



Contents lists available at ScienceDirect

## Applied Catalysis B: Environmental

journal homepage: [www.elsevier.com/locate/apcatb](http://www.elsevier.com/locate/apcatb)

## Insight into the superior activity of bridging sulfur-rich amorphous molybdenum sulfide for electrochemical hydrogen evolution reaction

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## ARTICLE INFO

## Keywords:

Bridging sulfur  
Amorphous molybdenum sulfide  
Electrocatalyst  
Hydrogen evolution reaction

## ABSTRACT

Hydrogen evolution reaction (HER) activity of the molybdenum sulfide-based electrocatalysts originates from diverse types of active sulfur (S) sites, different S configurations, the ratio of molybdenum to S, and the crystallinity. The bridging  $S_2^{2-}$  has been considered as the major active site for HER. However, to realize more efficient electrocatalysts, newer architectures based on molybdenum sulfide are required to allow more active S sites beyond the endemic structural limits. Hence, the facile aging approach is used to maximize the bridging  $S_2^{2-}$  in amorphous molybdenum sulfide by adding  $(NH_4)_2S_x$ , leading to the highest proportion of bridging  $S_2^{2-}$  (up to 67%). Additionally, the effect of S configuration on HER activity in molybdenum sulfide is systematically studied by controlling of the amount of bridging  $S_2^{2-}$ . The bridging S-rich electrocatalysts exhibits an excellent HER activity with low onset potential of  $-96$  mV and Tafel slope of  $46$  mV dec<sup>-1</sup>, and stability for 1000 cycles.

## 1. Introduction

The energy and environmental crisis facing the world have required clean, sustainable, and load-balanceable energy paradigm beyond the existing fossil fuel-based system. Molecular hydrogen ( $H_2$ ) produced by water splitting have been expected to realize the global demand for the energy. To popularize this process, numerous studies have been carried out to develop efficient and cheap electrocatalysts for the hydrogen evolution reaction (HER) [1–4]. Electrocatalysts based on molybdenum sulfides are some of the most promising materials for HER due to their low Gibbs free energy ( $\sim 0.08$  eV) for hydrogen adsorption [5]. Among the various kinds of molybdenum sulfides, crystalline molybdenum disulfide (c-MoS<sub>2</sub>) based electrocatalysts have been extensively investigated for decades [6–17]. However, c-MoS<sub>2</sub> exhibits less HER activity than platinum, which is commercially available one with the highest activity in acidic solutions. This results from a relatively narrow electrochemically active area in c-MoS<sub>2</sub>. It is known that only the edge of the c-MoS<sub>2</sub> was electrochemically active, while the basal plane was electrochemically inert [5].

Innovative designs for molybdenum sulfides have been considered to improve this critical issue [18–21]. Thiomolybdate clusters,  $[Mo_3S_{13}]^{2-}$  on a graphitic paper or carbon nanotubes, are known to have intrinsically exposed sulfur atoms throughout the surface of the clusters unlike c-MoS<sub>2</sub>, leading to the best activity among molybdenum sulfide based electrocatalysts [22,23]. It was experimentally proved by the selective removal of sulfur (S) that the major active sites in molybdenum sulfides were bridging S sites in the clusters, while the terminal S sites were electrochemically inert [24,25]. From a structural viewpoint, S atoms are preferentially bonded to molybdenum as terminal S rather than bridging S configuration, since the terminal S with saturated  $S^{2-}$  state is more stable than the bridging S with unsaturated  $S_2^{2-}$  state. Therefore, it is necessary that bridging S-rich molybdenum sulfides should be newly designed to enhance HER activity up to the level of platinum.

Recent studies reported a simple strategy to synthesize molybdenum sulfides with higher S/Mo ratio, in order to increase the bridging  $S_2^{2-}$  configuration in molybdenum sulfides [8]. Ye et al. synthesized MoS<sub>x</sub>/CNT nanospheres ( $x = 3.8$ ) by ultrasonic spray and pyrolysis at 300 °C

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