

Article

Metal Ionic Liquid-Mediated Highly Dispersed Ru-Cu Bimetallic Nanomaterials for Electrocatalytic Urea Production

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Abstract

Traditional urea synthesis is energy-intensive and has a high carbon footprint, making the direct electrocatalytic synthesis from CO₂ and NO₃[−] under mild conditions highly attractive. However, designing efficient bimetallic catalysts that promote C–N coupling while suppressing side reactions remains a key challenge. This study reports a metal ionic liquid-mediated pyrolysis strategy for constructing carbon nanofibers embedded with highly dispersed Ru–Cu bimetallic nanoparticles (Ru/Cu@CF). A self-synthesized salicylic acid-imidazole metal ionic liquid served as a trifunctional precursor, enabling 10 nm level dispersion and stable anchoring of the metals within the carbon matrix after programmed carbonization. The resulting Ru/Cu@CF features a 3D porous fibrous structure, high surface area, abundant defects, and amorphous/highly dispersed Ru–Cu species. For electrocatalytic co-reduction of CO₂ and NO₃[−] to urea, Ru/Cu@CF achieved a high urea yield of 57.8 mmol g^{−1} h^{−1} and a Faradaic efficiency of 25.4% at a mild potential of −0.5 V vs. RHE, along with good stability. Comparative studies confirmed the crucial role of Ru–Cu synergy in enhancing activity and selectivity.

Keywords: metal ionic liquid; nanocomposite; urea synthesis; bimetallic catalyst

1. Introduction

Urea is an indispensable nitrogen source in agricultural fertilizers, playing a crucial role in promoting crop growth [1,2], and it is also a promising raw material in fuel cell systems [3,4]. Currently, urea is industrially produced via the Bosch–Meiser process involving liquid NH₃ and CO₂ [5]. As a conventional chemical process, Bosch–Meiser suffers from high energy input (150–200 °C and 100–200 atm) and high CO₂ emissions. Alternatively, it can be synthesized via the Haber–Bosch process, which, however, relies on fossil fuel resources and is considered one of the most significant contributors to CO₂ emissions. The current urea synthesis processes are plagued by high energy consumption and the utilization of valuable ammonia, falling far short of the demands for sustainable development [6]. Consequently, there have been continuous efforts to explore green and sustainable strategies for urea synthesis [7,8]. Electrochemical methods for urea synthesis



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have garnered significant attention from the scientific community due to their potential to reduce the current levels of CO₂ emissions associated with urea production [9]. Electrocatalytic urea synthesis has emerged as one of the promising alternatives to conventional urea production, enabling urea generation under milder conditions [10–12]. A particularly promising route is the electrocatalytic C–N coupling for urea synthesis, which efficiently utilizes CO₂ and NO₃[−] as reactants under mild conditions. Compared to indirect methods involving ammonia production first, the direct co-activation and coupling of carbon dioxide (CO₂) and nitrate (NO₃[−]) waste for urea synthesis plays a pivotal role in simultaneously reducing the global carbon footprint, maintaining nitrogen balance, and reforming the urea industry [13].

The co-activation of carbon and nitrogen sources, coupled with the electrocatalytic C–N coupling of in situ generated species, points the way forward for urea synthesis. However, the most formidable challenge lies in preparing highly active and stable selective catalysts that can efficiently perform C–N coupling following moderate hydrogenation of reactants while suppressing their conversion into by-products such as NH₃ and CO [14]. In recent years, researchers have extensively investigated several electrocatalytic systems designed for efficient urea production. Transition metals [15–18], bimetallic nanomaterials [19,20], metal oxides [21–23], metal-carbon-based nanocomposites [24–26], heteroatom-doped nanomaterials [27,28], single-atom catalysts [29–31], and several other materials [32,33] have all been reported in the literature for this purpose. Among the numerous catalytic systems, one strategy to optimize electrocatalyst selectivity is the use of bimetallic materials [5]. Combining two metals with distinct properties can modulate the adsorption energies for reactants and intermediates, as well as intramolecular bond energies. Furthermore, strain effects occur when one metal atom is forced into positions different from its equilibrium positions in the bulk material, leading to alterations in the surface electronic structure [34–36]. The use of bimetallic materials for urea electrosynthesis is not surprising, as the catalyst should provide optimal affinity for the intermediates required in the two parallel reactions (CO₂ and NO₃[−] electrochemical reduction), whose surface requirements differ significantly. Despite these advances, the scalable synthesis of bimetallic electrocatalysts still faces several challenges: (1) Due to the need for specialized equipment and a lack of ideal economic and environmental feasibility, current methods are difficult to apply effectively to the industrial production of bimetallic catalysts. (2) The homogeneity and stability of catalysts prepared by current methods require further improvement due to unresolved issues of structural non-uniformity. (3) Bimetallic catalysts often lack ideal conductivity and electrocatalytic performance due to large particle sizes and suboptimal elemental composition.

Ionic liquids, owing to their properties such as non-flammability, high ionic conductivity, and unique solvation capabilities, play a multifunctional role in the fabrication of metal nanomaterials [37–39]. The dual role of ionic liquids as structure-directing agents and reaction media addresses the persistent limitations in traditional composite synthesis, particularly the key challenge of achieving uniform metal dispersion within a carbon matrix. This opens up new avenues for preparing bimetallic electrocatalysts for urea production. Based on this, this study innovatively employs metal-based salicylic acid-imidazole metal ionic liquids simultaneously as trifunctional reagents—structure templates, reactive monomers, and metal precursors. Through controlled pyrolysis, a carbon nanofiber composite material with highly dispersed ruthenium–copper nanoparticles (Ru/Cu@CF) was prepared. The inherent coordination properties of the metal ionic liquids ensured exceptional dispersion stability of the Ru–Cu metal particles within the carbon matrix. The strong coordination between the ionic liquid and metal ions guaranteed uniform distribution of metal atoms at the atomic level during material preparation and in the fixed state, resulting

in the formation of Ru/Cu@CF with a homogeneous catalytic structure. The integration of carbon nanofibers with Ru-Cu bimetallic species achieved significantly improved electrocatalytic performance. The Ru/Cu@CF electrocatalyst exhibited a high urea yield of up to $57.8 \text{ mmol g}^{-1} \text{ h}^{-1}$ and a high Faradaic efficiency of 25.4%.

2. Experimental Section

2.1. Instruments and Reagents

Morphological characterization was performed using a Hitachi S-4800 (Hitachi, Japan) field emission scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM) measurement was conducted using a JEOL 2010 (Japan Electron Optics Laboratory Co., Ltd., Japan) transmission electron microscope at 200 keV. X-ray diffraction (XRD) patterns were measured using X-ray D8 (Bruker, Germany) Advance Instrument operated at 40 kV and 20 mA and using Cu K_{α} radiation source with $\lambda = 0.15406 \text{ nm}$. X-ray photoelectron spectroscopy (XPS) was conducted using a PHI 5700 ESCA spectrometer (Physical Electronics, USA) with monochromatic Al K_{α} radiation. Raman measurement was carried out by using an InVia laser micro-confocal Raman spectrometer (Renishaw, UK). Miniature pulse sensor a working current of 0.1–0.5 mA and a voltage of 1.5 V was purchased from Huakang medical technology Co., Ltd., China. Nitrogen physisorption isotherms at 77 K were obtained using a Quantachrome Autosorb iQ analyzer (Quantachrome Instruments, USA). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The wettability of the fiber membrane was characterized using a contact angle tester (OCA15EC) (Dataphysics, Germany). All chemical reagents were of analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used as received. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the metal concentration in Ru/Cu@CF.

2.2. Preparation of Ru/Cu@CF Composite

[Salicylic acid][N,N'-carbonyl diimidazole] ionic liquid was synthesized by mixing an aqueous solution of salicylic acid (60 mL, 0.1 mol L^{-1}) with N,N'-carbonyl diimidazole (60 mL, 0.1 mol L^{-1}) and stirring for 30 min. Copper(II) chloride or ruthenium(III) chloride (10 mL, 0.1 mol L^{-1}) was added and magnetically stirred at 65°C for 60 min to obtain a homogeneous solution. Subsequently, liquid–liquid extraction was performed using dichloromethane ($3 \times 50 \text{ mL}$). The organic phase was separated, concentrated by rotary evaporation, and vacuum-dried at 75°C for 12 h to obtain a viscous fluid, which was the target ruthenium-based metal ionic liquid or copper-based metal ionic liquid.

A total of 10 g of ODA (4,4'-oxydianiline) and 10 g of PMDA (pyromellitic dianhydride) were dried separately at 100°C for 30 min. Further, 8.0096 g of ODA was weighed and placed in a three-necked flask. Further, 86.5695 g of N,N-dimethylformamide (DMF) was added, and the mixture was stirred in an ice-water bath until completely dissolved. Then, 9 g of PMDA dissolved in 10 g of DMF was added slowly with stirring. After continuing to stir for 60 min, 16.3 g of DMF was added for dilution, obtaining a spinning solution with a concentration of 13 wt%. Finally, a film was prepared using the electrostatic spinning method. The electrostatic spinning conditions were: positive voltage 15 kV, negative voltage 2 kV, speed 0.06 mm/min, temperature 30°C , humidity 30%, with a distance of 10 cm maintained between the nozzle and the roller collector.

Furthermore, 3 g of the dried polymer membrane was dispersed in a mixture of 3 g of the prepared ruthenium-based and copper-based (Molar ratio 1:1) ionic liquids, 50 mL of ethanol was added, and the mixture was sonicated for 10 min, followed by vacuum drying. It was then transferred to a tube furnace. The temperature was raised to 100°C at a heating rate of 2°C/min , held for 60 min, then raised to 200°C at the same rate and held for 60 min,

then raised to 300 °C and held for 60 min, and finally raised to 800 °C at a heating rate of 5 °C/min and held for 120 min. After natural cooling, Ru/Cu@CF was obtained. Ru@CF and Cu@CF were prepared separately using methods involving only one type of metal ionic liquid. Additionally, CF was prepared following the above steps but without the addition of metal ionic liquids; all other steps were identical. Pure metallic Ru/Cu particles were acquired by completely oxidizing the carbon framework of the Ru/Cu@CF composite. Ru/Cu@CF was placed in a tubular furnace, first maintained at 500 °C for 60 min in an air atmosphere, and then reduced at 350 °C for another 60 min in a hydrogen atmosphere, ultimately yielding Ru/Cu particles.

2.3. Electrocatalytic Urea Synthesis

Electrocatalytic urea synthesis was performed on a CHI830D workstation equipped with an H-type electrolytic cell system. The H-cell system consisted of a carbon paper (1 cm × 1 cm) coated with Ru/Cu@CF as the working electrode, a standard Ag/AgCl electrode as the reference electrode, and a platinum plate (1 cm × 1 cm) as the counter electrode. A Nafion 117 membrane was used to separate the cathode and anode compartments. The working electrode was prepared as follows: 2 mg of Ru/Cu@CF was dispersed in a mixture containing 950 µL of ethanol and 50 µL of a 5 wt% Nafion solution. The resulting solution was ultrasonicated for 30 min to prepare the Ru/Cu@CF ink. Then, 20 µL of the ink was drop-cast onto the surface of the carbon paper (1 cm × 1 cm), which was then dried overnight under vacuum at 60 °C.

Electrocatalytic urea synthesis was conducted in a 0.1 M KNO₃ aqueous solution saturated with CO₂ gas at ambient temperature. During the reaction, a constant CO₂ flow rate of 30 mL min^{−1} was maintained. Potentials measured versus the Ag/AgCl reference electrode were converted to the RHE reference scale using the following formula: $E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 \text{ V} + 0.0591 \times \text{pH value}$ (pH = 6.8). To avoid interference from atmospheric O₂, the electrolyte was purged with argon gas for over 30 min prior to use. Qualitative and quantitative analyses of urea were carried out using nuclear magnetic resonance and validated using the diacetyl oxime method and high-performance liquid chromatography.

3. Results and Discussion

3.1. Synthesis of Ru/Cu@CF Composite

The immobilization and dispersion of metal nanoparticles on the polyamic acid membrane is key to preparing highly active Ru/Cu@CF. To obtain small-sized Ru/Cu nanoparticles with good dispersion, an ionic liquid-mediated synthesis route was developed. The synthesis process first involved the preparation of ruthenium-based and copper-based ionic liquids, where N,N-carbonyl diimidazole underwent ion exchange with salicylic acid to form N,N-carbonyl diimidazolium salicylate ionic liquid. Subsequently, ruthenium chloride or copper chloride coordinated with this ionic liquid to generate ruthenium-based or copper-based salicylic acid N,N-carbonyl diimidazolium metal ionic liquids. In this reaction, each copper ion forms coordination bonds with two salicylate ions, creating a stable copper-based salicylate anion, while each ruthenium ion forms coordination bonds with three salicylate ions, forming a stable ruthenium-based salicylate anion. This coordination structure prevents metal ion aggregation, ensuring the formation of small metal nanoparticles during reduction. After preparation of the ionic liquids, the affinity between the ionic liquids and the polymer membrane was utilized to achieve uniform dispersion of the ruthenium-based and copper-based salicylic acid N,N-carbonyl diimidazolium ionic liquids on the polymer membrane. This affinity and dispersion effect promoted the three-dimensional distribution of the ruthenium-based and copper-based

ionic liquids on the polymer membrane fibers, significantly enhancing the dispersion of the metal nanoparticles and their interaction with the support. The uniform distribution of Ru/Cu nanoparticles on the fibers not only increased the activity of the composite membrane but also enhanced its stability. Serving as precursors providing both carbon and metal sources, the ruthenium-based and copper-based ionic liquids also acted as structure-directing templates for uniform nanoparticle formation and as stabilizers preventing Ru/Cu atom migration. During the high-temperature reduction process, a multi-stage carbonization program was employed: holding at 100 °C, 200 °C, and 300 °C for one hour each to facilitate better imidization of the polymer, ensuring the stability of the fiber structure, while the Ru/Cu in the metal ionic liquids were preliminarily reduced, allowing Ru/Cu atoms to be stably anchored on the polymer membrane. In the final stage, rapid heating at 5 °C/min to 800 °C for carbonization generated zero-valent Ru/Cu nanoparticles embedded on conductive carbon nanofibers. Simultaneously, the high-temperature carbonization improved the material's conductivity, which is crucial for enhancing electrochemical performance. Inductively coupled plasma mass spectrometry (ICP-MS) was used for quantitative analysis of the Ru/Cu content in the Ru/Cu@CF composite. The results indicated that the total Ru/Cu content in Ru/Cu@CF was 8.35 wt.%, the total Ru content in Ru@CF was 6.92 wt.% and the total Cu content in Cu@CF was 4.77 wt.%.

3.2. Structural Characterization

The synthesized Ru/Cu@CF was characterized using SEM, TEM, XRD, XPS, Raman spectroscopy, and contact angle measurement. As shown in Figure 1B, the Ru/Cu@CF structure is stable, possessing a well-defined three-dimensional porous fiber skeleton. Compared to the base material CF (Figure 1A), it shows a distinctly rougher surface and uniform nanoparticle distribution. In Ru/Cu@CF (Figure 1B–D), Ru/Cu nanoparticles with an average particle size of about 10 nm are uniformly distributed on the carbon fiber skeleton, the TEM characterization (Figure 1J,K) also confirms this result. In addition, HRTEM (Figure 1L) showed that Ru/Cu metal particles formed an alloy structure, but due to carbon hybridization coverage or incomplete crystal structure, the lattice stripes were not particularly clear. Each fiber is uniformly covered with dispersed Ru/Cu nanoparticles, exhibiting excellent dispersion. Elemental mapping analysis further supports this observation (Figure 1E). The elemental maps for carbon (C), ruthenium (Ru), copper (Cu), and nitrogen (N) (Figure 1F–I) reveal their spatial distribution within the composite. The results show that carbon, nitrogen, and Ru/Cu are uniformly distributed on the carbon skeleton, confirming the stable loading and uniform dispersion of Ru/Cu nanoparticles. This is attributed to the crucial role of the ruthenium-based and copper-based metal ionic liquids during material preparation. The results further demonstrate the excellent dispersing ability of the ionic liquids on the polymer fibers, which is essential for achieving stable loading, uniform distribution of Ru/Cu nanoparticles, and optimizing the activity of the composite material.

The XRD pattern of the Ru/Cu@CF composite (Figure 2A) shows two intense diffraction peaks at 26.5° and 43.7°, attributed to the characteristic diffraction of the carbon framework. No obvious metal diffraction peaks were found, indicating that the Ru and Cu species are primarily amorphous or highly dispersed, confirming the uniform Ru/Cu distribution observed in the HRTEM and elemental mapping analysis. The small size of the Ru/Cu nanoparticles, combined with the fixation and barrier effect of the ionic liquids, restricts the formation of more complete crystals, resulting in fewer exposed crystalline facets. This amorphous and hybrid state allows the Ru/Cu@CF composite to expose more active sites, thereby enhancing its catalytic activity. This nanoscale dispersion prevents particle agglomeration while maximizing accessible active sites—a key

factor for the enhanced capability of Ru/Cu@CF in reducing CO_2 and NO_3^- . The Raman spectrum of Ru/Cu@CF (Figure 2B) displays two characteristic peaks, 1332.27 cm^{-1} and 1583.61 cm^{-1} , corresponding to graphitic carbon layers (G band) and disordered/defective carbon structures (D band), respectively. The high intensity ratio of the D band to the G band (I_D/I_G) indicates a high density of structural defects and limited graphitization degree, consistent with the carbon nanofiber structural morphology observed in SEM. Nitrogen adsorption–desorption analysis (Figure 2C) revealed a specific surface area of $641.6\text{ m}^2\text{ g}^{-1}$. The higher specific surface area is more conducive to CO_2 accumulation and the exposure of more active sites, demonstrating the material's high metal loading capacity and rich accessibility of active sites. These structural features—the defect-rich carbon matrix and porous structure—synergistically improve charge transfer efficiency.

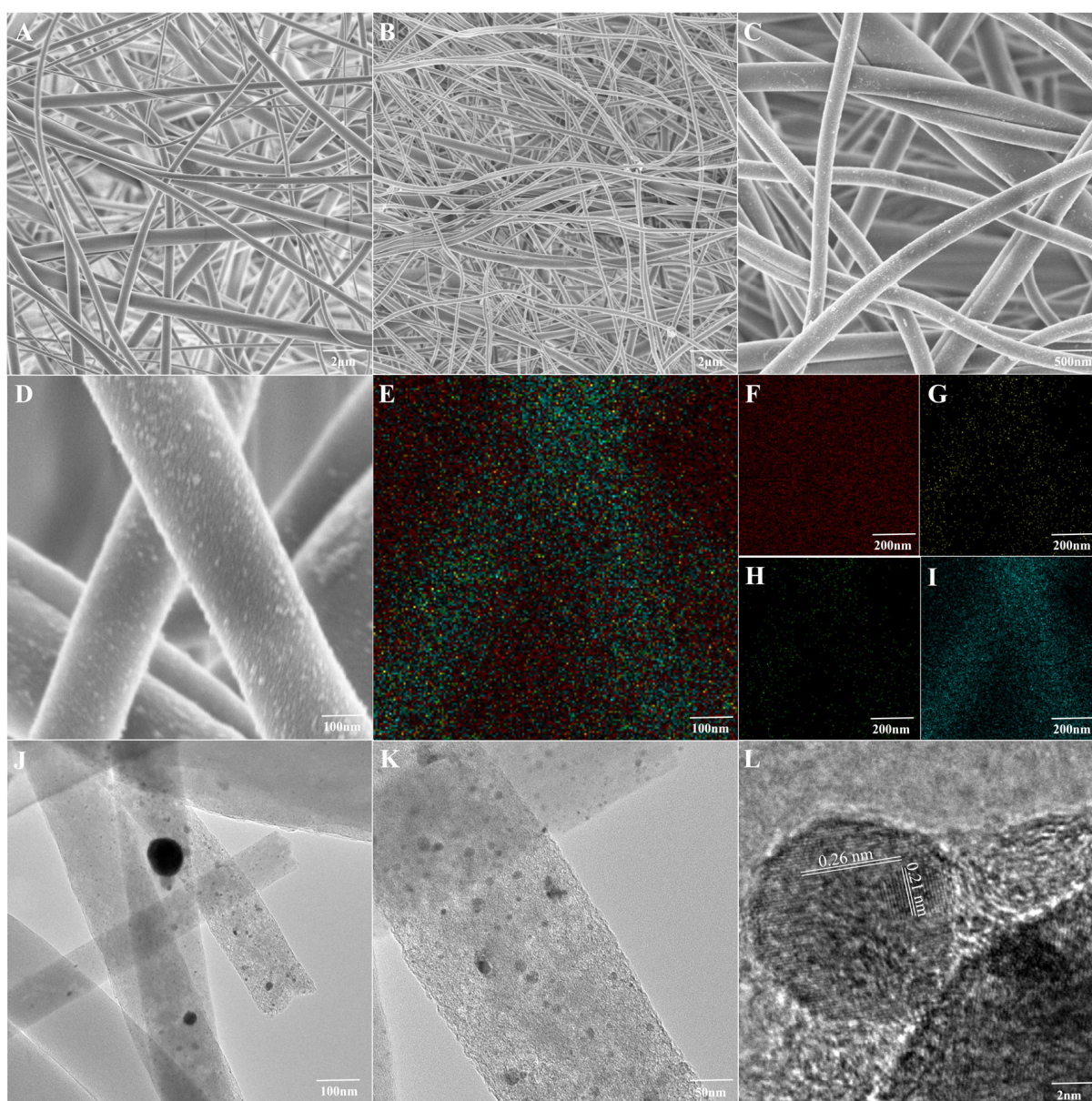


Figure 1. The SEM (A–D) and corresponding EDS element mappings of C (F), Ru (G), Cu (H), N (I) and layered image (E), TEM (J,K) and HRTEM (L) of Ru/Cu@CF.

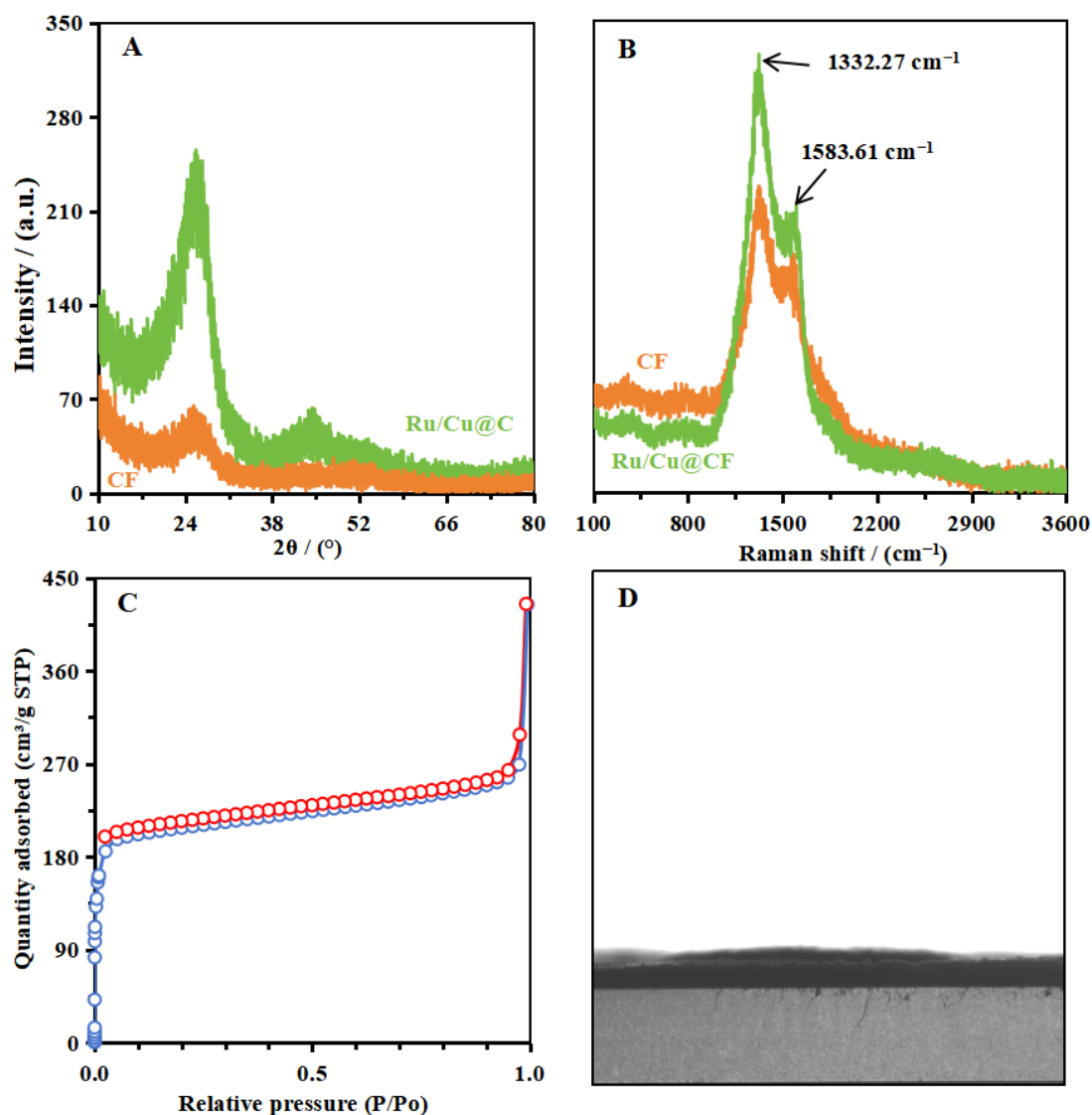


Figure 2. The XRD (A), Raman (B), BET (C) spectra and contact angle images (D) of Ru/Cu@CF.

In summary, the characterization results confirm that Ru/Cu atoms are uniformly dispersed on the carbon nanofibers in the form of atomic clusters or ultra-small nanoparticles with an amorphous morphology. This amorphous and hybrid state allows the Ru/Cu@CF composite to expose more active sites. The unique structural configuration maximizes the exposure of electroactive sites while preventing particle aggregation, directly contributing to the exceptional electrocatalytic performance of Ru/Cu. Additionally, contact angle tests (Figure 2D) indicate that Ru/Cu@CF possesses strong hydrophilicity, which is one reason for its high catalytic activity. The strong hydrophilicity enhances the contact between the electrode material and water molecules, thereby improving mass transfer and ion transport efficiency. Consequently, CO_2 molecules and NO_3^- ions can more easily reach active sites, and the produced urea disperses at a faster rate, which is more favorable for promoting the reaction towards urea production and thus increases the reaction rate.

The carbon nanofiber (CF) substrate in the Ru/Cu@CF composite plays multiple critical roles beyond merely serving as a physical support. First, its three-dimensional interconnected porous fibrous network provides a high specific surface area, which offers an ideal scaffold for the highly dispersed and stable anchoring of Ru-Cu nanoparticles, effectively preventing their agglomeration. Second, CF itself possesses good electronic conductivity, forming an efficient charge-transport skeleton that ensures rapid electron

delivery to the active sites during electrocatalysis. Furthermore, Ru/Cu@CF, after modification and carbonization via the metal ionic liquid, exhibits strong hydrophilicity, which significantly improves the wettability at the electrode/electrolyte interface and enhances the mass transport of reactants and products.

Figure 3 presents the overall XPS survey spectrum and high-resolution spectra of C 1s, N 1s, O 1s, Ru 3d, and Cu 2p for Ru/Cu@CF. The XPS survey spectrum confirms that the material is primarily composed of C, N, O, Ru, and Cu. In the C 1s spectrum (Figure 3B), three peaks located at 284.3, 285.8, and 286.9 eV are assigned to C–C, C–O, and C=O bonds, respectively. The N 1s spectrum (Figure 3C) can be deconvoluted into three peaks corresponding to pyridinic N (399.2 eV), pyrrolic N (400.8 eV), and graphitic N (401.6 eV). The presence of graphitic N indicates that nitrogen atoms have been incorporated into the graphitic carbon plane and bonded with three carbon atoms, while the existence of pyridinic and pyrrolic N can help modulate the electronic structure of the carbon matrix, enhance electron transfer capability, and thereby improve the electrocatalytic activity of the material. The O 1s spectrum (Figure 3D) shows two peaks at 532.3 and 535.2 eV, corresponding to O–C and O=C species, respectively. The Ru 3d spectrum (Figure 3E) exhibits characteristic peaks at 462.8 eV (Ru 3d_{5/2}) and 484.5 eV (Ru 3d_{3/2}). The Cu 2p spectrum (Figure 3F) displays typical peaks at 932.3 eV (Cu 2p_{3/2}) and 952.8 eV (Cu 2p_{1/2}). Notably, compared with the monometallic reference samples (Ru@CF and Cu@CF), clear binding energy shifts are observed in both the Ru 3d and Cu 2p spectra of Ru/Cu@CF, indicating electronic interaction between Ru and Cu and further supporting the formation of a bimetallic alloy structure, which is consistent with the HRTEM characterization results.

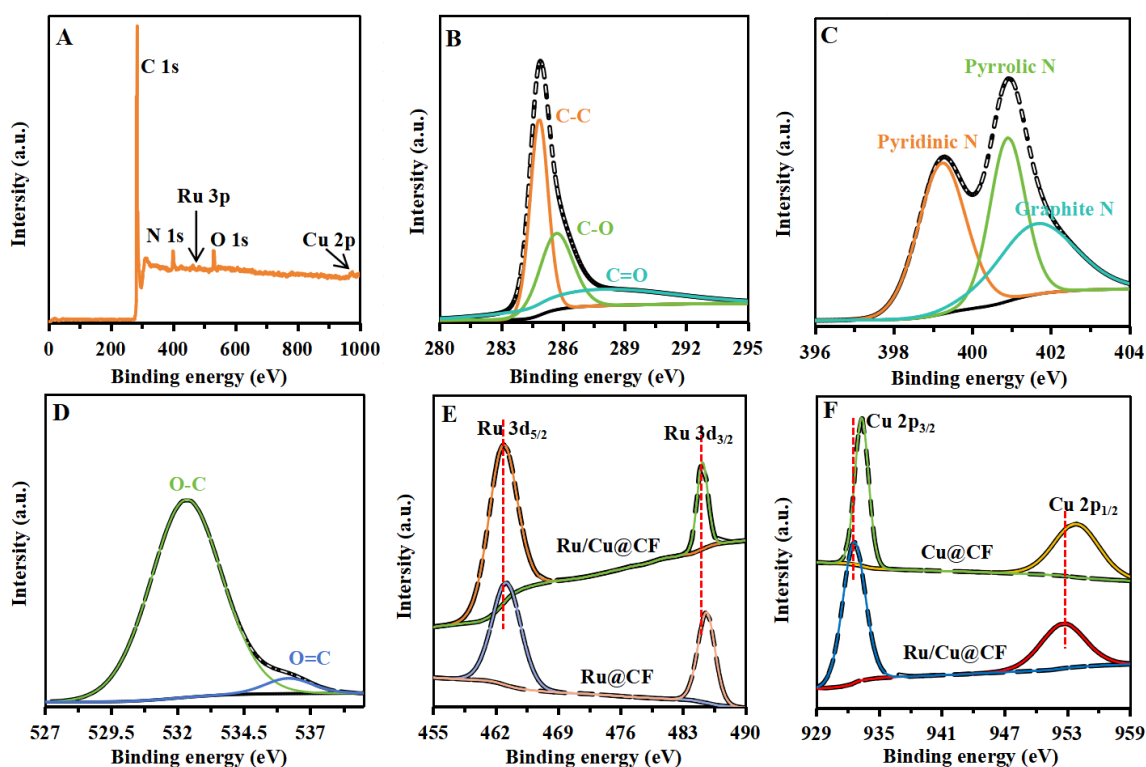


Figure 3. The total (A), C 1 s (B), N 1 s (C), O 1 s (D), Ru 3d (E) and Cu 2p (F) XPS spectra of Ru/Cu@CF.

3.3. Electrocatalytic Performance for Urea Synthesis

Urea synthesis was employed as a model reaction to evaluate the electrocatalytic performance of Ru/Cu@CF. Figure 4A shows the LSV curves of the Ru/Cu@CF electrode in 0.1 M KNO₃ (or K₂SO₄) electrolyte saturated with Ar (or CO₂), at potentials between

−1.8 and 0 V. When the potential is above −0.9 V in Ar-saturated 0.1 M K_2SO_4 electrolyte, the LSV current density is close to zero, indicating no redox reactions of Ar and SO_4^{2-} occur on the electrode. However, when the potential is below −0.9 V, the current density slightly increases with decreasing potential. This is due to the reduction of H^+ ions from the electrolyte on the electrode surface. Due to the presence of abundant metal cations, Ru/Cu@CF strongly repels H^+ ions approaching the electrode surface. This property leads to a very high overpotential for H^+ ion reduction on the Ru/Cu@CF electrode. The high overpotential inhibits the reduction of H^+ ions, resulting in very low current density. Because the NO_3^- reduction reaction (NO_3^- RR) involves more frequent electron transfer than the CO_2 reduction reaction (CO_2 RR), the current increase in $\text{K}_2\text{SO}_4/\text{CO}_2$ is lower than that in KNO_3/Ar . The above results indicate that Ru/Cu@CF can catalyze the reduction of NO_3^- and CO_2 . When tested using 0.1 M KNO_3 solution saturated with CO_2 as the electrolyte, the current density reached its maximum. This is attributed to the coupling of CO_2 reduction with NO_3^- reduction to form urea, creating a C–N bond. Furthermore, Figure 3A also shows that when the potential is −0.1 V, the current density is below zero, confirming that urea synthesis can proceed at a potential of −0.1 V. The low reduction potential indicates that Ru/Cu@CF possesses excellent electrocatalytic activity for urea synthesis. Figure 4B–D present the *i*-*t* curves, urea yield, and Faradaic efficiency of the Ru/Cu@CF electrode in CO_2 -saturated 0.1 M KNO_3 electrolyte at potentials of −0.3, −0.4, −0.5, −0.6, and −0.7 V vs. RHE for a reaction time of 60 min. At all applied potentials, the current density was below zero, indicating that CO_2 and NO_3^- can be reduced within the potential range of −0.3 to −0.7 V. As the potential becomes more negative, the reduction of CO_2 and NO_3^- accelerates, leading to an increase in current density (Figure 4B). However, the changes in urea yield and Faradaic efficiency do not follow this trend. When the potential is more negative than −0.5 V, the urea yield increases rapidly (Figure 4C), reaching a maximum value ($57.8 \text{ mmol g}^{-1} \text{ h}^{-1}$) and the highest Faradaic efficiency (25.4%) at a potential of −0.5 V (Figure 4D), before decreasing. To achieve high urea yield and avoid severe side reactions, −0.5 V was selected as the working potential for electrocatalytic urea synthesis catalyzed by Ru/Cu@CF.

The FE values for the production of H_2 , NH_3 , CO, NO_2^- , and urea using the Ru/Cu@CF catalyst in CO_2 -saturated 0.1 M KNO_3 electrolyte at a potential of −0.5 V for 60 min are shown in Figure 5A. The FE for urea synthesis is as high as 25.4%, surpassing the FE values for H_2 (1.9%), NH_3 (17.4%), and CO (7.6%). Although the FE for NO_2^- is 41.8%, higher than that for urea, it can be converted into urea upon further reduction. The above results indicate good selectivity for urea synthesis on Ru/Cu@CF. To evaluate the contribution of different components in Ru/Cu@CF to the catalytic activity, four other electrocatalysts were prepared, including CF, Ru@CF, Cu@CF, and Ru/Cu nanoparticles, and used for urea synthesis following the same procedure. Figure 4B displays the FE for urea synthesis using different catalysts. Compared to Ru/Cu@CF, the Ru/Cu nanoparticles show similar efficiency. Catalysts containing bimetallic species all exhibit higher FE than those containing only single metals or the base material, with the bimetallic catalysts achieving the maximum FE at −0.5 V vs. RHE. Among the investigated catalysts, Ru/Cu@CF shows the highest FE of 25.4% at −0.5 V vs. RHE. Meanwhile, Ru@CF and Cu@CF show higher FE at −0.6 V and −0.7 V, respectively, indicating that the Ru–Cu bimetallic system effectively lowers the potential required for urea synthesis. Figure 4C presents the urea yields on Ru@CF, Cu@CF, CF, Ru/Cu, and Ru/Cu@CF electrodes in CO_2 -saturated 0.1 M KNO_3 electrolyte at a potential of −0.5 V for 60 min.

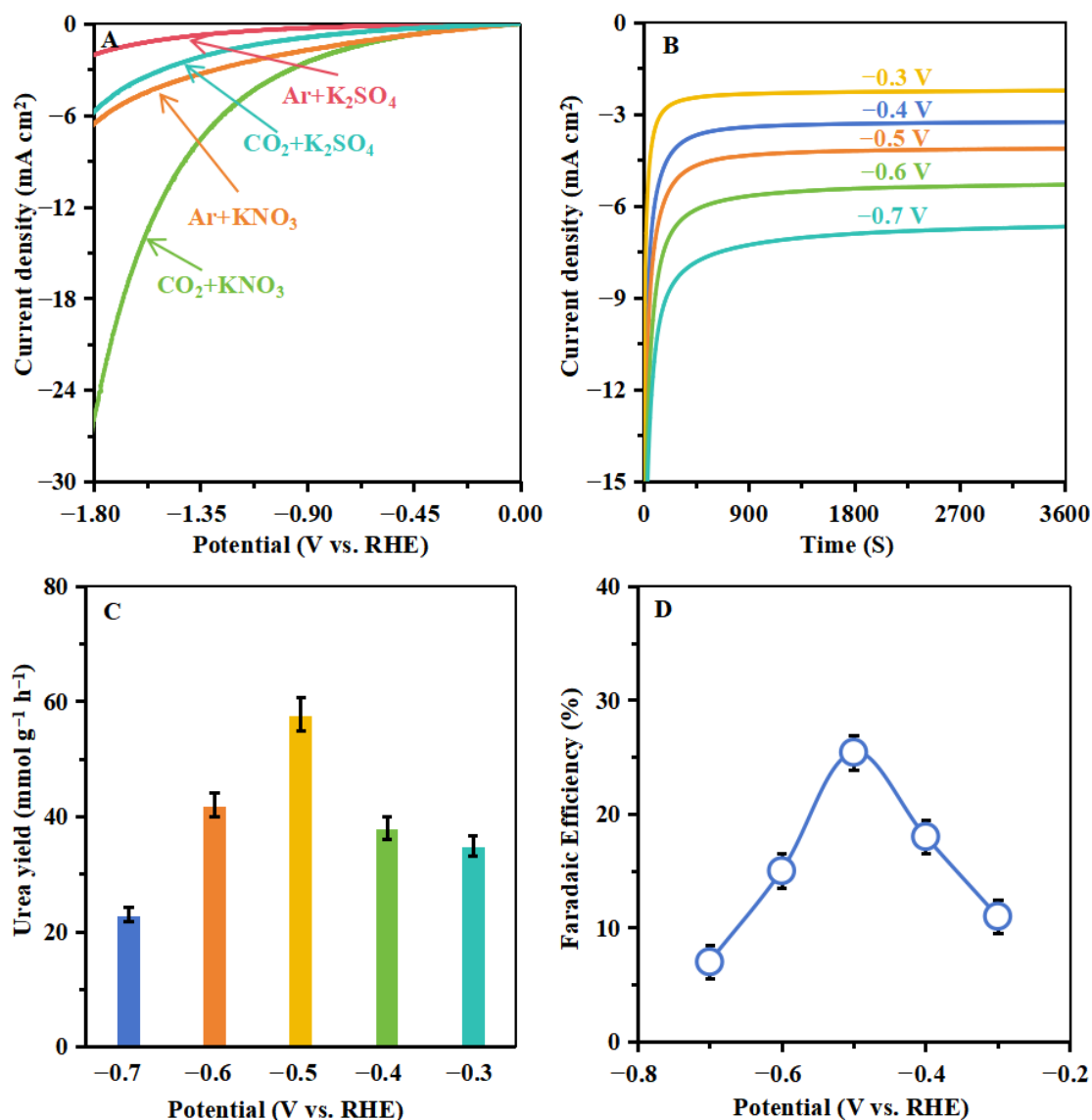


Figure 4. LSV curves (A) of Ru/Cu@CF electrode at potential between -1.8 and 0 V in the Ar-(or CO₂)-saturated 0.1 M KNO₃ (or K₂SO₄) electrolyte, i-t curves (B), urea yields (C) and Faraday efficiencies (D) of Ru/Cu@CF electrode at -0.3 , -0.4 , -0.5 , -0.6 and -0.7 V vs. RHE in the CO₂-saturated 0.1 M KNO₃ electrolyte for 60 min.

Although Ru/Cu@CF achieved a high urea yield rate of $57.8 \text{ mmol g}^{-1} \text{ h}^{-1}$ at -0.5 V vs. RHE, the corresponding Faradaic efficiency (FE) of 25.4% reflects the significant presence of competing parallel reaction pathways within this co-reduction system. As shown in Figure 5A, under identical testing conditions, the partial reduction of NO₃[−] to NO₂[−] claims the largest share of electron allocation (FE = 41.8%), indicating its thermodynamic and kinetic favorability. Concurrently, a considerable portion of electrons is diverted toward the formation of by-products such as NH₃ (FE = 17.4%) and CO (FE = 7.6%). The existence of these parallel reactions, particularly the facile conversion of NO₃[−] to NO₂[−], substantially divert the electrons available for the C–N coupling step, thereby limiting the selectivity toward urea synthesis. Furthermore, at more negative potentials (e.g., -0.6 V and -0.7 V), while the total current density increases, the hydrogen evolution reaction (HER) and the over-reduction of nitrogen intermediates to NH₃ are exacerbated, leading to a decline in the urea FE (Figure 4D). Consequently, the Faradaic efficiency obtained at -0.5 V is a result of the inherent complexity and competitive kinetics of the reaction network. Future efforts to further tailor the adsorption energies of key intermediates on the catalyst surface or to

modulate the local reaction microenvironment may suppress side reactions and enhance the selectivity for C–N coupling.

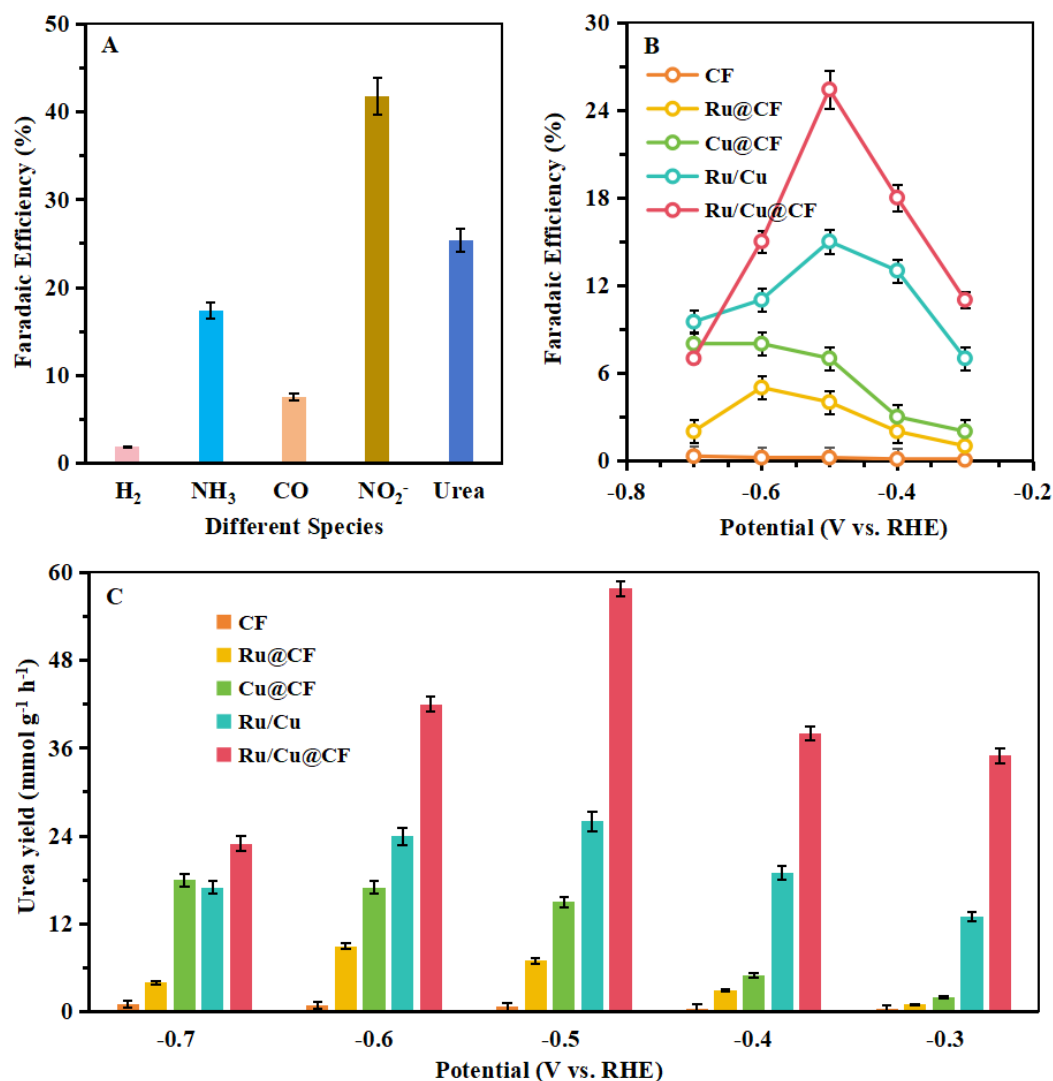


Figure 5. Faraday efficiencies for electrocatalytic synthesis (A) of H₂, NH₃, CO, NO₂⁻ and urea in CO₂-saturated 0.1 M KNO₃ electrolyte at −0.5 V for 60 min under catalysis of Ru/Cu@CF, urea yields (B) and Faraday efficiencies (C) of CF, Ru@CF, Cu@CF, Ru/Cu and Ru/Cu@CF electrode at −0.3, −0.4, −0.5, −0.6 and −0.7 V vs. RHE in the CO₂-saturated 0.1 M KNO₃ electrolyte for 60 min.

Control experiments confirm that pure CF alone exhibits very low catalytic activity for urea synthesis (Figure 5B,C), underscoring that its primary function is to provide an optimized conductive network and structural platform. By synergizing with the highly dispersed Ru–Cu active sites, the CF substrate collectively enhances the overall electrocatalytic performance. The superior urea synthesis performance of Ru/Cu@CF compared to its single-metal counterparts (Ru@CF, Cu@CF) and the bare carbon support (CF) (Figure 5B,C) is primarily attributed to the synergistic catalytic effect between the Ru and Cu bimetallic components. This synergy likely operates through the following mechanisms: (1) Bifunctional activation: Cu sites exhibit high activity for CO₂ reduction, facilitating the generation of carbon intermediates like *CO, while Ru sites are more effective in promoting the step-wise reduction of NO₃⁻ to nitrogenous intermediates such as *NH_x. Their close proximity creates a favorable microenvironment for C–N bond coupling. (2) Electronic structure modulation: The electronic interaction between Ru and Cu alters the electronic states of the surface metal atoms, optimizing the adsorption strength for key reaction intermediates

(e.g., $^*\text{CONH}_2$) and thereby lowering the energy barrier for C–N coupling. (3) Suppression of competing reactions: The bimetallic structure may modulate the hydrogen adsorption energy on the surface, partially suppressing the hydrogen evolution side reaction. Simultaneously, by balancing the reduction depths of CO_2 and NO_3^- , it minimizes their tendencies to be fully reduced to CO and NH_3 , respectively, steering the reaction pathway toward urea synthesis. Therefore, the synergy between Ru and Cu is key to achieving high activity and selectivity. Among the five electrocatalysts used, Ru/Cu@CF provides the best electrocatalytic activity, followed by Ru/Cu. Such excellent catalytic activity is attributed to the synergistic effects arising from the various components. More importantly, the above results provide new insights for us to improve electrocatalytic activity through rational catalyst design.

For comparison, the electrocatalytic behaviors of reported electrocatalysts for urea synthesis are listed in Table 1. Table 1 shows that, compared to reported electrocatalysts, Ru/Cu@CF can provide superior electrocatalytic performance. Compared to previously reported high-performance bimetallic catalysts [19], the salient advantages of the present work include the following: (1) The introduction of an innovative synthesis method based on metal ionic liquid precursors and pyrolysis, which offers uniqueness and controllability in achieving atomic-level dispersion of metals. (2) The obtained catalyst delivers a high urea yield rate of $57.8 \text{ mmol g}^{-1} \text{ h}^{-1}$ at a relatively mild potential (-0.5 V vs. RHE), demonstrating promising energy efficiency. (3) The material exhibits excellent cycling stability, retaining over 95% of its initial activity after 10 consecutive tests. (4) The synthesis strategy possesses good generality, opening a new avenue for the rational design and controllable preparation of high-performance bimetallic and even polymetallic catalytic materials.

Table 1. Electrocatalytic performance of different catalysts for urea synthesis.

Electrocatalyst	Nitrogen Source	Urea Yield ($\text{mmol g}^{-1} \text{ h}^{-1}$)	Potential (V vs. RHE)	Faradaic Efficiency (%)	Ref.
RhCu alloys	0.1 M KNO_3	26.81 ± 0.62	-0.6	34.82 ± 2.47	[19]
Pd4Cu1- FeNi(OH) ₂	0.1 M KNO_3 + 0.1 M KHCO_3	436.9	-0.6	66.5	[40]
CoRuN ₆	0.1 M KNO_3	8.98	-0.6	25.31	[41]
AuCu self-assembled nanofiber	0.01 M KNO_2 + 0.5 M KHCO_3	64.76	-1.55	24.70	[42]
PdCu alloy/TiO ₂	N ₂	3.36	-0.4	8.92	[43]
Ru/Cu@CF	0.1 M KNO_3	57.8	-0.5	25.4	This work

The superior performance of the Ru/Cu bimetallic system, compared to its monometallic counterparts, necessitates a deeper mechanistic inquiry into the origin of the observed synergy, which we propose stems from a concerted integration of compartmentalized reactant activation and a facilitated C–N coupling at the bimetallic interface. The electrochemical behavior of the monometallic controls provides initial clues, as Ru@CF achieves its peak FE for urea at a more negative potential (-0.6 V) than Cu@CF (-0.7 V), suggesting divergent intrinsic activities. Based on established literature [19,40–43] where Cu-based catalysts are highly effective for CO_2 reduction to CO and other C_1 intermediates while Ru is renowned for the stepwise reduction of NO_3^- to NH_x species, it is inferred that in Ru/Cu@CF, Cu sites preferentially activate and reduce CO_2 , whereas Ru sites are more active toward the stepwise hydrogenation of NO_3^- , thereby creating a local environment rich in both carbonaceous and nitrogenous intermediates on adjacent sites. Beyond this compartmentalization, the key synergy likely originates at the Ru–Cu interface or within the alloyed nanoparticles, where the electronic interaction between the metals, indicated by

the amorphous/alloyed structure in HRTEM, modifies the local electronic density of states to optimize the adsorption energy of the key transition state for C–N coupling; for instance, the interface may stabilize the $^*\text{CONH}_2$ intermediate more effectively than individual metal surfaces, significantly lowering the activation energy barrier for the C–N bond-forming step, which is consistent with Ru/Cu@CF achieving its highest yield and FE at a less negative potential (-0.5 V) than either monometallic catalyst. Furthermore, this bimetallic synergy suppresses competing reactions by weakening the binding of $^*\text{H}$ to mitigate the hydrogen evolution reaction and by providing an optimized pathway for intermediate coupling, which reduces the surface residence time of $^*\text{CO}$ and NH_x species and thus their chance of further reduction to by-products like CO or NH_3 [11–13]. In summary, the synergy in Ru/Cu@CF is a concerted effect where Cu and Ru sites cooperate compartmentally in initial activation, and their intimate contact creates an interfacial region that electronically promotes the critical C–N coupling step, leading to high urea yield and selectivity at reduced overpotentials, with future theoretical and in situ spectroscopic studies being valuable to precisely map the adsorption energies and validate this proposed mechanism.

Isotope labeling experiments were performed to identify the nitrogen source in the synthesized urea products. As shown in the direct NMR spectra (Figure 6A–D), characteristic doublet signals corresponding to $\text{CO}(^{15}\text{NH}_2)_2$ and singlet signals corresponding to $\text{CO}(^{14}\text{NH}_2)_2$ were clearly observed, confirming that urea originated from the electrocatalytic coupling of CO_2 with $^{15}\text{KNO}_3$ and $^{14}\text{KNO}_3$, respectively. Furthermore, the NMR analysis allowed clear identification of $^{15}\text{NH}_4^+$ derived from $\text{CO}(^{15}\text{NH}_2)_2$ based on distinct spectral features: a triplet splitting pattern from ^{14}N and a doublet splitting pattern from ^{15}N . These signals matched well with the calibration curves obtained from authentic $^{14}\text{NH}_4^+$ (derived from $\text{CO}(^{14}\text{NH}_2)_2$) and $^{15}\text{NH}_4^+$ (derived from $\text{CO}(^{15}\text{NH}_2)_2$), thereby providing direct evidence that urea was produced via the electrocatalytic C–N coupling of CO_2 and NO_3^- [13].

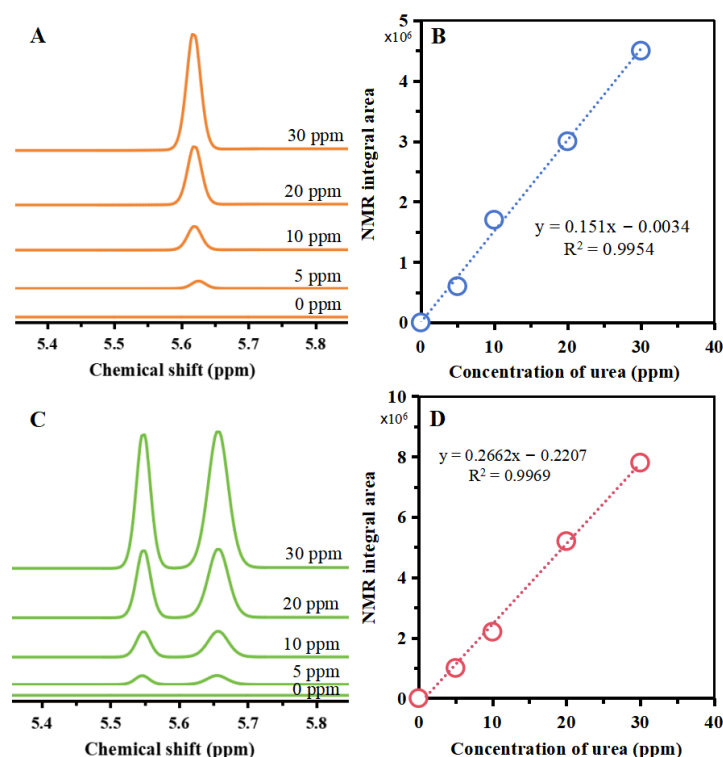


Figure 6. NMR spectra and calibration curves for quantification of urea. (A) NMR spectra of $\text{CO}(^{14}\text{NH}_2)_2$ with various concentrations. (B) The calibration curves for $\text{CO}(^{14}\text{NH}_2)_2$. (C) NMR spectra of $\text{CO}(^{15}\text{NH}_2)_2$ with various concentrations. (D) The calibration curves for $\text{CO}(^{15}\text{NH}_2)_2$.

Figure 7A,B show the urea yield and Faradaic efficiency values for the Ru/Cu@CF electrode during a 10-cycle test in CO₂-saturated 0.1 M KNO₃ electrolyte at a potential of −0.5 V. As can be seen from Figure 7A, after 10 cycles, the urea yield remains at 55.3 mmol g^{−1} h^{−1}, with an FE of 24.8%. This result indicates minimal changes in urea yield and FE after 10 cycles. This demonstrates the good cycling stability of Ru/Cu@CF, with catalyst deactivation and loss of electroactive components due to electrode material detachment or side reactions being almost negligible.

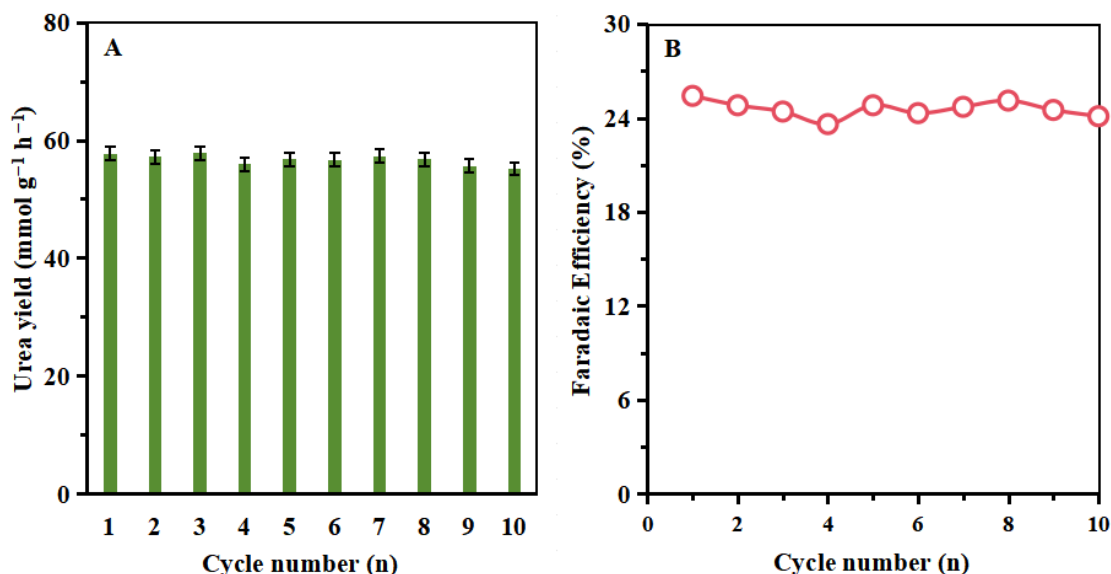


Figure 7. Urea yields (A) and Faraday efficiency values (B) of Ru/Cu@CF electrode in the CO₂-saturated 0.1 M KNO₃ electrolyte at −0.5 V for 10-cycle test.

4. Conclusions

This study successfully developed a novel synthesis strategy based on metal ionic liquids for constructing highly dispersed and structurally stable bimetallic nanocatalytic materials. By leveraging the multiple roles of functionalized metal ionic liquids, this strategy achieved uniform dispersion and firm anchoring of ruthenium–copper bimetallic components within the carbon matrix, effectively addressing the challenges of dispersion and stability commonly faced in the synthesis of traditional bimetallic catalysts. The prepared ruthenium–copper/carbon nanofiber composite material exhibits a unique three-dimensional porous structure and abundant active sites. In the electrocatalytic co-reduction of carbon dioxide and nitrate for urea synthesis, this material demonstrates excellent catalytic activity, high selectivity, and good cycling stability. Experiments indicate that the synergistic effect between ruthenium and copper is a key factor in enhancing its catalytic performance. This work not only provides an efficient and stable catalyst for electrocatalytic urea synthesis under mild conditions but, more importantly, the developed ionic liquid-mediated synthesis strategy opens a new pathway for the rational design and controllable preparation of high-performance bimetallic and even polymetallic catalytic materials. This research holds positive scientific significance for advancing the development of green and low-carbon catalytic technologies and achieving sustainable chemical synthesis.

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