Sulfur defect-rich WS_{2-x} nanosheet electrocatalysts for N₂ reduction

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ABSTRACT Seeking catalysts with high electrocatalytic activity for ambient-condition N₂ reduction reaction (NRR) remains an ongoing challenge due to the chemical inertness of N₂. Herein, defect-rich WS₂ nanosheets (WS_{2-x}) were designed as an efficient electrocatalyst for NRR, which were prepared *via* vulcanizing the oxygen-vacancy-rich tungsten oxide in a vacuum tube. The sulfur defects were conducive to the adsorption and activation of N₂. In neutral electrolyte of 0.1 mol L⁻¹ Na₂SO₄ at -0.60 V vs. reversible hydrogen electrode, such WS_{2-x} offered a high Faradaic efficiency of 12.1% with a NH₃ generation rate of 16.38 μg h⁻¹ mg_{cat}⁻¹.

Keywords: electrocatalysis, nitrogen reduction reaction, transition metal sulfide, WS_{2-x}, sulfur vacancy

INTRODUCTION

NH₃ has been considered as one of the most important fundamental chemicals in the world and has great applications in industry and agriculture [1,2]. It is also a promising green energy carrier and sustainable fuel [3]. The urgent demand for the practical application of NH₃ has aroused people's strong interest in the transformation of N₂ to NH₃ [4,5]. At present, more than 90% of the synthetic NH₃ is produced from N₂ and H₂ *via* industrial Haber-Bosch process at extreme reaction conditions (300–550°C, 200–350 atm) [6]. This process is energy-intensive, accounting for 1%–3% of global energy consumption and causing massive greenhouse gas emission [7–9]. Thus, a new, gentler and more efficient alternative is desired. The electrocatalytic reduction of N₂ to NH₃ can be driven by renewable electrical energy, representing a potential green and energy-saving strategy [6,10]. How-

ever, designing highly active catalysts for electrochemical N₂ reduction reaction (NRR) remains an ongoing challenge due to the intrinsic chemical inertness of N₂. Thus, many nanomaterials have been explored, such as Au [11], Ru [12], Pd [13], as well as transition metal compounds of Fe₂O₃-carbon nanotube [14], MoO₃ [15], Mo₂N [16] and CoP [17] and even non-metallic catalysts of B₄C [18], N-doped porous carbon [19] and poly(*N*-ethyl-benzene-1,2,4,5-tetracarboxylic diimide) [20]. Among them, transition-metal-based ones are widely concerned because of their high abundance, low cost and promising catalytic activity for NH₃ synthesis.

Recent studies suggest that tungsten-based compounds such as WO₃ and W₂N₃ are active for the NRR [21,22]. However, WO₃ shows weak catalytic activity in neutral condition, while, the preparation process of W₂N₃-based NRR catalyst suffers from the complex preparation process. Single-layer WS₂ nanosheets are composed of S-W-S sandwich arrays, which show a graphene-like structure with high electron mobility, moderate band gap, and abundant active sites [23,24], and have been applied in many fields, such as photocatalysis [25], and lithium/sodium storage [26]. In addition, defect engineering is an effective strategy to tune the electronic structure and increase the number of reactive sites, leading to a reduction in the reaction energy barrier [27]. Accordingly, it was reported that the sulfur vacancies (S-vacancies) in WS₂ nanosheets are more likely to be generated than other defects due to the low formation energy of S-vacancies [28,29]. Theoretical calculations have indicated the possible feasibility of S-vacancies in improving the performance of WS₂ as an NRR catalyst [30,31], but no such

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catalysts have been reported experimentally. Therefore, it is meaningful to prepare defect-rich WS_2 (WS_{2-x}) as an NRR catalyst in a relatively simple and environment-friendly way.

Herein, WS_{2-x} nanosheets were prepared *via* vulcanizing the oxygen-vacancy-rich tungsten oxide in a vacuum tube. The WS_{2-x} catalysts exhibited high electrocatalytic NRR activity under neutral conditions ($0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$). Under the operating voltage of -0.60 V vs. reversible hydrogen electrode (RHE), these catalysts could achieve Faradaic efficiency (FE) of 12.1% and NH_3 generation rate (R_{NH_3}) of $16.38 \mu\text{g h}^{-1} \text{ mg}_{\text{cat.}}^{-1}$. The performance of WS_{2-x} was superior to the precursor WO_3 with oxygen vacancies (WO_3 : $7.69 \mu\text{g h}^{-1} \text{ mg}_{\text{cat.}}^{-1}$ and 3.8%) and commercial WS_2 (WS_2 : $3.63 \mu\text{g h}^{-1} \text{ mg}_{\text{cat.}}^{-1}$ and 0.35%). In addition, the WS_{2-x} catalysts also exhibited a high degree of electrochemical and structural stability.

EXPERIMENTAL SECTION

Chemicals

Ultra-high-purity N_2 (99.999%) was purchased from Qingdao Dehai Weiye Technology Co., Ltd. (Qingdao, China). Nafion (5 wt% in aliphatic alcohols and water), salicylic acid, ethanol, *para*-(dimethylamino) benzaldehyde, sodium nitroferricyanide dehydrate, ammonium chloride, sodium citrate dehydrate, sodium hypochlorite solution, sodium sulfate, sodium hydroxide, hydrochloric acid, sodium tungstate dehydrate, citric acid, glucose, hydrazine monohydrate, amorphous boron powder, and sulfur powder all at analytical grade were purchased from Shanghai Macklin Biochemical Co. Ltd., China. Hydrophobic carbon paper (CP) and Nafion membrane were received from Shanghai Hesen Electric Co., Ltd. (Shanghai, China). Deionized (DI) water ($18.2 \text{ M}\Omega \text{ cm}$) from a

Milli-Q ultrapure system (Qingdao, China) was used throughout all experiments.

Materials synthesis

Preparation of WO_3 precursor

WO_3 were synthesized by a two-step process [32]. Briefly, $1 \text{ mmol L}^{-1} \text{ Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was initially added into 30 mL of H_2O to prepare a transparent solution, into which 1.5 mmol L^{-1} citric acid and 5 mmol L^{-1} glucose were then added in order. HCl solution (3 mL , 6 mol L^{-1}) was added into the mixed solution, followed by 30 min stirring. The mixture was transferred into a 50-mL Teflon-lined autoclave, which was then sealed and heated at 120°C for 24 h . After the autoclave cooled down to room temperature, the precursor was separated by centrifugation, washed with water and anhydrous ethanol for several times until the organics were completely removed. Finally, the precursor was dried at 60°C in vacuum oven for 12 h . Then the WO_3 was synthesized by calcining the precursor at 400°C with a heating rate of 2°C min^{-1} in Ar atmosphere for 2 h . After being cooled to room temperature, the obtained dark-blue powder was collected.

Preparation of WS_{2-x}

The preparation process of WS_{2-x} is shown in Scheme 1 [33]. Stoichiometric amounts (1:1) of boron and sulfur powders were mixed and placed in a separate fused silica tube of the same size as the one for WO_3 nanosheets. The constituent materials (WO_3 nanosheets, boron powder and sulfur powders) reacted in the molar ratio of 1:2:2. To ensure a complete reaction of metal oxides, S was loaded 10% more than the stoichiometric amounts. The whole container was flame-sealed after evacuating through a vacuum line ($\sim 10^{-4} \text{ bar}$), the container was kept at 550°C ,

Scheme 1 The preparation process of WS_{2-x} and diagram of the three-electrode system of the unit used in NRR.

for 24 h, and subsequently cooled radiatively to room temperature. After the reactions, the lower tube was empty, which indicated complete consumption of boron. The silica reaction tubes were intact, and there was no visible indication of corrosion on the inner surface of the tubes. The products were cleaned several times with carbon disulfide and DI water (or methanol) to wash off unreacted S, B₂S₃, and the by-product B₂O₃.

Materials characterization

X-ray diffraction (XRD) patterns were obtained from a Shimadzu XRD-6100 diffractometer accompanied by Cu K α radiation (40 kV, 30 mA) with a wavelength of 0.154 nm (Japan). Scanning electron microscopy (SEM) images were acquired from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). Transmission electron microscopy (TEM) images, high resolution TEM (HRTEM) images, and the corresponding energy dispersive X-ray spectroscopy (EDX) elemental mapping images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. Atomic force microscopy (AFM) images were obtained from BRUKER Dimension Edge. Brunauer-Emmett-Teller was tested with micromeritics TriStar II 3020. The nitrogen temperature programmed desorption (N₂-TPD) was recorded on micromeritics AutoChem II 2920. X-ray photoelectron spectroscopy (XPS) measurements were assigned on an ESCALABMK II X-ray photoelectron spectrometer in which the Mg element was used as the exciting source. The absorbance data of spectrophotometer were measured on SHIMADZU UV-1800 spectrophotometer. The room temperature electron spin resonance (ESR) spectra were recorded on an X-band (ν_{mw} = 9.84 GHz) EMXmicro BRUKER spectrometer.

Preparation of the working electrode

The CP was cut into a rectangle of 1 × 2 cm² and was cleaned *via* brief sonication with ethanol and water for several times. The WS_{2-x} catalyst (5.0 mg) was mixed with 325 μ L of water, 625 μ L of ethanol, and 20 μ L of Nafion (5 wt%), and sonicated for at least 30 min to form a homogeneous ink. The homogeneous ink (20 μ L) was evenly drop on CP (1 × 1 cm²) and dried under ambient conditions.

Electrochemical measurements

Electrochemical measurements were performed using a gas-tight H-type dual-chamber electrolytic cell under the ambient conditions [34] (Scheme 1). Before NRR mea-

surement, the Nafion membrane was pretreated by heating in H₂O₂ (3 wt%), 0.5 mol L⁻¹ H₂SO₄, and ultrapure water at 80°C for 2 h, respectively. Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using an Ag/AgCl electrode as the reference electrode, a Pt foil as the counter electrode and WS_{2-x}/CP as the working electrode. All experiments were performed at ambient conditions. Before the NRR measurements, the Na₂SO₄ electrolyte (0.1 mol L⁻¹) was bubbled with high-purity N₂ (99.999%) for 45 min. All potentials reported in this work were calibrated to RHE, using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{\text{Ag/AgCl}} \quad (1)$$

Determination of NH₃ and N₂H₄

The NH₃ concentration was determined by indophenol blue spectrophotometry measurement with salicylic acid [35]. The N₂H₄ content in 0.1 mol L⁻¹ Na₂SO₄ after electrolysis was detected by Watt and Chrisp's method [36]. Detailed experimental procedures refer to the Supplementary information.

Calculations of NH₃ generation rate and Faradaic efficiency

NH₃ generation rate was calculated using the following equation:

$$\text{NH}_3 \text{ generation rate } (\mu\text{g h}^{-1} \text{ mg}_{\text{cat.}}^{-1}) = (C_{\text{NH}_4^+} \times V \times 17) / (18 \times t \times m_{\text{cat.}}), \quad (2)$$

where $C_{\text{NH}_4^+}$ ($\mu\text{g mL}^{-1}$) is the measured NH₄⁺ concentration, V (mL) is the volume of electrolyte (35 mL), t (s) is the reduction reaction time and $m_{\text{cat.}}$ (mg) is the mass loading of catalyst on CP.

Faradaic efficiency in 0.1 mol L⁻¹ Na₂SO₄ was calculated according to following equation:

$$\text{Faradaic efficiency} = 3 \times F \times C_{\text{NH}_4^+} \times V / (18 \times Q) \times 100\%, \quad (3)$$

where F is the Faraday constant (96,500 C mol⁻¹); Q (C) is the quantity of applied electricity.

RESULTS AND DISCUSSION

As shown in Fig. 1a, diffraction peaks of the as-prepared catalyst at 14.32°, 28.88°, 33.57°, 39.54°, 43.90°, 49.68°, 58.42°, 60.51°, 66.48°, and 69.14° are indexed to the (002), (004), (101), (103), (006), (105), (110), (112), (114) and (201) planes of WS₂ (JCPDS No. 08-0237), confirming the intrinsic WS₂ crystallinity of the as-prepared WS_{2-x}. The blue line shows that WO₃ (JCPDS 83-0951) was also successfully prepared without any impurities. The morphology of the materials was confirmed by SEM and

TEM, respectively. The SEM images indicate that WS_{2-x} features flake structure with about 400 nm in lateral dimension (Fig. 1b, c), and their sheet-like structure is thinner than WO_3 nanosheets (Fig. S1a) and WS_2 (Fig. S1b). TEM image of WS_{2-x} (Fig. 1d) shows a nanosheet structure with a regular and smooth surface, further confirming the SEM analysis results. HRTEM image of WS_{2-x} (Fig. 1e) exhibits clear lattice fringes with lattice spacings of 0.266 and 0.249 nm, corresponding to the (101) and (102) crystal facets of WS_2 , respectively. The high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image and the corresponding element distribution spectra (EDS) illustrate the uniform distribution of W and S elements on the as-obtained WS_{2-x} (Fig. 1f). The thickness of WS_{2-x} catalyst was characterized by AFM (Fig. 1g), showing that the thickness of WS_{2-x} catalyst was about 4.5 nm.

The chemical states of W and S elements of WS_{2-x} were investigated by XPS. As indicated in Fig. 2a, three peaks at 31.8, 33.8 and 37.2 eV correspond to the orbits of W $4f_{7/2}$, W $4f_{5/2}$ and W $4f_{3/2}$, respectively, fitting well with W^{4+} [37]. In the S 2p region (Fig. 2b), two peaks appearing at 161.2 and 162.7 eV should be ascribed to the S $2p_{3/2}$ and S $2p_{1/2}$ of S^{2-} , respectively [37]. Compared with the XPS spectrum of WS_2 , the binding energies of WS_{2-x} shift to lower binding energy due to the sulfur vacancies [38]. To determine the presence of defects, ESR spectroscopy tests were performed. It can be seen that WS_{2-x} shows a clear signal at $g = 2.004$ (Fig. 2c), being recognized as an electron trapped on the defects [39]. Meanwhile, the solid photoluminescence (PL) spectra show that the PL emission intensity of WS_{2-x} was much lower than that of WS_2 (Fig. 2d). This is because most of the electrons excited by light may be trapped by defects,

resulting in non-radiative centers and thus reduced emission intensity. The PL spectra further prove that there are abundant defects in WS_{2-x} . All the above evidence indicates the successful synthesis of the WS_{2-x} . The XPS spectra of O and N exclude the possibility of WO_3 residue and N-source (Figs S2, S3).

An electrochemical NRR test was carried out at ambient temperature and pressure to study the NRR activity of WS_{2-x} . CP coated with WS_{2-x} ($\text{WS}_{2-x}/\text{CP}$) was used as the working electrode. All voltages were converted to RHE. Indophenol blue and Watt and Chrisp's methods were used to detect NH_3 and N_2H_4 , respectively [35,36]. Figs S4, S5 exhibit the corresponding calibration curves, respectively. To study the electrochemical NRR performance of the catalysts, the linear sweep voltammetry (LSV) curves of WS_{2-x} were first collected in the N_2 - and Ar-saturated electrolyte ($0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$), respectively. As indicated in Fig. 3a, the potential in the N_2 -saturated electrolyte is more negative than that in Ar-saturated one, and the current density increases significantly, indicating that the NRR was initiated on $\text{WS}_{2-x}/\text{CP}$. In $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ with continuous N_2 bubbling, the NRR activity of the WS_{2-x} was systematically studied at different potentials. Fig. 3b shows the chronoamperometry curves at the corresponding potentials. The indophenol blue method was used to analyze the electrolytes at different potentials and blank electrolytes to detect the produced NH_3 (Fig. 3c). It shows that the highest absorbance value of NH_3 for WS_{2-x} is at -0.6 V , and the blank electrolyte has a very low absorbance background. N_2H_4 is a possible byproduct, which was evaluated by the Watt and Chrisp's method, while no N_2H_4 was produced in the present work (Fig. S6). The NH_3 generation rate and the corresponding Faradaic ef-

Figure 1 (a) XRD patterns of WS_{2-x} and WO_3 nanosheets. (b, c) SEM images; (d) TEM and (e) HRTEM images; (f) HAADF-STEM image and EDS mapping; (g) AFM image and the corresponding line profiles of WS_{2-x} .

Figure 2 XPS patterns of (a) W 4f and (b) S 2p for WS_{2-x} and WS_2 . (c) Comparison chart of ESR of WS_{2-x} and WS_2 . (d) PL spectra of WS_{2-x} and WS_2 .

efficiency of WS_{2-x} are shown in Fig. 3d. The blank electrolyte produces almost no ammonia, and NH_3 generation rate and Faradaic efficiency are the highest at the potential of -0.6 V, which are $16.38 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and 12.1%, respectively. We noticed that the Faradaic efficiency of WS_{2-x} is more favorable than the studies on similar tungsten-based or sulfide catalysts under similar neutral conditions [40–42]. In addition, with the negative movement of the applied potential, the values of NH_3 generation rate and Faradaic efficiency drop sharply. The reason is that the adsorption of hydrogen species gradually exceeds the N_2 on the electrode surface, which causes the hydrogen evolution reaction as the main reaction in the electrocatalytic system [18].

The cyclic voltammetry (CV) curves of the three materials (Fig. 4a–c) were collected for calculating the double layer capacitor (C_{dl}) at the solid-liquid interface to compare the electrochemically active surface area (ECSA) of each sample. It can be seen from Fig. 4d, the C_{dl} value of $\text{WS}_{2-x}/\text{CP}$ (0.053 mF cm^{-2}) is markedly higher than that of WO_3/CP (0.033 mF cm^{-2}) and WS_2/CP (0.007 mF cm^{-2}). The results indicate that the WS_{2-x}

possesses more exposed active sites, which are favorable for substantially enhancing the NRR activity of WS_{2-x} compared with the WO_3 and WS_2 [43]. In addition, the N_2 -TPD was conducted to gain insight into the adsorption ability of catalysts toward N_2 . As shown in Fig. 4e, WS_{2-x} exhibits physical adsorption of N_2 at around 100°C . The occurrence of chemisorption of N_2 after 300°C was observed for WS_{2-x} , and the large area suggests their adsorption capacity. In contrast, the binding strength of N_2 on WS_{2-x} is higher than that on WO_3 and WS_2 , indicating that the adsorption of WS_{2-x} to N_2 is stronger than that of WO_3 and WS_2 , resulting in higher activity of WS_{2-x} [44]. The specific surface areas of the catalysts were obtained by the BET method (Fig. 4f). The specific surface areas of WS_{2-x} , WO_3 , WS_2 are 25.73, 13.46 and $12.55 \text{ m}^2 \text{g}^{-1}$, respectively. A larger specific surface area of the WS_{2-x} indicated more active sites exposed on the as-prepared catalysts.

In order to rule out the possibility of contamination, the performance of WS_{2-x} was tested in Ar-saturated electrolyte at -0.60 V, open circuit potential (OCP) in N_2 -saturated electrolyte, and blank CP in N_2 -saturated elec-

Figure 3 (a) Comparison of LSV of WS_{2-x} under N_2 and Ar in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (scan rate: 5 mV s^{-1}). (b) $I-t$ curves at different potentials tested in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ for 2 h. (c) UV absorbance at different potentials after 2 h of electrochemical test. (d) NH_3 yields and Faradaic efficiencies of WS_{2-x} under a series of potential tests.

Figure 4 4 CV curves of (a) $\text{WS}_{2-x}/\text{CP}$, (b) WO_3/CP and (c) WS_2/CP at different scan rates. (d) Plots of current density differences ($\Delta j_{0.05\text{V}}/2$) vs. scan rate at 0.05 V vs. AgCl to calculate the C_{dl} values of $\text{WS}_{2-x}/\text{CP}$, WO_3/CP and WS_2/CP . (e) Comparison of N_2 -TPD adsorption on the surface of WS_{2-x} , WO_3 and WS_2 . (f) N_2 adsorption-desorption isotherms of WS_{2-x} , WO_3 and WS_2 .

Figure 5 (a) Comparison of UV absorbance of electrocatalytic test of WS_{2-x} under Ar, OCP, N₂ and blank sample. (b) Comparison of NH₃ yield and Faradaic efficiency of WS_{2-x}, WS₂ and WO₃. (c) Long time-dependent current density curve of WS_{2-x} at -0.60 V. (d) Recycling test for eight times at a potential of -0.60 V.

trolyte at -0.60 V, respectively. The UV-visible absorption spectrum of blank electrolyte obtained using the indophenol blue method shows negligible NH₃ (Fig. 5a). Similarly, when WS_{2-x} was electrolyzed in Ar-saturated electrolyte at -0.60 V and N₂-saturated one under the OCP, the NH₃ is below the detection limit. It further eliminates the interference from external conditions. WS₂ and WO₃ constant-potential N₂ reduction tests were also performed at the same potential (-0.60 V), to prove the superior NRR performance of WS_{2-x}. As shown in Fig. 5b, the performance of WS₂ (3.63 $\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ and 0.35%) and WO₃ (7.69 $\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ and 3.8%) are far lower than that of WS_{2-x}. These reflect the performance advantages of high conductivity and the promotion of NRR activity by the defects of WS_{2-x}. The stability of the catalyst is very vital for practical applications. Stability tests were performed through long-term electrolysis and continuous cycle electrolysis at -0.60 V. No significant change was obtained in the total current density (Fig. 5c) during the long-term electrolysis of 24 h. And in eight consecutive cycles of tests, the NH₃ production rate of WS_{2-x} remains 91.3% (Fig. 5d). It confirmed the high

catalytic stability of the WS_{2-x}, which should be ascribed to its stable structure and composition. As evidenced, the valence states of the W and S elements in WS_{2-x} did not change significantly after electrolysis (Fig. S7a). Moreover, the HAADF-STEM image (Fig. S7b) clearly shows that WS_{2-x} still appears as a nanosheet structure, and the TEM image (inset in Fig. S7b) further confirms the well-maintained morphology of WS_{2-x}.

CONCLUSIONS

In short, WS_{2-x} nanosheets were prepared *via* vulcanization of oxygen-vacancy-rich tungsten oxide in a vacuum tube. Defects in WS_{2-x} were conducive to improving the efficiency of the NRR. In 0.1 mol L⁻¹ Na₂SO₄ solution, WS_{2-x} has a high-efficiency and stable electrochemical N₂ fixation. The NH₃ production rate of WS_{2-x} was 16.38 $\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$, and it can achieve high Faradaic efficiency (12.1%) under normal temperature and pressure conditions. This performance is better than those of WO₃ (7.69 $\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ and 3.8%) and WS₂ (3.63 $\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ and 0.35%). This work further expands the possibility of low-cost and easily prepared W-

based catalysts for electrocatalytic NRR.

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Author contributions Xu Y and Li J conceived the idea and wrote the manuscript. Ma L and Kong W carried out the synthesis, characterization and performance measurements and wrote the manuscript. Jin Z, Han Y, Sun J, and Liu J participated in the general discussion. Liu M contributed to the data analysis. Xu Y and Li J revised the manuscript.

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Supplementary information Supporting data are available in the online version of the paper.

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硫缺陷工程设计的 WS_{2-x} 纳米片电催化剂用于还原 N_2

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摘要 由于 N_2 的化学惰性, 实现高效的 N_2 还原反应(NRR)亟需发展高活性的电催化剂. 本文中, 我们设计了富含缺陷的 WS_2 纳米片(WS_{2-x})作为NRR的有效电催化剂, 该催化剂是在合成具有氧空位的二维 WO_3 纳米片的基础上通过真空封管法硫化方法制备而成. 这种单层的 WS_2 纳米片是由S-W-S夹心阵列组成的类石墨烯结构, 具有高电子迁移率, 中等带隙和丰富的活性位点, 同时硫缺陷有利于 N_2 的吸附和活化. 在相对于可逆氢电极为 -0.60 V 的 Na_2SO_4 (0.1 mol L^{-1})中性电解质中, 使用该 WS_{2-x} 催化剂可得到12.1%的法拉第效率和 $16.38\text{ }\mu\text{g h}^{-1}\text{ mg}_{\text{cat}}^{-1}$ 的产氮量.