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Copper- and Nitrogen-Codoped Graphene with Versatile Catalytic Performances for Fenton-Like Reactions and Oxygen Reduction Reaction

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Abstract: Copper- and nitrogen-codoped reduced graphene oxide material (Cu/N-rGO) was prepared with a hydrothermal method. Its versatile catalytic performances were demonstrated toward the oxidative degradation of rhodamine B (RhB) and oxygen reduction reaction (ORR). The Cu and N codoping of graphene enhanced not only its activation ability toward H_2O_2 , but also its electrocatalytic ability for ORR. It was observed that the use of 3%Cu/N-rGO together with $40 \text{ mmol}\cdot\text{L}^{-1} \text{H}_2\text{O}_2$ and $4 \text{ mmol}\cdot\text{L}^{-1} \text{Na}_2\text{CO}_3$ could remove more than 94% of the added RhB ($30 \text{ mg}\cdot\text{L}^{-1}$) in 20 min through a catalytic Fenton-like degradation. Quenching experiments and electron paramagnetic resonance (EPR) measurements indicated that the main reactive species generated in the catalytic oxidation process were surface-bound $\cdot\text{OH}$. The modified graphene also showed good electrocatalytic activity for ORR reaction in alkaline media through a four-electron mechanism. On the electrode of Cu/N-rGO, the ORR reaction exhibited an onset potential of -0.1 V and a half-wave potential of -0.248 V , which were correspondingly close to those on a Pt/C electrode. In comparison with a Pt/C electrode, the 3%Cu/N-rGO electrode showed much greater tolerance to methanol. Such outstanding catalytic properties are attributed to the abundant active sites and the synergism between Cu and N in Cu/N-rGO.

Keywords: Cu–N-codoped graphene; versatile catalyst; oxidative degradation; oxygen reduction reaction

1. Introduction

Due to serious challenges from environmental pollution and energy shortages, various catalysts have been developed to enhance the related pollutant degradation reactions and energy conversion reactions, especially for Fenton-like reactions, and hydrogen evolution and oxygen reduction reactions [1–5]. Typical investigations are focused on the designs of heterogeneous catalysts with high catalytic activity and selectivity by using noble metals (Pt and Au) [6,7], metal oxides (Fe_3O_4 and $\text{ZnO}/\text{Co}_3\text{O}_4$) [8,9], and metal nitrides [10]. These catalysts may have the demerits of either high cost (due to noble metals) or poor durability (due to the less noble metals), which are unfavorable to their large-scale deployment. To overcome this problem, it is interesting and important to develop carbon-based versatile catalysts that have good catalytic performances for both the Fenton-like reactions (in the field of environmental chemistry) and electrochemical oxygen reduction reaction (in the field of energy chemistry).

In fact, carbon-based catalytic materials have recently attracted much attention, such as carbon nanotubes (CNTs) [11,12], graphene [13,14], graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [15–17], and carbon

nanospheres [18,19]. For example, Peng et al. [11] illustrated that CNTs could effectively accelerate the decomposition of H_2O_2 via a nonradical activation mechanism. Kannan and Kumar [13] reviewed the current status in the design and development of graphene-based oxygen reduction reaction (ORR) catalysts for microbial fuel cell applications. Cui et al. [15] demonstrated a g- C_3N_4 catalyst that activated H_2O_2 to generate reactive hydroxyl radicals and had good Fenton-like catalytic performance in the visible-light-driven degradation of contaminants. Mahajan et al. [18] developed a grape-like carbon nanosphere as photocatalyst and electrocatalyst, which activated the formation of oxidizing radical species under UV-light irradiation and exhibited excellent electrocatalytic activity, respectively. Heteroatom doping of metal (Fe, Cu, Co) or non-metal (N, S, B) in carbon may also enhance the catalytic performances [2,20–24]. The N atom, as an electron donor, provides electron carriers and decreases the band gap energy, which is used to dope into carbon [21,23,25]. The N-doped carbon catalysts are applied to the field of catalysis. Wang et al. [23] developed N-doped graphene as Fenton-like catalysts, which efficiently catalyze the activation of persulfates for the destruction of organic contaminants. Qu et al. [25] reported N-doped graphene as metal-free electrodes for ORR, which presented much better electrocatalytic activity. Another way of improving the catalytic performances of carbon is to fabricate composites of carbon with other components. Tang and Wang used Fe_3O_4 /multiple-walled carbon nanotubes(MWCNT) composites to activate H_2O_2 for the degradation of sulfamethazine, in which MWCNTs have a rich surface area for adsorbing pollutants and for the circulation of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ [26]. These authors also fabricated the Fe@MesoC catalyst that the Fe-based magnetic nanoparticles embedded into mesoporous carbon [27]. The Fe@MesoC catalyst exhibited enhanced catalytic activity for sulfamethoxazole degradation.

In the doping of carbon-based materials, there are few reports on the codoping by both a metal atom and a non-metal atom. We investigated well the N-doped graphene as a Fenton-like catalyst [23], and observed the strong effect of Cu species on the catalytic performances of carbon- and non-carbon-based substrates [28–31]. Furthermore, previous reports suggested that some M–N/C catalysts showed better catalytic activity and stability than those containing only a single metal [5,31–33]. As an extension of our previous investigations, we aimed to develop a Cu-containing nitrogen-doped carbon composite as a versatile catalyst. In this carbon-based catalyst (Cu/N-rGO), the doping of heteroatoms N into reduced graphene oxide (rGO) can be useful to trap and bond the Cu atoms, constructing the nitrogen-coordinated copper; and the transition metal related to Lewis acid could be prone to bind with N (Lewis base) to form a strong M–N coordination coupled with carbon, forming double active sites. By investigating its catalytic performances toward the degradation reaction and ORR, it was found that the 3%Cu/N-rGO catalyst could not only efficiently catalyze the degradation of rhodamine B by H_2O_2 , but also provide the electrochemical catalytic ability for ORR being close to that of the traditional Pt-C electrocatalyst.

2. Results and Discussion

2.1. Characterizations of Cu/N-rGO

The morphologies of 3%Cu/N-rGO and 100%Cu/N-rGO were observed by transmission electron microscopy (TEM). As shown in Figure 1a, 3%Cu/N-rGO exhibited intrinsic graphene structures, which were composed of crumpled wave-like layers. It was evident that no copper species particles were observed due to its low-content Cu doping. Even at high magnification (5 nm), no lattice fringes from Cu particles were observed (Figure 1b). When the doping content of Cu was increased, the TEM image of 100%Cu/N-rGO in Figure 1c clearly reveals that CuO particles were dispersed on the surface of the graphene. The elemental mapping images (Figure 1d–h) confirm that the 3%Cu/N-rGO catalyst consisted of four elements, i.e., oxygen, carbon, nitrogen, and copper. The evenly distributed strong signals of Cu and N suggested that both copper and nitrogen were successfully doped in the 3%Cu/N-rGO material.

Figure 1. TEM images of (a,b) 3%Cu/N-rGO and (c) 100%Cu/N-rGO. (d) High angular annular dark field image and elemental mapping images of (e) oxygen, (f) carbon, (g) nitrogen, and (h) copper elements of 3%Cu/N-rGO.

The X-ray diffraction (XRD) patterns of rGO, N-rGO, 3%Cu/N-rGO, and 100%Cu/N-rGO are shown in Figure 2a. For all samples, two distinct characteristic peaks of the graphite (002) plane at $2\theta = 26.5^\circ$ and (100) plane at $2\theta = 43^\circ$ were observed, which demonstrated the graphitic crystal structure. However, no copper-based characteristic peaks were detected in the patterns of the 3%Cu/N-rGO sample, due to the low Cu content, poor crystallinity of Cu-based compounds, and/or the formation of Cu-N. For 100%Cu/N-rGO, new reflection peaks at 35.6° and 38.9° can be indexed to the (−111) and (111) planes of CuO (JPCDS card no. 45-0937), indicating the presence of CuO species. This was consistent with the TEM observation.

Figure 2b shows the Raman spectra of rGO, N-rGO, 3%Cu/N-rGO, and 100%Cu/N-rGO. In all the spectra, there were two peaks at around 1350 cm^{-1} and 1603 cm^{-1} , corresponding to the D band and G band of graphene, respectively [23]. In comparison with the I_D/I_G value of rGO (1.55), the values of N-rGO, 3%Cu/N-rGO, and 100%Cu/N-rGO were decreased to 1.11, 1.08, and 1.10, respectively, due to the incorporation of N and Cu atoms. This suggested the formation of the increased number of hopping defects in the graphene layers. The increased number of defect sites can be beneficial to the enhancement of the catalytic activity.

To obtain the specific surface area of rGO, N-rGO, 3%Cu/N-rGO, and 100%Cu/N-rGO, we measured the adsorption–desorption isotherms of N_2 (Figure S1). It was found that the pore sizes distribute mainly in the range of 2–20 nm. The specific surface area of 3%Cu/N-rGO ($425.21\text{ m}^2\cdot\text{g}^{-1}$) was larger than that of N-rGO ($398.05\text{ m}^2\cdot\text{g}^{-1}$), 100%Cu/N-rGO ($186.45\text{ m}^2\cdot\text{g}^{-1}$), and rGO ($177.98\text{ m}^2\cdot\text{g}^{-1}$) (Table S1). The specific surface area declined when the doping context of Cu was 100%, which may be because the CuO species anchored onto the surface of 100%Cu/N-rGO.

Figure 2. (a) XRD patterns and (b) Raman spectra of rGO, N-rGO, 3%Cu/N-rGO, and 100%Cu/N-rGO.

The X-ray photoelectron spectroscopy (XPS) was applied to analyze the surface chemical state of rGO, N-rGO, and 3%Cu/N-rGO, as shown in Figure 3a. From the survey scan of 3%Cu/N-rGO, it can be seen that the 3%Cu/N-rGO catalyst contained four kinds of elements, i.e., carbon (70.85%), oxygen (21.84%, Table S2), nitrogen (6.70%), and copper (0.61%). Apparently, the metallic Cu signal was very weak, and the content was only 0.61%. The C 1s spectra (Figure 3b) of rGO, N-rGO, and 3%Cu/N-rGO could be deconvoluted into the following bands: C=C/C–C (284.38 eV), C=N/C–OH (285.6 eV), epoxy C–O–C (286.7 eV), C=O/C–N (288.9 eV), and O–C=O (291.5 eV), respectively [23,34]. Similarly, the N 1s XPS spectra of 3%Cu/N-rGO (Figure 3c) could be deconvoluted into three peaks around 398.3 eV, 400.0 eV, and 401.2 eV, which were attributed to pyridinic-type N (47.31%, Table S3), pyrrolic-type N (31.54%), and graphitic-type N (6.76%), respectively [23,35]. In addition, there was a particular additional peak at 399.2 eV, which was ascribed to the Cu-coordinated nitrogen (14.39%) [35,36]. The high ratio of pyridinic N (47.31%, Table S3) in 3%Cu/N-rGO could enhance the ORR activity as compared to that of N-rGO (43.10%) [10]; meanwhile, the Cu-coordinated nitrogen could provide new active sites. In the Cu 2p XPS spectrum in Figure 3d, the main peak between 932.1 and 934.5 eV was similar to the values previously reported [36,37], which demonstrated that the valence states of the Cu species in 3%Cu/N-rGO was situated between Cu⁰ and Cu²⁺. This result indicated that the Cu^{δ+} (0 < δ < 2) nature of the Cu-coordinated nitrogen was dominant on the surface of the Cu species, which conforms with previous literature [38,39].

2.2. H₂O₂ Activation Catalyzed by Cu/N-rGO for the Oxidative Degradation of Rhodamine B (RhB)

In our previous work [23], we explored the persulfate activation ability of N-rGO toward the oxidative degradation of organic pollutants. As a green oxidizing agent, H₂O₂ is superior to persulfate because the activation of the latter disposes of unfavorable sulfates into the natural environment. Therefore, we investigated the H₂O₂ activation catalyzed by 3%Cu/N-rGO toward the oxidative degradation of RhB. Figure 4a displays the removal of RhB in different systems. It was certain that under the tested conditions the total removal of RhB was contributed to from both the pre-adsorption and the followed degradation. There was no adsorption capacity in the system of H₂O₂ and H₂O₂ + Na₂CO₃. After adding the catalysts, the adsorption capacity (Figure 4b) of these samples followed the order 3%Cu/N-rGO (345 mg·g^{−1}) > N-rGO (232 mg·g^{−1}) > rGO (208 mg·g^{−1}). Therefore, the doping N and Cu improved the pre-adsorption capacity of RhB on rGO, which may be attributed to more active sites and a larger specific surface area (as confirmed in Figure S1). After the pre-adsorption, the oxidative degradation of RhB was started by adding H₂O₂. In the absence of any catalyst, the degradation removal of RhB in 20 min was only 3% by adding 40 mM H₂O₂, and it was increased slightly to 13% by

co-adding 4 mM Na_2CO_3 . The enhancement induced by the introduction of Na_2CO_3 may be attributed to the greater number of free radicals originating from the interaction between CO_3^{2-} and $\bullet\text{OH}$ [40,41]. This result was consistent with previous reports that carbonates may enhance the degradation of organic pollutants [40,42]. When N-rGO was used as the catalyst system in the presence of H_2O_2 and Na_2CO_3 , RhB was partly degraded, giving a corresponding total RhB removal of 47%. Surprisingly, the RhB removal efficiency was increased to be more than 94% when 3%Cu/N-rGO was introduced. This improved activation performance may be ascribed to the increased number of defect sites and the synergism between Cu and N doped in Cu/N-rGO. The transition metal related to Lewis acid can be prone to bind with N (Lewis base) to form a strong M-N coordination coupled with carbon, which contributes to excellent catalytic activity. The nature of the metal-nitrogen species (M-N_x) resulted in an irregular charge distribution and distribution [20,43,44], which ameliorated the RhB adsorption and degradation. Moreover, the transition metal provided new active sites, which was beneficial to the catalytic activation because of its vacant 3D orbital and variable valence state [27].

Figure 3. (a) Wide survey XPS spectra of rGO, N-rGO, and 3%Cu/N-rGO; (b) C 1s spectra of rGO, N-rGO and 3%Cu/N-rGO; (c) N 1s spectra of N-rGO and 3%Cu/N-rGO; (d) Cu 2p of 3%Cu/N-rGO.

Figure 4. (a) Adsorption and degradation of RhB in different systems: H_2O_2 , $H_2O_2 + Na_2CO_3$, $rGO + H_2O_2 + Na_2CO_3$, $N-rGO + H_2O_2 + Na_2CO_3$, and $3\%Cu/N-rGO + H_2O_2 + Na_2CO_3$. (b) Adsorption kinetics of RhB on rGO , $N-rGO$, and $3\%Cu/N-rGO$.

Figure 5 gives the effects of various reaction parameters (Cu load, H_2O_2 concentration, Na_2CO_3 concentration, and temperature) on the adsorption and degradation of RhB over $Cu/N-rGO$, where the insets are the dependence of the apparent rate constant of RhB degradation on the specified reaction parameter. In order to know the practical Cu load in the different catalysts, we determined that the actual Cu -doping contents of the $Cu/N-rGO$ samples were obtained by the atomic absorption spectroscopy, as listed in Table S4. From Figure 5a, it was found that the total removal of RhB in 20 min was increased from 43% for $N-rGO$ (zero Cu load) to 67%, 79%, and 94% for Cu -loading amounts of 0.5, 1.0, and 3.0 wt.%, respectively. The differences in the total RhB removal observed between the various $Cu/N-rGO$ catalysts were mainly attributed to the effect of the Cu content on the catalytic degradation of RhB. Because the degradation rate in the initial time period (0–1 min) was very fast, we used only the experimental data in the initial one minute to fit with the pseudo first-reaction kinetic model. The calculated rate constant (k) in the oxidation stage was increased from 0.11 for undoping condition to 0.16, 0.25, and $0.27\ min^{-1}$ for Cu -adding amounts of 0.5, 1.0, and 3.0 wt.%. When the Cu -loading amount was increased to 100 wt.%, the RhB oxidative degradation was not significantly enhanced in relation to 3% $Cu/N-rGO$, and the apparent rate constant was only about $0.33\ min^{-1}$. The above results confirmed that the degradation performance of RhB was best when the Cu -loading amount was 3.0 wt.%. The good performance of 3% $Cu/N-rGO$ was attributed to the moderate coordination of copper and nitrogen atoms, and then the formation of $Cu-N_x$ (2 or 4) active sites that exhibited the strong Lewis acid–base interaction [37,45].

The effect of the initial concentration of H_2O_2 for RhB degradation in the 3% $Cu/N-rGO$ system was studied, as shown in Figure 5b. With increasing H_2O_2 concentrations from 5.0 mM to 40.0 mM, the degradation efficiency improved from 73% to 94% and the k value increased from 0.19 to $0.27\ min^{-1}$. The enhanced efficiency can be attributed to the greater generation of radical species at higher H_2O_2 concentrations. The use of 60 mM H_2O_2 did not further increase the degradation efficiency with a k value of $0.25\ min^{-1}$. This was due to insufficient catalytic sites and self-quenching of the generated superfluous $\bullet OH$. The performance of the 3% $Cu/N-rGO$ catalyst and the values in the previous articles are shown in Table S5.

Figure 5. Effects of different reaction parameters on the adsorption and degradation of RhB over Cu/N-rGO: (a) Cu load, (b) H_2O_2 concentration, (c) Na_2CO_3 concentration, and (d) temperature. The insets give the dependence of the apparent rate constant of RhB degradation on the specified reaction parameter.

Figure 5c displays the effect of Na_2CO_3 on the catalytic degradation of RhB. It was easily observed that the k value increased from 0.19 to 0.27 min^{-1} with the increasing Na_2CO_3 concentrations from 0 to 4 mM, but the addition of 8 mM Na_2CO_3 induced little further enhancement of the RhB degradation. It seemed that 4 mM Na_2CO_3 was optimal. This was explained by the fact that the co-existence of the H_2O_2 molecules and carbonate radicals resulted in the generation of $\text{CO}_3^{\bullet-}$, which triggered a series of reactions to generate other radicals (including the superoxide ion and singlet oxygen) for pollutant degradation as suggested by the equations below [40,41], involving the following reactions:

The degradation of RhB over 3%Cu/N-rGO was investigated at temperatures in the range of 10–55 °C, as shown in Figure 5d. The k value was roughly linearly increased from 0.24 min^{-1} to 0.36 min^{-1} with increasing temperatures from 10 °C to 55 °C. The activation energy (E_a) of the degradation of RhB in the 3%Cu/N-rGO- H_2O_2 - Na_2CO_3 system was calculated according to the Arrhenius equation of $\ln k = \ln A - E_a/RT$, where R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}$). The E_a value was obtained as $6.93 \text{ kJ}\cdot\text{mol}^{-1}$, indicating the high catalytic activity of 3%Cu/N-rGO.

It was reported $\bullet\text{OH}$, $\bullet\text{O}_2^-/\text{HO}_2^\bullet$, and singlet oxygen ($^1\text{O}_2$) could be generated to the reactive oxygen species for RhB in the H_2O_2 - Na_2CO_3 system. To determine the main free radicals for determining the degradation process, electron paramagnetic resonance (EPR) and quenching experiments were carried out. Figure 6a displays the EPR spectra of the tested catalytic system, which were typical for TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)- $^1\text{O}_2$, DMPO ($5,5$ -dimethyl-1-pyrroline N-oxide)- $\bullet\text{OH}$, and DMPO- $\bullet\text{O}_2^-/\text{HO}_2^\bullet$. Strong characteristic peaks of DMPO- $\bullet\text{OH}$ were detected, but the signals for DMPO- $\bullet\text{O}_2^-/\text{HO}_2^\bullet$ were weak and no signals were observed for TEMPO- $^1\text{O}_2$. This suggested that $\bullet\text{OH}$ was primarily important in the degradation process. Furthermore, thiourea, benzoquinone, and NaN_3 were used as the radical scavenger for $\bullet\text{OH}$, $\bullet\text{O}_2^-/\text{HO}_2^\bullet$, and ($^1\text{O}_2$) [46,47], respectively. According to Figure 6b, the RhB degradation was inhibited significantly after adding thiourea, and the removal was decreased from 94% to 53.6%. When benzoquinone or NaN_3 was used as the radical scavenger in the 3%Cu/N-rGO/ H_2O_2 / Na_2CO_3 system, the degradation efficiency declined slightly as compared with that without adding any radical scavenger. This result illustrated that the dominant free radical was $\bullet\text{OH}$ rather than $\bullet\text{O}_2^-/\text{HO}_2^\bullet$ and $^1\text{O}_2$ during the catalysis process, which was consistent with the reported literature [48].

Figure 6. (a) Electron paramagnetic resonance (EPR) spectra in the systems for the degradation of RhB over Cu/N-rGO, being trapped as typical DMPO- $\bullet\text{O}_2^-/\text{HO}_2^\bullet$, DMPO- $\bullet\text{OH}$, and TEMPO- $^1\text{O}_2$. (b) Effect of quenching agents on the adsorption and degradation of RhB for 3%Cu/N-rGO.

2.3. Electrocatalytic Performance of Cu/N-rGO

The electrocatalytic activity of 3%Cu/N-rGO for the ORR was evaluated with cyclic voltammetry (CV), which was conducted in 0.1 M KOH at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. As shown in Figure 7a,b, the obtained cyclic voltammogram of N-rGO and 3%Cu/N-rGO in the N_2 -saturated solution was typically capacitive without an observable electrocatalytic active reaction occurring in the potential window from -1.0 to 0.2 V (vs. Ag/AgCl). However, both the electrodes of N-rGO and 3%Cu/N-rGO exhibited an obvious oxygen reduction peak around -0.285 V in the O_2 -saturated electrolyte, and the peak current ($0.7 \text{ mA}\cdot\text{cm}^{-2}$) on 3%Cu/N-rGO was more than two times ($0.26 \text{ mA}\cdot\text{cm}^{-2}$) that on N-rGO. This was indicative of an excellent ORR electrocatalytic activity of 3%Cu/N-rGO. To further support the result, we compared the linear sweep voltammetry (LSV) of rotating disk electrodes (RDEs) of 3%Cu/N-rGO and other materials including Pt/C at a rotation rate of 2500 rpm in O_2 -saturated

0.1 M KOH. As shown in Figure 7c, these catalysts gave onset potentials (E_{onset}) in the order of Pt/C (-0.086 V) > 3%Cu/N-rGO (-0.1 V) > 100%Cu/N-rGO (-0.143 V) > N/rGO (-0.146 V) > rGO (-0.178 V), half-wave potentials ($E_{1/2}$) in the order of Pt/C (-0.163 V) > 3%Cu/N-rGO (-0.248 V) > rGO (-0.31 V) > 100%Cu/N-rGO (-0.351 V) > N/rGO (-0.365 V), and limiting current density in the order of 3%Cu/N-rGO (-6.83 mA·cm $^{-2}$) > Pt/C (-6.34 mA·cm $^{-2}$) > 100%Cu/N-rGO (-5.18 mA·cm $^{-2}$) > N/rGO (-4.78 mA·cm $^{-2}$) > rGO (-3.34 mA·cm $^{-2}$). These results were close to or higher than the values previously reported in the literature (Table S6). It should be mentioned that both the much higher limiting current density and more positive onset potential (and half-wave potential) of 3%Cu/N-rGO proved that the electrocatalytic activity of 3%Cu/N-rGO was much better than 100%Cu/N-rGO, rGO, and N-rGO, and very close to that of Pt/C, indicating that the existence of Cu species played a key role in the catalytic activity. Such outstanding catalytic properties may be attributed to the abundant active sites and the synergism between Cu and N in the Cu/N-rGO.

Figure 7. Cyclic voltammetry (CV) curves of (a) 3%Cu/N-rGO and (b) N-rGO in N_2 -saturated and O_2 -saturated in 0.1 M KOH. (c) Linear sweep voltammetry (LSV) curves of the rotating electrodes of rGO, N/rGO 3%Cu/N-rGO, 100%Cu/N-rGO, and 20% Pt/C at 2500 rpm. (d) LSV curves of 3%Cu/N-rGO at different rotating rates (inset: corresponding Koutecky–Levich plots). (e) Tafel plots of 3%Cu/N-rGO and commercial 20 wt% Pt/C in O_2 -saturated 0.1 M KOH at a scan rate of 10 mV·s $^{-1}$. (f) Current–time (I–t) curves of Cu–N/C and Pt/C at 0.55 V in 0.1 M KOH after addition of 10 mL methanol.

The kinetics of ORR reaction pathways of various catalysts were studied by LSV. The LSV curves (Figure 7d) of the 3%Cu/N-rGO catalyst illustrated that the current densities were increased with the increasing rotation speed, which was due to the increased mass transport, considering a kinetics-controlled process of ORR. As a comparison, the LSV data of rGO, N-rGO, 100%Cu/N-rGO, and Pt/C are plotted in Figure S2. The corresponding Koutecky–Levich (K–L) plots showed nearly parallel fitting lines (inset of Figure 7d), validating that the transferred electron numbers per oxygen molecule in ORR were almost the same. The electron transfer number (n) of 3%Cu/N-rGO was calculated to an average value of 4.04, indicating a better selectivity of the $4e^-$ pathway to directly reduce O_2 to H_2O . However, the corresponding values (insets of Figure S2a,b) of rGO and N-rGO were 1.51 and 2.16, respectively, suggesting the presence of a less efficient $2e^-$ pathway. For both 100%Cu/N-rGO and Pt/C, the electron transfer number (insets of Figure S2c,d) was close to 4. However,

the catalysis ability of 100%Cu/N-rGO decreased greatly compared with 3%Cu/N-rGO, due to the existence of CuO species.

Figure 7e presents the Tafel plots of 3%Cu/N-rGO and 20 wt% Pt/C. The Tafel slope value for the 3%Cu/N-rGO catalyst was calculated to be $84.31 \text{ mV}\cdot\text{dec}^{-1}$, which was very close to that of Pt/C ($84.1 \text{ mV}\cdot\text{dec}^{-1}$). This demonstrated that it was easy to drive a larger catalytic current density at a lower overpotential and had a favorable electron transfer kinetics. In a methanol fuel cell, methanol may permeate from the anode to the cathode, leading to the poisoning and deactivation of the cathode catalyst. The durability of 3%Cu/N-rGO was evaluated by chronoamperometric measurements into 0.1 M KOH. As observed in Figure 7f, the 3%Cu/N-rGO catalyst still retained 97.5% of its original current after methanol (AR, 99.5%) injection, whereas the 20%Pt/C displayed a dramatic decline (current loss of 23.9%), illustrating the superior tolerance toward methanol of 3%Cu/N-rGO comparable to that of 20%Pt/C. The result was higher than the values previously reported in the literature (Table S6).

3. Materials and Methods

3.1. Reagents and Materials

Rhodamine B (RhB), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2 , 30 wt.%), Na_2CO_3 (99.8%), NaNO_3 , $\text{NH}_3\cdot\text{H}_2\text{O}$ (30%), KMnO_4 , and H_2SO_4 (98%) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphite powder was purchased from American Bay Carbon (Bay City, MI, USA). All the reagents were chemical grade or higher and used without further purification.

3.2. Preparation of the Cu/N-rGO Catalyst

Graphene oxide (GO) was prepared according to a modified Hummers method (see Supplementary Materials for more details) [23,49], and the GO suspension was obtained by dispersing GO in deionized water. Typically, a 12.5 mL portion of GO ($4 \text{ mg}\cdot\text{mL}^{-1}$) suspension was added to 32.5 mL of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ aqueous solution. Afterward, the mixture was treated by ultrasonication for 30 min. Then, 5 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ were added with magnetic stirring. The mixture was then transferred into a 100 mL Teflon-lined autoclave and heated at 180°C for 6 h. Subsequently, the black precipitates were filtrated and washed with distilled water several times. Finally, the product was dispersed in water as Cu/N-rGO dispersions. N-rGO and rGO samples were similarly prepared in the absence of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ and/or $\text{NH}_3\cdot\text{H}_2\text{O}$, respectively. In the present work, the Cu/N-rGO catalysts were referred to as $x\%\text{Cu/N-rGO}$, where x represented the Cu^{2+}/GO mass ratio.

3.3. Characterizations

The morphology and the element distribution of the catalysts were characterized by transmission electron microscopy (TEM, FEI Tecnai G2 F20, Hillsboro, TX, USA) and energy-dispersive spectroscopy (EDS) (Fei company, Hillsboro, TX, USA). X-ray diffraction (XRD) was applied to obtain the crystal structure by using an X-ray diffractometer (Bruker D8 Advance, Thermo Fisher Technology Co., Ltd, Walsham, MA, USA) under the condition of Cu K_α irradiation with operating voltage and current of 40 kV and 40 mA. The surface chemical composition and valence state were analyzed with X-ray photoelectron spectroscopy (XPS) on a VG Multilab 2000 spectrometer (Thermo Fisher Technology Co., Ltd, Walsham, MA, USA) with Al K_α radiation (300 W). Raman spectra were obtained on a Thermo Fisher DXR Raman spectrometer (Thermo Fisher Technology Co., Ltd, Walsham, MA, USA) with laser power (532 nm). The free radicals in the $\text{DMPO}\cdot\text{OH}$, $\text{DMPO}\cdot\text{O}_2^-/\text{HO}_2^\bullet$, and $\text{TEMPO}\cdot\text{O}_2^-$ systems were trapped by electron paramagnetic resonance (EPR) spectra (Bruker, Beijing, China).

3.4. Adsorption and Degradation Experiments

The adsorption and catalytic degradation experiments were carried out in a 100 mL beaker at 298 K. The given amount of Cu/N-rGO (40 mg/L) was added to 50 mL solution of RhB (30 mg/L), and the

dispersion was magnetically stirred for 16 min to achieve the adsorption/desorption equilibrium between the solution and the Cu/N-rGO solid. Then, a specified amount of $\text{H}_2\text{O}_2 + \text{Na}_2\text{CO}_3$ was added to the above suspension to initiate the degradation. Afterward, aliquots (1 mL) were sampled at given time intervals and centrifuged by using an EBA-21 centrifuge (13000 rpm) to remove Cu/N-rGO. The RhB concentration in the supernatant was determined by monitoring its absorbance at $\lambda_{\text{max}} = 554 \text{ nm}$ on a Cary 60 UV-VIS spectrophotometer (Agilent, Palo Alto, CA, USA).

3.5. Electrochemical Measurements

The electrocatalytic activity of Cu/N-rGO for ORR was investigated at room temperature by using a CHI 660A electrochemical station with a standard three-electrode system consisting of a rotating disk electrode with a geometric area of 0.196 cm^2 coated with the catalyst, a Ag/AgCl reference electrode (saturated with 1 M KOH), and a Pt foil counter electrode. The primary catalyst ink was prepared by dispersing 5 mg of Cu/N-rGO into 5 mL of N, N-dimethylformamide (DMF) within 50 μL of 5% naphthol. The as-obtained ink was coated onto the disk electrode, yielding a catalyst loading of $0.1 \text{ mg}\cdot\text{cm}^{-2}$. The ORR reaction of the catalyst was investigated by cyclic voltammetry (CV) in the N_2/O_2 -saturated 0.1 M KOH electrolyte solution, with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. Linear sweep voltammetry (LSV) curves were measured at various rotating speeds, with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ under O_2 condition. The stability of the catalysts was also evaluated by acquiring current–time (I–t) curves at 0.55 V in O_2 -saturated 0.1 M KOH solution.

4. Conclusions

A versatile catalyst of Cu- and N-codoped graphene was synthesized by a hydrothermal process. The Cu load in the catalyst and several other parameters were optimized in terms of the catalytic activity. It was confirmed that the 3%Cu/N-rGO catalyst showed superior catalytic activity in the H_2O_2 - Na_2CO_3 system. Its use achieved a total removal of 94% of the added RhB within 20 min with an apparent degradation rate constant of 0.27 min^{-1} . Furthermore, the 3%Cu/N-rGO catalyst was applied to oxygen reduction reaction, and displayed a four-electron pathway and excellent tolerance to methanol in ORR. The better catalytic and ORR performances were attributed to the abundant active sites and the synergism between Cu and N in the Cu/N-rGO.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/11/1326/s1>; Table S1: Specific surface area and pore diameter of rGO, N-rGO, 3%Cu/N-rGO, and 100%Cu/N-rGO. Table S2: Elemental compositions of rGO, N-rGO, and 3%Cu/N-rGO catalysts determined by XPS. Table S3: Relative percentage of N species for N-rGO and 3%Cu/N-rGO catalysts. Table S4: The actual Cu-doping contents of 0.5%Cu/N-rGO, 1.0%Cu/N-rGO, 3.0%Cu/N-rGO, and 100%Cu/N-rGO from Atomic absorption spectroscopy. Table S5: The performance of M-N catalysts in previous articles. Table S6: ORR performances of some M-N catalysts in previous articles. Figure S1: (a) N_2 adsorption/desorption isotherms and (b) pore distributions of rGO, N-rGO, 3%Cu/N-rGO, and 100%Cu/N-rGO. Figure S2: LSV curves of (a) rGO, (b) N/rGO, (c) 100%Cu-N/rGO, and (d) 20% Pt/C.

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