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Hierarchical molybdenum carbide/N-doped carbon as efficient electrocatalyst for hydrogen evolution reaction in alkaline solution

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ABSTRACT

Development of highly-active and noble-metal-free electrocatalysts for hydrogen evolution reaction (HER) is of critical challenge for water splitting, and optimizing the structure and the composition of the relative materials is very necessary to obtain the high-quality catalysts. Herein, a novel molybdenum carbide/N-doped carbon (Mo_2C/NC) hybrid is fabricated by using the hierarchical polyaniline tube network as a carbon source and a reactive template, and the as-fabricated Mo_2C/NC hybrid possesses a uniform hierarchical tube structure. The coupling of the ultrafine Mo_2C nanoparticles and the N-doped carbon substrate provides the abundant active sites and accelerates the charge transfer process. The final Mo_2C/NC catalyst gives the excellent catalytic activity for HER in alkaline condition, which shows a lower overpotential of 142 mV at 10 mA cm^{-2} and a small Tafel slope of 61 mV $decade^{-1}$ in 1 M KOH.

Introduction

Hydrogen (H_2) is a sustainable and renewable energy resource because of its high energy density and the clean nature [1,2]. However, current industrial production of H_2 always involves fossil fuels, which inevitably produce greenhouse gases under most conditions [3]. Water splitting by electrolysis to generate hydrogen has attracted much attention since the production process of H_2 from water is relatively simple and environmental friendly [2,4,5]. Hydrogen evolution reaction (HER) is a half-reaction of water electrolysis, in which platinum is the most active and catalytically stable catalyst; however, its scarcity and high cost make it impractical for global-scale applications [4]. Therefore, the search of platinum-free electrocatalysts, based on transition-metal elements (such as Fe, Co, Ni and Mo, W)-based materials, is particularly important for the development of hydrogen energy [6–10].

Transition-metal carbides are potential substitutes for platinum because of their low cost, high catalytic activity, selectivity, and good electrochemical stability under rigorous conditions [11]. Among carbide-based hydrogen evolution catalysts, molybdenum carbide is considered to be a promising one due to its "platinum-like" d-band structure and encouraging HER catalytic activity [12]. However, bare molybdenum carbide particles possess some drawbacks, such as poor process ability and easy aggregation. In order to enhance

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the HER performance, rational design of catalysts is very important, which contributes to expose the more Mo active sites of molybdenum carbide and to promote the diffusion and transport kinetics of HER [13–17].

Dispersing molybdenum carbide nanoparticles on conductive supports, such as carbon nanotubes or graphene, is usually used to enhance the catalytic performance of the catalysts [15,18]. It is well known that the hierarchical three-dimensional (3D) architecture can endow catalysts with high specific surface areas and porosity that facilitates fast diffusion of reaction species and consequently realizes high utilization efficiency of electrocatalysts. Furthermore exploration of interesting nitrogen doped carbon as a support to disperse molybdenum carbide nanocrystals is a valuable solution to achieve a high HER performance. Nitrogen-containing polymers, such as polypyrrole, polyaniline (PANI) and polydopamine, have been reported as template materials for constructing nitrogen-doped carbon matrix [19,20]. Although much progress has been achieved, these reported nitrogen-doped carbon shows a single morphology structure. On the other hand, molybdenum carbide-based HER catalysts are usually well in the acidic environment. However, many water-alkali electrolyzers need catalysts to perform actively and durably in a basic environment to couple with the oxygen evolution reaction. Unlike the acid condition, the hydrogen generation is much harder in alkaline solution, because this process needs to break the H-O-H bond before adsorbing active hydrogen atom in the surface of the catalyst, which introduces an accessional energy barrier and confines the total reaction rate [21]. The introduction of N atoms in carbon-based composite could tune the electronic structure of carbon skeleton and strengthen the interaction of H_2O on the surface through hydrogen bonding, which may accelerate the Volmer step and thus promote the overall HER process [22]. On the other hand, the nitrogen-containing carbon precursor also could introduce the N-Mo bond into the Mo_2C, which is a new active site for the HER [23]. Based on these considerations, it is necessary to obtain the molybdenum carbide catalysts in hierarchical nitrogen doped carbon substrate that possesses excellent performance under basic condition.

In this work, the hierarchical PANI tube was directly used as a template and single carbon source for the preparation of molybdenum carbide, and hierarchically porous molybdenum carbide hybrids were formed by in-situ high temperature solid-phase reaction. The PANI undergoes carbonization and helps the deoxygenation of ammonium molybdate, leading to the in-situ generation of the Mo_2C nanoparticles on N-doped carbon. The as-fabricated Mo_2C/NC hybrid exhibited excellent HER activity with a low overpotential of 142 mV for driving cathodic current density of 10 mA cm^{-2} in basic media, a small Tafel slope of 61 mV dec^{-1} and good stability.

Experimental section

Chemicals and materials

Aniline monomer (An, Sinopharm Chemical Reagent Corp, China) was distilled under reduced pressure before used. Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), citric acid monohydrate (CA), and ammonium persulfate (APS) were purchased from Sinopharm Chemical Reagent Co. Ltd, all of which were used as received. The commercial Pt/C powder (10 wt% Pt) was from the Aladdin Reagent Co. Ltd, Shanghai, China. All the experiments were carried out using the deionized water.

Synthesis of catalysts

Synthesis of PANI: The PANI was synthesized using a simple procedure [24]. 5 mmol CA and 10 mmol An were dissolved in 50 mL DI water with magnetic stirring to get a clear solution. Then the 25 mL APS aqueous solution (5 mmol) was added into the above mixed solution, and the reaction was carried out overnight below 5 °C. The resulting PANI precipitate was separated by filtration and washed with water several times. Finally, the green product was dried in an oven at 60 °C for 12 h.

Preparation of Mo_2C/NC Hybrids: First, 100 mg PANI was immersed in 0.05 M $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution for 24 h. After that, the precipitate was collected by filtration and dried under 60 °C overnight. To prepare the Mo_2C composite, the precursor was carbonized at 800 °C under argon/hydrogen (95%/5% in volume ratio) atmosphere for 3 h with a heating rate of 5 °C min^{-1}. For comparison, the Mo_2C/NC samples obtained with different reaction temperature and concentration of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were denoted as Mo_2C-700, Mo_2C-800, and Mo_2C-900, Mo_2C-0.01, Mo_2C-0.05, Mo_2C-0.1, respectively. The Mo_2C/NC hybrid represented the optimal HER performance sample of Mo_2C-800-0.05 unless otherwise specified.

Material characterization

The morphologies of the samples were observed by field emission scanning (FESEM; Hitachi S-4800, Japan) and transmission (TEM; JEOL, JEM-2100, Japan) electron microscopes. Powder X-ray diffraction patterns were recorded on a diffractometer equipped with Cu Ka radiation $\lambda = 1.5406$ Å (XRD; Bruker D8 Advance diffractometer). The micromeritics Tristar 3020 analyzer was used to measure nitrogen adsorption/desorption isotherms at the liquid nitrogen temperature. Raman spectrometry (Renishaw inVia) was obtained at the 514 nm laser under ambient conditions, and chemical state analysis of the sample was performed by X-ray photoelectron spectroscopy (XPS; AXIS Ultra DLD).

Electrochemical measurements

All electrochemical catalytic tests were performed with a standard three-electrode in CHI 660D electrochemical workstation (Chenhua Instruments Co, Shanghai, China) at room temperature. The working electrode was prepared as follows: 5 mg of catalyst was dispersed in 0.5 mL of ethanol containing 10 μL of 0.5 wt% Nafion. Then, the mixture was sonicated for 30 min to obtain the homogeneous slurry. Finally, 10 μL of the slurry was dropped onto glassy carbon electrodes (GCE) (diameter: 5 mm) and dried at room temperature to achieve catalyst modified electrode. The GCE modified with samples was applied as the working electrode, and a Ag/AgCl (saturated KCl) as the reference electrode and a graphite rod (Alfa

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