In this work, the photocatalytic performance of electrochemically exfoliated graphite (EG) with low copper addition (≤ 5 wt.%) was studied. Composites of EG/Cu/Cu$_2$O were successfully prepared by microwave-assisted in situ reduction method. FTIR spectra of the samples showed that the main functional groups of graphite were detected in the samples. XRD characterization further proved the presence of EG, Cu, and Cu$_2$O in the samples. The higher proportion of Cu$_2$O presented in the samples prepared with a higher amount of Cu$^{2+}$. SEM analysis showed that Cu$_2$O/Cu particles were homogeneously deposited on the surface of EG. The composites of EG, Cu, and Cu$_2$O with a varied amount of Cu (1 and 5 wt. %) in EG / Cu$^{2+}$ mixture were examined as photocatalyst in the degradation process of Rhodamine B (RhB). The photocatalytic degradation of RhB was analysed by observing its decolorization within a set time of irradiation. UV-Vis analysis revealed that the degradation of RhB in EG/Cu/Cu$_2$O A and B for 105 minutes was 26 and 35 %, respectively. The result demonstrates that the sample with a larger amount of Cu$_2$O (sample B, Cu 5 wt.%) shows higher photocatalytic activity in the degradation of RhB.

Keywords: photocatalysts, exfoliated graphite/copper composite, rhodamine B

1. Background

Exfoliated graphite (EG) refers to graphite with a degree of separation of a substantial portion of the carbon layers in the graphite [1]. This material has been gaining tremendous attention due to its excellent properties, including large surface area, high porosity, and high charge carrier mobility [2]. These properties make EG suitable for the application as catalyst support, gaskets, and anode of lithium battery [1,3,4]. EG is also easy to fabricate using several top-down processes from graphite precursor, such as chemical exfoliation [5], thermal exfoliation [6], and electrochemical exfoliation [7]. Among them, the electrochemical exfoliation technique is considered more accessible, environmentally friendly, economically profitable, and applicable to mass production [7,8].

Our previous research has demonstrated the efficient graphite exfoliation via the electrochemical process with the aid of H$_2$SO$_4$/H$_2$O$_2$ pretreatment [9]. This method can cut down the processing time that is typically needed to exfoliate graphite using other complex processes. Moreover, unlike the chemical exfoliation method, which involves the reduction process to transform an oxidized form of EG or Exfoliated Graphite Oxide (EGO) to its reduced form (rEGO), this method does not need the reduction process to produce EG [5].

To this day, the research of EG has been evolving dynamically. Functionalization and deposition of EG have been involved in improving its properties to be applied in various applications [10,11]. Among materials that have been studied, metals [12] and metal oxides [10,13] have been frequently deposited on the EG surface.

There are several ways to deposit metals and metal oxides on the surface of EG, such as in situ chemical reduction [10,14], solvothermal/hydrothermal [15], and electrodeposition [16]. Among them, the in situ reduction process has been utilized to deposit metal on several types of carbonaceous, such as EG [17], rGO [14], and CNT [18]. In our previous work, we intended to deposit Cu on the GO surface through the microwave-assisted reduction of Cu$^{2+}$ ions to produce rGO/Cu composites [14]. However, it was revealed that depends on the added amount of copper precursor, Cu species
presented in various forms, i.e., Cu, Cu$_2$O, and CuO. It was also demonstrated that the species of Cu, determined the electrical conductivity of the resulted rGO composites. Samples prepared with a higher content of copper oxides (Cu$_2$O and CuO) showed lower electrical conductivity due to the semiconducting/insulating properties of copper oxide. Whereas, the sample with a higher content of metallic Cu showed higher electrical conductivity due to the nature of metallic Cu.

Despite its low electric conductivity, copper (I) oxide (Cu$_2$O), along with other semiconducting metal oxides such as TiO$_2$[19], ZnO [20], and SnO$_2$ [21], are known to have the ability to perform the photocatalytic reaction. These materials can absorb light to excite electrons from the valence band (VB) to conduction band (CB) and leave holes in the VB [22]. The generated electron-hole pairs move to the surface of the material to perform a redox reaction with the organic compounds. However, this process is commonly hampered by the fast recombination of electron-hole pairs, reducing photocatalytic efficiency.

Many researchers have attempted to composite photocatalyst materials with support materials, commonly carbonaceous materials, to improve photocatalytic efficiency. Among the carbonaceous material, EG is one of candidates as photocatalyst support material due to its exceptional properties, including high charge carrier conductivity and large surface area, which are beneficial for photocatalytic application. High charge carrier conductivity is responsible for preventing fast recombination of electron-hole pairs [3,23]. Meanwhile, a large surface area is beneficial to provide more active sites for photocatalytic reaction [2,24]. In addition to EG, Cu metals could also improve the transport of photoelectrons, which leads to efficient charge (electron-hole) separation [25,26]. Therefore, the enhancement of photocatalytic performance is expected to be achieved by compositing EG, Cu, and Cu$_2$O.

Previously, our group has studied the effect of compositing rGO with a small amount of copper (≤ 5 wt.%), from which we have obtained rGO, Cu, and Cu$_2$O composite. However, despite the expected excellent performance, there has been no report about its photocatalytic performance. In this study, EG which resembles the characteristics of rGO was mixed with Cu$^{2+}$ ions. The mixture then underwent a reduction procedure under microwave irradiation with hydrazine as a reducing agent, following a similar procedure in our previous work [14]. EG was prepared using the electrochemical exfoliation method which is more efficient than the modified Marcano method that was studied in our previous research. The action is expected to produce a composite of EG/Cu/Cu$_2$O due to the incomplete reduction of Cu$^{2+}$ ions. The obtained EG/Cu/Cu$_2$O composites were characterized using XRD, FT-IR, and SEM to assess the effect of Cu/Cu$_2$O addition on the exfoliation, functionalization, and morphology of EG, respectively. Hereinafter, the photocatalytic activity of the obtained EG/Cu/Cu$_2$O composite was evaluated through the decolorization process of rhodamine B (RhB).

2. Methodology

2.A. Preparation of Exfoliated Graphite/Copper (EG/Cu/Cu$_2$O) Composites

In this study, EG was produced via electrochemical exfoliation of graphite following the procedure demonstrated in our previous work [9]. The graphite precursor was immersed in a mixed solution of H$_2$SO$_4$ 98% with H$_2$O$_2$ 50%, with the ratio of H$_2$SO$_4$ to H$_2$O$_2$ 95:5. After 5 minutes of immersion, the graphite precursor was then exfoliated employing an anodic electrochemical process. This process was conducted at the potential of 15 V, inside a beaker glass containing 0.1 M aqueous solution of (NH$_4$)$_2$SO$_4$ as an electrolyte. The obtained sample was rinsed using DI water and ethanol. After washing, the sample was then dried in the oven at 60 °C for 2h. This sample is labeled as raw EG.

EG/Cu/Cu$_2$O composites were fabricated by firstly preparing EG suspensions by mixing raw EG in ethylene glycol (Merck, 1 ml for 1 mg EG). The mixture was sonicated for 30 minutes and then vacuum filtrated to separate its residue and supernatant. After that, a certain amount of Cu(NO$_3$)$_2$·2H$_2$O (Merck) was added to the supernatant to obtain EG/Cu$^{2+}$ dispersion with Cu composition of 1 and 5 wt. %. The dispersion was stirred for 15 minutes and followed by sonication and homogenization process using Ultra-Turrax homogenizer for 40 minutes. The reduction process was conducted by adding hydrazine (Merck, 1 ml for 1 g of EG), followed by stirring for 15 min and low mode microwave treatment (Panasonic Microwave 2.45 MHz, 800 W) for 20 min. The obtained sample was rinsed using DI water and
ethanol and followed by drying in an oven at 80°C for 2h. The obtained samples were labeled as EG, EG/Cu/Cu$_2$O A, and EG/Cu/Cu$_2$O B for 0 wt.%, 1 wt.%, and 5 wt.% Cu [in the form of Cu(NO$_3$)$_2$.2H$_2$O] added to the EG, respectively.

2.B. Characterization of EG/Cu Composites

The obtained EG/Cu/Cu$_2$O composites were characterized using Fourier Transform Infra-Red (FTIR) Spectrometer Prestige 21 Shimadzu and Bruker D8 Advance X-Ray Diffractometer (XRD) with Cu-Kα radiation ($\lambda$=1,54056 Å) to analyze the functional group and the structure of the composites. Meanwhile, the morphology of the samples was observed using a Scanning Electron Microscope - SEM Hitachi SU3500.

2.C. Photocatalytic Activity Measurement

The photocatalytic activity of the EG/Cu/Cu$_2$O composite was evaluated by observing the degradation process of RhB. For this measurement, 0.02 g of EG/Cu/Cu$_2$O composite was mixed with 50 mL of RhB aqueous solution (2 mg/L). In the dark, the mixtures were then irradiated by three UV blacklight lamps with a power of 10 W. Afterward, 3 mL of each mixture was drawn at regular intervals of 15, 45, 75, and 105 min, then membrane filtrated to remove the catalyst. The supernatant was then measured using Micro pack UV-Vis-NIR light DH-2000-BAL at the range of 400-750 nm. The concentration of RhB in each supernatant was determined using the following Lambert – Beer equation

$$A = abcC,$$

where $A$, $a$, $b$, and $c$ are absorbance, molar attenuation coefficient, optical path length, and solution concentration, respectively. The calibration curve which showed a linear response ($r^2$=0.9906) was obtained by measuring the absorbance of a series RhB standard solution (0.50-3.00 mg/L) at $\lambda_{max}$ of 554 nm.

3. Results and Discussion

Figure 1 shows FTIR spectra of the raw EG and EG/Cu/Cu$_2$O composites. All spectra show several dominant peaks which are commonly present in graphitic materials such as peaks at 2930 cm$^{-1}$, 1080 cm$^{-1}$, and 1500-1650 cm$^{-1}$, each corresponds to stretching of C-H, stretching of C-O, and asymmetric stretching vibration of C=C, respectively. At the range of C=C vibration characteristic, there are two peaks that are located at ca. 1580 cm$^{-1}$ and 1630 cm$^{-1}$. The C=C peak at 1580 cm$^{-1}$ is known to correspond to the vibrational mode of substituted aromatic rings in graphitic material, which corresponds to the introduction of oxygen-containing functional group in graphitic material [27]. Meanwhile, the C=C peak at 1630 cm$^{-1}$ corresponds to the unoxidized sp$^2$ graphitic network [28].

Figure 1 shows that the intensity of C=C peak at 1580 cm$^{-1}$ tends to decrease with respect to C=C peak at 1630 cm$^{-1}$ with the increasing amount of Cu loading. This result indicates that the higher Cu amount leads to a lower oxygen-containing functional group in EG. The broad and strong peak related to the vibration of the hydroxyl (-OH) group also can be seen from all samples at a wavenumber of 3000-3700 cm$^{-1}$. However, the width of -OH peak tends to be narrower with the more addition of Cu to EG. The narrowing of -OH peak is related to lower content of hydroxyl group in the sample EG/Cu/Cu$_2$O B than other samples [29,30]. This phenomenon is allegedly caused by the ability of Cu$^{2+}$ to work as a reducing agent in the reduction of oxygenated carbonaceous compounds under microwave irradiation. A similar result has been reported by Li et al. in the process of graphene oxide reduction by metallic Cu [31].

Figure 2 (a) shows the x-ray diffractograms of raw graphite, EG, EG/Cu/Cu$_2$O A, and EG/Cu/Cu$_2$O B. A peak at 2θ of 26.3°, which corresponds to (002) plane of graphitic structure (JCPDS-41-1487), can be seen from all samples. However, the intensity of the peak significantly decreased in the EG, EG/Cu/Cu$_2$O A, and EG/Cu/Cu$_2$O B samples compared to the raw graphite sample, indicating
the disruption of graphene layer stacking along c-axis in these samples. This result implies that graphite was exfoliated into fewer layers as reported by several studies [32–34].

Inset Figure 2(a) shows the intensity normalized diffractograms of all samples. It can be seen that the (002) peak was shifted from 2θ of 26.46° (graphite sheet) to 26.40° (EG), which also confirmed the exfoliation of graphite [33,34]. The calculation result of (002) plane interlayer spacing (d_{002}) using Bragg Equation, shown in table 1, revealed that interlayer spacing of (002) plane increased from 3.364 (raw graphite) to 3.371 Å (EG).

The addition of Cu to EG also affected the interlayer spacing of (002) plane of EG. The interlayer spacing of EG increased to 3.379 and 3.382 Å in the samples prepared with the addition of 1 and 5 wt. % of Cu, respectively. The increasing of interlayer spacing in EG sample with Cu addition might be attributed to partial insertion of Cu or Cu_{2}O particle between interlayer of graphite layers [35]. As the increasing amount of Cu addition, more particles were inserted into graphite interlayer which caused the larger interlayer spacing of EG/Cu/Cu_{2}O B than EG/Cu/Cu_{2}O A. Not only had it caused the increase of interlayer spacing of (002) plane, exfoliation of graphite, and addition of Cu also caused the decrease of crystallite size of the graphitic plane. It can be seen from Table 1 that the crystallite size of (002) plane decreased from 184.19 (graphite sheet) to as low as 127.59 Å (EG/Cu 5 wt. %).

Figure 2 (b) exhibits the diffractograms of graphite, raw EG, EG/Cu/Cu_{2}O A, and EG/Cu/Cu_{2}O B at range 2θ of 30°-80°. In this figure, there are several peaks represent EG, Cu, and Cu_{2}O in the sample which is not visible in Figure 2 (a) due to the dominant intensity of (002) graphitic peak. The peak at 2θ of 44.5° and 55.0° correspond to (101) and (004) plane of EG, respectively. The peaks at 2θ of 44° and 52° correspond to (111) and (200) planes of Cu (JCPDS-04-0836). Meanwhile, peaks that appeared at 2θ of 36°, 42.5°, 61.5°, 74°, and 78° correspond to (111), (200), (311), and (222) planes of Cu_{2}O, respectively (JCPDS-05-0667).

Upon the addition of hydrazine, the reduction process of Cu^{2+} caused the formation of Cu and Cu_{2}O. Cu_{2}O was formed due to incomplete reduction of Cu^{2+} which possibly caused by the lack amount of hydrazine. Another mechanism of Cu_{2}O formation was probably due to reduction reaction of oxygen functional group in EG by nascent metallic Cu. As indicated by XRD and FTIR characterization, the reduction of EG by Cu may cause the re-oxidation of the Cu. Higher peak intensities of Cu and Cu_{2}O can be seen clearly from the EG sample prepared by the addition of 5 wt. % of Cu, noting the higher amount of Cu_{2}O added. It also can be seen that the Cu_{2}O phase is more dominant than the Cu phase in this sample, as peaks correspond to Cu_{2}O were more to be found.

Quantitative analysis comparing the peak area of Cu_{2}O to peak area of Cu (Table 1) in both samples prepared with the addition of Cu_{2}O also showed the same trend. The sample prepared by adding 5 wt. % of Cu_{2}O showed a higher ratio of Cu_{2}O to Cu compared to that of prepared with 1 wt. % of Cu_{2}O. This phenomenon allegedly happened because the amount of hydrazine involved in the reduction was
not enough to ultimately reduce Cu$^{2+}$ to Cu(s) in this sample.

SEM characterization was conducted to study the effect of the addition of different copper concentration on the morphology of EG/Cu/Cu$_2$O composites. The SEM images of EG/Cu/Cu$_2$O A and EG/Cu/Cu$_2$O B are shown in Figure 3 (a) and (b), respectively. As can be seen from the images, small particles were deposited on the surface of both samples. Indeed, more particles can be observed on the surface of the sample with a higher copper content (EG/Cu 5 wt. %). This result corresponds to XRD analysis that demonstrated a higher intensity of Cu and Cu$_2$O peaks in the sample prepared with a larger amount of copper addition. Larger copper addition also caused the Cu and Cu$_2$O particles evenly decorated the surface EG than that of samples with the smaller copper amount. The larger amount and more evenly distribution of Cu/Cu$_2$O particles are expected to provide larger active sites for enhancing photocatalytic performance.

The photocatalytic activities of EG/Cu/Cu$_2$O A and EG/Cu/Cu$_2$O B composites were principally evaluated by degradation of hazardous of RhB, a kind of cationic dyes which gives pinkish-red color when dissolved in water. Absorbance spectra of RhB aqueous solution measured using a UV-Vis spectrophotometer at 400-700 nm are shown in figure 4. Figure 4 (a) and (b) show absorbance spectra on RhB solution with the addition of EG/Cu/Cu$_2$O A and EG/Cu/Cu$_2$O B, respectively. The spectra were taken after irradiation of RhB solution for particular irradiation time (0, 15, 45, 75, and 105 mins). It can be seen from both cases that absorbance peaks at $\lambda_{max}$ of 554 nm decreased with increasing irradiation time. However, the EG/Cu/Cu$_2$O B generally showed higher activity than the EG/Cu/Cu$_2$O A.

The photocatalytic activities of EG/Cu/Cu$_2$O composites on the degradation process of RhB were also demonstrated via the plot of degradation efficiency (h(%)) as a function of time (min). The degradation efficiency (h(%)) was calculated using the formula of $h(\%) = (1 - C/C_0) \times 100\%$, where $C$ is the concentration of the RhB at a reaction time of $t$ min and $C_0$ is the concentration of RhB at a reaction time of 0 min [36].

The data in Figure 4.c demonstrated that samples prepared with 5 wt. % of Cu showed an efficiency value of 35 %, higher than that of

### Table 1. Comparison of d$_{002}$ and L of synthesized materials.

| Sample                  | 20 (deg) | FWHM (deg) | d$_{002}$ (Å) | L (Å) | Cu$_2$O/Cu peaks area |
|-------------------------|----------|------------|--------------|-------|-----------------------|
| Graphite                | 26.46    | 0.46       | 3.364        | 184.19| -                     |
| Raw EG                  | 26.40    | 0.53       | 3.372        | 159.84| -                     |
| EG/Cu/Cu$_2$O A        | 26.34    | 0.66       | 3.379        | 128.88| 0.63                  |
| EG/Cu/Cu$_2$O B        | 26.32    | 0.67       | 3.382        | 127.59| 1.51                  |

$d_{002}$ = interplanar spacing (derived from Bragg Law)
FWHM = full width at half maximum of a diffraction peak
L = average crystallite size (derived from Debye-Scherrer equation)

Figure 3. SEM images of (a) EG/Cu/Cu$_2$O A and (b) EG/Cu/Cu$_2$O B.

Figure 4. The UV-Vis spectra of RhB aqueous solution measured with increasing irradiation time (a) with EG/Cu/Cu$_2$O A and (b) EG/Cu/Cu$_2$O B as the photocatalyst. (c) The photocatalytic degradation efficiency versus irradiation time with EG/Cu/Cu$_2$O A and EG/Cu/Cu$_2$O B as the photocatalyst.
prepared with a smaller amount of Cu (1 wt. %) with an efficiency value of 26 % during 105 min of irradiation. This phenomenon probably happened due to the higher amount of CuO compound presented in the sample with 5 wt. % of Cu.

As explained previously, CuO may act as a photocatalyst that increases the photodegradation rate of RhB. Han et al. [37] reported the significance of CuO in the photocatalytic activity of CuO/TiO2 composite. Photocatalyst with a higher content of CuO showed higher photocatalytic activity in degrading the dye pollutant [37]. Zhao et al. have also reported that compositing CuO with rGO could improve the photocatalytic activity of the catalyst to degrade methylene orange [24]. The narrow bandgap of Cu2O (~ 2 eV) allows the absorption of the photon at the visible region to excite an electron from the conductance band to the valence band in Cu2O [38]. During this process, a pair of electron-hole is generated, and each may indirectly reduce or oxidize organic dyes. The electrons that are flowing through EG reacts with an O2 molecule generating an unstable -O2- molecule. Meanwhile, the photogenerated holes (h+) with strong oxidation ability could interact with H2O to produce radical hydroxyl (·OH) [39]. The generated species (·O2-, ·OH) can degrade the RhB and other organic dyes [24,37].

4. Conclusion

In this study, EG/Cu/Cu2O composite was successfully prepared. The addition of hydrazine to EG/Cu salt mixture caused the reduction of Cu2+ to form Cu and Cu2O, as confirmed by XRD. The more significant proportion of Cu2O was observed from the sample prepared with a higher amount of Cu2+ (EG/Cu/Cu2O B). This occurrence allegedly happened due to incomplete reduction of Cu2+ affected by the lack of a reducing agent (hydrazine).

It was demonstrated that samples with a larger amount of Cu2O showed higher photocatalytic activity in the degradation of RhB with optimum efficiency of 35% after 105 min of irradiation.

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