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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 C₂H₂, 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

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 transfers 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$_2$O. 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$_2$R 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 Cu/N$_2$C (nitrogen-doped carbon) interface and found that CO$_2$ has a strong interaction with the Cu/N$_2$C interface and is enriched on N$_x$C, 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 *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 g-C$_3$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]. g-C$_3$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$_2$R. The interaction of g-C$_3$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 Cu-C$_3$N$_4$ to provide experimental evidence for the calculation of the g-C$_3$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$_2$R of Cu-C$_3$N$_4$ was still hydrogen (>50%). This suggests that the g-C$_3$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 g-C$_3$N$_4$ and copper oxide to enhance electrochemical CO$_2$R and its selectivity.

In this work, starting with the material structure of electrocatalysts, CuO/g-C$_3$N$_4$ was prepared based on copper oxide catalysts using g-C$_3$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 CuO/g-C$_3$N$_4$ electrode were comprehensively analyzed.

2. Results and Discussion

2.1. Electrochemical Activity Tests

LSV curves of the CuO SP, CuO NS and CuO/g-C$_3$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$_2$R. Under the same solution conditions, CuO/g-C$_3$N$_4$ also exhibited a smaller onset potential than the CuO NSs and CuO SPs. Additionally, CuO/g-C$_3$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$_2$R 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 mV·dec$^{-1}$ and 33.6 mV·dec$^{-1}$), the slope of CuO/g-C$_3$N$_4$ exhibits a significant decrease (17.2 mV·dec$^{-1}$), which provides the further evidence
of the better intrinsic properties of the CuO/g-C$_3$N$_4$ surface. The advantageous current density is also attributed to the lower charge transfer resistance of CuO/g-C$_3$N$_4$, 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.

The ECSA of the CuO SP, CuO NS and CuO/g-C$_3$N$_4$ 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-C$_3$N$_4$ (3.6 mF·cm$^{-2}$) is much higher than that of the CuO NSs (2.3 mF·cm$^{-2}$), indicating that CuO/g-C$_3$N$_4$ has a larger electrochemical active surface area and more exposed active sites, which are advantageous for boosting the CO$_2$R activity. This also proves that the larger active surface area is caused by the g-C$_3$N$_4$ 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 CO$_2$ Reduction Performance Tests

Furthermore, the CO$_2$RR gaseous product distributions of the CuO SPs, CuO NSs and CuO/g-C$_3$N$_4$ 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 CH$_4$ production in all the testing potential regions, while the C$_2$H$_4$ 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 CH$_4$ was suppressed for the CuO NSs. At the best applied
potential of \(-1.0\) V, the \(^1\text{C}_2\text{H}_4\) production increased from 16.5% to 31.7%, and some ethane was produced as well (Figure 2b). However, in terms of the \(\text{CuO}/\text{g-C}_3\text{N}_4\) electrocatalyst, the \(^1\text{CH}_4\) and CO productions were considerably further suppressed, totaling less than 6% at the potential of \(-1.0\) V, as Figure 2c shows, while the \(\text{CuO NS}\) catalyst had an 8.1% Faradaic efficiency of \(^1\text{C}_2\) gaseous products at the same potential. Meanwhile, the \(^1\text{C}_2\text{H}_4\) selectivity in \(\text{CuO}/\text{g-C}_3\text{N}_4\) was significantly improved, whereas the \(^2\text{H}_2\) production caused by the HER side reaction clearly decreased. In particular, at the potential of \(-1.0\) V, the \(^1\text{C}_2\text{H}_4\) Faradaic efficiency reached as high as 37.0%, which was accompanied with \(^2\text{H}_2\) formation at 25.8%. A very small amount of HC(OOH) (8.8%) was also detected at this potential in the liquid products. Ethanol was reliably detected as well. At \(-0.8--1.0\) V, its Faradaic efficiency varied in the small range of 27.3–28.2%. The Faradaic efficiency for \(^1\text{C}_2\) was 64.7% for \(\text{CuO}/\text{g-C}_3\text{N}_4\) at the respective optimal potential for \(^1\text{C}_2\) electroreduction. In brief, the \(\text{CuO}/\text{g-C}_3\text{N}_4\) catalyst achieves a further improvement in the selectivity of \(^1\text{C}_2\) products.

**Figure 2.** Faradaic efficiencies of \(^2\text{CO}_2\) electroreduction products as a function of the potential: (a) \(\text{CuO SPs}\), (b) \(\text{CuO NSs}\) and (c) \(\text{CuO}/\text{g-C}_3\text{N}_4\). (d) Stability tests for \(\text{CuO SPs}\), \(\text{CuO NSs}\) and \(\text{CuO}/\text{g-C}_3\text{N}_4\) at \(-1.0\) V vs. RHE.

Figure S3 compares the geometric partial current densities of several products for various electrodes. At each potential, the \(^2\text{H}_2\) formation rate for the electrodes follows the trend \(\text{CuO}/\text{g-C}_3\text{N}_4 < \text{Cu NSs} < \text{CuO SPs}\), illustrating the \(^2\text{H}_2\) production caused by the competing HER was well controlled on \(\text{CuO}/\text{g-C}_3\text{N}_4\). Meanwhile, the maximum \(^1\text{C}_2\text{H}_4\) and \(^1\text{C}_2\) partial current densities occurred at \(-1.0\) V in \(\text{CuO}/\text{g-C}_3\text{N}_4\), reaching 14.0 mA cm\(^{-2}\) and 24.5 mA cm\(^{-2}\), respectively. The above results show the exceptional performance of \(^2\text{CO}_2\)R compared to that of the previously reported Cu-based electrocatalysts (Table S2).

\(\text{CuO}/\text{g-C}_3\text{N}_4\) 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 \(^1\text{C}_2\text{H}_4\) selectivity, especially for \(\text{CuO}/\text{g-C}_3\text{N}_4\)). The \(\text{CuO}/\text{g-C}_3\text{N}_4\) and \(\text{Cu NSs}\) displayed an excellent stability in these two hours. In terms of \(\text{CuO}/\text{g-C}_3\text{N}_4\), the total cathodic current density tended to smooth out and was still maintained at 37.0 mA cm\(^{-2}\) at the end of the stability test. Its corresponding \(^1\text{C}_2\text{H}_4\) selectivity experienced an initial increase and was then retained at over 37.0% throughout the electroreduction. The \(\text{CuO SPs}\) 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$_2$H$_4$ 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$_3$N$_4$ 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$_3$N$_4$ is more than that of the CuO NSs, demonstrating that CuO/g-C$_3$N$_4$ 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$_3$N$_4$, as obtained, are 7.62 m$^2$/g and 11.2 m$^2$/g, respectively. Meanwhile, a higher average pore volume of 0.048 cm$^3$·g$^{-1}$ is observed in CuO/g-C$_3$N$_4$ (versus 0.029 cm$^3$·g$^{-1}$ of the CuO NSs sample). In a word, g-C$_3$N$_4$ 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$_3$N$_4$.

![Figure 3. N$_2$ adsorption–desorption isotherm and BJH pore size distribution plots (insets) of CuO NSs and CuO/g-C$_3$N$_4$.](image)

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$_3$N$_4$ 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$_3$N$_4$ composite allows for the observation of both g-C$_3$N$_4$ 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$_3$N$_4$ (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$_3$N$_4$. This evidence prove that the two elements, g-C$_3$N$_4$ and CuO, coexist in the CuO/g-C$_3$N$_4$ material.
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-C₃N₄ 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-C₃N₄ composite allows for the observation of both g-C₃N₄ 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-C₃N₄ (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-C₃N₄. This evidence proves that the two elements, g-C₃N₄ and CuO, coexist in the CuO/g-C₃N₄ 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: 2p₃/2 and 2p₁/2. 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-C$_3$N$_4$, CuO and CuO/g-C$_3$N$_4$ were confirmed using FESEM (Figure 6) and TEM (Figure S5). In Figure 6a, the pure g-C$_3$N$_4$ 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-C$_3$N$_4$ 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-C$_3$N$_4$ 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-C$_3$N$_4$ 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-C$_3$N$_4$ structure and the close contact between them.

![Figure 6](image)

**Figure 6.** FESEM images of (a) g-C$_3$N$_4$, (b) CuO NSs, (c) CuO/g-C$_3$N$_4$, and (d–g) elemental mapping results of C (red), N (blue), O (green), and Cu (orange) of CuO/g-C$_3$N$_4$.

### 3. Materials and Methods

#### 3.1. Materials

Urea, polyvinyl pyrrolidone K30 (PVP-K30), Cu(NO$_3$)$_2$$\cdot$3H$_2$O, sodium acetate (C$_2$H$_3$NaO$_2$), NaOH, KHCO$_3$, isopropanol (C$_3$H$_8$O) and acetone (C$_3$H$_6$O) were purchased from Sinopharm Chemical Reagent. Sodium dodecyl sulfate (SDS), ethanol (99.7%), Nafion-117 solution (~5%) and CuO SPs (40 nm, 99.5%) were purchased from Macklin. Carbon paper (GDS180S) was purchased from Ce Tech. Each chemical was used directly as received, and UP water (>18.2 × 10$^6$ Ω·cm) was employed to dispense the whole aqueous solution.

#### 3.2. Preparation of Catalysts

##### 3.2.1. Preparation of g-C$_3$N$_4$

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-C$_3$N$_4$ sample was obtained.

##### 3.2.2. Preparation of CuO NSs

A total of 0.238 g Cu(NO$_3$)$_2$$\cdot$3H$_2$O, 0.173 g C$_2$H$_3$NaO$_2$, 0.500 g PVP-K30 and 0.295 g SDS were dissolved in 100 mL H$_2$O. Then, under continuous rapid stirring, 0.1 M NaOH was added dropwise until a pH > 12 was obtained. The suspension was filled in a 200 mL stainless-steel autoclave with a Teflon lining and heated for 24 h at 170 °C. The resultant sample was obtained by centrifuging the suspension, repeatedly washing it in H$_2$O and EtOH, and then heating it to 550 °C (5 °C min$^{-1}$) and holding it there for two hours in air.
3.2.3. Preparation of g-C\textsubscript{3}N\textsubscript{4}

The procedure was similar to that of CuO NSs, except for the fact that 0.100 g g-C\textsubscript{3}N\textsubscript{4} 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\alpha. 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° (2θ) at room temperature. Fourier transform infrared spectrometer (FTIR) spectra were measured in the 400–4000 cm\textsuperscript{-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 N\textsubscript{2} adsorption mode.

3.4. Electrochemical Measurements

The carbon paper was pre-treated with acetone and washed at least 3 times with H\textsubscript{2}O and EtOH before being air-dried. A total of 4 mg of the sample (CuO/g-C\textsubscript{3}N\textsubscript{4}, CuO NSs or CuO SPs) was dispersed in 1 mL isopropanol and 30 \mu\text{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 × 2 cm\textsuperscript{2}) and dried on a hot plate, and then it was divided into working electrodes with a surface area of 1 × 1 cm\textsuperscript{2}.

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. CO\textsubscript{2}-saturated (pH ≈ 6.8) or Ar-saturated 0.1 M KHCO\textsubscript{3} (pH ≈ 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:

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

The \( iR_u \) was determined by potentiostatic electrochemical impedance spectroscopy measurements under an open circuit potential (OCP) at frequencies ranging from \( 10^5 \) Hz to 0.1 Hz. The linear sweep voltammery (LSV) was tested in the same environment at a sweep rate of 10 mV·s\textsuperscript{-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 ± 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:

\[ FE_{\text{gas}} = \frac{nCGP \times 96485}{IRT} \quad (2) \]

Above, \( n \) is the amount of e\textsuperscript{-} that is transferred to the product formation. \( C \) is the concentration (ppm) of the gases revealed by GC. \( G \) is rate of CO\textsubscript{2}. \( I \) 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:

\[
FE_{\text{liquid}} = \frac{cV \cdot ne \times 6.022 \times 10^{23}}{Q} \tag{3}
\]

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-C\(_3\)N\(_4\) catalyst was fabricated by a simple hydrothermal method and achieved highly active and selective electrochemical CO\(_2\)R to C\(_2\) 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 C\(_2\)H\(_4\) 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 C\(_2\) 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-C\(_3\)N\(_4\). Moreover, the structure and morphology characterizations demonstrated that the composite is based on g-C\(_3\)N\(_4\)-supported uniform polycrystalline copper oxide. The introduction of g-C\(_3\)N\(_4\) increases the specific surface area, which promotes the mass transfer kinetics and provides new opportunities for the adsorption of CO\(_2\) and the exposure of active sites. Additionally, the interaction of pyridine N with copper oxide was confirmed, which further increases the reaction activity of CO\(_2\) reduction. This work provides an effective strategy that can be used to improve the selectivity and activity of C\(_2\) formation during the electrochemical reduction of CO\(_2\) and bridges the gap between the laboratory-based conversion of CO\(_2\) 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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