

Study on the active sulfur site of thiomolybdate clusters on carbon nanotubes for hydrogen evolution reaction

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Introduction

Hydrogen has been one of the most promising energy sources and it could innovatively change the current fossil fuel system which induce energy and environmental crisis. Producing hydrogen by an environmentally friendly pathway is a critical issue and electrolysis of water using highly active catalysts is one of ways for realizing cost effective hydrogen production. Even though platinum has been used as a catalyst, there are efforts to develop alternatives due to high cost of platinum. Molybdenum sulfides exhibited an excellent hydrogen evolution reaction (HER) activity and stability due to the low Gibbs energy at edge sites of molybdenum sulfides. However, it is well known that only edge sites are reactive and basal plane of the molybdenum sulfides is inactive for HER.¹⁻³ Therefore, it should be studied to increase active sites of molybdenum sulfides for using them as practical catalysts.

In this study, a simple and solid transition from amorphous MoS₃ to the [Mo₃S₁₃]²⁻ clusters was demonstrated using an addition of sulfur sources, which resulted in synthesis of highly active and reliable clusters after being loaded on commercial multiwall carbon nanotubes.

Materials and Methods

MoS₃ of 0.1 g was dispersed in 40 mL of 25~28 % ammonium hydroxide solution (NH₄OH, Daejung, Korea) by bath-sonication for 10 min. Then, the mixture was kept for 1, 2, 3, 4, and 7 days at room temperature. Precipitates were collected by filtration and washing using DI water followed by freeze drying. MWCNTs (TMC 220-05, Nano Solution, Korea) of 0.1 g were dispersed in 100 mL of HNO₃ (30 wt%) and H₂SO₄ (70 wt%) mixture using a bath sonicator. The mixture was reacted in a round flask with an installed condenser. The reaction was carried out with magnetic stirring for 6 h at 50 °C. Subsequently, the resulting suspension was diluted by adding DI water slowly. Finally, O-CNT was obtained by filtration and washing using DI water followed by drying in vacuum oven at 60°C.

Mo₃S₁₃/O-CNT of 0.1 g was placed in a quartz tube and heated to 280, 340, 400, and 460 °C, respectively, with heating rate of 5 °C/min, and maintained at the corresponding temperature for 30 min. After cooling to room temperature, electrocatalysts were obtained. All heat treatments were conducted in N₂ flowing atmosphere at 200 sccm.

Results and Discussion

The resulting electrocatalysts, [Mo₃S₁₃]²⁻/MWCNT, showed excellent electrochemical HER activity with onset potential of ~ 100 mV, Tafel slope of ~ 40 mV/decade, and stability for 1,000 cycles with ~ 5% decay. After an additional low temperature treatment, an active sulfur bonding

was identified using XPS and electrochemical analyses. It was observed that electrocatalytic activity of catalysts decreased significantly when bridge sulfur in the cluster was selectively removed. Therefore, it is evident that bridge and apical sulfurs play an important role to realize the highly active and stable catalysts.⁴

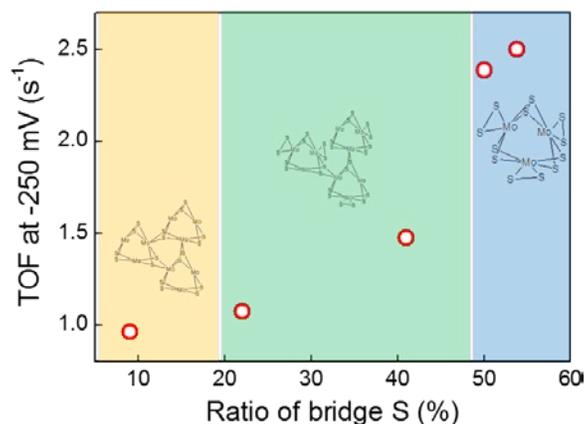


Figure. Turnover frequency at 250 mV as a function of ratio of bridge sulfur

Conclusions

The electrocatalyst, $[\text{Mo}_3\text{S}_{13}]^{2-}$, using amorphous MoS_3 was synthesized, and its structural transition was investigated. During an affordable heat treatment, amorphous MoS_3 changed to molybdenum sulfide clusters, and some amounts of molybdenum sulfide clusters were completely degraded to S and Mo ions, simultaneously. Subsequently, remaining molybdenum sulfide clusters and S ions were reacted. Finally, Mo_3S_{13} crystals were formed and they were loaded on O-CNTs. The as-synthesized $\text{Mo}_3\text{S}_{13}/\text{O-CNT}$ showed good electrochemical HER performance and stability for 1000 cycles with a low overpotential of -137 mV at 10 mA/cm² and Tafel slope of 40 mV/decade.

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