

Study of the Graphene Oxide Nanosheets Synthesized from Pencil Electrode Using Electrochemical Method and Solar Energy as a Source of Power

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Abstract

Graphene Oxide nanosheets were synthesized using electrochemical exfoliation of pencil electrodes in aqueous solution containing 2% of magnesium sulfate salt. A solar panel of 20V was used as a power supply to turn the synthesis into a green method. Several measurements were carried out to investigate the product, namely: Raman scattering, X-ray diffraction, photoluminescence, UV-VIS-NIR spectroscopy, and FTIR spectroscopy. Raman scattering showed the existence of both D-band and G-band, which are an indication of graphene oxide existence. The D-to-G band ratio was 1.5. The results of X-ray showed a diffraction peak at $2\theta = 20.7^\circ$ corresponding to the space distance between graphene oxide nanosheets and a diffraction peak at $2\theta = 26.25^\circ$ corresponding to the short range interplanar spacing. Photoluminescence showed two peaks of emission (at wavelengths 355nm & 701nm) regarding to the π - π^* transition. UV-VIS-NIR spectroscopy exhibited a 4.2eV photon energy absorption peak corresponding to the aromatic C=C bonds and 5.4eV photon energy absorption peak corresponding to the carbonyl groups. FTIR showed peaks related to hydroxyl groups, hydrogen-bonded OH groups of COOH, and functional groups such as C-OH (1375 cm^{-1}), and C-O (1039 cm^{-1}). FTIR results approved that graphene oxide nanosheets are functionalized. TEM images show that the synthesized graphene oxide is single-, double-, and multi-layer stacks with an amount of impurities.

1. Introduction

Graphene is now the subject of interest in various applications such as photovoltaics [1]. Graphene has unique properties that allow it to be incorporated in different ways in solar cells fabrication such as nanocomposites [2], buffer layers in organic solar cells [3], and active layer materials [2]. Graphene is considered one of the thinnest materials. It was first synthesized and characterized by Novoselov et al., in 2004 [4]. Before this invention, scientists thought that such planar benzene-ring structure can be unstable compared to spherical structure such as fullerene or cylindrical structure such as carbon nanotubes [4]. However, this nanosheet material has shown outstanding optical, electrical, and mechanical properties [4]. Graphene also exhibits high stability at wide range

of ambient temperature [4]. The nature of graphene requires only a few layers of nanosheets to fabricate high quality thin films with high transparency and conductivity. In addition, composite materials can also take advantage of graphene as incorporation with other materials.

Pristine graphene has an electron mobility of $103\text{cm}^2/\text{V}\cdot\text{s}$ [5], a film of $\sim 10\text{nm}$ thick has electrical conductivity of $1250\text{S}/\text{cm}$ with a transparency of more than 70% over the wavelength range of $1000\text{-}3000\text{nm}$ [6]. The delocalization of charges within each plane graphene sheet produces high conductivity [4]. The mechanical strength of a single graphene sheet is extremely high due to the strong π -bond in its honeycomb crystal lattice, for instance a graphene paper exhibits a tensile strength up to 35 GPa [7].

Solution processed graphene nanosheets usually have lattice defects that create trap centers causing a decrease in the sheet conductivity. This can be overcome by synthesizing multi-layer graphene sheets. Moreover, graphene is made with two different edge configurations: zigzag and armchair [8]. The first configuration is metallic, while the latter can be either metallic or semiconducting. The bandgap of armchair graphene is tunable and is mainly dependent on the width of graphene sheet -- for instance the bandgap of 15nm wide graphene nanoribbon is 0.2eV [9]. The ability to tune the bandgap of graphene in addition to its high conductivity and transparency, are some of the advantages of graphene that makes it an implicit material for solar cells application.

Graphene can be chemically modified to produce graphene oxide (GO), which allows graphene to be soluble in many solvents and can be further attached with many functional groups depending upon different applications. GO can be viewed as a graphene sheet with defects on its basal plane: mainly oxygen containing functionalities, such as carbonyl, ether, and/or hydroxyl groups. However, this form of graphene is easy to functionalize, and this can increase the potential of wide applications. A second benefit is that functionalization improves solubility which helps to ease the fabrication methods of solution processed graphene sheets. GO can also be reduced resulting in similar properties of pure graphene.

One method that can produce graphene oxide directly is the electrochemical exfoliation of graphite. In this method, graphite is used as an electrode in acidic or saline media. This method has several advantages such as simplicity, low-cost synthesis, and short synthesis time [10]. The method requires a source of electric power to be applied to the electrode to accelerate the electrolysis. Using photovoltaic (PV) panel as a source of power can turn the method into a green technique. Moreover, graphite electrode is relatively expensive. Using inexpensive pencils of high graphite content can be a good substitute. In this work, GO nanosheets were synthesized using a green and eco-friendly electrochemical method by using a PV panel as a source of electric power. 5B pencil in a saline medium is used as an electrode to turn the method into a very inexpensive technique. The method can produce a high quantity of GO in a very short time.

2. Experimental Procedure

GO nanosheets were synthesized using the electrochemical exfoliation technique. Two electrodes of high content graphite pencil (5B) were immersed in Epsom salt electrolyte consisting of 2% of magnesium sulphate (MgSO_4) dissolved in distilled water. Epsom salt is chosen because it is highly water-soluble, so that we can obtain high concentration easily. PV panel of 20V rated voltage is used as a power source to exfoliate graphene from the electrodes. The experimental setup is shown in Figure (1). A charge controller with 12V DC was used to regulate the PV voltage. The amount of current passing through the circuit can be controlled by three factors: the distance between electrodes, the applied voltage, and the electrolyte concentration. In the current experiment, the space between electrodes was set to be 2cm . The passing current through the electrolyte was 290mA . Higher current can cause vigorous exfoliation resulting in producing graphite instead of graphene. The exfoliation time was set to be 15min . Graphene oxide dispersion was obtained as shown in Figure (1-f). Some of the dispersion was filtered and dried out into a powder in an oven at 70°C , so that it can be characterized. The fluorescent properties of the dispersion were studied using spectrofluorometer (type RF-5301PC). Raman scattering of the GO powder was investigated using a Horiba Jobin HR800 with a spectrometer with a grating of $600\text{lines}/\text{mm}$. The excitation source was a 633nm He-Ne laser. The spot size focused by the microscope is $\sim 0.01\text{mm}^2$. Optical transmission of GO samples dropcast on glass slides were investigated using Shimadzu double beam UV-VIS-IR spectrophotometer. The crystal structure of the powder was studied using X-ray diffraction (type Angstrom AD2700) in 2θ range of 5° to 60° . Fourier-Transform Infrared (FTIR) analysis was performed on GO powder using FTIR spectroscopy

(type Nicolet™ iS™ 10 FTIR Spectrometer) from Thermo Fisher Scientific company. Transmission electron microscopy (TEM) was used to investigate the existence of GO sheets. JEM-2100F JEOL with 80kV acceleration was used in this study. A few drops of GO aqueous dispersion were deposited onto a holey-carbon coated copper grid, and left to dry before being placed inside the TEM chamber.

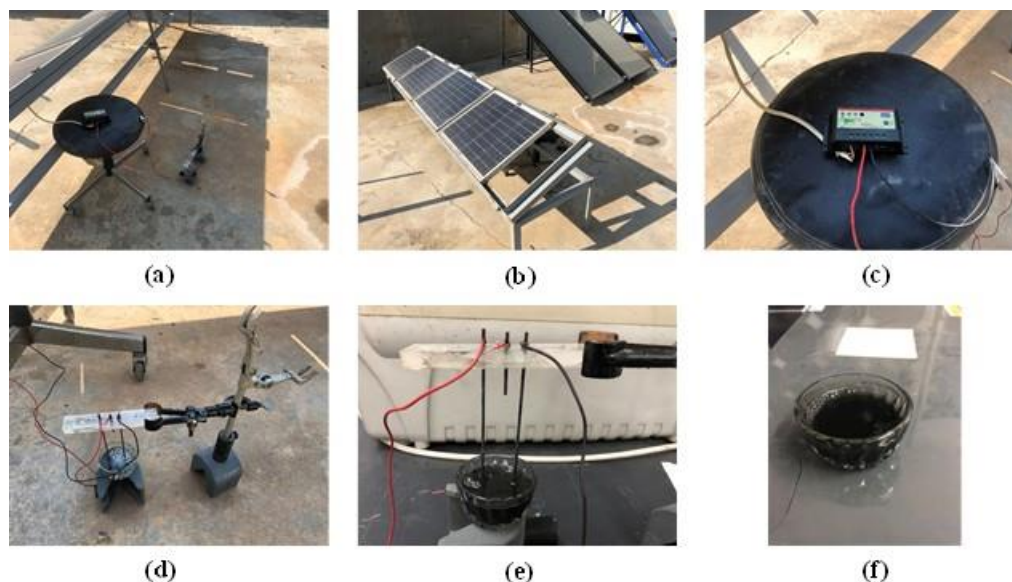


Figure 1. (a) The experimental setup, (b) the PV panel used, (c) the charge controller, (d) the electrochemical setup, (e) a close-up look of the electrochemical setup, and (f) the GO dispersion.

3. Results and Discussion

Raman shift of GO is illustrated in Figure (2). The G band is located at 1593 cm^{-1} , which corresponds to the in plane stretching motion. The D band is located at 1329 cm^{-1} and it is assigned to the breathing mode. Both bands are shown in the Raman spectrum. Generally speaking, an ideal graphene sheet is comprised of sp^2 hybridized carbon atoms only, whereas graphene oxide is comprised of a mix of sp^2 and sp^3 hybridizations because of the covalent bonds with oxygen in the form of epoxy and hydroxyl groups [11]. Therefore, the intensity ratio between the D and G bands (I_D/I_G) can be considered a measure of the lattice disorder. The I_D/I_G ratio is 1.5, which is reasonably consistent with the literature in the case of GO sheets, in which the D band intensity is higher than the G band intensity [12].

The XRD spectrum of GO films deposited on a glass substrate is displayed in Figure (3). Several peaks are shown in the spectral pattern. Some of them are for electrolyte residues and the impurities of the pencil. However, GO peaks are clear in the pattern. The $(0\ 0\ 2)$ diffraction peak at $2\theta = 20.7^\circ$ is attributed to the space distance between GO nanosheets, which indicates multilayer sheets [13]. The diffraction peak at $2\theta = 26.25^\circ$ corresponds to the short range interplanar spacing [14].

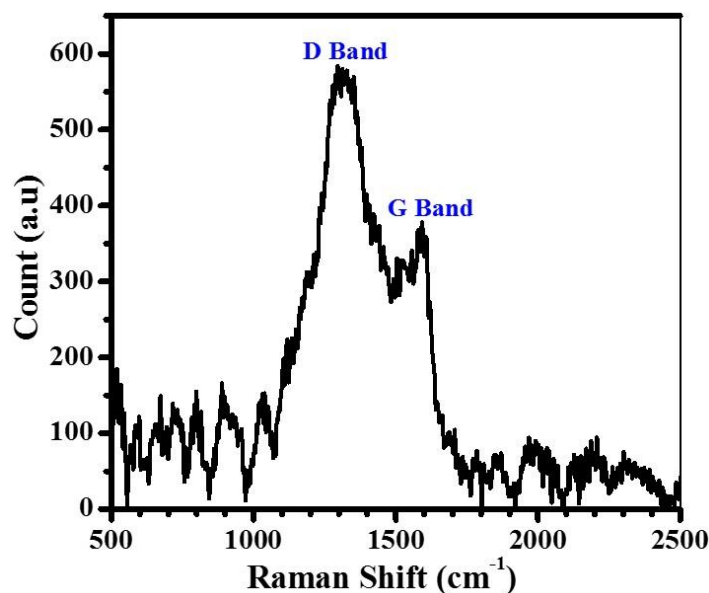


Figure (2). Raman spectrum of GO recorded with 633 nm laser line.

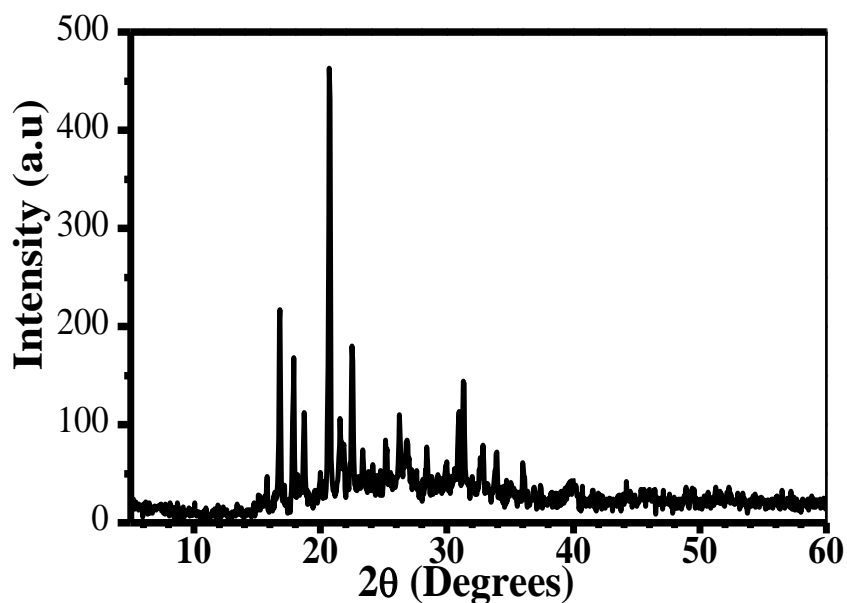


Figure (3). XRD diffraction pattern of GO nanosheets.

The photoluminescence (PL) of GO suspension is illustrated in Figure (4). The excitation wavelength used is 350nm and the PL signal is integrated from 350nm to 800nm. Photoluminescence in GO is arising from oxygen-based functional groups. In these groups, the emission has occurred from the transition of π - π^* transition [15]. Because of the existence of a wide size of sp^2 hybridization distribution in GO, the bandgap is varied along a wide range (from UV to Near IR region) [15]. Therefore, we can see two peaks of PL emission (at wavelengths 355nm and 701nm).

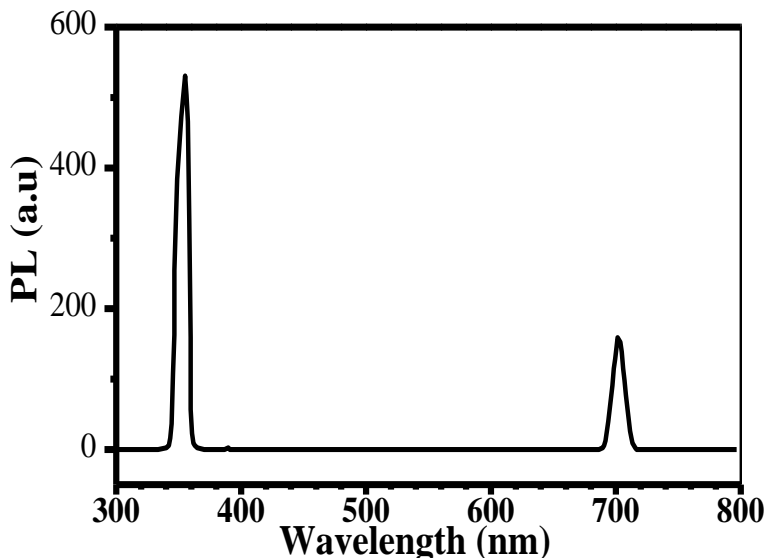


Figure (4). Photoluminescence of 2% GO aqueous solution excited at 350nm.

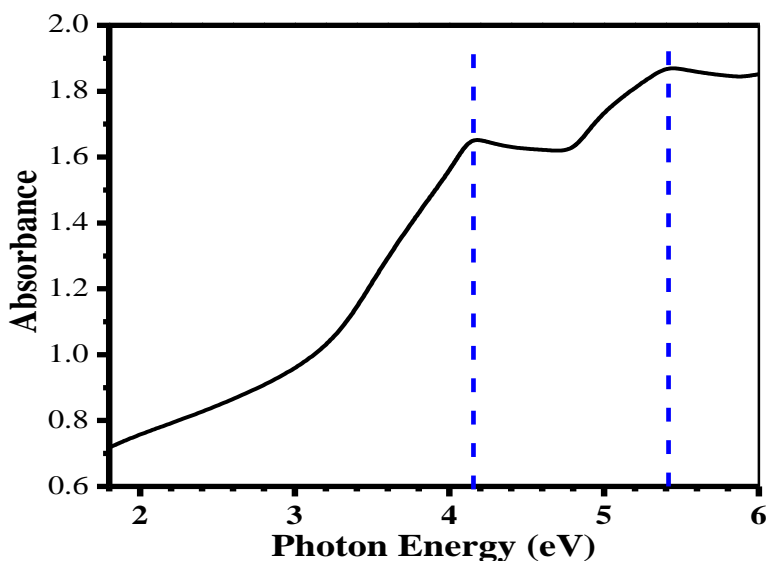


Figure (5). UV-VIS-NIR spectroscopy of GO thin film dropcast onto glass substrates.

Spectral absorbance shown in Figure (5) reveals a 4.2eV photon energy absorption peak corresponding to the aromatic C=C bonds and a 5.4eV photon energy absorption peak corresponding to the carbonyl groups [10]. This result shows the fingerprint of GO nanosheets. FTIR transmittance spectrum of GO is presented in Figure (6). The broadband transmittance peak at 3430 cm^{-1} is attributed to the stretching vibrations of hydroxyl groups, which may have been caused by the remaining water in GO [16]. The two adjacent peaks (2928 & 2846 cm^{-1}) are corresponding to the hydrogen bonded OH groups of COOH [16]. The bands at 1735 cm^{-1} and 1614 cm^{-1} are corresponding to the C=O stretching vibrations [16]. Functional groups such as C-OH (1375 cm^{-1}), and C-O (1039 cm^{-1}) can be observed in the low frequency region. Results of FTIR show that graphene nanosheets are functionalized and can rather be considered as graphene oxide nanosheets.

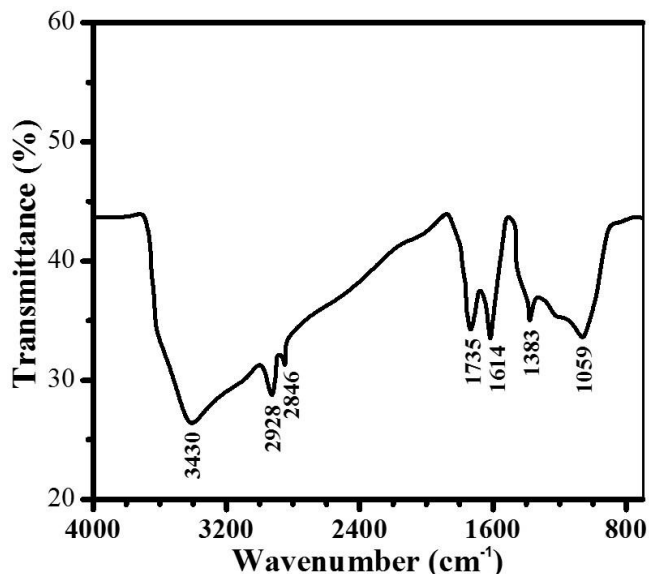


Figure (6). FTIR spectrum of GO nanosheets deposited on a glass substrate.

TEM images of ten times diluted of GO solution in distilled water are shown in Figure (7). The image in Figure (7-a) shows an agglomeration of graphene containing either a double layer or multilayer. However, single-layers can be noticed. Agglomeration issue can be solved using platinum catalyst support [17]. Since the graphite used in the synthesis is not pure, impurities can be existed with the GO sheets and can be seen in the image as black spots. Figure (7-b) shows GO deposited on a holey carbon grid support. In addition to, the impurities and the stack of double- and multi-layers, we can see single layers' GO at the carbon grid.

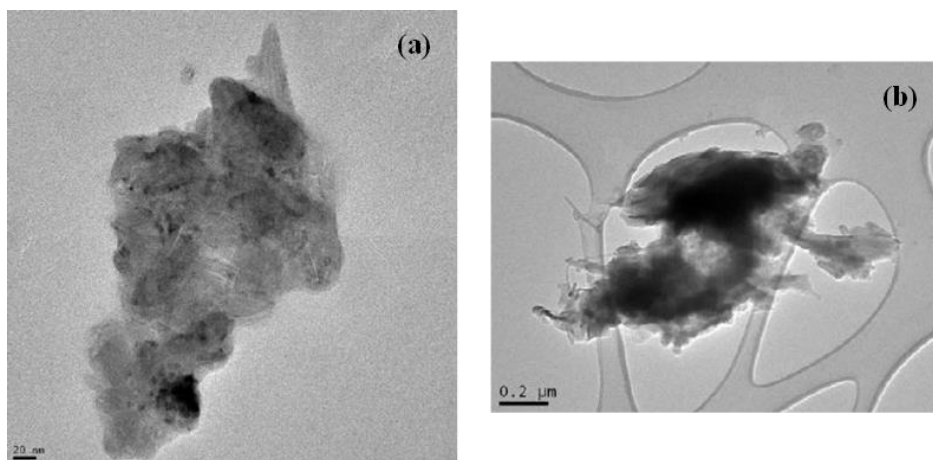


Figure (7). TEM images of GO: (a) agglomerated sheets, and (b) stack of single and multi-layer sheets.

The electrochemical exfoliation in this work is done using PV panel as a source of electric power. This is considered as a green method. The amount of CO₂ reduction can be calculated by the amount of energy used in the exfoliation. In our setup, 20V of applied photovoltage and 290mA of passing photocurrent were applied. This corresponds to a power of 6mW. The experiment time is 15min (900s). Hence, the amount of green energy obtained from the PV is 1.5Wh. Since each Wh of energy corresponds to 0.7g of CO₂, therefore, the reduction of CO₂ in this microscale experiment is 1.0g. This small amount of avoided CO₂ will be significant if the experiment scale is enlarged to a mass production.

4. Conclusions

Electrochemical exfoliation is a simple and inexpensive technique that can be used to synthesize GO nanosheets in a lab scale and even in a mass production scale. The method requires relatively low power and hence a small

PV panel can be used successfully as a source of electric power. This can result in a reduction in CO₂ that can be noticeable in the large scale production. Electrodes can be pencil graphite rods, which are dirt cheap electrodes. The product showed impurities due to the residues of the electrolyte and functional groups resulting in graphene oxide sheets instead of pristine graphene sheets. This requires further research to introduce a purification procedure.

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Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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