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RAPID COMMUNICATION

Hierarchical carbon nanopapers coupled with ultrathin MoS_2 nanosheets: Highly efficient large-area electrodes for hydrogen evolution

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Abstract
Design of large-area hybrid paper for directly using as electrodes in hydrogen evolution reaction (HER) can provide an efficient approach for the extension of electrochemical hydrogen industry. Here we construct MoS_2 decorated hybrid carbon papers (MoS_2-CPs) that consist of tiny MoS_2 nanosheets coupled with 3D graphene-carbon nanofiber papers. MoS_2-CPs can function as large-area working electrodes for HER with an overpotential (at 10 mA/cm^2) of 80 mV in acid media and 186 mV in basic media, surpassing the Mo-based catalysts ever reported thus far in acid and basic solution respectively. It is the highly coupled interface of carbon frameworks and MoS_2 components that resulted in the formation of patched and few-layer MoS_2 nanosheets with rather small size and thus ensured the abundance of exposed active edge sites. Stability tests through long-term potential cycles and extended electrolysis confirm the outstanding durability of MoS_2-CPs in both acid and basic electrolytes.

Introduction

With the energy crisis becoming more and more serious, hydrogen is considered as one of the most promising candidates substituting the fossil energy [1]. The search for high stability and low-cost sustainable electrodes for the splitting of water into hydrogen gas is one of the noble missions of hydrogen energy [2,3]. Pt based catalyst, the

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best hydrogen evolution reaction (HER) catalyst, is often deposited on electrodes to promote electrochemical hydrogen production [4]. As the most electroactive catalyst, Pt catalyst just requires negligible overpotential, even at high reaction rates [5]. However, the high price and scarcity have critically impeded the extensive applications of these electrochemical techniques for practical preparation of hydrogen fuels.

Recently, transition metal phosphides and chalcogenides as the non-precious metal catalysts have shown a striking electrocatalytic performance for HER [6–21]. Among these transition-metal based catalysts, layered molybdenum disulfide (MoS_2) has been widely used in both industry and fundamental researches as a cheap alternative of platinum with noble-metal-like catalytic activities [22–29]. There is a consensus that the catalytic sites of layered MoS_2 mainly arise from the active edges of two-dimensional layers and the (0001) basal planes of MoS_2 are catalytically inert. The bulk phase is relatively inert because the (0001) basal planes are the major on the surface [17]. Consequently, nanostructured MoS_2 catalysts have been well engineered to maximize the amount of exposed edges of the MoS_2 layers and thus boost their catalytic activity, including HER activity [30–32].

With respect to the practical use of those MoS_2 nanocatalysts, large-area electrodes with mesoscale to microscale pores are essential for releasing hydrogen bubbles via HER. Considering the intrinsic low electrical conductivity of MoS_2 with a band gap of 1.69 eV, the resistance of MoS_2 nanomaterials could be further elevated by a factor of several orders of magnification due to the increased number of grain boundaries in nanoscale [33]. Current efforts are thus mainly focused on painting the ink of nanocatalysts with binder to a conductive substrate (e.g. commercial carbon papers, Ni foams or even graphene-coated Ni foams) with microscale subunits to fabricate large-area MoS_2 thick films as practical electrodes [34–36]. Such a process obviously lead to a decrease in the HER activity as compared with that over glass carbon electrode (GCE), presumably due to the poor distribution of the MoS_2 nanocatalysts over the support [34]. Direct deposition of defect-rich and ultra-fine MoS_2 nanocatalysts on large-area conductive paper composed of nanoscale subunits promises great room for significantly elevating the HER activity of noble-metal-free electrocatalysts for practical applications [35,37–39].

Herein, we highlighted the fabrication of ultra-thin MoS_2 nanosheets decorated carbon papers (MoS_2-CPs) as large-area electrodes for HER. The defect-rich MoS_2 nanosheets with a size smaller than 15 nm and a mean layer number around 2–3 layers can function as electrocatalytic active sites here. The highly coupled MoS_2-CPs hybrid papers show superb activity and stability in both acid and basic media when directly used as electrode for HER.

Experimental section

CPs aerogels synthesis

The bacterial cellulose (BC) pellicles were kindly provided by Ms CY Zhong (Hainan Yeguo Foods Co., Ltd., Hainan, China). In a typical synthesis, the BC pellicles were first washed with deionized water and then dipped in a urea aqueous solution for 24 h. After frozen by liquid nitrogen and dried in a bulk dryer, white BC aerogels were generated. The resulting BC aerogels were transferred into a crucible with flowing-nitrogen and heated at 600 °C at a rate of 1 °C min^{-1}, kept this temperature for 1 h. This was followed by further heating at a rate of 1 °C min^{-1} to reach a temperature of 1000 °C and maintaining at that temperature for 1 h. The sample was then cooled naturally to room temperature within nitrogen gas, resulting in black and ultralight carbon papers (CPs).

Preparation of MoS_2-CPs

Briefly, 0.1 mL of $N_2H_4 \cdot H_2O$ and 55 mg of $(NH_4)_2MoS_4$ were dispersed into 10 mL of DMF solution containing under sonication. The as-obtained CPs (weight: 11 mg) were dipped into the mixed solution. All these precursors were then transferred into a 100 mL Teflon-lined autoclave and heated at 200 °C for 12 h. The as-formed MoS_2-CPs were washed with distilled water and ethanol repeatedly for 6 times to remove DMF and free-standing nanoparticles.

Electrochemical measurements

Firstly, the MoS_2-CPs were used as direct electrodes for HER. A standard caliper was employed to define the 1 cm^2 electrode area by cutting scissors. The loading of MoS_2 species in MoS_2-CPs was estimated to be 0.875 mg cm^{-2} via inductively coupled plasma (ICP) analysis. And the polytetrafluoroethene wapped platinum wire clip was used to connect the MoS_2-CPs electrode with an external circuit. The electrolyte was 0.5 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} KOH solution, the counter and the reference electrodes were a platinum net and a saturated calomel electrode, respectively. Linear scanning voltammetry (LSV) measurements were performed in an N_2-saturated electrolyte at a sweep rate of 0.5 mV s^{-1}. Cyclic voltammetry (CV) was conducted from −0.2 to 0.2 V vs RHE at a scan rate of 10 mV s^{-1} in N_2-saturated 0.5 mol L^{-1} H_2SO_4 solution to investigate the cycling stability. The electrochemical impedance spectroscopy (EIS) measurements for the MoS_2-CPs and CPs 1000, 900, 800 were performed in N_2-saturated 0.5 mol L^{-1} H_2SO_4 solution with the frequencies range from 10 KHz to 0.1 Hz with an AC voltage of 5 mV. For measurements on glassy carbon electrode, the MoS_2-CPs were ground into fine powder. Then, 4 mg of the ground powder catalyst and 80 μL of 5 wt% Nafion solution were mixed in 1 mL of 4:1 v/v water/ethanol by sonication for 30 min to form a homogeneous ink. Then, 7 μL of the slurry was loaded onto the surface of a glassy carbon (GC, 3 mm in diameter) electrode. And electrochemical tests were also performed in a three-electrode system like with MoS_2-CPs measurement. All data of our bench-marked samples presented in this work were corrected for *iR*. All measurements were conducted at room temperature.

Characterization

The SEM measurements were performed on a FEI Nova NanoSEM 2300. The TEM and HRTEM measurements were