

Photocatalytic Activity of Cu-based Nanoparticles Synthesized by Glycine-Nitrate Combustion Technique

Hsuhui Cheng^{1*}, Liangwei Jang², Shiaoshing Chen^{2*} and Huamin Chen¹

¹School of Environmental and Chemical Engineering, Zhaoqing University, Zhaoqing, 526061, China

²Institute of Environment Engineering and Management, National Taipei University of Technology, 1, Sec.3 Chung-Hsiao E. Rd., Taipei 10643, Taiwan, China

E-mail: hhcheng1126@gmail.com; fl0919@ntut.edu.tw

Abstract. The copper based nanoparticles was synthesized by glycine-nitrate process (GNP), using copper nitrate trihydrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$ as main starting materials and glycine $[\text{C}_2\text{H}_5\text{NO}_2]$ as complexant and incendiary agent. The as-prepared powders were characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM) techniques. Results of the photocatalytic degradation of Nonylphenol polyethoxylates (NP9EO) in a custom-made photoreactor indicated that the maximum degradation (more than 94% and 70% TOD removal) of NP9EO occurred with $\text{CuO}+\text{Cu}_2\text{O}$ composite catalyst (dosage of 0.3 g/L) when a combination of ultraviolet (UV) irradiation for 600 min, and a heterogeneous system was used.

1. Introduction

Nano-sized of transition metal oxides (TMO) has attracted great attention due to their unique applications in various fields, such as chemical, catalysts [1], photo-catalysts [2], solar cells [1], and gas sensors [3] etc. Preparation of high quality nanostructures of defined, controllable size and morphology are the main determinant of the catalytic performance [4]. Among them, transition metal oxides (TMOs)-based catalysts offers an active sites with low activation potential for hydrogen evolution systems [3], especially noble metals (such as gold, silver, and platinum) are widely employed optimize the catalytic efficiency of these. On the other hand, high cost of noble metals are still major obstacles in developing stable highly efficient catalysts. Consequently, reducing the amount of noble metals without compromising their catalytic performance is an urgent task.

Compared with noble metal catalysts, being cheap, quite abundant and safe, copper has recently drawn the attention as co-catalyst for photoreforming [5]. The Cu oxides (Cu_xO_y , where $x:y = 1:1$ or $1:2$) is as TMO catalysts, is a p-type semiconductor having monoclinic structure with a bandgap of 1.7–2.17 eV [6], and high theoretical photocurrent density of -14.7 mA/cm^2 [6-8], which makes it a promising material in application of catalysis. In this paper, we present a glycine nitrate process (GNP) methods with varying G/N ratio conditions, it is possible to obtain Cu_xO_y and metallic copper catalysts. Meanwhile, this study aimed to investigate the heterogeneous copper oxides (including metallic copper) catalyst degradation of nonylphenol polyethoxylates (NP9EO) under ultraviolet (UV) irradiation in a custom-made photoreactor.



2. Experimental

2.1. Catalyst Preparation

To synthesize Cu based materials by using the GNP route, copper nitrate trihydrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$ (Merck, USA, 99.5% purity) and glycine $[\text{C}_2\text{H}_5\text{NO}_2]$ (Merck, USA, 99.7% purity) were dissolved in distilled water. The glycine (fuel) was added into the metal nitrate (oxidizer) solution at the various glycine-nitrate (G/N) ratio (G/N=0.3, 0.5, 0.7). The glycine-nitrate solution was then mixed and heated overnight on a hot plate stirrer (Corning, USA) at 105°C to form clear, homogeneous and viscous gel-like solutions. The gel was then placed in a ceramic bowl, and place it in the oven, further heated to the temperatures of 200°C until the gel was self-ignited, producing a catalyst ash.

2.2. Characterization

The crystal structure of the samples was determined by powder X-ray diffraction (XRD) using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) on a Rigaku DMAX 2200VK/PC diffractometer (Tokyo, Japan). All peaks measured using XRD were assigned by comparison to those of the Joint Committee on Powder Diffraction Standards (JCPDS) data. The morphology of the synthesized samples were analyzed by scanning electron microscope (SEM, Hitachi S-4800) coupled with EDS (energy dispersive X-ray spectroscopy) measurements.

2.3. Photocatalytic experiments

NPEOs (reagent grade) with an average of 9 EOs (Sigma-Aldrich, USA, purity $\geq 99.7\%$) was chosen as model compound. The photocatalytic reaction was carried out in a custom-made photoreactor (Panchum Scientific Co., PR-2000) as illustrated in Fig. 1. The photocatalytic activities of Cu oxides samples under UV irradiation were evaluated based on the degradation rate of nonylphenol polyethoxylates (NPEOs) in a quartz reactor (120/115 mm OD/ID, Height: 240 mm) containing 0.3 g of Cu oxides (G/N=0.3) and 1 L of a 100 mg/L NPEOs aqueous solution. The system was open to the atmosphere, and the cylindrical quartz reactor was surrounded by a total of 14 light tubes. The UV light tubes were germicidal lamps with a wavelength of 254 nm (Sankyo Denki Co., Ltd.). The photo-degradation rates of NPEOs solutions was determined by high performance liquid chromatography (HPLC) (Agilent 1100 series; Agilent Technologies, USA) with Wondasil-C18 ($4.6 \times 150 \text{ mm}$, $5 \mu\text{m}$), and a 2487-UV detector at a wavelength of 277nm.

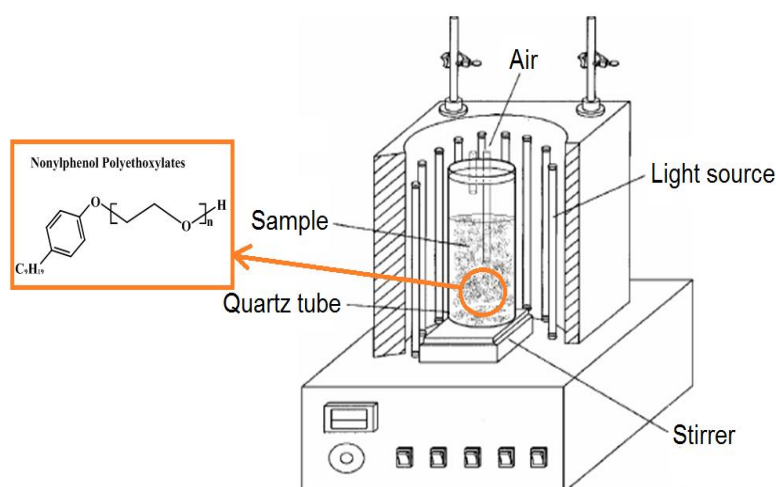


Figure 1. Schematic drawing of the custom-made photoreactor

3. Results and discussion

3.1 Characterization of Cu-Based nanoparticles catalyst

Fig. 2 exhibits the XRD pattern of the as-synthesized copper based nanoparticles by GNP method with different G/N ratio conditions. At the stoichiometric G/N ratio of 0.5 (see Sample (b) in Fig. 2), intense reflections are observed with 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° correspond to the (111) plane of divalent copper (II) oxide (CuO) whereas the reflections at 29.5° , 36.8° , 42.3° and 61.4° corresponding to (110), (111), (200), and (220) planes of cuprite, respectively (JCPDS File No. 01-078-0428), indicate the formation of cubic copper (I) oxide (Cu₂O) nanocrystals (JCPDS File No. 01-077-0199). In addition, the zero-valent copper (Cu⁰) peaks at 50.5° and 74.2° correspond to the (200), and (220) peaks were observed, respectively. This obviously illustrates that the Cu⁰ nanoparticles formed in the chemical reduction stage go through decomposition due to limited stability of Cu [9,11], and Cu₂O might be formed by oxidation [10-11]. When the G/N ratio was increased to 0.7, broad reflections due to a highly dispersed Cu⁰ phase was shown in sample (c) of Fig. 2. The XRD pattern (111), (200), and (220) of Cu⁰ planes at 43.4° , 50.5° , and 74.2° , respectively, which are in good agreement with the bulk copper crystallographic data (JCPDS File No. 01-085-1326). The results clearly show that the formation of Cu⁰ as a favoured product with increased glycine (fuel) content in the combustion synthesis [12]. When the G/N ratio was decreased to 0.3, the sample (a) contains a large number of primary CuO phases and a few number of Cu₂O phases (about 9.5%) were observed. This indicates that the nanocrystalline CuO reduces to a stable Cu₂O phase rather than forming metallic copper directly [13].

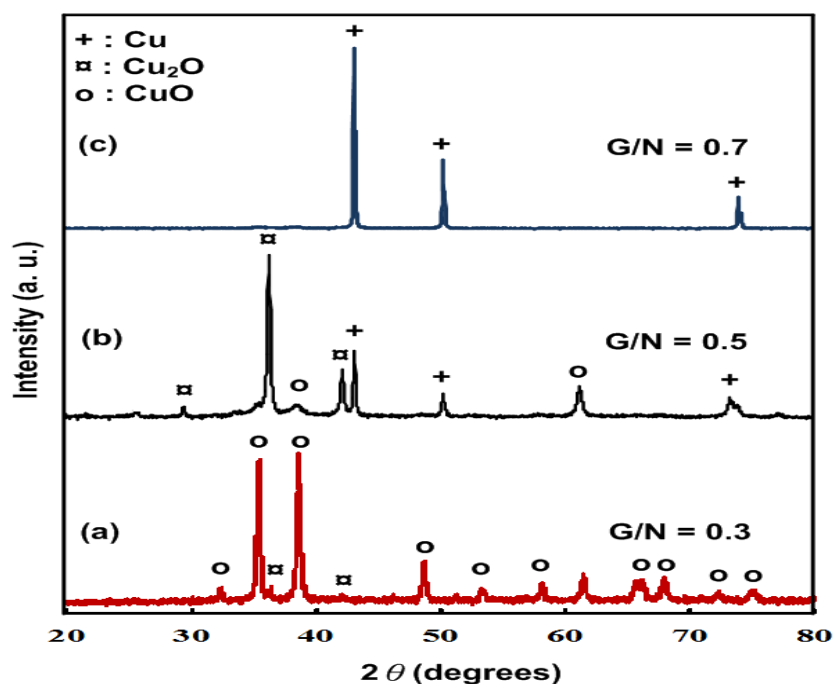


Figure 2. The XRD pattern of combustion synthesized products of copper-based materials with various glycine-nitrate ratio (G/N) = 0.3(a), 0.5(b), and 0.7(c)

Fig. 3 shows the scanning electron microscope (SEM) with EDS images of prepared Cu based nanoparticles at various G/N ratios. The typical EDS spectrum from the particles in Figure 5 indicates that the particles were composed of copper (Cu), and oxygen (O). From SEM photographs, the catalysts formed a sponges-like aggregates containing some small nanoparticles with the broad-sized distribution (~5–100 nm), and some irregular granules with a high degree of shape anisotropy. It could be noticed that prepared Cu based nanoparticles were not single-domain particles. Obviously, the particles shape and size in homogeneity was typical for combustion syntheses as well as the presence of sponges or flake-like structures. The results indicate that the high amount of gas evolution during the combustion process affects the porosity of solid products [14]. Moreover, high combustion temperature promotes nanoparticles agglomeration and crystal grains growth [15].

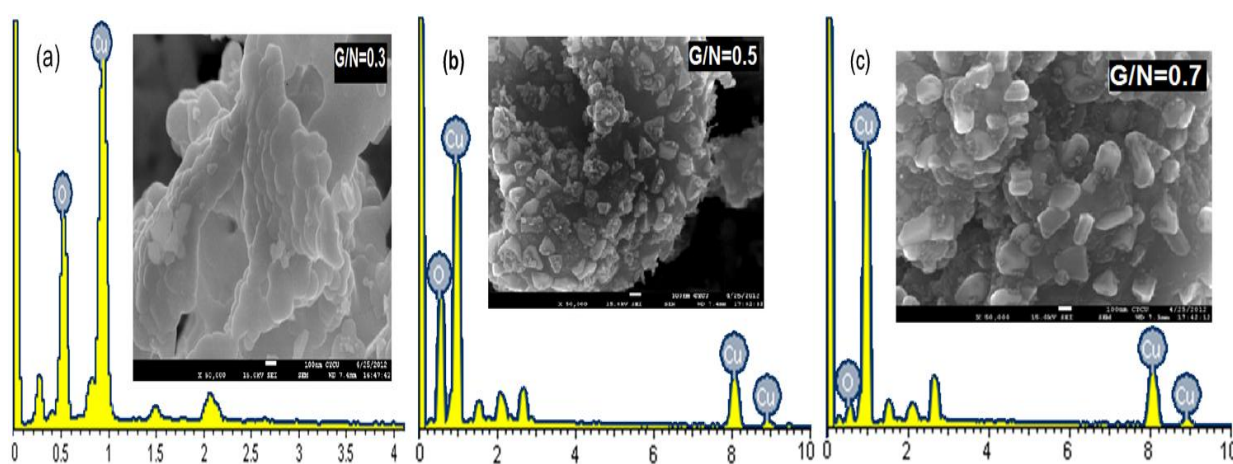


Figure 3. The SEM with EDS images of prepared Cu based nanoparticles at glycine-nitrate ratio (G/N) = 0.3(a), 0.5(b), and 0.7(c).

3.2 Degradation of NP9EO in batch photoreactor

Fig. 4 shows the photocatalytic NP9EO degradation curves for copper/oxygen catalysts synthesized at different G/N ratios. The photocatalytic activity evolves as follows: $G/N=0.5 > G/N=0.7 > G/N=0.3$. The G/N=0.5 catalysts shows the highest photocatalytic activity and leads to 94.6% NP9EO degradation in 600 min. This clearly suggests that G/N=0.5 conditions, catalysts have a higher photocatalysts for the photodegradation of NP9EO. The Cu_2O (bandgap of around 2.2 eV) has superior electric conductivity to CuO (bandgap of around 1.6 eV) [6], and thus a better removal effect in a photocatalytic system. Besides, Cu_2O and CuO are more stable at a higher potential for photoelectrochemical (PEC)/hydrogen evolution reaction (HER) because a high potential restrains the photoreduction of Cu_2O (or CuO) to metal copper [16]. Consequently, for the copper-based catalysts for heterogeneous system, the best photocatalytic performance with a glycine/nitrate ratio of 0.5. Furthermore, in our results, TOC is consistently lower than the removal efficiency of NP9EO, indicating other than mineralization to CO_2 , some of the intermediates were also generated [17]. The main reason for NP9EO cannot, therefore, be effectively mineralized.

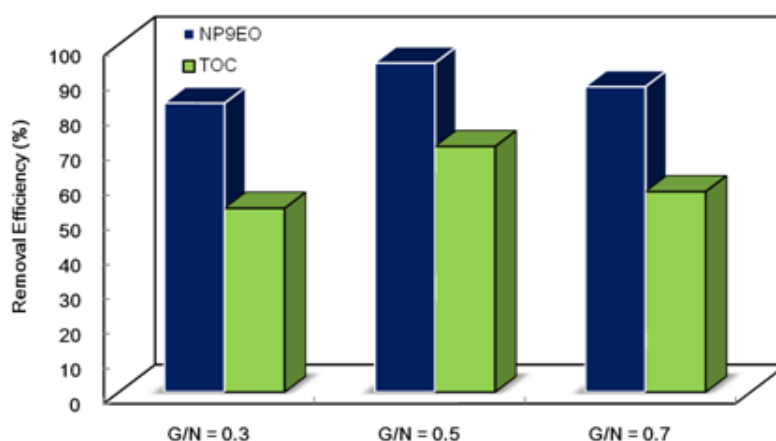


Figure 4. NP9EO degradation curves for copper/oxygen catalysts synthesized at different G/N ratios

4. Conclusions

Nanocrystalline Cu-based heterogeneous catalyst was successfully synthesized using combustion synthesis with glycine as the fuel and nitrate as the oxidizer. For the Cu-based catalysts for heterogeneous system, the best photocatalytic performance with a glycine/nitrate (G/N) ratio of 0.5, which leads to 94.6% NP9EO degradation and 70.5% TOC reduction were obtained after 600 min. Furthermore, in our results, TOC is consistently lower than the removal efficiency of NP9EO, indicating other than mineralization to CO₂, some of the intermediates were also generated.

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