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Nickel Doping in Atomically Thin Tin Disulfide Nanosheets Enables Highly Efficient CO₂ Reduction

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Abstract

Engineering the electronic properties by elemental doping represents a direct strategy to design efficient catalysts towards CO_2 electroreduction. Herein, we modified atomically thin SnS_2 nanosheets with Ni doping for efficient electroreduction of CO_2 . The introduction of Ni into SnS_2 nanosheets significantly enhanced the current density and Faradaic efficiency for carbonaceous product relative to pristine SnS_2 nanosheets. When the Ni content was 5% in atomic percentage, the Ni doped SnS_2 nanosheets achieved a remarkable Faradaic efficiency of 93% for carbonaceous product with a current density of 19.6 mA cm⁻² at -0.9 V vs RHE. Mechanistic study revealed that the Ni doping gave rise to a defect level and lowered the work function of SnS_2 nanosheets, resulting in the promoted CO_2 activation and thus improved performance in CO_2 electroreduction.

Keywords: nickel doping; tin disulfide; atomically thin nanosheet; CO₂ electroreduction



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Electroreduction of CO_2 into value-added fuels represents a promising strategy to meet the ever-increasing energy demands, because the electricity can be powered by abundant renewable sources such as solar energy and wind energy.^[1,2] In CO_2 electroreduction, the critical bottleneck lies in the activation of CO_2 into a radical anion (CO_2) which requires a high reduction potential of -1.9 V vs NHE.^[3,4] Generally, the CO₂ activation concerns an electron transfer from catalysts to a CO₂ molecule, which was closely associated with the electronic structure of catalysts.^[5,6] A powerful method to tailor the electronic structure of catalysts is elemental doping, because the introduction of heteroatoms leads to the hybridization of energy levels between dopants and pristine catalysts.^[7,8] Typically, the elemental doping has been reported to engineer the band structure, d-band centre, valence state of active site, and charge redistribution, resulting in the enhanced electrochemical activity. For example, n-type doping of MoS₂ nanosheets with the Zn dopants shifted the Fermi energy into the conduction band of MoS₂, thereby modulating the hydrogen evolution activity.^[9] Besides, the incorporation of P into Ni-based multi-metal oxides promoted the oxidation of Ni²⁺ to Ni⁴⁺ which was highly active towards oxygen evolution reaction.^[10] Moreover, the incorporated quaternary N atoms in graphene induced charge redistribution in the p-conjugated system, endowing the adjacent C atoms with enhanced binding strength of O_2 and hence accelerating the oxygen reduction reaction.^[11] In addition, the introduction of isolated Cu into Pd lattice elevated the *d*-band centre of Cu site for improved CO₂ activation, boosting the conversion of CO₂ to CH₄.^[12] Therefore, elemental doping provided a promising opportunity to facilitate CO₂ activation and thereby improve the performance of CO₂ electroreduction by modifying the electronic structure of catalysts.

Herein, we modified atomically thin SnS_2 nanosheets with Ni doping for enhanced performance towards CO₂ electroreduction. The Ni doped SnS_2 nanosheets exhibited higher current density and Faradaic efficiency (FE) for carbonaceous product than those of the pristine SnS_2 nanosheets. When the Ni content was 5% in atomic percentage, the Ni doped SnS_2 nanosheets achieved a remarkable FE of 93% for carbonaceous product with a current density of 19.6 mA cm⁻² at -0.9 V vs RHE. During the potentiostatic test, the Ni doped SnS_2 nanosheets remained a steady FE for carbonaceous product without obvious decay of current density. Mechanistic study revealed that Ni doping generated a defect level at conduction band edge and decreased the work function of SnS_2 nanosheets, which benefited the activation of CO₂ and accordingly improved the catalytic performance in CO₂ electroreduction.

In the standard synthesis of atomically thin Ni doped SnS_2 nanosheets, different amounts of NiCl₂ and a certain amount of SnCl₄ were added into anisole solution containing oleylamine and CS₂, followed by heating at 190 °C for 24 h. Pristine SnS₂ nanosheets were also prepared for comparison through the similar procedure except for the addition of NiCl₂. Determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) results, the atomic ratios of Ni/(Ni+Sn) were 1%, 3%, 5% and 7%, denoting these samples as 1%Ni-SnS₂, 3%Ni-SnS₂, 5%Ni-SnS₂, and 7%Ni-SnS₂ nanosheets, respectively. As shown by the transmission electron microscopy (TEM) images, the products with the Ni content from 1% to 5% took the nanosheet morphology, whereas excessive Ni content of 7% led to the formation of inhomogeneous nanoparticles on the nanosheets (Figs. 1A and S1). Notably, the doped Ni content of 6.3% corresponded to the nucleation point of NiS supersaturation (Table S1). The high-resolution transmission electron microscopy (HRTEM) images show that pristine SnS_2 and homogeneously doped Ni-SnS₂ nanosheets were highly crystalline with hexagonal structure (Figs. 1B and S2). The interplanar spacings of two distinct lattice fringes were both 0.32 nm, which can be assigned to (100) and (010) planes. As such, all the nanosheets were orientated along <001> axis. The atomic force microscopy images showed the thicknesses of all the nanosheets were around 1.2 nm (Fig. S3), around two S-Sn-S layers^[13]. As indicated by the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and corresponding energy dispersive X-ray (EDX) elemental mapping of a freestanding 5%Ni-SnS₂ nanosheet, Ni, S, and Sn elements were homogeneously distributed in the whole nanosheet (Fig. 1C). Such homogeneous distribution was further confirmed by the line-scan profiles and EDX spectrum (Figs. 1D and S4). In addition, the HAADF-STEM image and elemental mapping spectra of an individual 7% Ni-SnS₂ nanosheets indicate the existence of NiS_x nanoparticles (Fig. S5).

To further investigate the structure of atomically thin Ni doped SnS₂ nanosheets, we carried out a series of characterizations including X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. As evidenced by XRD patterns, Ni doped SnS₂ nanosheets with Ni content lower than 5% exhibited similar diffraction peaks which corresponded to hexagonal SnS₂ (Fig. 1E). As the Ni content increased to 7%, extra diffraction peaks assigned to NiS appeared, indicating 7%Ni-SnS₂ nanosheets were inhomogeneous with NiS phase. We further performed XPS measurements to elucidate the chemical states of Ni. As shown in the XPS survey spectra, the weak signals of Ni were recorded in Ni doped SnS₂ nanosheets (Fig. S6).

Figure 1F shows the Ni 2p XPS spectra of 5%Ni-SnS₂ nanosheets and 7%Ni-SnS₂ nanosheets. The peaks at 871.0 eV and 853.7 eV were attributed to Ni $2p_{1/2}$ and Ni $2p_{3/2}$ of 5%Ni-SnS₂ nanosheets, respectively. The binding energies of Ni were higher than that of reported NiS and Ni₂S₃, suggesting that Ni was most likely to occupy the substitution site of Sn in SnS₂.^[14] In the case of 7%Ni-SnS₂ nanosheets, Ni $2p_{1/2}$ and Ni $2p_{3/2}$ are dominated by the peaks at the same position with that of 5%Ni-SnS₂ nanosheets. Another set of peaks are located at 870.1 eV and 852.9 eV, which are ascribed to the binding energy of Ni $2p_{1/2}$ and Ni $2p_{3/2}$ of NiS.^[15] In Sn 3*d* and S 2p XPS spectra of pristine SnS₂ and Ni doped SnS₂ nanosheets, the XPS peaks of Sn and S were slightly shifted to lower binding energies with the increase of Ni content, which was attributed to the electron transfer from the doped Ni to Sn and S (Figs. S7 and S8).^[16]

The catalytic performance of pristine SnS_2 and Ni doped SnS_2 nanosheets for CO_2 electroreduction was explored in an H-cell containing 60 mL of 0.1 M KHCO₃ (Fig. S9). As shown in Figure 2A, the geometrical current densities of SnS₂ nanosheets enhanced with the increase of Ni contents, which was confirmed by the IR-corrected linear sweep voltammetry measurements (Fig. S10). At overpotentials of -0.9 V and -1.0 V vs RHE, 5%Ni-SnS₂ nanosheets exhibited considerable current densities of 19.6 mA cm⁻² and 29.5 mA cm⁻², respectively. The promotion of current density by the Ni doping was further confirmed by the cyclic voltammetry curves in N₂ and CO₂ saturated KHCO₃ electrolyte (Fig. S11).Quantified by gas chromatography and ¹H NMR analysis, the product in CO₂ electroreduction included formate, CO, and H₂ over pristine SnS₂ and Ni doped SnS₂ nanosheets. The molar quantity of formate was measured by internal standard method of ¹H NMR (Fig. S12). Figure 2B shows the FE for carbonaceous product (CO and formate), which reflects the efficiency of CO₂ reduction. At -0.9 V vs RHE, the 5%Ni-SnS₂ nanosheets exhibited the highest FE of 93% for carbonaceous product. By comparison, the FE for carbonaceous product over the 7%Ni-SnS2 nanosheets obviously reduced to 71%. The decreased selectivity was attributed to that NiS in 7%Ni-SnS₂ nanosheets preferred hydrogen evolution to CO₂ reduction during the electrochemical reaction.^[17] These results demonstrate that the homogeneous incorporation of Ni into SnS₂ nanosheets promoted the activity and selectivity for CO₂ electroreduction.

Through the introduction of Ni into SnS_2 nanosheets, the formation of formate as the major product significantly increased at the expense of hydrogen evolution (Fig. 2C and Fig. S13). At -0.9 V vs RHE, the maximum FE for formate production over 5%Ni-SnS₂ nanosheets reached

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80%, which was 1.6-fold higher than that of pristine SnS_2 nanosheets. The FE for H₂ production significantly decreased from 38% over pristine SnS₂ nanosheets to 7% over 5%Ni-SnS₂ nanosheets. Figure S14 shows the yield rates for formate and CO formation over pristine SnS₂ and Ni doped SnS₂ nanosheets at -0.9 V vs RHE. Specifically, the formate yield rates over 5%Ni-SnS₂ nanosheets were 587.5 mmol h^{-1} g⁻¹, 293.7 mmol h^{-1} cm⁻², and 4.16 µmol C⁻¹ based on the catalyst loadings, geometric areas and charges through the system, respectively. Figure S15 shows the energy conversion efficiency for formate production (Φ_{formate}), which was used to evaluate the utilization of electricity. At -0.7 V vs RHE, the 5%Ni-SnS2 nanosheets achieved the highest Φ_{formate} value of 57% among the Ni doped SnS₂ nanosheets. Considering that the partial current density for formate production ($i_{formate}$) represents the production rate of formate, we further compared the *j*_{formate} values in this work with that of the recently reported Sn-based catalysts (Fig. S16). Due to the low overpotential and high partial current density, the 5% Ni-SnS₂ nanosheets represented one of the best catalysts for formate production. During an 8-h potentiostatic test at -0.9 V vs RHE, the 5%Ni-SnS₂ nanosheets exhibited less than 3% decay in geometrical current density, with a steady FE of more than 90% for carbonaceous product (Fig. 2D). Moreover, the Ni 2p XPS spectrum after the durability test and ICP results demonstrated that the chemical states of Ni in 5%Ni-SnS₂ nanosheets exhibited negligible changes during the electrochemical reaction (Fig. S17).

Inspired by the boosted performance of CO₂ electroreduction via the Ni doping, we investigated the relevant reaction kinetics of pristine SnS₂ and 5%Ni-SnS₂ nanosheets. The double-layer capacitance (C_{dl}) values slightly increased from 6.2 mF cm⁻² of pristine SnS₂ nanosheets to 6.7 mF cm⁻² of 5%Ni-SnS₂ nanosheets (Fig. 3A and Fig. S18). Given that the C_{dl} value is positively correlated with the electrochemical active surface area (ECSA), the geometrical current density was normalized by C_{dl} values to evaluate the intrinsic activity of catalysts. The C_{dl} -normalized current density demonstrated that the slightly increased ECSA was not the main reason for the enhanced current density after Ni doping (Fig. S19). Figure 3B shows the plot of geometrical current density at -0.9 V vs RHE against C_{dl} values for pristine SnS₂ and 5%Ni-SnS₂ nanosheets to 3.4 mA mF⁻¹ of 5%Ni-SnS₂ nanosheets, demonstrating that Ni doping promoted the intrinsic activity of SnS₂ nanosheets. The tafel slopes of the two

nanosheets were both close to 118 mV dec⁻¹, indicating that the activation of CO₂ serves as the rate-limiting step in the system of SnS₂ nanosheets.^[18] Figure 3D shows the Nyquist plots and the corresponding equivalent circuit of the two nanosheets. Based on the diameter of semicircular Nyquist plots, the 5%Ni-SnS₂ nanosheets exhibited the charge-transfer resistance (R_{CT}) of 3.0 Ω , which was lower than that (5.0 Ω) of pristine SnS₂ nanosheets. Therefore, the charge-transfer process of SnS₂ nanosheets was accelerated after the Ni doping during CO₂ electroreduction.

To rationalize the dramatic difference in the charge-transfer process of CO₂ electroreduction, we explored the electronic structures of pristine SnS₂ and Ni doped SnS₂ nanosheets. Figure 4A shows the calculated density of states (DOS) of a single-layer SnS₂ slab and Ni doped SnS₂ slab by density functional theory methods. Compared with the pristine SnS_2 , Ni doped SnS_2 exhibited a defect level below the conduction band, which effectively narrowed the band gap from 2.3 eV of pristine SnS_2 to 1.9 eV of Ni doped SnS_2 . Figure 4B shows the charge density distribution of Ni doped SnS₂ slab near the defect level. The abundant electrons in the vicinity of Ni atom demonstrate that the defect level was attributed to the Ni doping. We further verified the defect level through the UV-vis spectra of pristine SnS₂ and 5%Ni-SnS₂ nanosheets (Fig. 4C). Due to the low-energy photoexcitation of valance band to defect level, 5% Ni-SnS₂ nanosheets exhibited enhanced absorption at long wavelength (600-900 nm).^[19] As the electrons in defect level are easier to be transferred to molecules compared with that in conduction band, the Ni doping is expected to facilitate the Faradaic process of SnS₂ nanosheets. Figure 4D shows the secondary electron cutoff of the ultraviolet photoelectron spectroscopy (UPS) spectra. The work function decreased from 4.1 eV of pristine SnS₂ nanosheets to 3.7 eV of 5%Ni-SnS₂ nanosheets.^[20] It has been reported that the decreased work function improves the electron transfer process of electrocatalysts, and thus enhances the performance of CO₂ electroreduction.^[21] Therefore, the Ni doping benefited the Faradaic process of SnS₂ nanosheets in CO₂ electroreduction because of the defect level and lowered work function.

To verify the promoted Faradaic process through Ni doping, we analyzed the CO₂ activation process of pristine SnS₂ and 5%Ni-SnS₂ nanosheets. In CO₂ adsorption isotherms, 5%Ni-SnS₂ nanosheets attained a CO₂ adsorption capacity of 186 μ mol g⁻¹ under 1 atm at 25 °C, which was 1.9 times larger than that of pristine SnS₂ nanosheets (Fig. 4E). This result suggests that Ni doping favored the CO₂ adsorption of SnS₂ nanosheets, which was the pre-requisite step for triggering further CO₂ reduction process. We further evaluated the chemisorption abilities of CO₂

on pristine SnS_2 and 5%Ni-SnS_2 nanosheets by CO₂ temperature programmed desorption measurements (Fig. 4F). The temperature of CO₂ desorption peak increased from 166 °C for pristine SnS₂ nanosheets to 225 °C for 5%Ni-SnS₂ nanosheets. Accordingly, the chemical adsorption of CO₂ on SnS₂ nanosheets enhanced after Ni doping. To further understand the reaction mechanism for CO₂ conversion, we analyzed the corresponding proton coupling process on 5%Ni-SnS₂ nanosheets by adjusting the pH values of electrolyte (Fig. S20). The *j*_{formate} kept almost unchanged with the variation of pH values, demonstrating the proton coupling process was not the rate-determining step. Therefore, the Ni doping strengthened the chemical adsorption of CO₂, facilitating the activation process and thus boosting the CO₂ conversion to formate.

In conclusion, we developed atomically thin Ni doped SnS_2 nanosheets for efficient electroreduction of CO₂. The current density and FE for carbonaceous product exhibited a dramatic increase through the introduction of Ni into SnS_2 nanosheets. At -0.9 V vs RHE, the 5%Ni-SnS₂ nanosheets exhibited a remarkable FE of 93% for carbonaceous product, with a considerable current density of 19.6 mA cm⁻². Moreover, the 5%Ni-SnS₂ nanosheets remained a steady FE for carbonaceous product without obvious decay of current density during potentiostatic test. Mechanistic study revealed that the improved performance of SnS₂ nanosheets by Ni doping originated from the defect level at conduction band edge and decreased work function. This work not only developed Ni doped SnS₂ nanosheets as promising catalysts for CO₂ electroreduction, but also provided a strategy for the design of electrocatalysts.

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Figure 1. (A) TEM image of 5%Ni-SnS₂ nanosheets. (B) HRTEM image of 5%Ni-SnS₂ nanosheets. (C-F) HAADF-STEM and STEM-EDX elemental mapping images of an individual 5%Ni-SnS₂ nanosheet. (G) Line-scanning profiles of Ni, S, and Sn along the yellow line in panel C. (H) XRD patterns of pristine SnS₂ and Ni doped SnS₂ nanosheets. (I) Ni 2*p* XPS spectra of 5%Ni-SnS₂ nanosheets and 7%Ni-SnS₂ nanosheets.



Figure 2. (A) Geometrical current densities over pristine SnS_2 and Ni doped SnS_2 nanosheets. (B) Faradaic efficiencies for carbonaceous product (C-product) over pristine SnS_2 and Ni doped SnS_2 nanosheets. (C) Faradaic efficiencies for formate production over pristine SnS_2 and Ni doped SnS_2 nanosheets. (D) Plot of geometrical current density (*j*) and Faradaic efficiencies for carbonaceous product versus time over the 5%Ni-SnS₂ nanosheets at a constant potential of -0.9 V vs RHE.



Figure 3. (A) Charging current density differences plotted against scan rates for pristine SnS_2 and 5%Ni-SnS₂ nanosheets. The fitting slopes are twice that of the C_{dl} values. (B) Geometrical current density at -0.9 V vs RHE plotted against C_{dl} for pristine SnS₂ and 5%Ni-SnS₂ nanosheets at different loadings. (C) Tafel plots of pristine SnS₂ and 5%Ni-SnS₂ nanosheets. (D) Nyquist plots of pristine SnS₂ and 5%Ni-SnS₂ nanosheets.



Figure 4. (A) Calculated DOS of SnS₂ and Ni doped SnS₂ slabs. (B) The distribution of charge density at the defect level of Ni doped SnS₂ slab. (C) UV-vis-NIR diffuse reflection spectra of pristine SnS₂ and 5%Ni-SnS₂ nanosheets. (D) Secondary electron cutoff of the UPS spectra for pristine SnS₂ and 5%Ni-SnS₂ nanosheets. (E) CO₂ adsorption isotherms of pristine SnS₂ and 5%Ni-SnS₂ nanosheets at 25 °C. (F) CO₂-TPD spectra of pristine SnS₂ and 5%Ni-SnS₂ nanosheets.