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Highly dispersed few-layer MoS₂ nanosheets on S, N co-doped carbon for electrocatalytic H₂ production

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ABSTRACT

Ultrathin small MoS₂ nanosheets exhibit a higher electrocatalytic activity for the hydrogen evolution reaction. However, strong interactions between MoS₂ layers may result in aggregation; together with the low conductivity of MoS₂, this may lower its electrocatalytic activity. In this paper we present a method that we developed to directly produce solid S, N co-doped carbon (SNC) with a graphite structure and multiple surface groups through a hydrothermal route. When Na₂MoO₄ was added to the reaction, polymolybdate could be anchored into the carbon materials via a chemical interaction that helps polymolybdate disperse uniformly into the SNC. After a high temperature treatment, polymolybdate transformed into MoS₂ at 800 °C for 6 h in a N₂ atmosphere at a heating rate of 5 °C/min, owing to S²⁻ being released from the SNC during the treatment (denoted as MoS₂/SNC-800-6h). The SNC effectively prevents MoS₂ from aggregating into large particles, and we successfully prepared highly dispersed MoS₂ in the SNC matrix. Electrochemical characterizations indicate that MoS₂/SNC-900-12h exhibits a low onset potential of 115 mV and a low overpotential of 237 mV at a current density of 10 mA/cm². Furthermore, MoS₂/SNC-900-12h also had an excellent stability with only ~2.6% decay at a current density of 10 mA/cm² after 5000 test cycles.

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1. Introduction

Hydrogen energy is clean and one of the most promising candidates for replacing fossil fuels in the future [1]. The electrocatalytic hydrogen evolution reaction (HER) is considered to be one of the most common and efficient pathways to produce H₂. Currently, the most efficient HER electrocatalysts are noble metals such as Pt [2,3]. However, the high price and limited reserve of noble metals inhibit their large scale application in

practice. Thus, developing a low cost, highly efficient electrocatalyst is urgently needed to progress sustainable energy infrastructure [4–8].

Over the past few years, MoS₂-based electrocatalysts have attracted increased research attention because they are low-cost, highly efficient alternatives to Pt [9,10]. Both experimental and theoretical studies have confirmed that the HER activity of MoS₂ strongly depends on the number of catalytically active edge sites [11–13]. Therefore, developing MoS₂ elec-

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trocatalysts with both abundant active edge sites and good crystallinity is an efficient way to simultaneously achieve high a HER performance and long-term stability of the catalyst. Jaramillo and coworkers [11] reported a highly ordered double-gyroid MoS₂ bicontinuous network with preferentially exposed active edge sites that led to an outstanding improvement in HER performance. Recently, Cui's group [14] prepared MoS₂ films with vertically aligned layers; this geometry allows the edges to be maximally exposed on the film's surface. Meanwhile, Xie's group [15] synthesized MoS₂ ultrathin nanosheets with controllable defects leading to the exposure of additional active edge sites.

To improve the HER activity of MoS₂, two aspects should be considered. First, strong van der Waals interactions between the lamellar crystals will result in aggregation, which decreases the number of active sites as well as the overall electrocatalytic activity [16]. This means that larger, multilayer MoS₂ nanosheets cannot provide enough active sites. Second, the poor conductivity of MoS₂, which is caused by the lateral transfer of electrons along the lamella structure of the MoS₂ nanosheets, restricts the efficient transfer of electrons as well as hindering related electrochemical kinetic processes [17]. Therefore, designing MoS₂ catalysts with few layers that are small and can be highly dispersed would be an effective strategy to generate more active sites, thus enhancing the electrocatalytic HER. A good electrocatalyst would thus be nanoscale MoS₂ crystallites supported on carbon-based materials, since those are conducting but otherwise inert [18–20]. Recently, Rao *et al.* [21] prepared a MoS₂ composite with nitrogen doped reduced graphite oxide, which showed excellent HER activity; this implies that nitrogen incorporated graphene should improve the catalytic activity of their composite because N doped graphene has an enhanced ability to donate electrons. N-doped carbon materials have a high electronic conductivity owing to their p-delocalization and high thermal conductivity.

Taking these factors into account, carbon materials are ideal supports to improve electrocatalytic activity. However, MoS₂ nanosheets are difficult to grow on traditional carbon nanofibers owing to the inert carbon surface, which has few anchor sites on which the MoS₂ can bond. Here, we present a new synthesis route that we developed to produce carbon nanostructures with high content of N and S, which can thus anchor MoO₄²⁻ onto the carbon nanostructures. A subsequent high temperature treatment causes S²⁻ to be released from the carbon, thus transforming MoO₄²⁻ into MoS₂. Owing to the confinement of the carbon materials, the as-formed MoS₂ has only a few layers, large active sites, and is highly dispersed in the carbon matrix. We demonstrate that this MoS₂/SNC composite is a good catalyst for electrochemical hydrogen evolution as it exhibits a low overpotential and high stability.

2. Experimental

2.1. Reagents and materials

Na₂MoO₄·2H₂O was purchased from Tianjin Chemical Reagent Co., Ltd. Sulfuric acid (H₂SO₄, GR, 95.0–98.0%) and Dime-

thyl sulfoxide (DMSO, AR) were purchased from Beijing Chemical Works. Isopropyl alcohol was purchased from Sinopharm Chemical Reagent Co., Ltd. *N,N*-diphenyl thiourea (DPU, 99%) was obtained from Adamas Reagent Co., Ltd. Citric acid (CA) anhydrous (≥99.8%) was purchased from Tianjin Fuchen Chemical Reagents Factory. Platinum catalyst (20 wt% Pt/C) and nafion solution (5 wt%) were obtained from Alfa Aesar. α-Aluminum oxide polishing powder (≥99%, *d* = 0.5 μm and *d* = 50 nm), Pt foil, Ag/AgCl (saturated KCl), and glassy carbon electrodes were purchased from Tianjin Aidahengsheng Technology. All chemicals were used without further purification. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ/cm.

2.2. Synthesis of compounds

Typically, 0.242 g (1 mmol) Na₂MoO₄·2H₂O, 0.192 g (1 mmol) CA and 0.685 g (3 mmol) DPU were dispersed into 5 mL of DMSO. After the solution was dispersed via ultrasonication for about 1 h, it was transferred into a 10 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 14 h. After cooling naturally to room temperature, a polymolybdate salt (PMS)/SNC solid rod was collected, which was subsequently immersed into DI water and acetone to remove any small molecules and inorganic salts from it; this sample was dried in air at 60 °C overnight. The obtained solid powder was dark green. The powder was thermally treated in a conventional tube furnace at 700–950 °C for either 6 or 12 h in a N₂ atmosphere at a heating rate of 5 °C/min, thereby obtaining MoS₂/SNC-*T-t* powder, where *T* stands for treatment temperature and *t* for treatment time. SNC-*T-t* was also prepared for comparison under the same conditions but in the absence of Na₂MoO₄·2H₂O.

2.3. Characterizations

X-ray diffraction (XRD) was carried out using a PANalytical X'Pert instrument. The samples were prepared by dropping the catalyst powders onto glass substrates. The Raman spectra of the powder samples were recorded on a LabRAM HR Raman microscope with a laser excitation wavelength of 514.53 nm. X-ray photoelectron spectroscopy (XPS) spectra were collected on a SSI S-Probe XPS spectrometer. The XPS samples were prepared by casting an isopropyl alcohol suspension of the catalyst powders onto Si wafers. Scanning electron microscopy (SEM) images were recorded on a Hitachi US8010. The SEM samples were prepared by casting an isopropyl alcohol suspension of the catalyst powders onto Si wafers. Transmission electron microscopy (TEM) images were collected on an FEI Tecnai G2 F20 TEM instrument. Samples were prepared by dropping a diluted suspension of the catalyst powders in isopropyl alcohol onto copper grids covered with porous carbon films.

2.4. Electrochemical characterization

The electrochemical measurements were performed in a

Table 1

The elemental analysis of SNC and SNC-900-12h.

Catalyst	C (%)	H (%)	O (%)	N (%)	S (%)
SNC	51.2	5.0	19.6	7.0	17.2
SNC-900-12h	87.7	1.6	1.2	3.3	6.2

H₂SO₄ solution (0.5 mol/L) using an Autolab electrochemical workstation (Autolab PGSTAT302N). A graphite rod was used as the counter electrode, Ag/AgCl (saturated KCl) as the reference electrode, and the catalyst powders casted onto the glassy carbon electrode were used as the working electrode. The glassy carbon electrodes (GCE) used each had a diameter of 5 mm. They were polished using alpha alumina powder (0.5 μm and 50 nm in size) suspended in DI water on a Nylon polishing pad. To prepare the working electrode, the catalyst (4 mg) and 5 wt% nafion solution (80 μL) were dispersed in isopropyl alcohol (920 μL) and sonicated for at least 1 h to form a homogeneous mixture. Then, the mixture (14 μL) was drop casted onto the glassy carbon electrode and left to dry at room temperature. The catalyst loading density was determined to be 0.285 mg/cm².

The H₂SO₄ solution (0.5 mol/L) was purged with N₂ for 1 h to completely remove O₂ prior to the experiment. Cyclic voltammograms (CVs) were recorded between 0 and −0.6 V versus Ag/AgCl (saturated KCl) at a scan rate of 100 mV/s. CVs were scanned for 50 cycles. Linear sweep voltammograms (LSVs) were measured from 0 to −0.8 V versus Ag/AgCl (saturated KCl) with a scan rate of 5 mV/s. Tafel slopes were calculated from the LSV curves by plotting the overpotential (η) against the logarithm of the current density, j . Accelerated stability tests were performed in H₂SO₄ solution (0.5 mol/L) for 5000 cycles with potential cycling between 0 and −0.3 V versus the reversible hydrogen electrode (RHE) and a sweep rate of 100 mV/s. At the end of the cycling test, the electrode was used to investigate the polarization curves at a sweep rate of 5 mV/s. Electrochemical impedance spectroscopy (EIS) tests were conducted in the same configuration at $\eta = -0.2$ V from 10⁶–10^{−2} Hz with an AC voltage of 5 mV. All the potentials were calibrated with the RHE using the equation $E_{\text{vs. RHE}} = E_{\text{vs. Ag/AgCl}} + E_{\text{Ag/AgCl}} + 0.059$ pH. All data were iR-corrected.

3. Results and discussion

It is well-documented that CA and urea or thiourea can be used to produce graphite carbon dots under hydrothermal conditions [22,23]. Here, urea was replaced by DPU to increase

Fig. 1. SEM images of SNC (a); PMS/SNC (b); SNC-900-12h (c); and MoS₂/SNC-900-12h (d).

the conjugation of the *sp*² domain. When the reaction time was less than 12 h, carbon dots were produced in DMSO solutions. To our surprise, when CA and DPU in DMSO was transferred into an autoclave at 180 °C for 14 h, a yellowish-brown solid was obtained. After the hydrothermal reaction, all the reactants turned solid, indicating that DMSO also took part in the carbonization process to form carbon materials with high S and N content. Element analysis results indicate that the N and S content reached 7.0% and 17.2%, respectively (Table 1). Fig. 1(a) shows a SEM image of the as-prepared SNC after the hydrothermal reaction. It shows a solid rod that is composed of particles with diameters of 200–300 nm. Those results imply that this route could be an effective one for obtaining high N and S doped carbon materials.

To fabricate the MoS₂/SNC composite, Na₂MoO₄ was added into the reaction as a Mo source. Typically, 1 mmol Na₂MoO₄·2H₂O, 1 mmol CA, and 3 mmol DPU were dispersed in 5 mL of DMSO. Since Na₂MoO₄ dissolves in DMSO at high temperatures, MoO₄^{2−} can react with the −NH₂ groups on the carbon dots produced during the initial stage of the reaction to form PMS, which helps the Mo to disperse uniformly in the solution as well as helping the carbon materials formed later to disperse. After the hydrothermal reaction, a dark green solid rod was obtained. The synthesis route of MoS₂/SNC-*T-t* is shown in Scheme 1. Fig. 1(b) displays a SEM image of the PMS/SNC composite. The morphology of the composite shows that nanoparticle aggregates remain after the addition of PMS. The SEM image further reveals that the solid rod is composed of particles with diameters of 100–200 nm. Then we treated

Scheme 1. Schematic illustration of the synthetic process for the generation of the MoS₂/SNC-*T-t* composites.

Fig. 2. TEM (a) and HRTEM (b) images of MoS₂/SNC-900-12h.

the PMS/SNC composite at a high temperature to convert the PMS to MoS₂ owing to the S²⁻ and NH₃ released from the SNC at high temperature. Fig. 1(c) and (d) show SEM images of the SNC and PMS/SNC after calcination at 900 °C for 12 h; both samples exhibit particle aggregates with reduced particle sizes (~100 and ~50 nm, respectively). Fig. 2(a) and (b) shows TEM images of MoS₂/SNC-900-12h at different magnifications. The TEM images reveal that the samples consisted of highly dispersed and ultrafine MoS₂ nanosheets with few layers, which massively increases the availability of catalytic edge sites. A high resolution TEM (HRTEM) image (Fig. 2(b)) shows that graphite lattice fringes can be observed in the background, indicating that the as-prepared carbon materials are graphite phase.

Fig. 3(a) shows the XRD patterns of MoS₂/SNC-900-12h, SNC-900-12h, PMS/SNC, and bulk MoS₂. The XRD patterns have two diffraction peaks at 22.8° and 43.7°, which are related to the (002) and (101) peaks of the graphite of the SNC-900-12h sample [24]. This indicates that the SNC is in the graphite phase after the high temperature treatment. For PMS/SNC, no obvious diffraction peaks related to MoS₂ are observed besides the carbon diffraction peaks. Fig. 3(a) and (b) shows the XRD pattern of the MoS₂/SNC-*T*-*t* sample for *T* = 700, 800, 900, and 950 °C for *t* = 6 and 12 h. The data clearly shows that the height of the MoS₂ diffraction peaks is insignificant when the PMS/SNC sample is treated at 700 °C for 12 h, indicating that the MoS₂ is not fully formed. When the treatment temperature increases to 800 °C, diffraction peaks at 33.3 and 58.9° appear; these are assigned to the (100) and (110) diffraction peaks of hexagonal MoS₂ (2H-MoS₂, JCPDS 37-1492). This indicates that MoS₂ forms at this temperature. Compared with bulk MoS₂, no peak was observed at $2\theta = 14.2^\circ$, which is attributed to the (002) diffraction peak and indicates that the material is highly oriented in the (100) direction. No (002) diffraction peak implies that the MoS₂ has only a few layers owing to the PMS uniformly dispersing it in the carbon material matrix; this result agrees with the TEM results. Fig. 3(c) shows the XRD patterns of MoS₂/SNC-900-12h prepared using various feeding amounts of Na₂MoO₄. The diffraction peaks of MoS₂ became stronger and sharper with an increase in Na₂MoO₄, indicating that the size of

Fig. 3. (a) XRD patterns of bulk MoS₂, SNC-900-12h, and MoS₂/SNC-900-12h; (b) XRD patterns of MoS₂/SNC-*T* at various annealing temperatures and annealing durations; (c) XRD patterns of MoS₂/SNC-900-12h with various Na₂MoO₄·2H₂O loadings; (d) Raman spectra of SNC-900-12h and MoS₂/SNC-900-12h.

MoS₂ increases according to the Scherrer equation. Fig. 3(d) displays the Raman spectra of MoS₂/SNC-900-12h and SNC-900-12h. Both the SNC-900-12h and MoS₂/SNC-900-12h composites exhibit two dominant Raman peaks at 1341 and 1584 cm⁻¹, respectively; these are a good match with the D and G bands of graphite, respectively. In general, the relative intensity ratio of the D and G bands, I_D/I_G , is an indication of the graphite quality, which means the delocalized π conjugation is partially restored during the hybridization process. The I_D/I_G value of the MoS₂/SNC-900-12h hybrid ($I_D/I_G = 0.99$) is close to that of SNC-900-12h ($I_D/I_G = 0.98$), indicating that both samples have a similar degree of graphitization.

Elemental analysis of SNC-900-12h (Table 1) illustrates that some N and S are lost in the form of NH₃ and H₂S during the high temperature treatment. 3.3% N and 6.2% S, respectively, remained in SNC-900-12h to form N and S co-doped carbon materials. XPS was used to further confirm the composition and valance state of all elements in the composite. In Fig. 4(a) the XPS full-scan spectrum of SNC-900-12h shows that the material is mainly composed of C and O, while the S and N content is quite low, indicating that the S and N on the surface of the carbon material is lost during the high temperature treatment. For MoS₂/SNC-900-12h, strong Mo and S signals can be observed at 234 and 163 eV, respectively. The N 1s XPS signal is still quite weak, though. Fig. 4(b) shows a high resolution C 1s XPS spectrum of SNC-900-12h, which has four different peaks corresponding to C=C/C-C (284.6 eV), C-C (*sp*³, 284.9 eV), C-O (286.1 eV), and COOR (288.9 eV) groups. Fig. 4(c) shows a high resolution C 1s XPS spectrum of MoS₂/SNC-900-12h, which has five different peaks corresponding to C=C/C-C (284.6 eV), C-C (*sp*³, 284.9 eV), C-O (285.9 eV), and COOR (289.4 eV) groups;

further, another peak is visible at 286.8 eV, which corresponds to C-S/C-N, indicating S and N doped graphite. High-resolution XPS data of the composite in the Mo 3d region is shown in Fig. 4(d). It can be deconvoluted into three peaks, one of which is at 226.8 eV; this one actually corresponds to the S 2s of MoS₂. The two-main intense Mo 3d_{5/2} (229.4 eV) and Mo 3d_{3/2} (232.6 eV) components are characteristic of MoS₂, while the high binding energy peak of Mo 3d (235.8 eV) corresponds to MoO₃, which may result from the oxidation of the catalyst sample in air [25, 26]. The sulfur species were determined from the high-resolution XPS S 2p spectrum (Fig. 4(e)). The main doublet located at binding energies of 162.2 and 163.5 eV corresponds to the S 2p_{3/2} and S 2p_{1/2} (C-S-C) lines of MoS₂ [25]. Meanwhile, a peak at the binding energy at 164.9 eV suggests the existence of bridging disulfides S₂²⁻ and/or apical S²⁻ ligands (C=S), which may be related to high activity HER species [27]. The high-energy components at 168.1 and 169.2 eV can be assigned to high valance S species C-SO_x-C [28,29]. Fig. 4(f) shows the high resolution N 1s XPS spectrum of MoS₂/SNC-900-12h, which has three peaks at 395.5, 398.5, and 401.4 eV corresponding to Mo 3p_{3/2} in MoS₂, pyridinic, and graphitic N, respectively, which contribute to the electron density of the π -conjugated system via a pair of π -electrons in the graphitic carbon layers.

To investigate the catalytic activity of the MoS₂/SNC-900-12h composite toward HER, LSVs of the various catalysts were measured in a N₂ saturated H₂SO₄ solution (0.5 mol/L) using a typical three-electrode configuration. Commercial Pt/active carbon, bulk MoS₂, and SNC-900-12h were used as references. The samples were deposited on a glassy carbon electrode (5 mm diameter) with a loading of 0.285 mg/cm². Fig.

Fig. 4. XPS survey spectra of the SNC-900-12h (1) and MoS₂/SNC-900-12h composites (2) (a); High-resolution C 1s XPS spectra of SNC-900-12h (b) and MoS₂/SNC-900-12h (c); High-resolution XPS spectra of the MoS₂/SNC-900-12h Mo 3d and S 2s (d); S 2p (e); and N 1s (f).

Fig. 5. (a) HER polarization curves and (b) the corresponding Tafel plots of 20% Pt/C, bulk MoS₂, SNC-900-12h, and MoS₂/SNC-900-12h recorded on GCE with a catalyst loading of 0.285 mg/cm² at a potential scan rate of 5 mV/s in H₂SO₄ solution (0.5 mol/L); (c) HER polarization curves of 20% Pt/C and MoS₂/SNC-*T-t*; (d) HER polarization curves of 20% Pt/C and MoS₂/SNC-900-12h with addition of Na₂MoO₄·2H₂O.

Fig. 5(a) shows the HER polarization curves of 20% Pt/C, bulk MoS₂, SNC-900-12h, and MoS₂/SNC-900-12h. The bulk MoS₂ and SNC-900-12h show much higher overpotentials. Fig. 5(c) shows the polarization curves of PMS/SNC treated at different temperatures for either 6 or 12 h. The data show that the electrocatalytic activity continuously improves after the thermal treatment. When PMS/SNC was treated at 800 °C for 6 h, the onset overpotential and the potential at a current density of 10 mA/cm² were 165 and 322 mV vs. RHE, respectively. Both the onset potential and potential at 10 mA/cm² reduce as the treatment temperature is increased. However, the electrocatalytic performance of MoS₂/SNC-950-6h was decreased. From Fig. 5(a), it can be seen that the MoS₂/SNC-900-12h composite catalyst shows the smallest onset overpotential of 115 mV for hydrogen evolution, beyond which the cathodic current density rises rapidly under more negative potentials. The onset overpotential of MoS₂/SNC-900-12h is lower than that of the other samples, indicating good catalytic activity of the MoS₂/SNC-900-12h composite for HER. Moreover, the MoS₂/SNC-900-12h composite displayed the largest cathodic current density of all the test samples except for the commercial Pt/active carbon sample. MoS₂/SNC-900-12h also exhibited the lowest overpotential (237 mV) at a current density of 10 mA/cm². We also studied the effect of adding Na₂MoO₄ into the

hydrothermal reaction. Fig. 5(d) shows the composite produced from adding between 0.5 and 2 mmol of Na₂MoO₄. When 1 mmol of Na₂MoO₄ was added into the reaction, MoS₂/SNC-900-12h gave the best catalytic activity. A Tafel plot obtained from the overpotential vs. the logarithm of the current density (η vs. $\log(j)$) are shown in Fig. 5(b), which can be used to perform a quantitative kinetics analysis of HER [30]. The Tafel slopes can be determined by fitting the linear portions of the Tafel plots to the Tafel equation ($\eta = b \log(j) + a$, where b is the Tafel slope). The values of the Tafel slope from Fig. 5(b) were 184, 151, 78, and 30 mA/decade for SNC-900-12h, bulk MoS₂, MoS₂/SNC-900-12h, and 20% Pt/C, respectively. Although the Tafel slopes of the MoS₂/SNC-900-12h composites were lower than those of the MoS₂/graphene catalyst [31], this may be because of some active sites were lost owing to the MoS₂ embedded in the carbon matrix.

The interfacial reactions and electrode kinetics of the MoS₂/SNC-900-12h composite catalyst in HER can be further demonstrated by EIS. The Nyquist plot of the samples and the corresponding electrical equivalent circuit diagram are given in Fig. 6(a) and (b), respectively, while the impedance parameters determined by fitting the EIS response are listed in Table 2. The ohmic series resistance (R_s) was determined via the intercept of the semicircle and the real axis, and the charge transfer re-

Fig. 6. (a) Electrochemical impedance spectra of bulk MoS₂, SNC-900-12h, and MoS₂/SNC-900-12h composites in HER at -0.20 V (vs. RHE); (b) Equivalent circuit of MoS₂/SNC-900-12h; (c) Electrochemical impedance spectra of MoS₂/SNC-*T-t* in HER at -0.20 V (vs. RHE); (d) Electrochemical impedance spectra of MoS₂/SNC-900-12h with addition of Na₂MoO₄·2H₂O in HER at -0.20 V (vs. RHE).

distance (R_{ct}) and the corresponding interfacial capacitance were determined by fitting the semicircle of the Nyquist plot in terms of the equivalent circuit model shown in Fig. 6(b). The R_s of all the samples falls within the range of 4–5 Ω, which is a manifestation of the good conductivity of the electrolyte. In addition, the charge transfer resistance (R_{ct}) of the MoS₂/SNC composites follow the sequence MoS₂/SNC-900-12h (124 Ω) < bulk MoS₂ (7.18 kΩ) < SNC-900-12h (9.88 kΩ), which is in accordance with the HER results shown in Fig. 5(a). We believe a synergistic effect between MoS₂ and SNC promotes the change in conductivity. At the same time, MoS₂ formation during the high temperature treatment may also enhance the graphitization and conductivity of SNC. It has been well established that R_{ct} is related to the electrocatalysis kinetics and that a lower R_{ct} value corresponds to a faster reaction rate. Thus, a fast charge transfer during the electrocatalytic reaction coupling with the large exposed active surface area of the catalyst likely contributes to the superior electrocatalytic activity of the MoS₂/SNC-900-12h composite. Fig. 6(c) shows the Nyquist

plots of PMS/SNC treated at different temperatures for either 6 or 12 h; the results are in accordance with the HER results shown in Fig. 5(c). Fig. 6(d) shows the Nyquist plots of the composite produced from adding between 0.5 and 2 mmol Na₂MoO₄·2H₂O; the results are in accordance with the HER results shown in Fig. 5(d).

Furthermore, to probe the HER stability of the MoS₂/SNC-900-12h composite, we cycled the catalyst continuously for 5000 cycles between 0 and -0.3 V vs. RHE at 100 mV/s. After cycling, the catalyst was measured at the same applied potential range as for the initial test. As shown in Fig. 7(a), the current density of the MoS₂/SNC-900-12h composite catalyst had decreased slightly ($\sim 2.6\%$) compared with the initial value (at a current density of 10 mA/cm²) after 5000 continuous cycles, indicating that the MoS₂/SNC-900-12h composite catalyst exhibits excellent HER activity with long-term stability. We also characterized the sample after 5000 cycles; Fig. 7(b) shows that the XRD pattern of MoS₂/SNC-900-12h after 5000 cycles. Another new peak was observed at $2\theta = 16.5^\circ$, which corresponds to the (002) diffraction peak. This indicates that a small amount of MoS₂ may aggregate during the test. Fig. 7(c) and (d) show the TEM and HRTEM images of MoS₂/SNC-900-12h after 5000 test cycles. A small amount of multi-layer MoS₂ was observed. Most of the MoS₂ was still in a few-layers state, however, to which we attribute the excellent stability of MoS₂/SNC-900-12h.

Table 2

Impedance parameters determined from fitting the EIS responses of the various catalysts.

Catalyst	R_s (Ω)	R_{ct} (Ω)
MoS ₂ /SNC-900-12h	4.92	124
Bulk MoS ₂	4.35	7180
SNC-900-12h	5.28	9880

Fig. 7. (a) Stability test for the MoS₂/SNC-900-12h recorded on GCE with a catalyst loading of 1 mg/cm². A small degradation of HER activity is observed after 5000 cycles between 0 and -0.3 V (vs. RHE) at a potential scan rate of 100 mV/s in H₂SO₄ solution (0.5 mol/L); (b) XRD patterns of MoS₂/SNC-900-12h before and after 5000 cycles; (c) TEM and (d) HRTEM images of MoS₂/SNC-900-12h after 5000 cycles.

4. Conclusions

In summary, we developed a simple synthesis route to prepare graphite S, N co-doped carbon solid powder using a one-step hydrothermal method. SNC possesses a porous structure and multiple functional group because it is prepared using a bottom-up route. MoO₄²⁻ was further introduced into the reaction to fabricate a MoS₂/SNC composite, which can chemically bond with the functional groups on the carbon materials. This results in the MoO₄²⁻ being uniformly dispersed into the carbon materials. A high temperature treatment helps MoO₄²⁻ transfer into MoS₂ since S²⁻ can be released from SNC during the high temperature treatment. Only few-layered MoS₂ can be formed during the thermal treatment because the MoO₄²⁻ is embedded in the carbon materials. After treatment at 900 °C for 12 h, the MoS₂/SNC-900-12h material exhibits good electrocatalytic properties with a small onset of the overpotential at 115 mV, a large cathodic current density, and small Tafel slope of 78 mV per decade. At the same time, the MoS₂/SNC-900-12h exhibits excellent stability.

References

- [1] M. S. Dresselhaus, I. L. Thomas, *Nature*, **2001**, 414, 332–337.
- [2] Z. H. Wen, J. Liu, J. H. Li, *Adv. Mater.*, **2008**, 20, 743–747.
- [3] D. V. Esposito, S. T. Hunt, A. L. Stottlemeyer, K. D. Dobson, B. E. McCandless, R. W. Birkmire, J. G. Chen, *Angew. Chem. Int. Ed.*, **2010**, 49, 9859–9862.
- [4] S. J. Liu, X. Zhang, J. Zhang, Z. G. Lei, X. Liang, B. H. Chen, *Sci. China Mater.*, **2016**, 59, 1051–1061.
- [5] H. Zhong, J. Wang, F. Meng, X. Zhang, *Angew. Chem. Int. Ed.*, **2016**, 55, 9937–9941.
- [6] F. Meng, H. Zhong, D. Bao, J. Yan, X. Zhang, *J. Am. Chem. Soc.*, **2016**, 138, 10226–10231.
- [7] Z. L. Wang, X. F. Hao, Z. Jiang, X. P. Sun, D. Xu, J. Wang, H. X. Zhong, F. L. Meng, X. B. Zhang, *J. Am. Chem. Soc.*, **2015**, 137, 15070–15073.
- [8] J. Wang, K. Li, H. X. Zhong, D. Xu, Z. L. Wang, Z. Wu, X. B. Zhang, J. Wang, H. X. Zhong, Z. Jiang, *Angew. Chem. Int. Ed.*, **2015**, 54, 10530–10534.
- [9] D. Merki, X. L. Hu, *Energy Environ. Sci.*, **2011**, 4, 3878–3888.
- [10] Y. Yan, B. Y. Xia, Z. C. Xu, X. Wang, *ACS Catal.*, **2014**, 4, 1693–1705.
- [11] J. Kibsgaard, Z. B. Chen, B. N. Reinecke, T. F. Jaramillo, *Nat. Mater.*, **2012**, 11, 963–969.
- [12] H. I. Karunadasa, E. Montalvo, Y. J. Sun, M. Majda, J. R. Long, C. J. Chang, *Science*, **2012**, 335, 698–702.
- [13] Q. Tang, D. E. Jiang, *ACS Catal.*, **2016**, 6, 4953–4961.
- [14] D. S. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, Y. Cui, *Nano Lett.*, **2013**, 13, 1341–1347.
- [15] J. F. Xie, H. T. Zhang, S. Li, R. X. Wang, X. Sun, M. Zhou, J. F. Zhou, X. W. D. Lou, Y. Xie, *Adv. Mater.*, **2013**, 25, 5807–5813.
- [16] W. J. Zhou, D. M. Hou, Y. H. Sang, S. H. Yao, J. Zhou, G. Q. Li, L. G. Li, H. Liu, S. W. Chen, *J. Mater. Chem. A*, **2014**, 2, 11358–11364.
- [17] C. G. Morales-Guio, L. A. Stern, X. L. Hu, *Chem. Soc. Rev.*, **2014**, 43, 6555–6569.
- [18] D. H. Youn, S. Han, J. Y. Kim, J. Y. Kim, H. Park, S. H. Choi, J. S. Lee, *ACS Nano*, **2014**, 8, 5164–5173.
- [19] D. McAteer, Z. Gholamvand, N. McEvoy, A. Harvey, E. O'Malley, G. S. Duesberg, J. N. Coleman, *ACS Nano*, **2016**, 10, 672–683.
- [20] J. Wang, H. X. Zhong, Z. L. Wang, F. L. Meng, X. B. Zhang, *ACS Nano*, **2016**, 10, 2342–2348.

Graphical Abstract

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Highly dispersed few-layer MoS₂ nanosheets on S, N co-doped carbon for electrocatalytic H₂ production

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Highly dispersed few-layer MoS₂ nanosheets on S, N co-doped carbon were synthesized using a simple hydrothermal, high temperature annealing route. More catalytic active sites were thus exposed and the electrocatalytic properties were greatly enhanced for the hydrogen evolution reaction.

- [21] U. Maitra, U. Gupta, M. De, R. Datta, A. Govindaraj, C. N. R. Rao, *Angew. Chem. Int. Ed.*, **2013**, 52, 13057–13061.
- [22] D. Qu, M. Zheng, L. G. Zhang, H. F. Zhao, Z. G. Xie, X. B. Jing, R. E. Haddad, H. Y. Fan, Z. C. Sun, *Sci. Rep.*, **2014**, 4, 5294.
- [23] D. Qu, M. Zheng, P. Du, Y. Zhou, L. G. Zhang, D. Li, H. Q. Tan, Z. G. Zhao, Z. C. Xie, Z. Sun, *Nanoscale*, **2013**, 5, 12272–12277.
- [24] D. F. Yan, S. Dou, L. Tao, Z. J. Liu, Z. G. Liu, J. Huo, S. Y. Wang, *J. Mater. Chem. A*, **2016**, 4, 13726–13730.
- [25] H. W. Wang, P. Skeldon, G. E. Thompson, *Surf. Coat. Technol.*, **1997**, 91, 200–207.
- [26] P. Li, Z. Yang, J. X. Shen, H. Q. Nie, Q. R. Cai, L. H. Li, M. Z. Ge, C. C. Gu, X. A. Chen, K. Q. Yang, L. J. Zhang, Y. Chen, S. M. Huang, *ACS Appl. Mater. Interfaces*, **2016**, 8, 3543–3550.
- [27] X. L. Zheng, J. B. Xu, K. Y. Yan, H. Wang, Z. L. Wang, S. H. Yang, *Chem. Mater.*, **2014**, 26, 2344–2353.
- [28] Y. Ito, W. T. Cong, T. Fujita, Z. Tang, M. W. Chen, *Angew. Chem. Int. Ed.*, **2015**, 54, 2131–2136.
- [29] W. Kiciński, M. Szala, M. Bystrzejewski, *Carbon*, **2014**, 68, 1–32.
- [30] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Hørch, I. Chorkendorff, *Science*, **2007**, 317, 100–102.
- [31] Y. G. Li, H. L. Wang, L. M. Xie, Y. Y. Liang, G. S. Hong, H. J. Dai, *J. Am. Chem. Soc.*, **2011**, 133, 7296–7299.

高分散超薄二硫化钼/硫、氮共掺碳复合材料的电催化析氢性能滑世新^a, 曲丹^{a,b,c}, 安丽^a, 席广成^d, 陈戈^a, 李钊^a, 周志军^e, 孙再成^{a,*}^a北京工业大学环境与能源工程学院, 化学与化学工程系, 绿色催化与分离北京市重点实验室, 北京100124^b中国科学院长春光学精密机械与物理研究所, 发光学及应用国家重点实验室, 吉林长春133033^c中国科学院大学, 北京100049^d中国检验检疫科学研究院, 纳米材料与产品研究中心, 北京100000^e中国工程物理研究院核物理与化学研究所, 四川绵阳621000

摘要: 氢气是一种清洁可再生能源, 有望在未来替代化石燃料成为最主要的能源物质。电催化析氢技术是最有效的产氢途径之一。目前, 电催化析氢催化剂主要是贵金属铂, 由于其昂贵的价格限制了它的大规模应用。所以在不减少催化剂活性的前提下尽量减少贵金属的使用或者寻找替代物质, 降低成本是工业化大规模使用析氢反应(HER)催化剂的前提。二硫化钼基催化剂因其价格低廉、资源丰富且具有优异的催化析氢性能而引起研究者的广泛关注。实验和理论研究都证明了二硫化钼的催化性能和其催化活性位点有关。所以, 开发一种具有丰富的活性位点、良好的导电性的二硫化钼基催化剂可以获得高的产氢性能和良好的稳定性。因此, 对于提高MoS₂的电催化析氢性能的研究主要集中于增加MoS₂暴露活性位点的个数和导电性。然而, 二硫化钼层与层之间的相互作用可能导致其发生聚集, 较低的导电率都有可能降低它的电催化活性。

我们通过水热的方法直接制备出了固体的硫、氮共掺杂的、具有石墨化结构的碳复合材料(SNC)。将钼酸钠加入到反应中后, 多钼酸盐通过化学交互作用均匀地嵌入、分散到SNC中。经高温处理后, SNC放出S²⁻, 多钼酸盐结合S²⁻生成二硫化钼。SNC有效地防止了二硫化钼聚集成为大的颗粒。我们成功地制备出具有较好析氢性能的、高度分散于SNC中的二硫化钼纳米片。通过透射电子显微镜(TEM)、扫描电子显微镜(SEM)、X射线衍射(XRD)、拉曼光谱(Raman)、元素分析、X射

线光电子能谱(XPS)等测试手段对材料进行了表征,通过电催化析氢、电化学阻抗以及稳定性测试等手段研究了其电催化性能.

由MoS₂/SNC-900-12h的TEM图片可以看出,二硫化钼纳米片高度分散于碳复合材料中,且层数只有一到几层,暴露出了更多的催化活性位点.拉曼光谱图的D带(1341 cm⁻¹)和G带(1584 cm⁻¹)体现出了材料具有较好的石墨化结构,提高了材料的导电性. XPS C 1s谱图中存在C-S和C-N键, S 2p谱图中存在C-S-C、C=S和C-SO_x-C键, N 1s谱图中存在吡啶氮和石墨氮,结合元素分析,说明该碳材料确为硫氮共掺杂的碳; Mo谱测试显示出Mo 3d_{5/2} (229.4 eV)和Mo 3d_{3/2} (232.6 eV),证明了二硫化钼成功地嵌入到了碳材料中. 电化学性能表征显示MoS₂/SNC-900-12h在H₂SO₄溶液(0.5 mol/L)中展现出较低的起始电位(115 mV)以及低的过电位(237 mV). 电化学阻抗测试显示在H₂SO₄溶液(0.5 mol/L)中过电位为-0.2 V (vs. RHE)时R_{ct}只有124 Ω. 此外,在-0.3–0 V (vs. RHE)下,经5000圈稳定性测试后性能只有约2.6% (10 mA/cm²)的衰减,说明MoS₂/SNC-900-12h同样具有优异的电化学稳定性.

关键词: 二硫化钼纳米片; 硫、氮共掺杂的碳; 电催化析氢; 复合材料; 析氢反应

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