C6_NPE_Formation_of_Graphene_Oxide

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Formation of graphene oxide from carbon rods of zinc-carbon battery wastes by audiosonic sonication assisted by commercial detergent

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ABSTRACT

This study aims to determine the effect of audiosonic sonication in normal modes on the formation of graphene oxide (GO) from carbon rods of zinc-carbon (ZnC) battery wastes. The method used in this study was sonication with an audiosonic frequency in normal modes, assisted by a surfactant solution derived from a commercial detergent. A graphite-detergent solution was exposed to audiosonic waves using a frequency of 170 Hz for 3 h with a pattern on the surface of the solution. The graphite solution was a mixture of 0.8 g of graphite powder and 100 ml of distilled water that was mixed using a blender for 2 min. 25 ml of the solution was then taken and dripped with two drops of detergent solution containing 0.2 g detergent powder dissolved into 100 ml distilled water, so that a graphite-detergent solution was obtained. The tools used in this study included UV–Visible spectroscopy (UV–Vis), Fourier Transform InfraRed spectroscopy (FTIR), and a Scanning Electron Microscope (SEM). The solution that was audiosonicated showed a strong visible nodal pattern on its surface. The UV–Vis spectroscopy produced absorbance peaks at wavelengths of 225 nm and 270 nm, and the FTIR indicated the presence of OH and C=C functional groups, which suggested the existence of GO. The SEM images showed GO in the form of coral-like materials.

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1. Introduction

Graphene oxide (GO) is a class of nanomaterial formally considered a precursor for producing graphene material. Nevertheless, GO itself has many applications such as glucose detection in medical diagnostics,[1] use as a supercapacitor using fibrillar polyaniline doped with GO,[2] wireless humidity sensing,[3] natural organic matter removal in water filtration systems,[4] and use in high energy batteries.[5] Because of its importance, preparation and synthesis of GO is still a subject of active studies, especially in those using simple and affordable equipment to produce good quality GO material. The most common method in synthesizing GO or graphene is Hummers' method. However, this method produces chemical compounds that are potentially dangerous to the environment.[6] Therefore, green synthesis of GO is considered an intriguing alternative in producing GO, or graphene, such as through electrolytic oxidation.[7] Another method for preparing and synthesizing GO[8,9] with fewer chemically involved materials is using liquid sonication exfoliation (LSE).[10,11] Usually, this method involves using commercial detergent.[12] In sonication, ultrasonic frequencies higher than 20 kHz are used. This is a standard procedure in the exfoliation of GO through cavitation.[13,14]

While ultrasonication has been a standard method in the synthesis of GO or graphene materials, very few studies have been conducted to investigate the effect of audiosonic frequencies on exfoliation of graphite. Audiosonic is the range of frequencies that the average human may hear, i.e., 20 Hz to 20 kHz, which is well below the ultrasonic range. The advantages of audiosonication include its ability to leave the composition of the material intact, and its ability to decompose the material purely through mechanical vibration. Hence, in this study, we constructed a simple, custom-made audiosonic sonicator in order to study the formation of GO from carbon rod zinc carbon (ZnC) battery wastes.[15] From a previous study,[16] ZnC batteries have been shown to be one of the wastes that can be used as precursors for producing GO materials. Moreover, the audiosonic frequencies used are based on the normal modes[17,18] of the solution being sonicated. These normal modes are produced because of the resonance between the audiosonic generator and the solution. Visible and active vibration of the solution is observed when the solution is placed in a container above the speaker. This vibration is due to the audiosonic waves coming out of the speaker. The boundary type of the sample container affects the vibration pattern, which helps in the exfoliation of graphene layers.

Commercial detergent is utilized to assist the exfoliation of graphite oxide.[19] The exfoliation occurs because the surfactants enter spaces between adjacent graphene layers and rearrange themselves such that their tails are attached to the graphene layers, whereas their heads are attached to other heads in the solution. Consequently, the distance

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Fig. 1. The materials used in this study are (A) graphite powder from the battery waste, (B) commercial detergent, and (C) a ZnC battery.

between two adjacent graphene layers increases, and through added normal mode vibrations, the exfoliation occurs.

2. Materials and method

Materials used in this study included (1) graphite powder (Fig. 1(A)) from carbon rods of ZnC battery wastes (Fig. 1(C)), (2) commercial detergent (Fig. 1(B)), and (3) distilled water as solvent. The household detergent used in this study was 'So Klin' brand. The active ingredient in this detergent is sodium alkylbenzene sulfonate ≤25% in each package. Sodium alkylbenzene sulfonate is a surfactant, which has an important role in the exfolation of the graphite powder.

The tools used in this study were (1) a digital scale, (2) a blender, (3) an audio generator [Csi/Speco Model SS-1], (4) an amplifier [Uchida TA-2MS], (5) an oscilloscope (CRO) [BK PRECISION 20 MHz Oscilloscope Model 2120B], (6) a mic condensor, (7) empty water bottle, (8) a loudspeaker, and (9) sample bottles. Some equipment can be observed in Fig. 2, including audiosonicator apparatus (Fig. 2(A)), an audio generator (Fig. 2(B)), and the amplifier (Fig. 2(C)). The audiosonicator apparatus used was a custom-made sonicator with components consisting of a loudspeaker, attached to a container that served as a sample container. The container was made from a truncated water bottle. The loudspeaker was connected to the amplifier, and the amplifier was connected to the audio generator, which was set to a frequency of 170 Hz. The audiosonicator apparatus design can be observed in Fig. 3.

A preliminary observation was conducted to determine the best frequency for the audiosonicator for the exfoliation process. This was done by varying the audio generator from 20 Hz to 20 kHz and simultaneously observing the solution in the sample container. By varying the frequency of the audio generator back-and-forth, a certain frequency was chosen that resulted in the most active vibrations on the surface of the solution. In this case, the most active and vibrant solution was obtained at a frequency of 170 Hz. Furthermore, to establish that the audiosonicator worked properly, a CRO was attached to the loudspeaker and the amplifier, as shown in Fig. 3, to determine the frequency coming out of the loudspeaker. Finally, in order to determine the vibration frequency of the solution, a mic condensor attached to the CRO (seperate from the audiosonicator) was placed into the solution so that vibration profiles were observed on the screen of the CRO (see Fig. 4). These profiles were used to determine the frequency of the solution.

The method of exfoliation of GO used in this study was sonication using audiosonic frequencies, aided by a surfactant derived from the commercial detergent. Audiosonic waves were exposed to the graphite-detergent solution using a frequency of 170 Hz for 3 h. The graphite solution used was a mixture of 0.8 g of graphite powder and 100 ml of distilled water, which was mixed using a blender for 2 m. 25 ml graphite solution was then poured into the sample container part of the audiosonicator apparatus. The solution (inside the sample container) was then dripped with 2 drops of detergent solution, which was obtained by mixing 0.2 g detergent powder and 100 ml distilled water. A graphite-detergent solution was thus obtained. The audiosonicator apparatus was turned on at a frequency of 170 Hz, so that vibrations occurred in the solution. After 3 h, the apparatus was

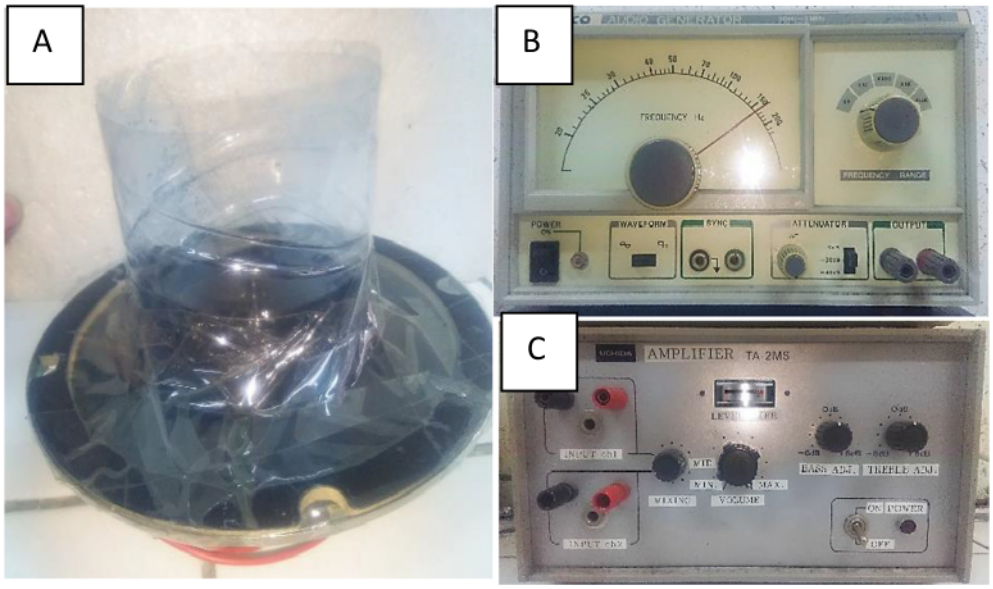

Fig. 2. Equipment used in this study: (A) sonicator apparatus, (B) audio generator, and (C) an amplifier.

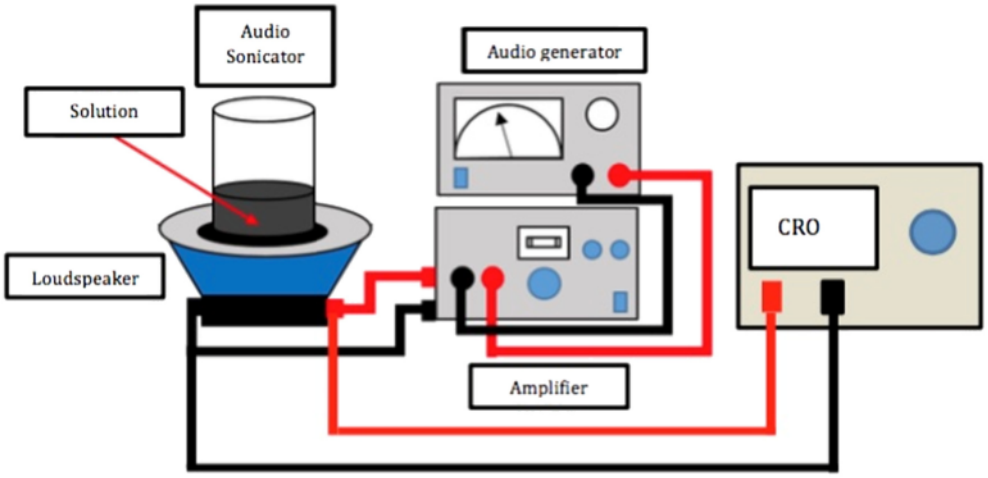

Fig. 3. The custom-made audiosonicator equipment design.

turned off and the solution placed in a sample bottle. Finally, the solution was left to equillibrate overnight.

Subsequently, the solution was analyzed. The analysis carried out in this study included UV–Vis (Shimadzu UV-2550), FTIR (Nicolet Avatar), and SEM (Hitachi SU3500). The UV-VIS and FTIR analyses of the solution were conducted in the liquid phase, whereas the SEM was done in the solid phase.

3. Results and discussion

A wave pattern occurring on the surface of the solution (Fig. 5(A)) was a result of audiosonic vibration with a frequency of 170 Hz. The boundary of the solution followed the geometry of the container, which was spherical. This boundary determined the form of the vibration pattern on the solution. The pattern consisted of nodes and antinodes, where the nodes were seen as clear or white stripes on the solution. This pattern was a normal mode of the vibration at 170 Hz. At first, the graphite materials were scattered around and vibrated as a result of the wave pattern. After a while, the materials tended to settle down on the bottom of the container. The upper part of the solution seemed to be clear. Therefore, we found that the normal mode at 170 Hz could exfoliate the graphene layers in the graphite-detergent solution, aided by the surfactant in the commercial detergent. The frequency of 170 Hz was chosen as this is the frequency that produced the most active vibrations on the surface of the solution. For comparison, it was observed that a frequency of just 100 Hz produced small vibrations, whereas a frequency of 20 kHz (ultrasound) did not produce any vibration.

Moreover, in order to determine the frequency of the loudspeaker at an audio generator frequency of 170 Hz, a CRO was connected to the loudspeaker. The result showed that the frequency of the loudspeaker averaged 178.57 Hz, which was not too different from that of the audio generator. The difference of around 8.57 Hz may have been caused by the beats occuring in the apparatus. Finally, to confirm the resonance of the solution at 170 Hz, a test was conducted by submerging a mic condenser into the solution (Fig. 4). The result of the vibration profile was observed on the screen of the CRO. It could be observed that the vibration pattern was not smooth. This was expected, as surrounding background noise also contributed to the vibration profile on the CRO. However, the calculation of the frequency from the CRO produced a frequency averaging 178 Hz, similar to the frequency of the loudspeaker, which indicated the occurrence of resonance in the solution.

The solution that resulted from the audiosonic sonication and being left overnight can be observed in Fig. 4(B) [inset]. The solution shows the separation between lighter and heavier particles (sediment at the bottom of the solution). The upper part of the liquid, which was clear, was used for the UV–Vis, FTIR, and SEM analyses.

UV–Vis analysis is one way to determine the presence of GO materials through a graph of the relationship between wavelength and absorbance. GO has a wavelength in the range of 223 nm to 270 nm.[20]

Fig. 4. A test to determine the frequency of the solution (A) by submerging a mic condensor into the solution (B).

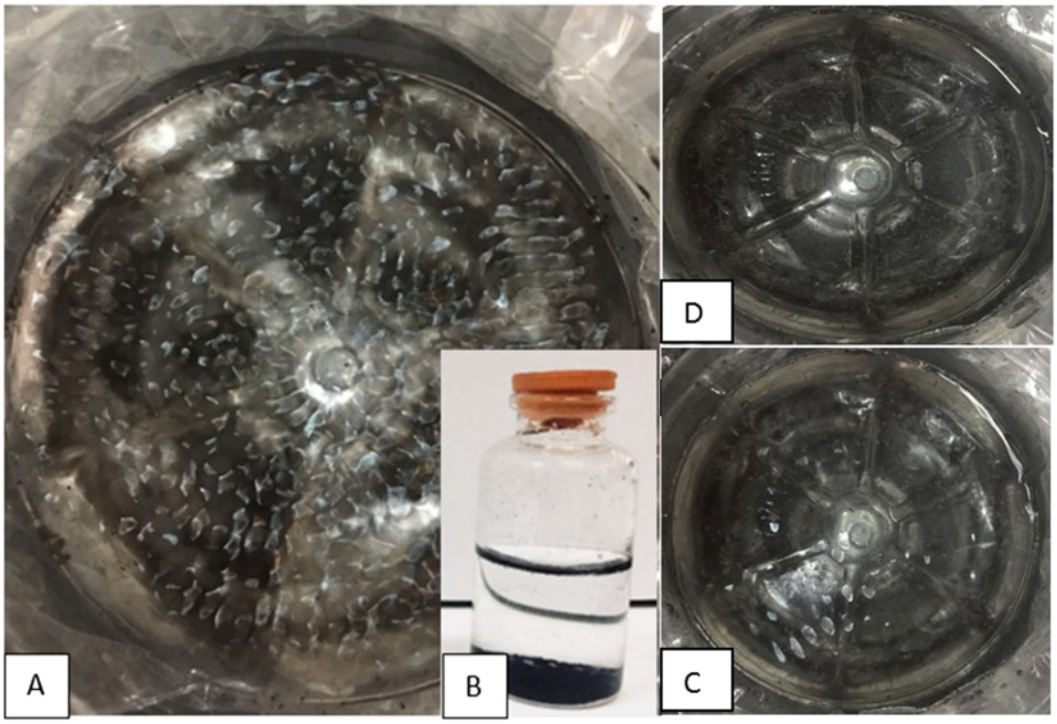

Fig. 5. The solution being sonicated at frequencies of 170 Hz (A), 100 Hz (C), and 20 kHz (D), and after being sonicated in a sample bottle (B).

The UV–Vis results with (blue-dashed line) and without (solid-red line) sonication can be observed in Fig. 6. The UV–Vis result without sonication indicated the presence of graphite material with a peak at around 300 nm. This is in accordance with Kumar *et. al* (2014),[21] who found the UV–Vis peak of graphite powder to be 271 nm. A red shift toward the GO peaks for the UV–Vis profile with audiosonic sonication occurred at peaks of 225 nm and 270 nm. The first peak at 225 nm showed the existence of $\pi \rightarrow \pi^*$ molecular transitions, whereas the second shouldering peak at 270 nm indicated $n \rightarrow \pi^*$ molecular transitions (shown by green arrows on Fig. 6). Moreover, it can be observed that the absorbance of the solution with audiosonic sonication tended to increase compared with the absorbance without audiosonic sonication, especially at the peaks. This increase may have been caused by the increase of GO material produced by the sonication process.

The FTIR results for the solutions with (solid-blue line) and without (dashed-red line) sonication can be observed in Fig. 7. The FTIR profiles for both solutions (with and without audiosonication) showed functional groups that are contained in the sample solutions. These results were in accordance with the FTIR results obtained by Gurunathan *et. al* (2015),[22] especially for the RES-rGO in aqueous solutions. There are, in fact, missing oxygen-containing functional groups in the FTIR results in Fig. 7 that commonly occur for GO material, such as C—O, C-OH, and C═O. The solutions

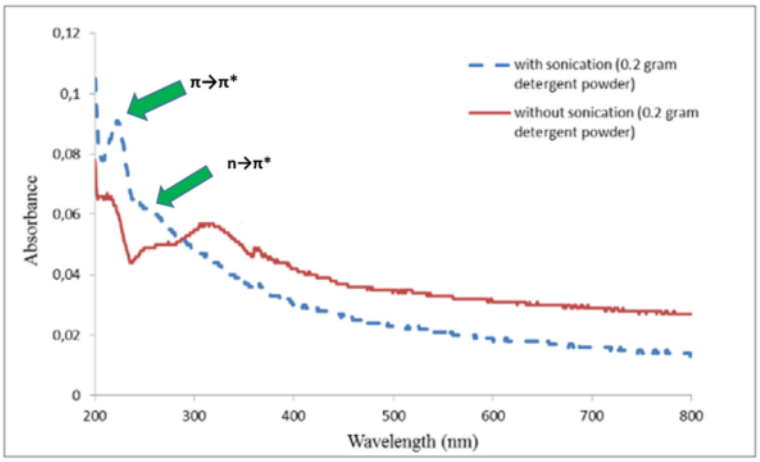

Fig. 6. UV–Vis results for the solutions without (solid-red line) and with (dashed-blue line) audiosonications.

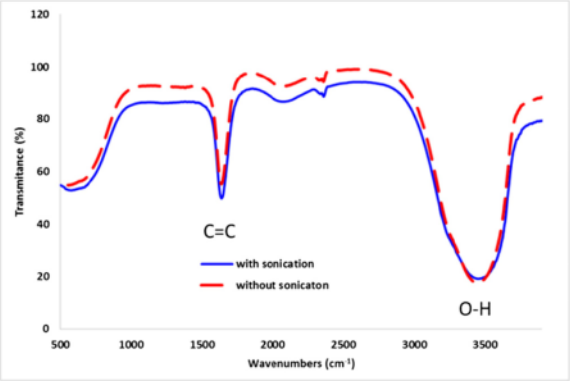

Fig. 7. FTIR results for the solutions without (dashed-red line) and with sonication (solid-blue line).

based on Fig. 7 contained hydroxyl (OH) groups at a band around 3400 cm^{-1} and C=C groups at a band around 1600 cm^{-1}. These functional groups may still have indicated the existence of GO for the solutions with sonication as there were carbon and oxygen atoms in the solution. Moreover, it may be observed that the FTIR profiles for the solutions with and without audiosonication were quite similar, with no difference observed in the FTIR bands. This shows that the audiosonication did not change the chemical composition or content in the solutions. The audiosonication produced mechanical vibrations that only effected the physical changes in the solution, i.e., exfoliation of graphene layers (assisted by the detergent), and not effecting or producing chemical reactions that would give rise to chemical changes in the solutions, as in cavitation caused by ultrasonication. This is further supported by the finding that the difference occurring in Fig. 7 concerns the transmittance or absorbance values of the solutions with and without the audiosonication. The absorbance values for the solution with sonication were higher compared with the solution without sonication, except at the hydroxyl band. This was in accordance with the UV–Vis results in Fig. 6.

SEM images from the sample with audiosonication can be observed in Fig. 8 at various magnifications. Fig. 8(A) is the SEM image of the sample with 500× magnification, showing piling of large islands of particles and smaller particles scattered around them. Increasing the magnification further to 1000× (Fig. 8(B)) showed coral-like grains of particles in stacks, not joined together, but, rather, in clumps. With the magnification increased to 5000× (Fig. 8(C)), the more obvious clumps of material were observed stacked on top of each other. Finally, Fig. 8(D) clearly shows layers of materials, laminated over each other, resembling coral-rock piles. These images are in accordance with the SEM images of GO produced by Wu, *et. al* (2017)[23] and Drewniak, *et. al* (2016).[24] In addition, there were also spherical particles (indicated by a yellow circle), which were suspected of being surfactant particles derived from the use of the commercial detergent.

4. Conclusions

The solution that is being audiosonicated using a frequency of 170 Hz for 3 h produces a strong, visible nodal pattern on the surface of the solution. The UV–Vis analysis shows a red shift at 225 nm and 270 nm that indicates electronic transitions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Furthermore, the FTIR analysis results indicate the presence of OH and C=C functional groups. The SEM images point out the presence of coral-like materials. These characterization show that the solution being audiosonicated can produce GO materials. Further investigation is needed to comprehensively understand the effect of audiosonication on the formation of GO, which may include varying the concentrations of the graphite or detergent solutions. Further analyses by taking cross-sectional SEM images, using XRD, XPS, or TEM, may shed further light on the properties of the GO obtained, which was not conducted in this study.

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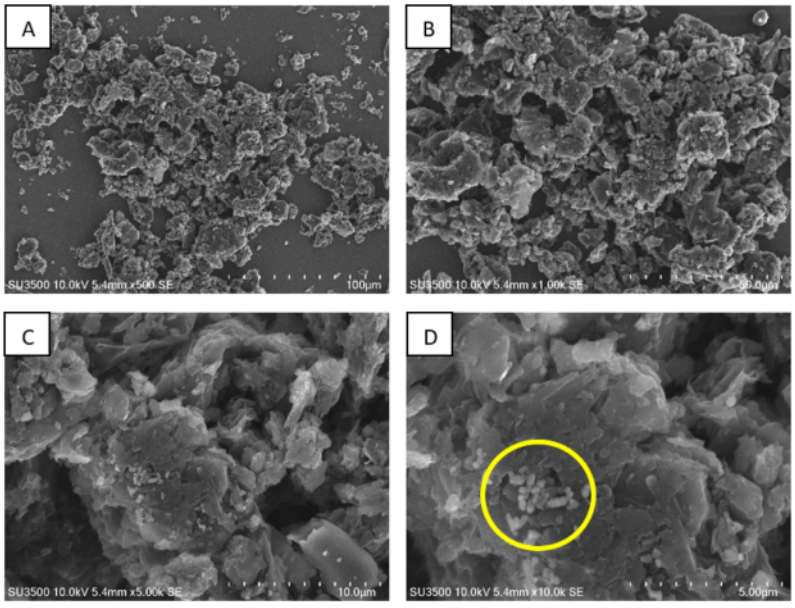

Fig. 8. SEM images of the solution with audiosonication with (A) 500×, (B) 1000×, (C) 5000×, and (D) 10,000× magnifications.

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