Decisive Intermediates Responsible for the Carbonaceous Products of CO2 Electro-reduction on Nitrogen-Doped sp2 Nanocarbon Catalysts in NaHCO3 Aqueous Electrolyte

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Decisive intermediates responsible for the carbonaceous products of CO₂ electro-reduction on nitrogen doped sp² nanocarbon catalysts in NaHCO₃ aqueous electrolyte


Abstract: Nitrogen doped sp²-nanocarbon materials have been considered as promising catalysts for CO₂ electro-reduction. However, fundamental understanding about the product selectivity and the reaction routes is still lacking. In this report, the reaction mechanism on nitrogen doped sp²-nanocarbon materials is resolved by clarifying the authentic origin of the carbonaceous products: CO and HCO₂⁻. Two carbon-reduction pathways are identified based on a series of comparative studies using differential electrochemical mass spectrometry and in-situ CO adsorption experiments: a dominant pathway leading to CO from CO₂ and a secondary pathway leading to HCO₂⁻ from HCO₃⁻. Neither hydrocarbon (C₂H₄), nor alcohol or aldehyde (C₂H₅O) was detected in the reduction of CO₂, however CO which is generally regarded as an intermediate to be transformed into these products on metal catalysts can undoubtedly be produced and adsorbed on nitrogen doped sp²-nanocarbon catalysts during the reaction.

A promising path to reduce carbon dioxide emissions into the atmosphere is the transformation of carbon dioxide into valuable chemicals through electrochemical means, using renewable energy sources.[1-3] A landmark discovery in this area was made by Hori in 1985, who found that CO₂ can be reduced to CO, HCO₂⁻, C₂H₄ and C₂H₅O on a bulk copper electrode.[4] Later, precious metals (Ag, Au and Pd) and other non-precious transition metals (Sn, Ni and Fe) have received tremendous attention in the field and it was found that the product distribution varied over a broad range with different metals.[2,5]

Recently, nitrogen doped sp²-nanocarbon (NDSN) materials have emerged as a class of metal-free catalysts with reasonable activity for the electro-reduction of CO₂ (Table S1). The idea behind is exploring the potential of metal-free catalysis for this important reaction. Kumar and co-workers have reported direct conversion of CO₂ to CO over nitrogen doped carbon nanofibers in ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate.[6a] The same conversion was also observed separately by Ajayan et al. and Strasser et al. that CO was the dominant carbonaceous product on nitrogen doped carbon nanostructures (NCNT)[6b,c] and nitrogen doped porous carbon black[6d] in a 0.1 M KHCO₃ solution. However, HCO₂⁻ was reported as the main product instead of CO using NCNT as catalyst in 0.1 M KHCO₃ solution by Zhang et al.[6e] The reason behind such inconsistent product distribution remains unclear and solving it requires insights into the reduction mechanism.

Although a variety of C1 or C2 compounds could be produced from the electro-reduction of CO₂ on metal catalysts (as listed in Table S2), only CO and HCO₂⁻ could be obtained using NDSN materials as catalysts.[6] Theoretical computation suggested that the absence of C₂H₄ or C₂H₅O should be ascribed to the poor adsorption capability of CO on NCNT[6b,c]. However, recent theoretical calculation from Guo et al. suggested that CO adsorbed on strong bonding sites of (6, 0) NCNT could be reduced to HCHO and CH₂OH owing to its high degree of curvature.[8] Unfortunately, there lacks an experimental proof to elucidate the determining factor for the product distribution of NDSN catalysts.

Under realistic situation, however, the reaction system is not as ideal as those described in computational studies. In particular, electrolyte species are involved during the course of CO₂ reduction and their participation should not be ignored. For example, water in the electrolyte not only acts as a proton source for CO₂ reduction but also as a competing reactant for electrons during the cathode process on NDSN and metal catalysts.[2,5] The Faradaic efficiency (FE) of H₂ increased (20-90 %) with raising potentials thus the FE of carbonaceous reduction products was inhibited especially under high potentials. In addition, bicarbonate salt electrolyte has been frequently employed to increase the solubility of CO₂ in aqueous electrolyte (CO₂ has a solubility of 30 mM in pure water at standard ambient temperature and pressure) as a measure to improve the FE of the CO₂ reduction.[6-9] In such a case, the presence of relatively concentrated HCO₃⁻ species (100-500 mM), created another possible origin of the products during the cathode process. Despite that the dissolved CO₂ was generally regarded as the dominant carbon source for electro-reduction,[2,5] the possibility of the direct reduction of HCO₂⁻ species was still in dispute[10] and this matter had been commonly ignored. Previous studies have reported CH₄, C₂H₆, HCHO, CH₂OH and other carbonaceous products on Cu and Pt electrodes[10d] in a bicarbonate electrolyte in the absence of CO₂ and HCO₂⁻ could be produced from HCO₃⁻ on Pd impregnated polymer electrodes[10e] or metallic Pd electrodes.[10d] Furthermore, a recent spectroscopy study by Innocent et al. showed that HCO₂⁻...
was the only electroactive species to produce HCO$_2^-$ on Pb electrodes in HCO$_3^-/CO_2$ solution.$^{[10d]}$ It is important to unravel the decisive intermediates responsible for the carbonaceous product distribution, particularly there is only a few reports paid some attention to this aspect for NDSN catalysts.

The present work aimed to identify the possible reaction routes and mechanism governing the carbonaceous product distribution of CO$_2$ electro-reduction on NDSN catalysts in HCO$_3^-/CO_2$ solution. Onion-like carbon (OLC),$^{[11]}$ carbon nanotube (CNT) and graphene were selected as representative sp$^2$-nanocarbon materials for the investigation. Ammonia post-treatment was conducted to introduce nitrogen species into the carbon framework.$^{[12]}$ The N-doped nanocarbons were referred as NOLC, NCNT and NG, respectively. The structural details and metal residuals were provided in the supporting information. (Figures S1, S2, Tables S3 and S4). By combining differential electrochemical mass spectrometry (DEMS)$^{[13]}$ and a series of in-situ CO adsorption experiments, we are able to unravel the authentic carbon source of the formed CO and HCO$_2^-$ during CO$_2$ electro-reduction on NDSN catalysts in HCO$_3^-/CO_2$ solution.

![Figure 1](image_url)

**Figure 1.** Normalized DEMS characterization (loading gas, Ar, 1 mL min$^{-1}$) of oxidized CNT (OCNT, a) and NCNT (b) in Ar saturated NaHCO$_3$ electrolyte at 25°C. The inset was the corresponding electrochemical data (scan rate, 1 mV s$^{-1}$).

First of all, the product distribution and FE of each product were examined using potential-controlled electrolysis, which was performed in a 0.5 M NaHCO$_3$/CO$_2$ electrolyte at ambient temperature. For the investigated NDSN catalysts, CO (Figure S3a) was the major product detected by an online gas chromatography. Only a trace amount of HCO$_2^-$ with a FE in the range of 0.2-3 % was detected by $^1$H nuclear magnetic resonance (NMR) (Figures S3b and S3c). Neither hydrocarbon (C$_2$H$_2$) nor alcohol/aldehyde (C$_2$H$_4$O$_2$) was detected, even at an applied potential higher than -2.0 V vs Reversible Hydrogen Electrode (RHE). This result with CO as the major product was consistent with the previous literature, except for the result from Zhang et al.$^{[6]}$ Specially, it should be noted that the normalized activity for CO production for all the NDSN catalysts should be an integrated result of the nitrogen content, conductivity and electroactive surface area of catalysts (Figures S4 and S5).

Since the selectivity cannot be simply tuned by modulating the morphology of sp$^2$ carbon framework or the composition of nitrogen species, our attention was shifted to the intermediates derived from the reduction of possible carbon sources. It has been pointed out that the carbonaceous products could either come from the fed CO$_2$ or the HCO$_3^-$ in the electrolyte.$^{[14]}$ The authentic source of reduction products (particularly CO and HCO$_2^-$) was still unclear. Hence, we employed DEMS to in-situ quantify the gas products without supplying CO$_2$. For oxidized CNT (OCNT), after the reaction occurred at -1.1 V (1100 s), the amount of gas products (without any CO) increased until the reaction ended at -1.5 V (1500 s, Figure 1a). The delayed gas signal (which ended at about 2500 s) was due to the slow diffusion of gas products to the detector in mass spectrometer. In view of the e/2O$_2$ ratio (4, (0.93 μmol)/(0.2325 μmol)), it can be concluded that O$_2$ was the only oxidation product, which was generated from the water splitting (2H$_2$O $\rightarrow$ 4H$^+$ + 4e$^-$ + O$_2$) at the anode. The detected CO$_2$ signal indicated that the HCO$_3^-$ could decompose to CO$_2$ at a slow rate of $1.8 \times 10^4$ μmol s$^{-1}$ ((0.072 μmol)/(400 s)). Two possible reaction pathways (HCO$_3^-$ $\rightarrow$ CO$_2$ + OH$^-$; HCO$_3^-$ + H$^+$ $\rightarrow$ CO$_2$ + H$_2$O) might take place at the same time.$^{[14]}$ In addition, H$_2$ (2H$^+$ $\rightarrow$ H$_2$) was collected at the cathode. The value of the e/H$_2$ ratio (2.21, (0.93 μmol)/(0.42 μmol)) was higher than 2.0, which indicated that a part of the electrons was consumed by the reduction of carbonaceous species into products other than CO. This agreed with the well-known fact that OCNT or undoped CNT cannot promote the conversion of CO2 to CO.$^{[6]}$ The electrolyte was analyzed using $^1$H NMR after the reaction, and HCO$_2^-$ was the only detectable carbonaceous product.

In contrast to OCNT, CO was detected during the reduction with NCNT as the catalyst (Figure 1b). This indicated that the doped nitrogen could promote the reduction of CO$_2$ generated from the decomposition of HCO$_3^-$ CO$_2$. This was supported by the much higher decomposition rate of HCO$_3^-$ (4.8 $\times$ 10$^4$ μmol s$^{-1}$, (0.25+0.09 μmol)/(700 s)) vs 1.8 $\times$ 10$^4$ μmol s$^{-1}$ in NCNT) as the conversion of CO$_2$ to CO may accelerate the decomposition of HCO$_3^-$. Considering the lower ratio of e/(-H$_2$ + CO) (2.04, (1.86 μmol)/(0.09 μmol)), it was reasonable that fewer HCO$_2^-$ was produced since less electrons left after they were consumed by the reduction to H$_2$ and CO at the cathode.

In addition, the FE for CO production in NaHCO$_3$/Ar electrolyte (Figure 1b) was much lower than that in the NaHCO$_3$/CO$_2$ solution (Figure S3a), whereas the FE of HCO$_2^-$ in Ar was slightly higher (Figures 1b and S3c). This suggested that the CO$_2$ fed from outside should be the main origin of CO. The increased FE of CO should be ascribed to the abundance of the fed CO$_2$ which could not be achieved by the slow decomposition rate of HCO$_3^-$. Moreover, the increased CO$_2$ (of weak acidity) concentration can...
suppress the adsorption of HCO$_3^-$ (of weak basicity) to the NCNT (of weak basicity) and thus the FE of HCO$_3^-$ decreased. Ultimately, the carbon-reduction pathway was validated by an electrolysis experiment (Figure S6) in the H$_2$O/CO$_2$ electrolyte where the concentration of HCO$_3^-$ could be negligible and only CO was obtained without any HCO$_2^-$.

It was clear that HCO$_3^-$ could be reduced from HCO$_2^-$ in absence of CO related intermediates, and vice versa. HCO$_2^-$ could not be produced without HCO$_3^-$ while CO was generated from CO$_2$. These results suggested that HCO$_3^-$ should be the true source of HCO$_2^-$, rather than other intermediates relating to the CO generated by CO$_2$ reduction. This conclusion was consistent with the in-situ reflectance spectroscopy result in the literature. Moreover, it was more reasonable that HCO$_3^-$ did not originate from the CO related intermediates, otherwise it should also be feasible to produce other carbonaceous reduction products (C$_2$H$_4$ or C$_2$H$_2$O$_3$ besides HCO$_2^-$ by the further reduction of adsorbed CO. In fact, no other carbonaceous reduction product (C$_2$H$_4$ or C$_2$H$_2$O$_3$) was observed apart from CO and HCO$_2^-$ in this study.

In case of the electro-reduction of CO$_2$ on metal surface, it has been proposed that the product distribution of CO$_2$ reduction depends on the binding energy of CO to electrode surface. Metals that adsorb CO weakly such as Zn, Au and Ag (Table S5) could only produce CO, as CO can easily desorb from the surface before it can be further reduced to C$_2$H$_4$ or C$_2$H$_2$O$_3$. This was also supposed as the reason of why C$_2$H$_4$ or C$_2$H$_2$O$_3$ was hardly generated on NDSN catalysts (Table S5). However, recent studies showed that C$_2$H$_4$, C$_2$H$_2$O$_3$ could be produced on Zn, Au and Ag at high potentials (after -1.0 V vs RHE). Therefore, the high binding energy of CO may not be indispensable for the formation of C$_2$H$_4$ or C$_2$H$_2$O$_3$. This suggested that producing C$_2$H$_4$ or C$_2$H$_2$O$_3$ on NDSN catalysts may be possible under a specific condition in spite of their low CO adsorption capability.

A series of CO adsorption experiments were conducted to study the adsorption capability of CO which is supposed as intermediates for further reduction. Firstly, the CO pulsed adsorption experiment (Figure S7) revealed that the adsorption of CO on the surface of NDSN catalysts could be negligible without an applied electric field, which agreed well with the calculation results. However, the linear polarization test in Ar or CO$_2$ (Figure S8) suggested that CO could be adsorbed on the surface of NDSN catalysts when there was an electric field. Similar results have been reported on the metal catalysts. Clearly, the different CO adsorption behaviour was caused by the applied electric field. This led us to conduct a cyclic voltammetry (CV) experiment (Figure S9) to investigate the CO adsorption in-situ during the reaction.

As shown in Figure 2a, when the terminal potential in the negative direction was fixed at -0.1175 V vs RHE, no CO oxidation peak was found. After the potential was raised to -0.5175 V vs RHE, a weakly broad peak at about 0.67 V vs RHE was observed. With raising the terminal potential, the peak current at 0.67 V vs RHE gradually increased to reach saturation. The peak current at each terminal potential was plotted in Figure 2b. Furthermore, the CO production currents based on the total current (from CV curves in Figure 2a) and FE (Figure S3a) were also presented in Figure 2b. Two valuable conclusions could be drawn: 1) CO can be adsorbed on the surface of NCNT when there was a negatively polarized electric field; 2) with increasing overpotential, the desorption rate would accelerate which implied the low CO binding energy and finally led to a steady adsorption state. Similar results for other NDSN catalysts were shown in supporting information (Figure S10).

The equilibrium potential for the formation of C$_2$H$_4$ or C$_2$H$_2$O$_3$ usually lies in the range of 0.02 V to -0.50 V vs RHE (Table S2). However, neither C$_2$H$_4$ nor C$_2$H$_2$O$_3$ was observed when NDSN materials were used as catalysts, even if the applied potential was higher than -2.0 V vs RHE. Although a considerable amount of CO could be adsorbed on NDSN catalysts with an applied electric field, it cannot be transformed into other carbonaceous products. Thus we supposed that the activation energy was too high to further reduce the adsorbed CO. This was different from the reduction mechanism on the metals (Zn, Au and Ag) discussed above on which the barrier for the reduction of CO to C$_2$H$_4$ or C$_2$H$_2$O$_3$ could be overcome by raising the potential (higher than -1.0 V vs RHE).

Combining the above observations, we were able to draw a more explicit mechanism for the CO$_2$ electro-reduction on NDSN catalysts. The proposed reaction mechanism including two reaction routes was shown in Figure 3. CO$_2$ reduction was the dominant pathway, which proceeded via an initial rate-determining charge transfer of one electron to CO$_2$ to form CO$_2^-$; as supported by the Tafel analysis (Figure S5). CO$_2^-$ can then be reduced to CO with the participation of two protons and
another electron. As suggested by the in-situ CO adsorption experiment, the low CO binding energy could result in the release of CO, instead of further being reduced to C_{2}H_{4} or C_{2}H_{2}O_{2}. The secondary pathway was the reduction of HCO_{3} to HCO_{2}. It should be noted that the terminal proton source should be H_{2}O (Figure S11). If the CO reduction energy barrier could be overcome with a relatively low potential under which the adsorbed CO would not be completely released and the H_{2} evolution reaction should not be promoted to consume all the electrons generated at the anode, further electro-reduction of CO to form other carbonaceous products (C_{2}H_{4} or C_{2}H_{2}O_{2}) could be possible. For instance, the ionic liquid may meet this requirement. Very recently, Han et al. synthesized the nitrogen doped graphene-like materials for the CO_{2} electro-reduction catalysts.[21] They found that nitrogen doped carbon catalysts were very efficient for the electrochemical reduction of CO_{2} to C_{2}H_{4} (CH_{4}) when using ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate) as the electrolyte. This results were different from Kumar et al., where they observed that CO_{2} was converted to CO over nitrogen doped carbon nanofibers in ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate).[22] Furthermore, these results also proved that the electrolyte had a profound effect on the electrolysis process and consequently changed the product distribution of CO_{2} electro-reduction. Therefore, the study of the decisive intermediates responsible for the carbonaceous products of CO_{2} electro-reduction is of great importance for the development of CO_{2} electro-reduction.

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Keywords: nitrogen doped sp^{2}-nanocarbon • carbon dioxide electro-reduction • reaction route • reaction mechanism


Acknowledgements

Figure 3. The proposed reaction mechanism on the surface of NDSN materials (RDS: rate determining step).


The reaction mechanism on nitrogen doped sp²-nanocarbon materials is resolved by clarifying the authentic origin of the carbonaceous products: CO and HCO₃⁻. Two carbon-reduction pathways are identified: a dominant pathway leading to CO from CO₂ and a secondary pathway leading to HCO₃⁻ from HCO₃⁻. Neither hydrocarbon (CₓHᵧ), nor alcohol or aldehyde (CₓHᵧOₓ) was detected in the reduction of CO₂.

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