Tunable and Efficient Tin Modified Nitrogen-Doped Carbon Nanofibers for Electrochemical Reduction of Aqueous Carbon Dioxide

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Abstract
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Keywords: carbon dioxide reduction, electrocatalysis, tin nanoparticle, atomically dispersed tin, nitrogen-doped carbon nanofiber

Efficient and selective earth-abundant catalysts are highly desirable to drive the electrochemical conversion of CO₂ into value-added chemicals. In this work, a low-cost Sn modified N-doped carbon nanofiber hybrid catalyst is developed for switchable CO₂ electroreduction in aqueous medium via a straightforward electrospinning technique coupled with a pyrolysis process. The electrocatalytic performance can be tuned by the structure of Sn species on the N-doped carbon nanofibers. Sn nanoparticles drive efficient formate formation at a high current density of 11 mA cm⁻² and a faradaic efficiency of 62% with a moderate overpotential of 690 mV. Atomically dispersed Sn species promote conversion of CO₂ to CO with a high faradaic efficiency of 91% at a low overpotential of 490 mV. The interaction between Sn species and pyridinic-N may play an important role in tuning the catalytic activity and selectivity of these two materials.
1. Introduction

Electrochemical reduction of CO\textsubscript{2} (CO\textsubscript{2}ER) into value-added chemical feedstocks and liquid fuels using renewable energy is a promising route for CO\textsubscript{2} recycling\textsuperscript{[1-3]} The key challenges are the sluggish reaction kinetics of CO\textsubscript{2}ER and the competitive hydrogen evolution reaction (HER) in aqueous medium.\textsuperscript{[4]} The realisation of efficient electrocatalysts is the key to lowering the overpotential and improving product selectivity. Common heterogeneous catalysts are metals, particularly nanostructured noble metals such as Au, Ag and Pd. They have demonstrated impressive catalytic activity and selectivity for CO or formate production.\textsuperscript{[5-12]} However, the low abundance and high cost of these precious metals limits their large-scale application. Inexpensive, robust and selective electrocatalysts with high energy efficiency are highly desirable to drive the development of CO\textsubscript{2}ER.

Tin, a nontoxic earth-abundant metal, has attracted attention due to its high selectivity for producing formate or formic acid.\textsuperscript{[13-18]} The electrocatalytic activity is highly sensitive to the surface structure including the particle size,\textsuperscript{[13]} oxide layer thickness,\textsuperscript{[14]} and morphology,\textsuperscript{[19]} as well as pH of the electrolyte.\textsuperscript{[20,21]} The tin oxide (SnO\textsubscript{x}) layer facilitates CO\textsubscript{2}ER by effectively stabilizing the CO\textsubscript{2}•• intermediate; and in the absence of the oxide layer H\textsubscript{2} evolution predominates.\textsuperscript{[16,22]} The catalytic activity can be optimised by balancing the binding ability of CO\textsubscript{2}•• intermediates against the poor electron conductivity of the oxide layer.\textsuperscript{[13,14,23]} Nanostructured Sn electrodes such as mesoporous SnO\textsubscript{2} nanosheets,\textsuperscript{[15]} grain-boundary-rich SnO\textsubscript{2} nanowires,\textsuperscript{[18]} and hierarchical Sn dendrites,\textsuperscript{[19]} afford much larger faradaic efficiency (FE) and current density compared to conventional Sn electrodes due to an increase in accessible active sites.

The electrocatalytic activity of Sn-based catalysts can also be tuned by neighbouring active species in Sn-based binary or multicomponent metallic catalysts.\textsuperscript{[13,19]} For example, SnO\textsubscript{x} decorated Cu nanostructures exhibited Sn-thickness dependent product selectivity: with a thicker SnO\textsubscript{x} shell (> 1.8 nm) Sn metal-like activity for formate formation was observed,
whereas with a thinner shell (< 1 nm) CO formation predominated.\textsuperscript{[21,24-26]} Theoretical calculations suggested that the interaction between Cu and Sn active sites on the thinner SnO\textsubscript{x} modified Cu electrodes favoured the adsorption of COOH\textsuperscript{*} intermediates and promoted CO formation.\textsuperscript{[26]}

The local electronic environment from the supporting materials affects the electrocatalytic activity of Sn as well. Compared with carbon black support, graphene sheet supported Sn nanoparticles (NPs) exhibited enhanced electron donation, promoting the adsorption of CO\textsubscript{2} and CO\textsubscript{2}\textsuperscript{−} and thus facilitating formate formation.\textsuperscript{[13,27]} Nitrogen-doping can be used to tailor the electronic structure of graphitic carbons,\textsuperscript{[28]} leading to increased electronic conductivity, high surface energy and tunable chemisorption ability favouring electrochemical reactions such as the oxygen reduction reaction and HER.\textsuperscript{[29]} Pyridinic-N doped carbons themselves can act as active sites for CO\textsubscript{2}-to-CO conversion due to their capability of binding CO\textsubscript{2} and protons.\textsuperscript{[30]} The introduction of HER-active metal atoms such as Fe,\textsuperscript{[31,32]} Mn,\textsuperscript{[32]} or Ni,\textsuperscript{[33]} can further improve catalytic activity by turning the pyridinic-N sites to more active metal-N moieties for CO production. However, the research on the interaction between N-doped carbons and p-block metals with intrinsic CO\textsubscript{2}ER activity such as Sn is limited.

Herein, we have developed a Sn modified N-doped porous carbon nanofiber (Sn-CF) catalyst for CO\textsubscript{2} electroreduction using a straightforward electrospinning and pyrolysis technique. The electrocatalytic activity of this hybrid catalyst can be tuned to predominantly generate either formate or CO, by controlling the structure of Sn and N species. The pyridinic-N-doped carbon nanofibers supported Sn nanoparticles demonstrated a high formate partial current density of 11 mA cm\textsuperscript{-2} and a FE of 62% at a moderate overpotential of 690 mV in 0.5 M KHCO\textsubscript{3} solution. The nanofibers containing only atomically dispersed Sn species switched to selectively reduce CO\textsubscript{2} to CO with a FE of 91% at a low overpotential of 490 mV in 0.1 M KHCO\textsubscript{3}. 
2. Results and Discussion

The fabrication of Sn-CFs catalysts involved an electrospinning process from a precursor solution containing polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA) and SnCl$_2$; followed by a pyrolysis process at 1000 °C in Ar/H$_2$ atmosphere to form a Sn-containing fiber membrane (Figure 1a). During the pyrolysis, the PAN was transformed to N-doped carbon; SnCl$_2$ was reduced to Sn; and PMMA was decomposed to create pores on the nanofibers.[34,35] The resultant material was denoted Sn-CF1000. Using this electrode structure for CO$_2$ reduction resulted in formic acid as the dominant product, whereas after a simple acidic leaching treatment CO was the major product. This facile and straightforward synthesis method provides a new avenue to fabrication of Sn-based electrocatalysts for efficient tunable CO$_2$ electroreduction processes in aqueous medium.

The Sn-CF1000 composite consists of nanofibers decorated with microspheres (Figure 1b). These nanofibers are typically in a diameter of ~ 250 nm and a length of tens of microns. They were interconnected into a porous three dimensional (3D) network favouring the mass transport. Those microspheres are in a diameter of 0.5-3 µm with smooth surfaces (Figure 1c). They are identified as Sn (JCPDS 82-2264) by XRD analysis (Figure S1, Supporting Information), which was formed by outward diffusion and aggregation of metallic Sn on the carbon nanofibers. In addition, a large number of nanosized pores (dark parts) and nanoparticles (bright dots) were observed on the nanofiber surface, as revealed by the dark field scanning transmission electron microscopy (STEM) (Figure 1d-e). These nanodots in a diameter of ~ 2.5 nm were tightly anchored on the surface. A set of fine lattice fringes with a space of 0.34 nm are identified (Figure 1f), which can be ascribed to the (110) plane of SnO$_2$ (JCPDS 41-1445). The SnO$_2$ may be formed from the spontaneous oxidation of Sn in air. No obvious lattice fringes of carbon can be observed, indicating its amorphous nature. The elements Sn and N species were uniformly distributed along the carbon nanofiber, as revealed by the STEM energy-dispersive X-ray spectroscopy (EDS) mapping (Figure 1g).
content was evaluated from the thermogravimetric analysis (Figure S2), and was ~ 53 wt%. The relative N content evaluated from the X-ray photoelectron spectroscopy (XPS) analysis was 2.35 atm% (Table S1, supporting information). The N\textsubscript{2} adsorption/desorption isotherm exhibited a typical type-IV hysteresis loop at relative pressure P/P\textsubscript{0} > 0.5 (Figure S3), suggesting the existence of mesopores in the nanofibers.\[^{36}\] This material presented a hierarchical mesoporous structure, as evidenced by the presence of three different peaks at ~ 4.0 nm, 6.5 nm and 11.7 nm on the Barrett-Joyner-Halenda (BJH) pore-size-distribution curve (inset of Figure S3). These results are consistent with the TEM observations (Figure 1d). According to the Brunauer-Emmett-Teller (BET) method, the specific surface area was found to be 286 m\textsuperscript{2} g\textsuperscript{-1} with a pore volume of 0.25 cm\textsuperscript{3} g\textsuperscript{-1} (for pores smaller than 330 nm). The hierarchical mesoporous structure and large surface area may provide more open channels and active sites for CO\textsubscript{2} reduction.

The structure and chemical state of Sn and N species on Sn-CF\textsubscript{1000} were further analysed by high-resolution XPS. The Sn3d\textsubscript{3/2} and Sn3d\textsubscript{5/2} spectra (Figure 1h) fit into three groups at binding energies of 495.6 and 487.4 eV for Sn\textsuperscript{4+}, 495.0 and 486.7 eV for Sn\textsuperscript{2+}, and 493.2 and 484.7 eV for Sn\textsuperscript{0};\[^{17}\] indicating a mixture of SnO\textsubscript{x} and Sn. The presence of Sn\textsuperscript{4+} is consistent with the observance of SnO\textsubscript{2} in the HRTEM analysis. As revealed by the deconvoluted N\textsubscript{1s} spectrum (Figure 1i), the N-doped carbon was mainly ascribed to pyridinic-N (398.0 eV) and graphitic-N (400.8 eV) with abundance of 24.8\% and 75.2\%, respectively.\[^{34}\] It exhibited two broad peaks at 1346 and 1585 cm\textsuperscript{-1} in the Raman spectrum (Figure S4), corresponding to the defect-induced band (D) and graphitic-induced band (G) of carbon.\[^{34,37}\] The intensity ratio of D/G band (I\textsubscript{D}/I\textsubscript{G}) is ~ 1.30, reflecting a disordered carbon structure and agreeing with the HRTEM result.

The effect of pyrolysis temperature on the structure of Sn and N species in Sn-CF composites was investigated. Two more samples were obtained after annealing the Sn-containing fiber membrane at 900 and 1100 °C. The resulting Sn-CF\textsubscript{900} and Sn-CF\textsubscript{1100} were
fully characterized using SEM, TEM and XPS (Figure S5-7). They displayed similar structure with Sn-CF1000: interconnected carbon nanofibers with Sn microspheres decoration; uniform distribution of Sn and N species along the nanofiber (Figure S5-6). However, the content of Sn and N, particularly the pyridinic-N, decreased with increased temperature (Table S1, Figure S7). No pyridinic-N can be detected on Sn-CF1100; instead small graphite nanosheets with a thickness of ~2 nm and a lateral size of ~20 nm were formed (Figure S6). The pyridinic-N defects are active for CO$_2$-to-CO conversion due to the ability to bind CO$_2$ and protons.$^{[30]}$ The abundance of pyridinic-N in Sn-CF900 and Sn-CF1000 may promote the electrocatalytic activity for CO$_2$ER.

Electroreduction of CO$_2$ on these three different Sn-CF hybrid catalysts was investigated and results are summarized in Figure 2. During CO$_2$ reduction Sn-CF1000 and Sn-CF900 presented similar iR-corrected total current densities, much higher than those of Sn-CF1100, especially at potentials more negative than -0.7 V (Figure 2a). The positive shift in the onset potential (e.g. the potential where current density reaches 0.5 mA cm$^{-2}$, Table S2) for Sn-CF900 and Sn-CF1000 indicates a higher catalytic capability for CO$_2$ER. These three electrodes all generated H$_2$, CO and HCOOH but with different faradaic efficiencies (FEs) (Figure 2b-d). At -0.5 V, the HER prevailed and the dominant product from CO$_2$ER was CO. The FE for H$_2$ evolution (FE$_{H_2}$) decreased with the negatively shifting potential and reached a minimum at ~ -0.8 V. Meanwhile, the dominant CO$_2$ER product changed from CO to HCOOH. This selectivity change may be attributed to the potential-dependent formation of different intermediates HCOO$^*$ and COOH$^*$ (respectively for HCOOH and CO formation) on the N-doped carbon with active Sn sites.$^{[38]}$ Sn-CF1100 displayed a catalytic behaviour typical of Sn metal: the formate production is promoted by the increased overpotential, as demonstrated for Sn nanoparticles,$^{[13]}$ Sn nanowires,$^{[18]}$ and Sn dendrites.$^{[19]}$ Sn-CF900 and Sn-CF1000 demonstrated a FE$_{HCOOH}$ maximum at -0.9 V and -0.8 V, respectively. At -0.8 V (corresponding to an overpotential of 690 mV for HCOOH formation), a maximum FE$_{HCOOH}$
7 of 65% was reached on Sn-CF1000, and the hydrogen evolution was highly suppressed (FEH2 ~ 12%). The HCOOH partial current density (jHCOOH) for Sn-CF900 and Sn-CF1000 was similar, much higher than that for Sn-CF1100 (Figure S8). Sn-CF1000 exhibited a jHCOOH of 4.7 mA cm\(^{-2}\), about five times larger than that obtained using Sn-CF1100 (0.97 mA cm\(^{-2}\)).

To confirm that the products HCOOH and CO were generated from CO\(_2\) rather than from the carbonaceous catalysts, electrolysis of Sn-CF1000 catalyst was carried out in an Ar-saturated CO\(_2\)-free electrolyte at a potential of -0.8 V vs. RHE (Figure S9). Only H\(_2\) was detected, ruling out the possibility of decomposition or transformation of carbon structures into HCOOH and CO.

The effect of electrolyte concentration on the rate of formation of HCOOH (jHCOOH) on the Sn-CF1000 electrode was investigated (Figure 2e). At -0.8 V, the jHCOOH increased from 7.1 mA cm\(^{-2}\) to 12.1 mA cm\(^{-2}\) when the bicarbonate concentration ([HCO\(_3^-\)]) was increased from 0.1 M to 1.0 M, with the FEHCOOH decreased slightly from 65% to 57%. The plot of log (jHCOOH) versus log ([HCO\(_3^-\)]) showed a slope of 0.27 (Figure S10), indicating that HCO\(_3^-\) may be involved in the rate determining step for HCOOH formation. The rate and FE for H\(_2\) evolution was also improved with increased [HCO\(_3^-\)], whereas the CO production was not much affected; as previously reported.\(^{[20,39]}\) Notably, a high jHCOOH of 11.0 mA cm\(^{-2}\) can be obtained in 0.5 M KHCO\(_3\) while maintaining a high FEHCOOH of 62%. The jHCOOH of 11.0 mA cm\(^{-2}\) at a reduction potential of -0.8 V (vs. RHE) is higher or comparable to some state-of-the-art Sn-based catalysts such as Sn porous nanowires,\(^{[18]}\) Ag-Sn core-shell nanoparticles,\(^{[23]}\) and even some Sn-based gas-diffusion electrodes (Table S3).\(^{[39-41]}\) This demonstrates the intrinsic high catalytic activity of Sn-CF1000 and excellent mass transport in the electrodes. The electrocatalytic performance of Sn-CF1000 may be further improved by using rationally designed gas diffusion electrodes in a flow cell electrolyzer owing to the improved mass transport and reaction kinetics obtained.\(^{[42-44]}\) The stability of the Sn-CF1000 electrode for CO\(_2\)ER was evaluated under optimal conditions: electrolyte concentration was 0.5 M KHCO\(_3\)
and using a potential of -0.8 V vs. RHE (Figure 2f). In the first 20 h of electrolysis, the current density slowly increased from 16.6 to 19.3 mA cm\(^{-2}\). This may be mainly attributed to increased accessibility of electrolyte containing reactants (proton and CO\(_2\)) to Sn active sites, and enhanced electron transport related to the reduction of SnO\(_x\). The electric-field-induced increase of cation concentration in cathode compartment may also contribute. The FE\(_{H2}\) and FE\(_{CO}\) were almost uninfluenced stabilizing around 16\% and 26\%, respectively over this 20 hr period. The FE\(_{HCOOH}\) at the end of the electrolysis was 63\%, which is slightly higher than 62\% for the first 50 min of electrolysis. No obvious changes in electrode surface morphology were observed after electrolysis for 24 h (Figure S11), indicating the structural stability of the Sn-CF1000 catalyst.

To obtain some insight into the mechanism of formate formation on these three electrodes, Tafel plots were performed (Figure S12). The slope of the Tafel curve for Sn-CF900 and Sn-CF1100 was respectively 105 mV dec\(^{-1}\) and 134 mV dec\(^{-1}\), close to the 120 mV dec\(^{-1}\) expected for a rate determining step (RDS) of one-electron transfer forming adsorbed CO\(_2^*\) (Equation S2 in Figure S12).\(^{[45]}\) In comparison, Sn-CF1000 exhibited a Tafel slope of 79 mV dec\(^{-1}\), which is close to the theoretical value of 59 mV dec\(^{-1}\) for a rapid one-electron transfer step followed by a RDS.\(^{[15,45]}\) This RDS may be the protonation of adsorbed CO\(_2^*\) (Equation S3). These results suggest that Sn-CF1000 can bind the CO\(_2^*\) intermediates much more strongly than the other two electrodes. This may account for the increased formate formation at a relatively low overpotential. However, it should be noted that this assignment of RDS has to be tentative given the experimentally determined Tafel slope value and the complexity of CO\(_2\)ER.\(^{[15]}\) Future mechanistic studies are required to determine the reaction kinetics.

The different catalytic performance of these three electrodes may mainly be attributed to the coverage of Sn species on nanofiber surface and their interaction with N-doped carbon supporting. Compared with Sn-CF1100, higher content of Sn in Sn-CF900 and Sn-CF1000 and a larger coverage of Sn nanodots on the nanofiber surface (Figure S2 and S6, Table S1),
would contribute to the higher catalytic current density observed. The low Sn coverage in Sn-CF1100 may afford big Sn particles a dominant role in formate production, leading to a typical Sn-like catalytic behavior. The pyridinic-N defects can improve the electron donating ability of graphitic carbon frameworks due to the lone pair of electrons present.\textsuperscript{[28,30]} Due to the abundance of pyridinic-N, carbon nanofibers in Sn-CF900 and Sn-CF1000 would have stronger electronic interactions with the anchored Sn nanodots, making Sn nanodots more negatively charged than those in Sn-CF1100. The enhanced electronic donation capability of Sn nanodots may promote the adsorption of CO\textsubscript{2} and CO\textsubscript{2} bring, thus facilitating CO\textsubscript{2} reduction at relatively low overpotentials.\textsuperscript{[13,46]} The Sn-CF1000 have a relatively low Sn coverage on the nanofiber surface compared with Sn-CF900; however, it may have a stronger Sn-N interaction, as reflected by its smaller Tafel slope (Figure S12). A balance between Sn coverage and Sn-N interaction may lead to the increased formate selectivity of Sn-CF1000.

To demonstrate the role of atomically dispersed Sn species on the N-doped carbon nanofibers for CO\textsubscript{2}ER, the Sn particles were removed via a simple acidic leaching process. The Sn-CF1000 composite with the best CO\textsubscript{2}ER performance was chosen as a case study. The resultant atomically dispersed Sn catalyst (denoted AD-Sn/N-C1000), exhibited only two distinct peaks at ~26.1° and 43.2° in the XRD pattern (Figure S13), which can be ascribed to the (002) and (101) planes of the graphitic carbon frameworks.\textsuperscript{[47]} No peaks attributable to Sn or SnO\textsubscript{x} were detected. Moreover, no Sn nanodots were detected in the bright field and dark field STEM images (Figure 3a-b). The weight loss was approximately 99% after being annealed at 650 °C in air (Figure S14). All of these evidenced that big Sn particles were effectively removed. The Aberration-corrected high-angle annular dark field scanning TEM (HAADF-STEM) imaging was then used to investigate the atomic structure of the AD-Sn/N-C1000 catalyst. A number of atomically dispersed bright spots are observable in-between the carbon layers or on the surface (Figure 3c-d), which may be ascribed to Sn atoms or clusters. The isolated Sn atoms can be discerned in the carbon support because of the different Z
contrasts of Sn, N and C. The elements Sn and N were homogeneously dispersed along the carbon nanofiber (STEM-EDS analysis, Figure 3e). The AD-Sn/N-C1000 demonstrated different binding energy in the Sn3d XPS spectrum compared to Sn-CF1000 (Figure 3f). The binding energy of the Sn3d_{3/2} peak (486.3 eV) was higher than that for Sn^0 (484.7 eV) and lower than that for Sn^{2+} (486.7 eV), revealing the ionic Sn^{δ+} (0 < δ < 2) nature of Sn in AD-Sn/N-C1000. This unique valence state is similar to that recently reported for Ni in pyridinic-N coordinated Ni-single-atoms catalyst.\[33\] In light of the abundance of pyridinic-N defects in Sn-CF1000, it may be reasonable to propose that Sn atoms in AD-Sn/N-C1000 are coordinated by pyridinic-N, and the formed Sn-N moieties may act as new active sites for CO2ER.

The CO2ER activity of the AD-Sn/N-C1000 catalyst is summarized in Figure 4 with N-doped carbon nanofibers (N-C1000) as control. The AD-Sn/N-C1000 catalyst exhibited a much larger current density, and a more positive onset potential of ~ - 0.4 V (vs. RHE) compared to ~ - 0.8 V for N-C1000 (Figure 4a). At - 0.8 V, the current density of AD-Sn/N-C1000 reached 5.12 mA cm\(^{-2}\), ~ 7.6 times larger than 0.67 mA cm\(^{-2}\) for N-C1000. These results indicate that the incorporation of Sn atoms enhanced the electrocatalytic activity of N-doped carbon nanofibers. The primary products produced using AD-Sn/N-C1000 and N-C1000 were CO and H\(_2\). They showed a similar volcano-like FE\(_{CO}\) dependence on the applied potentials, peaking around - 0.6 V (Figure 4b), yet the AD-Sn/N-C1000 exhibited substantially higher FE\(_{CO}\) and j\(_{CO}\). At - 0.6 V (corresponding to an overpotential of 490 mV for CO formation), the AD-Sn/N-C1000 attained a maximum FE\(_{CO}\) of 91% and a j\(_{CO}\) of 1.75 mA cm\(^{-2}\), much higher than those (64%, 0.2 mA cm\(^{-2}\)) for N-C1000. This performance is comparable to the recently reported 3D N-doped graphene foam,\[48\] Fe-N-C,\[31,32\] Mn-N-C,\[32\] Ni-N-C,\[33\] and Cu-Sn catalysts (Table S4).\[25\] It may be further improved by promoting the mass transport via the use of rationally designed electrode and reactor structures (i.e. use of a gas diffusion electrode in a flow cell).\[49\] Due to the low content of Sn doping (~ 1 wt%), the
mass specific CO partial current density of AD-Sn/N-C1000 was over 16 times larger than that of N-C1000 over a moderate overpotential range of - 0.6 to - 0.8 V (Figure S15). In addition, the AD-Sn/N-C1000 catalyst exhibited an excellent stability. During the electrolysis of 24 h, the current density was almost kept stable around 1.55 mA cm\(^{-2}\), and the FE\(_{\text{CO}}\) only slightly decreased from 91\% to 84\% (Figure 4c). This implies that the structure of this catalyst was stable, since no obvious morphology changes were observed after this prolonged electrolysis time (Figure S16).

AD-Sn/N-C1000 demonstrated a Tafel slope of 140 mV dec\(^{-1}\) (Figure 4d), which is close to the theoretical 120 mV dec\(^{-1}\) for a mechanism that the initial single-electron transfer forming CO\(_2\)\(^{2-}\) intermediates is the rate-determining step for CO\(_2\)-to-CO conversion.\(^{[45]}\) In contrast, N-C1000 exhibited a slope of 239 mV dec\(^{-1}\), evidencing its sluggish kinetics. This result is in agreement with other reported N-doped carbons.\(^{[30,48,50]}\) It should be noted that the catalytic behaviors and structure of AD-Sn/N-C are very similar to active transition metal doped N-carbons,\(^{[31-33]}\) in which metal-N moieties are active sites for CO formation. It is reasonable to infer that Sn-N moieties are the active centers in AD-Sn/N-C1000 catalyst. The acid treated N-C1000 showed nearly identical catalytic current densities to the untreated samples, ruling out the contribution to the improved performance on AD-Sn/N-C1000 from functional groups generated during the acidic treatment (Figure S17). Given the same content and structure of N species in these two samples (Figure S18) and a larger specific surface area for N-C1000 (Figure S19), the improved kinetics for CO formation on AD-Sn/N-C1000 may be mainly attributed to the enhanced stabilization of CO\(_2\)\(^{2-}\) and subsequently facilitated formation of COOH* intermediates on the Sn-N moieties. This may also account for the high selectivity and activity for CO formation on the Sn atoms modified N-doped carbon nanofibers.

3. Conclusion
In summary, the catalytic activity of Sn modified N-doped porous carbon nanofiber for CO$_2$ER can be tuned by the structure and content of Sn and N species. The abundance of Sn active sites and the strong electronic interaction between pyridinic-N doped carbon and Sn nanodots may contribute to the promoted CO$_2$-to-HCOOH conversion on Sn-CFI1000 by improving the binding strength of CO$_2$•••intermediates. The high activity and selectivity for CO production over the Sn atoms modified nanofibers may arise from the intrinsically high activity of the formed Sn-N moieties. Future mechanistic studies are needed to understand the reaction kinetics behind it. This work may provide a route to development of switchable non-precious hybrid electrodes for conversion of CO$_2$ to valuable HCOOH or CO as demanded. It should be also pointed out that this well-established electrospinning technology is readily employed to produce other metal-based hybrid catalysts integrated with heteroatom-doped carbon nanofibers (i.e. N, B, P) for CO$_2$ER, further expanding the materials family and promoting the research.

4. Experimental Section

Materials: Polymethylmethacrylate (PMMA, M$_w$ ~ 35000) and N,N-Dimethylformamide (DMF, 99.5%) were purchased from Sinopharm Chemical Reagent. Tin (II) chloride dehydrate (SnCl$_2$·2H$_2$O, 98%) was from Xilong Chemical Company. Polyacrylonitrile (PAN, M$_w$ ~ 150000), potassium bicarbonate (KHCO$_3$, ≥99.95%), and Nafion® 117 solution (5 wt %) were purchased from Sigma-Aldrich. Carbon paper (SIGRACET® GDL 38AA, 225 ± 30 µm) was purchased from SGL Carbon GmbH, and Nafion® 117 membrane was from Alfa-Aesar. Ultrapure Milli-Q water (18.2 MΩ·cm) was used in this work.

Synthesis of Sn modified nitrogen-doped carbon nanofibers: The hybrid nanofibers were prepared via an electrospinning method. Briefly, PAN (0.35 g) and PMMA (0.35 g) were dissolved into DMF (7 g) forming a homogeneous colloidal solution. After adding 0.68 g of SnCl$_2$·2H$_2$O, the solution was magnetically stirred for 4 h at 50 °C to form a transparent
solution. Then it was transferred into a plastic syringe (10 mL) equipped with a capillary and needle head (0.5 mm in diameter). Under a high voltage of ~ 8.5 kV, the syringe was propelled by a peristaltic pump at a speed of 0.4 mL h\(^{-1}\), and the fibers were sprinkled from the metallic needle and collected with an aluminium collector. The distance between the needle and collector was 12 cm. The fibers were then dried in a vacuum oven at 60 °C for 12 h. Finally, they were subjected to a pyrolysis process in a tube furnace at three different temperatures, 900, 1000 and 1100 °C for 2 h in Ar/H\(_2\) gas (8% H\(_2\)) to form the Sn decorated N-doped carbon nanofibers. The heating rate was 3 °C min\(^{-1}\).

To prepare the Sn atoms modified nitrogen-doped carbon nanofibers (AD-Sn/N-C1000), the Sn-CF1000 powder was immersed into 3 M HCl solution for 8 h at 90 °C, and collected by centrifugation and washed with copious water to neutral pH. The catalyst was dried at 60 °C for 12 h in a vacuum oven. The pure N-doped carbon fibers (N-C1000) were also treated with the same procedures as control sample.

**Structural Characterization:** The crystal structure was analysed by X-ray diffraction (XRD, GBC MMA diffractometer) with Cu Kα radiation at a scan rate of 4 degree min\(^{-1}\). The morphology was investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-7500FA) and scanning transmission electron microscopy (STEM, JEOL ARM200F) equipped with energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) was conducted on a SPECS PHOIBOS 100 Analyser with X-ray excitation provided by Al Kα radiation (\(h\nu = 1486.6\) eV) at a high voltage of 12 kV and a power of 120 W. The XPS binding energy spectra were recorded at a pass-energy of 20 eV in the fixed analyser transmission mode. All the spectra were calibrated by C 1s = 284.6 eV. Raman spectra were performed with a confocal Raman spectrometer (Jobin Yvon HR800, Horiba) using a 632.8 nm diode laser. **Thermal gravimetric analysis (TGA)** was conducted on a Pyris Diamond thermogravimetric/differential thermal analyzer at a heating rate of 5 °C min\(^{-1}\) in air flow.
Fabrication of Working Electrode: The catalyst inks were prepared by mixing 15 mg of the obtained carbon nanofiber samples, 5 mg Ketjen carbon blacks, ethanol/water (2:3 v/v, 1.9 mL) solution and Nafion solution (5 wt%, 0.1 mL) under sonication for 90 min. An aliquot of the catalyst ink (130 µL) was dropped uniformly on one side of carbon paper (1 cm × 1 cm), and kept at room temperature overnight to evaporate most of the solvents. After being annealed in an oven at 70 °C for 3 h, these catalyst covered carbon papers were used as working electrodes.

Electrochemical Measurements: All the experiments were carried out on a potentiostat (CHI 650D) in a two-compartment gastight glass H-cell. The cathodic and anodic compartments were separated by Nafion membrane. Each compartment holds 30 mL of electrolyte and leaves a headspace of about 20 mL. A piece of platinum gauze (2 cm × 2 cm) and a Ag/AgCl (3 M NaCl, BASi) electrode are served as counter electrode and reference electrode. The KHCO₃ aqueous solution was used as electrolyte directly without any purification. All the applied potentials (E_{Ag/AgCl}) were set according to the equation, E_{RHE} = E_{Ag/AgCl} + 0.21 + 0.0591 × pH, where E_{RHE} was the potential on reversible hydrogen electrode (RHE) scale. The E_{Ag/AgCl} was corrected using the automatic iR compensation function on the potentiostat. The pH of CO₂-saturated 0.1 M, 0.3 M, 0.5 M, 0.7 M and 1.0 M KHCO₃ was 6.8, 7.2, 7.5, 7.6 and 7.8, respectively. The current density reported in this work was normalized to the geometric area.

Prior to the CO₂ reduction, the cathodic electrolyte was saturated with CO₂ (99.99%, BOC Australia) at a flow rate of 20.0 mL min⁻¹ controlled by a mass flow controller (GFC17, Aalborg®) for at least 20 min under a stirring rate of 700 rpm. During the chronoamperometry electrolysis, CO₂ was continuously bubbled into the cathodic compartment and vented directly into the gas-sampling loop (1 mL) of a gas chromatograph (GC, 8610C, SRI). This GC was equipped with a packed MolSieve 5A column and a packed Haysep D column with argon as carrier gas. The separated gases were analyzed by a thermal conductivity detector.
(for H₂) and a flame ionization detector with methanizer (for CO, CH₄, C₂H₆ etc.). Quantification of the products was performed by an external standard method. A standard gas mixture composed of H₂, CO, CH₄, C₂H₄, C₂H₆ and CO₂ (BOC Australia) was used to obtain the calibration curve for each component. The first GC run was initiated at the 10th min, and thereafter re-initiated every 16 min for twice. The average of the results from these three measurements was used in the data analysis. Liquid products were analysed on a 400 MHz NMR spectrometer (Bruker Avance) and quantified according to our previous report.[25]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Published online: ((will be filled in by the editorial staff))
References


Figure 1. (a) Schematic illustration of the fabrication process of Sn modified N-doped carbon nanofiber electrocatalysts for HCOOH and CO production; (b) SEM image and (c) bright field TEM image of Sn-CF1000 composite; (d-e) Dark field STEM images under different magnifications, (f) HRTEM image and (g) STEM-EDS mapping results of a single nanofiber; (h-i) High-resolution Sn3d and N1s XPS spectra of Sn-CF1000.
Figure 2. (a) Stationary CO$_2$ER average current densities and (b-d) the corresponding faradaic efficiencies of HCOOH, CO and H$_2$ during 50 min of electrolysis in CO$_2$-saturated 0.1 M KHCO$_3$ for three Sn-CFs catalysts. (e) Faradaic efficiencies (columns) and partial current densities (points) of three products on Sn-CF1000 at -0.8 V vs. RHE in CO$_2$-saturated KHCO$_3$ solution with different concentration; (f) Stability of Sn-CF1000 at -0.8 V for 24 h in CO$_2$-saturated 0.5 M KHCO$_3$. Dash lines to guide the eye.
Figure 3. (a) Bright field STEM image the AD-Sn/N-C1000 catalyst; (b-d) HAADF-STEM images of AD-Sn/N-C1000 under different magnifications; (e) EDS mapping results of the nanofiber in (b); (f) High-resolution Sn3d XPS spectra for AD-Sn/N-C1000 and Sn-CF1000.
Figure 4. (a) Stationary CO$_2$ER average current densities at different potentials in CO$_2$-saturated 0.1 M KHCO$_3$ for AD-Sn/N-C1000 and N-C1000 catalysts; (b) CO faradaic efficiency and partial current density for these two catalysts; (c) Prolonged electrolysis of AD-Sn/N-C1000 at -0.6 V vs. RHE for 24 h; (d) Tafel plots of AD-Sn/N-C1000 and N-C1000 catalysts for CO production. Dash lines to guide the eye.
Supporting Information

Tunable and Efficient Tin Modified Nitrogen-doped Carbon Nanofibers for Electrochemical Reduction of Aqueous Carbon Dioxide

Yong Zhao, Jiaojiao Liang, Caiyun Wang*, Jianmin Ma*, Gordon G Wallace*

**Figure S1** XRD pattern of the Sn-CF1000 (a), Sn-CF900 and Sn-CF1100 (b).
Figure S2 TGA curves of Sn-CF1000 (a), Sn-CF900 and Sn-CF1100 (b) in air at a heating rate of 5 °C min⁻¹.

The content of tin in the Sn-CF1000 composite was evaluated by TGA, as shown in Figure S2a. The weight loss of 1.5% observed below 250 °C is attributed to the evaporation of adsorbed water. With the increase of temperature, the carbon in the composite is combusted in air (C + O₂ → CO₂) and the metallic tin is oxidized to SnO₂ (Sn + O₂ → SnO₂). The combustion reaction leads to weight loss, whereas the oxidation results in weight increase. The TGA curve almost keeps stable from 250 °C to 400 °C, probably due to the balance of the two opposite processes. The rapid weight loss from 400 °C to 560 °C may be caused by the fast combustion reaction of carbon. It should be noted that the formed thick SnO₂ layer may hinder the further oxidation of Sn micropsheres. The weight gain over 560 °C to 720 °C may be from the oxidation of metallic Sn at the core of Sn microspheres.

Given that only SnO₂ would remain after TGA test, the Sn content in the composite could be evaluated according to the following equation:

\[
Sn \text{ (wt\%)} = \frac{m_2}{m_1} \times \frac{M_{Sn}}{M_{SnO_2}} \times 100\%
\]

where the \(m_1\) is the mass at 250 °C and \(m_2\) is the mass at 720 °C, and \(M_{Sn}\) and \(M_{SnO_2}\) are the molar weight of Sn and SnO₂, respectively.

According to this method, the Sn weight percentages of Sn-CF900, Sn-CF1000 and Sn-CF1100 are calculated to be ~ 50%, ~ 53%, and ~ 43%, respectively.
Table S1 Relative content of Sn, O, N and C in the Sn-CF composites estimated from XPS analysis.

<table>
<thead>
<tr>
<th>Atomic content (%)</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-CF900</td>
<td>62.81</td>
<td>2.83</td>
<td>28.56</td>
<td>5.79</td>
</tr>
<tr>
<td>Sn-CF1000</td>
<td>71.77</td>
<td>2.35</td>
<td>23.98</td>
<td>1.90</td>
</tr>
<tr>
<td>Sn-CF1100</td>
<td>94.41</td>
<td>1.21</td>
<td>4.22</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Figure S3 Nitrogen adsorption/desorption curve of Sn-CF1000, inset is the corresponding Barrett-Joyner-Halenda (BJH) pore distribution curve.
**Figure S4** Raman spectrum of the Sn-CF1000 composite.

**Figure S5** SEM images of the Sn-CF900 (a-b) and Sn-CF1100 (c-d) composites at different magnifications.
Figure S6 TEM characterizations of the Sn-CF900 (a-c) and Sn-CF1100 (d-f): (a, d) are dark field STEM images; (b, e) are bright field HRTEM images and (c, f) are the EDS mapping results.

Sn nanodots are densely anchored on the surface of the Sn-CF900 nanofiber, while the density of Sn nanodots is relatively low for the Sn-CF1100 nanofiber. It can be concluded that the density of Sn species on the nanofiber surface decreases with the increase of pyrolysis temperature from 900 to 1100 °C. This tendency is consistent with the XPS results in Table S1.
Figure S7 XPS Sn3d spectra (a) and N1s spectra (b-c) of the Sn-CF900 and Sn-CF1100 composites.
Table S2 Onset potentials of the three Sn-CF electrodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sn-CF900</th>
<th>Sn-CF1000</th>
<th>Sn-CF1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset potential (V vs. RHE)</td>
<td>-0.50</td>
<td>-0.61</td>
<td>-0.69</td>
</tr>
</tbody>
</table>

Figure S8 HCOOH partial current densities on the three Sn-CF electrodes in CO₂-saturated 0.1 M KHCO₃ at different potentials.
Figure S9 (a) Electrolysis curves of Sn-CF1000 in Ar-saturated (pH ~ 7.0) and CO₂-saturated (pH ~ 6.4) 0.1 M K₂HPO₄/KH₂PO₄ (KPi) at -0.8 V vs. RHE. (b) The subsequent electrolysis in 0.1 M KHCO₃ (pH ~ 6.8) using the same electrode at -0.8 V vs. RHE.

The product distribution tested in KPi is different from that tested in KHCO₃, particularly the FE₉₂. This may be caused by the chemically adsorbed phosphate ions on Sn sites during the electrolysis which are able to accelerate the catalytic hydrogen evolution rate.\textsuperscript{[1]} The simple control experiment in (b) may shed light on this effect.

Figure S10 The relationship of log ([HCO₃⁻]) and log (j₃COOH) for the Sn-CF1000 electrode.
Table S3 Comparison of different Sn-based catalysts for CO$_2$-to-HCOOH conversion

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Loading mass (mg cm$^{-2}$)</th>
<th>Electrolyte</th>
<th>Potential (V vs. RHE)</th>
<th>FE$_{\text{HCOOH}}$</th>
<th>$j_{\text{HCOOH}}$ (mA cm$^{-2}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/SnO$_x$ /Ti foil</td>
<td>N/A</td>
<td>0.5 M NaHCO$_3$</td>
<td>-0.7</td>
<td>58%</td>
<td>1.04</td>
<td>[2]</td>
</tr>
<tr>
<td>Electrodeposited Sn GDE</td>
<td>3.0</td>
<td>0.5 M NaHCO$_3$</td>
<td>-1.1</td>
<td>71%</td>
<td>5.77</td>
<td>[3]</td>
</tr>
<tr>
<td>SnO$_2$ GDE</td>
<td>N/A</td>
<td>0.5 M KHCO$_3$</td>
<td>-1.28</td>
<td>68%</td>
<td>4.08</td>
<td>[4]</td>
</tr>
<tr>
<td>Sn GDE</td>
<td>5.0</td>
<td>0.5 M KHCO$_3$</td>
<td>-1.11</td>
<td>~ 73%</td>
<td>~ 9.82</td>
<td>[5]</td>
</tr>
<tr>
<td>Sn foil</td>
<td>N/A</td>
<td>0.5 M KHCO$_3$</td>
<td>-1.37</td>
<td>63.5</td>
<td>17.78</td>
<td>[6]</td>
</tr>
<tr>
<td>Sn/Nafion GDE</td>
<td>0.7</td>
<td>0.5 M NaHCO$_3$</td>
<td>-1.17</td>
<td>70%</td>
<td>18.9</td>
<td>[7]</td>
</tr>
<tr>
<td>SnO$_2$/graphene</td>
<td>0.21</td>
<td>0.1 M NaHCO$_3$</td>
<td>-1.16</td>
<td>93.6%</td>
<td>9.55</td>
<td>[8]</td>
</tr>
<tr>
<td>SnO$_2$/carbon black</td>
<td>0.21</td>
<td>0.1 M NaHCO$_3$</td>
<td>-1.16</td>
<td>86%</td>
<td>4.64</td>
<td>[8]</td>
</tr>
<tr>
<td>Porous Sn NWs</td>
<td>4.0</td>
<td>0.1 M KHCO$_3$</td>
<td>-0.8</td>
<td>80.1%</td>
<td>4.81</td>
<td>[9]</td>
</tr>
<tr>
<td>Sn NPs</td>
<td>4.0</td>
<td>0.1 M KHCO$_3$</td>
<td>-0.8</td>
<td>58%</td>
<td>1.39</td>
<td>[9]</td>
</tr>
<tr>
<td>SnO$_2$ dendrite /Sn foil</td>
<td>N/A</td>
<td>0.1 M NaHCO$_3$</td>
<td>-1.16</td>
<td>56.9%</td>
<td>7.97</td>
<td>[10]</td>
</tr>
<tr>
<td>Ag-Sn core-shell NPs</td>
<td>1.0</td>
<td>0.5 M NaHCO$_3$</td>
<td>-0.8</td>
<td>80%</td>
<td>15.6</td>
<td>[11]</td>
</tr>
<tr>
<td>Sn-CF1000</td>
<td>0.97</td>
<td>0.5 M KHCO$_3$</td>
<td>-0.8</td>
<td>62%</td>
<td>11.0</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: 1) GDE is the abbreviations of gas-diffusion electrode. 2) The potentials were converted to RHE scale based on the equation, $E$ (vs. RHE) = $E$ (vs. Ag/AgCl) + $E$ (Ag/AgCl) + 0.0591*pH, by assuming the pH of CO$_2$-saturated 0.5 M and 0.1 M NaHCO$_3$ or KHCO$_3$ is 7.2 and 6.8, respectively. 3) If the FE$_{\text{HCOOH}}$ and $j_{\text{HCOOH}}$ values were not specifically stated, they were derived from graphical results or calculated with the available information.
Figure S11 SEM images of Sn-CF1000 electrode before (a,b) and after (c,d) 24 h of electrolysis in CO$_2$-saturated 0.5 M KHCO$_3$ solution at -0.8 V vs. RHE. The small particles are carbon blacks.

Figure S12 Tafel plots of the three Sn-CF electrodes. The elementary steps (Equation S1-S5) for formate formation are proposed based on previous reports$^{[8,12,13]}$. The proton donor is assigned to HCO$_3^-$ rather than H$^+$, which may be supported by the positive linear correlation of log ([HCO$_3^-$]) and log ($j_{HCOOH}$) in Figure S10.
**Figure S13** XRD pattern of the AD-Sn/N-C1000 (Sn-CF1000 after acidic leaching).

**Figure S14** TGA curves of Sn-CF1000 and AD-Sn/N-C1000. The weight percentage of Sn in AD-Sn/N-C1000 is evaluated to approximately 1% according to the method in Figure S2.
Table S4 Comparison of different catalysts for CO$_2$-to-CO conversion

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Loading mass (mg cm$^{-2}$)</th>
<th>Electrolyte</th>
<th>Potential (V vs. RHE)</th>
<th>FE$_{CO}$</th>
<th>$j_{CO}$ (mA cm$^{-2}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-doped 3D graphene foam</td>
<td>0.3 ~ 0.5</td>
<td>0.1 M KHCO$_3$</td>
<td>-0.58</td>
<td>~ 80%</td>
<td>1.54</td>
<td>[14]</td>
</tr>
<tr>
<td>Mn-N-C</td>
<td>0.79</td>
<td>0.1 M KHCO$_3$</td>
<td>-0.6</td>
<td>~ 73%</td>
<td>~ 3.9</td>
<td>[15]</td>
</tr>
<tr>
<td>Fe-N-C</td>
<td>0.79</td>
<td>0.1 M KHCO$_3$</td>
<td>-0.6</td>
<td>~ 79%</td>
<td>~ 2.35</td>
<td>[15]</td>
</tr>
<tr>
<td>FeN$_4$-C</td>
<td>1.0</td>
<td>0.1 M NaHCO$_3$</td>
<td>-0.6</td>
<td>91%</td>
<td>~ 4.1</td>
<td>[16]</td>
</tr>
<tr>
<td>Ni-N-C</td>
<td>5.0</td>
<td>0.5 M KHCO$_3$</td>
<td>-0.9</td>
<td>71.9%</td>
<td>~ 5.2</td>
<td>[17]</td>
</tr>
<tr>
<td>Cu-Sn NWs</td>
<td>N/A</td>
<td>0.1 M KHCO$_3$</td>
<td>-0.7</td>
<td>82%</td>
<td>0.96</td>
<td>[18]</td>
</tr>
<tr>
<td>Cu-Sn alloy</td>
<td>N/A</td>
<td>0.1 M KHCO$_3$</td>
<td>-0.6</td>
<td>~ 90%</td>
<td>1.12</td>
<td>[19]</td>
</tr>
<tr>
<td>AD-Sn/ N-C1000</td>
<td>0.97</td>
<td>0.1 M KHCO$_3$</td>
<td>-0.6</td>
<td>91%</td>
<td>1.75</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: If the FE$_{CO}$ and $j_{CO}$ values were not specifically stated, they were derived from graphical results or calculated with the available information.
Figure S15 Comparison of the mass specific CO partial current densities of the AD-Sn/N-C1000 and N-C1000 catalysts under four different potentials.

Figure S16 SEM images of AD-Sn/N-C1000 electrode before (a-c) and after (d-f) 24 h of electrolysis in CO$_2$-saturated 0.1 M KHCO$_3$ solution at -0.6 V vs. RHE. The small particles are carbon blacks.
Figure S17 Electrolysis curves of N-C1000 (a) and acid treated N-C1000 (b) at -0.7 V and -0.8 V vs. RHE in CO₂-saturated 0.1 M KHCO₃.

Figure S18 N1s XPS spectra of the AD-Sn/N-C1000 (a) and N-C1000 (b).
Figure S19 Nitrogen adsorption/desorption curves of the AD-Sn/N-C1000 and N-C1000 composites and the corresponding BJH pore distribution curves.

References


