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Fabrication of Graphene Oxide from Graphite Rod of a disposed battery

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***Abstract*— We report a new electrochemical exfoliation method to produce graphene oxide (GO) on a large scale from disposed graphite rod, recycled from a zinc-carbon battery. GO is exfoliated with plasma from the tip of the cathode. The properties of GO are characterized by Raman, SEM and EDX analysis. A moderate ratio of I_D/I_G ~ 0.75 in Raman spectra indicates that the product includes a mix of GO and graphite.**

***Keywords*— graphene oxide, plasma-assisted exfoliation, battery recycling, disposed graphite**

I. INTRODUCTION

Since the discovery of graphene in 2014, two-dimensional (2D) materials are attracting considerable interest, for example, as ribbon FETs to be introduced in mainstream CMOS ,. Graphene exhibits outstanding mechanical, thermal and electronic properties [1] and can be synthesized by a variety of methods such as Chemical vapor deposition (CVD), epitaxial growth, scotch tape method, and exfoliation of graphite in solution. CVD methods can be employed at scale [2], however, mass production of graphene by CVD has still proved to be a challenge due to the high cost of production in an inert environment at high temperature. Plasma-assisted electrochemical exfoliation is a highly efficient method to fabricate graphene/graphene oxide from graphite [3]. The purpose of this study is to investigate a continuous production of GO from recycled graphite, recovered from a zinc-carbon battery. The safe disposal of batteries is the leading cause of environmental concern, due to pollution from toxic metals and graphite rods [4]. The advantage of reutilization of graphite rods from battery is reduced pollution as well as cheap and sustainable methods of production of graphene/graphene oxide (GO).

II. EXPERIMENTAL

The electrolytic solution in this work was prepared by dissolving KOH in 200 ml H_2O and $(NH4)_2SO_4$ in 40 ml H_2O. KOH and $(NH4)_2SO_4$ solutions were prepared separately, subsequently mixed and stirred for 10 minutes. An anode and a cathode were obtained from disposed graphite rods with the diameter of 6 mm (Pinaco, the eagle brand). The tip of the cathode was prepared by grinding to a diameter of ~ 200 μm. All electrodes were cleaned in acetone, isopropanol (IPA), and annealed in 24 hours at 130ºC. The experiment was conducted in an electrochemical chamber illustrated in Fig. 1(a), with a cap designed to have a freely moving cathode. All electrodes were connected to a DC power supply with the bias voltage increased gradually to 60 V. The initial temperature of the chamber was recorded at 30ºC. To exfoliate graphene, the cathode was slowly moved downwards in steps of 20 μm until a plasma occurred around the tip of the cathode (Fig. 1(a)). At this moment, several bubbles were released at the anode and a gas was exhausted out the chamber as shown in Fig 1(b). During the experiment, GO was exfoliated and floated on the surface of the electrolyte solution, and the plasma was maintained for more than 1 hour. GO was washed in deionized (DI) water and collected using vacuum filtration through Poly(vinylidene fluoride) (PVDF) membrane with an average pore size of 0.45 μm. It was subsequently dried at 50ºC for 2 hours. Hitachi FE-SEM S-4800 with Horiba EDX system was employed to obtain Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX). Fourier transform infrared (FTIR) spectra were recorded by Thermo Nicolet 6700 FT-

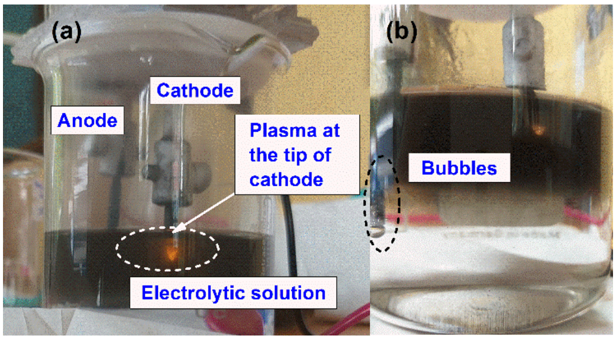


Figure 1: An electrochemistal cell, indicating the placement of the cathode and anode. The cathode can be moved freely along an axis perpendicular to a bottom of the chamber. Plasma occurs at a surface when inside the electrolytic solution.

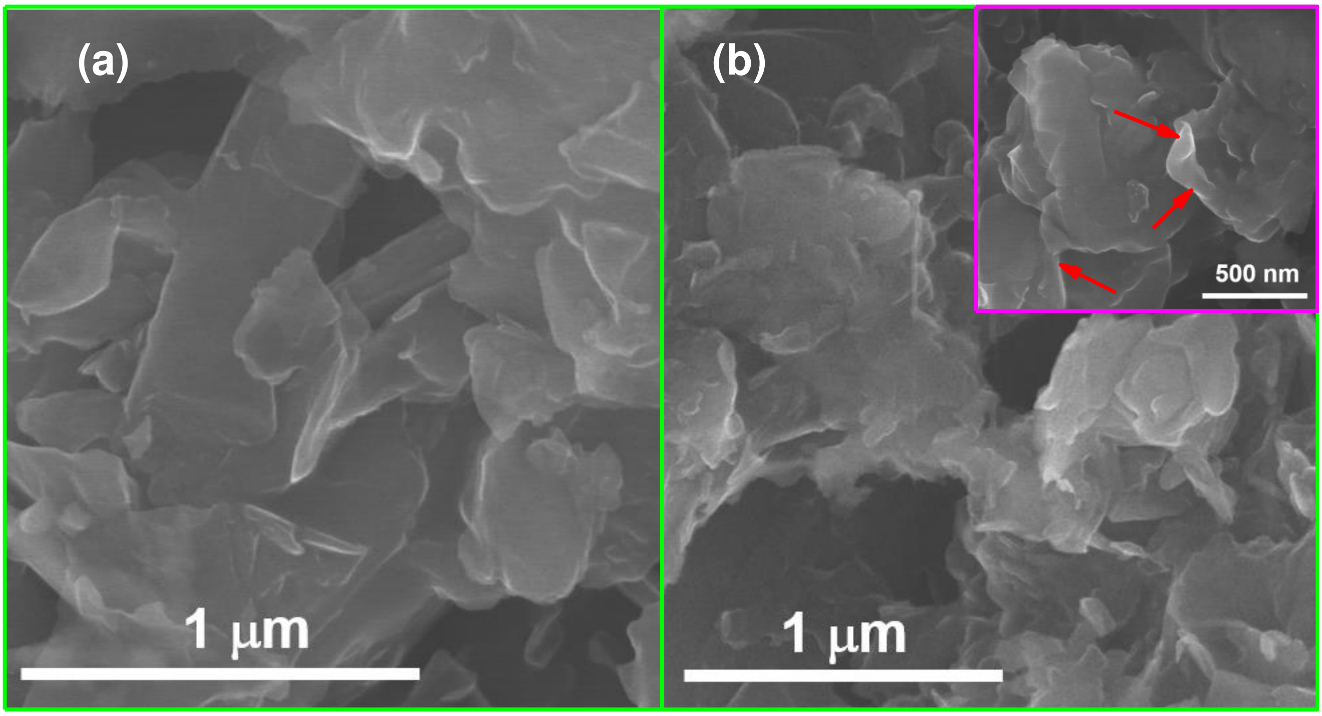


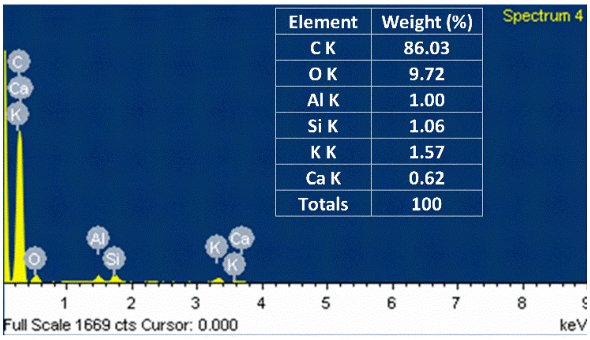
Figure 2: SEM image of (a) graphite and (b) graphene oxide obtained from plasma-assisted exfoliation method. Inset of figure b is a magnification of this figure. A stacked layer and bulk structure of graphite is observed in figure a, while crumped nano-sheets are obtained in figure b. Graphene oxide is scrolled illustrated by red arrow in the inset of figure b.

IR optical spectrometer, and Raman spectra were measured by Horiba XploRA ONE system.

III. RESULTS AND DISCUSSION

Fig. 2 shows the field emission scanning electron microscope (FESEM) images of graphite powder, directly ground from the graphite rod, and exfoliated graphene oxide collected after filtration, for comparison. A stacked layer structure of graphite is observed in graphite powder in Fig. 2(a), whereas the plasma-assisted electrochemical exfoliation creates randomly crumpled nano-sheets, closely associated with each other due to strong π−π bonds in Fig. 2(b). The exfoliated product includes several nanometer-scale plates (Fig.2(b)). At high magnification, GO sheets are observed to be scrolled as indicated by red arrows in the inset of Fig. 2(b). The purification of GO after filtration, is determined in EDX spectrum as shown in Fig. 3. It is found that oxygen dominates ~ 10% in weight in filtration products, while other metals, including Al, Si, K, and Ca, are observed within the marginal errors of EDX measurement (less than 2%). There are no toxic materials observed.

Fig. 4 shows the FTIR spectra of graphite power and graphene oxide. The highly intense peak at 3432.7 cm^{-1} is due to the O-H stretching vibration, indicating the present of OH or COOH functional groups. The symmetry and asymmetry stretching vibration of C-H bond is clearly



Element	Weight (%)
C K	86.03
O K	9.72
Al K	1.00
Si K	1.06
K K	1.57
Ca K	0.62
Totals	100

Figure 3: EDS spectrum of GO after filtration. There is not toxic metal observed in the samples.

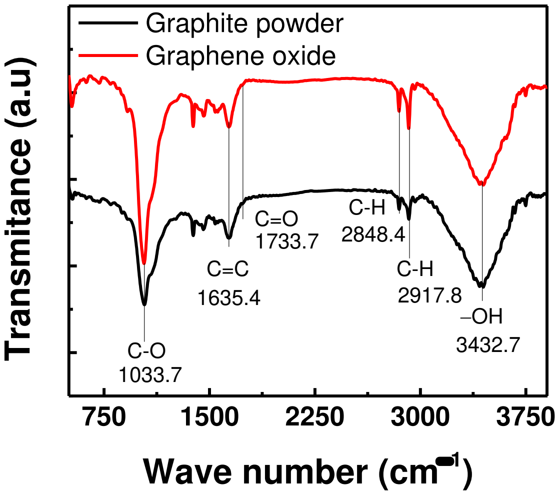


Figure 4: FTIR spectra of graphite powder (obtained from the disposed graphite rod in battery) and graphene oxide. Many oxygen containing functional groups were observed.

TABLE I. ASSIGNMENT OF CHARACTERISTICS FTIR ABSORPTION BANDS OF G AND GO

No.	***Wave number*** **(cm^{-1})**	***Functional groups***
1	3432.7	–OH Stretching Vibration
2	2917.8 2848.4	Symmetric and asymmetric stretching vibration of –CH2–
3	1733.7	–C=O stretching vibration
4	1635.4	C=C stretching Vibration
5	1033.7	C–O stretching of alkoxy group

observed at 2848.4 and 2917.8 cm–1. Very weak stretching vibration is observed for the carbonyl C=O peak at 1733.7 cm^{-1}. The peak at 1635.4 cm–1 is assigned to an un-oxidized C=C stretching vibration. The most intense peak is at 1033.7, which is related to the C-O stretching vibration of the alkoxy group. The results obtained from FTIR (Table 1) indicate the present of several oxygen containing functional groups in agreement with those reported in [5-9]. The FTIR spectrum of the graphene oxide powder is similar to that of the graphite powder, indicating that the graphite rod is oxidized before exfoliation.

Figure 5 shows Raman spectra of graphite and exfoliated graphene oxide, which reveals structural changes during the chemical conversion from graphite to graphene oxide. The principle is that C=C double bonds give rise to high intensity in the Raman spectra [10]. For graphite (black line), the highest intensity is at 1568.8 cm-1, representing the G band, due to the first order scattering of the E_{2g} phonon of sp^2 C atoms [11]. All sp^2 carbon materials such as graphite, amorphous carbon, carbon nanotube, and graphene exhibit the G band. Weak bands are related to D band at 1342.3 cm^{-1} and 2D band at 2682.3 cm^{-1}. The D band is known as a defect band derived from edge effects, structural defects, and the sp^2 bond that breaks the symmetry. The 2D peak is due to the linear dispersion of its electronic bands, giving rise to triple or double resonance. The Raman spectra of graphene oxide depends not only on the phonon properties but also on their electronic structures. In Fig. 5, the frequencies of D, G, and 2D bands are shifted to higher values, reaching 1354.4, 1581.6, and 2703.2 cm^{-1}, respectively, in agreement with previous reports [5, 12]. It is seen that G and D bands change significantly during the exfoliation of graphite to graphene oxide, illustrated by a broadening and a right shift of these bands shown in Fig. 5. The right shift of the G band is supposed to be the higher resonance frequency of isolated double bonds present in a single layer GO [13]. An increase in I_D/I_G ratio from 0.18, corresponding to graphite (black line), to 0.75, for graphene oxide (red line), in Fig. 5 indicates that the size and crystallinity of graphitic materials decreases, increasing in isolated graphene domains [11, 12]. The observed results are in agreement with those reported in [5]. The results indicate that graphite has been exfoliated to GO. It is also known that the intensity ratio of the D and G bands (I_D/I_G) helps to estimate the defects in GO sample, where higher ratio implies more defects in the graphene sheet.

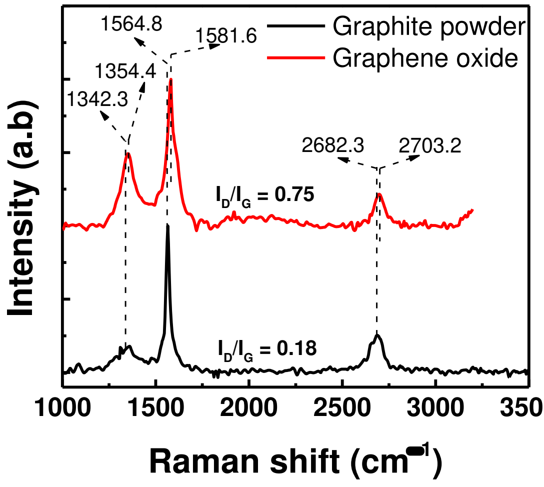


Figure 5: Raman spectra of graphite powder (black line) and graphene oxide (red line). Spectrum of graphene oxide broadens and shifts to the right, indicating the present of isolate double bond in single layer graphene oxide.

IV. CONCLUSION

In conclusion, the disposed graphite of a battery is used to produce graphene oxide. The process is designed to work for more than 1 hour. The SEM, EDX, and Raman characteristics verify the obtained GO. There are no toxic elements observed in the exfoliated GO, so this study opens a new way to sustainably produce cheap GO and protect the environment from battery waste.

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