Preparation and NRR application of transition metal nanosheets on carbon nanofiber membranes

Shengmei Huang¹, Meng Zhang¹, Yi-Tao Liu¹,²,*

¹College of Textiles, Donghua University, Shanghai, 201620, China
²Innovation Center for Textile Science and Technology, Donghua University, Shanghai, 200051, China
*liu-yt03@dhu.edu.cn

Abstract. Electrocatalytic Nitrogen Reduction (NRR) is a green and sustainable method of artificial nitrogen fixation, but it is still a serious challenge due to the lack of efficient and selective catalysts. In this paper, carbon nanofiber membranes (NFMs) were prepared by electrospinning technology as the skeleton structure of electrocatalytic materials, and Sn doped MoSe₂ nanosheets on carbon NFMs (Sn doped MoSe₂@C NFMs) were synthesized by a one-step hydrothermal synthesis method. Compared with pure MoSe₂@C NFMs, Sn doped MoSe₂@C NFMs will create vacancies, increase the reactive sites of the NRR catalyst, and make Sn doped MoSe₂@C NFMs have better ammonia yield (1.61 ×10⁻¹⁰ mol s⁻¹ cm⁻²) and Faraday efficiency (14.51%). This research provides a new idea for designing the structure design of NRR catalyst.

1. Introduction
Ammonia (NH₃) is mainly used in the production of fertilizers and plays an important role in plastics, cosmetics, agriculture, pharmaceuticals, and textiles. Nitrogen (N₂) is abundant in nature, people cannot directly use it because of the high bonding energy of N≡N (940.95 kJ mol⁻¹). [1] At present, the Haber-Bosch process is the main method used in industrial ammonia synthesis. However, the Haber-Bosch causes excessive energy consumption and emissions of greenhouse gases. [2] Electrocatalytic nitrogen reduction reaction (NRR) has been widely studied because it is clean, sustainable and has achieved under environmental conditions. [3]

In order to effectively nitrogen fixation, a highly active electrocatalyst is required. In the past, a large number of electrocatalytic materials and noble metal catalyst materials have been limited due to their extremely slow reaction kinetics and selectivity, while transition metal disulfide has high catalytic activity, layered structure, unique photoelectric properties in the field of electrocatalysis. [4] This paper proposes to use electrospinning carbon NFMs as a framework material, Sn doped MoSe₂@C NFMs were synthesized by hydrothermal method. The doping of Sn makes the MoSe₂@C NFMs produce vacancies and increases the reaction of the material. The active site shows excellent activity and high selectivity, and its Faraday efficiency is relatively high at 14.51%.
2. Experiment

2.1. Preparation of carbon nanofibers
The polyacrylonitrile (PAN) NFMs was prepared by electrospinning and annealing procedures. First of all, the 13% PAN/DMF precursor solution was obtained by PAN and N, N-dimethylformamide (DMF), and stirred for 12 hours under environmental conditions. Then, the precursor solution was spun on a DXES-4 electrospinning device, at spinning voltage of 30 kV, and perfusion rate of 1 mL/h. The electrospinning was performed at temperature 25 ± 2°C and humidity 45 ± 2%. Finally, the PAN NFMs was pre-oxidized, annealed in nitrogen to prepared carbon NFMs.

2.2. Preparation of Sn doped MoSe$_2$@C
In a typical experiment, 0.6197 g of Se, 0.5486 g of Na$_2$MoO$_4$, 0.1037 g of SnCl$_4$ were dissolved in a 40 ml solution (including 20 ml C$_2$H$_6$O and 20 ml H$_2$O), then 0.12 g of NaBH$_4$ were pour into the above solution. Immediately perform rapid stirring on a magnetic stirrer. After stirring for 1h, the mixed solution was transferred to 50 ml of Teflon-lined stainless autoclave. Then, 40 mg of carbon NFMs were immersed in the solution, and put into the reaction kettle, sealed and heated in a blast oven for 24 hours at 220°C. After the reactor was cooled to ambient, Sn doped MoSe$_2$@C NFMs were taken out, rinsed repeatedly with H$_2$O and ethanol, and dried for 4h at 80°C.

2.3. Characterization
SEM was performed by Hitachi SU 5000 microscope operated at voltage of 20 kV. XPS was analyzed by ULVAC-PHI 5300 spectrometer. The Bruker D8 Advance diffractometer was used to test XRD. EPR was performed by a Bruker EMX-8 spectrometer. Absorbance was measured at room temperature by UV-vis spectrophotometer.

2.4. Electrochemical nitrogen fixation
The NRR experiment was carried out under environmental condition, the two-chamber electrocatalytic tank was filled with 50ml 0.1M Na$_2$SO$_4$. Two chambers were separated with Nafion 211 membrane. The sample size of 0.5×0.5 cm was tested, and bubbles of nitrogen or argon of high purity (99.999%) were pumped into the electrolytic cell for at least 30 minutes to completely remove the air. All electric potentials need to be converted into reversible hydrogen electric potential (RHE), the formula is:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.245 \text{V} \quad (1)$$

3. Analysis
The comparison of field emission electron microscopy images of carbon NFMs and Sn doped MoSe$_2$@C NFMs shows (Figure 1a, b) that both are composed of randomly oriented nanofibers with a length of tens of nanometers. Comparing with smooth carbon NFMs, the surface of Sn doped MoSe$_2$@C NFMs is clearly rougher, with petal-shaped growth on the surface.

![Figure 1 SEM images showing (a) carbon NFMs, and (b) Sn doped MoSe$_2$@C NFMs.](image-url)
Figure 2 (a) XRD patterns of MoSe$_2$@C NFMs and Sn doped MoSe$_2$@C NFMs, (b) EPR spectra, (c) Mo 3d, and (d) Sn 3d spectra.

The characteristic peaks of MoSe$_2$@C NFMs and Sn doped MoSe$_2$@C NFMs are shown in Figure 2a, and the characteristic peaks of 2H-MoSe$_2$ can be observed.\[5\] To verify that Sn doping will create vacancies for MoSe$_2$@C NFMs, an EPR was performed. When g=2.0039, the signal of Sn doped MoSe$_2$@C NFMs is significantly higher and wider than that of MoSe$_2$@C NFMs (Figure 2b), indicating that the former has more defects than the latter.\[6\] The XPS was conducted to make clear the valence states. Figure 2c shows Mo 3d spectra. For Sn doped MoSe$_2$@C NFMs, the two absolute peaks at 232 eV and 228.8 eV that are assigned to the Mo 3d$_{3/2}$ and 3d$_{5/2}$ orbitals of Mo$^{4+}$.\[7\] It is worth noting that Sn doped MoSe$_2$@C NFMs has a slight negative shift in the binding energy shift of Mo 3d, which is caused by the existence of the Sn atom substitution sites, indicating that the Sn doped MoSe$_2$@C NFMs electrons density increases.\[8\] Figure 2d shows the high-resolution Sn 3d, in which the characteristic peaks at 494.64 eV and 486.25 eV correspond to the 3d$_{3/2}$ and 3d$_{5/2}$ orbital of Sn$^{4+}$.\[9\]
The NRR reaction is carried out in a double-chamber electrolytic cell, then subjected to linear sweep voltammetry (LSV) to verify the electrocatalytic activity of the material. As shown in Figure 3a that the two curves in N$_2$ and Ar shown significantly different in the current density, indicating that NRR possible between $-0.35$ to $-0.75$ V vs. RHE. After the sample was electrolyzed in the electrolytic cell for 2h, the electrolyte of the cathode was sampled, and the absorbance of the electrolyte was tested by UV/Vis. According to the standard ammonia curve equation: $y = 0.26x + 0.048$, combined with the accumulated charge and ammonia concentration information, we can calculate the ammonia yield and Faraday efficiency (Figure 3b). The highest at $-0.45$ V vs. RHE, the ammonia yield is $1.61 \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$, and the Faraday efficiency is 14.51%. As shown in Figure 3c, the results can illustrate the superiority of Sn doped MoSe$_2$@C NFMs as a NRR catalyst. Through the test under the conditions of nitrogen and argon (Figure 3d), the influence of trace ammonia pollution in the system on the final result of this experiment was eliminate.

4. Conclusion
In summary, the creation of vacancies by Sn doped MoSe$_2$@C NFMs increases active sites and improves the electrocatalytic activity of NRR catalysts for nitrogen fixation in the environment. The carbon NFMs can evenly load MoSe$_2$ on it, prevent the occurrence of agglomeration, and further improve the NRR performance of the Sn doped MoSe$_2$@C NFMs. Sn doped MoSe$_2$@C NFMs can be used as a self-
supporting electrocatalyst with great ammonia yield ($1.61 \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$) and Faraday efficiency (14.51%).

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