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Controllable Synthesis of Caterpilliar-like Molybdenum Sulfide @carbon Nanotube Hybrids with Core Shell Structure for Hydrogen Evolution

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ABSTRACT

Ultrathin molybdenum sulfide (MoS_x) nanosheets were uniformly grown on multiwalled carbon nanotubes (MWCNTs) via a solvothermal process. These MoS_x nanosheets possess high density of active sites, full of the basal MoS_x edges and unsaturated S atoms, and their one-dimensional (1D) core-shell architecture facilitates electron transfer and charge transport, leading to a superior performance in H_2 evolution reaction (HER). These caterpillar-like MoS_x@MWCNT hybrids show a high HER capability in 0.5 M H_2SO_4 solution with a low overpotential of 102 mV vs standard hydrogen electrode (SHE) and a small Tafel slope of 35 mV dec^{-1} at 10 mA cm^{-2}. Their HER activity presents no significant decay during potential polarization at 150 mV vs SHE for over 5 h.

1. Introduction

Hydrogen is a promising clean and renewable energy resource. As an alternative to fossil energy, its large-scale usage can halt environmental deterioration and maintain long-term sustainable development of human society [1]. Among the strategies for H_2 production, electrochemical water electrolysis attracts great attention due to its low cost, high efficiency and environmental friendliness [2,3]. Currently, Pt and its alloy ranks among the top electrocatalysts used in hydrogen evolution reaction (HER), but Pt is scarce in earth, and thus the expensive price limits its wide use in H_2 production[4,5].

A great deal of efforts are made to open up an earth-abundant HER catalysts as a substitute for this noble metal and alloy. Transitional metal sulfides and selenides, such as MoS_2, WS_2, $MoSe_2$, $CoSe_2$ and $NiSe_2$, have attracted considerable attention recently as inorganic electrocatalysts for HER because of their low cost, high chemical stability and excellent electrocatalytic properties [6,7]. Among HER catalysts, two-dimensional (2D) MoS_2 is a promising alternative to Pt and its alloy, and its HER activity can rival the state-of-the-art catalysts in solar-driven photoelectron chemical cells [8–11]. The HER activity of MoS_2 springs from its edge sites [12]. Therefore, many works focus on controllable synthesis of MoS_2 hybrids with various nanostructures as an aim to maximize the density of edge sites, including nanowire [13], nanotubes[14], nanoflakes[15], nanoplates [16] and nanosheets with porous, vertically-aligned three-dimensional (3D) structure [4] or assembling superstructure[17]. In addition, further nanostructure engineering can make MoS_2 full of edge sites and surface defects. Lukowski et al exfoliated MoS_2 bulk with n-butyl lithium, the lithiation reaction will produce porous metallic 1T MoS_2 nanosheet [18]. Ye at al treated the pristine monolayer MoS_2 by oxygen plasma exposure and thermal hydrogenation. These treatments will favor the formation of defects at the scale from macroscopic continuum to discrete atoms [19]. However, the nanostructure engineering involves in laborious and even dangerous procedures, and the active sites of the resulting crystalline MoS_2

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are confined in its edge. In comparison, amorphous MoS_x intrinsically possesses an abundance of defect sites, which are distributed throughout the entire surface of HER catalyst [20]. Moreover, the scale synthesis of MoS_x is available via a facile solvothermal process or electrodeposition approach. Yan et al reported a solvothermal synthesis of ultrathin MoS_2 nanoplates. This MoS_2 nanostructure shows a low HER onset potential of 0.09 V vs SHE and a small Tafel slope of 53 mV dec^{-1}. The superior HER activity can be attributed to the bridging S_2^{2-} in an amorphous state of MoS_2 nanoplates. The unsaturated sulfur atom can favor the formation S-H bonds, leading to H_2 generation eventually [16]. Note that the conductivity of amorphous MoS_x is poor, and the conductivity will also affect HER performance of MoS_2. A solution to this problem is to hybridize MoS_2 with carbon materials, such as active carbon [21], carbon fiber [22], graphene [23] and carbon nanotubes (CNTs) [24]. CNT is a desirable MoS_2 support due to its great specific areas, high electrical conductivity and excellent chemical stability [25]. McAteer et al used CNT as an additive for liquid-exfoliated MoS_2 nanosheet multilayer to improve its conductivity and mechanical capacity. This MoS_2-CNT multilayer composites show a thick-dependent HER capability with a Tafel slope in the range 100-150 mV dec^{-1} [26]. Liu et al synthesized MoS_2 nanosheets on single-walled carbon nanotube film. This flexible catalyst exhibited a high HER activity with a low overpotential (~150 mV vs SHE at 10 mA cm^{-2}) and small Tafel slope (41 mV dec^{-1}) [27]. Li et al deposited subnanometer-sized MoS_x on CNT, these MoS_x/CNT hybrids achieved a small Tafel slope of 37 mV dec^{-1} and a low overpotential of 106 mV vs SHE at 10 mA cm^{-2} [24].

Herein, we developed a facile solvothermal strategy to prepare ultrathin MoS_x nanosheets uniformly grown the surface of CNT. The as-prepared MoS_x@CNT hybrids take the shape of caterpilliar with core shell structure. This protocol will enrich this ultrathin MoS_x nanosheets with basal edges and unsaturated S atoms on its entire surface, which will increase the density of active sites by a large margin. In addition, for MoS_x@CNT hybrids, the inside CNTs can act as nano-collector, which will substantially improve the conductivity and mechanical capacity of amorphous MoS_x, and the 1D core-shell structure may favor electron transfer at the electrode interface. Expectedly, the as-prepared MoS_x@CNT hybrids will show superior HER activity and stability. This work may provide a useful insight to the intrinsic catalytic nature in MoS_2 and pave the way for the rational design of MoS_2-based HER catalysts and their related applications.

2. Experimental

2.1. Materials.

$(NH_4)_2MoS_4$ (95%) and Dimethyl formamide (DMF, 99%) were purchased from Acros, and the purified multiwalled carbon nanotube (MWCNT) was obtained from Chengdu organic Chemics Co., Ltd (purity > 95% out diameter 10-20 nm, length 30 μm).

2.2. Synthesis of MoS_x@MWCNT hybrids

15 mg MWCNTs and 25-100 mg $(NH_4)_2MoS_4$ (95%) were dispersed completely by sonicator in the mixture solution of DMF and water with a volume ratio of 2:1. The mixture solution was transferred into 50 ml reactor, and the reactor was sealed and heated at 200 °C for 12 h. The resulting MoS_x@MWCNT hybrids were recovered by centrifugation, rinsed with alcohol and water to remove the adsorbed ions and molecules, and then dried at 100 °C for 24 h in vacuum for characterization and electrochemical investigation.

The pure MoS_x powder was prepared in the strategy similar to that of MoS_x@MWCNT hybrids without introduction of MWCNTs.

2.3. Composition Characterization

The MoS_x@MWCNT hybrids were imaged by scanning electron microscope (SEM, Hitachi S-4800) under an accelerating voltage of 5 kV, and further characterized by transmission electron microscopy (TEM, JEOL 2010) with the electron beam energy of 200 KeV. The composition of the MoS_x@MWCNT hybrids was determined by the inductively coupled plasma-atom emission spectroscopy (ICP-AES, TJA Atomscan Advantage instrument) and further investigated by the X-ray photoelectron spectroscopy (XPS, ESCALAB-MKII spectrometer) with a monochromated Al Kα (1486.7 eV) as the X-ray source. The crystal structure of MoS_x@MWCNT hybrids was measured by X-ray powder diffraction (XRD, Philips PW3040/60) with Cu Kα radiation (λ = 0.15406 nm). Raman spectra were collected on a Renishaw inVia confocal micro-Raman spectroscopy system with a 488 nm excitation laser.

2.4. Electrochemical Investigation

The electrochemical analysis was performed in a typical three-electrode cell set-up interfaced with CHI 750 C. MoS_x and MoS_x@MWCNT hybrids (2.5 μg) were coated on glassy carbon (GC) (3 mm) with the binder nafion@117, and the Pt/C catalysts were used as control for HER. The saturated calomel electrode (SCE) and platinum net were used as reference and counter electrodes, respectively. The HER was performed in 0.5 M H_2SO_4 solution, and the electrolyte solution was stirred using magnet to release gas during electrolysis. All the electrode potentials were referred to the standard hydrogen electrode (SHE). The HER activity was investigated by linear scan voltammetry (LSV) at the scan rate of 5 mV s^{-1}. The LSV currents presented were corrected against the ohmic potential drop. The relative electrochemical surface area can be estimated from the double layer capacitance (C_{dl}), which was determined by cyclic voltammetry (CV). The long-term durability was tested by chronoamperometry (CA). The kinetic was studied by the electrochemical impedance spectroscopy (EIS) in the frequency ranged from 10^6 to 0.01 Hz with ac voltage amplitude of 5 mV.

3. Results and discuss:

Fig. 1 show the typical TEM images of MoS_x@MWCNT hybrids, MoS_x nanosheets were averaged to be about 10 nm in size, and uniformly grown on MWCNT surface with dense interconnected ripples and corrugation to form a caterpillar-like shape, indicative of the basal-edge-rich feature of 2D MoS_x. The high resolution TEM image reveals the edge thickness of MoS_x nanosheets is estimated to be less than 2 nm, and the lateral view of some MoS_x multilayer show that its interplanar distance is about 0.65 nm, which can be indexed as (002) spacing of two-dimensional MoS_x, and consistent with the natural layered structure of MoS_2 along the *c*-axis [28]. The selected area electron diffraction (SAED) pattern shows a typical ring pattern, indicative of amorphous MoS_x. For comparison, the bulk MoS_x was also prepared. The typical shape of MoSx is presented as nanoplate with a size of 20-100 nm. (Fig. S1)

The MoS_x loading on MWCNTs can be tuned by controlling the mass ratio of $(NH_4)_2MoS_4$ and MWCNTs in the solvothermal process. Fig. 2 shows the morphology of MoS_x@MWCNT hybrids with different MoS_x loading. The uniform deposition of MoS_x nanoheet can be observed from their microscopic images. Even the mass ratio of MoS_x and MWCNT increases from 0.5 to 2, the thickness of MoS_x cover is almost about 10-20 nm, and its variation can be negligible, but the density of MoS_x nanosheets packing around MWCNT grows observably. For convenience, MoS_x@MWCNT hybrids are defined as MoS_x@MWCNT hybrids (1:2), MoS_x@MWCNT hybrids (1:1) and