

Article

Heterostructured Cu/CuO Nanoparticles Embedded within N-Doped Carbon Nanosheets for Efficient Oxygen Reduction Reaction

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Abstract: The development of cost-effective and highly efficient oxygen reduction reaction (ORR) electrocatalysts is an essential component of renewable clean energy technologies, such as fuel cells and metal/air cells, but remains a huge and long-term challenge. Here, novel heterogeneous Cu/CuO nanoparticles embedded within N-doped carbon nanosheets (Cu/CuO@NC-900) are successfully synthesized by combining a facile hydrothermal route with a solid calcination technique. Benefitting from the electronic interaction between Cu and CuO, the generated abundant highly active Cu-N_x active sites and the high conductivity of the N-doped carbon nanosheets, the resulting Cu/CuO@NC-900 material shows superior ORR performance in alkaline media, exhibiting a high half-wave potential of ~0.868 V, and a robust stability and methanol tolerance, even outperforming commercial 20 wt% Pt/C. Our study opens up a new avenue for the rational design and fabrication of efficient and durable noble-metal-free Cu-based electrocatalysts for energy conversion and storage.

Keywords: Cu/CuO; heterogeneous nanostructure; electrocatalyst; oxygen reduction reaction



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1. Introduction

Energy is closely related to human civilization, and energy crisis and environmental pollution problems have been the two major problems faced by human survival and the development process [1–5]. To build a clean, low-carbon, secure and efficient energy system, efforts have been made to develop green renewable energy storage and conversion devices [6–10]. Among them, metal–air cells and fuel cells have received widespread attention due to their low cost, high efficiency, and clean and pollution-free characteristics. Electrochemical oxygen reduction reaction (ORR) is the core step of their reactions and, due to the slow reaction kinetics, is also the main cause of their voltage loss [11–13], so it is of great significance to seek stable and efficient catalytic electrodes for improving the oxygen reduction reaction. It is well known that platinum-based materials exhibit good catalytic activity for ORR, but there are problems, such as low abundance, high price and stability in alkaline solutions, and poor methanol tolerance, which greatly hinder its wide application.

In recent years, nonprecious-metal-based catalysts have attracted a great deal of attention from researchers, with great progress being made in particular with sulfides [14–18], oxides [19,20], and phosphides [21–23]. The transition metal copper (Cu) is abundant in the earth and its low price and high electrical conductivity have been extensively studied in many fields [24–26]. Copper oxides have the potential to be efficient oxygen reduction catalysts due to their variable oxidation states and stronger O₂ adsorption capacity [27,28]. Nonetheless, CuO has poor electrical conductivity and tends to aggregate during high-temperature synthesis, making it difficult to expose the active site, so how to improve

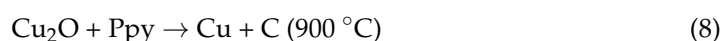
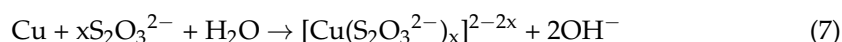
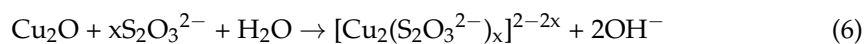
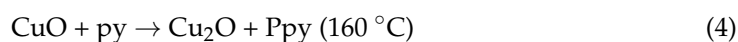
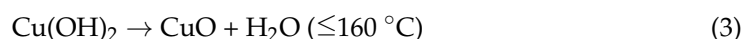
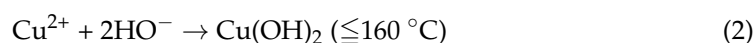
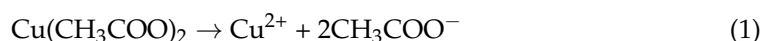
its catalytic activity and stability remains a key research issue. It has been reported that the thermal decomposition of copper complexes with carbon carriers is an effective way to solve the instability problem of copper composite catalysts in ORR [29,30]. The combination with carbon carrier can not only improve the conductivity of the material, but also as a carrier can make the nanoparticles more dispersed and expose more active sites. Notably, metal/metal oxides with heterojunctions have also received extensive attention because the electron density of different redox active sites can remain at the interface, thus facilitating charge transfer and allowing the intrinsic activity of the material's electrocatalysis to be enhanced [31–33]. In addition, it has been reported that DFT calculations confirm that N-doped carbon-based materials can also modulate the electronic structure of metals and that the Cu-N_x site is the main active site for copper-based catalysts used in ORR. As reported by Zhang Q et al. [34], the introduction of Cu-N_x sites effectively reduced the generation of HO²⁻ on the catalyst during the catalytic process and prevented its possible carbon corrosion caused by the autocatalytic Fenton process, thus giving the SA-CoCu/Cu@Cu/CoNP catalyst excellent electrocatalytic activity and long ORR period durability under alkaline conditions. Based on the above considerations, the preparation of Cu/CuO heterostructures with Cu-N_x modification is an effective way to find efficient and stable ORR catalysts [35–37].

Herein, we reported a coupling strategy to successfully synthesize novel heterogeneous Cu/CuO nanoparticles embedded within N-doped carbon nanosheets (Cu/CuO@NC-900) via a hydrothermal route and a solid calcination technique. Due to the presence of Cu/CuO heterostructures promoting electronic interactions between Cu and CuO, the large number of highly active Cu-N_x active sites generated, and the high electrical conductivity of N-doped carbon nanosheets, Cu/CuO@NC-900 exhibits excellent ORR activity, long-term durability, and resistance to methanol toxicity. These findings open up new avenues for the rational design of noble-metal-free electrocatalysts with the advantages of high efficiency and high stability for energy conversion and storage devices.

2. Results and Discussion

2.1. Structural and Morphological Characterizations

The synthesis process of the Cu/CuO@NC-900 nanocomposite was illustrated in Figure 1. Using Cu(CH₃COO)₂·H₂O as the copper source and pyrrole monomer as the carbon source, Cu₂O/CuO/Cu@Ppy was firstly produced by a hydrothermal reaction at 160 °C for 10 h. Then, Cu and part of Cu₂O in Cu₂O/CuO/Cu@Ppy suffered from the etching of sodium thiosulfate solution for 1 h, thus resulting in the Cu₂O/CuO@Ppy (Figure S3), which was further calcined at 900 °C for 2 h under an Ar protective atmosphere, eventually generating the target product Cu/CuO@NC-900. If this etching step was not carried out, only red metallic copper rather than the black Cu/CuO@NC-900 hybrid was synthesized in the resulting material (Figure S1), which can be confirmed by the XRD pattern of Figure S2. This result can be explained, as without the etching, Cu₂O and CuO in Cu₂O/CuO/Cu@Ppy just exactly reacted with Ppy to generate Cu. The rational synthetic mechanism of Cu/CuO@NC-900 can be speculated as follows [33,38]:



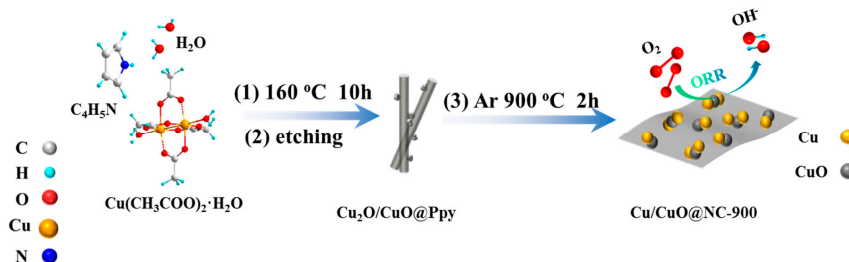


Figure 1. Schematic illustration for the synthesis process of Cu/CuO@NC-900.

In the hydrothermal reaction, copper acetate was firstly hydrolyzed to form $\text{Cu}(\text{OH})_2$, which was further decomposed to form CuO. Then, CuO underwent the reduction conversion to different extents to produce a $\text{Cu}_2\text{O}/\text{CuO}/\text{Cu}$ hybrid, and meanwhile the pyrrole was converted into polypyrrole by the oxidation polymerization reaction [33], eventually forming the precursor $\text{Cu}_2\text{O}/\text{CuO}/\text{Cu}@Ppy$. Afterwards, part of Cu_2O and Cu in $\text{Cu}_2\text{O}/\text{CuO}/\text{Cu}@Ppy$ took part in a complexation reaction with sodium thiosulfate solution as the etching agent, and then was etched to generate $\text{Cu}_2\text{O}/\text{CuO}@Ppy$, of which the Cu_2O was further reduced to Cu by Ppy in the pyrolysis condition of 900°C , integrating with CuO to form a Cu/CuO heterojunction anchored on the N-doped carbon nanosheets, denoted as Cu/CuO@NC-900.

The phase compositions of the as-synthesized samples were characterized by a powder X-ray diffractometer (XRD). In the XRD pattern of Cu/CuO@NC-900 in Figure 2a, the corresponding peaks of the monoclinic CuO (NO. 80-1916), cubic Cu (NO. 85-1326), and C can be observed. The characteristic peaks of CuO appear at 32.48° , 35.49° , 38.68° , and 48.66° , corresponding to (110), (-111), (111), and (-202) crystal planes, respectively. To obvious diffraction peaks of (111), (200), and (220), the plane diffraction of Cu are located at 43.32° , 50.45° , and 74.12° , respectively. Meanwhile, the diffraction peak appearing at $\sim 26^\circ$ can be attributed to the (002) crystal plane of graphitic carbon [39]. These results indicate that Cu/CuO@NC-900 was composed of Cu, CuO, and carbon. In addition, the sizes of the sample Cu and CuO crystals were calculated by using Scherrer's formula as shown in Tables S1 and S2. The data in the tables show that the particle size of Cu/CuO@NC-900 for CuO (12.781 nm) was smaller than that of Cu (59.394 nm). The XRD pattern of the samples treated with different heat treatment temperatures showed that the diffraction peaks of Cu/CuO@NC-800 and Cu/CuO@NC-1000 were similar to those of Cu/CuO@NC-900 and no new phases were generated, illustrating that the temperature had no effect on the phase composition of the samples (Figure S4). The Raman spectra of the synthesized samples were illustrated in Figure 2b and Figure S5, where the peaks near 1340 and 1580 cm^{-1} corresponded to the D and G bands of the carbon structure, respectively. Notably, the D band was related to the degree of disorder of the carbon at the sp^2 -hybridization, whereas the G band represented the degree of graphitization [40]. The D/G intensity ratio (I_D/I_G) of Cu/CuO@NC-900 was only 0.93, lower than that of Cu/CuO/NC-800 (0.94), Cu/CuO@NC-1000 (0.97), Cu@NC-900 (0.94), and CuO@NC-900 (0.98), indicating that the Cu/CuO@NC-900 sample has the highest degree of graphitization and best conductivity, which is more favorable for electron transfer and enhances the catalytic reaction kinetics.

The microstructure features of the synthetic samples were investigated by SEM and TEM measurements. As shown in Figure S6, the precursors $\text{Cu}_2\text{O}/\text{CuO}/\text{Cu}@Ppy$ and $\text{Cu}_2\text{O}/\text{CuO}@Ppy$ showed the morphology of nanoparticle-attached nanowires, but the number of nanowires in $\text{Cu}_2\text{O}/\text{CuO}@Ppy$ was significantly reduced. By further characterization, the TEM image of $\text{Cu}_2\text{O}/\text{CuO}/\text{Cu}@Ppy$ precursors revealed that the nanowires were composed of Cu_2O , CuO, and Cu, and the nanowire surface was covered by Ppy nanoparticles (Figure S9). Due to the polymerization of pyrrole monomers adsorbed on their specific crystalline planes, the formation of nanowires covered by polypyrrole was thus induced [41]. As depicted in Figure 3a, Cu/CuO@NC-900 was composed of a large number of nanoparticles, which may be due to the conversion of the precursor

Cu₂O/CuO@Ppy from nanowires to nanoparticles through a pyrolytic reduction conversion process. The TEM images of Cu/CuO@NC-900 in Figure 3b and Figure S10 further verify that it was composed of nanoparticles. As depicted in Figure 3c,d, the HRTEM images of Cu/CuO@NC-900 with two diverse components of hetero-nanoparticles show that the lattice fringes reveal 0.232 nm corresponding to the (111) plane of CuO, 0.208 nm belonging to the (111) plane of Cu, and the Cu/CuO hetero-nanoparticles were embedded within N-doped carbon nanosheets. In addition, the selected area electron diffraction (SAED) pattern of Cu/CuO@NC-900 (inset Figure 3c) demonstrates several bright rings that were assigned to the (−111), (202) planes of CuO and the (111), (200) planes of Cu, indicating that the structure of Cu/CuO@NC-900 was polycrystalline. The STEM image and the corresponding EDS mapping (Figure 3e–i) disclose that the Cu, O, N, and C elements were uniformly distributed in Cu/CuO@NC-900. The formation of a heterogeneous interface between Cu and CuO provides more interfacial area, enhances the surface reaction sites, increases the number of active sites, widens the channels, and also increases the electron transfer rate, which in turn accelerates the kinetics of electrocatalytic oxygen reduction reactions.

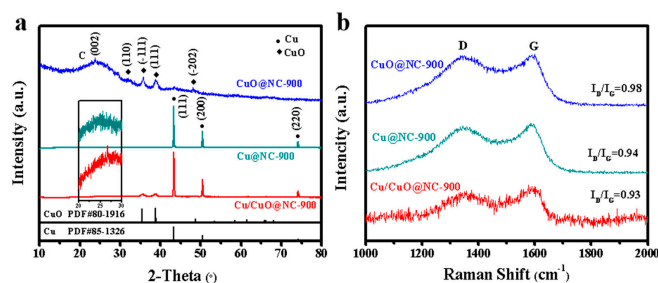


Figure 2. (a) XRD patterns (Inset: XRD partial magnification of Cu/CuO@NC-900 and Cu@NC-900) and (b) Raman spectra of CuO@NC-900, Cu@NC-900 and Cu/CuO@NC-900 electrocatalysts.

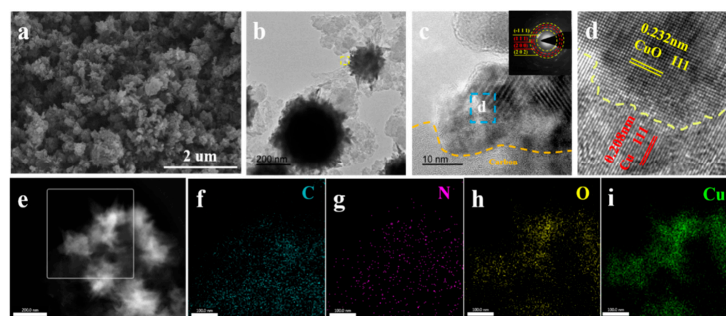


Figure 3. Morphologic characterization of Cu/CuO@NC-900. (a) SEM image; (b) TEM image; (c) HRTEM image taken from the yellow dotted frame of Figure 3b (inset: SAED pattern of the Cu/CuO@NC-900); (d) Enlarged HRTEM image from Figure 3c; (e) STEM image (The white box is the selected area of EDX mapping images) and corresponding (f–i) EDX mapping images of C, N, O, and Cu elements in Cu/CuO@NC-900.

To further elaborate, the chemical composition and electronic state of the heterostructured Cu/CuO@NC-900 catalyst were investigated by XPS. As revealed in the survey XPS spectrum of Figure S12, Cu, O, N, and C elements were observed in Cu/CuO@NC-900. The C 1s XPS spectrum of Cu/CuO@NC-900 was deconvoluted into three peaks at ~284.60, ~285.86, and ~287.14 eV (Figure 4a), which belonged to C-C, C-N, and C=O, respectively [12,42,43]. In Figure 4b, Cu/CuO@NC-900 showed five XPS fitting peaks at 398.18, 398.96, 400.04, 400.82, and 401.72 eV corresponding to pyridine N, M-N (M=Cu), pyrrole N, graphite N, and oxidized N [44–47], respectively, and it was noteworthy that the atomic ratio of metallic N (M-N: Cu-N) in Cu/CuO@NC-900 reached 18.06%, which was higher than Cu@NC-900 (8.19%) and CuO@NC-900 (16.61%). This means that there was a predominance of Cu-N in Cu/CuO@NC-900 (Figure S14) and indicates that the presence of a

large number of Cu-N_x high active sites in Cu/CuO@NC-900 enhanced the ORR [48,49]. The O 1s spectrum of Cu/CuO@NC-900 can be deconvoluted into three peaks at 529.77, 531.27, and 532.51 eV (Figure 4c), attributed to Cu-O, C-O/C=O, and adsorbed water [50], respectively. It was noteworthy that the Cu-O peak position in Cu/CuO@NC-900 shows a significant negative shift compared to the pure CuO@NC-900 sample, which was due to the increased electron state density of O in Cu/CuO@NC-900. In the Cu 2p spectrum of Cu/CuO@NC-900 (Figure 4d), the peaks at 933.33 and 953.44 eV were attributed to Cu 2p_{2/3} and Cu 2p_{1/2} of Cu^I, the peaks at 935.06 and 955.23 eV were ascribed to Cu 2p_{2/3} and Cu 2p_{1/2} of Cu^{II}, accompanied with three satellite peaks at 941.13, 943.53, and 962.27 eV [51–53]. Notably, the Cu 2p peak in Cu/CuO@NC-900 has a slight positive shift compared to Cu@NC-900 and CuO@NC-900, indicating that the Cu center in CuO of Cu/CuO@NC-900 produces more positive charge (δ^+), which facilitates the electrocatalytic reaction. Furthermore, as shown in Table S3, it was found that the metal content of Cu/CuO@NC-900 (3.42%) was much higher than that of CuO@NC-900 (0.42%) and Cu@NC-900 (0.44%), which further indicates that more metal elements can be loaded onto the carbon substrate when Cu and CuO form a heterostructure, which facilitates the formation of a large number of active sites for promoting the catalytic reaction.

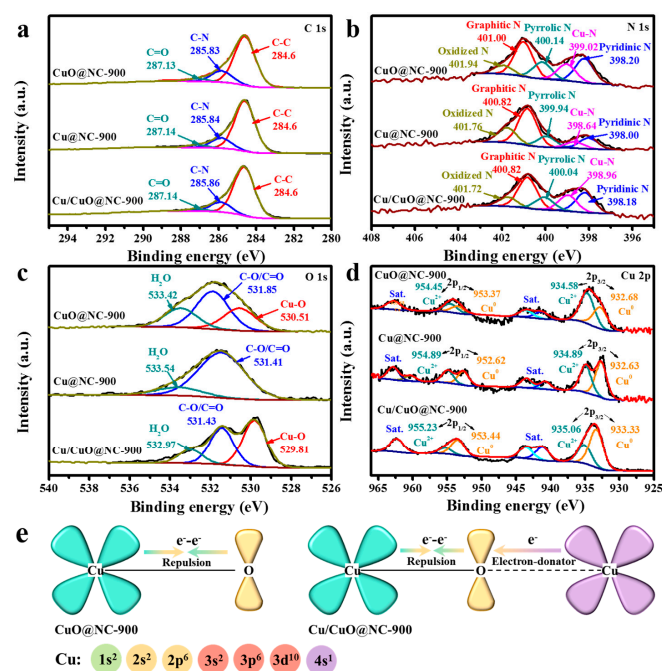


Figure 4. High-resolution XPS spectra of CuO@NC-900, Cu@NC-900, and Cu/CuO@NC-900 samples: (a) C 1s; (b) N 1s; (c) O 1s; (d) Cu 2p. (e) Schematic representations of the electronic coupling among Cu and O in CuO@NC-900 and Cu/CuO@NC-900.

The synergistic electronic interactions between CuO and Cu were elaborated from the perspective of electronic coupling (Figure 4e). The electron aggregation on the Cu site and O₂-bridge site in CuO creates the mutual repulsive force between them, leading to the improper electron interactions that were not favorable for oxygen adsorption and thus affected the reaction rate. However, the XPS results of Cu/CuO@NC-900 indicate that CuO acts as an electron acceptor and Cu acts as an electron donor in Cu/CuO@NC-900, and Cu atoms with electron-rich d orbitals can transfer electrons to bridging O atoms, thus improving the number of electrons between Cu and O in CuO, optimizing the electron density balance, regulating the oxygen adsorption/desorption behavior, enhancing the intrinsic catalytic activity of the catalyst, and favoring the charge transfer and reaction kinetics of ORR [54].

2.2. Electrochemical Evaluation of Cu/CuO@NC-900 for ORR

The electrocatalytic ORR performance of the as-fabricated Cu₂O/CuO/Cu@Ppy, Cu₂O/CuO@Ppy, Cu@NC-900 (XRD: Figure 2a, SEM: Figure S7a, TEM: Figure S11 and survey XPS spectrum: Figure S13), CuO@NC-900 (XRD: Figure 2a, SEM: Figure S7b, TEM: Figure S11 and survey XPS spectrum: Figure S13), Cu/CuO@NC-900, Cu/CuO@NC-800 (SEM: Figure S8a), Cu/CuO@NC-1000 (SEM: Figure S8b), and 20 wt% Pt/C samples were evaluated by using a rotating ring disc electrode (RRDE) in an O₂-saturated 0.1 M KOH solution. Firstly, linear scanning voltammograms (LSVs) of the samples were collected, and as revealed in Figure 5a, the precursors Cu₂O/CuO/Cu@Ppy and Cu₂O/CuO@Ppy exhibited almost no ORR characteristics. However, the ORR performance of the three catalysts was greatly enhanced after the high-temperature heat treatment, probably due to the formation of more stable nitrogen-doped carbon after the high-temperature treatment of polypyrrole, which led to the improved conductivity of the catalysts and the formation of Cu-N ligands to excite the catalytic activity of the copper species [55–57]. The order of the ORR activity of the catalysts was as follows: Cu@NC-900 < CuO@NC-900 < 20 wt% Pt/C < Cu/CuO@NC-900, which was evident by an onset potential of 1.010 V (vs. RHE) and a half-wave potential of 0.868 V (vs. RHE) for Cu/CuO@NC-900, which were more positive than those of CuO@NC-900 (E_{onset} : 0.982 V vs. RHE, $E_{1/2}$: 0.830 V vs. RHE), Cu@NC-900 (E_{onset} : 0.915 V vs. RHE, $E_{1/2}$: 0.750 V vs. RHE), and even more positive than those of 20 wt% Pt/C (E_{onset} : 0.987 V vs. RHE, $E_{1/2}$: 0.845 V vs. RHE) (Figure 5a and Figure S21). As displayed in Figures S19a and S21, the onset potential and half-wave potential of the Cu/CuO@NC-900 were also higher than those of Cu/CuO@NC-800 (E_{onset} : 0.905 V vs. RHE, $E_{1/2}$: 0.740 V vs. RHE) and Cu/CuO@NC-1000 (E_{onset} : 0.940 V vs. RHE, $E_{1/2}$: 0.800 V vs. RHE). The normalized LSV curve of ORR with ECSA also suggested that the high ORR electrocatalytic activity of Cu/CuO@NC-900 was attributable to the abundant catalytic active sites and intrinsic catalytic activity (Figures S15–S17). Impressively, the excellent electrocatalytic ORR activity of Cu/CuO@NC-900 was comfortably ahead of those currently reported Cu-based electrocatalysts (Table S4). Next, in order to evaluate the reaction kinetics and corresponding mechanisms of Cu/CuO@NC-900, measurements at the rotating ring disc electrode (RRDE) were recorded at different speeds from 400 to 2500 rpm (Figure 5b), showing that the onset potential remained constant with increasing speed and that the limiting current density of the catalyst increased with increasing speed. The ORR kinetics of Cu/CuO@NC-900 can be further observed by the Koutecky–Levich curve inset in Figure 5b. The good linearity and parallelism between j^{-1} and $\omega^{-1/2}$ indicate that the number of electron transfers (n) per oxygen molecule at different potentials in the ORR was almost the same. The calculation of the K-L diagram gives an electron transfer number (n) of 3.95–3.98 for Cu/CuO@NC-900 between 0.4–0.70 V, which was close to the theoretical four-electron transfer pathway in the reduction of oxygen to OH[−], indicating a four-electron transfer pathway per oxygen molecule in the ORR. The Tafel plots can further reveal the ORR mechanism of the catalysts, and the Cu/CuO@NC-900 catalyst shows the smallest Tafel slope of 113 mV dec^{−1} (Figure 5b), which was smaller than the other catalysts (20 wt% Pt/C: 151 mV dec^{−1}, CuO@NC-900: 154 mV dec^{−1}, Cu@NC-900: 169 mV dec^{−1}, Cu/CuO@NC-800: 172 mV dec^{−1}, Cu/CuO@NC-1000: 157 mV dec^{−1}) (Figure 5b and Figure S19b), indicating that the Cu/CuO@NC-900 catalyst has the fastest electrochemical ORR reaction kinetics. The exchange current density (j_0) of Cu/CuO@NC-900 was 6.01 mA cm^{−2} at the same overpotential, which was higher than that of 20 wt% Pt/C (5.17 mA cm^{−2}), CuO@NC-900 (4.77 mA cm^{−2}), Cu/CuO@NC-1000 (4.49 mA cm^{−2}), Cu@NC-900 (4.05 mA cm^{−2}), and Cu/CuO@NC-800 (3.72 mA cm^{−2}) (Figures S18 and S20). The larger exchange current density of the Cu/CuO@NC-900 sample implies that this sample has the best ORR catalytic activity. In addition, the calculated electron transfer number (n) and hydrogen peroxide (H₂O₂%) yields were displayed in Figure 5d, and n for the Cu/CuO@NC-900 catalyst was ~3.98, which was in general agreement with the 20 wt% Pt/C catalyst (n = 3.97), and the H₂O₂% yield was lower than 3%, suggesting that the Cu/CuO@NC-900 catalyst follows an ideal four-electron transfer pathway. It can be inferred that the dissociation of O₂ on CuO occurs when the adsorption site consists of one copper atom and one O atom. Here, the d-electron-rich Cu, which forms a heterogeneous

structure with CuO, can effectively regulate the electron structure in CuO, which helps CuO to rapidly supply electrons to O₂, thus improving the ORR reaction kinetics [54,58,59].

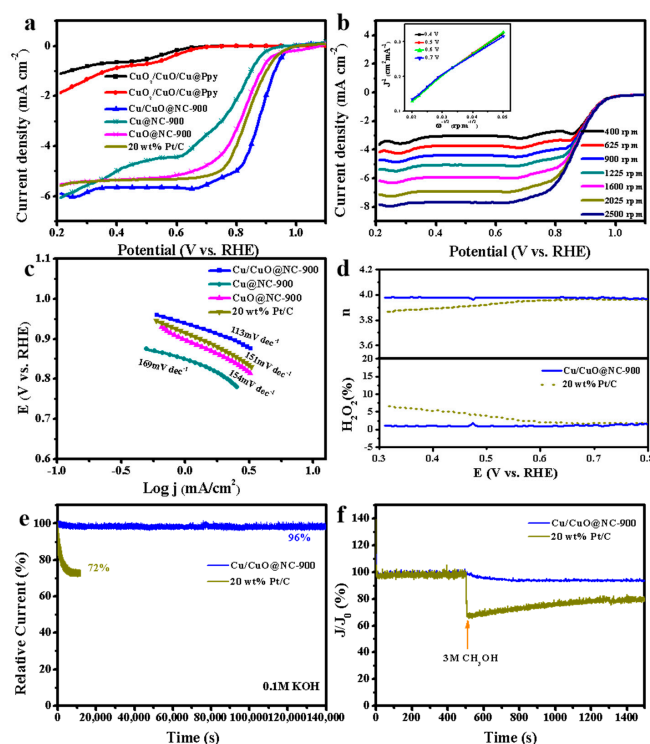


Figure 5. (a) RRDE curves of Cu₂O/CuO/Cu@Ppy, Cu₂O/CuO@Ppy, Cu/CuO@NC-900, Cu@NC-900, CuO@NC-900, and 20 wt% Pt/C at a sweep rate of 5 mV s⁻¹ and a rotation speed of 1600 rpm; (b) LSV curves of Cu/CuO@NC-900 catalyst at a sweep rate of 5 mV s⁻¹ and different rotation speeds ranging from 400 to 2500 rpm, and the Koutecky–Levich plots (insets); (c) the corresponding Tafel curves derived from (a); (d) electron transfer number *n* and H₂O₂ yield of Cu/CuO@NC-900 and commercial Pt/C; (e) current versus time (*i*-*t*) chronoamperometric response of the Cu/CuO@NC-900 and Pt/C at 0.7 V in O₂-saturated 0.1 M KOH at 200 rpm; (f) the stability evaluation for Cu/CuO@NC-900 and Pt/C catalysts in O₂-saturated 0.1 M KOH with the injection of 3 M methanol.

To estimate the stability of the catalysts in practical applications, the chronoamperometry test (*i*-*t*) at a constant current density of 4 mA cm⁻² as shown in Figure 5e further revealed the durable stability of Cu/CuO@NC-900; however, the 20 wt% Pt/C catalyst decreases in stability to 72% after 12,000 s. Microstructural analysis of the Cu/CuO@NC-900 catalyst after 140,000 s of stable operation was carried out, and it was observed that the nanoparticles' structure not only remained intact (Figure S22a,b), but also showed lattice stripes with a spacing of 0.232 nm and 0.208 nm in HRTEM (Figure S22c), which were the CuO (111) crystal plane and the (111) crystal plane of Cu, and there was still a strong interface between CuO and Cu. The results demonstrate that Cu/CuO@NC-900 has superior ORR catalytic activity and long-lasting stability. The catalyst tolerance to methanol was also particularly important in practical applications. As illustrated in Figure 5f, it was clear that after the addition of 10 mL of 3.0 M methanol solution to a 0.1 M KOH solution containing saturated O₂ at the 500 s, the performance of the 20 wt% Pt/C catalyst dropped dramatically with a rapid loss of current density approaching 30%. Nevertheless, the performance of the Cu/CuO@NC-900 catalyst quickly returned to normal levels after a brief, slight disturbance. This result indicates that Cu/CuO@NC-900 has good methanol tolerance performance. It was found that the catalytic activity of the sample was not almost decreased after the *i*-*t* test, further demonstrating the good methanol tolerance of Cu/CuO@NC-900.

3. Experimental

3.1. Chemicals and Reagents

Copper(II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, A.R.), ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$, A.R.), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, A.R.), pyrrole ($\text{C}_4\text{H}_5\text{N}$, C.P.), and potassium hydroxide (KOH, A.R.) were purchased from Sinopharm Group Chemical Reagent Co., Ltd., Beijing, China with no further purification. Nafion solution (5%) and platinum on activated carbon (20 wt% Pt/C) was purchased from Sigma-Aldrich. Highly purified water ($>18 \text{ M}\Omega \text{ cm}$ resistivity) was provided using a PALL PURELAB Plus system.

3.2. Synthesis of $\text{Cu}_2\text{O}/\text{CuO}@Ppy$

The $\text{Cu}_2\text{O}/\text{CuO}@Ppy$ hybrid was prepared by an improved hydrothermal method [41]. Generally, 0.2 g of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was dissolved in 40 mL of ultrapure water to form light blue solution A, and 69 μL of pyrrole was dissolved in 9.21 mL ultrapure water to form light yellow solution B. Subsequently, solution B was slowly dropped into solution A with continued stirring for 0.5 h to form the uniform mixed solution. The mixed solution was then transferred to a hydrothermal reactor lined with polytetrafluoroethylene and reacted at 160°C for 10 h. The generated product was filtered and washed alternately with alcohol and ultrapure water several times. The obtained samples were dried in a vacuum oven at 60°C for 12 h to result in the precursor $\text{Cu}_2\text{O}/\text{CuO}/\text{Cu}@Ppy$, which was quantitatively etched with 1 M sodium thiosulfate solution for 1 h. The as-prepared product was washed with ultrapure water and dried in an oven at 60°C for 12 h, denoted as $\text{Cu}_2\text{O}/\text{CuO}@Ppy$.

3.3. Synthesis of $\text{Cu}/\text{CuO}@NC$

The as-prepared $\text{Cu}_2\text{O}/\text{CuO}@Ppy$ was transferred into a porcelain boat, and then was calcined at 900°C for 2 h with a heating rate of $10^\circ\text{C min}^{-1}$ in an Ar atmosphere to obtain $\text{Cu}/\text{CuO}@NC$. For comparative studies, two more samples were prepared by altering the reaction temperature (800 and 1000°C) and keeping the rest of the synthetic conditions the same. The corresponding sample was denoted as $\text{Cu}/\text{CuO}@NC-x$ (x indicates the reaction temperature).

3.4. Synthesis of $\text{Cu}@NC$

The prepared $\text{Cu}_2\text{O}/\text{CuO}@Ppy$ was transferred into a porcelain boat and then kept under a mixed H_2/Ar atmosphere at 900°C for 2 h with a heating rate of $10^\circ\text{C min}^{-1}$, resulting in the $\text{Cu}@NC$ material.

3.5. Synthesis of $\text{CuO}@NC$

The prepared $\text{Cu}/\text{CuO}@NC$ sample was treated with 1 M sodium thiosulfate solution for 24 h and then washed several times with ultrapure water. Finally, the samples were dried at 60°C overnight to obtain $\text{CuO}@NC$.

3.6. Materials Characterization

XRD patterns of the material were collected with X-ray diffractometer (D/MAX-2200PC, Rigaku, Akishima-shi, Japan) within the range of $10\sim 80^\circ$, and Cu $K\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV was used for studying the phase and crystal structures of the catalysts (scan rate: $8^\circ/\text{min}$). The morphology and microstructure of the materials were observed via field emission scanning electron microscopy (SEM, S4800, Hitachi, Tokyo, Japan) and transmission electron microscope (TEM, FEI Tecnai G2 F20 S-TWIN, FEI, Hillsboro, USA). The Raman spectra were obtained using a Renishaw-in via a microscopic confocal laser Raman spectrometer with 532 nm as the excitation laser. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Surface Science Instruments Spectrometer with a monochromatic Al $K\alpha$ source.

3.7. Electrochemical ORR Measurements

Electrocatalytic oxygen reduction reaction (ORR) measurements were performed on the rotating disc electrode (RDE) or rotating ring disc electrode (RRDE) of the MSR electrode rotating device model AFMSRCE from RIKEN (Hong Kong) Ltd. A platinum counter electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively, during the test with 0.1 M KOH (pH = 13) as the electrolyte. Before the ORR test, a saturated O₂ electrolyte was required for measurements. All potentials needed to be calibrated to RHE according to the following equation: $E_{vs\ RHE} = E_{vs\ SCE} + 0.2415 + 0.059\ pH$, and the current density (J) was normalized to the geometrical area of the working electrode (0.2376 cm²). The electrochemical-activity-specific surface area (ECSA) was calculated by testing the electrochemical double-layer capacitance (electrochemical double-layer capacitance, C_{dl}) at different sweeps. The RRDE (rotating ring-disk electrode) was tested at 1600 rpm with a scan rate of 10 mV/s. The number of electron transfers (n) and the percentage of peroxide (HO₂[−]) were calculated according to the following equations:

$$n = 4 \times \frac{I_d}{I_d + I_r/N'} \quad (9)$$

$$HO_2^- \% = 200 \times \frac{I_r/N}{I_d + I_r/N'} \quad (10)$$

where I_d is the disk current and I_r is the ring current. The RRDE current collection efficiency N was 0.38.

4. Conclusions

In summary, a novel nanocomposite of heterogeneous Cu/CuO nanoparticles (Cu/CuO@NC-900) embedded within N-doped carbon nanosheets was successfully synthesized using a facile technique combining a hydrothermal route and a solid calcination technique. The excellent ORR performance of the resulting Cu/CuO@NC-900 material in alkaline media was mainly attributed to the promoted electronic interactions between Cu and CuO, the generated large number of highly reactive Cu-N_x active sites, and the high electrical conductivity of the N-doped carbon nanosheets. As expected, Cu/CuO@NC-900 not only has excellent ORR activity, but also maintains long-term durability, at least after 140,000 s of operation. These findings open up new avenues for the rational design and fabrication of efficient and stable noble-metal-free electrocatalysts for energy conversion and storage.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13020255/s1>, Figure S1: Color of (a) Cu/CuO@NC-900 sample and (b) unetched sample; Figure S2: XRD pattern of unetched sample; Figure S3: XRD patterns of Cu₂O/CuO@Ppy and Cu₂O/CuO/Cu@Ppy electrocatalyst; Figure S4: XRD patterns of CuO/Cu@NC-800, CuO/Cu@NC-900, and CuO/Cu@NC-1000 electrocatalysts; Figure S5: Raman spectra of CuO/Cu@NC-800, CuO/Cu@NC-900, and CuO/Cu@NC-1000 electrocatalysts; Figure S6: SEM images of Cu₂O/CuO/Cu@Ppy (a) and Cu₂O/CuO@Ppy (b); Figure S7: SEM images of Cu@NC-900 (a) and CuO@NC-900 (b); Figure S8: SEM images of Cu/CuO@NC-800 (a) and Cu/CuO@NC-1000 (b); Figure S9: TEM images of Cu₂O/CuO/Cu@Ppy (a) and Cu₂O/CuO@Ppy (b); Figure S10: TEM image in Cu/CuO@NC-900; S11: TEM image in Cu/CuO@NC-900; Figure S12: The survey XPS spectrum of CuO/Cu@NC-900 electrocatalyst; Figure S13: The survey XPS spectra of Cu@NC-900 and CuO@NC-900 electrocatalysts; Figure S14: The contents of pyridinic N, Cu-N, pyrrolic N, graphitic N, and oxidized N (obtained from XPS) of CuO@NC-900, Cu@NC-900, and CuO/Cu@NC-900 electrocatalysts; Figure S15: (a) CV curves measured by different sweeps of Cu/CuO@NC-900, (b) Cu@NC-900, (c) CuO-900, and CuO@NC-900 and (d) 20 wt% PtC in saturated N₂ alkaline electrolyte; Figure S16: Current density slope curve (Cdl fit line) for Cu/CuO@NC-900, Cu@NC-900, CuO@NC-900, and 20 wt% PtC catalysts; Figure S17: LSVs normalized by ECSA of ORR under alkaline conditions; Figure S18: Exchange current densities of Cu/CuO@NC-900, Cu@NC-900, CuO@NC-900, and 20 wt% Pt/C in alkaline electrolyte saturated with oxygen; Figure S19: (a) RRDE curves of Cu/CuO@NC-800, Cu/CuO@NC-900, and Cu/CuO@NC-1000 at a sweep rate of 5 mV^{−1} and a

rotation speed of 1600 rpm; (b) the corresponding Tafel curves derived from (a); Figure S20: Exchange current densities of Cu/CuO@NC-800, Cu/CuO@NC-900 and Cu/CuO@NC-1000 in alkaline electrolyte saturated with oxygen; Figure S21: Onset potential (Eonset) and half-wave potential (E1/2) plots of Cu/CuO@NC-900, CuO@NC-900, Cu@NC-900, Cu/CuO@NC-800, Cu/CuO@NC-1000, and 20 wt% Pt/C in O₂-saturated 0.1 M KOH solution with a rotation speed of 1600 rpm and a sweep rate of 10 mV/s; Figure S22: (a–c) TEM image of Cu/CuO@NC-900 after maintaining ORR stability for 140,000 s in 0.1 M KOH solution; Figure S23: LSV curves of Cu/CuO@NC-900 before and after i–t test for methanol tolerance; Table S1: The strongest peak properties of Cu/CuO@NC-900 and Cu@NC-900; Table S2: The strongest peak properties of Cu/CuO@NC-900 and CuO@NC-900; Table S3: Analytical results of elemental content in the prepared catalysts determined by XPS; Table S4: Electrocatalytic ORR performance of the Cu/CuO@NC-900 electrode compared with that of reported Cu-based electrocatalysts in KOH electrolyte.

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Data Availability Statement: Data available on request from the authors. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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