Short Communication

Graphene Loading Molybdenum Carbide/Oxide Hybrids as Advanced Electrocatalysts for hydrogen evolution reaction

Xinxin Li [a,b,c], Suqin Ci [a,**], Jingchun Jia [b,c], Zhenhai Wen [b,c,*]

[a] Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, PR China
[b] Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China
[c] Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

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ABSTRACT

The rational design of cost-effective and high-activity electrocatalyst for hydrogen evolution reaction (HER) is a crucial field of research for achieving the best way to promote "green energy". Here, we develop a simple route to prepare nanohybrids of three-dimensional graphene loading MoO_2-Mo_2C nanoparticles (MoO_2-Mo_2C/G), which were characterized using X-ray diffractometer (XRD), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), demonstrating the MoO_2-Mo_2C/G has unique features with high conductivity, robust structure, and high surface area. The as-developed MoO_2-Mo_2C/G nanohybrid shows great potential to replace Pt-based electrocatalyst for hydrogen evolution reaction (HER) due to its cheapness, high catalytic activity and considerable stability.

Introduction

Hydrogen (H_2), as a renewable clean fuel, has attracted worldwide research interest with purpose to develop efficient and low-cost strategy for its large-scale production [1–8]. Hydrogen evolution reaction (HER), as the half reaction of electrolysis of water, is the most promising route for achieving scale-up production [9]. The platinum-based material is generally recognized as the most active catalyst for HER [10]. Unfortunately, scarcity and high cost of platinum limited its application [11,12]. In this regard, it is a highly desirable for developing Pt-alternative electrocatalyst of HER. Accordingly, a variety of Pt-alternative electrocatalysts have recently been

* Corresponding author. Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China.
** Corresponding author.
E-mail addresses: sqci@nchu.edu.cn (S. Ci), wen@fjirsm.ac.cn (Z. Wen).

reported [3,9], including sulfides [13,14], borides [15], carbides [16,17], phosphides [18,19], nitrides [20,21]. Within the last year transition metal compounds (TMX, X = S, B, C, P, N) have also emerged as highly active and acid stable HER catalysts. Especially to deserve to be mentioned, due to the low cost and highly catalytic activity, Mo-based electrocatalyst have been widely studied [22–24], however, the development of Mo-based electrocatalyst at least faced the following two challenges. On one hand, it still remains challenge to implement synthesis of high-activity Mo-based nanomaterial in a convenient and cost-effective way; On the other hand, the low conductivity of Mo-based electrocatalysts hinders it from achieving the optimal catalytic activity. Therefore, it is a challenge to get an advancing catalytic activity and conductivity of Mo-based HER electrocatalyst.

In order to overcome the above shotcomings, we herein report a convenient route to prepared graphene loading Mo-based nanohybrids (MoO_2–Mo_2C/G), in which MoO_2–Mo_2C nanoparticles cluster were uniformly distributed on hierarchical three dimensional (3D) structured graphene, with excellent HER performance. We know that molybdenum carbide is investigated mostly, because of its low cost, high melting point, and catalytic activity [25–27]. Moreover, MoO_2 possesses merits such as low electrical resistivity ($8.8 \times 10^{-5} \Omega cm^{-1}$), high melting point, high chemical stability, besides, the Mo edge and O edge are both active sites of MoO_2 which is the key factor that renders MoO_2 a catalyst [28]. However, the easy aggregation of Mo_2C and MoO_2 may affect the proton and electron transfer during hydrogen evolution reaction, meanwhile, the low conductivity could also lead to the occurrences of this phenomenon. Fortunately, the graphene possess large surface area and highly conductivity, on this basis, graphene Loading Molybdenum Carbide/Oxide Hybrids as Advanced Electrocatalysts can be avoided the aggregation of nanoparticles and improving conductivity of materials. Therefore, the addition of graphene lead to MoO_2–Mo_2C/G nanohybrid shows great potential to replace Pt-based electrocatalyst for hydrogen evolution reaction.

Experimental

Synthesis and materials characterization

MoO_2 (99%) was purchased from sigma-aldrich, and Mo_2C (99%) was purchased from Alfa Chemistry. $(NH_4)_2Mo_4O_{13} \cdot 4H_2O$ (99.9% metals basis), and aniline (≥99.0%) were purchased from Aladdin. All aqueous solutions were freshly acquired with deionized water (≥15 M Ω cm, Elix, France) for all experiments. The samples were characterized by using scanning electron microscope (SEM, NOVA NANO-SEM450), transmission electron microscopy (TEM, JEM-2010), powder X-ray diffraction (XRD, Bruker D8), and nitrogen adsorption desorption isotherm measurements (Micromeritics TriStar II 3020).

Graphene oxides (GO) were synthesized by using a modified Hummers' method [29]. $(NH_4)_2Mo_4O_{13} \cdot 4H_2O$ (2.5 g) and aniline (3.3 g) were mixed with GO powder (0.5 g) with the assistance of grinding. Finally, MoO_2–Mo_2C/G samples were obtained by heating the mixtures at 750 °C under Ar

atmosphere for 2 h. The MoO_2–Mo_2C was also prepared as reference sample using the same method just without adding GO powder. As comparison, MoO_2/G and Mo_2C/G samples were also prepared by mixing the commercial powder of MoO_2 and Mo_2C with graphene (w/w 10:1), respectively.

Electrochemical measurements

The electrochemical measurements were carried out in a conventional three electrode electrochemical cell with a platinum wire as the counter electrode, an Ag/AgCl (3 M KCl) electrode as the reference electrode, and an electrocatalyst modified glassy carbon electrode as the working electrodes, respectively. The working electrode was prepared as follows: 5 mg catalytic materials were suspended in 475 μL water followed by adding 25 μL Nafion; after ultrasonication for 10 min, 6 μL of suspensions were dropped onto glassy carbon electrode and dried at room temperature. The catalyst loading was ~0.85 mg cm^{-2} on glassy carbon electrode. For comparison, commercial Pt/C (20% Pt) modified electrode was prepared using the same method. Before testing, electrolytes were purged with N_2 for 20 min to remove dissolved oxygen.

Result and discussion

The entire procedure for preparing the MoO_2–Mo_2C/G is quite simple, which includes the mixture of the precursors, i.e. GO, $(NH_4)_2Mo_4O_{13} \cdot 4H_2O$ and aniline, and the subsequent calcination at 750 °C. The crystallographic structure and phase are tested by X-ray diffraction (XRD) measurement. Fig. 1a presents the XRD pattern of the final products, i.e. MoO_2–Mo_2C/G. The set of main peaks at 2 theta of around 26.3°, 36.8°, 54.2° and 66.4° are well indexed to the (111), (211), (312) and (402) crystal planes of the pure MoO_2 (JCPDS: 32-0671); the other three minor diffraction peaks at 2 theta of around 37.7°, 43.7° and 63.4° are attributed to the (111), (200) and (220) crystal planes Mo_2C (JCPDS: 15-0457). It should be pointed out that the reduced graphene oxide possess two diffraction peaks at 26.1° and 43.3°, corresponding with the graphite (002) and (100) planes, are overlapped with the diffraction peaks of MoO_2. These results suggest that the precursor's mixtures, upon annealing under inert atmosphere, evolved to Mo-based nanohybrids with a dominating amount of MoO_2 with a small amount of Mo_2C. The XRD patterns was further analyzed by calculating the integral area of MoO_2 peaks and Mo_2C peaks for both MoO_2/Mo_2C (not show) and MoO_2–Mo_2C/G, respectively; both samples show a similar ratio of integral area between MoO_2 and Mo_2C, suggesting the small amount of reduced graphene oxide (~5%) does not significantly affect the phase ratio of MoO_2–Mo_2C. Tests based on energy dispersive spectrometer indicate both MoO_2–Mo_2C and MoO_2–Mo_2C/G have a similar molar ratio (i.e. ~3.0) between MoO_2 and Mo_2C.

N_2 adsorption–desorption isotherms and BJH pore size distribution analysis are carried out to assess the specific surface area and the porosity structure of the MoO_2–Mo_2C/G nanohybrids. Fig. 1b shows the N_2 sorption isotherms and the pore-size distribution of the MoO_2–Mo_2C/G, demonstrating the MoO_2–Mo_2C/G has a BET surface area of 64.4 m^2/g with a pore volume of 0.13 cm^3/g. The plot of pore size distribution