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Full Length Article

Amorphous MoS_2 nanosheets grown on copper@nickel-phosphorous dendritic structures for hydrogen evolution reaction

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ABSTRACT

In this study, we introduce highly active, efficient, and Pt-free electrodes (Cu@Ni-P@a-MoS_2) fabricated on Ni foils, which have good conductivity and several a-MoS_2 edge sites for the hydrogen evolution reaction (HER). A porous Cu dendritic structure on Ni foil was made by electro-plating utilizing hydrogen bubbles, and a Ni-P film that covered the dendritic structure was made by electro-less plating. Vertically grown a-MoS_2 nanosheets were formed on the Cu@Ni-P dendritic structure by thermolysis. The structure has abundant active sites because of its particular structure, which was examined by SEM and TEM. XPS analysis was used to confirm that MoS_2 was reduced completely, and the a-MoS_2 nanosheet layer was characterized by Raman spectroscopy. Electrochemical experiments demonstrated that the electrode was highly effective for the HER with a low onset potential of 118.5 mV, and a current density of 10 and 100 mA/cm^2 for 186 and 345 mV versus the reversible hydrogen electrode potential (vs RHE), respectively, a small Tafel slope of 60.5 mV/dec, and was stable after 2000 cycles. This study demonstrates that highly porous Cu@Ni-P@a-MoS_2 electrodes, possessing a huge surface, are desirable for the HER and these findings will pave the way for a new form of highly efficient electrocatalysts.

1. Introduction

New energy sources are required because of global warming and the worldwide shortage of fossil fuels. Hydrogen is a promising alternative since it can be easily obtained by splitting of water and its supply is inexhaustible. One kilogram of hydrogen can produce about 35,000 kcal when it combines with oxygen, and from an energy viewpoint, this amount is about three times that obtained from butane, propane, gasoline, and kerosene. Unlike other fuels, hydrogen does not create carbon dioxide, which can pollute the air and global warming.

The most efficient candidate for a catalyst for the hydrogen evolution reaction (HER), which is the basic reaction in water splitting, is Pt, but its high cost and scarcity inhibit its application. Thus, earth abundant catalysts such as Ni-alloys and transition metal dichalcogenides (TMD) which is MX_2(M = Mo, W/X = S, Se) have been explored by researchers.

Strategies to make TMD-based catalysts more active include increasing conductivity with carbon material, exposing the active edge sites, and doping effective metals like Co. In order to achieve better conductivity of TMD-based catalysts, researchers have combined carbon materials such as graphene nanosheets [1–13], amorphous carbon [14,15], and carbon nanotubes (CNTs) [16]. Another method of improving conductivity is by using metallic 1T-MoS_2 instead of semiconducting 2H-MoS_2, but 1T-MoS_2 is unstable with increasing temperature [17–19]. Doping nanoparticles also enhances conductivity by reducing he charge transfer resistance [20–22]. Some groups have synthesized vertical MoS_2 to expose the edge sites, which are more active and efficient for the HER than the basal plane [23,24]. In addition to these methods, double gyroid networks [25], template synthesis [26,27], MoS_2 nanorose [28], defect-engineered MoS_2 [29–31], amorphous MoS_2 [32,33], pH controlled synthesis [34], MoS_2 edge modified by UV-ozone [35], and MoS_2/(Ni foam@Graphene) [36,37] have made the catalyst more active.

Nickel is known as an effective catalyst, but it is unstable in acid. There have been efforts to find reasonable over-potentials

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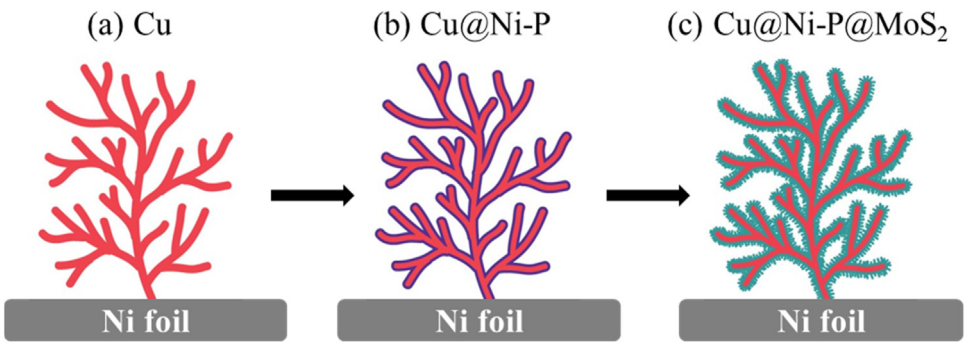

Fig. 1. Fabrication of a-MoS_2 nanosheets grown on Cu@Ni-P dendritic structure. (a) Electrodeposition of Cu dendrite, (b) electroless plating of Ni-P on Cu dendrite, (c) synthesis of a-MoS_2 nanosheets on Cu@Ni-P dendritic structure.

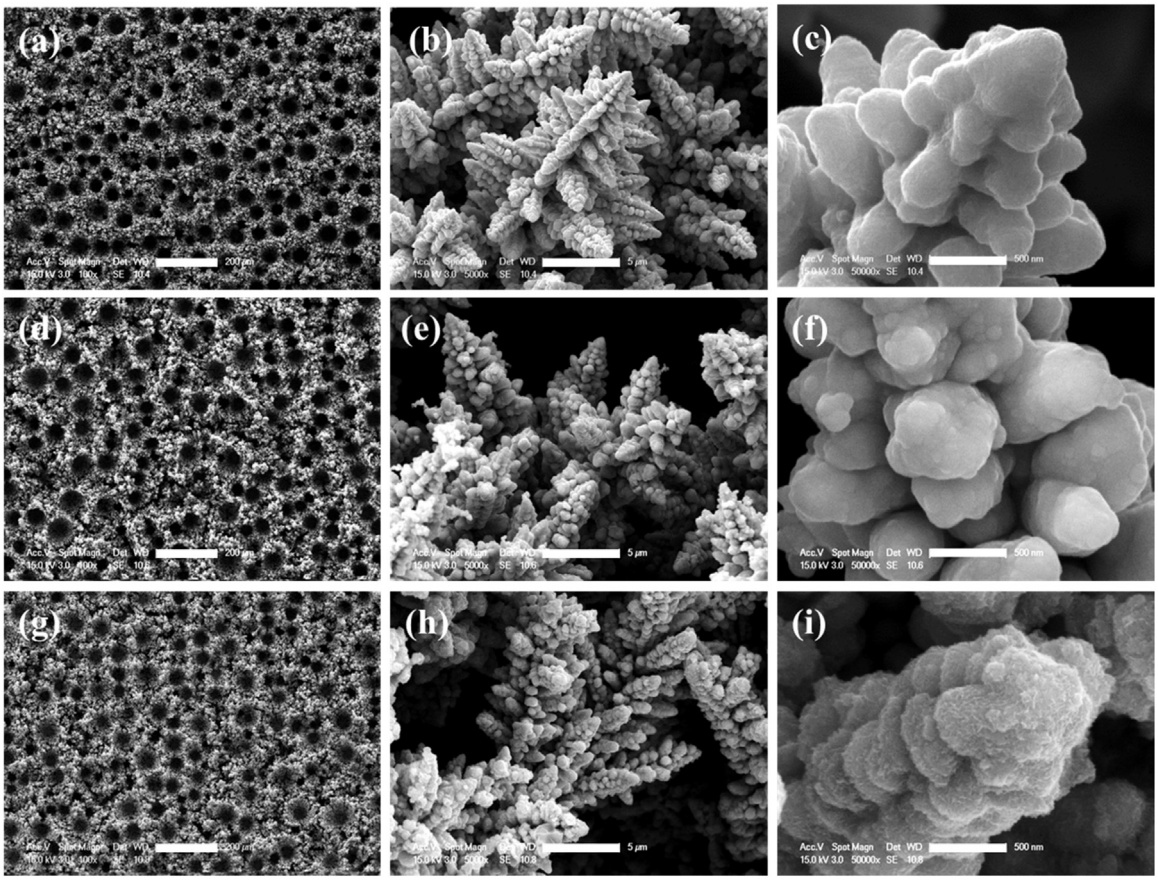

Fig. 2. SEM images of (a–c) Cu dendrites, (d–f) Cu@Ni-P dendrites, and (g–i) a-MoS_2 nanosheets grown on Cu@Ni-P dendrites (Cu@Ni-P@a-MoS_2). Panels (b, e, and h) and (c, f, and i) are high magnification top-view images, respectively. (Scale bar – 200 μm (a, d, g), 5 μm (b, e, h), 500 nm(c, f, i)).

that do not dissolve pure Ni foam in acid [38]. Recently, Fan et al. investigated atomically isolated nickel species anchored on graphitized carbon by starting with Ni based metal-organic framework (MOF). Its performance of 10 mA/cm^2 for −34 mV and a Tafel slope of 41 mV/dec is the best value so far for the HER compared to acid-stable and earth-abundant catalysts [39]. Other efforts to accomplish better performance for Ni-based HER catalyst have been made using Ni_3Se_2 nanoforests [40], high-index faceted Ni_3S_2 nanosheets [41], crystalline-amorphous Ni-NiO core-shell nanosheets [42], nickel phosphide nanoflakes [43], electrodeposited nickel-sulfide films [44], electro-deposited nickel-phosphorous nanoparticles film [45], nickel composites [46], nanostructured nickel sulfides [47], Ni_2P on MoS_2 hybrid [48], electrodeposited Ni-Co-S nanosheet film [49], and 3D-MoS_2@Ni Core-shell nanosheets [50].

In the present study, we report a unique structure consisting of a-MoS_2 nanosheets that have been prepared via electro-deposition, electro-less deposition, and thermolysis and investigate its catalytic properties. Unlike Ni foam, a Cu dendritic structure on Ni foil can achieve a higher surface area since its fabrication can be controlled by increasing or decreasing the deposition time. A Ni-P film is formed by electro-less deposition to cover the structure as Ni-P is more stable than Cu under acid [56]. The a-MoS_2 nanosheets were formed vertically on the structure to exploit the large surface area, which provides growth sites for a-MoS_2 (Fig. 1). The complete structure showed enhanced HER performance ascribed to the