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Glycine–Nitrate Combustion Synthesis of Cu-Based Nanoparticles for NP9EO Degradation Applications

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Abstract: Copper-based nanoparticles were synthesized using the glycine–nitrate process (GNP) by using copper nitrate trihydrate [Cu(NO₃)₂·3H₂O] as the main starting material, and glycine [C₂H₅NO₂] as the complexing and incendiary agent. The as-prepared powders were characterized through X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy analysis. Using Cu(NO₃)₂·3H₂O as the oxidizer (N) and glycine as fuel (G), we obtained CuO, mixed-valence copper oxides (CuO + Cu₂O, G/N = 0.3–0.5), and metallic Cu (G/N = 0.7). The XRD and BET results indicated that increasing the glycine concentration (G/N = 0.7) and reducing the particle surface area increased the yield of metallic Cu. The effects of varying reaction parameters, such as catalyst activity, catalyst dosage, and H₂O₂ concentration on nonylphenol-9-polyethoxylate (NP9EO) degradation, were assessed. With a copper-based catalyst in a heterogeneous system, the NP9EO and total organic carbon removal efficiencies were 83.1% and 70.6%, respectively, under optimum operating conditions (pH, 6.0; catalyst dosage, 0.3 g/L; H₂O₂ concentration, 0.05 mM). The results suggest that the removal efficiency increased with an increase in H₂O₂ concentration but decreased when the H₂O₂ concentration exceeded 0.05 mM. Furthermore, the trend of photocatalytic activity was as follows: G/N = 0.5 > G/N = 0.7 > G/N = 0.3. The G/N = 0.5 catalysts showed the highest photocatalytic activity and resulted in 94.6% NP9EO degradation in 600 min.

Keywords: glycine–nitrate process; copper-based nanoparticles; photocatalysis activity; NP9EO

1. Introduction

In recent years, many studies have attempted to develop nanomaterials through green synthesis to solve environmental issues. To synthesize nanoparticles with a high, specific surface area, it is also very important to control the size distribution of ultrafine particles [1]. The glycine–nitrate process (GNP) is effective, simple, and environmentally compatible for the efficient synthesis of various nanostructured metal oxides [2–5]. The GNP is highly suitable for synthesizing fine crystalline powders and nanometer-scale particles with desirable characteristics, such as high chemical homogeneity, high purity, and a narrow size distribution range of nanoparticles [6]. The GNP is a type of solution combustion synthesis, which involves a self-sustained reaction between an oxidizer, such as a metal nitrate solution, and a fuel, such as glycine [5,7,8]. Furthermore, glycine supplies the energy required...
for combustion and functions as a complexing agent. An advantage of the GNP is that the rapid evolution of a large volume of gaseous products during combustion dissipates heat from the process and limits temperature increases, which reduces the probability of local sintering among particles while facilitating fine powder formation [6].

Nanosized transition metal oxide (TMO) particles have recently attracted considerable attention because they have unique applications with various types of matter, such as catalysts [2,5], photocatalysts [8], solar cells [5], and gas sensors [9]. Preparation of high-quality nanostructures with defined and controllable size and morphology is the main determinant of catalytic performance [10]. Among nanocatalysts, TMO-based catalysts offer active sites with low activation potential for hydrogen evolution systems [11]; in particular, noble metals (e.g., gold, silver, and platinum) are widely used to optimize catalytic efficiency. However, the high cost of noble metals remains a major obstacle in the development of stable and highly efficient catalysts. Consequently, reducing the amount of noble metals without compromising their catalytic performance is an urgent requirement for catalysis.

Compared with noble metal catalysts, copper is relatively inexpensive and moderately abundant [12]. Copper oxides (Cu$_x$O$_y$, where x:y = 1:1 or 1:2) and metallic copper are widely used as TMO catalysts. Copper oxides are heterogeneous catalysts with high recyclability, high catalytic efficiency, and low band-gap energies [10]. Cu oxides are used as TMO catalysts; Cu$_2$O$_y$ catalysts are p-type semiconductors with a monoclinic structure, a bandgap of 1.7–2.17 eV [13], and a high theoretical photocurrent density of $-14.7 \text{ mA/cm}^2$ [14,15]; therefore, they are suitable for application in the photocatalysis field. Although these superior properties of copper oxide have been of great interest to researchers, the transformations of cubic copper (I) oxide (Cu$_2$O) to copper (II) oxide (CuO) and Cu are still unavoidable due to the thermodynamically feasible parasitic reactions of self-oxidation and self-reduction [16]. Nevertheless, the presence of both Cu$^+$ and Cu$^{2+}$ in oxides has been shown to be beneficial in some cases [17]. In all applications of Cu$_x$O$_y$ morphology, structure, size, and surface area are the main determinants of its catalytic performance [15,18]. Compared with other TMOs, such as titanium dioxide (TiO$_2$), zinc oxide (ZnO), iron oxide (Fe$_2$O$_3$), and cadmium sulfide (CdS) [18], only a few studies have described synthesis strategies for different Cu$_x$O$_y$ nanoparticles along with the introduction of their related applications.

Nonylphenol ethoxylates (NPEOs) are nonionic surfactants that belong to the alkylphenol ethoxylates (APEOs) family, and are used primarily in emulsifiers, detergents, wetting agents, and dispersing agents, etc. Of these, NPEOs with an average of nine ethylene oxide units (NP9EO) are well known for their commercial application [19]. The biodegradation of NPEOs in the environment leads to the formation of nonylphenol, which is a toxic xenobiotic compound, classified as an endocrine disrupter capable of interfering with living organisms. Directive 2003/53/EC of the European Union (EU) prohibited the use of NPEOs and nonylphenols (NP) and recommended replacing them by alcohol ethoxylates, which are expensive [20]. However, due to their low cost and higher efficiency, NPnEOs are still widely used in China. They are discharged continuously into the environment, and the occurrence of NPnEOs in environmental samples has been well documented [21].

In this study, we presented a low-GNP with varying glycine/nitrogen (G/N) ratios for synthesizing Cu$_x$O$_y$ and metallic copper catalysts. Furthermore, the degradation of NP9EO under ultraviolet (UV) irradiation was investigated using a heterogeneous Cu$_2$O$_y$ photocatalyst (and metallic copper) in a custom-made photoreactor. Moreover, the effects of operational parameters, such as catalyst activity, catalyst dosage, and H$_2$O$_2$ concentration, were examined. This study will provide useful evidence on the potential of this method as a treatment to remove toxic materials from the water environment.

2. Results and Discussion

2.1. Characterization of Cu-Based Nanoparticles

Figure 1 depicts the X-ray powder diffraction (XRD) pattern of as-synthesized copper-based nanoparticles synthesized through the GNP with different G/N ratios. The XRD pattern of the sample
(a) obtained at a stoichiometric G/N ratio of 0.3 displays peaks at 32.5°, 35.7°, 38.7°, 48.5°, 53.6°, 58.3°, 61.6°, 66.3°, and 68.1° for (110), (−111), (111), (−202), (020), (113), (022) (−311), and (220) planes, respectively, confirming the formation of the CuO monoclinic phase (JCPDS File No. 01-089-5897). At a stoichiometric G/N ratio of 0.5 (see sample (b) in Figure 1), intense reflections were observed at 2θ values of 29.5°, 36.8°, 38.7°, 42.3°, 43.4°, 50.5°, 61.4°, and 74.2°. The peaks at 38.7° corresponded to the (111) plane of divalent CuO, whereas the reflections at 29.5°, 36.8°, 42.3°, and 61.4° corresponded to the (110), (111), (200), and (220) planes of cuprite, respectively (JCPDS File No. 01-078-0428), which indicated Cu₂O nanocrystal formation (JCPDS File No. 01-077-0199) [22]. In addition, the peaks at 50.5° and 74.2°, which corresponded to the (200) and (220) peaks, respectively, of zero-valent copper (Cu⁰) were observed. These results clearly indicated that the Cu⁰ nanoparticles, formed during chemical reduction, underwent oxidation because of the limited stability of Cu [23,24], and Cu₂O might have been formed through oxidation [25]. When the G/N ratio increased to 0.7, broad reflections from a highly dispersed Cu⁰ phase were observed, as shown in sample (c) in Figure 1. The XRD patterns (111), (200), and (220) of CuO planes at 43.4°, 50.5°, and 74.2°, respectively, were consistent with bulk copper crystallographic data (JCPDS File No. 01-085-1326). The results clearly revealed that CuO formation was favored with an increase in glycine (fuel) content during combustion synthesis. When the G/N ratio was reduced to 0.3, sample (a) exhibited numerous primary CuO phases and a few Cu₂O phases (approximately 9.5%). These findings indicated that nanocrystalline CuO reduced to a stable CuO phase rather than forming metallic copper directly [26]. The average crystallite size was calculated from the XRD pattern according to the line width of the (200) plane refraction peak by using the Debye–Scherrer equation [27]:

\[
d = \frac{k_1 \times \lambda}{\beta \times \cos \theta}
\]

where \(d\) is the crystallite size (nm), \(k_1\) is the constant with a value of approximately 0.9, \(\lambda\) is the wavelength of the X-ray radiation (\(\lambda = 0.1542 \text{ Å} \text{CuKα}\)), \(\beta\) is the full width at half maximum intensity, and the value of \(2θ\) is the characteristic peak of the XRD pattern. The crystalline sizes of copper-based nanoparticles were 76.3 ± 2.2 nm (G/N = 0.3), 35.4 ± 1.0 nm (G/N = 0.5), and 99.4 ± 2.9 nm (G/N = 0.7), respectively, as presented in Table 1.

Figure 2 shows the SEM with EDS images of as-prepared Cu-based nanoparticles at various G/N ratios. The typical EDS spectra of the particles (Figure 2) indicated that the particles were composed of copper (Cu) and oxygen (O). The SEM photographs showed that the catalysts formed sponge-like aggregates containing some nanoparticles; the size distribution range of the synthesized particles was broad (5–100 nm), and some irregular granules with a high degree of shape anisotropy were observed. The prepared Cu-based nanoparticles were not single-domain particles. The lack of homogeneity in particle shape and size, as well as the presence of sponges or flake-like structures, was typical of combustion synthesis. The results indicated that the large amounts of gas that evolved during combustion affected the porosity of the solid products [28,29]. Moreover, high combustion temperatures promoted nanoparticle agglomeration and crystal grain growth [30]. This finding was consistent with the surface area (BET) analysis results in the present study (Table 1). The BET results indicated that increasing the glycine concentration and reducing the particle surface area promoted the formation of metallic Cu. Consequently, large-scale agglomerates were observed when the ratio G/N = 0.7 was used.

| Catalyst | Synthesis of Copper Oxide Nanoparticles Ratio Analysis [%] | Specific Surface Area (m² g⁻¹) | Crystallite Size (nm) |
|----------|----------------------------------------------------|-------------------------------|----------------------|
|          | CuO | Cu₂O | Cu |                          |                  |
| G/N = 0.3 | 90.5 | 9.5    | 0    | 166.9                      | 76.3             |
| G/N = 0.5 | 43.2 | 54.6   | 2.2  | 131.0                      | 35.4             |
| G/N = 0.7 | 0    | 24.8   | 75.2 | 92.1                       | 99.4             |
Figure 1. The X-ray diffraction (XRD) pattern of combustion synthesized products of copper-based materials with various glycine/nitrate ratios (G/N) = 0.3 (a), 0.5 (b), and 0.7 (c).

X-ray photoelectron spectroscopy (XPS) spectra of the selected catalysts were obtained to confirm the surface composition and oxidation state of copper from information derived from binding energy values. Copper oxidation states occurred during two semiconducting phases: cupric oxide (CuO) and cuprous oxide (Cu$_2$O) [31]. The binding energies in the XPS analyses were calibrated using the C 1s peak (BE = 284.6 eV), where the C 1s peak was attributed to residual carbon from the sample and adventitious hydrocarbons from the XPS instrument or adsorbed carbon. Figure 3 presents the three samples obtained from the XPS results. As displayed in Figure 3a, the main O 1s peak present at 532.8 eV was attributed to lattice oxygen in a metal oxide, such as CuO or Cu$_2$O. The deconvolution of the Cu 2p3/2 XPS core level spectra of Cu$_{x}$O$_{y}$ is illustrated in Figure 3b–d. Through spectral deconvolution, we observed that the binding energies of Cu$_2$O and CuO were in the ranges 933.1–933.7 and 934.3–934.5 eV for different samples, respectively [32,33]. In addition, two peaks were observed, and the feature at 932.4 ± 0.1 eV was attributed to metallic Cu (2p3/2) [31,32], as presented in Figure 3c,d, respectively.
Figure 2. SEM with EDS images of prepared Cu-based nanoparticles at various G/N ratios: G/N = 0.3 (a), G/N = 0.5 (b), and G/N = 0.7 (c).

Figure 3. X-ray photoelectron spectroscopy (XPS) wide-scan spectra (a) of all samples; deconvolution of XPS spectra of (b) (G/N) = 0.3, (c) (G/N) = 0.5, and (d) (G/N) = 0.7 samples.
2.2. Investigation of Photocatalytic Performance

NP9EO degradation was used in this study to evaluate the photocatalytic activity of the as-prepared samples; its chemical structure is demonstrated in Figure 4. Economically, catalyst dosage is a main parameter in degradation studies. As illustrated in Figure 5, the custom-made photoreactor (Panchum Scientific Co., PR-2000) was operated in the atmosphere and 14 UV light tubes functioned as germicidal lamps with a wavelength of 254 nm (Sankyo Denki Co., Ltd., Kanagawa, Japan), surrounding the cylindrical quartz reactor in sequence. Of these, a light with a power of approximately 10 mW/cm² was placed in the center of the reactor and measured by a power meter (Model 840-C Handheld). To optimize the dosage of nano-Cu for photocatalyst activity, experiments were performed by varying the nano-Cu (G/N = 0.3) amount from 0.1 to 1 g/L. Figure 6a illustrates that the degradation efficiencies for 0.1, 0.3, 0.5, 0.8, and 1.0 g/L nano-Cu (G/N = 0.3) were 80.1%, 83.1%, 78.2%, 73.6%, and 70.3%, respectively. Besides, the TOC value represents the total organic carbons concentration in the solution. It is an important indicator of mineralization [34]. Figure 6a also indicated that TOC removal efficiency and NP9EO degradation efficiency showed the same trend. TOC removal efficiency increased from 58.2% for a nano-Cu catalyst amount of 0.1 g to more than 70.5% for a nano-Cu catalyst amount of 0.3 g. However, the concentration of nano-Cu catalysts (G/N = 0.3) for 0.5 g/L was increased above the limiting value, and TOC removal efficiency decreased (the mineralization efficiency dropped from 60.7% to 54.9%) because of increasing suspension turbidity and decreasing light penetration from an increased scattering effect [35], as shown in Figure 6a. Therefore, the optimal dosage of nano-Cu catalysts (G/N = 0.3) in this custom-made photoreactor was 0.3 g/L in the present study.

![Figure 4. Chemical structure of NPnEO.](image)

![Figure 5. Schematic representation of the custom-made photoreactor.](image)
G/N = 0.3, \( 2 \cdot b \rightarrow 2 \cdot 2 \); which was represented as the degradation of NP9EO. This finding is consistent with the results of the experiment on photocatalytic performance, Cu catalysts, the highest exhibited NP9EO and TOC removal efficiencies were 83.1% and 70.6%, respectively; the rate of degradation increased due to the availability of the hydroxyl radical (·OH) by the decomposition of more \( \text{H}_2\text{O}_2 \) molecules [36]. Subsequently, NP9EO and TOC removal efficiency gradually decreased (70.3% and 60.1%, respectively) with increasing \( \text{H}_2\text{O}_2 \) concentration above 0.08 mM (Figure 6b). The propagation step in the oxidative cycle is hindered by an excess of \( \text{H}_2\text{O}_2 \), which scavenges the ·OH radicals in the solution due to the reaction between excess \( \text{H}_2\text{O}_2 \) and ·OH radicals (Reactions (2) and (3)), thereby reducing the amount of ·OH available for reaction with NP9EO [37,38].

\[
\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O} \\
\text{HO}_2 + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}
\]

(2) (3)

In addition, the effects of hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) concentration (0–0.1 M) on photocatalytic oxidation were investigated. The experimental results indicated that, initially, on increasing the \( \text{H}_2\text{O}_2 \) concentration up to 0.05 mM for nano-Cu catalysts, the highest exhibited NP9EO and TOC removal efficiencies were 83.1% and 70.6%, respectively; the rate of degradation increased due to the availability of the hydroxyl radical (·OH) by the decomposition of more \( \text{H}_2\text{O}_2 \) molecules [36]. Subsequently, NP9EO and TOC removal efficiency gradually decreased (70.3% and 60.1%, respectively) with increasing \( \text{H}_2\text{O}_2 \) concentration above 0.08 mM (Figure 6b). The propagation step in the oxidative cycle is hindered by an excess of \( \text{H}_2\text{O}_2 \), which scavenges the ·OH radicals in the solution due to the reaction between excess \( \text{H}_2\text{O}_2 \) and ·OH radicals (Reactions (2) and (3)), thereby reducing the amount of ·OH available for reaction with NP9EO [37,38].

The effect of different G/N ratios of Cu-based nanoparticles on photocatalytic activity was also investigated in this study (Figure 7). For photocatalytic activity, each respective dose of Cu-based nanoparticles was dispersed in 1L NP9EO aqueous solution, and then the suspension was stirred in a dark condition for 30 min to establish the adsorption–desorption equilibrium. Subsequently, the suspension was subjected to UV light irradiation. In addition, the background experiments, such as NP9EO, were performed to ensure that the actual photocatalytic activity came from the photocatalysts without the influence of direct pollutant degradation by light irradiation. Photolysis experiment was conducted in the reactor without photocatalysts at 254 nm UV light irradiation. The results in Figure 7 clearly indicate that no significant NP9EO photolysis was detected under UV light irradiation. The order of photocatalytic activity was as follows: G/N = 0.5 > G/N = 0.7 > G/N = 0.3. It was observed that the percentage of NP9EO degradations with different G/N ratios were 83.1%, 94.6% and 87.7%, respectively, and the corresponding TOC removal percentages were 52.8%, 70.6%, and 57.6%, respectively. These results clearly suggested that at G/N = 0.5, the catalyst exhibited a high activity, which was represented as the degradation of NP9EO. This finding is consistent with the results of the XPS analysis of the oxidation state of copper (see Table 1). Cu\(_2\)O (bandgap of approximately 2.2 eV) has a higher electric conductivity than CuO (bandgap of approximately 1.6 eV) [39]; therefore, in the experiment on photocatalytic performance, Cu\(_2\)O exhibited a higher removal effect than CuO under the UV-light irradiation system in our study. Furthermore, Cu\(_2\)O and CuO are more stable at a higher potential for photoelectrochemical/hydrogen-evolution reaction because a high potential restrains...
the photo-reduction of Cu$_2$O (or CuO) to metallic copper [40]. Dasineh et al. [39] reported that the integration of Cu$_2$O and CuO significantly increased charge collection and reduced the recombination rate inside the photocatalyst. Luna et al. [41] also reported that the Cu species modified catalysts presented a high photocatalytic activity which was attributed to an appropriate amount of copper phases acting as photogenerated electron traps, avoiding charge recombination. This indicates that Cu$_2$O and CuO improved optical absorption and facilitated charge transfer at the interface between the photocatalyst and electrolyte. Consequently, with copper-based catalysts in a heterogeneous system, the highest photocatalytic performance was obtained with a G/N ratio of 0.5. In our results, the efficiency of TOC removal was consistently lower than that of NP9EO removal, indicating that, in addition to CO$_2$ (formed by mineralization), some intermediates were generated (such as by-products) [42].

![Figure 7](image_url)

**Figure 7.** NP9EO degradation curves for Cu-based catalysts synthesized at different G/N ratios. Data presented are the average of duplicate experiments with relative standard deviation. (Catalyst dosage = 0.3g/L, NP9EO = 100 mg/L, H$_2$O$_2$ = 0.05 mM (1000 mg/L), pH = 6.)

### 2.3. Analysis of Variance (ANOVA) Study of Photocatalytic Activity

We further evaluated the effects of nano-Cu$_x$O$_y$ catalyst dosage (range 0.1–1 g/L), H$_2$O$_2$ concentration (range 0–0.1 mM), and different G/N ratios (range 0.3–0.7) on the degradation of NP9EO by using a one-way ANOVA analysis. The nano-Cu$_x$O$_y$ photocatalytic activity assays were performed in triplicates. For all statistical analyses, values were presented as the mean ± standard deviation, and the significance between different groups was examined ($p < 0.05$). According to the results in Table 2, the nano-Cu$_x$O$_y$ catalyst had significant effects as the $p$ values were $4.99 \times 10^{-7}$, $1.42 \times 10^{-13}$, and $9.46 \times 10^{-6}$ for catalyst dosage, H$_2$O$_2$ concentration, and different G/N ratio percentage removals, respectively. This suggests that there were significant differences in the effect of the nano-Cu$_x$O$_y$ catalyst on the percentage removal of dosage, H$_2$O$_2$ concentration, and different G/N ratios, hence this practice can be effectively used to explain the effect of nano-Cu$_x$O$_y$ on photocatalytic activity efficiency.
Cu-based materials were synthesized through the GNP. Copper nitrate trihydrate \([\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}]\) (Merck, Kenilworth, NJ, USA, 99.5% purity) and glycine \([\text{C}_2\text{H}_5\text{NO}_2]\) (Merck, Kenilworth, NJ, USA, 99.7% purity) were dissolved in deionized water. Various amounts of glycine (fuel) were added to the metal nitrate (oxidizer) solution to obtain three different glycine–nitrate (G/N) ratios \((\text{G/N} = 0.3, 0.5, \text{and 0.7})\). As shown in Figure 8, the glycine–nitrate solutions were then mixed and heated overnight over a hot-plate stirrer (Corning, Glendale, AZ, USA) at 105 °C to form clear, homogeneous, and viscous gel-like solutions. Each gel was then poured into a ceramic bowl that was placed in an oven. The gels were heated to 200 °C until they underwent self-ignition and produced catalyst ashes. Finally, we obtained various shades, from russet brown to dark brown, of copper oxide nanoparticles displayed in the forms of fine powder.

### Table 2. One-way ANOVA results of various Cu-based nanoparticles effects on the degradation of NP9EO.

| Source of Variation | Sum of Squares | Df | Mean Square | F Value | p Value | Decision |
|---------------------|----------------|----|-------------|---------|---------|----------|
| Catalyst dosage     |                |    |             |         |         |          |
| Between groups      | 329.96         | 4  | 82.49       | 62.24   | 4.99 × 10^{-7} | Significant |
| Within groups       | 13.25           | 10 | 1.32        |         |         |          |
| Total               | 343.22          | 14 |             |         |         |          |
| H\textsubscript{2}O\textsubscript{2} concentration | 4314.67         | 4  | 1078.67     | 1325.14 | 1.42 × 10^{-13} | Significant |
| Between groups      | 8.14            | 10 | 0.81        |         |         |          |
| Within groups       | 4322.81         | 14 |             |         |         |          |
| Total               | 4322.81         | 14 |             |         |         |          |
| G/N ratios          | 199.64          | 2  | 99.82       | 62.83   | 9.46 × 10^{-6} | Significant |
| Between groups      | 9.53            | 6  | 1.58        |         |         |          |
| Within groups       | 209.18          | 8  |             |         |         |          |
| Total               | 209.18          | 8  |             |         |         |          |

### 3. Materials and Methods

#### 3.1. Catalyst Preparation

The crystal structure of the samples was determined through XRD by using Cu Kα radiation (\(\lambda = 1.5418\ \text{Å}\)) on a Rigaku DMAX 2200VK/PC diffractometer (Tokyo, Japan). The allocation/distribution of all measured peaks from XRD was examined by converting the adsorption amount at \(P/P_0 = 0.3, 0.5, \text{and 0.7}\). As shown in Figure 8, the glycine–nitrate solutions were then mixed and heated \(\text{C}\) until they underwent self-ignition and produced catalyst ashes. Finally, we obtained various shades, from russet brown to dark brown, of copper oxide nanoparticles displayed in the forms of fine powder.

![Combustion Synthesis Schematic](https://example.com/combustion-synthesis-schematic.png)

**Figure 8.** Schematic illustration of combustion synthesis for the copper G/N reaction system.
3.2. Characterization

The crystal structure of the samples was determined through XRD by using Cu K\textsubscript{α} radiation (\(\lambda = 1.5418 \text{Å}\)) on a Rigaku DMAX 2200VK/PC diffractometer (Tokyo, Japan). The allocation/distribution of all measured peaks from XRD referred to the data from the Joint Committee on Powder Diffraction Standards (JCPDS) [43]. The XPS (VG Escalab 250 iXL ESCA, VG Scientific, West Sussex, UK) was applied to verify the chemical composition of the samples to obtain the chemical analysis. The specific surface area (m\(^2\) g\(^{-1}\)) was calculated by the BET equation [44], and the total pore volume (V\(_t\), m\(^3\) g\(^{-1}\)) was examined by converting the adsorption amount at \(P/P_0 = 0.95\) to the volume of the liquid adsorbate. The morphologies of the synthesized samples were analyzed through SEM (S-4800, Hitachi, Tokyo, Japan), coupled with EDS measurements.

3.3. Photocatalytic Experiments

The stock solutions of NP9EO were prepared in distilled water to obtain a concentration of 100 mg/L, which was then ultrasonicated for 30 min to obtain a stable emulsion. The emulsion was stored at 4 °C for a maximum of 4 weeks. The photocatalytic activities of nano-Cu samples under UV irradiation were evaluated based on the degradation rate of NP9EO in a quartz reactor (120/115 mm outer/inner diameter, height: 240 mm) containing 0.3 g of nano-Cu and 1 L of a 100 mg/L aqueous solution of NP9EO. The system was operated in the atmosphere and 14 UV light tubes functioned as germicidal lamps with a wavelength of 254 nm (Sankyo Denki Co., Ltd., Kanagawa, Japan), surrounding the cylindrical quartz reactor in sequence.

3.4. Analytical Procedures

The photo-degradation rate of NP9EO solution was determined through HPLC (Agilent 1100 series; Agilent Technologies, Santa Clara, CA, USA) with a Wondasil-C18 (4.6 × 150 mm, 5 µm), and a 2487-UV detector at 277 nm. TOC was measured by a model 1010 TOC analyzer (O.I. Analytical, College Station, TX, USA) following the NIEA W532.52C standard methods (Taiwan’s Environmental Protection Agency). Of these, the principle of TOC was calculated by the subtraction of the IC (inorganic carbon) value from the TC (total carbon) of the sample. The pH value was measured with a pH meter (Model TS-1, Suntex Co., New Taipei City, Taiwan).

4. Conclusions

A nanocrystalline Cu-based heterogeneous catalyst was synthesized using the GNP. The nature and amount of fuel were crucial factors controlling combustion and final product composition. The formation of CuO, mixed-valence copper oxides (CuO + Cu\(_2\)O), and metallic Cu was achieved by varying the G/N ratio, in which glycine was used as fuel. The effect of the G/N ratio on catalyst morphology was analyzed using SEM. With a G/N ratio of 0.7, agglomerate structure formation was observed. Furthermore, Cu-based catalysts exhibited high photocatalytic activity during NP9EO degradation in a custom-made photoreactor under UV light. The experimental results revealed that, under optimal reaction conditions, namely a catalyst dosage of 0.3 g/L and H\(_2\)O\(_2\) concentration of 0.05 mM, NP9EO and TOC removal efficiency was 83.1% and 70.6%, respectively. However, the concentration of nano-Cu catalysts (G/N = 0.3) for 0.5 g/L was increased above the limiting value, and TOC removal efficiency decreased because of increasing suspension turbidity and decreasing light penetration from an increased scattering effect. The NP9EO removal efficiency increased with H\(_2\)O\(_2\) concentration but decreased when H\(_2\)O\(_2\) concentration exceeded 0.05 mM. With Cu-based catalysts in a heterogeneous system, the highest photocatalytic activity was observed with a G/N ratio of 0.5. Furthermore, TOC was consistently lower than the removal efficiency of NP9EO, indicating that, in addition to the mineralization of CO\(_2\), some intermediates were also generated.

Author Contributions: S.-S.C. and H.-H.C. conceived and designed the experiments that produced/generat ed this paper. S.-S.C. proposed methodology and project administration related to the research areas. H.-H.C. wrote...
original manuscript, drew figures, reviewed and edited the article. H.-M.L. analyzed quantitative data, statistically analyzed data, reviewed original manuscript, and provided critical comments. L.-W.J. performed the experiments, collected and analyzed the data. S.-Y.C. performed data processing of the experiments, statistically analyzed, reviewed original manuscript, revised grammar and provided critical comments. H.-H.C. and S.-Y.C. contributed to the final revision of the paper. All authors contributed to the manuscript and discussed the results. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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