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Controlled morphology evolution of electrospun carbon nanofiber templated tungsten disulfide nanostructures

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ABSTRACT

Three-dimensional (3D) WS_2-nanoflower decorated and two-dimensional (2D) WS_2-nanosheet (NS) wrapped carbon nanofiber (CNF) nanostructures are constructed through a simple approach using $(NH_4)_2WS_4$ contained electrospun polyacrylonitrile nanofibers (W-PAN NFs) and S powder as the precursor. $(NH_4)_2WS_4$ are thermally decomposed into WS_2 nanoparticles (NPs) during a pre-oxidation treatment of W-PAN NFs. Interestingly, the introducing of S vapor during the carbonization of W-PAN NFs results in unexpected migration of WS_2 nanoparticles (WS_2 NPs) from the inside of CNFs to the surface to form WS_2 NSs or WS_2 nanoflowers. It is believed that S not only controls the initial nucleation of WS_2 on the surface of CNFs but also induces the migration of WS_2 NPs and directs the growth of WS_2 into various morphologies. The synthesized catalysts are directly used as the electrode for hydrogen evolution reaction (HER) and they exhibit good electrocatalytic activity.

1. Introduction

The discovery of the unique properties of graphene has prompted intensive studies into layered semiconducting transition metal dichalcogenides (TMDCs). These materials, such as those in the class MX_2 (M = Mo, W and X = Se, S), have electronic properties complementary to those of semimetallic graphene [1–10]. In recent years, the preparation of thinly-layered TMDCs has been of great interest to researchers due to their favourable properties, including semiconductivity, superconductivity, and superior field emissivity, and the ability to form charge density waves. These characteristics are of great importance for a number of applications, such as electronic devices, catalysis, supercapacitors, and battery systems [11–17].

Combinations of TMDCs with other functional materials have been widely studied as candidate components for a wide range of applications. Carbon nanomaterials ranging from 1D carbon nanotubes (CNTs) or CNFs, to 2D graphene nanosheets (NS) and 3D carbon fiber papers have been investigated as TMDC substrates due to their large specific surface areas, outstanding electronic conductivities, and high charge mobilities [13,18–24]. For instance, 2D WS_2 NS grown on a reduced graphene oxide (rGO) support were recently tested as a catalyst for enhancing the hydrogen evolution reaction. The superior catalytic performance of this hybrid material was attributed to the enhanced charge transfer kinetics that arose from the rapid electron transfer between the catalytic WS_2 NS and the rGO support [20].

WS_2 is a 2D, anisotropic material with a trigonal prismatic structure, formed by stacks of "sandwiches" consisting of a layer of W atoms between two layers of S atoms [25]. This structure gives rise to remarkable physical and chemical properties. However, the development of reliable methods for the batch production of layered WS_2 has lagged behind comparable efforts for MoS_2. Moreover, significant work is still required to explore the fundamental characteristics of WS_2 and adapt it for use in practical applications. Synthesis of high-quality WS_2 with 2D NS-like structures is of key importance in order to realize the potential of this material [26–28]. WS_2 sheets with thicknesses from one single layer to a few layers have been obtained via mechanical and chemical exfoliation [26,29,30]. These methods limit the amount of control that can be exerted over the physical features of the exfoliated sheets [29]. Solvothermal reactions are another path that may be used for the production of WS_2 NSs, but this method often results in solvent residues on the surfaces of the NSs, which are difficult to remove and may negatively impact the intrinsic properties of the NSs.

As is well known, chemical vapor deposition (CVD) has been used to grow several-layer nanoflakes of WS_2. One such process uses WO_3 thin films as a precursor material which is then

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subjected to a rapid sulfurization process under an inert environment (or in a mixed atmosphere with H_2 gas) [31–38]. Unfortunately, due to the structural differences between WO_x and MoO_3, sulfurization of the WO_x precursor tends to lead to the formation of 0D fullerene-like or 1D nanotube/nanorod-like WS_2 nanostructures [39,40]. As such, the lack of a facile, reliable method for the synthesis of WS_2 NSs has also prevented research into hybrid materials combining WS_2 and carbonaceous materials such as CNFs, despite their high potential for use in a number of applications.

In recent years, our group has studied the synthesis of TMDCs with controllable size, and hybrid materials on CNFs. These hybrid materials have high surface area and exhibit excellent performance in electrochemical catalytic applications [41–43]. In this work, the synthesis of 2D WS_2 NSs and 3D WS_2 nanoflowers on electrospun CNFs is reported using $(NH_4)_2WS_4$-containing electrospun PAN NFs (W-PAN NFs) as the precursor material.

Firstly, uniformly-distributed WS_2 nanoparticles (NPs) with diameters of ~3 nm were thermally decomposed from $(NH_4)_2WS_4$ contained in the W-PAN NFs. Subsequently, the PAN NFs contained WS_2 NPs were carbonized under higher temperature at Ar atmosphere. Furthermore, an efficient route has been developed to transfer these WS_2 NPs from inside CNFs into 3D WS_2 nanoflowers or 2D WS_2 NS forms grown on the outside surfaces of CNFs. This is accomplished by sublimating S powder into the Ar gas flow as a multifunctional reagent during carbonization of W-PAN NFs. Interestingly; the morphology of the resulting WS_2 can be tailored by adjusting the amount of S present in the system. A possible reaction pathway and a formation mechanism for 3D WS_2 surface nanoflowers and 2D WS_2 NSs were proposed. The synthesized catalysts were directly assembled as catalytic electrodes for electrocatalytic hydrogen production, which not only exploited the merits of CNFs, such as high surface area and good conductivity, but also avoided the usage of polymer binder to immobilize the catalyst which will benefit the practical application of the catalysts. The synthesized electrode treated by a small amount of S vapour (10 g) exhibits the best HER performance among these electrodes, in which the WS_2 catalyst with 3D flower like nanostructure exposed more active edge sites and the conductive CNFs provides a short path for fast charge transfer and transport.

2. Experimental

2.1. Synthesis of PAN nanofibers (PAN NFs) and $(NH_4)_2WS_4$ contained PAN nanofibers (W-PAN NFs) Mats

The PAN NFs were synthesized by electrospinning method. Typically, 3.86 g PAN powder was dissolved in 30 mL dimethyl formamide (DMF, 99.5%) under magnetic stirring to get a homogeneous solution. Therefore, the mass fraction of PAN in the DMF solution was 12 wt%. The solutions were transferred into a syringe with a stainless copper needle at the tip and then electrospun under a fixed voltage of 12 kV and the needle to collector distance was 12 cm with the flow rate at 0.01 mL min^{-1}. During electrospinning process the temperature was 25 ± 2 °C and the humidity was 45 %RH. The electrospun fibers were collected onto a piece of aluminium foil. W-PAN NFs were prepared by adding additional $(NH_4)_2WS_4$ powder in above PAN/DMF solution by electrospinning under the same condition. The concentration of $(NH_4)_2WS_4$ is 10 wt% based on the weight of PAN powder.

2.2. Preparation of carbon nanofibers (CNFs) and carbon nanofiber templated WS_2 nanostructures (WS_2-CNFs) Mats

The PAN and W-PAN NFs mats were collected and peeled off from the aluminium foil, cut into pieces, placed into a boat, and put into a CVD furnace for heat treatment. Typically, the nanofibrous mats were heated to 280 °C from room temperature within 1 h, and maintained for 6 h for the sufficient pre-oxidation of the nanofibrous mats as well as the thermal decomposition of $(NH_4)_2WS_4$. The furnace was then heated to 1000 °C within 2.5 h under Ar flow (150 sccm) and maintained for another 8 h for the graphitization of the nanofibrous mats. Finally, the products were cooled to room temperature under Ar atmosphere.

2.3. CVD Growth Process of S treated WS_2-CNFs (S_x-WS_2-CNFs, where x = 10 or 100) Mats

The W-PAN NFs mats with a certain size were placed in a boat and put at the center of the furnace. After 6 h thermal treatment of W-PAN NFs mats under air condition, the pressure in the chamber was reduced to 50 Pa for 10 min, and Ar (150 sccm) was then allow into the reaction tube, reaching a pressure of 400 Pa. The furnace was heated to 1000 °C within 2.5 h, then a boat with 10 or 100 mg of S powder was placed outside the furnace. This zone was wrapped with a heating belt, which was heated to a temperature of 150 °C. The furnace was maintained at 1000 °C for another 8 h. The typical thermal treatment under S vapor environment and temperature ramps for both the furnace and the heating belt is shown in Fig. S1.

2.4. Electrochemical characterization

The as-grown WS_2 catalysts on CNFs were tested in 0.5 M H_2SO_4 (aq) electrolyte (deaerated by N_2). The catalysts were cut into 1×1 cm^{-2} with the cross section diameter about 15-20 μm and fixed in a Teflon electrode clamp and directly used as the working electrode. Using a Pt mesh as the counter electrode, and a saturated calomel electrode (E(RHE) = E(SCE) + 0.265 V after calibration) as the reference electrode. Linear sweep voltammetry (LSV), cyclic voltammetrys (CVs) and electrochemical impedance spectroscopy (EIS) are recorded by CHI660E workstation (Shanghai Chenhua, Shanghai). LSV were conducted beginning at +0.3 V and ending at −0.6 V with a scan rate of 5 mV s^{-1}. EIS measurements were carried out at a constant −0.25 V vs RHE, while sweeping the frequency from 5 MHz to 20 mHz.

2.5. Characterization

The thermal properties of $(NH_4)_2WS_4$ powder, pure electrospun PAN NFs and W-PAN NFs with $(NH_4)_2WS_4$ content of 10 wt% were carried out on a Perkin-Elmer Pyris 1 Thermogravimetric analyzar (TGA) with a heating rate of 20 °C/min from 20 to 800 °C in a nitrogen atmosphere. The morphology of the prepared samples was observed by a JSM-6700F FE-SEM (JEOL, Japan) at an acceleration voltage of 3 kV. Transmission electron microscope (TEM) images and SAED patterns of all the samples were obtained with a JSM-2100 transmission electron microscopy (JEOL, Japan) at an acceleration voltage of 200 kV. X-ray photoelectron spectra of the samples were recorded using an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) Kα source (1486.6 eV). Raman spectra were recorded by a Renishaw inVia Raman microscope using a 514.5 nm laser excitation source. The high-angle annular dark field scanning TEM (HAADF STEM) mages, EDS mapping images, and were collected by a STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at an acceleration voltage of 300 kV.