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In situ growth of MoS_2 on carbon nanofibers with enhanced electrochemical catalytic activity for the hydrogen evolution

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ABSTRACT

Developing an effective and facile method to achieve mass production of MoS_2 nanostructures with abundant of edges may be the feasible way to meet the increasing demand for hydrogen evolution electrocatalysts. We developed a facile glucose-assisted hydrothermal method to *in-situ* grow MoS_2 nanosheets on the commercial carbon nanofibers (CNFs). The controlled growth of MoS_2 on CNFs (MoS_2@CNFs) is leveraged to reveal mass ratio- and structure-dependent catalytic activity in the hydrogen evolution reaction (HER). Due to the unique shell structure, abundant edges of the MoS_2 layer are exposed as active site, as well as the underlying CNFs effectively improves the conductivity, the resulting MoS_2@CNFs hybrid exhibited high electrocatalytic activity in HER. The catalyst demonstrated the lowest overpotential of 52 mV, the highest current density of 101.49 mA cm^{-2} at ~200 mV overpotential and the smallest Tafel slope of 49 mV/decade, suggesting the Volmer–Heyrovsky mechanism for the MoS_2-catalyzed HER.

Introduction

Hydrogen, as a promising energy carrier for the fuel, has been vigorously pursued to settle the energy crisis which arises from excess consumption of traditional unrenewable resources [1,2]. Recently, a great deal of works were engaged in producing hydrogen through sustainable photo-electro chemical process, such as water splitting at suitable overpotential [3,4] or photoelectrochemistry cells [5,6]. The hydrogen evolution reaction (HER), $2H^+ + 2e^- \rightarrow H_2$, is a fundamental of water splitting. Pt-based electrocatalysts have considered as the most effective HER activity [7–9], that the overpotential is nearly zero, however, the low abundant and high cost largely would be a large obstacle in their large scale hydrogen production. Therefore, developing a high-efficient, earth-abundant and low-price non-noble-metal alternatives that are appropriated for the water splitting and scalable in hydrogen economy is extremely urgent [10].

In the past few decades, numerous efforts have been devoted to exploits the effective noble-metal-free HER electrocatalyst. For instance, transition metal sulfides [11–14], carbides [15,16], nitrides [17], and selenides [18], as well as phosphides [19]. MoS_2, as a typical two-dimensional (2D) lamellar material, exhibits promising HER activity in crystalline [20–24], amorphous state [25], and molecular mimics [26]. Both the theoretical and experimental studies have demonstrated that the exposed active sites with enhanced HER

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activity mainly origins from the sulfided Mo edges of MoS_2 nanosheets, while the basal plane remains inert [27,28]. Unfortunately, the intrinsic poor conductivity of MoS_2, attributing to the lateral transfer of electrons along the lamella structure of MoS_2 nanoplates, restrains the efficient electron transfer as well as the associated electrochemical kinetics [29,30]. Therefore, not only increasing the number of sulfided Mo-edges of MoS_2 nanoplates but also incorporated carbon-based conductivity would be an efficient strategy to improve the overall HER activity [31,32]. For the choice of carbon-based materials, such as grapheme [33,34], conductive polymers [35], carbon nanotubes (CNTs) [36], combined with MoS_2 has been revealed to be effective. In the recent works, similar to CNTs, carbon nanofibers (CNFs) have been widely used in energy conversion and storage as the material owing to highly conductive and stable as well as a large functionalized surface area, making it an ideal host to confine the growth of MoS_2 nanosheets [37,38].

In this present work, we aim to fabricate an efficient and low-cost HER electrocatalyst that few-layers MoS_2 nanosheets vertically grows on the CNFs. CNFs act as a substrate not only prevent MoS_2 nanosheets from self-aggregation, which increasing the number of exposure active edge sites, but also accelerate electron transfer, resulting in highly improved overall conductivity. The glucose plays a key role during the process of in-situ growth of MoS_2 on the CNFs. To the best of our knowledge, this is the first report of employing the hydrothermal method to in-situ grow MoS_2 nanosheets on the CNFs, and the resulted composites exhibit an excellent HER activity comparable to commercial 20% Pt/C.

Experimental

Reagents and materials

Carbon Nanofibers (CNFs, purity >95 wt%) powder was purchased from Beijing Tebo Wande Technology Co. Ltd (Beijing, China). Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) was purchased from China Medicine Group Chemical Reagent Co., Ltd (Shanghai, China). Thiourea ($CS(NH_2)_2$) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). D-(+)-Glucose (98%) was purchased from Beijing J&k Technology Co., Ltd (Shanghai, China). All the reagents were used without further purification. Nafion and 20% Pt/C were purchased from Alfa Aesar (Johnson Matthey Public Limited Company, England). Other chemicals were of pure analytical grade and used without further purification. Milli-Q purified water (Millipore, Resistivity $\geq$18.2 MΩ cm at 25 °C) was used throughout the study.

Synthesis of MoS_2/CNFs composites

The preparation procedure of MoS_2/CNFs composites is schematically illustrated in Scheme 1. For the MoS_2/CNFs composites, the first step is to obtain the acid-treated CNFs. The functionalization of CNFs with carboxylic acid groups was achieved by hydrothermal in the mixed acid (the volume ratio of H_2SO_4 and HNO_3 is 3:1, 60 mL) for 8 h, then the CNFs precipitates was collected by centrifugation, washed thoroughly with water and ethanol until pH of 7, and finally dried at 70 °C for 12 h. For the synthesis of MoS_2/CNFs (the theoretical weight ratio is 5:1.), acid-treated CNFs (7.5 mg) were dispersed into glucose solution (40 mL, 0.025 M) by ultrasonication for 1 h. Then, 0.0566 g $Na_2MoO_4 \cdot 2H_2O$ was added into the solution. After being treated by ultrasonication for 20 min, 0.1808 g thiourea was added and treated by another 20 min ultrasonication. Then the solution was transferred into a Teflon-lined stainless steel autoclave (60 mL) and heated in an oven at 200 °C for 22 h. The autoclave was then removed from the oven and left to cool to room temperature. The black product was collected by centrifugation, washed with water and ethanol repeatedly for many times, and dried at 60 °C. The as-prepared catalyst is denoted as MoS_2@CNFs-5. For comparison, the composites with weight ratios of 2.5:1 and 15:1 were also synthesized, and were denoted as MoS_2@CNFs-2.5 and MoS_2@CNFs-15, respectively. The synthesis procedures of MoS_2 and the mixture of MoS_2 and CNFs were similar to that described above except for without the addition of CNFs and glucose.

Electrochemical measurements

Typically, 4 mg of as-prepared catalyst was dispersed in 1 mL 45% water–ethanol solution by ultrasonication for 1 h to form a homogeneous ink. Then 2.5 μL of the ink was loaded onto a conventionally pretreated glass carbon (GC) electrode of 3 mm in diameter by two times (loading approximately 0.283 mg cm^{-2}).

Electrochemical measurements of various samples were performed on a GC electrode using a typical three-electrode electrochemical workstation (CHI660C). Linear sweep voltammetry (LSV) beginning at 0 V and ending at −0.80 V vs. RHE with a scan rate of 5 mV s^{-1} was conducted in 0.5 M H_2SO_4 (deaerated by pure nitrogen) using Hg/Hg_2Cl_2 electrode as the reference electrode, a glassy carbon rod used as the counter electrode. The reversible hydrogen electrode (RHE) was calibrated using platinum as both working and counter electrode at a scan rate of 5 mV s^{-1}. In 0.5 M H_2SO_4, E (RHE) = E (Hg/Hg_2Cl_2) + 0.251 V. To measure electric double-layer capacitance, cyclic voltammograms taken three times at each of various scan rates (20, 40, 60, 80 mV s^{-1}, etc) were collected in the range of 0.15–0.35 V (vs. RHE). Time-dependence was conducted at the overpotential of 250 mV to investigate the catalyst stability. The Nyquist plots were measured with frequencies ranging from 100 kHz to 0.01 Hz at the overpotential of 280 mV with the AC voltage of 5 mV.

Apparatus

Morphology analysis was taken on a Hitachi S-4800 scanning electron microscope (SEM, Hitachi, Japan) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM), the high-angle annular dark field scanning TEM (HAADF-STEM), and STEM mapping were performed on a Tecnai G2 F20 microscope (FEI, USA) with an accelerating voltage of 200 kV at room temperature. The STEM mapping was recorded under STEM modes. Raman spectrum was conducted using a Horiba Jobin Yvon LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon) with a laser excitation wavelength of

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