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DOI
10.1002/advs.202102884

Publication date
2021

Document Version
Final published version

Published in
Advanced Science

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Citation for published version (APA):
Guo, J., Zhang, W., Zhang, L.-H., Chen, D., Zhan, J., Wang, X., Shiju, N. R., & Yu, F. (2021). Control over Electrochemical CO2 Reduction Selectivity by Coordination Engineering of Tin Single-Atom Catalysts. Advanced Science, 8(23), [2102884]. https://doi.org/10.1002/advs.202102884
Control over Electrochemical CO$_2$ Reduction Selectivity by Coordination Engineering of Tin Single-Atom Catalysts

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Carbon-based single-atom catalysts (SACs) with well-defined and homogeneously dispersed metal–N$_4$ moieties provide a great opportunity for CO$_2$ reduction. However, controlling the binding strength of various reactive intermediates on catalyst surface is necessary to enhance the selectivity to a desired product, and it is still a challenge. In this work, the authors prepared Sn SACs consisting of atomically dispersed SnN$_3$O$_1$ active sites supported on N-rich carbon matrix (Sn-NOC) for efficient electrochemical CO$_2$ reduction. Contrary to the classic Sn-N$_4$ configuration which gives HCOOH and H$_2$ as the predominant products, Sn-NOC with asymmetric atomic interface of SnN$_3$O$_1$ gives CO as the exclusive product. Experimental results and density functional theory calculations show that the atomic arrangement of SnN$_3$O$_1$ reduces the activation energy for $^*$COO and $^*$COOH formation, while increasing energy barrier for HCOO$^*$ formation significantly, thereby facilitating CO$_2$-to-CO conversion and suppressing HCOOH production. This work provides a new way for enhancing the selectivity to a specific product by controlling individually the binding strength of each reactive intermediate on catalyst surface.

1. Introduction

Electrochemical CO$_2$ reduction reaction (ECRR) has been recognized as one of the promising strategies to meet the CO$_2$ abatement goal of the world by converting it to value-added products.\(^1\)

However, ECRR usually involves the multiple proton-coupled electron transfer (PCET) steps and competes with the hydrogen evolution reaction (HER) causing poor selectivity and lower conversion efficiency. Designing catalysts with well-defined and homogeneously dispersed active centers can reduce the diversity of CO$_2$ reaction routes and weaken HER, thus improving selectivity to a specific product at low potentials.

Recently, carbon-based single-atom catalysts (SACs) with isolated single metal–N$_x$ (M–N$_x$) centers have emerged as new candidates for ECRR electrocatalysts.\(^2\) The defined structure and coordination environment provide a great opportunity to tune adsorption behavior of substrate and intermediates, thus controlling the reaction pathways for efficiently and selectively producing a desired product.\(^3\) Tin (Sn) SACs are generally regarded as catalysts for converting CO$_2$ to formic acid owing to their moderate adsorption energy for HCOO$^*$ intermediate.\(^4\) However, the currently reported SnN$_4$ structure exhibits poor selectivity for ECRR. For instance, Wei et al. reported a SnN$_4$ configuration embedded on a hierarchical integrated carbon nanosheet array showing 70% Faraday efficiency (FE) for HCOOH production with around 15% CO and 15% H$_2$ formation.\(^5\) The low selectivity was induced by the tiny thermodynamical difference in energy barriers for HCOOH, CO, and H$_2$ formation paths. Therefore, controlling the binding strength of various reactive intermediates on catalyst surface is necessary to enhance the selectivity to a desired product, and it is still a challenge.

Recent research has revealed that introducing the second coordination heteroatom can cause significant differences in the binding energy of active centers to intermediates, subsequently leading to a change in the reaction routes. For instance, a series of Fe$_x$N$_y$–O$_z$ (Fe$_x$N$_y$–O$_z$ site with axial Fe–O coordination),\(^6\) Cu–Sn$_x$,\(^7\) Mn–N$_x$Cl,\(^8\) Ni–N$_x$S$_y$, and Fe–N$_x$S$_z$ configurations have been reported and shown higher catalytic performance than symmetrical M–N$_x$ structure under the same conditions. In spite of the progress, the research about the effect of asymmetrically coordinated Sn single-atom sites on reaction pathways of ECRR is limited. Moreover, the determination of real active sites and how these single-atom sites boost ECRR are still not well understood.

In this work, we designed and synthesized Sn SACs consisting of atomically dispersed SnN$_3$O$_1$ active sites supported on...
N-rich carbon matrix (Sn-NOC), which displayed exceptional activity for the ECRR to CO with a maximum FE of 94% and a CO partial current density of 13.9 mA cm$^{-2}$ at −0.7 V (versus RHE). In contrast, for the reference tin phthalocyanine (Sn-Pc) with classic Sn-$N_4$ configuration, HCOOH and $H_2$ products dominated over the measured potential range. According to the number of active Sn atoms in Sn-NOC, the calculated TOF of ECRR to CO is 23 340.5 h$^{-1}$, which is more than 400 times over that of Sn-$N_4$ (57.5 h$^{-1}$) and superior over the advanced SACs in literature. Moreover, a linear relationship is established by plotting the $F_{ECO}$ versus the Sn-N content, proving that Sn$N_3O_1$ coordination is the real active site for ECRR in the Sn-NOC catalyst. Experimental results and density functional theory (DFT) calculations show that the Sn$N_3O_1$ configuration has an optimal adsorption capacity for $^*CO_2$ and $^*COOH$ intermediates, which is beneficial to the generation of CO, shifting the production from HCOOH to CO. Our finding offers a universal strategy for enhancing the catalytic performance of SAC and controlling its selectivity.

2. Results and Discussion

The atomically dispersed Sn$N_3O_1$ active sites supported on N-rich carbon matrix (NC) were synthesized by a gas transport strategy (Figure 1a).[11] NC was obtained by a simple pyrolysis of ZIF-8 precursor. SnO$_2$ powder, serving as the Sn and O sources, and NC were subsequently placed in two separate porcelain boats and were heated at high temperatures. In high temperature Ar flow, volatile Sn species, formed by the evaporation of SnO$_2$, migrated to the surface of NC and were trapped by heteroatoms in carbon basal plane, forming the isolated Sn-NOC electrocatalyst. Notably, the relative contents of Sn atoms in Sn-NOC samples can be controlled by varying the temperature from 950, 1000 to 1050 °C. The samples are denoted as Sn-NOC-950, Sn-NOC-1000 (i.e., Sn-NOC), and Sn-NOC-1050, respectively. This provides a possible way to correlate catalytic activity with the amounts of active sites, thereby identifying the real active sites for ECRR. This will be discussed in detail below.

Figure 1. a) The formation process of atomically dispersed Sn$N_3O_1$ active sites; b) HRTEM image, c,d) STEM images, and corresponding EDS mapping of Sn-NOC, e) XRD patterns of NC and Sn-NOC; f,g) AC HAADF-STEM images of Sn-NOC.
Transmission electron microscopy (TEM) images show that both NC and Sn-NOC (Figure S1, Supporting Information) retained the dodecahedral morphology of ZIF-8 without obvious surface distortion and structural collapse, and no obvious metal nanoparticles were observed. High-resolution TEM (HRTEM) image reveals that the microstructures of Sn-NOC sample have massive crystallites stacked by graphitic layers (Figure 1b). Raman spectra of the two samples show two obvious peaks near 1580 and 1348 cm$^{-1}$ corresponding to the stretching vibrations of sp$^2$-bonded (G-bond) carbon and defect-induced breathing mode of aromatic ring (D bond), further aligned with graphitic carbon structure (Figure S2, Supporting Information). The energy-dispersive X-ray spectroscopy (EDS) mapping research shows that the C, O, N, and Sn were dispersed evenly throughout the Sn-NOC (Figure 1c,d). X-ray diffraction (XRD) of the two samples show similar diffraction patterns with broad peaks located at 23° and 44° assigned to the (002) and (101) planes of graphitized carbon (Figure 1e).\cite{12} No obvious metallic Sn crystallites were detected, consistent with the results of HRTEM. For revealing the dispersion of Sn species more clearly, we also did the aberration-corrected high-angle annular dark-field scanning TEM (AC HAADF-STEM) and the images are shown in Figure 1f,g. The individual bright dots with a size of ≈0.13 nm are consistent with the size of Sn atom, validating that the Sn species are atomically isolated on the carbon matrix.\cite{13} The Sn contents in Sn-NOC-950, Sn-NOC-1000, and Sn-NOC-1050, analyzed by inductively coupled plasma atomic emission spectrometry (ICP-MS), are 0.27, 0.48, and 0.43 wt.%, respectively.

The chemical composition and elemental states of NC and Sn-NOC were analyzed by X-ray photoelectron spectroscopy (XPS, Figures S3 and S4 and Table S1, Supporting Information). High-resolution N1s spectrum shows distinct Sn-N bond at \(\sim 399.0\) eV, suggesting the direct coordination of Sn and N atoms (Figure 2a).\cite{14} Additionally, pyridine N (398.4 eV), pyrrole N (400.1 eV), and graphite N (401.4 eV) were also detected.\cite{15} The high-resolution O1s spectrum consists of three sub-peaks, C=O (531.1 eV),\cite{16} C–O (532.1 eV),\cite{17} and Sn–O (530.7 eV) (Figure 2b), implying Sn is also trapped by O atom. For Sn 3d

![Figure 2](image_url)

Figure 2. a–c) XPS spectra of N1s, O1s, and Sn3d of Sn-NOC; d) Sn K-edge XANES spectra; e) Fourier transform (FT) of the Sn K-edge EXAFS spectra; f) WT analysis of Sn-NOC, SnO$_2$, and Sn foil; g) The fitting curve of $k^3$-weighted EXAFS spectra; h) Schematic atomic interface model of Sn-NOC.
spectrum of Sn-NOC, the Sn 3d_{5/2} peak centers at 486.5 eV, higher than Sn⁰ (484.5–485.5 eV) and lower than Sn⁴⁺ (486.3–487.3 eV) indicating the valence of Sn is 0 < δ < 4 (Figure 2c).[18]

To further explore the chemical states and coordination environment of the atomically dispersed Sn atoms, Sn-NOC was further characterized by synchrotron-radiation-based X-ray absorption spectroscopy (XAS, consisted of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)). The Sn K-edge XANES shows that the oxidation state of the isolated Sn atoms in Sn-NOC is higher than Sn⁰ and lower than Sn⁴⁺ (Figure 2d), consistent with XPS analysis. The oxidation state of isolated Sn atom was further analyzed and found as +1 by the Linear Combination Fitting (LCF) of the XANES data (Figure S5 and Table S2, Supporting Information). The pre-edge features of the XANES spectra of Sn-NOC show a clear shift towards the left compared to that of Sn foil, indicating that Sn atoms in Sn-NOC can easily transfer electrons and interact with substrate, for example, CO₂. The FT-EXAFS curve of Sn-NOC shows a main peak at around 1.51 Å assigned to the Sn–N/O coordination (Figure 2f). Importantly, the characteristic peak of Sn–Sn bond at about 2.77 Å was not detected, confirming the isolated Sn atoms on the carbon skeleton. We also used wavelet transform (WT) to analyze the Sn K-edge EXAFS oscillations. The WT maximum for the Sn-NOC was found at 6.2 Å⁻¹ which could be assigned to the Sn–N/O. No signals assigned to Sn–Sn were detected as compared with WT plots for Sn foil and SnO₂ (Figure 2f). Based on the subsequent EXAFS fitting with the bond distances of Sn–N and Sn–O, the local atomic configuration of Sn atom in Sn-NOC is consistent with the SnN₃O₁ model (Figure 2g,h and Table S3, Supporting Information).

N₂ sorption isotherms for the two samples are essentially type I, indicating their microporous nature (Figure S6 and Table S4, Supporting Information). Remarkably, the pore volumes and surface areas of Sn-NOC have significantly increased compared with those of NC, meaning more physical adsorption sites for CO₂. In addition, a strong CO₂ chemisorption capacity of Sn-NOC was confirmed by CO₂ temperature-programmed desorption (CO₂-TPD) analysis (Figure S7, Supporting Information).[19]

To test activity and selectivity of the samples for ECRR, linear sweep voltammetry (LSV) analysis was first carried out in a three-electrode H-cell containing CO₂- or N₂-saturated 0.1 M KHCO₃ solution. As shown in Figure 3a and Figure S8, Supporting Information, Sn-NOC shows higher reduction current density starting at −0.5 V in the CO₂-saturated electrolyte than in the N₂-saturated electrolyte, implying an active response to ECRR. Moreover, this current density is higher than that of tin phthalocyanine (Sn-Pc) with a classic SnN₄ configuration, and that of NC in CO₂-saturated electrolyte. Impressively, the current density of Sn-NOC at −0.7 V could reach 14.81 mA cm⁻², which is much higher than Sn-Pc (8.42 mA cm⁻²) and NC (8.44 mA cm⁻²). The FE was evaluated through controlled potential electrolysis with the detection of the products by gas chromatography and ion chromatography. For Sn-NOC, CO was detected as the main reduction product, and FE CO reaches 94% at −0.7 V. A high selectivity of more than 80% can be retained at the potential range of −0.6 ~ −0.9 V (Figure 3b). In contrast, Sn-Pc, a control sample, exhibits a very low selectivity for CO (FE CO < 10%), while HER dominates with FE higher than 50.0% at the measured potential range (Figure 3c). Similarly, SnO₂ nanoparticles loaded on NC (denoted as SnO₂-NC)[20] also showed low CO selectivity and produced more HCOOH (Figures S9–S11, Supporting Information). The impressive selectivity for CO and excellent activity over a wide potential range enhances the CO partial current density (j_CO) for Sn-NOC, reaching 26.6 mA cm⁻² at −0.9 V, which is 13.4 and 4.2 times more than that for Sn-Pc and NC, respectively (Figure S12, Supporting Information). The Tafel slope...
Figure 4. a) In situ SERS spectra of ECRR at the Sn-NOC surface in 0.1 M CO₂-saturated KHCO₃. b) The formation of *COO⁻ and *COOH pathway on Sn-NOC. c) The calculated Gibbs free energy diagrams for CO₂-to-CO conversion. d) The calculated Gibbs free energy diagrams for CO₂-to-HCOOH conversion.

derived from CO partial current density was 110 mV dec⁻¹ for Sn-NOC, lower than that of NC (129 mV dec⁻¹) and Sn-Pc (281 mV dec⁻¹) (Figure S13, Supporting Information), further illustrating that the kinetics enhancement of Sn-NOC. The Tafel slope of Sn-NOC (110 mV dec⁻¹) is close to 118 mV dec⁻¹ indicating that the rate-determining step (RDS) is the initial electron transfer to CO₂ forming *COOH intermediate. Additionally, a stable current density with FEₐ,CO more than 90% was achieved for 8 h by Sn-NOC catalyst (Figure 3d). To explore the intrinsic activity of the as-prepared catalysts, the catalytic current was normalized with electrochemically active surface area (ECSA) extracted from double-layer capacitance (Cᵋ). The Sn-NOC catalyst showed a Cᵋ of 10.03 mF cm⁻² which is higher than NC (5.18 mF cm⁻², Figure S14, Supporting Information), indicating more ECRR active sites were exposed by the introduction of Sn atoms. The specific activity normalized to the measured ECSA of Sn-NOC is also more than that of the control samples (Figure S15, Supporting Information), further suggesting a high intrinsic catalytic activity of Sn-NOC for CO production. According to the number of active Sn atoms, the calculated TOF of ECRR to CO is 23 340.5 h⁻¹, which is more than 400 times over that of Sn-N₄ (57.5 h⁻¹) and superior over the advanced SACs reported in literature (Tables S5 and S6, Supporting Information), reflecting a highly enhanced intrinsic activity.

To further clarify the active sites of Sn-NOC in ECRR, thiocyanate (SCN⁻) poisoning experiments were carried out.[21] Generally, SCN⁻ can adsorb on the M-Nₓ moiety leading to the loss of catalytic activity, while SCN⁻ shows no obvious poisoning effect for heteroatom active sites, that is, N. Therefore, we prepared a series of Sn-NOC samples with different contents of single atomic Sn active sites by controlling the temperature of Ar flow at 950, 1000, and 1050 °C, respectively. During ECRR test, 10 mM KSCN was added to 35 mL CO₂-saturated 0.1 M KHCO₃ aqueous solution. As shown in Figures S16–S20, Supporting Information, Sn-NOC-1000 sample shows the highest conversion ability for CO₂ to CO over the measured potential range. Notably, a linear relationship is established by plotting the FEₐ,CO versus the Sn-N content, proving that atomically dispersed SnN₃O₁ coordination is the real active site for ECRR in the Sn-NOC catalyst (Figure 3e, Figure S21 and S22, and Table S7, Supporting Information).

To our best knowledge, there are limited studies on the identification of the real active sites in N-rich carbon catalyst for ECRR. To identify possible reaction intermediates leading to fundamental understanding of the ECRR mechanism, we conducted electrochemical in situ surface-enhanced Raman spectroscopy (SERS) under different potentials (Figure 4a). Four peaks (718, 998, 1030, and 1130 cm⁻¹) were observed from −0.3 to −0.6 V which can be assigned to the δ (COO⁻) from *COO⁻, the
symmetric stretch of $^{*}\text{OCO}$, the asymmetric stretch of $^{*}\text{OCO}$, and the stretch of $^{*}\text{CO}$ from $^{*}\text{COOH}$, respectively.[22] The signal changes from weak to strong and then weak with the increase of potential from $-0.1 \text{ V}$ to $-0.9 \text{ V}$, and a plateau appears at $-0.5 \text{ V}$ consistent with potential trend in activity evaluation, indicating the formation of $^{*}\text{COO}^-$ and $^{*}\text{COOH}$ pathway on Sn-NOC (Figure 4b). As the applied voltage increases, the driving force becomes larger and the reaction rate increases, resulting in rapid consumption of the intermediate and therefore weak signals in SERS at large FE.

Subsequently, DFT calculations were carried out to explore the catalytic mechanism of Sn$_3$O$_4$ for ECRR (Figures S23 and S24, Supporting Information). The free energy diagram (Figure 4e) shows that the ECRR on Sn$_4$ site is controlled by the desorption of $^{*}\text{CO}$ with $\Delta G = 1.72 \text{ eV}$.[21] The $^{*}\text{COOH}$ adsorption is facile on Sn$_4$. However, it is an endothermic process on Sn$_3$O$_1$, followed by an uphill step to form $^{*}\text{COOH}$ as the RDS consistent with Tafel plot analysis. SnN$_4$ exhibits a relatively lower energy compared to COFE of 94% and a CO partial current density of 13.9 mA cm$^{-2}$ at $-0.7 \text{ V}$. Further experimental results and DFT calculations show that the asymmetric atomic interface of Sn$_3$O$_4$ facilitates $^{*}\text{CO}$ and $^{*}\text{COOH}$ coordination and boosts CO formation with the suppression of HCOOH formation. Additionally, from the kinetic point of view, the asymmetric atomic interface facilitates the electron transfer and therefore promotes the protonation process of CO$_2$, ultimately accelerating the formation of CO.[7] Additionally, Sn$_3$O$_4$ increases the $^{*}\text{H}$ endothermic energy of HER, which is the main competitive reaction of ECRR (Figure S25, Supporting Information).

3. Conclusion

We demonstrate that a Sn single-atom catalyst (Sn-NOC) with an asymmetric Sn$_3$O$_4$ configuration is an efficient and robust CO$_2$-to-CO conversion catalyst. The Sn-NOC catalyst shows a maximum CO FE of 94% and a CO partial current density of 13.9 mA cm$^{-2}$ at $-0.7 \text{ V}$. Further experimental results and DFT calculations show that the asymmetric atomic interface in Sn$_3$O$_4$ reduces the energy barrier of rate determining step for CO formation while increasing the energy for $^{*}\text{OCO}$ adsorption, the key step for HCOOH production. Therefore, the asymmetric Sn$_3$O$_4$ structure shows an impressive FE for CO formation and suppress the formation of HCOOH, the main product for previously reported Sn-based catalysts. Our work provides an efficient method for controlling the catalytic path and switching the product selectivity of SACs. This approach can be extended to other PCET electrochemical conversions, thus has a wider scope.

4. Experimental Section

Chemicals: Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, AR 99%) and 2-methyl imidazole (2-MeIM, AR 98%) were obtained from Aladdin. Stan-
Keywords
asymmetric SnN₃O₁ configuration, CO selectivity, CO₂ reduction reaction, electrochemistry, single-atom catalysts

Received: July 5, 2021
Revised: August 9, 2021
Published online: October 24, 2021

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