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Impact of Cation Concentration on Graphene Oxide Properties Fabricated from Disposed Batteries

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ABSTRACT

Disposed batteries contain the hazardous sources that directly impact on the environment. Proper disposal of used batteries is a vital matter because of toxit component found in types of batteries. This study focuses on the reutilization of the disposed Zn-battery graphite to produce graphene oxide (GO) via electrochemical exfoliation. The influence of various electrolytes on the exfoliation process was investigated, and the optimal I_D/I_G values in Raman spectra were determined as 2.5% for KOH. Scanning electron microscopy (SEM) images confirmed the presence of multi-wall graphene oxide in the exfoliated samples. X-ray diffraction (XRD) spectra displayed a broadening of the peak at $2\theta = 26.5°$, further supporting the successful formation of graphene oxide. The exfoliated graphene oxide was found not to contain any toxic elements. This highlights the potential of using disposed batteries in producing low cost graphene oxide. The study contributes to environmental protection by repurposing graphite rods and reducing industrial waste.

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1. Introduction

In recent years, there has been a notable increase in battery consumption due to the arrival of the technological age. As a consequence, used batteries have become a hazardous form of waste, directly impacting the environment. Proper disposal of these batteries has become an urgent matter due to the unique chemical components found in each type [1]. Notably, graphite rods within Zinc-carbon batteries can serve as potential sources for recycling graphite. Therefore, the recycling of graphite rods from disposed batteries is crucial, aiming to reuse graphite in batteries, reduce pollution, and enable the production of graphene oxide (GO). Graphene oxide was initially synthesized through the process of oxidizing and exfoliating naturally crystalline graphite [2]. GO has 2D structure as graphene, however, layers of carbon are covalently bonded to oxygen-containing groups such as hydroxyl, epoxide, carbonyl, etc [3]. These functional groups are present both on the basal plane and at the edges, and they are introduced during the chemical exfoliation process of graphite flakes. The presence of these functional groups in GO enables easy processing and provides it with high colloidal stability in water, giving rise to a distinctive range of mechanical, colloidal, and optical properties [4]. The properties of GO can be enhanced using chemical engineering techniques, resulting in a wide range of applications such as solar cells [5], sensors [6], supercapacitors [7], cellular migration [8], drug delivery [9], membranes [10], multifunctional gels [11], water purification [12].

Electrochemical exfoliation [13] is a promising method to produce graphene and graphene oxide due to its possibility of the mass-production. In this method, the ions of electrolyte intercalate between the graphene layers, exfoliating them to singer layer or few layers. Numerous electrolytes and electrochemical conditions have been tested with excellent exfoliation efficiencies. Applied voltage and the type of electrolyte strongly affect the quality of graphene oxide, especially in the presence of negative ions such as SO^{4-}, NO^{3-}, Cl^{-}, etc [14], [15]. Using high voltage during the exfoliation also generates numerous oxygen groups on exfoliated graphene oxide and damages its structure [16]. To address this

issue, researchers have explored the use of negative potentials under cathodic conditions in the presence of positive intercalation ions like tetraalkylammonium cations. This approach aims to prevent the formation of oxygen functionalities and achieve higher-quality graphene [16]. However, it has been observed that the exfoliation efficiencies under cathodic conditions are generally lower compared to anodic conditions.

In this study, graphene oxide is fabricated using the electrochemical exfoliation of graphite rods obtained from disposed Zin-batteries. Because the cation concentration strongly affects the exfoliation efficiencies, the initial investigation of KOH concentration of 2.5% and 7.5% was conducted to see the impacts of the cation concentration on the properties of GO. The GO fabricated was thoroughly analyzed in terms of its morphology, structure, and crystalline properties, using scanning electron microscopy (SEM), Raman spectroscopy, and X-Ray diffraction analysis (XRD).

2. Experimental Procedure

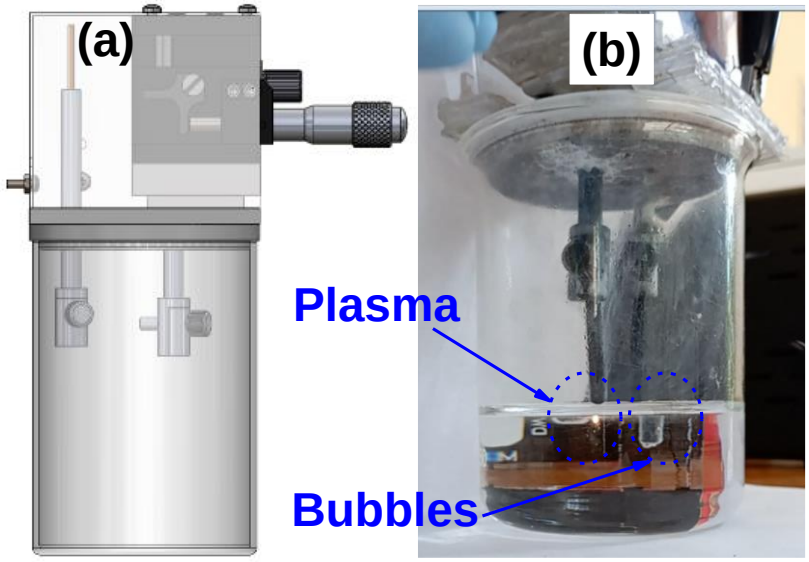
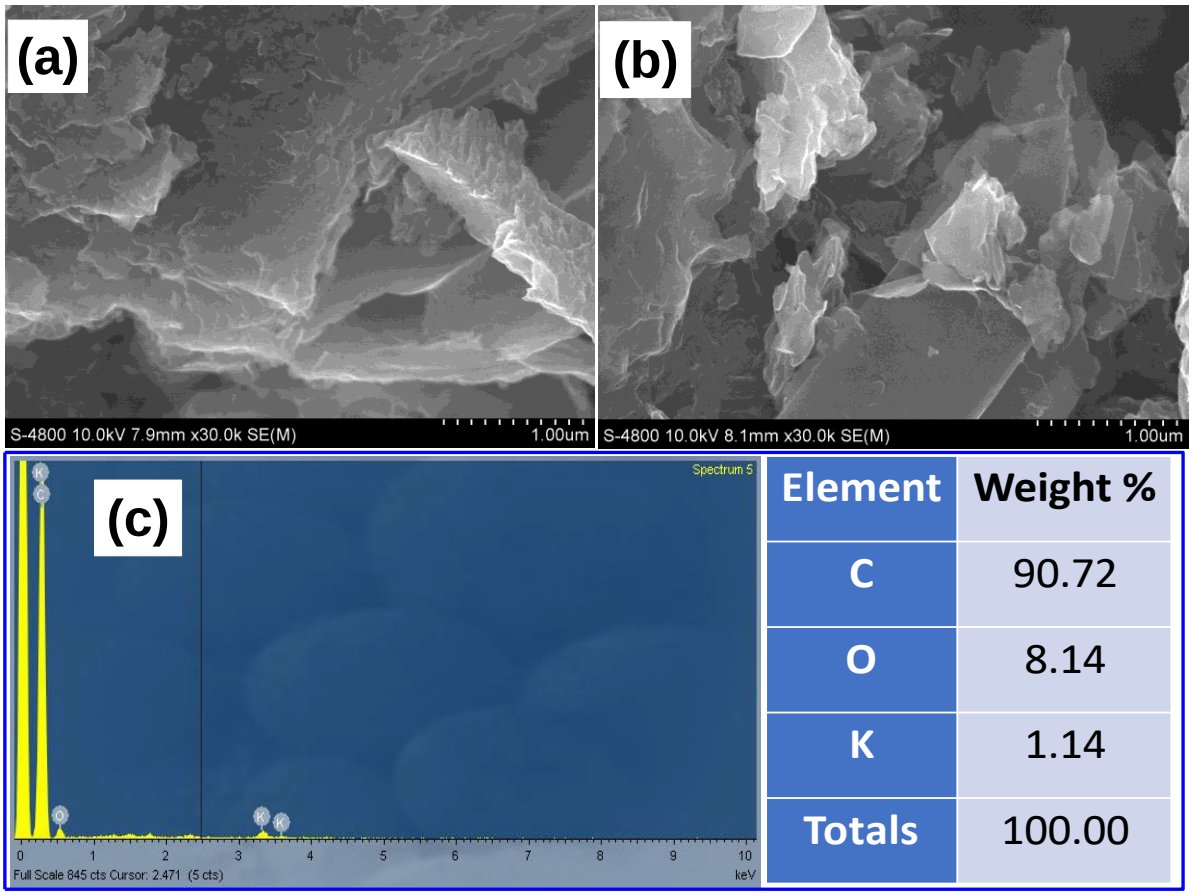


Figure 1. *(a) The electrochemical cell was illustrated schematically, clearly indicating the placement of the cathode and anode. Notably, the cathode was designed to be movable along a perpendicular axis with respect to the bottom of the chamber. (b) Observations revealed that plasma generation occurred specifically at the cathode, while bubbles were observed exclusively at the anode within the electrolyte solution.*

The electrolytic solution used in this study was created by dissolving KOH in 200 ml of water and $(NH_4)_2SO_4$ in 40 ml of water. The KOH and $(NH_4)_2SO_4$ solutions were prepared individually, then combined and stirred for 10 minutes. The anode and cathode were obtained from graphite rods with a diameter of 6 mm (Pinaco, the eagle brand). The tip of the cathode was ground to approximately 200 µm in diameter. Prior to the experiment, all electrodes underwent a cleaning process using acetone and isopropanol (IPA), followed by annealing at 130°C for 24 hours. The experimental setup involved an electrochemical chamber, as showed in Figure 1(a), where a specially designed cap allowed for unrestricted movement of the cathode. To begin the experiment, all electrodes were linked to a DC power supply, and the bias voltage was gradually raised up to 60 V. The initial temperature inside the chamber was noted as 30°C. In order to induce graphene exfoliation, the cathode was slowly lowered in increments of 20 µm until a plasma formed around its tip (as shown in Figure 1(a)). At this moment, numerous bubbles were emitted at the anode, and a gas was expelled from the chamber as illustrated in Figure 1(b). Throughout the experiment, graphene oxide (GO) underwent exfoliation, causing it to float on the surface of the electrolyte solution. The plasma state was sustained for over one hour. Subsequently, the GO was washed with deionized (DI) water and gathered by employing vacuum filtration through a Poly(vinylidene fluoride) (PVDF) membrane with an average pore size of 0.45 µm. The sample was then subjected to a drying process at a temperature of 50°C for a duration of 2 hours.

Hitachi FE-SEM S-4800 was utilized to obtain scanning electron microscope (SEM) images. The Raman spectra were obtained using the Horiba XploRA ONE system.

3. Results and Discussion



Element	Weight %
C	90.72
O	8.14
K	1.14
Totals	100.00

Figure 2. *The scanning electron microscope (SEM) images depict (a) graphite and (b) graphene oxide (GO) obtained using the plasma-assisted exfoliation method with 2.5%. In Figure 2(a), a stacked layer structure and bulk form of graphite are observed. Conversely, Figure 2(b) displays crumpled nanosheets resulting from the exfoliation process. Notably, Figure 2(b) illustrates the scrolled configuration of GO. Figure 2(c) presents the Energy-Dispersive X-ray Spectroscopy (EDS) spectrum of GO after the filtration process. The analysis reveals that no toxic metals are detected in the samples.*

Fig. 2 displays electron microscope images obtained from a field emission scanning electron microscope (FESEM). The images compare graphite powder, which was directly obtained by grinding a graphite rod, with exfoliated graphene oxide collected after filtration. In Fig. 2(a), the graphite powder exhibits a stacked layer structure, indicating the presence of multiple layers. On the other hand, Fig. 2(b) shows the result of plasma-assisted electrochemical exfoliation, where randomly crumpled nano-sheets are formed. The closely associated nano-sheets in the exfoliated product are a result of the strong π-π bonds between them. These nano-sheets form nanometer-scale plates, composing the exfoliated product. Notably, upon observation, the graphene oxide (GO) sheets can be seen to be scrolled, as indicated in the inset of Fig. 2(b). Figure 2(c) presents an investigation of the purification of exfoliated graphene oxide (GO) through an Energy-Dispersive X-ray (EDX) spectrum analysis. The analysis aimed to identify any toxic elements present in GO. Upon examination, it was determined that no toxic elements were detected. A small fraction of potassium (K) was observed within the marginal errors of the EDX measurement. This finding suggests that GO can be utilized for various applications without concerns regarding toxic heavy metal content.

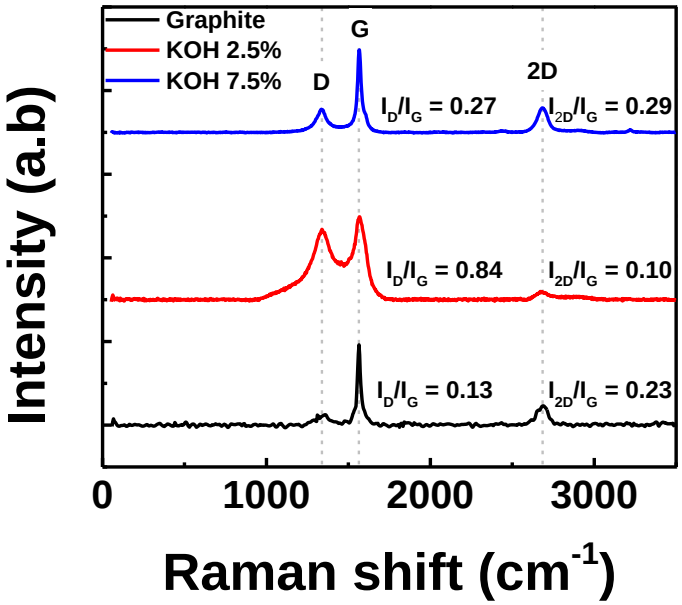


Figure 3. *The Raman spectra of graphite powder (black line) and graphene oxide (red and blue lines) reveal clear distinctions. Specifically, when the KOH concentration is 2.5%, the spectrum of graphene oxide shows broadening and shifting of peaks towards higher frequencies. This shift is indicative of isolated double bonds present in the single layer of graphene oxide.*

The influence of cations on the reduction of defects at the surface and edge of GO has been reported [16], even though exfoliation is facilitated by anions like SO^{4-}, NO^{3-}, Cl^{-}. Figure 3 illustrates the Raman spectra analysis exploring the effects of varying potassium concentrations on the properties of GO. In the electrolyte solution, the reaction between KOH and $(NH_4)_2SO_4$ can be represented by the following chemical equation:

$$2\ KOH + (NH_4)_2SO_4 \rightarrow K_2SO_4 + 2\ NH_3 + 2\ H_2O$$

In this reaction, potassium hydroxide (KOH) reacts with ammonium sulfate ($(NH_4)_2SO_4$) to form potassium sulfate (K_2SO_4), ammonia (NH_3), and water (H_2O). The presence of K^+ and SO^{4-} ions in the solution can be inferred from this observation. Raman spectra of graphite and GO in Fig. 3 illustrates structural changes during the chemical conversion from graphite to graphene oxide. It is well-known that C=C bonds exhibit high Raman intensities [17]. In the case of graphite spectra (represented by the black line), the peak with the highest intensity occurs at 1568.8 cm^{-1}, corresponding to its G bands. This peak results from the first-order scattering of the E_{2g} phonon of sp^2 carbon atoms [18]. The G band is observed in all sp^2 carbon materials, including graphite, amorphous carbon, carbon nanotubes, and graphene. Additional weak bands are associated with the D band at 1342.3 cm^{-1} and the 2D band at 2682.3 cm^{-1}. The D band is known as a defect band and arises from edge effects, structural defects, and the breaking of symmetry in sp^2 bonds. The presence of the 2D peak in the Raman spectra of graphene oxide is attributed to the linear dispersion of its electronic bands, resulting in either triple resonance or double resonance. It is important to note that the Raman spectra of graphene oxide are influenced not only by the phonon properties but also by its electronic structures.

In 2.5% KOH sample, the frequencies of the D band, G band, and 2D band experienced a shift towards higher values in this study. Specifically, the D band reached a value of 1348.45 cm^{-1}, the G band reached 1572.42 cm^{-1}, and the 2D band reached 2678.98 cm^{-1}. These findings align with previous reports [19], [20]. During the exfoliation process of graphite to graphene oxide, there are notable changes observed in the G and D bands. These changes can be seen in Fig. 3 as a broadening and rightward shift of these bands (red line). The rightward shift of the G band suggests a higher resonance frequency associated with isolated double bonds present in single layer graphene oxide [21]. Additionally, an increase in the I_D/I_G ratio from 0.13 (representing graphite, depicted by the black line) to 0.81 (representing graphene oxide, shown by the red line) in Fig. 3 indicates a decrease in the size and crystallinity of graphitic materials. This increase in the ratio signifies the presence of more isolated

graphene domains [18], [19]. These observations align with findings reported in [20]. When the concentration of KOH is increased to 7.5%, a noticeable shift in the frequencies of the D band, G band, and 2D band is also observed. This shift is opposite to that observed in the 2.5% KOH sample (represented by the blue line). In this sample, the D band frequency is measured at 1339.93 cm^{-1}, the G band frequency at 1567.66 cm^{-1}, and the 2D band frequency at 2683.91 cm^{-1}. The shift in these bands indicates that the high concentration of K^+ cations has a suppressive effect on the defects present on the surface and edges of the graphene. However, this higher concentration may result in a lower efficiency of exfoliation. This can be attributed to the strong bonds formed between the K^+ cations and SO^{4-} anions, which minimize the interlacement of SO^{4-} ions between the graphene sheets.

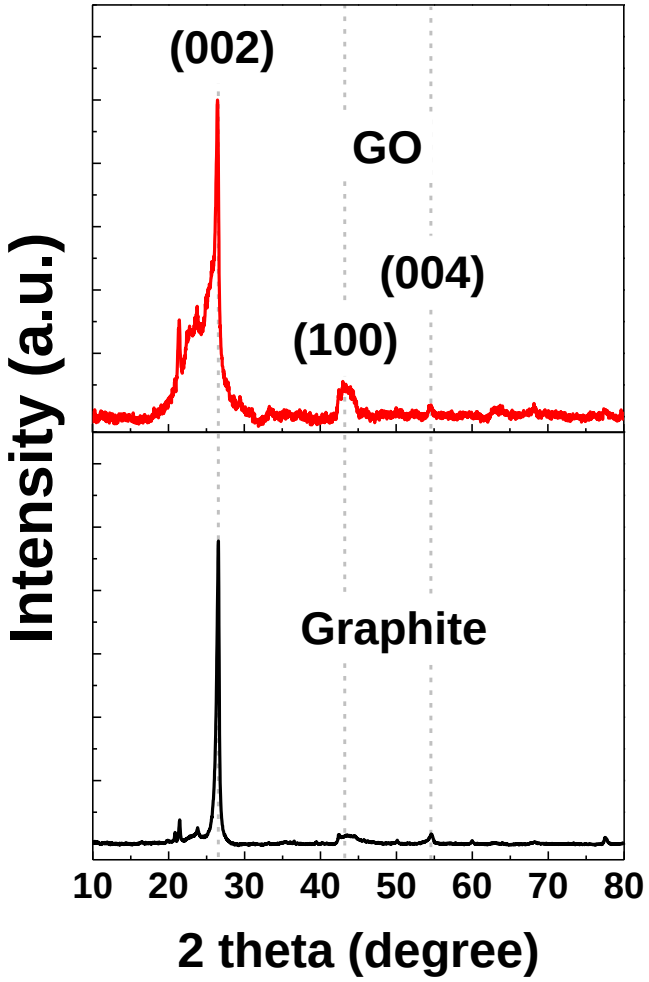


Figure 4. *XRD patterns recorded for graphite and graphene oxide obtained from plasma-assisted exfoliation.*

The graphite-based material (GF) was analyzed using X-ray diffraction (XRD) in Fig. 4 (black line). A distinct diffraction peak at $2\theta = 26.54°$ was observed, exhibiting a narrow peak width and high intensity. This peak corresponds to the crystal plane (002) of graphite, which possesses a hexagonal structure and an interlayer distance of d = 0.34 nm [22]. Additionally, a peak with small intensity at $2\theta = 54.5°$ was detected, corresponding to the crystal plane (004). The (004) peak is weaker as compared to the (002) peak because it is a result of a second-order diffraction [23]. The XRD pattern of the GO sample shows a significant shift and expansion towards lower angles. This broad peak locates from $2\theta = 20.53°$ to approximately $2\theta = 26.65°$, indicating an expanded interlayer distance ranging between 0.33 nm and 0.43 nm. These changes indicate that the graphite is exfoliated to GO during electrochemical exfoliation process. Additionally, a lower intensity peak at $2\theta = 42.60°$ (d = 0.21 nm) is observe, corresponding to the (100) peak. This peak can be attributed to the presence of disorder in carbon materials [24], [25]. The appearance of (100) peak is a result of the oxidation of SO^{4-} ions during the exfoliation process at the anode.

4. Conclusions

In conclusion, graphene oxide (GO) was successfully synthesized from disposed zinc batteries. The focus was on investigating the influence of potassium concentration on the properties of GO. Raman spectra analysis revealed that the presence of cation K+ effectively reduced defects on the graphene surface and its edges, presenting a promising approach to improve the quality of fabricated graphene oxide. X-ray diffraction (XRD) spectra demonstrated a broadening of the (002) peak of carbon, indicating the successful exfoliation of graphite layers to form graphene oxide. The confirmation of obtained GO was further supported by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis. Importantly, no toxic elements were detected in the exfoliated GO, emphasizing the potential of this study in producing cost-effective GO while contributing to environmental protection through the repurposing of discarded batteries.

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Conflict of Interest

The authors declare no conflict of interest.

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