

Application of carbon dioxide electrocatalytic reduction to medium carbon nanomaterials

Yinge Li

School of Science, Changchun University, Changchun, China

Abstract: *The purpose of this study was to explore the application of carbon nanomaterials in the electrocatalytic reduction of carbon dioxide. The results show that the larger the specific surface area of carbon materials, the more active sites are provided, which is conducive to the reduction of carbon dioxide. In addition, the doping of nitrogen can improve the selectivity of carbon materials in the electrocatalytic reduction of carbon dioxide, and the higher the nitrogen content, the more beneficial the carbon material is to reduce carbon dioxide to methane. In addition, in a certain temperature range, the graphitized nitrogen generated by high temperature carbonization can improve the selectivity of the material to methane. These results provide important theoretical basis and experimental guidance for the application of carbon nanomaterials in carbon dioxide electrocatalytic reduction.*

Keywords: *Carbon dioxide; Electrocatalytic reduction reaction; Carbon nanomaterials; Applied research*

1. Introduction

In recent years, with the continuous growth of global energy demand and the increasingly serious environmental problems, the efficient conversion and utilization of carbon dioxide has become one of the research hotspots.^[1] Carbon dioxide electrocatalytic reduction has great potential as a sustainable energy conversion method. Carbon nanomaterials, as an important class of catalysts in carbon dioxide electrocatalytic reduction, have attracted much attention due to their unique structures and properties.^[2] Carbon nanomaterials have high specific surface area and abundant active sites, which can provide good catalytic activity and selectivity. However, the application of carbon nanomaterials in the electrocatalytic reduction of carbon dioxide is still relatively few. Therefore, it is of great significance to explore the application potential of carbon nanomaterials in the electrocatalytic reduction of carbon dioxide for the efficient conversion and utilization of carbon dioxide.^[3] The aim of this paper is to study the application of carbon nanomaterials in carbon dioxide electrocatalytic reduction, explore their catalytic performance and mechanism, and provide a new way and theoretical basis for the efficient conversion and utilization of carbon dioxide.

In recent years, electrocatalytic CO₂ reduction reactions (CO₂RR) with the goal of decarbonization have attracted great research interest as a possible route to recover CO₂ into more valuable chemicals. Yusuf Bashir Adegbemiga; Yaseen Waleed et al. review the basic concepts of kinetic evolution in CO₂RR, including thermodynamic and kinetic characteristics of reactions, and then outline operational characterization methods for studying evolution in operational environments. The dynamic evolution properties of common catalytic materials, such as atomic rearrangement and changes in chemical states, have been extensively studied, especially the relationship between these properties and electronic properties such as catalytic performance, product selectivity and durability. The potential possibilities of the CO₂ pulsed commutation electrolysis process under development are highlighted.^[4] Starting from the industrialization and commercialization of electrocatalytic CO₂ technology, Peng Rezhi, Zhang Yang et al systematically summarized the development of catalysts, the influence of electrolytes, the progress of reactors and the types of membranes. Among them, the charge transfer and surface conversion steps in electrocatalytic CO₂ technology depend on catalysts with abundant effective active sites.^[5] Shah Syed Shoaib Ahmad; Sufyan Javed Muhammad et al ignored the metal sites of metal oxide catalysts and only considered the M-O (metal-oxygen bond) active sites for discussion, outlining recent strategies used to improve the performance of CO₂RR, such as advanced morphology development and interface and vacancy defect engineering. By illustrating the key role of catalyst (M-O) structures in efficiency and stability, this review also provides some future directions for the design and development of highly efficient metal-oxido-based CO₂RR electrocatalysts.^[6] Wei Helei; Tan Aidong et

al. synthesized a Ni-doped Bi nanosheet (Ni@Bi-NS) electrocatalyst for the electrochemical reduction of CO₂ to HCOOH. Physicochemical characterization methods are widely used to study the composition and structure of materials. The electrochemical results show that the obtained HCOOH product Ni@Bi-NS has an equivalent current density of 51.12 mA cm⁻² at -1.10V, which is much higher than that of pure Bi-NS (18.00 mA cm⁻² at -1.10V). In the wide potential range of -0.80 ~ -1.10V, HCOOH has a Faraday efficiency of more than 92.0%, with a maximum efficiency of 98.4% at -0.90V in particular. Both experimental and theoretical results show that Ni doping on Bi nanosheets has good activity and selectivity. Density functional theory calculation shows that the charge is transferred from Ni atom to the adjacent Bi atom after doping, and the P-orbital electron density state moves towards Fermi level. The strong orbital hybridization formed between Bi and CO₂'s π* orbitals is conducive to the formation of *OCHO intermediates and their activation. This study provides an effective strategy for developing active and selective CO₂RR electrocatalysts by modulating electron density states. [7] Kaifan Liu, Zongjun Li et al studied the controlled synthesis of two kinds of gold nanoclusters, Au₂₄NCs and Au₂₅NCs, and studied their catalytic activity on CO₂RR. The results showed that Au₂₄NCs /C had higher catalytic activity on CO₂RR. The different CO₂RR catalytic activities of Au₂₄ NCs and Au₂₅ NCs can be attributed to their different coordination structures. Au₂₄ NCs lacks a central atom compared with Au₂₅ NCs, so its peripheral ligands may be more easily shed during electrochemical processes, resulting in more Au active sites exposed, resulting in better CO₂RR catalytic performance of Au₂₄ NCs/C than Au₂₅ NCs/C. In addition, the different structures of Au₂₄ NCs and Au₂₅ NCs affect the electron distribution and surface atomic activity of the clusters, thus affecting their catalytic activity. [8]

2. Mechanism of electrocatalytic reduction of carbon dioxide

The electrocatalytic reduction reaction of carbon dioxide is a heterogeneous catalytic reaction, which is mainly a catalytic reaction between gaseous carbon dioxide and the solid catalyst in the electrolyte at the two-phase interface. It mainly includes three simple steps similar to other electrocatalysis: (1) CO₂ molecules are adsorbed to the surface of the cathode catalyst through chemisorption; (2) The transfer of electrons breaks the C-O bond or the transfer of protons forms the C-H bond; (3) The product is formed by the rearrangement reaction and then released from the electrode surface into the electrolyte. The second reaction is the most complex of the three steps, as it involves proton coupling involving the transfer of 2, 4, 6, 8, 12, 14, and 18 electrons. As shown in Figure 1. From the perspective of energy analysis, the reduction process of CO₂ is through the proton-coupled multi-electron transfer process. However, the actual details of the response are influenced by many factors.

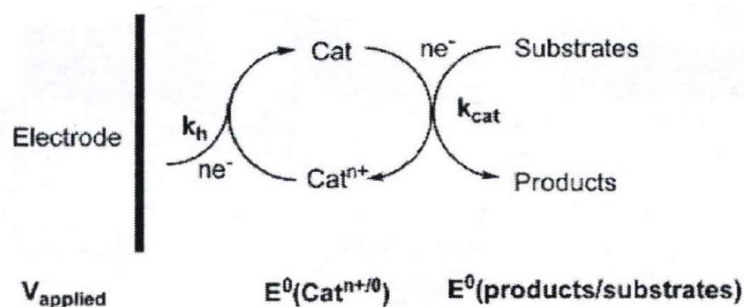


Figure 1: Steps of electrocatalytic reduction of carbon dioxide

Carbon dioxide electrocatalytic reduction reaction refers to the process of converting carbon dioxide into organic compounds using an electrocatalyst. The catalyst active site is formed on the electrode surface. This can be done by adsorbing metal catalysts or organic molecules to the electrodes. Carbon dioxide molecules are adsorbed to the catalyst active site. This is usually achieved by adsorption to oxygen atoms or vacancies on the metal surface. Adsorbed carbon dioxide molecules are activated, making them more likely to react. This can be done by providing electrons or protons. For example, a metal catalyst can supply electrons, while protons can be supplied through acidic conditions in a solution. The activated carbon dioxide molecules react with electrons and protons to form organic compounds. This step usually involves the formation and transformation of multiple intermediates, and the specific reaction path depends on the nature of the catalyst and reaction conditions. The resulting organic compounds are dissociated from the catalyst active site and released into the solution.

It should be noted that the mechanism of the carbon dioxide electrocatalytic reduction reaction can vary depending on the catalyst. In addition, the specific mechanism of this reaction is still an active area of research, and scientists are constantly exploring new catalysts and reaction paths to improve reaction efficiency and selectivity.

3. Application effect analysis of fluorine-nitrogen double-doped carbon nanomaterials in electrocatalytic reduction of carbon dioxide

1) Material synthesis

In the glove box, p-phenylphthalonitrile and zinc chloride were added to the quartz ampere tube according to the molar ratio of 1:5, mixed evenly, sealed, and vacuum sealed with a multi-station vacuum pipe sealing device. Subsequently, the sealed vacuum quartz ampoule is placed in the tube furnace and the temperature is raised from 30°C at a heating rate of 5°C/min: Rise to 400°C, continue for 20 hours at 400°C, when the temperature drops to 3 (TC), take out the quartz tube from the tube furnace, use a glass cutter, cut the quartz tube, take out the sample, rinse the sample with 5% dilute hydrochloric acid, rinse and filter it, and then rinse and filter it with N, N dimethylformamide (DMF). Finally, rinse with deionized water and filter until the washing solution is neutral. The samples were dried in a vacuum drying oven at 8 (TC) for 24 hours. Get material DCB. The preparation of TETCB, DCBP is prepared by the precursor and zinc chloride under the same conditions. The DCB was graphitized at different temperatures of 700,800,900,1000 for 2 hours to obtain NB-700, NB-800, NB-900, NB-1000 respectively. Figure 2 shows the synthesis of nitrogen-doped carbon materials.

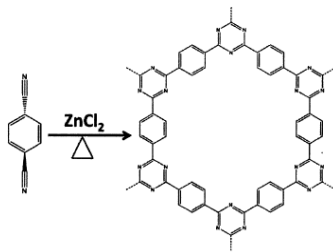


Figure 2: Schematic diagram of synthesis of carbon nanomaterials

2) Electrode preparation

5mg of DCB was added to a solution composed of 420 microliters of deionized water, 30 microliters of ethanol, and 50 microliters of nafion. Apply 100 microliters of uniform solution to 11 carbon paper and dry.

3) Electrochemical performance test

The three materials were respectively subjected to electrochemical tests under the same conditions in saturated carbon dioxide electrolyte and saturated nitrogen electrolyte. As shown in Figure 3, the curves of the three materials in saturated nitrogen gas and carbon dioxide gas differ greatly, but the three materials all showed a large electrochemical active area in saturated carbon dioxide gas.

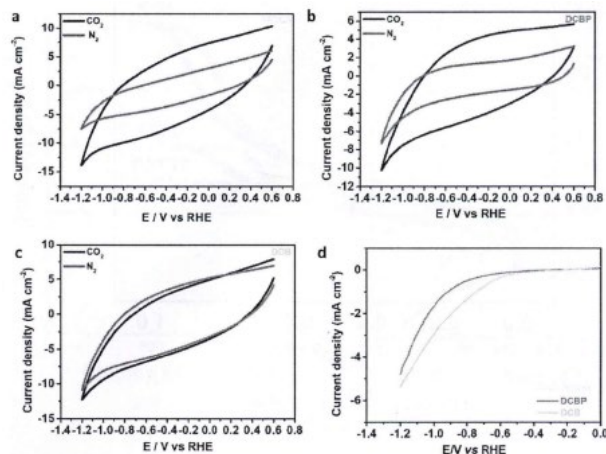


Figure 3: CV curve and LSV curve of DCB, DCBP and TETCB

It can be preliminarily judged that the three materials have certain electric reduction properties for carbon dioxide. In order to further study the electrocatalytic carbon dioxide reduction capability of the three materials, the LSV curve of the three materials in the saturated carbon dioxide electrolyte was obtained using the electrochemical workstation (FIG. 3d). It can be seen from the diagram that the absolute value of the initial potential of DCB is the smallest, and theoretically, the overpotential of DCB is the smallest. In other words, DCB has certain advantages for the electrochemical reduction of carbon dioxide. Combined with the above characterization analysis, the three materials are nitrogen-doped porous carbon materials, and through XRD powder diffraction test and XPS test, it is known that the three materials are pure carbon materials and do not contain other metal elements. In the XPS diagram of the materials, peaks appear at 398.1eV, 400.5eV, 401.2eV and 402.6eV positions. The corresponding are pyridine nitrogen, pyrrole nitrogen, graphitized nitrogen and nitrogen oxide. According to the Raman diffraction analysis pattern, the I_d/I_g value of the three materials is DCBP, but DCB has the largest specific surface area of the three materials and is a mesoporous material. In theory, the larger the specific surface area of the material, the more active sites the material is exposed to. It can be considered that in carbon materials, the specific surface area of the material has a greater impact on the electrochemical properties of the material.

4) Analysis of carbon dioxide electrocatalytic reduction products

The products of the three materials at different potentials were analyzed by gas chromatography, and the yields at different potentials were calculated according to the yields of different products, as shown in FIG. 4. The three materials in the saturated carbon dioxide electrolyte, under different potentials, the main products are carbon monoxide and methane, and there is a trace of hydrogen. At the same time, no liquid phase product was detected by nuclear magnetic resonance spectrometer. Because the reaction is carried out in a water system, HER reaction is inevitable, but the main products in the reaction are carbon monoxide and methane, indicating that the CO₂RR of the material has more competitive advantages. According to the analysis in Figure 4, the potentials with the highest Faraday efficiency of carbon monoxide of the three materials are all -0.8V(vs.RHE), and the order of the highest Faraday efficiency of carbon monoxide is DCB, DCBP and TETCB. It is worth noting that the highest Faraday efficiency of carbon monoxide in DCB can reach 74.98%. DCBP and TETCB are 47.59% and 42.39%, respectively. The highest Faraday efficiency potential of methane is -0.7V(vs.RHE), which is opposite to the highest Faraday efficiency of carbon monoxide. TETCB has the highest Faraday efficiency, reaching 42.52%, 0£8? The figures were 17.05% and 5.1% respectively. The order of carbon monoxide and methane production is consistent with the order of Faraday efficiency of the product, but the difference is large, indicating that these three materials are more likely to produce carbon monoxide under the same environmental conditions.

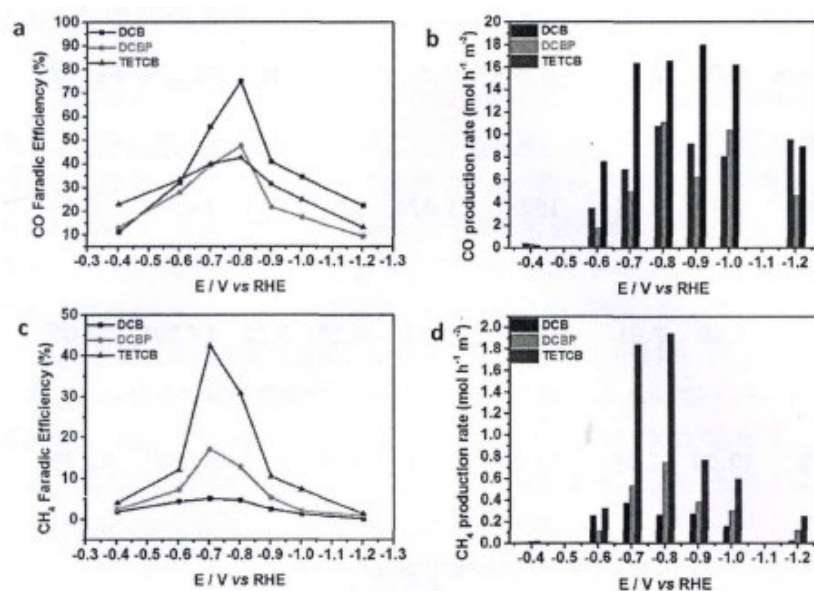


Figure 4: Faraday efficiency diagram and product yield diagram of DCB, DCBP and TETCB

The three materials are nitrogen-doped porous carbon nanomaterials, but the electrocatalytic carbon dioxide reduction performance of the three materials is significantly different. According to the characterization data of the three materials, as shown in Table 1, the nitrogen content of TETCB is

significantly higher than that of DCB and DCBP, and the specific surface area is close to that of DCB. The ID/IC value of TETCB differs little from that of DCB, but the Faraday efficiency of methane of TETCB is the highest in the process of electrocatalytic reduction of carbon dioxide, which is about 2.5 times that of DCBP and 9 times that of DCB. The Faraday efficiency of carbon monoxide in DCB is the highest, about twice that of DCBP and TETCB, and the Faraday efficiency of carbon monoxide in DCBP and TETCB is relatively close. Considering the three materials themselves, TETCB with the highest nitrogen content and higher specific surface area has the highest Faraday efficiency for methane; DCB with the largest specific surface area but lower nitrogen content has the highest Faraday efficiency for carbon monoxide; DCBP has the lowest specific surface area and nitrogen content, but DCBP has the highest ID/IC. The Faraday efficiency of carbon monoxide in DCBP is higher than that of TETCB, and that of methane is higher than that of the lowest DCB. Through the above analysis, it can be concluded that the larger the specific surface area of carbon materials, the more active sites are exposed, and the higher the total Faraday efficiency in the electrocatalytic carbon dioxide reduction process; The higher the nitrogen doping content in the carbon material with higher specific surface area, the better the material can reduce carbon dioxide to methane in the process of electrocatalytic reduction of carbon dioxide.

Table 1: Nitrogen content and types of DCB, DCBP, TETCB, BET, Faraday efficiency analysis table of products

Electrodes	DCB	DCBP	TETCB
$N_T/\%$	9.02	8.00	12.05
$N_S/\%$	9.46	7.52	12.57
S_{BET}/m^2g^{-1}	1824	1209	1716
I_D/I_G	1.075	1.108	1.062
N_i	0.83	0.21	4.04
N_{ii}	7.22	7.23	7.12
$FE_{CO}/\%$	74.99	47.58	42.43
$FE_{CH_4}/\%$	5.2	17.06	42.38

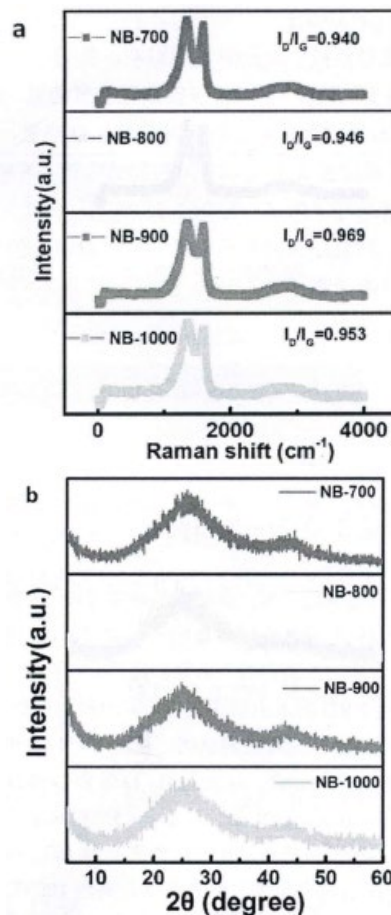


Figure 5: (a) XRD analysis diagram and (b) confocal Raman diffraction diagram

According to the above research on the electrocatalytic carbon dioxide performance of the three materials, it is found that the specific surface area and the doping amount of nitrogen have a great impact on the carbon dioxide reduction products. Interestingly, after further carbonization of the materials at high temperature, the performance of the materials in the electrocatalytic carbon dioxide has been significantly improved. In order to further study the influence of high-temperature carbonization on the material, the material was first characterized by XRD powder diffraction and Raman diffraction, as shown in Figure 5. Figure a shows the Raman diffraction performance characterization test diagram of the material. It can be seen from the figure that the peaks of the D and G bands are at 1400 and 1600 cm^{-1} respectively. The D band and G band are related to the sp^2 hybridization of carbon and the crystallinity of graphitic carbon in the material, respectively, and ID/IO indicates the structural defect of the material. After analysis, it can be seen that the crystallinity of the materials after high temperature carbonization is obviously improved, and the characterization value is decreased by IO / IG. However, with the increase of temperature, the ID/IG of the material increases, but when the temperature rises to 100 °C, the IO/Ia of the material begins to decline. The results show that high temperature is conducive to the generation of defects in the material within a certain temperature range. The XRD powder diffraction pattern of the material after carbonization is consistent with that before carbonization.

4. Conclusion

In this study, the application of carbon nanomaterials in carbon dioxide electrocatalytic reduction was studied, and the following conclusions were drawn. First, the larger the specific surface area of the carbon material, the more active sites can be provided, which is more conducive to the reduction reaction of carbon dioxide. Secondly, the doping of nitrogen can improve the selectivity of carbon materials in the electrocatalytic reduction of carbon dioxide. The higher the nitrogen content, the more favorable the carbon materials are to reduce carbon dioxide to methane. Finally, in a certain temperature range, the graphitized nitrogen produced by high temperature carbonization can improve the selectivity of the material to methane. These results provide important theoretical basis and experimental guidance for the application of carbon nanomaterials in carbon dioxide electrocatalytic reduction, and are expected to provide a new way for the efficient conversion and utilization of carbon dioxide.

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