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Preparation of graphite oxide using modified Tours method by using raw graphite powder from jewelry industry waste

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Abstract

In this study, we modified Tours Method for graphite oxide (GO) production. The raw graphite powder was collected from jewelry industry, in order to achieve the most beneficial value of graphite material instead of wasting several tons of graphite into landfill. To observe an alteration of the materials, the raw graphite powder and the produced GO were characterized their surface structures using scanning electron microscope (SEM) as well as transmission electron microscope (TEM) for greater magnification. The crystalline properties were determined by X-ray diffraction (XRD) and the attached functionalities were examined using Fourier transform infrared spectrometer (FTIR). Regarding to the study, the modified Tours Method showed a great potential for large-scale preparation of graphite oxide in order to utilize this material over a broad range application.

Keywords: Tours method, Graphite, Graphite oxide, Jewelry industry

1. Introduction

Graphite oxide (GO) is a carbon material that previously known as graphitic oxide or graphitic acid that composed of carbon, hydrogen and oxygen in variable ratio [1]. In order to synthesize GO, treating graphite with strong chemical oxidizing agents such as H_2SO_4, H_3PO_4 and HNO_3 are commonly used, known as oxidation method [1-3]. The most three common graphite oxidation methods that widely known are; Brodie's method, Staudenmaier, and Hummers method. Among the three methods, Hummers method had been widely used regarding to its effectiveness to manufacture graphite to GO, while maintaining relatively high C/O ratio [4].

Regarding to the promising methods to synthesize GO, mass production is a goal to achieve in order to apply GO into several applications, such as, gaskets, seal, packings, fire extinguisher agents, thermal insulators, electrodes, lubricant supports etc. [5]. As well as the other applications, GO for water purification has also caught a great attention regarding to the benefits of GO after underwent oxygenated functional groups through oxidation process such as, the increase of hydrophilicity and oxygen functional groups that can react with water, and non-polar solutions [6-7]. In addition, most of conventional water purification technologies required high surface area carbon materials to decolorize and eliminate heavy metal ions detention in which the benefits of GO can serve the application [6].

In this study, we applied Tours Method for GO synthesis and modified the process to make it becomes suitable in practice. We can assure its simplicity, less toxicity, no explosion, scalable ability, high yield, and less time consuming through the processes, which are the most important factors to be considered for GO production [8]. Due to the reason, this method is feasible in low cost GO by using graphite waste from jewelry industry, in order to attain the worthwhile value of graphite and provide the additional value to the industrial waste.

2. Materials and methods

2.1 Pre-treatment of raw graphite

Graphite waste was collected from jewelry industry, from residual graphite of graphite crucible lathing process. The residual graphite powder was ground using mortar, and consequently sieved through 40 mesh flour sifter (SAM, SM20916) before placing in a dry zip bag.

2.2 GO synthesis

GO was synthesized by the modified Tours method (Marcano et al., 2010). In detail, 3 g. of pre-treated graphite and 18 g. of $KMnO_4$ were carefully mixed and slowly added 9:1 mixture of concentration H_2SO_4/ H_3PO_4 (360:40 ml) storing in ice bath. Later the mixture was heated to 50 °C and then continuously stirred for 9 h. while the temperature was maintained. Consequently after stirring, the reaction was cooled to room temperature and slowly mixed with iced 400 ml DI water and 3 ml of 30% H_2O_2, and finally stirred the

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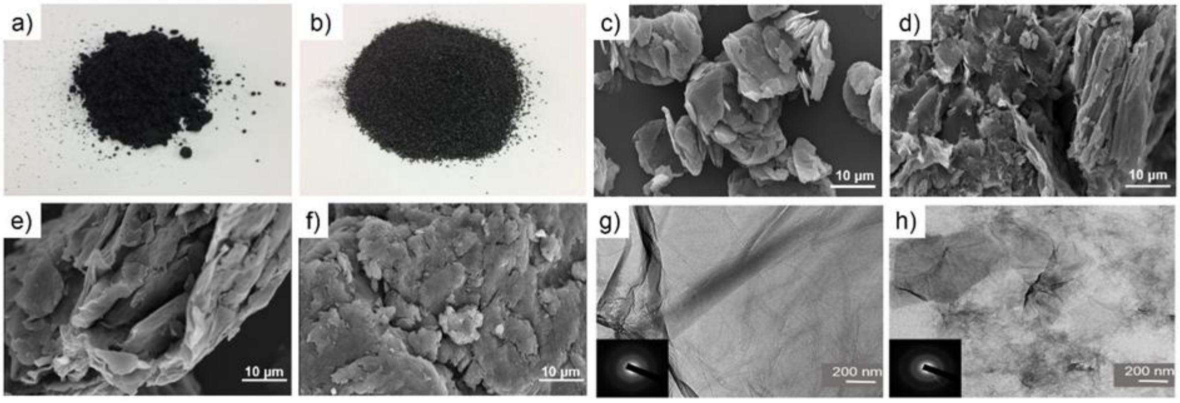

Figure 1 a) and b) The picture of graphite powder; c) and d) SEM image of graphite powder; e) and f) SEM image of GO; g) and h) TEM image of graphene oxide sheet and diffraction pattern (inset figures) obtained from GO

mixture for homogeneous mixing. In order to remove the residual burnt graphite from dissolved GO, metal testing sieve, Retsch® 300 µm, was use to separate undissolved solid graphite and subsequently filtered using filter paper, Whatman No.2. The suspension GO cake was trapped on the filter paper, and then was later washed with DI water, 30% HCl, and ethanol, respectively. The suspended solid was collected from the filter paper and carefully remove and rinsed with DI water. Since all the suspension was collected in a glass tray, consequently dried overnight in at 50 °C in the oven, and finally the dried suspension was harvested using stainless scrapper and placed in a zip lock bag and kept at room temperature.

2.3 Characterization of graphite oxide

The surface morphology of graphite and fabricated GO were studied under a scanning electron microscope (SEM) operating at 15 kV (JEOL, JSM-6400, Japan). GO was dissolved in DI water, and then exposed to sonication bath. The nanostructure sheet of graphene oxide was observed under a transmission electron microscope (TEM) (JEOL, JEMM-2100/HR, Japan). Likewise, X-ray diffraction (XRD) (Bruker AXS, Germany) was applied for phase identification of GO crystalline with Cu-K_{α} radiation in the 5 – 80 degree range. Moreover, functional groups of the GO were cultivated by using a Fourier transform infrared spectrometer (FTIR) (Thermo Scientific Nicolet iS5, United States).

3. Results

We compared physical properties of graphite from jewelry industry (sG) with commercial graphite (cG) as shown in the digital picture (Figure 1 a) and b)). The cG presents in fluttered-fine particles with deep black color, while sG is dark gray powder with coarse particle size. It is clearly observed that the sG has greater particle size comparing with cG. SEM was characterized in order to look at the surface structure of cG and sG, in which revealed that sG presents the particle size in the range of 50 – 100 µm while the cG was 10 – 20 µm (Figure 1 c) and d))

The oxidation process of graphite was carried out for both cG and sG. In order to compare the characteristics of the material, SEM was used to observe surface morphology and particle size of GO that produced by modified Tours method of both raw materials. The morphology of sG affirmed the character of vitality in particles (Figure 1 e)), while cG conceded swollen graphite layers as shown in Figure 1 f). It seems that the oxidation process of Tours method can achieve surface structure change of graphite with swollen graphite layers that is similar to Hummers method when oxidizing cG. However, the result of oxidation sG was differed regarding to the difference of particle size.

In addition, to examine whether the synthesized GO by Tours method can potentially offer thin-layer graphene oxide. We dissolved GO into DI water, using sonicator to disperse the suspension and probed graphene oxide nanosheet under TEM (Figure 1 g) and h)). The synthesized cGO and sGO were investigated and both presented the existing of graphene oxide nanosheet in which observed on the holey TEM grid. In Figure 1 g), the TEM image revealed that graphene oxide sheet that produced from cGO showed large area sheet with less aggregation, while the graphene oxide sheet obtained from sGO showed thickening sheet with obvious aggregation wrinkles (Figure 1 h)). The diffraction patterns were obtained to confirm the existing of graphene oxide sheets (inset figures), in which admitted the presence of complete ring diffraction pattern.

In Figure 2 a), XRD patterns were obtained in order to differentiate cG and sG. The lower intensity of carbon peak (002) at $2\theta=27.8°$ of sG was obviously seen, while the other peaks of carbon (100) and (004) showed comparable intensities. On the other hand, we investigated the exfoliation of graphite layers using XRD patterns from raw materials cG and sG (Figure 2 b)). The elevation of small carbon peak at $2\theta=10°$ was visibly found in sGO, while very low intensity of carbon peak was presented at the same position for cGO. In contrast, the XRD pattern of cGO revealed a dominant peak at $2\theta=27.8°$ indicated the peak of carbon (002).

The attached functionalities on GO that produced from both raw materials were examined by FTIR. As seen in Figure 3, the vibration of O-H functional groups (at 3100 cm^{-1}) is revealed in sGO can be dominantly observed from cGO. Likewise, the absorbance spectrum of sGO clearly presents single bonding strength of carbonyl compounds C-O (1100 cm^{-1}), epoxy (1225 cm^{-1}), carboxyl (1728 cm^{-1}) and aromatic ring (1624 cm^{-1}).

4. Discussion

In the beginning, we compare physical character of sG with cG, the particle size of sG was 2-fold greater than the particle of cG. From SEM images, the different particle size was showed and allowed us to affirm the shape of cG flake, while the sG particle inconstantly presented as compacted

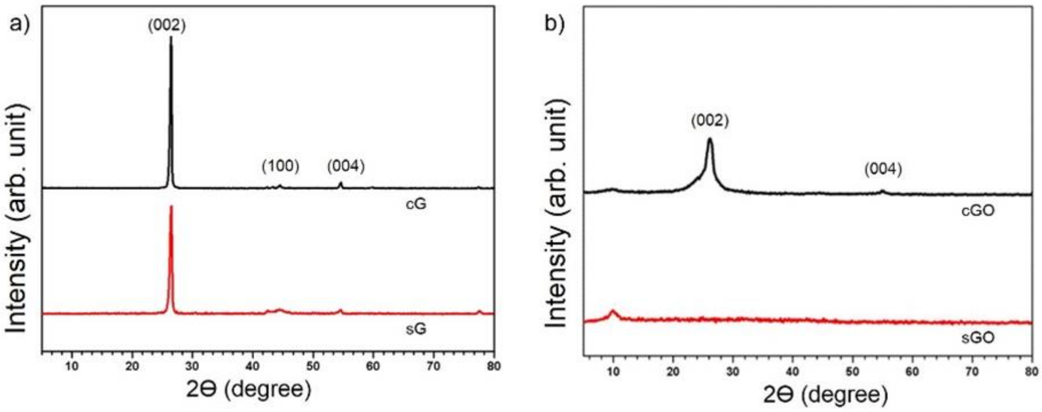

Figure 2 XRD patterns of a) graphite powder b) graphite oxide

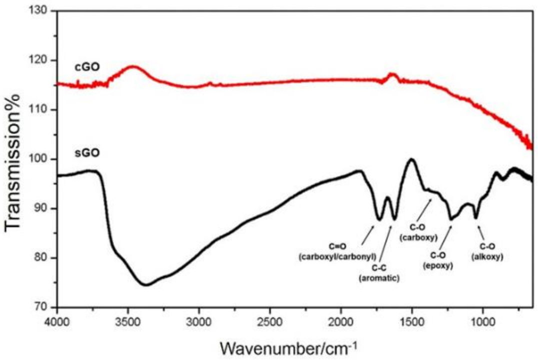

Figure 3 Fourier-transform infrared spectra of GO compare between cGO and sGO

structure. The surface structure of cGO showed a corrugated structure as mentioned in various studies [9-11]. On the other hand, the production of sGO was unclear to observe the change on the surface structure under SEM. Hence, we probed TEM in order to assure whether graphene oxide nanosheet was obtained. The results from TEM confirmed the production of sGO (Figure 1 h)). However, the ring diffraction pattern of sGO indicated that the obtained graphene oxide was composed of multiple-layer graphene oxide sheets [12].

We presented the XRD data to differentiate raw material graphite (cG and sG) through their crystallinities. The high intensity of carbon (002) peaked at 2θ=27.8° of cG indicated highly crystalline structure [13]. Additionally, the XRD patterns of Figure 2(b) provided the differentiation of sGO regarded to the elevation of carbon peak at 2θ=10° in which implied the spacing of graphite layers was expanded [14] as obviously seen from the XRD pattern of sGO. Meanwhile, we still observed the peak of carbon (002) from cGO. It is possibly determined that graphene oxide sheets that existed in the GO content underwent oxygen functional groups decreased during synthetic process and its slipped back close to the expanded graphite [15].

5. Conclusions

GO has been successfully prepared by modified Tours method using sG and cG as precursors. The method is easily controlled the occurrence of strong reaction and rapid rising temperature which can reduce toxic gases. The GO that produced by Tours method from different initial graphite presented different surface structure which could be probed by SEM and TEM. The XRD patterns of sGO represented the expansion of graphite layer from the existing of carbon peak at 2θ=10°. As well as the attached functionalities, FTIR spectrum of sGO evidenced an endurance of various oxygen-containing functionalities. The development of this methods showed a great potential for large-scale preparation of GO with comparable properties to Hummers' method.

6. Acknowledgements

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