{2+x}$-Cu$_2$O photocathodes were tested for hydrogen evolution under simulated AM 1.5 illumination (100 mW/cm$^2$). Figure 8b displays the current-potential curves in the dark and under illumination for a MoS$_{2+x}$-Cu$_2$O photocathode with a catalyst loading of 30 µg/cm$^2$. A photocurrent of -5.7 mA/cm$^2$ at 0 V vs. RHE was obtained at pH = 1. The onset potential is 150 mV more negative than that observed for an analogous photocathode with Pt nanoparticles as HER catalyst. However, the deposition of the conformal film protects the photocathode from corrosion in acid, improving the stability of the photoelectrode relative to analogous device without a sacrificial electron donor. The MoS$_{2+x}$-Cu$_2$O photoelectrode is also stable and active at neutral and basic pH. Stable currents of -4 and -2 mA/cm$^2$ were obtained at 0 V vs. RHE at pH = 4 and 9, respectively, for 10 h. The photoelectrochemical hydrogen evolution has a nearly quantitative Faradaic efficiency.

The catalyst loading can be varied from 10 to 100 µg/cm$^2$; the catalyst can be deposited in surface areas in the order of several square centimeters. Figure 8d shows a digital image of the catalyst after deposition of 100 nm thick catalyst. The resulting catalyst has properties and activity similar to our ammonium heptamolybdate, sodium sulfide, and sulfuric acid. Since our initial report in 2011, several other groups have worked in the development of analogous amorphous molybdenum sulfide catalysts. Benck et al. reported the synthesis of amorphous molybdenum sulfide particles from a solution of ammonium heptamolybdate, sodium sulfide, and sulfuric acid. The resulting catalyst has properties and activity similar to our chemically prepared MoS$_2$ catalyst.\textsuperscript{36} Laursen et al. electrochemically deposited amorphous MoS$_{2+x}$ films on activated carbon paper to achieve higher mechanical stability of the catalyst.\textsuperscript{37} Hsu et al. prepared amorphous molybdenum sulfide catalysts by low temperature thermolysis of ammonium tetratimolybdate precursor. Addition of NbCl$_3$ during the preparation of catalyst resulted in enhancement of HER activity.\textsuperscript{38} The same group also deposited amorphous molybdenum sulfide catalysts on high surface area, three-dimensional electrodes for electrochemical hydrogen production using this thermolysis method.\textsuperscript{39,40}

A number of highly active amorphous HER catalysts are recently developed using electrochemical deposition methods similar to the one developed for the deposition of amorphous molybdenum sulfide film catalysts.\textsuperscript{41-43} Tram et al. reported the electrodeposition of ternary sulfides of cobalt-tungsten and nickel-tungsten which showed good HER activity.\textsuperscript{42} Wang et al. reported a simple, one-step electrochemical copolymerization method to fabricate a hybrid film containing polypyrrole (PPy), a conductive polymer, and amorphous molybdenum sulfide catalyst. The hybrid system exhibited a remarkable HER activity.\textsuperscript{43} Sun et al. reported the electrochemical synthesis of amorphous Co-S catalyst that worked best in neutral water.\textsuperscript{44}

Our amorphous MoS$_{2+x}$ catalysts has also been adapted by other groups for photoelectrochemical hydrogen evolution. Seger et al. deposited the MoS$_{2+x}$ film catalyst on a Si photolistoide protected with a Ti layer.\textsuperscript{44} The resulting photocathode gave an impressive photocurrent under illumination. The same group also deposited this catalyst to Si photocathodes protected by a thin MoS$_2$ layer.\textsuperscript{45} Tran et al. reported similar work to use the MoS$_{2+x}$ film catalyst for photoelectrochemical hydrogen evolution on silicon nanowires.\textsuperscript{46} Bourgeois et al. applied the amorphous MoS$_2$ particles as HER catalyst to an organic solar cell for photoelectrochemical hydrogen evolution in acidic solutions.\textsuperscript{47} In a related work, Tang et al. deposited an amorphous molybdenum sulfide catalyst on CdSe-seeded CdS nanorods by microwave thermolysis of (NH$_4$)$_2$MoS$_4$.\textsuperscript{48} Characterization of the catalyst by XPS and extended X-ray absorption fine structure (EXAFS) spectroscopy revealed an active catalyst similar to our MoS$_2$ species. The catalyst promoted the photochemical hydrogen production from a buffered aqueous solution (pH = 7) using triethanolamine as the sacrificial electron donor.

**CONCLUSION AND PERPECTIVES**

Summing up, we have established amorphous molybdenum sulfides as a new class of non-precious HER catalysts. These catalysts can be conveniently synthesized either by electro-

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**Table 1.** Summary of electrochemical HER parameters of amorphous molybdenum sulfide catalysts developed in our group.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>preparation method (substrate)</th>
<th>catalyst loading / mg/cm$^2$</th>
<th>$\eta_{10,mA/cm^2}$ / mV</th>
<th>Tafel slope / mV/dec</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_{2+x}$ film$^a$</td>
<td>electrochemical (rotating disk GC)</td>
<td>0.2</td>
<td>160</td>
<td>40</td>
</tr>
<tr>
<td>M-MoS$_{2+x}$ film$^b$</td>
<td>electrochemical (GC)</td>
<td>0.013-0.014$^d$</td>
<td>181-192</td>
<td>39-43</td>
</tr>
<tr>
<td>MoS$_2$ particles$^c$</td>
<td>chemical synthesis (GC)</td>
<td>0.282</td>
<td>220</td>
<td>63</td>
</tr>
<tr>
<td>MoS$_{2+x}$ particles$^d$</td>
<td>chemical reduction (Vulcan®)</td>
<td>0.025</td>
<td>200</td>
<td>35</td>
</tr>
</tbody>
</table>

$^a$ Deposited by cyclic voltammetry from a [MoS$_4$]$^{2-}$ precursor solution.\textsuperscript{21} $^b$ Deposition from a bath containing a 1:3 ratio of MoCl$_3$ to (NH$_4$)$_2$[MoS$_4$] by cyclic voltammetry, where M = Fe, Co, Ni.\textsuperscript{24} $^c$ Chemical synthesis through acidification of a solution of MoO$_3$ and Na$_2$S.\textsuperscript{29,30} $^d$ Chemical reduction of [MoS$_4$]$^{2-}$ with NaBH$_4$.\textsuperscript{30} $^e$ Loading of Mo.
deposition or by a wet, chemical process. The mechanism for the electrodeposition has been unveiled and the active species has been identified as MoS\(_{2+x}\). The catalysts exhibit remarkable HER activity, especially in acidic solutions, rivaling the best known catalysts that are composed of only earth-abundant elements. Table 1 summarizes important performance parameters (i.e. apparent Tafel slope, catalyst loading and overpotential necessary to produce a current density of 10 mA/cm\(^2\)) for the amorphous molybdenum sulfide systems developed in our group and described in this account.

Parallel to our work, a large amount of research efforts have been invested in the development of nanostructured and single crystalline MoS\(_2\) nanoparticles.\(^{12}\) While our amorphous catalysts have similar activity to the best MoS\(_2\) nanocrystals, they can be prepared under ambient conditions using solution-based methods. The MoS\(_2\) nanocrystals, on the other hand, are normally prepared under elevated temperature, pressure, or vacuum. Clearly, the amorphous molybdenum sulfide catalysts are more processable and scalable. This aspect is demonstrated in several applications of the amorphous catalysts in photoelectrochemical hydrogen evolution including our own work on MoS\(_{2+x}\)-coated Cu\(_2\)O photocathodes.

The production of solar fuels is a grand technical challenge that has inspired numerous scientific endeavors. Not all work will lead to the ultimate solutions, if such a solution exists. Likewise, not all promising catalysts including the amorphous molybdenum sulfide catalysts described here may end up being used in an actual energy conversion device. The broader implication of our research in this field, however, is the concept of using amorphous materials as catalysts for hydrogen evolution. Amorphous materials are often accessible through simple solution-based synthesis under relatively milder conditions. The structural disorder in these materials might be detrimental to their electronic and photonic properties, but for catalytic applications, the resulting defect sites may serve as efficient reaction centers. We expect an emergence of amorphous catalysts for solar fuel production in the near future. The difficulty in the characterization and understanding of such catalysts will motivate the development of new analytical tools in catalysis.

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The authors declare no competing financial interest.

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Xile Hu was born in 1978 in Putian, China. He received a B.S. degree from Peking University (2000) and a Ph.D. degree from the University of California, San Diego (2004; advisor: Prof. Karsten Meyer). He carried out a postdoctoral study at the California Institute of Technology (advisor: Prof. Jonas Peters) before joining the École Polytechnique Fédérale de Lausanne (EPFL) as a tenure-track assistant professor in 2007. He is currently associate professor at the same institute. His research interests span from organometallic chemistry, synthetic methodology, and reaction mechanism to bio-mimetic and bio-spectacled coordination chemistry to electrocatalysis and artificial photosynthesis.

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REFERENCES


(26) The films are labeled M-MoS2x films here rather than M-MoSx in the original paper. This is because the active catalyst in various amorphous molybdenum sulfide catalysts is now known to be MoS2x. In the original paper, the MoSx label was referred to the precatalyst.


