



Article

Highly Selective Electrochemical CO₂ Reduction to C₂ Products on a g-C₃N₄-Supported Copper-Based Catalyst

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Abstract: Herein, a novel approach used to enhance the conversion of electrochemical CO₂ reduction (CO₂R), as well as the capacity to produce C₂ products, is reported. A copper oxide catalyst supported by graphite phase carbon nitride (CuO/g-C₃N₄) was prepared using a one-step hydrothermal method and exhibited a better performance than pure copper oxide nanosheets (CuO NSs) and spherical copper oxide particles (CuO SPs). The Faradaic efficiency reached 64.7% for all the C₂ products, specifically 37.0% for C₂H₄, with a good durability at −1.0 V vs. RHE. The results suggest that the interaction between CuO and the two-dimensional g-C₃N₄ planes promoted CO₂ adsorption, its activation and C-C coupling. This work offers a practical method that can be used to enhance the activity of electrochemical CO₂R and the selectivity of C₂ products through synergistic effects.

Keywords: electrochemical reduction of CO₂; graphite phase carbon nitride; copper oxide; C₂ products; hydrothermal preparation for advantageous electrocatalyst



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1. Introduction

According to statistics, the level of CO₂ in the air is rising, which has led to global warming [1]. Compared with other measures, the chemical transformation of CO₂ into carbon-containing chemicals is a promising option for CO₂ mitigation. Among these options, electrocatalysis is considered to have high potential because it uses clean energy generated by electrical power and reacts in an aqueous solution at room temperature and pressure under mild reducing conditions [2,3]. As a result, it is environmentally friendly and transforms CO₂ into fuels and chemical materials with significant added value [4].

Among the numerous metal catalysts, copper is the only one that has a moderate binding energy to intermediates, which can generate numerous C₁ and high-value C₂ and C₂₊ products [5,6]. Compared to copper, as a simple substance, oxide-derived copper catalysts at lower potentials exhibit a considerably enhanced CO₂ electroreduction to C₂ [7]. However, in conventional thermal conversion, it is difficult to meet the need for the increased reaction rates and selectivity of the target products at present. Although several novel synthetic strategies for copper-based catalysts have been reported, such as electrodeposition and plasma treatments [7–10], these complex synthesis methods often require the adoption of harsh reaction conditions and the use of expensive equipment, which hinder the widespread application of the related technologies. Consequently, it is necessary to create new methods that are simple and environmentally friendly for the preparation of catalysts.

Thus far, a wide range of CO₂R techniques for oxide-derived copper catalysts have been reported. Ager et al. [11] prepared oxide-derived Cu catalysts based on Cu₂O through electroreduction and obtained a selectivity of the C₂₊ products (FE = 60%) for at least 5 h at −1.0 V in 0.1 M potassium bicarbonate. Cui et al. [12] introduced N into Cu₂O to produce nitrogen-doped Cu₂O, which resulted in the enhanced CO₂ adsorption and

doubled Faradaic efficiency of ethylene (10%) compared to Cu_2O . However, despite the excellent electrocatalytic performance of copper metal in regard to CO_2 , it is still affected by its complex reduction products and poor single-product selectivity and CO_2R activity. Moreover, CO_2 is poorly soluble in water. Thus, the overpotentials related to C_2 generation reactions are high, which makes it more difficult for CO_2 to be adsorbed on the catalyst surface and renders the competing hydrogen precipitation side reactions significant [13,14]. In this regard, Luo et al. [15] proposed that high CO_2 pressure at the same concentration of the electrolyte can lead to a lower local pH, which will increase the surface coverage of CO, thus promoting the formation of C_2 products. Wang et al. [16] created a $\text{Cu}/\text{N}_x\text{C}$ (nitrogen-doped carbon) interface and found that CO_2 has a strong interaction with the $\text{Cu}/\text{N}_x\text{C}$ interface and is enriched on N_xC , which increases the selectivity of C_2 by 200–300%. Hence, there is a need to develop a novel catalyst that is more efficient and highly selective, following this line of reasoning.

Density functional theory (DFT) indicates that, for multi-carbon products, the ability of multiple $^*\text{CO}$ intermediates to engage in a C-C coupling process and influence the strength of $^*\text{CO}$ intermediate binding located in the catalytic active center are the determining factors [17]. In order to promote such an interaction, a number of enhancement studies have been undertaken, including the study of $\text{g-C}_3\text{N}_4$. It has a high thermal and chemical stability and special laminar structure, as well as a low cost, and its heterostructure provides a high CO_2 adsorption and activation efficiency [18,19]. $\text{g-C}_3\text{N}_4$ contains a large amount of pyridine N. Theoretical calculations indicate that, as the main active site for electrocatalytic reactions, pyridine N, as a substrate, can complex with the metal nanoparticles to stabilize them and also provides an active center for CO_2R . The interaction of $\text{g-C}_3\text{N}_4$ with metal also causes the metal surface to be highly electron-rich, thus enhancing the adsorption of reaction intermediates [20]. However, few experiments have been conducted to systematically verify this process. Jiao et al. [21] synthesized $\text{Cu-C}_3\text{N}_4$ to provide experimental evidence for the calculation of the $\text{g-C}_3\text{N}_4$ scaffold. In the synthesized samples, the analysis based on the N K-edge NEXAFS spectra and Cu 2p XPS confirmed the significant chemical interaction between N and Cu atoms. However, the main product of CO_2R of $\text{Cu-C}_3\text{N}_4$ was still hydrogen (>50%). This suggests that the $\text{g-C}_3\text{N}_4$ -loaded Cu-based catalysts still require further improvement. To date, there is no research that has been carried out to capitalize on the synergistic effects of $\text{g-C}_3\text{N}_4$ and copper oxide to enhance electrochemical CO_2R and its selectivity.

In this work, starting with the material structure of electrocatalysts, $\text{CuO}/\text{g-C}_3\text{N}_4$ was prepared based on copper oxide catalysts using $\text{g-C}_3\text{N}_4$ as a carrier by a straightforward hydrothermal method combined with calcination. The morphology and components were analyzed, and the electrochemical performance and catalytic activity were investigated by drop coating the catalysts on carbon paper. During the discussion, the control experiments were performed using CuO NSs and CuO SPs, and the reasons for the efficient catalytic reduction to C_2 products by the $\text{CuO}/\text{g-C}_3\text{N}_4$ electrode were comprehensively analyzed.

2. Results and Discussion

2.1. Electrochemical Activity Tests

LSV curves of the CuO SP, CuO NS and $\text{CuO}/\text{g-C}_3\text{N}_4$ catalysts in Ar- and CO_2 -saturated 0.1 M KHCO_3 solution are displayed in Figure 1a. In the CO_2 -saturated electrolyte, clearly, all of the investigated catalysts showed higher current densities compared to those in the Ar-saturated electrolyte, demonstrating their great inherent activity for electrochemical CO_2R . Under the same solution conditions, $\text{CuO}/\text{g-C}_3\text{N}_4$ also exhibited a smaller onset potential than the CuO NSs and CuO SPs. Additionally, $\text{CuO}/\text{g-C}_3\text{N}_4$ exhibited a noticeably improved current density from onset potential to -1.3 V vs. RHE relative to the other two CuO catalysts, thus implying its higher CO_2R performance. Tafel curves for the overpotential-log (C_2 current density) are plotted in Figure 1b. Compared with the CuO NSs and CuO SPs ($27.8 \text{ mV}\cdot\text{dec}^{-1}$ and $33.6 \text{ mV}\cdot\text{dec}^{-1}$), the slope of $\text{CuO}/\text{g-C}_3\text{N}_4$ exhibits a significant decrease ($17.2 \text{ mV}\cdot\text{dec}^{-1}$), which provides the further evidence

of the better intrinsic properties of the CuO/g-C₃N₄ surface. The advantageous current density is also attributed to the lower charge transfer resistance of CuO/g-C₃N₄, reflecting the improved charge transfer process at the interface of the electrode and surrounding electrolyte, according to the EIS measurements and the fitting results in Figure S1 and Table S1.

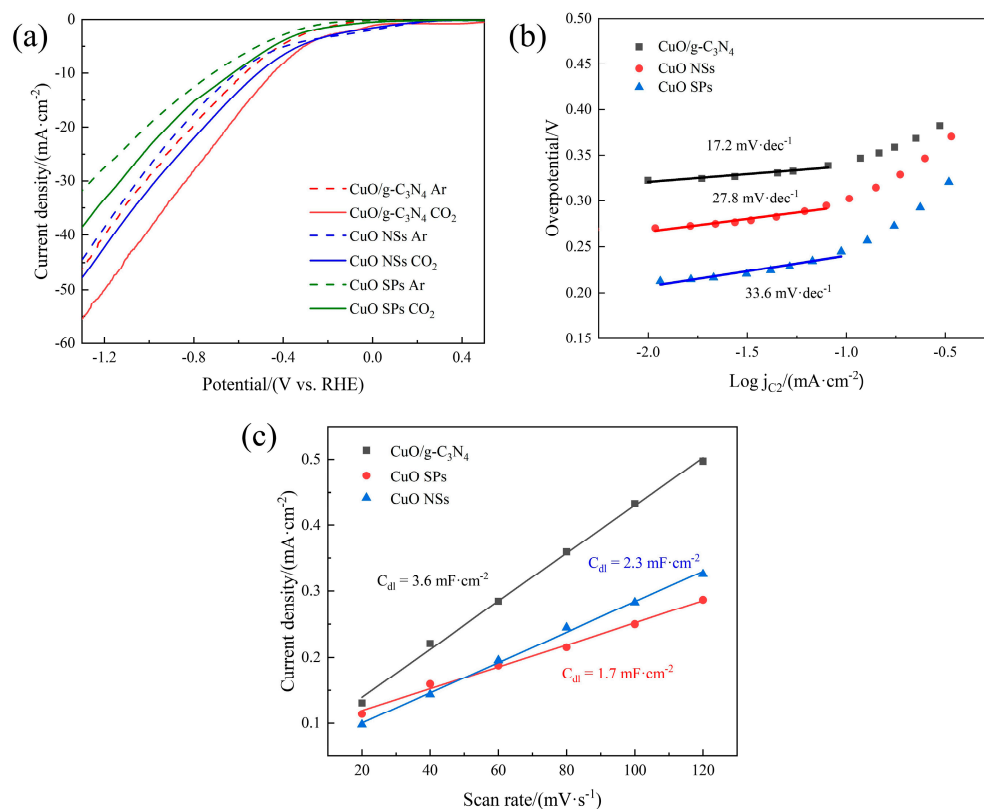


Figure 1. (a) LSV curves of CuO SPs, CuO NSs and CuO/g-C₃N₄ in Ar- and CO₂-saturated 0.1 M KHCO₃ solution, (b) Tafel slope calculation curves of CuO SPs, CuO NSs and CuO/g-C₃N₄, and (c) capacitive current at OCP as a function of the scan rate of CuO SPs, CuO NSs and CuO/g-C₃N₄ in CO₂-saturated KHCO₃ solution.

The ECSA of the CuO SP, CuO NS and CuO/g-C₃N₄ electrodes were studied by contrast with the corresponding C_{dl} (double-layer capacitance). The CVs of these three electrodes are presented in Figure S2. The slope of the non-faradaic capacitive current (current density at OCP) versus the scan rate was used to calculate the C_{dl} value. In Figure 1c, it is clear that the C_{dl} of CuO/g-C₃N₄ (3.6 mF·cm⁻²) is much higher than that of the CuO NSs (2.3 mF·cm⁻²), indicating that CuO/g-C₃N₄ has a larger electrochemical active surface area and more exposed active sites, which are advantageous for boosting the CO₂R activity. This also proves that the larger active surface area is caused by the g-C₃N₄ layer. Meanwhile, the C_{dl} of the CuO NSs is larger than that of the CuO SPs (1.7 mF·cm⁻²), suggesting that the nanosheets of CuO have a larger active surface area than the spherical nanoparticles of CuO.

2.2. Electrochemical CO₂ Reduction Performance Tests

Furthermore, the CO₂RR gaseous product distributions of the CuO SPs, CuO NSs and CuO/g-C₃N₄ were comparatively studied using a potential region of −0.8~−1.2 V vs. RHE. As given in Figure 2a, the CuO SPs consistently preferred CH₄ production in all the testing potential regions, while the C₂H₄ selectivity was very low (<20%). This result indicates that regardless of the applied potentials, CuO SPs do not exhibit a particularly high C-C coupling activity. Comparatively to the CuO SPs, whose Faradaic efficiency was not higher than 5% at −0.8~−1.2 V, that of CH₄ was suppressed for the CuO NSs. At the best applied

potential of -1.0 V, the C_2H_4 production increased from 16.5% to 31.7%, and some ethane was produced as well (Figure 2b). However, in terms of the CuO/g- C_3N_4 electrocatalyst, the CH_4 and CO productions were considerably further suppressed, totaling less than 6% at the potential of -1.0 V, as Figure 2c shows, while the CuO NS catalyst had an 8.1% Faradaic efficiency of C_1 gaseous products at the same potential. Meanwhile, the C_2H_4 selectivity in CuO/g- C_3N_4 was significantly improved, whereas the H_2 production caused by the HER side reaction clearly decreased. In particular, at the potential of -1.0 V, the C_2H_4 Faradaic efficiency reached as high as 37.0%, which was accompanied with H_2 formation at 25.8%. A very small amount of HCOOH (8.8%) was also detected at this potential in the liquid products. Ethanol was reliably detected as well. At $-0.8 \sim -1.0$ V, its Faradaic efficiency varied in the small range of 27.3–28.2%. The Faradaic efficiency for C_2 was 64.7% for CuO/g- C_3N_4 at the respective optimal potential for C_2 electroproduction. In brief, the CuO/g- C_3N_4 catalyst achieves a further improvement in the selectivity of C_2 products.

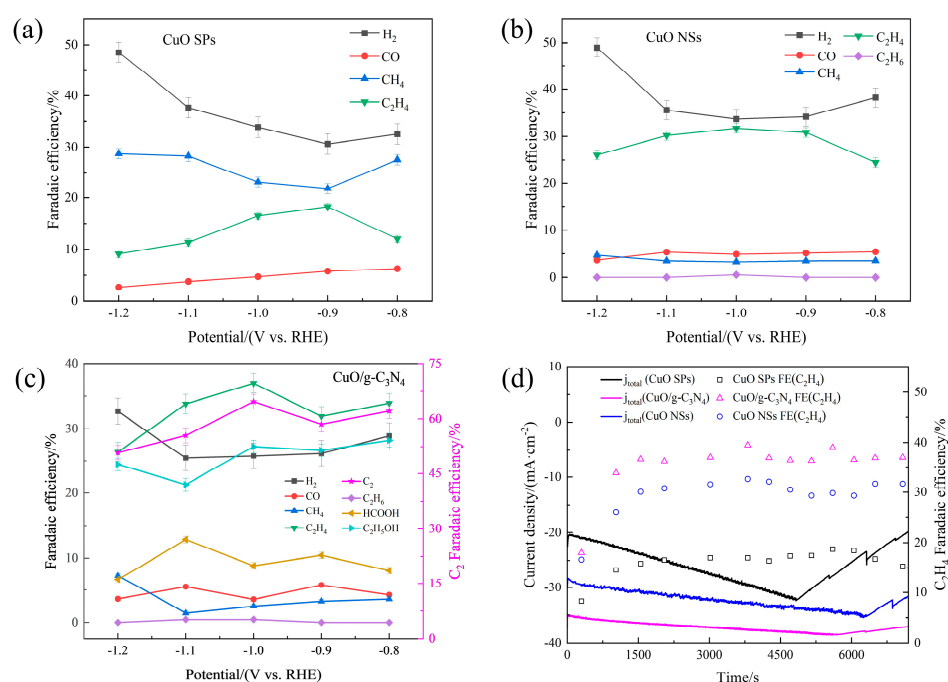


Figure 2. Faradaic efficiencies of CO_2 electroreduction products as a function of the potential: (a) CuO SPs, (b) CuO NSs and (c) CuO/g- C_3N_4 . (d) Stability tests for CuO SPs, CuO NSs and CuO/g- C_3N_4 at -1.0 V vs. RHE.

Figure S3 compares the geometric partial current densities of several products for various electrodes. At each potential, the H_2 formation rate for the electrodes follows the trend CuO/g- C_3N_4 < Cu NSs < CuO SPs, illustrating the H_2 production caused by the competing HER was well controlled on CuO/g- C_3N_4 . Meanwhile, the maximum C_2H_4 and C_2 partial current densities occurred at -1.0 V in CuO/g- C_3N_4 , reaching $14.0 \text{ mA} \cdot \text{cm}^{-2}$ and $24.5 \text{ mA} \cdot \text{cm}^{-2}$, respectively. The above results show the exceptional performance of CO_2R compared to that of the previously reported Cu-based electrocatalysts (Table S2).

CuO/g- C_3N_4 has an excellent activity and selectivity in addition to a good stability. Figure 2d shows its chronoamperometric responses after being biased for two hours at -1.0 V (corresponding to the highest C_2H_4 selectivity, especially for CuO/g- C_3N_4). The CuO/g- C_3N_4 and Cu NSs displayed an excellent stability in these two hours. In terms of CuO/g- C_3N_4 , the total cathodic current density tended to smooth out and was still maintained at $37.0 \text{ mA} \cdot \text{cm}^{-2}$ at the end of the stability test. Its corresponding C_2H_4 selectivity experienced an initial increase and was then retained at over 37.0% throughout the electroreduction. The CuO SPs catalyst, on the other hand, demonstrated a quick catalytic deactivation. The current density dropped rapidly by 40% after 5000s, and there

was also a downward trend in the Faradaic efficiency of C_2H_4 at the end, despite the fact that it experienced a spike during the previous experiment.

2.3. Structure and Morphology Characterizations

The surface characteristics of nano-adsorbents can be identified using N_2 adsorption/desorption measurements. In Figure 3, for the CuO/g- C_3N_4 material, there is a mesoporous structure, as evidenced by the large hysteresis loop from 0.47 to 1.00 of P/P_0 , which can also be proved by its pore size distribution using the BJH method. Remarkably, the adsorbed quantity of CuO/g- C_3N_4 is more than that of the CuO NSs, demonstrating that CuO/g- C_3N_4 has a more consistent pore structure and a greater surface area [22,23]. The BET surface areas of the CuO NSs and CuO/g- C_3N_4 , as obtained, are $7.62 \text{ m}^2/\text{g}$ and $11.2 \text{ m}^2/\text{g}$, respectively. Meanwhile, a higher average pore volume of $0.048 \text{ cm}^3 \cdot \text{g}^{-1}$ is observed in CuO/g- C_3N_4 (versus $0.029 \text{ cm}^3 \cdot \text{g}^{-1}$ of the CuO NSs sample). In a word, g- C_3N_4 contributes to the increase in the surface area as well as the pore volume. Thus, CO_2 can be better adsorbed, combined with the synergistic effects between CuO and g- C_3N_4 .

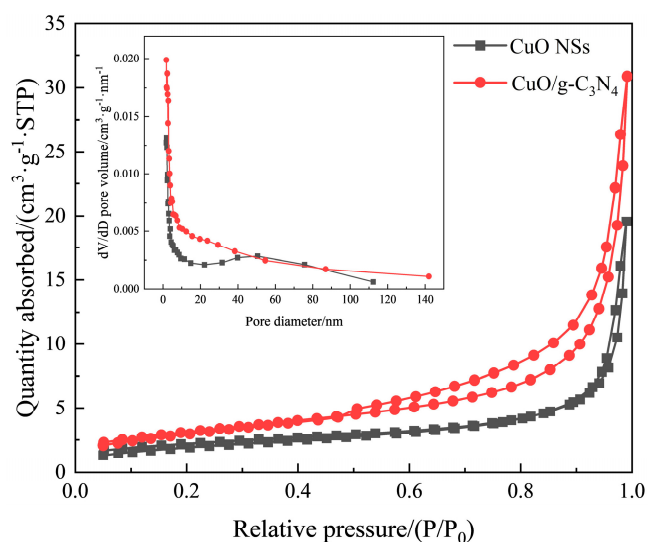


Figure 3. N_2 adsorption–desorption isotherm and BJH pore size distribution plots (insets) of CuO NSs and CuO/g- C_3N_4 .

The crystal phase of the synthesized catalysts was revealed by the XRD patterns. According to Figure 4a, the graphitic materials with two specific diffraction planes, (100) and (002), correspond to the two typical diffraction peaks of pure g- C_3N_4 at 13.08° and 27.17° , which are caused by the interlayer stacking of conjugated aromatic rings and the in-plane structure of tri-s-triazine motifs [24,25]. In terms of the CuO NSs, the main peaks at 32.50° , 35.50° , 38.73° , 38.96° and 48.73° can be attributed to the crystal facets (-110), (002), (111), (200) and (-202) of CuO (JCPDS#45-0937), some of which are also depicted in the HRTEM and SAED patterns (Figure S4). The CuO/g- C_3N_4 composite allows for the observation of both g- C_3N_4 and CuO XRD diffraction peaks, and the absence of any additional distinctive peaks indicates the high purity of the samples immediately after preparation. Meanwhile, the cluster bands between 1248 and 1631 cm^{-1} in the FTIR spectra of g- C_3N_4 (Figure 4b) can be classified as the classic stretching mode of C-N heterocycles, and the heptazine ring system is the source of the 805 cm^{-1} sharp peak. The peaks of Cu-O stretching vibrations are also very obvious. The distinctive bands seen in CuO NSs at 425 cm^{-1} correspond to the CuO Au mode, and those at the slightly higher wavenumber position of 496 cm^{-1} correspond to the CuO Bu mode [26–29]. All of them can be seen in CuO/g- C_3N_4 . This evidence prove that the two elements, g- C_3N_4 and CuO, coexist in the CuO/g- C_3N_4 material.

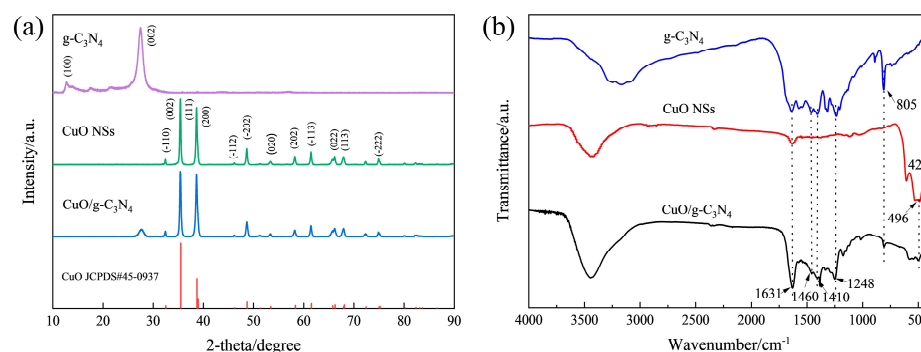


Figure 4. (a) XRD patterns of g-C₃N₄, CuO NSs and CuO/g-C₃N₄, (b) FTIR spectra of g-C₃N₄, CuO NSs and CuO/g-C₃N₄.

The elemental compositions of g-C₃N₄ and CuO/g-C₃N₄ were examined by XPS spectroscopy, and the binding energies obtained for each of them were compared. The investigated spectra in Figure 5a confirm that all the anticipated elements are present, namely N 1s and C 1s for g-C₃N₄ and O 1s, Cu 2p, N 1s and C 1s for CuO/g-C₃N₄. In Figure 5b, the Cu 2p high-resolution peak of the composite CuO/g-C₃N₄ is observed. The pattern of CuO/g-C₃N₄ presents with a pair of peaks discovered at 932.7 and 952.5 eV that are associated with two typical energy levels of copper: 2p_{3/2} and 2p_{1/2}. CuO crystals are present, according to the nearly 20 eV spin-orbit energy difference. This also indicates that the Cu in the sample is in the +II oxidation state. The small peaks at 940–945 eV are satellite peaks, which are generally seen in Cu ions in the oxidation state of +II. Furthermore, in Figure 5c, a C 1s binding energy peak is shown at 284.8 eV, which refers to g-C₃N₄ and CuO/g-C₃N₄, belonging to the C=N sp² bond and the interaction of the metal oxide with g-C₃N₄ in the mixture. Similarly, on the s-triazine ring of graphitic nitride of g-C₃N₄ and CuO/g-C₃N₄, there are sp² N-C=N bonds, which can be represented by the C 1s peaks at 288.1 and 287.9 eV. Assigned to pyridine nitrogen, pyrrolic nitrogen and graphitic nitrogen, respectively, the N 1s peak of g-C₃N₄ can be deconvoluted into three chemical states, i.e., the peaks at 398.5, 399.0 and 400.6 eV. In terms of pyridine N, the binding energy of the CuO/g-C₃N₄ sample (398.3 eV) is 0.2 eV lower than that of pure g-C₃N₄ (398.5 eV), impacting the interaction between the two molecules at the interface (Figure 5d) [30–35].

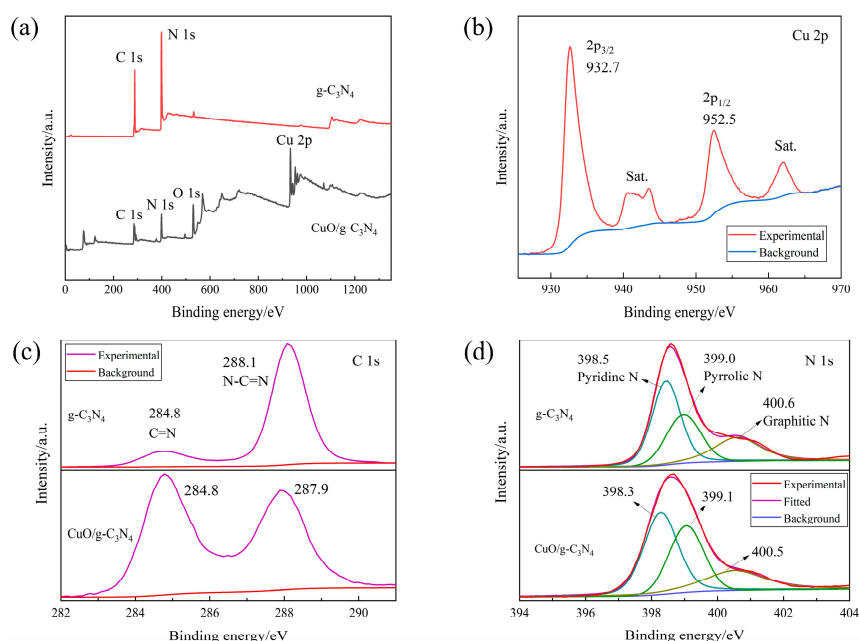


Figure 5. XPS spectra of g-C₃N₄ and CuO/g-C₃N₄: (a) full scan, (b) Cu 2p, (c) C 1s, (d) N 1s.

The morphology of g-C₃N₄, CuO and CuO/g-C₃N₄ were confirmed using FESEM (Figure 6) and TEM (Figure S5). In Figure 6a, the pure g-C₃N₄ is composed of irregular and loose aggregates of sheet-like structures. The lamellae are formed as a result of the thermal breakdown of the urea fracture while producing a large number of pores, and this rough appearance confers a very high functionalization on the g-C₃N₄ sheets. In Figure 6b, it can be seen that a large number of CuO nanosheets of varying lengths were synthesized, with an average width of about 300 nm. Figure 6c demonstrates that, in the case of the CuO/g-C₃N₄ composites, it is evident that the particles with smooth surfaces in the connected sheets of agglomerates are considered as CuO NSs loaded onto the g-C₃N₄ matrix. Meanwhile, the corresponding elemental mapping (Figure 6d–g) also shows that the C, N, O and Cu atoms are evenly distributed throughout the composite, indicating the emergence of the CuO/g-C₃N₄ structure and the close contact between them.

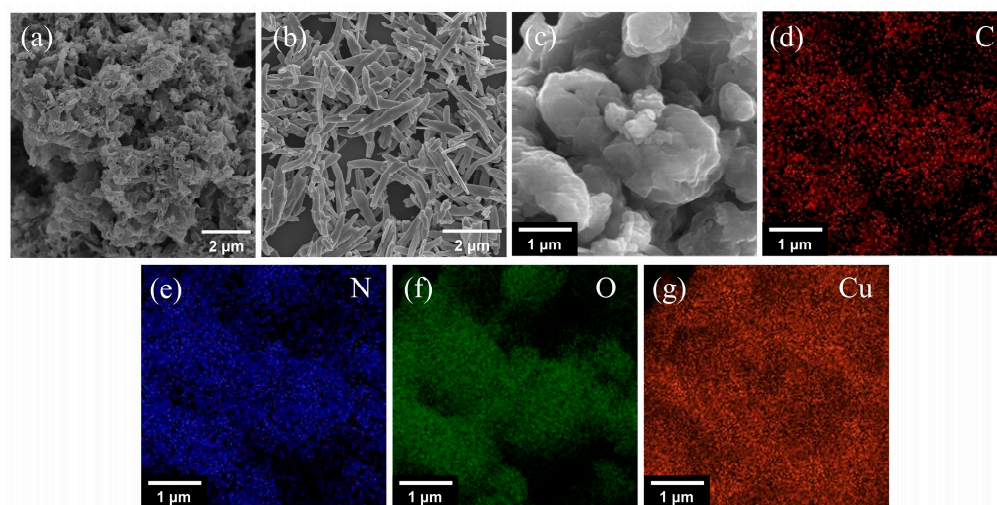


Figure 6. FESEM images of (a) g-C₃N₄, (b) CuO NSs, (c) CuO/g-C₃N₄, and (d–g) elemental mapping results of C (red), N (blue), O (green), and Cu (orange) of CuO/g-C₃N₄.

3. Materials and Methods

3.1. Materials

Urea, polyvinyl pyrrolidone K30 (PVP-K30), Cu(NO₃)₂·3H₂O, sodium acetate (C₂H₃NaO₂), NaOH, KHCO₃, isopropanol (C₃H₈O) and acetone (C₃H₆O) were purchased from Sinopharm Chemical Reagent. Sodium dodecyl sulfate (SDS), ethanol (99.7%), Nafion-117 solution (~5%) and CuO SPs (40 nm, 99.5%) were purchased from Macklin. Carbon paper (GDS180S) was purchased from Ce Tech. Each chemical was used directly as received, and UP water (>18.2 × 10⁶ Ω·cm) was employed to dispense the whole aqueous solution.

3.2. Preparation of Catalysts

3.2.1. Preparation of g-C₃N₄

A total of 20 g urea was placed into a 50 mL crucible, and after that, the prepared sample was placed in a muffle furnace, directly heated for 2 h in air conditions at 540 °C and a rate of 10 °C min^{−1}. After allowing it to naturally drop to an ambient temperature, the g-C₃N₄ sample was obtained.

3.2.2. Preparation of CuO NSs

A total of 0.238 g Cu(NO₃)₂·3H₂O, 0.173 g C₂H₃NaO₂, 0.500 g PVP-K30 and 0.295 g SDS were dissolved in 100 mL H₂O. Then, under continuous rapid stirring, 0.1 M NaOH was added dropwise until a pH > 12 was obtained. The suspension was filled in a 200 mL stainless-steel autoclave with a Teflon lining and heated for 24 h at 170 °C. The resultant sample was obtained by centrifuging the suspension, repeatedly washing it in H₂O and EtOH, and then heating it to 550 °C (5 °C min^{−1}) and holding it there for two hours in air.

3.2.3. Preparation of g-C₃N₄

The procedure was similar to that of CuO NSs, except for the fact that 0.100 g g-C₃N₄ was introduced in the first instance.

3.3. Characterization

The morphology and structure of the studied samples were characterized by field emission scanning electron microscopy (FESEM, Regulus 8100, 5 kV) and transmission electron microscopy (TEM, Tecnai G2 F20, 200 kV). Energy-dispersive X-ray spectroscopy (EDS) mapping was conducted using FESEM Regulus 8100. The atomic valence states and some molecular structures were investigated by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250), and the source gun type was Al K α . X-ray diffraction (XRD) was carried out using D8 Advance, produced by German Bruker-AXS, operating at 40 kV and 40 mA with an accuracy of 0.01° (2 θ) at room temperature. Fourier transform infrared spectrometer (FTIR) spectra were measured in the 400–4000 cm^{−1} range using a Nicolet iS50 FT-IR spectrometer, with the samples prepared as KBr pellets. Brunauer–Emmett–Teller (BET) surface area measurements were performed at 77 K using a TriStar II 3020 adsorption analyzer in the N₂ adsorption mode.

3.4. Electrochemical Measurements

The carbon paper was pre-treated with acetone and washed at least 3 times with H₂O and EtOH before being air-dried. A total of 4 mg of the sample (CuO/g-C₃N₄, CuO NSs or CuO SPs) was dispersed in 1 mL isopropanol and 30 μ L Nafion solution, followed by sonication for 30 min to create the sample ink. Then, the ink was homogeneously added drop by drop onto the carbon paper (2 $\times$ 2 cm²) and dried on a hot plate, and then it was divided into working electrodes with a surface area of 1 $\times$ 1 cm².

The electrochemical measurements were performed using an electrochemistry workstation (Gamry Reference 300) in a three-electrode system. A Nafion-117 membrane divided the two compartments of the H-cell. As the counter electrode and reference electrode, respectively, platinum grid and Ag/AgCl electrode (saturated KCl) were employed. CO₂-saturated (pH $\approx$ 6.8) or Ar-saturated 0.1 M KHCO₃ (pH $\approx$ 8.3) was used as the electrolyte. Additionally, each measurement potential was standardized to the reversible hydrogen electrode (RHE) reference scale, together with manual internal resistance compensation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197 - iR_u \quad (1)$$

The iR_u was determined by potentiostatic electrochemical impedance spectroscopy measurements under an open circuit potential (OCP) at frequencies ranging from 10⁵ Hz to 0.1 Hz. The linear sweep voltammetry (LSV) was tested in the same environment at a sweep rate of 10 mV·s^{−1}. The current density equals the testing current divided by the geometric surface area of working electrode. The double-layer capacitance method was used to conduct the electrochemical active surface area (ECSA) tests. The potential range was OCP $\pm$ 50 mV, and cyclic voltammetry was performed at different sweep speeds. Gas chromatography (Agilent GC 8890) was used to identify the resulting gas phase products, and NMR (AVANCE III HD 400 MHz) was used to detect the products in the liquid phase.

3.5. Calculation of the Faradaic Efficiency

The following equation was used to calculate the Faradaic efficiency of the gas products:

$$FE_{gas} = \frac{nCGP \times 96485}{IRT} \quad (2)$$

Above, n is the amount of e[−] that is transferred to the product formation. C is the concentration (ppm) of the gases revealed by GC. G is rate of CO₂. I is the cell current. $P = 1.01 \times 10^5$ Pa. R is the universal gas constant. $T = 273.15$ K.

The Faradaic efficiency of the liquid products was calculated by following equation:

$$FE_{liquid} = \frac{cV \cdot ne \times 6.022 \times 10^{23}}{\frac{Q}{e}} \quad (3)$$

Above, c is the concentration of the product. V is the total volume of the cathodic electrolyte and e is the electron. Q is the number of the transfer charge.

4. Conclusions

In summary, a CuO/g-C₃N₄ catalyst was fabricated by a simple hydrothermal method and achieved highly active and selective electrochemical CO₂R to C₂ products. The catalyst demonstrates a significant advantage over pure CuO nanosheets and spherical CuO particles and shows a high Faradaic efficiency of 37.0% for C₂H₄ at −1.0 V vs. RHE. It also has an ethylene catalytic stability that lasts for at least two hours. Meanwhile, the Faradaic efficiencies of all the C₂ products of the composite are 64.7%, performing better than many other Cu-based catalysts, which indicates a synergistic promotion of C-C coupling between CuO and g-C₃N₄. Moreover, the structure and morphology characterizations demonstrated that the composite is based on g-C₃N₄-supported uniform polycrystalline copper oxide. The introduction of g-C₃N₄ increases the specific surface area, which promotes the mass transfer kinetics and provides new opportunities for the adsorption of CO₂ and the exposure of active sites. Additionally, the interaction of pyridine N with copper oxide was confirmed, which further increases the reaction activity of CO₂ reduction. This work provides an effective strategy that can be used to improve the selectivity and activity of C₂ formation during the electrochemical reduction of CO₂ and bridges the gap between the laboratory-based conversion of CO₂ to economically valuable chemicals and its industrial application.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ijms232214381/s1>. Refs. [36–47] are cited.

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