Copper-Graphene Composite: Electrochemical Synthesis and Structural Characterization

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Abstract. Graphene utilization as multifunctional conductive material still has been obstacle in the scaling up process. Some methods, such as mechanical exfoliation only results few products, otherwise Chemical Vapor Deposition (CVD) needs high cost and high temperature. Synthesis of copper modified graphene by electrochemical with low cost has been studied in this research. Cu-Graphene composite was characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM). XRD analysis indicates conformity with simulated pattern peaks 2θ at 26.73°; 31.9° and 45.8°, that shows presence of graphene and Cu. In addition, SEM analysis shows that the Cu-Graphene morphology was in exfoliated flake structure. The electrochemical method performed here is expected can be used for scaling up the Cu-graphene production.

1. Introduction

Recently graphene material has attracted due to its high charge mobility carry, up to 200,000 cm² Vs. In Indonesia, graphene synthesis has not been developed. The most common method of graphene synthesis are mechanical exfoliation by peeling mechanical on graphite and Chemical Vapor Deposition (CVD). However, the mechanical exfoliation method only produces a small amount of graphene [1]. In addition, the CVD method requires high temperatures, inert systems and relatively high cost [2]. An alternative method of graphite exfoliation to form graphene under development is the chemical process [3]. Chemically reduction of graphene oxide can produce large single-layered graphene with relatively low cost [4]. To improve its conductivity, graphene can be combined with transition metals such as Ti, Cu, Zn, Sc, and Fe. Several methods of combining metals with graphene over reported are hydrothermal [5], microwave-assisted [6], self-assembly [7] and electrolysis [8]. Cu metal is selected as particles embedded
in graphene because of its considerable abundance in nature, low cost and it has better electrical and thermal conductivity. Cu-Graphene composites would be suitable for electrofriction materials with low coefficient of friction and can be used on electric motors and generators [9]. In this research, graphene synthesis using sonication method continued electrolysis to produce copper-graphene composite. Copper-graphene composite have higher electrical and thermal conductivity than copper for various applications [2].

2. Experimental

2.1 Materials and equipment

Graphite as raw material, certain amounts of aquades, NaCl 98% (Sigma Aldrich), KMnO₄ 98% (Sigma Aldrich), H₂SO₄ 98% (Sigma Aldrich), and H₂O₂ 30% (Sigma Aldrich), carbon rod and copper plate 99% as electrodes. The equipments are pH meter, power supply, ultrasonic cleaner, oven MEMMERT (type 67 UN30), Hot plate Termo Scientific CIMAREX.

2.2 Graphene oxide synthesis

Graphene oxide synthesis was prepared using Hummer and sonication method based on the reported procedures [5]. 2 g of graphite was dissolved in 46 mL H₂SO₄ 98% then was stirred for 30 minutes in the ice bath. 6 g KMnO₄ was added to the mixture then was stirred for 1 hour. The mixture was continuously stirred at 35 °C for 20 hours. 92 mL of deionized H₂O was slowly added to the mixture and stirred 2 hour then 280 mL of deionized H₂O was diluted for 15 minutes. 20 mL H₂O₂ was added to the dilute mixture then stirred for 15 minutes. The precipitate was separated and washed by deionized H₂O until its pH was neutral then it was dried at 60 °C for 12 hours to obtain graphene oxide. 1 g of graphite oxide was diluted into 100 mL deionized H₂O then it was sonicated for 1 hour to obtain graphene oxide.

2.3 Cu-Graphene composite synthesis

Due to the lack of previous study [10] that reduction of graphene oxide using hydrogen with inert system was not simple and highly cost, we provide a simple electrochemical method of graphene reduction. 0.5 g of graphene oxide and 0.1 M of NaCl were diluted into 25 mL of deionized H₂O, stirred to get homogenous mixture. Electrolysis was carried out in a electrochemical cell under 3 and 5 Volt for 30 minutes at room temperature using carbon rod as cathode and copper plate as anode. Finally the yellow-black precipitate was dried at 100 °C for 1 hour.

Figure 1. The schematic of electrolysis method for Cu-graphene synthesis
2.4 Characterization

The X-ray powder diffraction data were collected on Rigaku Miniflex 600 Benchop. The morphology of the final materials were recorded using scanning electron microscopy (SEM) type: inspect S50-FEI.

3. Results and Discussion

Graphene was prepared through graphite oxidation to form graphite oxide. KMnO$_4$ and H$_2$SO$_4$ were used as oxidation agent. In order to disperse multilayer structure of graphite, graphite oxide was sonicated to form graphene oxide. After that, graphene oxide was reduced through electrochemical synthesis to form graphene. Conterminous with Cu plate used as anode was oxidized and deposited at graphene surface forming Cu-graphene. Illustration of graphite change to be Cu-graphene was shown in Figure 2.

![Graphene Oxide and Cu-graphene Illustration](image)

**Figure 2.** Illustration of Synthesis route of Cu-graphene

The diffraction pattern of the obtained materials is confirmed through similarities with the standard pattern of graphene and Cu which is generated from ICSD Number: 040290. Diffragogram of Cu-Graphene is shown at Figure 3. The peak detected at 2θ: 28° indicating the presence of graphene and two peaks at 2θ 31.8° dan 45.83° may be assigned that Cu metal was successfully deposited into active sites to form Cu-Graphene composite.
According to the SEM analysis (Figure 3), morphology of graphite oxide is a flake structure. After being reduced to form graphene, the shape was changed to be exfoliated layer of Cu-graphene with increase pore size distribution.

Figure 3. Diffractogram of graphite, Cu-Graphene synthesized by electrolysis method using 3 and 5 volt

Figure 4. Pore size histogram of graphite (A) and Cu-graphene under electrolysis using 3 volt (B) and 5 volt (C) and their SEM images.
4. Conclusion

In this present study, we synthesized Cu-Graphene via sonication and electrolysis method. The result indicates that the presence of graphene and copper on the obtained materials. Moreover, the graphene morphology is exfoliated structure with increase pore size distribution. Due to low cost and simplicity, electrolysis method can be applied for upscale graphene.

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