INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–9

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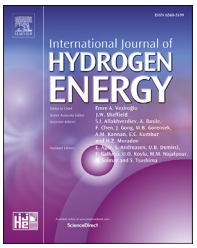

Highly efficient electrocatalytic hydrogen production via MoS_x/3D-graphene as hybrid electrode

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ARTICLE INFO

Article history:
Received 10 December 2016
Received in revised form
10 April 2017
Accepted 18 April 2017
Available online xxx

Keywords:
Molybdenum sulfide (MoS_x)
Hydrogen evolution reaction (HER)
Electrocatalytic reaction
Graphene

ABSTRACT

Molybdenum sulfide (MoS_x) has recently emerged as a promising catalyst for the hydrogen evolution reaction (HER) in water splitting that may replace the noble metal, such as platinum, as a cost-effective and high catalytic materials. It has been reported that two-dimensional structured MoS_x exhibit significant amount of exposed S-edge, which can be an active electrocatalytic catalyst for hydrogen production. However, the current reports mainly focusing on the planar electrode, where the catalyst utilization and the number of active sites are limited due to the lower exposed specific surface area (SSA) of supporting electrodes. In this work, we utilize the freeze-drying method to produce a porous three-dimensional (3D) structure assembled by graphene flakes. The as-prepared 3D graphene scaffold shows high surface area, high porosity while low density, which makes it as an ideal conductive electrode for supporting of MoS_x catalysts. Moreover, it was found out that the crystallinity of MoS_x, controlled by thermolysis temperature of thiosalts precursor ($(NH_4)_2MoS_4$), shows significantly influence the performance of HER. The optimized annealing temperature for the designed hybrid electrodes (MoS_x/3D-graphene) was found to create a lot of active sites, which facilitate the electrocatalytic performance for water splitting (overpotential of 163 mV @10 mA/cm^2 and a Tafel slope of 41 mV/dec). The study provides a potential material, which could pave the way for future applications of hydrogen energy.

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Introduction

It is an urgent task to search for the renewable and sustainable energy. Hydrogen energy is regarded as a clean and one of the most promising candidates for future energy carrier. Noble metal, such as platinum, was frequently used as a metal catalyst for electrochemical reaction and shows excellent efficiency in the hydrogen evolution reaction (HER) [1,2]. However, the expensive cost and poisoning induced degradation hinder its mass production and practical usage. Thus it becomes urgent to develop novel materials to yield highly catalytic activity for the electrochemical HER, these including precious metal, metal alloys [3,4], metal phosphides [5,6], metal sulfides [7], metal hydroxides [8–11], and carbides complexes [12,13]. Currently, the molybdenum disulfide (MoS_2) was regarded as a potential HER catalyst due to its large

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http://dx.doi.org/10.1016/j.ijhydene.2017.04.199
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Please cite this article in press as: Hung Y-H, Su C-Y, Highly efficient electrocatalytic hydrogen production via MoS_x/3D-graphene as hybrid electrode, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.04.199

amount of exposed reactive sulfur sites at the edges, which have attracted intense interest in the research society [14–16]. However, it is critical to increasing the exposed edge sites of MoS_2 to facilitate the HER performance since MoS_2 layered structure were easily re-stacked, thus decreases the amount of exposed active sites [17–20]. Therefore, a particular structure, like vertically aligned MoS_x, is considered to avoid this issue by sustaining a large number of exposed reactive edge sites [21].

In addition, the carbon-related materials such as fullerene, carbon nanotubes (CNTs), and graphene, has been evidenced to be ideal supporting electrodes that could facilitate the charge transfer efficiently through carbon materials to catalysts [22]. Graphene, a honeycomb lattice, arranged by carbon atoms with sp^2 bonding, shows high electrical conductivity, chemical stability and high specific surface area, which was a promising scaffold electrode to uniformly distribute and support versatile and functional nanoparticles [23]. Among various graphene materials by different synthesis approaches [24,25], graphene oxide (GO) has frequently been selected as supporting materials for catalyst due to the scalable production and cost-effective procedures [26]. Moreover, it has been reported that the 3D macroporous graphene monolithic can be made by self-assembly of GO flakes, which was regarded as ideal hybrid composite electrodes for electrochemical applications due to their high specific surface area and electrical conductivity. Therefore, until now, intensive efforts have been devoted to the synthesis of MoS_2/graphene composites by solvothermal and microwave methods [20,27–29], which shows high electrocatalytic activity in HER. However, most the reported works fabricate the 3D hybrid electrodes by randomly mixing MoS_2 with graphene flakes [15,30], where the as-prepared electrodes show higher internal series resistance and higher charge transfer resistance, leading to the limit enhancement on HER performance. Moreover, the procedures are time-consuming and show lower efficiency on active sites (inside the electrode) accessibility [15,30]. The ideal structure of MoS_x catalyst conformably supported on 3D graphene electrode have not yet been reported.

In this work, we report a simple approach to the in-situ synthesis of MoS_x nanoparticles supported on the high porosity of 3D graphene electrode by self-assembly of reduced graphene oxide (rGO), demonstrating a controllable crystallinity of MoS_x/rGO composites as catalysts for HER applications. In contrast to the hybrid composite made by hydrothermal method, where the non-efficient charge transfer result in degradation of HER performance. The present work composed a two-step procedure: (1) Self-assembly of 3D graphene by freeze drying process and (2) the formation of nanosized MoS_x decorated on the surface of 3D-graphene by a thermolysis method [29,31,32]. The morphology and crystallinity of as-prepared MoS_x/rGO composite electrode were investigated. The electrochemical characterizations on HER were comprehensively investigated. Moreover, the different degree of MoS_x crystallinity on 3D graphene was adjusted by altering various annealing temperatures. It was found out that 3D-graphene scaffold plays a crucial role as an ideal conductor in the hybrid electrode, which provides lots of charge transport pathway and high SSA of exposed MoS_x nanoparticles for high electrocatalytic activity. The result shows an optimized thermolysis condition at 100 °C, where the MoS_x/rGO composite shows the excellent catalytic activity of HER with higher current densities and lower overpotential.

Experimental section

Synthesis of graphene oxide (GO)

Graphene oxide (GO) were prepared from natural graphite powder by the improve Hummers method [33]. The detailed procedure was as follows: 3 g of graphite powder was mixed with the mixture solution of concentrated H_2SO_4 (96%) and H_3PO_4 (85%) (3:1 in 360 mL). Then 18 g of $KMnO_4$ was slowly added to the mixture, followed by stirring in an ice-bath for 10 min. The solution was kept at a reaction temperature below 50 °C and stirred for another 12 h. Afterward, 30 mL of H_2O_2 (30%) and then 400 mL of DI water were added into the mixture under an ice-bath. The obtained solution was centrifuged at 9000 rpm and dissolved in an HCl solution (1:10) to remove the residual metal ion, followed by rinsing with a large amount of DI water repeatedly until the pH reached neutral. The segregated GO was obtained after centrifuging at 9000 rpm for 30 min, and then it was weighted and re-dispersed in DI water to get a GO aqueous solution (10 mg/mL).

Preparation of MoS_x/3D-graphene hybrid electrodes

To prepare the 3D-graphene sponge, the GO aqueous solution (the optimized concentration is 10 mg/mL in regards to the mechanical strength of the graphene monolith) was firstly frozen by liquid nitrogen. Then it was placed into a freeze dryer chamber, followed by sublimation of the resulting solid ice under a pressure of 1×10^{-3} Torr for 24 h. Before the decoration of MoS_x catalyst on graphene electrodes, an additional thermal reduction process was performed in a typical furnace under a mixture gas of H_2/Ar (20/80 sccm) at 1000 °C for 15 min. The volume of 3D-graphene sponges for all conditionals were cut to ~$0.1 \times 0.5 \times 1.5$ cm^3. The average loading amount of MoS_x ($x = 2.6–1.8$) catalyst were estimated to be 0.69 mg/cm^3 ($MoS_{2.6}$) and 0.55 mg/cm^3 ($MoS_{1.8}$).

The active MoS_x catalyst, supported on 3D graphene sponge (denoted as MoS_x/rGO in followed discussion), was synthesized by thermolysis method as follows: First, the MoS_x precursor was prepared from an ammonium thiomolybdate solution, where 50 mg of $(NH_4)_2MoS_4$ was added into 5 mL of DMF and then sonicated for 30 min. Next, the 3D-graphene sponge was immersed in the MoS_x precursor under vacuum for 15 min, follow by baking at 100 °C for 20 min. Then, the MoS_x/3D-graphene were annealing in H_2/Ar (20:80 sccm) atmosphere in a furnace at various temperature (100 °C, 200 °C, 300 °C, 400 °C).

Characterizations

The SEM images were performed in a JEOL-6330F instrument. XPS was obtained using a Ulvac-PHI 1600 spectrometer with monochromatic Al KR X-ray radiation (1486.6 eV). The Raman spectra were recorded in an HORIBA confocal Raman microscopy system (Jobin Yvon HR800; the laser wavelength was 532 nm, the laser spot size was ~0.5 μm, and the Si peak at

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