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- Authors: Chunjun Chen, Xupeng Yan, Shoujie Liu, Yahui Wu, Qiang Wan, Xiaofu Sun, Qinggong Zhu, Huizhen Liu, Jun Ma, Lirong Zheng, Haihong Wu, and Buxing Han

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Highly Efficient Electroreduction of CO₂ to C2+ Alcohols on Heterogeneous Dual Active Sites

Chunjun Chen,^[a,b] Xupeng Yan,^[a,b] Shoujie Liu,^[c] Yahui Wu,^[a,b] Qiang Wan,^[a,b] Xiaofu Sun,^[a,b] Qinggong Zhu,^[a] Huizhen Liu, ^[a,b] Jun Ma, ^[a] Lirong Zheng,^[f] Haihong Wu, ^[e] and Buxing Han,^{[a,b,d,e]*}

Abstract: Electroreduction of CO2 to liquid fuels such as ethanol and n-propanol, powered by renewable electricity, offers a promising strategy for controlling the global carbon balance and addressing the need for the storage of intermittent renewable energy. In this work, we discovered that the composite composed of nitrogen-doped graphene quantum dots (NGQ) on CuO-derived Cu nanorods (NGQ/Cu-nr) was outstanding electrocatalyst for CO2 reduction to ethanol and npropanol. The Faradaic efficiency (FE) of C2+ alcohols could reach 52.4% with a total current density of 282.1 mA • cm⁻². This is the highest FE for C2+ alcohol with commercial current density to date. Control experiments and density functional theory (DFT) studies demonstrated that the NGQ/Cu-nr could provide dual catalytic active sites, and could stabilize the CH₂CHO intermediate to enhance the FE of alcohols significantly through further carbon protonation. The NGQ and Cu-nr had excellent synergistic effect for accelerating the CO₂ reduction reaction to alcohols.

Electrochemical CO₂ reduction reaction (CO₂RR) has attracted increasing attention, which can not only reduce the CO₂ concentration in the environment, but also can facilitate the storage of renewable energy at large scale.^[1-5] In recent years, various valuable products have been obtained, and the C2+ products are more attractive due to their high energy densities and high economic value per unit mass.^[6-10] Among the various C2+ products, alcohols (e.g. ethanol and n-propanol) are highly desirable, which can be either used directly as a fuel or blended

[a]	Dr. C. Chen, X. Yan, Y. Wu, Q. Wan, Prof. Dr. X. Sun, Dr Q. Zhu,
	Prof. Dr. H. Liu, Dr. J. Ma, Prof. Dr. B. Han
	Beijing National Laboratory for Molecular Sciences, CAS Key
	Laboratory of Colloid and Interface and Thermodynamics, CAS
	Research/Education Center for Excellence in Molecular Sciences,
	Institute of Chemistry, Chinese Academy of Sciences
	Beijing 100190, China
	E-mail: hanbx@iccas.ac.cn
[b]	Dr. C. Chen, X. Yan, Y. Wu, Q. Wan, Prof. Dr. X. Sun, Prof. Dr. H.
	Liu, Prof. Dr. B. Han
	School of Chemistry and Chemical Engineering, University of
	Chinese Academy of Sciences
	Beijing 100049, China
[c]	Dr. S. Liu
	Chemistry and Chemical Engineering of Guangdong Laboratory,
	Shantou 515063, China.
[d]	Prof. Dr. B. X. Han
	Physical Science Laboratory, Huairou National Comprehensive
	Science Center, No. 5 Yangi East Second Street, Beijing 101400,
	China
[e]	Prof. Dr. B. Han, Prof. Dr. H. Wu
	Shanghai Key Laboratory of Green Chemistry and Chemical
	Processes, School of Chemistry and Molecular Engineering, East
	China Normal University, Shanghai 200062, China
[f]	Dr. L. Zheng
	Institute of High Energy Physics, Chinese Academy of Sciences,
	Beijing 100049, China.
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with gasoline to give an overall cleaner-burning fuel.^[11-12] However, the selectivity for C2+ alcohols was too low at high current density,^[13-15] and designing of highly efficient and robust electrocatalysts is crucial to solve the problem.

The Cu-based catalysts are the most promising electrocatalysts for converting CO₂ to C2+ products.^[16-19] However, the most Cu-based catalysts generally favor the production of ethylene during CO₂RR.^[20-23] In order to improve the selectivity of C2+ alcohols, different methods have been applied to modify the Cu-based catalysts, including modifying morphology,^[24] using two metals,^[25] doping heteroatom,^[26] and modifying with other molecules.^[27] These methods mainly increase the production of the key C1 intermediate (CO) by another component to further enhance the production of alcohols, due to the selectivity of C2+ products can be tuned by the coverage of CO.^[28] In spite of these impressive efforts, the Faradaic efficiency (FE) of C2+ alcohols remains below 43% at commercial current density ($\geq 100 \text{ mA} \cdot \text{cm}^{-2}$). Moreover, it is unclear how the electrocatalytic performance of Cu is influenced by another component, mainly because microstructural features such as interfaces and defects influence CO2RR and are difficult to control.

It is known that the ethylene and ethanol usually share a penultimate reaction intermediate: *C₂H₃O. Thus, it is crucial to modify the catalyst structure to stabilize and hydrogenate this intermediate to promote alcohol production.[29] Nitrogen (N)doped nanostructured carbon materials are of interest in catalyzing CO₂ reduction into CO and C2 products (especially for ethanol).^[30, 31] For example, the N-doped mesoporous carbon could efficiently catalyze electroreduction CO₂ to ethanol with very high FE of 77%, but the reaction rate was very slow with current density of less than 1 mA•cm^{-2.[31]} The density functional theory (DFT) calculations demonstrated that N-doped carbon catalysts could enhance the adsorption of oxygen-containing reaction intermediates (*OCHx, *OH and *O) during the CO2RR due to its high oxophilicity, which prefer to the generation of deep reduction products.^[32] Furthermore, the FE of ethanol reached up to 63% over the composite composed of Cu nanoparticles on N-doped carbon nanospike film, although the current density was less than 2 mA•cm⁻².^[33] Thus, we can assume that the N-doped carbon species may be effective active sites for modifying the Cu-based catalysts to improve the selectivity of alcohols.

Herein, we used N-doped graphene quantum dot (NGQ) as the second component to modify CuO-derived Cu nanorod (Cunr), due to its high electroactivity, excellent chemical stability and, very importantly, its high oxophilicity. As a result of this strategy, outstanding efficiency of CO₂ to C2+ alcohols was achieved with a FE of 52.4% at a current density of 282.1 mA • cm⁻². Experimental and DFT studies indicate that the dual active sites and the oxophilicity of the NGQ/Cu-nr played a key role for highly efficient C2+ alcohols production.

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The NGQ/CuO-nr was first prepared blending NGQ and CuO nanorod (CuO-nr), and the NGQ/Cu-nr was then formed in-situ by electroreduction of the CuO-nr in the NGQ/CuO-nr. The CuO-nr was obtained from $Cu(OH)_2$ nanorod by calcination under N_2 atmosphere, and the NGQ was synthesized through in-situ N doping of graphene oxide in the dimethylformamide (DMF) solvent.^[30] The obtained CuO-nr had a diameter about 40 nm (Figure S1). The NGQ had a narrow lateral size distribution of 2-5 nm (Figure S2). The NGQ/CuO-nr hybrid was prepared by blending NGQ and CuO-nr in DMF with the assistance of sonication (see Methods for experimental details). Scanning electron microscope (SEM) and transmission electron microscopy (TEM) revealed that the NGQ/CuO-nr also exhibited the nanorod morphology (Figure 1A, 1B), which was similar to the original CuO-nr. High-resolution transmission electron microscopy (HR-TEM) suggests direct interfacial contact between NGQ and CuOnr (Figure 1C), and the corresponding lattice distance of NGQ and CuO were observed in the HR-TEM image. The energy dispersive X-ray spectroscopy maps show that the elements of Cu and N uniformly dispersed over the catalyst (Figure 1D, 1E and 1F), which confirm that the NGQ was successfully dispersed on the CuO-nr.



Figure 1. (A) The SEM image of the NGQ/CuO-nr. (B) The TEM image of the NGQ/CuO-nr. (C) HR-TEM image of the NGQ/CuO-nr. (D, E and F) The energy dispersive X-ray spectroscopy (EDS) maps of the NGQ/CuO-nr. (G) XPS spectra of N1s orbits of the NGQ/CuO-nr. (H) The XRD patterns of different catalysts. (I) The Raman spectra of different catalysts.

X-ray photoelectron spectroscopy (XPS) was employed to study the chemical states and composition of the catalysts. The N 1s spectra of NGQ was fitted with three components, including pyridinic N (398.8 eV), pyrrolic N (399.9 eV) and graphitic N (401.1 eV),^[34, 35] and the content of N in the NGQ was about 5.2 mol%, in which the amounts of pyridinic N, pyridonic N, and graphitic N in the NGQ were 63%, 12%, and 25% (Figure S2E). For the NGQ/CuO-nr, the content pyridinic N decreased to 41% and pyridonic N increased to 26% (Figure 1G), due to the interaction between the NGQ and CuO. According to previous literature, most of the pyridinic N would locate at the edge sites in NGQ, due to the lower formation energy of N doping at the edge sites than the basal planes.^[36, 37] The Cu valence state in the NGQ/CuO-nr was similar to that in the CuO-nr (Figure S3). Besides, XRD was also used to characterize the NGQ/CuO-nr

(Figure 1H). It is noted that the NGQ vibrational features were not observed for the NGQ/CuO-nr, which confirms that the small NGQ was uniformly dispersed on the CuO-nr. Raman spectroscopy was further used to characterize the NGQ/CuO-nr hybrid (Figure 1I). Signature vibrational peaks of NGQ can be discerned in the spectrum, which indicates that the NGQ/CuO-nr hybrid was successfully prepared.

Due to the electronic structure of Cu can influence the CO₂ reduction, we carried out operando X-ray adsorption spectroscopy (XAS) to monitor the local structure of Cu during CO₂RR. For both the NGQ/CuO-nr and CuO-nr, only peaks corresponding to metallic Cu were observed once a negative potential had been applied during CO₂RR (Figure 2 and Figure S4-S5), indicating that the CuO was rapidly reduced to metallic Cu. Thus, NGQ/Cu-nr or Cu-nr was the catalyst in the reaction. We also characterized NGQ/Cu-nr after 100 h electrolysis by SEM, TEM and EDS (Figure S6). No obvious change in morphology and structure was observed, showing the excellent stability of NGQ/Cu-nr in the reaction. Moreover, we used the ARTEMIS programs of IFEFFIT to fit the Cu-Cu coordination number of the NGQ/Cu-nr and Cu-nr during CO₂RR (Figure S7-S8 and Table S1). No obvious difference of Cu-Cu coordination number and bond distance was observed for the NGQ/Cu-nr and Cu-nr throughout CO₂RR process. These results indicate that the NGQ did not change the coordination property of Cu during CO₂RR.

The electrocatalytic activity and selectivity of catalysts towards CO_2 reduction were evaluated in a flow cell (Figure S9) employing 1 M aqueous KOH as an electrolyte. The polytetrafluoroethylene (PTFE) membrane with average pore size of 220 nm was used as the gas diffusion electrode (Figure S10).^[1] The gaseous and liquid products were analyzed by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy (Figure S11), respectively.



Figure 2. (A) XANES spectra at the Cu K-edge for NGQ/Cu-nr at different potentials during CO₂RR. (B) The corresponding Fourier transforms $FT(k^3w(k))$ for NGQ/Cu-nr at different potentials during CO₂RR.

It can be clearly observed that NGQ/Cu-nr obtained outstanding efficiency for CO₂ reduction to C2+ products (Figure 3A). The FE of C2+ products (FE_{C2+}) could reach up to 80.4% with a current density of 282.1 mA•cm⁻² at -0.9 V vs RHE. Especially, the FE of C2+ alcohols could reach 52.4%, which is significantly higher than that of ethylene. The FE_{C2+} for the Cu-nr was 64.6%, and the FE of C2+ alcohols was only 28.1% at -0.9 V vs. RHE

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(Figure 3B). The partial current density (current density times FE) of C2+ alcohols over NGQ/OD-Cu-nr could reach 147.8 mA•cm⁻² at -0.9 V vs. RHE, which is about 2 times that of over Cu-nr (Figure S12). The FEs of all products generated in the reaction are given in Figure S13, and the total FE was around 100 %. Compared with the state of the art catalysts, the FE for C2+ alcohol over NGQ/Cu-nr was the highest with commercial current density (Figure 3C and Table S2). In addition, we assembled a full cell system with NGQ/Cu-nr as the cathode catalyst for the CO₂RR and commercial IrO₂ catalyst (Figure S14) as the anode for oxygen evolution. The system delivered C2+ alcohols FE of 51.6% with a current density of 132 mA• cm⁻² at a cell voltage of 3.6 V in 1.0 M KOH, and the C2+ alcohols full-cell energy conversion efficiency (EE) was 16.4% (Figure S15). These results indicate that NGQ/Cu-nr can significantly enhance the selectivity of C2+ alcohols. In the meantime, the alcohol-to-ethylene ratio was enhanced from 0.81 on the Cu-nr to 2.18 on the NGQ/Cu-nr (Figure 3D), while overall C2+ selectivity only increased 1.2 times. It indicates that the selectivity mainly shifts from producing ethylene to alcohols. Moreover, using labelled ¹³CO₂, we further confirmed that the carbon source of products was only from CO2 (Figure S16). Furthermore, continuous CO2 reduction was performed at -0.9 V vs. RHE for 100 h to elucidate the electrode stability of the NGQ/Cu-nr. As shown in Figure 3E, there was no obvious change in both current density and FE of the products.



Figure 3. (A, B) The distribution of C2+ products at different potentials over NGQ/Cu-nr and Cu-nr. (C) Plot of C2+ alcohol partial current density versus maximum C2+ alcohol FE for various catalysts, and the source of literatures are listed in supporting information (Table S2). (D) FE of C2+ alcohols (ethanol and propanol) and ethylene on different catalysts at the potential of -0.9 V versus RHE. The five-pointed star show the corresponding FE ratio of alcohols to alkenes. (E) The current density and FE of C2+ products on NGQ/Cu-nr at -0.9 V vs. RHE with 100-hour potentiostatic electrolysis tests.

The intrinsic reason for the enhanced CO_2 conversion to alcohols was further investigated. The electrochemical active

surface areas (ECSAs) and Nyquist plots were measured (Figure S17-S18), we can observe that the ECSAs and charge transfer resistance (R_{ct}) for the NGQ/Cu-nr were similar to that of the Cu-nr, which suggested that the improved C2+ alcohols generation resulted not mainly from the slight change of the ECSAs and electronic conductivity.

Our experiment showed that the bare NGQ could produce CO and C2 products (Figure S19), and the coverage of CO on catalysts could alter the selectivity of C2+ products. In order to explore the role of the local CO concentration on the activity of the NGQ/Cu-nr and Cu-nr, CO elctroreduction reaction (CORR) in 1 M KOH was conducted in the flow cell. For the Cu-nr (Figure S20), we can observe that the FE of oxygenic products (ethanol, acetate and n-propanol) was higher than that of in CO₂RR, and the FE of C2+ alcohols can reach up to 35.1% at -0.7 V vs. RHE. However, for the NGQ/Cu-nr (Figure 4A), the FE of C2+ alcohols was 75.3% at -0.7 V vs. RHE, which is significantly higher than that of Cu-nr, and the FE of n-propanol could reach up to 27.2% at -0.7 V vs. RHE over NGQ/Cu-nr, which is one of the highest FE of C3 alcohols (Table S3). In the meantime, the alcohol-to-ethylene ratio was also compared in CORR (Figure 4B), we can observe that the NGQ/Cu-nr exhibited distinct high alcohol-to-ethylene ratio (about 9.8), which is 10.6 times than that of Cu-nr. These results indicate that the significant difference of C2+ alcohols selectivity between Cu-nr and NGQ/Cu-nr was not due to the different CO concentration. Thus, we can assume that the increasing FE of C2+ alcohols over NGQ/Cu-nr was mainly from the improved stability of the oxygenic C2 intermediates. The hypothesis can also be verified by the enhancement of n-propanol, since the n-propanol was produced by the stable oxygenic C2 intermediates and CO.^[13] Therefore, the introduced-NGQ can significantly increase the stability of oxygenic C2 intermediates.



Figure 4. (A) The distribution of C2+ products at different potentials over NGQ/Cu-nr in CORR. (B) FE of C2+ alcohols (ethanol and propanol) and ethylene on different catalysts at the potential of -0.9 V versus RHE in CORR. The five-pointed star shows the corresponding FE ratio of alcohols to alkenes.

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(C) The in-stiu Raman spectra for NGQ/Cu-nr at different potentials during $\mbox{CO}_2\mbox{RR}.$

We further investigated the role of the NGQs by varying its content in the NGQ/Cu-nr (Figure S21). The ratio of alcohols to ethylene gradually increased with the loading of NGQ on the CuOnr and reached the maximum when the content was 5 wt%. A further increase of the NGQ loading led to decreasing the selectivity of both C2+ products and alcohols, which may result from the fact that too many Cu sites were covered by the NGQs. Thus, we can conclude that the selectivity of alcohols was affected by both NGQ and Cu-nr.

To gain mechanistic insight into the cooperative effect of the NGQ and Cu-nr substrate, the in situ Raman spectroscopy was carried out to reveal the reaction intermediates during CO₂ reduction. A custom-built Raman setup was used to probe the surface of NGQ/Cu-nr and Cu-nr electrodes during CO₂ reduction at different potentials (Figure S22).

For the Cu-nr, the presence of adsorbed *CO on Cu was demonstrated by the appearance of Raman peaks located at 282-288, 364-368, and 2024-2044 cm⁻¹, which correspond to the restricted rotation of adsorbed *CO on Cu, Cu-CO stretching, and C=O stretching, respectively (Figure S23).^[38] These peaks were also observed on NGQ/Cu-nr, showing the vibration of adsorbed *CO on Cu sites (Figure 4C). There was no obvious difference in these peaks on Cu-nr and NGQ/Cu-nr, indicating that the adsorbed *CO on Cu was not influenced by the added NGQ. Combining with the results of CORR, it can be deduced that the enhancement of alcohols was not from the high local CO via spillover or tandem effects. We can observe that the signature vibrational peaks of NGQ can be discerned at every potential, indicating that the NGQ were stable on NGQ/Cu-nr during CO₂RR.

From the above results, we can propose that the high FE of C2+ alcohols over the NGQ/Cu-nr was mainly from the synergistic effect of NGQ and Cu-nr, not the high local CO via spillover or tandem effects and electronic structure of Cu. Both NGQ and Cu-nr can produce C2 products, suggesting that they both have active sites for producing C2+ products. Thus, we can assume that the NGQ/Cu-nr can provide dual active sites (NGQ and Cu) for the CO₂ reduction to C2+ products. Previous study also showed that the synergistic effect of dual active sites can promote generation of C2 products, although the selectivity of C2 products was low.^[32]

In order to further verify the hypothesis, the N-doped carbon quantum dots (NCQ) was prepared (Figure S24), the size of NCQ was similar to that of the NGQ. The NCQ could promote transformation of CO₂ to CO, and the FE was 62% at -1.3 V vs. RHE (Figure S25), but there were no C2+ products or CH₄, indicating that desorption of CO was easy and the C-C coupling cannot be occurred on the NCQs. For the NCQ/Cu-nr, the FE of C₂H₄ was higher than that of Cu-nr at high potential (Figure S26).Thus we believe that the increase of C₂H₄ over NCQ/Cu-nr is because that CO produced on NCQs transferred to the Cu surface, which further transformed into C₂H₄. However, the alcohol-to-ethylene ratio is similar to that on the Cu-nr. Therefore, the ability of C-C coupling over NGQ played a vital role for the enhancement of producing alcohols, and the NGQ and Cu showed a synergistic effect.



Figure 5. (A) Proposed reaction paths for CO₂ reduction to C₂H₅OH and C₂H₄ over NG/Cu(111). (B) Reaction Gibbs free energy diagram from the adsorbed C₂H₃O intermediate to ethylene (blue lines) and ethanol (red lines) on Cu(111). (C) Reaction Gibbs free energy diagram from the adsorbed C₂H₃O intermediate to ethylene (blue lines) and ethanol (red lines) on NG/Cu(111). (D) Reaction Gibbs free energy diagram from the adsorbed C₂H₃O intermediate to ethylene (blue lines) and ethanol (red lines) on NG/Cu(111). (D) Reaction Gibbs free energy diagram from the adsorbed C₂H₃O intermediate to ethylene (blue lines) and ethanol (red lines) on Cu(111) after applying a -0.5 V bias potential. (E) Reaction Gibbs free energy diagram from the adsorbed C₂H₃O intermediate to ethylene (blue lines) and ethanol (red lines) on NG/Cu(111) after applying a -0.5 V bias potential.

DFT calculations were then performed to gain insight into the outstanding performance of the NGQ/Cu-nr. From the results of CO_2RR of NGQ/Cu-nr, we can observe that n-propanol (C_3H_7OH) and ethanol (C_2H_5OH) follow a similar selectivity trend at the applied potentials, indicating that ethanol and n-propanol share common intermediates along their reaction pathways. Thus, we used ethanol as a proxy for the alcohols in the DFT study.

From the results of CO_2RR , it is known that the increase of C2+ alcohols was mainly from the decrease of ethylene. According to previous literature,^[29] ethylene and ethanol share a penultimate reaction intermediate: CH_2CHO intermediate (* C_2H_3O). Thus, the alteration of selectivity for C2 products was attributed mainly to the stability of intermediate on catalyst surface. As shown in Figure 5A, the adsorbed * C_2H_3O may change to ethanol through further carbon protonation, or to ethylene by leaving an oxygen atom adsorbed on the surface. Therefore, we used DFT to study the effect of surface modifications on the thermodynamics of the adsorbed CH_2CHO intermediate, and in turn on the selectivity for ethylene versus ethanol production.

The Cu(111) surface was selected as the model of Cu-nr (Figure S27), due to the main crystal plane is (111) (Figure S28). A layer of N-doped graphene (NG) was covered on the surface of Cu (111) to represent the model of the NGQ/Cu-nr. Then, the energy barriers of every step were characterized over Cu (111) and NG/Cu(111), starting with the bound $*CH_2CHO$ intermediate (Figure S29-32 and Table S4).

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For the Cu (111) surface, the formation of ${}^{*}C_{2}H_{4}O$ is endergonic, and the free energy barrier is 1.22 eV (Figure 5B). This indicates that transform of the adsorbed ${}^{*}C_{2}H_{3}O$ to ethanol through further carbon protonation is unfavourable. In contrast, the formation of $C_{2}H_{4}$ is exergonic, indicating that the C-O bond of ${}^{*}C_{2}H_{3}O$ is prone to break and leave an oxygen atom adsorbed on the Cu (111) surface. Furthermore, the Gibbs free energy diagrams were charaterized at -0.5 V applied potential (Figure 5D), which is the requirement to overcome the C-C coupling step. The ethanol pathway remains endergonic, and the ethylene pathway becomes more favorable, due to the energy barriers of ${}^{*}OH$ formation becomes lower. These results show that the ethylene is more favorable to be produced on Cu (111) surface, which is consistent with the experimental results and previous literature.^[39]

Interestingly, for the NG/Cu(111), the O atom of ${}^{*}C_{2}H_{3}O$ is preferentially attached to the NG (Figure 5A and Figure S31). This is mainly attributed to the strong oxophilicity properties of NG. Meanwhile, the formation of ${}^{*}C_{2}H_{4}O$ become exergonic, and the free energy barrier is -0.26 eV (Figure 5C), which is lower than that of the formation of $C_{2}H_{4}$ (-0.10 eV). Furthermore, the free energy barrier of the ${}^{*}C_{2}H_{4}O$ formation is still lower than that of the $C_{2}H_{4}$ formation at -0.5 V applied potential, and the desorption of $C_{2}H_{5}OH$ becomes easier (Figure 5E). These results indicated that the ethanol pathway is more favorable on NG/Cu (111) surface, which is in agreement with the experimental results.

In summary, we designed NGQ/Cu-nr catalyst for electroreduction CO₂ to C2+ alcohols. The FE of C2+ alcohols could reach up to 52.4% with a current density of 282.1 mA cm⁻². Based on the detailed study, the dual active sites mechanism was verified, which can significantly enhance CO₂ reduction to alcohols. DFT calculations suggested that the combination of the NGQ and Cu-nr can enhance the stabilization of oxygenic C2 intermediate, and the formation of ethanol is favorable on the NGQ/Cu-nr. We believe that the efficient catalyst has potential of application in CO₂ reduction to C2+ alcohols, and that design of dual active sites catalysts is a promising way for preparing other highly efficient electrocatalysts.

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Keywords: carbon dioxide • electrocatalysis • dual active sitesl • alcohols • green chemistry

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

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The electrocatalyst composed of nitrogen-doped graphene quantum dots (NGQ) on CuO-derived-Cu nanorod (NGQ/Cu-nr) is reported, which is outstanding electrocatalyst for CO₂ reduction to ethanol and npropanol. The Faradaic efficiency of C2+ alcohols could reach 52.4% with a total current density of 282.1 mA•cm⁻². Control experiments and DFT studies indicate that the NGQ/Cu-nr can provide dual active sites and stabilize the oxygenic C2 intermediates, thus resulting in a great improvement of CO2 reduction to alcohols.



Chunjun Chen, Xupeng Yan, Shoujie Liu, Yahui Wu, Qiang Wan, Xiaofu Sun, Qinggong Zhu, Huizhen Liu, Lirong Zheng, Haihong Wu, Buxing Han *

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Highly Efficient Electroreduction of CO₂ to C2+ Alcohols on Heterogeneous Dual Active Sites