Preparation of Graphene by Recycling Graphite Rods From Electrical Storage Devices -Microwave Treatment Effect.

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ABSTRACT/RESUME

Abstract: *Despite their utilities, batteries can because of the toxicity of certain constituents, represent a real danger for the environment. Due to the use of constituents with non-renewable resources, the manufacture of batteries is threatened for future generations. But today we can limit this by recycling.*
In this study, we focused on the large scale preparation of graphene (G) by recycling graphite from electrical storage devices using an affordable and simple electrochemical technique, after which the latter has undergone treatment microwave to re-exfoliate the graphene (GE) sheets and obtain a more pure graphene (GE-MW).
The characterization of our materials was examined using Raman spectroscopy, X-ray diffraction, SEM scanning electron microscope and the X-Ray Fluorescence Spectrometer.

I. Introduction

The theoretical structure of a graphite plane was studied as early by Wallace [1]. McClure wrote the graphite wave equation and the similarity to the Dirac equation was discussed by Semen off [2]. The difficulty was in isolating a single graphene plane large enough to be identified and characterized.
In the 1960s, thin films of graphite on the surface of metals were observed after reaction with hydrocarbons .On the other hand, Van Bommel et al [3], observed a monolayer of graphite on the surface of a SiC substrate annealed under ultra-high vacuum, without using the term graphene. The first to give the graphene name to the atomic carbon monoplane was Boehm in 1986. [4].

Until 2004 scientists were convinced that obtaining a stable layer of monoatomic carbon was impossible; Andre Geim and Konstantin Novoselov have shown the opposite, with a very simple method, they extracted graphene sheets from a graphite crystal, exfoliating them with an adhesive tape, and then depositing them on the silicon.

They even managed to make the first electrical measurements.
Recently, it has become possible to make large sheets of graphene. Using quasi-industrial methods, 70 cm wide leaves were produced [5].
Since graphene is a transparent conductor, it can be used in applications such as touch screens, light panels and solar cells, where it can replace the rather fragile and expensive indium-tin-oxide (ITO).
In this work, graphene was synthesized by recycling of graphite of electrical storage devices by the electrochemical exfoliation process in which the sulfuric acid dissolved in deionized water. The re-exfoliation of graphene was carried out by a microwave.

II. Materials and methods

In this study we used graphite (as electrodes) and the electrolyte baths (electrochemical cell) composed of sulfuric acid and water for exfoliation process. In this work, we performed the electrochemical exfoliation of graphite in sulfuric

acid to obtain high quality and large-area graphene thin sheets.

In a typical electrochemical process two-electrode system has been used in which a graphite rod acts as an anode and another rod acts as a cathode in a solution of sulfuric acid H_2SO_4. The electrolyte consisted of 100 ml of aqueous solution with a volume ratio of 1/4 of H_2SO_4 and H_2O. A DC voltage of 10 V was applied until the total consumption of the graphite rod which was converted to graphene sheets within 1.5 hours.

The aqueous solution of a graphene ink was centrifuged and washed several times with distilled water after sonication for half an hour. Finally our graphene is dried for 24 hours at 333° K. After drying our graphene electrochemically (GE) this material subjected a microwave treatment for 30 seconds to separate the sheets of graphene from each other the latter will be named (GE-MW).

III. Results and discussion

III.1. Raman Characterization

The experimental part of this research includes the preparation of the raw material, graphene (G) with electrochemical method.

Raman spectroscopy is a non-destructive technique for observation and characterization allowing the analysis of the molecular composition and the structure of material.

Our samples were analyzed using a Renishaw Invia microspectrometer tuned for monochromatic (Ar +) laser radiation with a wavelength of 514.5 nm.

Raman spectroscopy is a useful technique for characterizing the sp^2 and sp^3 hybrid carbon atoms, including those of graphite (Fig 1), fullerenes, carbon nanotube and graphene (Fig 2). Single, double and multilayer graphene were also differentiated by their Raman imprints.

Mode G is about 1583 cm^{-1} from the stretching of the C-C bond in graphitic materials and is common to all sp^2 carbon systems. The G band is very sensitive to stress effects in the sp^2 system and can therefore be used to probe the change in the graphene surface.

Mode D is due to a disordered structure of graphene. The presence of disorder in hybrid sp^2 carbon systems results in resonance Raman spectra and makes Raman spectroscopy one of the most sensitive techniques for characterizing the disorder of sp^2 carbon materials.
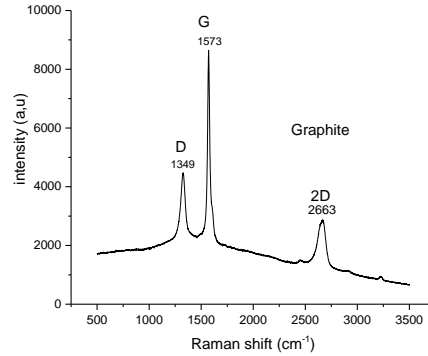

Figure 1. *Raman spectrum of graphite(display a disordered D peak at 1349 cm^{-1} ,G peak at 1573cm^{1-} and a 2D peak at 2663cm^{-1})*
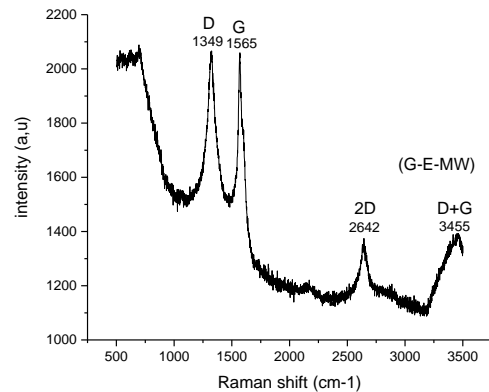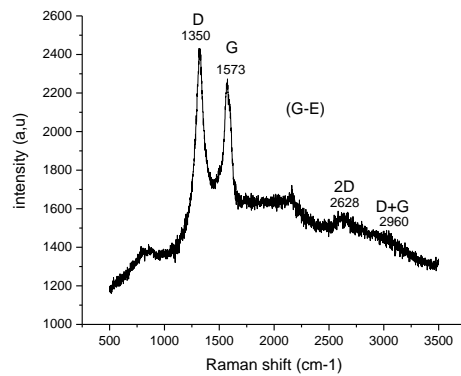

Figure 2. *Raman spectrum of graphene (GE) (display a disordered D peak at 1350 cm^{-1} ,G peak at 1573cm^{-1} and a 2D peak at 2628cm^{-1}) and graphene (GE-MW) (display a disordered D peak at 1349 cm^{-1} ,G peak at 1565$cm-1$,2D peak at 2642 cm^{-1} and a D+G peak at 3455 cm^{-1})*

In Raman spectroscopy, bands D and G are normally located at 1350 cm^{-1} and 1574 cm^{-1}, respectively. The existence of D and G bands confirms the formation of graphene with fewer defects and a crystalline structure (Fig 2). In addition, an increase in the intensity of the D-line around 1355 cm^{-1} indicates a considerable reduction in the size of the sp^2 domains in the plane due to the

oxidation processes and the formation of graphene nanofiles having a structure crystalline highly oriented.

To fully accomplish the protocol for quantifying pointlike defects in graphene GE and GE-MW using Raman spectroscopy, we use different excitation laser lines in ion-bombarded samples and measure the D to G peak intensity ratio.

***Table 1.** Raman Analysis Values for graphite, GE, and (GE-MW).*

Sample	D position (Cm^{-1})	D Intensity (u.a)	G position (Cm^{-1})	G Intensity (u.a)	2D position (Cm^{-1})	2D Intensity (u.a)	D+G position (Cm^{-1})	D+G Intensity (u.a)	ID/IG
Graphite	1328	4411	1573	8565	2824	2663	/	/	0.52
GE	1322	2427	1573	2260	2628	1560	2960	1464	1.07
GE-MW	1322	2059	1565	2054	2642	1356	3455	1383	1.00

In the Raman spectrum of graphene-based nanowires, the intensity of the D-line around 1350 cm^{-1} has considerably decreased due to the increase in the size of graphitic domains and thickness of the graphitic structure after heat treatment.

The ID / IG ratio, which has been validated as a measure of the inter-defect distance in graphene, is not reliable when applied to GO and Rgo [6-7].Ferrari and Robertson defined an amorphization trajectory, in which the ID / IG ratio of carbon (sp2) would increase with the spread of the defects, proportional to the square of the crystallite size [8]. In this way, they define a transition between carbons which have a crystallite size less than ~ 2 nm, which should obey the Ferrari - Robertson relationship, and those with larger crystallites, which obey the Tuinstra - Koenig relationship. The discontinuity in the relation to structure is attributed to the distortion of aromaticity at very high defect densities.

Kurniasari have shown that if the defect intensity ratio (ID / IG) increases, implying the increase of defect number. [9].

The decrease of the ratio of the intensities of the D and G bands (ID / IG ratio) (table 1) and the displacement of their position towards lower wavelengths indicate a less extensive graphitic domain, attributed to an increase in the degree of disorder of the sp2 bonds, and an increase in the number of sp^3 bonds in the structure. The lower the ratio ID / IG is lower (graphite) this results in an increase in the density of defects [10].

III.2. Characterization by X-ray diffraction

This technique allows the analysis of the crystalline phases contained in a sample. Information on its microstructure (size of the crystallites, micro stresses) can also be extracted.

X-ray diffraction is based on the recording of a diffractogram, which allows you to identify / quantify the phases, calculate the crystallographic parameters and determine the average size of the crystallites by different methods (Scherrer, Williamson-Hall).

Our samples were analyzed using a D8 Advance Eco diffractogram (Bruker) operating with a copper tube (λ = 1.54Å)

The X-ray spectrum of the graphite powder (Figure 3) shows the hexagonal structure according to the (002) orientation, as revealed by the single peak at 2θ = 25 ° which corresponds to a spacing of about 3, 4 A ° between the graphite planes.
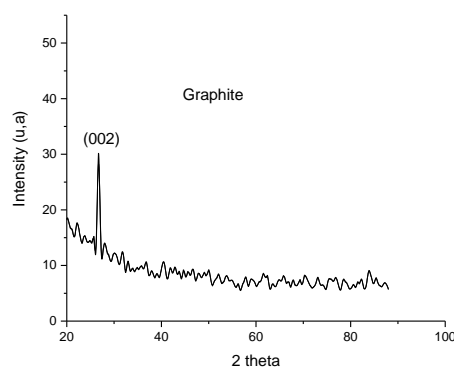
***Figure 3.** XRD patterns of Graphite XRD*

The graphene X-ray spectra (GE ;GE-MW) (Figure 4) show the absence of the diffraction peak in comparison with graphite (2θ = 26.4 °). This indicates the removal of the periodicity in the structure of Graphene exfoliated. In fact, the increase in the inter-spacing following the oxidation of the graphite comes from the intercalation of the oxygen-containing groups between the layers of the graphite thus weakening the van der Waals forces between the layers, which allows an exfoliation easy via sonification in an aqueous medium.
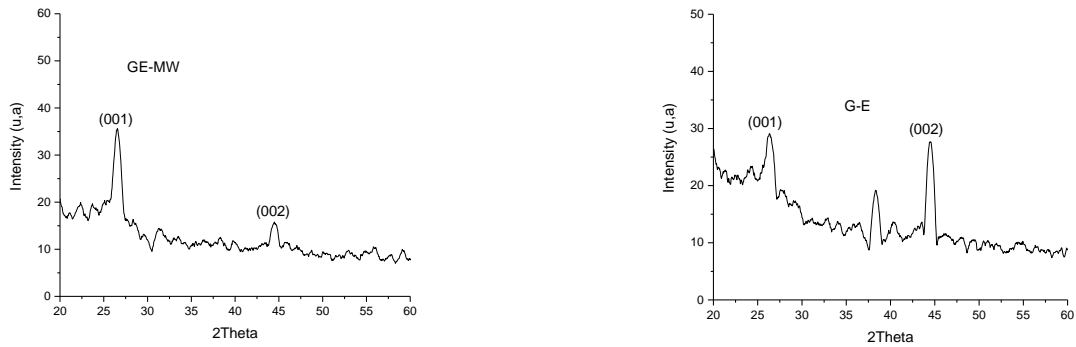
Figure 4. XRD patterns of GE, and GE-MW

III.3. Characterization by Scanning electron microscope (SEM)

The SEM were used to analyze the morphology and structural characteristics of "nano-composite samples, in order to check the condition of our studied materials, and to better observe the morphology of our samples we used a SEM type Quanta FFG 250.

Figure 5 shows the enlargement of the graphite grains. This scanning electron microscopy image shows a more homogeneous expansion on the milled sample. From the figure (6.7) It is clear that the images of our products show the dynamic form of graphene and confirm the existence of homogeneity in the microscopic structure.

These images show large, intact GE, GE-MW sheets entangled on top of each other. With a bigger magnification.
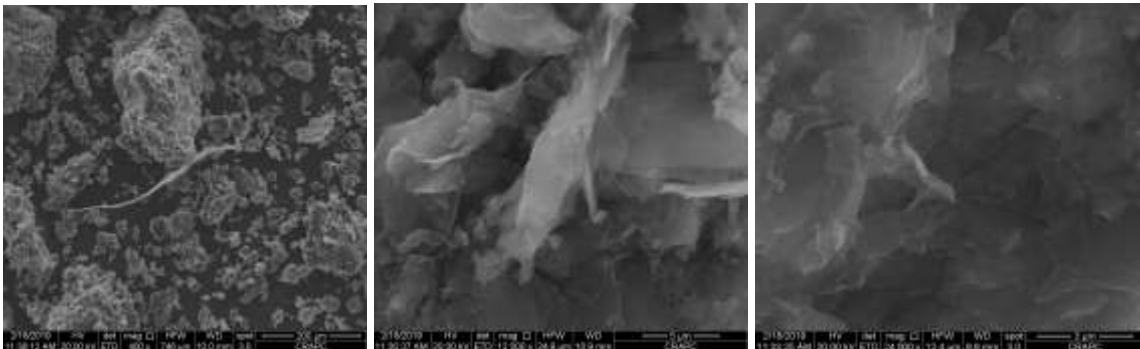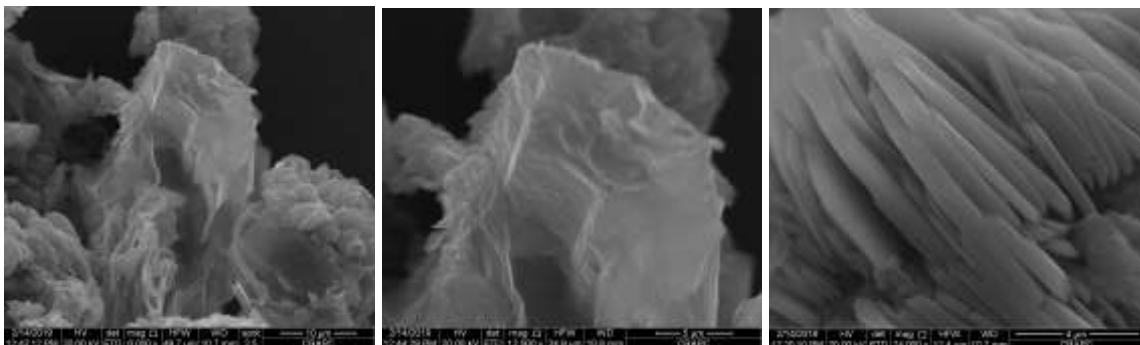

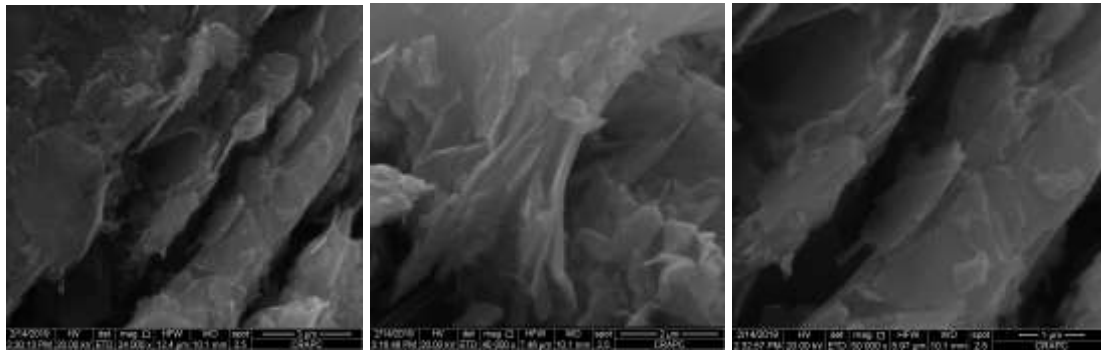*Figure 5. SEM of Graphite*

Figure 6. SEM of GE

Figure 7. SEM of GE-MW

III.4. Characterization by X-Ray Fluorescence Spectrometer

FRX is a method of spectroscopic analysis of matter, based on the principle of X-ray fluorescence. It is one of the most used methods for the qualitative and quantitative determination of the elementary composition of a sample. in liquid, solid or powder form.

Our samples were analyzed using spectroscopic analysis type ZSX Primus II.

Table 2. *The values of the FRX analysis.*

Sample	C wt. %	O wt %	others wt %
Graphite	50.1	31.1	18.8
GE	67	26.3	6.7
GE-MW	74.2	13.7	12.1

These results indicate that the mass percentage of carbon is (67% C, 26.3% W) in GE and after microwave treatment the oxygen percentage has decreased by 12.6% between GE and GE-MW and that the percentage of carbon increased by 7.2% which confirms that our samples are graphene by direct exfoliation of graphite.

IV. Conclusion

The graphene (G) were fabricated by electrochemical methods threated by microwave irradiation for 15 second, this is an eco-friendly approach to synthesize graphene nanoplatelets. The graphene synthesized by this method are highly pure and have high aspect ratio.

V. References

1. Wallace, P.R. the Band Theory of Graphite. *PhysRev.*(1947)71.622
2. Niemi, A. J; Paranjape, M. B.; Semenoff, G. W. Electric Charge of the Magnetic Monopole. 1984.
3. Van Bommel ,A.J.; Crombeen, J.E.; ,Van Tooren, A. Leed and auger electron observations of the SiC(0001) surface. 1975.
4. Boehm, H.; Setton, R.; Stumpp, E. Nomenclature and terminology of graphite intercalation compounds, *Carbon* 24(1986)241 - 245.
5. Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils, *Science* 324 (2009)1312-1314.
6. Kotchey, G. P. the Enzymatic Oxidation of Graphene Oxide, *ACS Nano* 5 (2011) 2098–2108.
7. Stankovich, S. Synthesis of graphene-based nano sheets via chemical reduction of exfoliated graphite oxide, *Carbon* 45(2007) 1558–1565.
8. Ferrari, A.; Robertson, C. Interpretation of Raman spectra of disordered and amorphous carbon, *J. Phys. Rev.* B. 61 (2000) 14095–14107.
9. Kurniasari. IOP *Conf. Ser.: Mater. Sci. Eng*. 196 (2017) 012021
10. Lucchese, M. ; Stavale, M. ; Ferreira, F.; Vilani, .E. ; Moutinho ,C.; Achete, R. *Carbon* 48 (2010) 1592-1597.