Understanding the Origin of Selective Reduction of CO₂ to CO on Single-Atom Nickel Catalyst

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Abstract

Electrochemical reduction of CO₂ to CO offers a promising strategy for regulating the global carbon cycle and providing feedstock for the chemical industry. Understanding the origin that determines the faradaic efficiency (FE) of reduction of CO₂ to CO is critical for developing a highly efficient electrocatalyst. Here, by constructing a single-atom Ni on the nitrogen-doped winged carbon nanofiber (NiSA-NWC), we find that the single-atom Ni catalyst possesses the maximum CO FE of over 95% at -1.6V vs. Ag/AgCl which is about 30% higher than the standard Ni nanoparticles on the same support. The Tafel analysis reveals that the single-atom Ni catalyst has a preferred reduction of CO₂ to CO and a slower rate for the hydrogen evolution reaction. We propose that the domination of singular Ni¹⁺ electronic states and limited hydrogen atom adsorption sites on the single-atom Ni catalyst lead to the observed high FE for CO₂ reduction to CO.

1. Introduction

The continuously increasing concentration of carbon dioxide (CO₂) in the earth atmosphere has raised a global concern about the greenhouse effect.¹ In the past decades, many efforts have been put on reducing the emission of CO₂ by converting CO₂ to the useful industrial chemical products.² Among them, the electrochemical reduction of CO₂ to fuels is a clean and sustainable approach for generating value-added gaseous products (CO, CH₄, etc.) and liquid products (HCOOH, CH₃OH, C₂H₅OH, etc.).³⁻⁴ In those possible electrochemical CO₂ reaction products, reduction of CO₂ to CO is one of the most promising reaction pathways because CO can be used as feedstock for the Fischer-Tropsch reaction.⁵⁻⁶ However, one of the major challenges for the CO₂ reduction to CO is that the equilibrium potentials for production of CO overlap with that of hydrogen evolution reaction (HER) in aqueous phase.⁷⁻⁸ Hence, it is important to maximize the selectivity of CO₂ reduction to CO over the HER in water.

In early studies, precious metal nanoparticles, especially Au or Ag, had been used as CO₂ electrocatalyst with more than 80% CO selectivity.⁹⁻¹⁰ The electronic structures of the Au and Ag nanocrystals can stabilize *COOH intermediate as well as selectively suppress HER pathway. For practical applications, utilizations of low-cost, earth-abundant transition metals (TM) to replace the precious metals have attracted the great attention. Currently, reduction of CO₂ on TM catalysts including Fe, Co and Ni nanoparticles have all been hindered by the accompanied HER reactions.¹¹⁻¹² For example, a catalyst made of 30-40 nm nickel nanoparticles supported on the carbon nanotube displayed more than 90% preferential selectivity to the HER in CO₂ reduction.¹³ A few recent studies suggested that the efficiency of CO₂ to CO on TM catalysts can be significantly improved once the TM

was supported on the doped carbon material.¹⁴⁻¹⁵ Strasser et al. had reported that Ni supported on nitrogen doped porous carbon can reach CO faradic efficiency (FE) of 80%.¹⁶ Jiang et al. demonstrated that the catalyst of atomic dispersing Ni on the 2D nitrogen-doped graphene nanosheet can procure the maximal CO faradic efficiency of more than 95% under an overpotential of 550 mV.¹³ More recently, Pan et al. showed that the edge-hosted Fe-N₄ catalyst present the maximal 93% CO FE.¹⁷ They explained that the edge-hosted metal-N₂₊₂ located at the two armchair-like graphitic layers bridge could further stimulate fast charge transfer from the active site to the adsorbed CO₂.¹⁷ Therefore, development of an ideal substrate that can confine metal active site sizes to the atomic level with designed coordination environment may enhance the selectivity of CO₂ reduction to CO.

In order to understand the origin of selective CO₂ reduction to CO, we design and synthesize a Ni single atom electrocatalyst consisting of isolated Ni atoms anchored on an N-doped and winged 3D-graphene carbon nanofiber (NWC). The morphology of Ni single atom was identified by aberration-corrected scanning transmission electron microscopy (STEM). The single-Ni-atom electrocatalyst showed high intrinsic selectivity of CO₂ reduction to CO. The maximal CO Faradaic efficiency (FE) of more than 95% at -1.6V vs Ag/AgCl in 0.1M NaHCO₃ solution was observed. We speculate that the enhancement of CO selectivity relative to the HER is attributed to domination of singular of Ni¹⁺ electronic states and limited hydrogen atom adsorption sites on the NiSA-NWC.

2. Experimental Section

Synthesis of winged carbon nanotubes (WC): In a standard procedure, 200 mg of stacked-cup carbon nanofiber with an average diameter of 100 nm (from the Pyrograf Product. Inc) and 1.0 g of sodium nitrate (NaNO₃) were mixed in 40 ml concentrated

sulfuric acid (H_2SO_4) in an ice bath. Then 6 g potassium permanganate (KMnO_4) was slowly added to the solution. The mixture was stirred at 0 °C for 1.5 h and then kept at room temperature for 1 h. After that the mixture was poured slowly into 250 ml ice-cooled water. Then 10 ml of H_2O_2 aqueous solution (30 wt%) was added dropwise. The color of the mixture changed from dark purple to black after stirring for 10 min. The oxidized CNT (Ox-CNT) was collected by vacuum filtration, followed by washing with water until pH-neutral. Then the Ox-CNT was re-dispersed in DI water (20 mg/ml). This mixture was tip sonicated for 30 min to form winged CNT with high concentration of defects (WCNT).

Synthesis of single-atom Ni on nitrogen doped winged carbon nanofiber (NiSA-NWC and Ni-WC): 2.4 mg nickel nitrate ($\text{Ni}(\text{NO}_3)_2$) was dissolved in 8 ml DI water, followed by adding 2.5ml Ox-CNT solution. Then 0.66 g cyanamide was added as the nitrogen source. The solution was well mixed in a centrifuge tube and stayed in liquid nitrogen for 15 min. The solidified mixture was freeze dried for two days. In the following pyrolysis process, the resultant powder was heated to 550 °C in 30 min and kept at this temperature for 2 h. Then the temperature was raised to 750°C in 30 min and kept for 1 h. The resultant product was washed by the 1M HCl to remove impurities. The procedure of making Ni-WC was similar to the procedure of the NiSA-NWC except for the addition of the cyanamide.

Synthesis of Ni nanoparticle on nitrogen doped winged carbon nanofiber (NiNP-NWC): Specifically, 12 mg nickel nitrate ($\text{Ni}(\text{NO}_3)_2$) in 8 ml of DI water was used in the same procedure above to prepare NiNP-NWC catalysts in this study. The resultant product was not washed by the 1M HCl to preserve the nature of the Ni nanoparticle on the NWC.

Electrochemical CO₂ Reduction: Typically, 5 mg of catalyst was ground into fine powder and then added to 2 ml of DI water, followed by the addition of 100 μ l Nafion solution (5 wt% in water). Then the mixture was sonicated for 30 min to form a uniform ink. Carbon paper was cut into 0.8 cm x 2 cm and 10 μ l of the prepared catalyst ink was drop-dried onto the carbon paper as the working electrode (WE). The working electrode was vacuum dried for 30 min before use.

Electrocatalytic tests of NiSA-NWC were conducted with a potentiostat (BioLogic) in a three-electrode setup with commercial Ag/AgCl electrode as the reference. 100 mM potassium carbonate (KHCO₃) aqueous solution was used as both the catholyte and the anolyte. Two chambers were separated by Nafion 115 membrane. Pure CO₂ gas was flowed into both chambers at a flow rate of 10 ml/min. The gas in working chamber was flowed into the IR chamber for characterization of reduction product. The calibration process follow the reports before.¹⁸ Potentials were corrected for the uncompensated ohmic loss (i_{Ru}) by the EIS following the procedure in the literature.¹⁹⁻²⁰

Mass spectroscopy for H₂ product detection: argon (Ar, Ultra High Purity) and CO₂ (CO₂, Ultra High Purity) were obtained from Airgas and used as a carrier gas. The gas flow rate was controlled individually by mass flow controllers (Aalborg) at 10ml/min. The gaseous product was analyzed by a quadrupole mass spectrometer (Hiden, HPR-20) equipped with a Faraday cup detector. For measurement, at least 30 min elapsed before reaching steady state and three sequential measurements were made to determine the steady-state concentration of each gas and the associated reaction rates and uncertainties. The 2 atomic mass unit (amu) signal was used to quantify the H₂ production rate.

Additional Characterizations: Morphologies of the prepared catalysts were imaged with a scanning electron microscope (SEM, FEI XL30) and a transmission electron microscope (TEM, FEI Tecnai G² Twin). The crystal structure and elemental analysis were studied with X-Ray diffractometer (XRD, Panalytical X'Pert PRO MRD HR XRD System) and X-Ray photoelectron spectrometer (XPS, Kratos Analytical Axis Ultra). The gaseous product was analyzed in a Nicolet 380 FT-IR.²¹ An EPR instrument (Bruker EMX/plus spectrometer, Germany) was serviced to detect the Ni states in the NiSA-NWC with parameters as follows: center field 3460 G, sweep width 100 G, microwave frequency 9.3 GHz(X-band), microwave power 19.71 mW.

3. Results and Discussion

The morphology and other characterization results of Ni single atom catalyst supported on nitrogen doped winged carbon nanofiber (NiSA-NWC), which was synthesized by the procedure shown in Scheme 1, were displayed in Figure 1. It can be observed that in Figure 1a and 1b, the CNF core has a loose strip-type structure and curly edges with tens of micrometers in length, binding with the graphene wing. It is worth noting that no metallic NPs were found in Figure 1a and 1b. In contrast, when the amount of the nickel salts increased, many nickel nanoparticles with 10-20 nm were clearly seen in the TEM image of the nanoparticle nickel catalyst (Figure S1b). The X-ray elemental mapping in Figure 1c reveals that NiSA-NWC possess uniform distribution of C, N, and Ni species across the entire tubular structure. The atomic level dispersion of Ni atoms on the NWC was further confirmed by the aberration-corrected scanning transmission electron microscopy (AC-STEM). The bright dots representing for the heavier Ni atoms homogenously disperse

throughout the whole NWC in the Figure 1d. A combination of the X-ray elemental mapping and AC-STEM results implies the successful preparation of Ni single-atom catalyst on the NWC surfaces.

To explore selectivity of CO₂ reduction influenced by the nanoparticle structure, we have also synthesized Ni nanoparticle catalysts on the NWC (NiNP-NWC) (see details in the experimental section). The morphology of Ni nanoparticle catalyst has been confirmed by the STEM in Supplemental Figure S2. The lattice structure of NiNP-NWC was also studied by the XRD. As shown in Figure S10, the sharp diffraction peaks at 44.5°, 51.9°, and 76.3° can be ascribed to the (111), (200), and (208) diffraction peaks of Ni metal in accordance with the standard pdf card 00-004-0850. And the peak at 26.4° belongs to the carbon lattice of carbon nanofiber support.²² For the NiSA-NWC samples, no Ni nanoparticle diffraction peak can be found, indicating there is no long-range ordered Ni structure in the NiSA-NWC. At first, the linear scan voltammetry (LSV) of NiSA-NWC and NiNP-NWC were recorded in aqueous 0.1 M KHCO₃ solution under an N₂ atmosphere. The reduction current shown in the N₂ saturated solution is typically attributed to the sole HER (Figure 2a). Upon saturating the solution with CO₂, the onset potential of NiSA-NWC starts at 200 mV lower than its value in the N₂ saturated solution whereas the onset potential of NiNP-NWC in CO₂ saturated solution remains close to its value in N₂ saturated solution. The electrochemical CO₂ reduction behavior of NiSA-NWC and NiNP-NWC was further differentiated by the determination of products where the gaseous products of CO₂ reduction under different applied potential were monitored for 2h by both inline infrared spectrometer and mass spectrometer (Figure S4, S5). Each product FE is shown in Figure 2b. A careful inspection of Figure 2b shows the NiSA-NWC possesses the maximum CO

FE over 95% at -1.6 V vs. Ag/AgCl which is about 30% higher than the standard Ni nanoparticles on the same support. And only 3% FE of H₂ was detected at the same potential, implying that NiSA-NWC selectively catalyzes CO₂ reduction to the CO in aqueous solution. In addition, liquid CO₂ reduction products were analyzed by NMR (Supplementary Fig. S6). Similar ¹H NMR spectrums were found in the spectra of before and after CO₂ reduction. These observations suggest that no liquid products from CO₂ reduction were detected in the potential range from -0.4 to -2 V versus Ag/AgCl. Moreover, we use Tafel analysis to elucidate the kinetics of the mechanism of CO₂ reduction, and the results are presented in Figure 2c. The potential range of Tafel analysis is -1.35 – 1.45 V vs. Ag/AgCl for the NiSA-NWC and -1.45 - -1.55 V vs. Ag/AgCl for the NiNP-NWC. As for the kinetics of CO formation on the NiSA-NWC, the Tafel slope of 134 mV dec⁻¹ was obtained from the CO partial current but a high Tafel slope of 199 mV dec⁻¹ is observed for the NiNP-NWC catalyst. The lower Tafel slopes confirm that the CO₂ reduction to CO is much easier on the NiSA-NWC.²³ The Tafel analysis was also used to evaluate the HER kinetics at the potential of CO formation based on the LSV results of the N₂-saturated solutions in Figure 2a. This evaluation method has been reported in a previous study of HER activity.²⁴ In Figure S7, the NiSA-NWC exhibits a Tafel slope of 468 mV dec⁻¹ in 0.1M NaHCO₃ electrolytes, which is similar to the Tafel slope of HER inert Au nanoparticle in previous studies.²⁰ However, the NiNP-NWC has much lower Tafel slope of 213 mV dec⁻¹, suggesting a fast HER kinetics on NiNP-NWC. Regarding the structure-activity relationship of the nickel catalyst, higher Tafel slope of single-atom Ni catalyst indicates the suppression of the HER by dispersing the single-atom Ni on the NWC. Such observation was further confirmed by the Nyquist plots shown in Figure 2d. It can be seen

clearly that the single-atom Ni catalyst has a more substantial charge transfer resistance for the HER in accordance with the sluggish HER kinetics. Collectively, these results derive that confining the size of the Ni particles to single atoms can significantly improve the selectivity of CO₂ reduction to CO and suppression of the side reaction (HER).

Next, the nitrogen doping effects exerted on the catalytic activity and selectivity of the CO₂ reduction are evaluated. A single atom nickel catalyst without nitrogen has been prepared, and the atomic dispersion of the Ni had been confirmed by the AC-STEM shown in Figure S2c. As demonstrated in Figure 3a, the current density of NiSA-NWC increased more than 30% in CO₂-saturated solution compared to that of Ni-WC from -1.4V to the -2.0V vs. Ag/AgCl.²⁵ Additionally, the advantages of NiSA-NWC are further exemplified by nearly double of CO production rates and 50% higher CO FE than the Ni-WC shown in Figure 3b, 3c. Finally, the NiSA-NWC catalyst maintains a stable current density of 5 mA/cm² with a CO selectivity of 90% for more than 2 hours of continuous operation (Figure 3d), demonstrating an excellent electrocatalytic durability. Based on these observations, the preferential response of NiSA-NWC to CO₂ reduction could be mainly attributed to the synergistic effect of both doped N and dispersion of Ni single atoms.

In order to explore the fundamental origin leading to the high selectivity of CO₂ to CO in this single atom Ni catalysts, the chemical state of nickel and nitrogen atoms of the catalyst were firstly analyzed by the XPS. As shown in Figure 4a, the spectrum of Ni 2p_{3/2} in NiSA-NWC was singularly centered at 855.0 eV. This singular Ni peak had been attributed to the Ni¹⁺ by Yang et al.²⁶ To address the issue of low signal to noise ratio Ni2p XPS spectra of NiSA-NWC, we also have used the Electron paramagnetic resonance (EPR) spectroscopy to characterize Ni unpaired electrons in NiSA-NWC, and the result is

displayed in Figure S9. An unsplit EPR band with one g factor of 2.28 was observed, which can be assigned to the $3d^9$ electronic configuration of Ni with $S=1/2$ spin state.²⁶ The combination of the XPS and EPR result confirm that the electronic structure of the Ni in the NiSA-NWC is Ni^{1+} . In contrast, the XPS spectrum of Ni $2p_{3/2}$ in NiNP-NWC appeared two peaks at 853.5 eV and 855.9 eV which correspond to metallic Ni^0 and Ni^{2+} respectively.²⁷ A small satellite peak centered at around 862.1 eV is also found. The local environment of the nickel atoms is further studied by the analysis of XPS spectra in N_{1s} region. Compared with the N_{1s} spectrum of NWC in Figure 4b, a new peak associated with the Ni-N bond emerges at 399.3 eV in the NiSA-NWC and NiNP-NWC. Also, the N_{1s} spectra of NiSA-NWC and NiNP-NWC can be deconvoluted into pyridinic (~ 398.2 eV), Ni-N (~ 399.5 eV), and pyrrolic (~ 400.5 eV) peak.²⁸⁻²⁹ The prevalent lower electronegativity of pyridinic N binding to the Ni atoms lead to the formation of Ni^{1+} but the pyrrolic N in NiNP-NWC cause the formation of the Ni^{2+} .³⁰ Strikingly, 40% higher Ni-N contents were observed in NiSA-NWC than that in NiNP-NWC. It is rather apparent that the lower percentage of Ni-N content may result from a large component of uncoordinated metallic Ni atoms in NiNP-NWC catalyst which results in the Ni^0 . Besides, after incorporating the nickel and nitrogen atom, the structure of carbon support was characterized by the Raman spectroscopy displayed in Figure 4d. The G-band peaked at 1592 cm^{-1} is associated with the E_{2g} mode of graphite,³¹ and the D-band located at 1330 cm^{-1} is ascribed to the defect-induced mode.³² A common method to quantify the amount of defects in carbon materials is to use the integrated area ratio of D to G band intensities I_D/I_G .³¹ Larger I_D/I_G in NiNP-NWC (2.1) and NiNP-NWC (1.8) can be found than that of CNF (1.4), demonstrating a relatively low graphitization degree and a higher density of

defect sites after the nitrogen doping. The increasing defect density in carbon lattice can arise from the successful incorporation of the nitrogen atoms into the carbon lattice.³³ The accurate atomic concentration of Ni on the NiSA-NWC surface determined by the XPS survey scans are displayed in Figure 4c. Closer inspection of Figure 4c reveals there is only 0.44 at% of Ni on NiSA-NWC surface, which is only half of its concentration on the surface of NiNP-NWC. Thus, the XPS results confirm that Ni atoms in NiSA-NWC are dominated with Ni¹⁺ state on the NWC instead of the mixed state of Ni⁰ and Ni²⁺ as in the NiNP-NWC catalyst.

In this study, we found that single-atom Ni catalyst possesses the maximum CO FE of over 95% at -1.6V vs. Ag/AgCl which is about 30% higher than the standard Ni nanoparticles on the same support. Their disparities in the electronic and atomic structure of the active site usually determine their different CO₂ reduction and HER activity. In Figure 4c, XPS analysis shows that the dominance of Ni(I) sites on the surface was confined by the strong metal–nitrogen interaction. The abundance of Ni(I) is known to help the delocalization of the charge to the antibonding of the CO₂ for assisting the desorption of *CO intermediate.²⁶ This benefit can be clearly shown by the Tafel analysis of CO₂ to CO reaction process because recent studies had demonstrated that Tafel slope is an effective descriptor for the CO₂ reduction rate-determining steps.³⁴ The Tafel slope of the single-atom nickel was calculated to be 133mV dec⁻¹ which is close to the theoretical value of 118 mV dec⁻¹, suggesting that initial electron transfer to generate a surface adsorbed *COOH species is the rate-determining step for CO evolution. However, the Tafel slope of Ni nanoparticle catalyst is 199 mV dec⁻¹, which is close but lower than the 270 mV dec⁻¹, indicating that the desorption of *CO constitutes the rate-determining step of CO₂

reduction. The higher Tafel slope of Ni nanoparticle catalyst reveals that it binds too strongly to CO which indeed block CO desorption from the catalyst surface. Therefore, the metal valence can play a deceiving role in changing the rate determining steps of CO₂ reduction between single-atom Ni and Ni nanoparticle catalyst.³⁵ For the side reaction (HER), in single-atom Ni catalyst, a single H atom can only attach to the top of the isolated Ni site (shown in Figure S8a), whereas more Ni atoms on the Ni nanoparticle catalyst surface provide more bridge and hollow sites (shown in Figure S8b, 8c) between metal atoms for the adsorption of more hydrogen atoms.³⁶ Previous calculation studies have shown that adsorption of hydrogen atom prefers the bridge or hollow sites to a top site because the hydrogen intermediate is destabilized when it is adsorbed on the top site.³⁷ As a result, the adsorption of hydrogen atoms on the single-atom Ni catalyst is less favorable than the Ni nanoparticle catalysts so that the side reaction HER is successfully suppressed. In addition, low coverages of the hydrogen atoms on the single-atom Nickel catalyst provide more proportion available sites for the CO₂ reduction, thus enhancing the selectivity of CO₂ reduction. These analyses indicate that both the enhancement of CO₂ reduction and the suppression of HER on single atom Ni catalyst resulted in the higher selectivity toward CO₂ reduction to CO at the lower overpotential than the Ni nanoparticle catalyst.

4. Conclusion

In conclusion, we have successfully prepared single-atom Ni and Ni nanoparticles catalyst supported on the nitrogen-doped carbon nanofiber to study the origin of selectivity in CO₂ reduction to CO in aqueous media. We found that the CO₂ reduction to CO becomes more dominating on the single-atom Ni supported on nitrogen-doped carbon

nanofiber. It is concluded that the unique electronic structure and ensemble effects lead to a high faradaic efficiency for CO₂ reduction to CO as well as suppression of the HER on single-atom Ni nitrogen-doped carbon nanofiber. These results offer an insight into the correlation between the CO₂ reduction to CO and HER activity to the Ni catalyst structure, enabling the rational design of high-performance electrocatalysts for CO₂ reduction.

ASSOCIATED CONTENT

Supplementary material (e.g., structure characterization of NiNP catalysts, additional characterization of NiNP catalysts, modeling of catalytic sites etc.) is available in the online version of this article at

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NOTES

The authors declare no competing financial interest

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Scheme 1. Synthetic routine of the NiSA-NWC and NiNP-NWC

Figure 1. Characterization of NiSA-NWC (a) Scanning electron microscopy (SEM) image; (b) transmission electron microscopy (TEM) image; (c) EDS mapping where red, green and yellow spots correspond to the carbon, nickel, and nitrogen, respectively; (d) AC-STEM-annular dark-field (ADF) images showing the atomic dispersion of Ni in NiSA-NWC.

Figure 2. (a) The linear scan voltammetry (LSV) curves of NiSA-NWC and NiNP-NWC where the solid black and dotted purple line denoted as NiSA-NWC in CO₂ and N₂ saturated solution, respectively. The solid red and dotted blue line represent NiNP-NWC in CO₂ and N₂ saturated solution respectively; (b) Faradic efficiency of CO and H₂ at different applied potential; (c) Tafel plots of the partial CO current density for the NiSA-NWC, and NiNP-NWC at different applied potentials; (d) Nyquist plots for NiSA-NWC, and Ni-WC in N₂.

Figure 3. CO₂ reduction performance. The linear scan voltammetry (LSV) curves of: (a) NiSA-NWC, Ni-WC and NWC in N₂ and CO₂ saturated 0.1 M KHCO₃ solution; (b) CO regions of an infrared absorbance spectrum of online gas measurement when apply -1.6V vs. Ag/AgCl. The region was chosen based on the results from the ref 18; (c) Faradaic efficiency of CO for the NiSA-NWC, Ni-WC and NWC; (d) Chronoamperometry during 2 h electrolysis of CO₂ in 0.1 M KHCO₃ at -1.6V vs Ag/AgCl.

Figure 4. (a) XPS spectra for Ni 2p; (b) N 1s in NiSA-NWC, NiNP-NWC, and NWC; (c) Element content of NiSA-NW-CNF determined from the survey scan; (d) Raman spectra of NiSA-NW-CNF, NiNP-NW-CNF, and NW-CNF.

TOC Figure