Chemical Engineering Journal 315 (2017) 355–363

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Aerosol synthesis of molybdenum diselenide–reduced graphene oxide composite with empty nanovoids and enhanced hydrogen evolution reaction performances

Seung-Keun Park [a,1], Gi Dae Park [b,1], Dongjin Ko [a], Yun Chan Kang [b,*], Yuanzhe Piao [a,c,*]

[a] Program in Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, 145 Gwanggyo-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-270, Republic of Korea
[b] Department of Materials Science and Engineering, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea
[c] Advanced Institutes of Convergence Technology, 145 Gwanggyo-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-270, Republic of Korea

HIGHLIGHTS

- $MoSe_2$–rGO composite powders with empty nanovoids are prepared by spray drying process.
- Tafel slopes for bare $MoSe_2$ and $MoSe_2$–rGO composite powders are 120 and 57 mV dec^{-1}, respectively.
- $MoSe_2$–rGO composite powders with unique porous structure showed outstanding HER performances.

ARTICLE INFO

Article history:
Received 17 October 2016
Received in revised form 19 December 2016
Accepted 10 January 2017
Available online 11 January 2017

Keywords:
Molybdenum diselenide
Porous structure
Reduced graphene oxide
Hydrogen evolution reaction
Spray drying

ABSTRACT

$MoSe_2$–reduced graphene oxide (rGO) composite powders with unique structures containing empty nanovoids and excellent hydrogen evolution reaction (HER) performances were prepared using a pilot-scale spray-drying process. One-step post-treatment of the spray-dried powders produced the macroporous $MoSe_2$–rGO composite with empty nanovoids through an intermediate MoO_3–Se–GO composite. Ultrafine $MoSe_2$ nanocrystals, which consisted of a few layers and were several nanometers in size, were uniformly dispersed on the surfaces of the $MoSe_2$–rGO composite powders with the optimal rGO contents. The $MoSe_2$–rGO–M composite (20 wt% rGO) had the optimized porous structure with a uniform distribution of $MoSe_2$ nanocrystals and enough the rGO content for a fast electron transport, and thus exhibited the highest HER activity. The $MoSe_2$–rGO–M composite powders exhibited a current density of 10 mA cm^{-2} at a small overpotential of 0.21 V, which was lower than that of bare $MoSe_2$ (10 mA cm^{-2} at 0.31 V). The Tafel slopes for bare $MoSe_2$ and $MoSe_2$–rGO–M composite powders were 120 and 57 mV dec^{-1}, respectively. The synergistic effects of rGO sheets and $MoSe_2$ nanocrystals and the unique porous structure resulted in outstanding HER performance with a small Tafel slope and overpotential.

1. Introduction

Ever-increasing needs for energy consumption and depletion of conventional fossil fuels call for innovation in sustainable energy conversion technologies. Hydrogen, a promising energy carrier, has been widely utilized as an important fuel in sustainable energy conversion systems to replace conventional fossil fuels owing to its environmental friendliness and high energy density [1–3]. As for the production of hydrogen, the electrochemical water splitting has been proved to be eco-friendly and the most efficient technique, where hydrogen is generated from the electrochemical reduction of H^+ [1–5]. Platinum (Pt) and its alloy have been widely known as the best catalysts owing to their extremely high catalytic activity and small overpotential. However, the mass production of hydrogen has been hampered by the low abundance and high cost

* Corresponding authors at: Department of Materials Science and Engineering, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea (Y.C. Kang). Program in Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, 145 Gwanggyo-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-270, Republic of Korea (Y. Piao).
E-mail addresses: yckang@korea.ac.kr (Y.C. Kang), parkat9@snu.ac.kr (Y. Piao).
[1] These two authors contributed equally to this work.

http://dx.doi.org/10.1016/j.cej.2017.01.032
1385-8947/

of Pt. Considering this, many studies have centered on replacing Pt with earth-abundant catalysts having high activity.

Layered transition metal dichalcogenides (MX_2, M = Mo, W; X = S, Se), a class of two-dimensional (2D), graphene-like materials, have attracted extensive interest in many fields, including electrocatalysis, energy storage, and gas sensing [1–8]. Nanostructured MX_2 materials with the maximum number of active edge sites and high electrocatalytic activity have recently been studied as noble metal-free electrocatalysts for the hydrogen evolution reaction (HER) [9–11]. Indeed, electrochemical water splitting has been demonstrated to be an eco-friendly and highly efficient technique in which hydrogen is generated from the electrochemical reduction of H^+. Substantial efforts have been focused on maximizing the number of active edge sites and the conductivity of MX_2-based electrocatalysts to enhance their HER performance [12,13]. The nanostructured MX_2 composites with carbon-related materials, such as carbon nanotubes (CNTs) and graphene, have also been studied to improve the HER performance by ameliorating the low conductivity of metal dichalcogenides [14–16]. Such carbon-related materials can also maximize the number of active edge sites of MX_2 by minimizing the crystal growth during the preparation process [17–19].

Among the various transition metal dichalcogenides, MoS_2 materials have been widely studied because of their high chemical stability and excellent electrocatalytic performance [20–22]. The improved HER performances of composites of MoS_2 and carbon-related materials have also been investigated. $MoSe_2$'s crystal structure is similar to that of MoS_2 [23,24]. Therefore, a few research groups have studied the synthesis and HER performances of composites of $MoSe_2$ and carbon-related materials [25–28]. Mao et al. demonstrated a high-performance HER catalyst composed of a 3D graphene network supporting perpendicularly oriented $MoSe_2$ nanosheets [15]. Qu et al. synthesized ultrathin $MoSe_2$ nanosheets with rich defects grown on the surface of carbon fiber cloth by a facile solvothermal method [27]. The resulting nanosheets exhibited excellent HER activity, including a small onset potential, a large exchange current density, and a small Tafel slope. Huang et al. synthesized a unique hierarchical nanostructure consisting of few-layered $MoSe_2$ nanosheets that were perpendicularly grown on CNTs through a one-step solvothermal reaction [29]. Their nanosheets exhibited HER activity with a low onset potential of −0.07 V vs. the reversible hydrogen electrode (RHE), a small Tafel slope of 58 mV dec^{-1}, and excellent long-term cycling stability. In previous studies, the composites of MoS_2 and carbon-related materials have mainly been prepared via liquid solution processes. However, the use of an easily scalable process to produce composite powders of $MoSe_2$ and carbon-related materials with regular morphologies has not been investigated.

The spray-drying process, which is a gas-phase reaction process, has been established as a powerful and efficient method for the pilot-scale production of composites of metal compounds with carbon-related materials, including reduced graphene oxide (rGO), CNTs, and amorphous carbon [30–37]. The energy storage-related electrochemical properties of nanostructured metal oxides, sulfides, and selenides composited with carbon-related materials prepared by a simple spray-drying process have been widely studied [31,33–36]. However, to the best of our knowledge, the synthesis of $MoSe_2$–rGO composite materials with high rGO contents and their HER performances have not been studied. Here, the $MoSe_2$–rGO composite powders that have unique structures including empty nanovoids and exhibit excellent HER performances were prepared via a pilot-scale spray-drying process.

2. Experimental

2.1. Sample preparation

$MoSe_2$–rGO composite powders with three different rGO contents were prepared by a simple two-step process. The composite powders of ammonium molybdate, selenous acid, and GO nanosheets were prepared from a spray solution by a pilot-scale spray-drying process, as shown in Fig. S1. The temperatures at the inlet and outlet of the spray dryer were fixed at 250 °C and 120 °C, respectively. A two-fluid nozzle was used as an atomizer, and the atomization pressure was 2.0 bar. The concentration of ammonium molybdate was fixed at 0.063 M. The molar quantity of water-soluble SeO_2 added to the spray solution exceeded 800% of the stoichiometric amount required to form $MoSe_2$. The SeO_2 was dissolved in water to form selenous acid (H_2SeO_3). GO nanosheets were synthesized from graphite flakes by a modified Hummers method, as described previously [38]. The appropriate amount of GO nanosheets was then redispersed in the spray solution containing ammonium molybdate and selenous acid. The spray-dried product was post-treated at 300 °C for 12 h in a 10% H_2/Ar gas atmosphere to form the $MoSe_2$–rGO composite powders.

2.2. Characterization

The crystal structures of the $MoSe_2$–rGO composite powders were investigated using X-ray diffractometry (XRD) (X'pert PRO MPD) with Cu K_α radiation (λ = 1.5418 Å). The morphological features were investigated using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100F) at a working voltage of 200 kV. The chemical states and molecular environments of the composite powders were examined using X-ray photoelectron spectroscopy (XPS), (ESCALAB-210) with Al K_α radiation (1486.6 eV). Thermogravimetric analysis (TGA; SDT Q600) was performed in air at a heating rate of 10 °C min^{-1} to determine the rGO contents in the composite powders. The specific surface areas of the composite powders were calculated by performing a Brunauer–Emmett–Teller (BET) analysis of nitrogen-adsorption measurements (TriStar 3000).

2.3. Electrochemical measurements

The prepared samples (5 mg) were dispersed in 1 mL of a binary mixture of N,N-dimethylformamide (DMF)/deionized (DI) water (1:1 v/v%) with 50 μL of Nafion (5 wt%, Aldrich) by sonication for at least 30 min to form a homogeneous ink. We used a DMF solvent for better dispersity of the samples. Then, 10 μL of the above ink was dropped onto a glassy carbon electrode (GCE, 5 mm in diameter) to obtain a modified GCE. For comparison, a commercially available Pt/C (20 wt%, Johnson Matthey) modified electrode was prepared in the same manner. Electrochemical measurements were performed using an Autolab potentiostat (Metrohm, PGSTAT 302N) in a standard three-electrode cell, in which a Pt sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All of the potentials were calibrated relative to the RHE. The electrocatalytic activity of the catalysts was examined via linear sweep voltammetry (LSV) in N_2-purged, 0.5-M H_2SO_4 at a scan rate of 10 mV s^{-1} at 298 K. To create Tafel plots, the linear regions were fit with the Tafel equation. Alternating current (AC) impedance measurements were conducted from 10^{-1} to 10^6 Hz with an AC amplitude of 5 mV (CHI, 660E). No iR compensation was applied to any of the electrochemical measurements.