

UV-Visible Optical Absorbance of Graphene Oxide Synthesized from Zinc-Carbon Battery Waste via a Custom-Made Ultrasound Generator based on Liquid Sonication Exfoliation Method

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Abstract

The objectives of this study are i) to synthesize graphene oxide (GO) from the waste materials of zinc-carbon (ZnC) batteries via the liquid sonication exfoliation (LSE) method using tweeter piezoelectric probes as speakers, and ii) to study the optical absorbance of the GO produced using a UV-Vis spectrophotometer by varying the mass of the graphite materials obtained from ZnC battery waste. The graphite materials are obtained from the carbon rods of the ZnC batteries, which are ground into powder. The powder is then mixed with distilled water, with powder mass variations of 0.4, 0.6, 0.8, and 1.0 grams. The solutions obtained are sonicated with a frequency of 30 kHz for six hours using a custom-made ultrasound generator based on piezoelectric probes. The effect of graphite material mass variation is studied by observing the UV-Vis spectrophotometer data before and after sonication. The results of this study show absorbance peaks at wavelengths of 221 nm to 227.5 nm, and shouldering peaks at 260 nm to 270 nm, indicating the presence of GO materials for all graphite mass variations. The best GO performances based on the UV-Vis results are obtained in samples with 0.8 and 1.0 grams of graphite powder, which undergo a red shift from 223.5 nm to 227.5 nm, respectively. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) are conducted upon the sample of 1.0 grams of graphite powder before and after sonication treatment. The SEM results before sonication show graphite materials forming in large chunks, whereas after sonication smaller islands of GO materials consisting of thin, transparent flakes are observed. The EDX results reveal that the sample material after sonication consists of 88% carbon, 11% oxygen, and a remaining 1% of aluminum, silicon, sulphur, ferrum, and zinc

Abstrak

Absorbansi Optis UV-Visibel Graphene Oxide yang Disintesis dari Limbah Baterai Zinc-Carbon Menggunakan Generator Ultrasound. Buatan Sendiri Berdasarkan Metode Eksfoliasi Sonikasi Cair. Tujuan dari penelitian ini adalah i) mensintesis grafena oksida (*graphene oxide* – GO) dari bahan limbah baterai zinc-carbon (ZnC) berdasarkan metode eksfoliasi sonikasi cair menggunakan tweeter piezoelektrik sebagai pengeras bunyi dan ii) mempelajari absorbansi optis material GO yang dihasilkan menggunakan spektrofotometer UV-Vis dengan memvariasi massa bahan grafit limbah baterai ZnC. Bahan grafit diperoleh dari batang karbon baterai ZnC yang dibuat menjadi bubuk. Bubuk tersebut dilarutkan dalam aquades dengan variasi massa bubuk grafit sebanyak 0,4; 0,6; 0,8; dan 1,0 gram. Campuran yang diperoleh selanjutnya disonikasi dengan frekuensi 30 kHz selama 6 jam menggunakan generator *ultrasound* buatan sendiri. Pengaruh fisis dari variasi massa bahan grafit dipelajari dengan mengamati data spektroskopi UV-Vis sebelum dan setelah sonikasi. Hasil dari penelitian ini menunjukkan puncak-puncak absorbansi pada panjang gelombang 221 nm sampai 227,5 nm dan puncak-puncak bahu pada 260 nm sampai 270 nm yang mengindikasikan keberadaan material GO untuk semua variasi massa grafit. Bahan GO yang paling baik berdasarkan hasil UV-Vis diperoleh untuk bahan grafit bermassa 0,8 dan 1,0 gram yang mengalami pergeseran merah dari 223,5 nm menuju 227,5 nm. *Scanning electron microscopy* (SEM) dan *energy dispersive X-ray* (EDX) juga dilakukan terhadap sampel GO yang dihasilkan dari bahan grafit bermassa 1,0 gram, baik sebelum maupun sesudah perlakuan sonikasi. Hasil SEM sebelum sonikasi menunjukkan bahan grafit dalam bongkahan, sedangkan setelah sonikasi teramati lempengan bahan GO yang tipis dan transparan. Hasil EDX mengungkapkan sampel setelah sonikasi terdiri dari 88% karbon, 11% oksigen, dan sisa 1% terdiri dari aluminium, silikon, belerang, ferrum, dan seng.

Keywords: graphene oxide, UV-Vis spectrophotometer, liquid sonication exfoliation, zinc-carbon battery waste

Introduction

Zinc-carbon (ZnC) batteries are still an important source of energy nowadays. They are widely used for operating various electrical devices and appliances, such as remote controls, radio receivers, small television sets, flashlights, toys, clocks, and electronic calculators. However, for non-rechargeable or single use batteries, only limited usage is available until the batteries are no longer functional and need to be renewed. This leads to waste disposal of the used ZnC batteries. This battery waste does not easily decompose [1]. It contains metals [2,3] such as mercury, lead, and zinc, which may be potentially hazardous for people and the environment [4-6]. The general method for dumping and burying used batteries in landfills may not be sufficient to prevent possible leakage of waste materials (gases or liquids) into the environment [7-9]. Hence, more innovative procedures are needed, which should focus on reusing and recycling used batteries using harmless green technologies, e.g. hydrometallurgy [10], solvent extraction [11-13], chemical precipitation [14,15], electro-chemistry [16], calcinations [17], and mechanochemistry [18].

A ZnC battery contains graphite material in the form of a rod which serves as the cathode for the battery [19]. In principle, the rod is made from solidified carbon, graphite, and binding materials, and is formed by an extrusion process and burning. The rod is designed so as to have the smallest electrical resistance possible. However, the effects, as a waste product, of the graphite material in used ZnC batteries have not yet been fully studied. In fact, most active research in the recycling of disposal batteries is focused on regaining important metals, such as zinc. One way to manage the carbon material is to reuse it as a desulphurizer in biogas with chemical treatments [20,21]. In this study, we propose an alternative treatment of ZnC batteries, especially for the carbon rods: synthesizing them into graphene oxide (GO) material. The liquid sonication exfoliation (LSE) method is utilized in the preparation and synthesis of the GO from the carbon rods, providing an easy and inexpensive method to produce GO materials.

GO is a precursor material for the production of graphene. Nevertheless, it has many physical, biological, and optical applications, such as in bio-sensors and transparent conductive films [22,23]. Furthermore, the method in producing GO from graphite materials is already well established. Geim and Novoselov [24] initiated the first procedure in producing graphene via a mechanical exfoliation (ME) method using duct tape. This method produces limited graphene with superior properties. However, the production of graphene or GO in larger quantities is in demand, so it may be implemented in everyday products. Various methods have been put forward to satisfy this demand. Arguably the most common method in producing GO or graphene



Figure 1. The Materials Treated in this Study: (a) a Used ZnC Battery; (b) Carbon Rods from the Battery; and (c) Carbon Powder Obtained from the Carbon Rods

is using chemical reactions, known as the Hummers method [25,26]. Other methods also exist, such as liquid exfoliation (LE) [27-29] and chemical vapour disposition (CVD) [30]. In the LE method, equipment such as a blender [31,32] or sonicator [33] is used to exfoliate graphite materials. Here, we use a custom-made sonicator, using piezoelectric probes for the speakers [34].

Ultraviolet-visible (UV-Vis) spectroscopy is a quantitative measurement technique applied in order to study the light absorbance of a sample, especially that of ultraviolet and visible wavelengths, i.e.: 200 nm to 400 nm and 400 nm to 800 nm, respectively. In principle, a sample is placed between a light source, e.g. tungsten, and a photodetector. The photodetector captures the light that goes through the sample so that the absorbance of the sample may be determined. The absorbance may be plotted with respect to the wavelengths of light. The plot may consist of peaks which indicate the presence of specific substances in the sample corresponding to electronic transitions caused by light absorbance inside the sample. GO material has an absorbance peak of around 223 nm [35] to 230 nm [36], and a shouldering peak of 300 nm. For reduced GO, the peak is shifted to a longer wavelength of 270 nm [23].

Method

The materials used in this study are: i) used ZnC batteries; ii) carbon powder from the carbon rods of used ZnC batteries; and iii) distilled water used as a solvent. The first and second material may be observed in Fig. 1.

The equipment in this study consists of: i) a blender; ii) a digital scale; iii) a sonicator system; iv) an audio generator; v) an amplifier; and vi) sample bottles. Some pieces of equipment may be observed in Fig. 2. The sonicator system which is utilized in this study is custom-made by using piezoelectric probes as speakers.



Figure 2. The Equipment Employed in this Study, viz.: the Sonicator System (top-left), Sonicator Control Panel (top-right), Csi/Speco Audio Generator Model SS-1 [20 Hz – 2 MHz] (bottom-left), Uchida Amplifier TA-2MS (bottom-right), and Piezoelectrics (Middle-Right)

Using the control panel, the sonicator can be turned on or off. An ultrasound frequency may be selected using an audio generator, and amplified. In order to exfoliate the carbon powder, the piezoelectric probes are submerged into the solution, exposing it to ultrasound for a given period of time.

The procedure of the experiment was as follows: i) extract the carbon rod inside a used ZnC battery by carefully opening the battery casing; ii) grind the extracted carbon rod into powder; iii) weigh the carbon powder using a digital scale for mass variations of 0.4, 0.6, 0.8, and 1.0 grams; iv) prepare distilled water to be used as a solvent with a constant volume of 100 ml for all mass variations; v) mix the carbon powder with the prepared distilled water; vi) mix the solution with a blender for about three minutes in order to obtain a well-mixed solution; vii) take a small amount of each of the mass variation samples to be tested using a UV-Vis spectrophotometer; viii) sonicate the carbon solutions of each mass variation with a frequency of 30 kHz for six hours; ix) leave the sonicated solutions overnight; x) test the sonicated solutions using the UV-Vis spectrophotometer; xi) compare the UV-Vis results of the solutions for all mass variations before and after sonication, and finally xii) perform SEM-EDX upon the samples obtained from 1.0 gram of graphite solution before and after sonication treatment.



Figure 3. The Solutions with Powder Mass Variations before (top) and after (bottom) Sonications

Results and Discussion

This study is concerned with the synthesis of GO using the LSE method, where the quality of the synthesis results are observed optically via the UV-Vis spectrophotometer and SEM-EDX. The solutions obtained before and after sonication (and after being left overnight) may be observed in Fig. 3.

As seen in Fig. 3, the solutions for all mass variations before sonication are colorless and contain some sediment at the bottom of the bottles. The sediments are of course graphite from the carbon rod, which does not dissolve in the solution. This physical appearance seems to be similar for solutions after sonication (and after being left overnight), but with less sediment at the bottom. This indicates that the sonication process has an effect in transforming the graphite materials from the carbon rod into thinner layers which may be further dissolved in the solution. Furthermore, after the sonication process, the solutions appear to become more feculent as the powder mass increases.

The UV-Vis results of the solutions before sonication may be viewed in Fig. 4. The figure shows the UV-Vis results of carbon powder mass variations of 0.4, 0.8, and 1.0 grams.

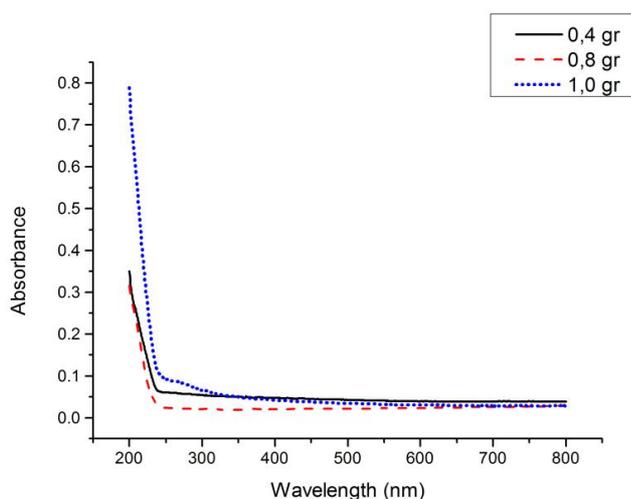


Figure 4. The UV-Vis Results of the Solutions before Sonication for the Powder Mass Variations of (in grams) 0.4 (Solid-black line), 0.8 (Dashed-red line), and 1.0 (Dotted-blue line)

The UV-Vis results for all mass variation samples before sonication in Fig. 4 do not show any wavelength that corresponds to a maximum peak. This indicates that GO materials have not yet been produced in the solutions, as no maximum peak is observed around 223 nm to 230 nm. At this stage, it is unlikely that there is exfoliation of the graphite layers in the solutions. Moreover, this also shows that exfoliation of the graphite layers may not take place under rotating blender blades after a short period of time, viz.: three minutes in this case.

Exfoliation of the graphite layers of the carbon rod is conducted using ultrasound with a frequency of 30 kHz for six hours. The UV-Vis results of the solutions after sonication and being left overnight can be observed in Fig. 5. The UV-Vis results in Fig. 5 are obtained for mass variations of 0.4, 0.6, 0.8, and 1.0 grams. All of the UV-Vis results visibly show peaks at certain corresponding wavelengths. This is of course in contrast to the UV-Vis results before sonication in Fig. 4. For powder masses of 0.4, 0.6, 0.8, and 1.0 grams, the absorbance peaks are obtained for wavelengths of (in nm) 221, 221, 223.5, and 227.5, respectively. These peaks correspond to the $\pi \rightarrow \pi^*$ transitions. Moreover, shouldering peaks are also observed. For carbon powder mass of 0.4 grams the shouldering peak occurs at 270 nm, and for 0.6, 0.8, and 1.0 grams of powder masses the shouldering peaks are located at 260 nm. These peaks correspond to the $n \rightarrow \pi^*$ transitions which indicate certain functional groups.

Wavelengths at maximum absorbance (peak) for the solutions with carbon powder masses of 0.4 and 0.6 grams are slightly smaller than the 223 nm obtained in [35],

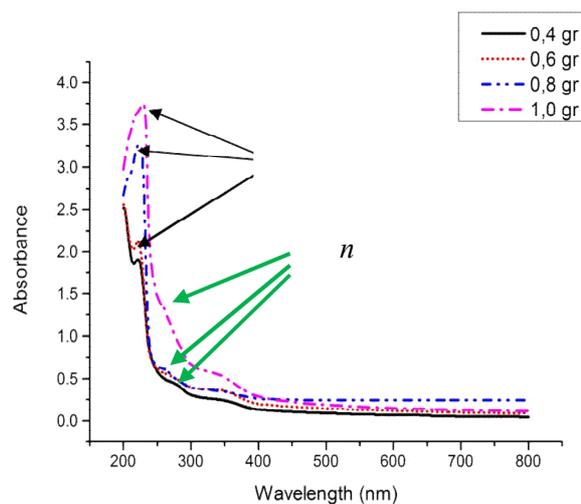


Figure 5. UV-Vis Results of the Sample Solutions after Sonication and being Left Overnight with Varying Carbon Powder Masses of (in grams) 0.4 (Solid-black line), 0.6 (Dotted-red line), 0.8 (Dashed-double dotted-blue line), and 1.0 (Dashed-dotted pink line)

which means that there might be GO materials produced. For the solution with 0.8 grams of carbon powder, the wavelength at maximum absorbance is significantly close to 223 nm. This indicates that more GO materials are produced with the increase of the carbon powder mass. Furthermore, for a higher carbon mass of 1.0 gram, the wavelength is 227.5 nm, which is close to the 230 nm observed in [36]. This is also an indication of GO materials forming in the solution. In summary, the four samples of different carbon powder masses yielded GO materials, as indicated by the presence of absorbance peaks at 221 nm to 227.5 nm and shouldering peaks at 260 nm to 270 nm. Furthermore, it may be observed that as the mass of the carbon powder increases, the absorbance peak value also increases. This is of course in accordance with the Lambert-Beer law.

Finally, Fig. 6 provides a closer look at the comparison between the UV-Vis results of the solutions before and after the sonication process for the powder masses of 0.8 and 1.0 grams. We only consider these two powder masses as these produced the most GO material based on the wavelengths at the absorbance peaks. The two lower lines of Fig. 6 represent the UV-Vis results of the solutions before sonication; as previously mentioned, no peaks were observed. However, after sonication the UV-Vis results show peaks at 223.5 nm and 227.5 nm for the solutions with masses of 0.8 grams and 1.0 grams, respectively (upper lines of Fig. 6). By comparing the UV-Vis results before and after sonication, we may identify a red shift (arrow) from no absorbance peak towards absorbance peaks of 223.5 nm and 227.5 nm.

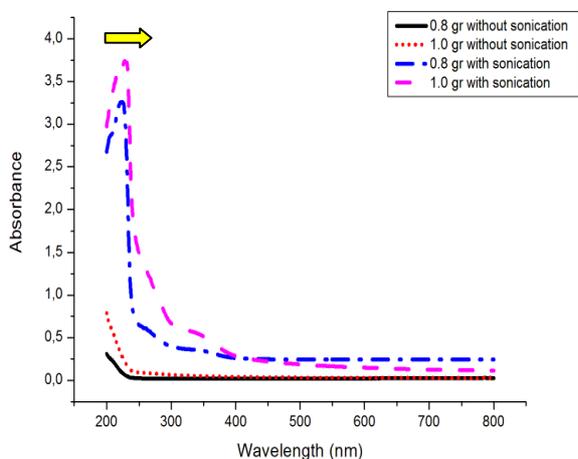


Figure 6. Comparison of the UV-Vis Results of the Samples before and after the Sonication Process for 0.8 and 1.0 grams of Carbon Powder. The Arrow Shows a Red Shift in the UV-Vis Results Before and After the Sonication Process

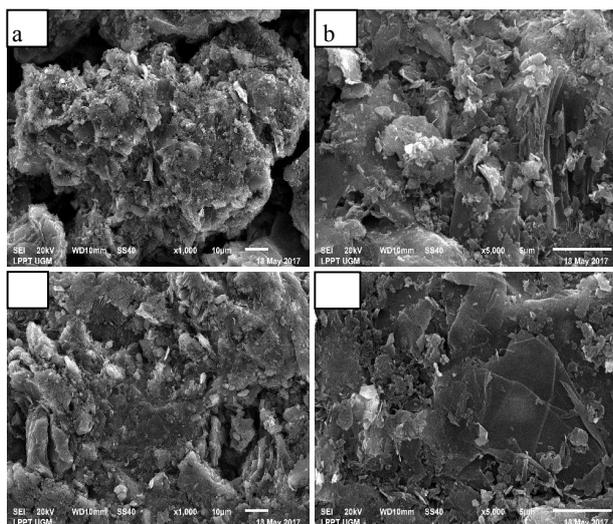


Figure 7. SEM Results from 1.0 gram of Graphite Powder Samples before Sonication with Magnifications of 1000X (a) and 5000X (b), and Also After Sonication with Magnifications of 1000X (c) and 5000X (d)

In order to further verify the existence of GO materials, SEM-EDX characterization was performed. The SEM results of the solidified sample solutions before and after the sonication for 1.0 grams of carbon powder are shown in Fig. 7. The top pictures, i.e. Fig. 7(a) and 7(b), show that the sample material before sonication clusters in large chunks. However, after sonication it seems that the sample material forms smaller clusters consisting of thin and transparent flakes, as seen in Fig. 7(c) and 7(d). It can be clearly observed in Fig. 7(b) that the sample material before sonication with 5000X magnification

consists of a thick layer of bulky materials. A different surface morphology is observed in Fig. 7(d), which shows thin and transparent layers in the material after sonication with 5000X magnification. Hence, we may conclude that the sonication treatment succeeded in producing GO materials.

Further evidence of GO is given by the EDX results shown in Fig. 8. The graph provides the sample composition of 1.0 grams of carbon powder after the sonication process. The EDX results reveal that the highest atomic percentage in the sample is of carbon and oxygen, viz.: 88% and 11%, respectively. The remaining materials, comprising less than 1% of the sample are aluminum, silicon, sulphur, ferrum, and zinc. The majority composition of carbon and oxygen in the sample shows the presence of GO material.

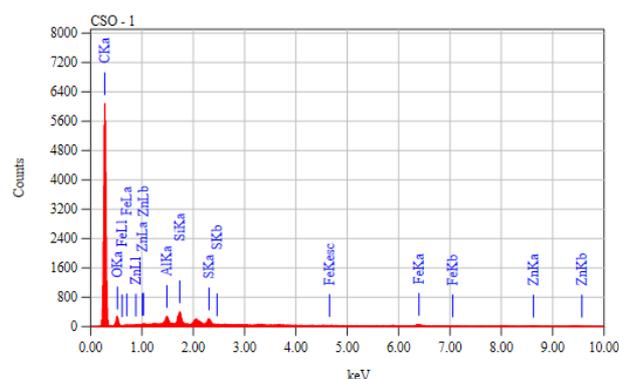


Figure 8. The EDX Results of 1.0 Grams of Graphite Powder Solution After Sonication

Conclusion

Sonication using a custom-made ultrasound generator based on piezoelectric probes with a frequency of 30 kHz for six hours can exfoliate graphite materials from carbon rods of ZnC battery wastes into GO. The UV-Vis absorbance peaks at wavelengths of 221 nm to 227.5 nm, and shouldering peaks at 260 nm to 270 nm were observed in sample solutions after sonication for all graphite mass variations. The best GO performances were obtained for graphite powder masses of 0.8 and 1.0 grams, which underwent a red shift from 223.5 nm to 227.5 nm, respectively. The SEM-EDX results of the sample after sonication show transparent and thin layers of GO material, corresponding to 88% and 11% of carbon and oxygen compositions, respectively. All in all, carbon rods from used ZnC batteries are potential raw materials for producing GO using simple and inexpensive equipment.

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