

# Synthesis of Graphene Nano-Sheets By Electrochemical Method Using Solar Energy

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## Abstract

Graphene nanosheets were combined utilizing electrochemical shedding of pencil anodes in watery arrangement containing 2% of magnesium sulfate salt. Sunlight based charger of 20V was utilized as a force supply to transform the combination into a green strategy. A few estimations were completed to examine the item, specifically: X-beam diffraction, photoluminescence, UV-VIS-NIR, and FTIR. The aftereffects of X-beam showed a diffraction top at  $2\theta = 20.7^\circ$  comparing to the space distance between graphene nanosheets and a diffraction top at  $2\theta = 26.25^\circ$  relating to the short reach interplanar separating. Photoluminescence showed two pinnacles of discharge (at frequencies 355nm and 701nm) worried to  $\pi$ - $\pi^*$  change. UV-VIS-NIR spectroscopy displayed a 4.2eV photon energy retention top comparing to the sweet-smelling C=C bonds and 5.4eV photon energy assimilation top relating to the carbonyl gatherings. FTIR showed tops identified with hydroxyl gatherings, hydrogen reinforced OH gatherings of COOH, and useful gatherings like C-OH (1375 cm<sup>-1</sup>), and C-O (1039 cm<sup>-1</sup>). FTIR results supported that graphene nanosheets are functionalized.

## 1. Introduction

Recently, many efforts have been directed at the use of multidimensional carbon allotropes (namely: the 0-D fullerenes, 1-D nanotubes and 2-D graphene sheets) in a plethora of applications and most notably in optoelectronic devices [1]. They have been utilized successfully in a wide range of photovoltaic-based applications: nanocomposites [2], buffer layers in organic solar cells [3], and active layer materials [2]. Each of these allotropes has unique properties that allow them to be incorporated in a number of technologies, with graphene being touted as the most attractive due to the surge of current research thrusts.

Graphene, the thinnest known manmade material ever, was first synthesized and described by Novoselov *et al.*, in 2004 [4]. Since then, this material has been intensively investigated as a result of its outstanding electrical, optical, chemical, and mechanical properties, as well as its stability under ambient conditions [4]. In the past, it was thought that such planar benzene-ring structure would be unstable compared to the structures such as fullerene or carbon nanotubes [4]. Due to the planar nature of graphene, it requires only a few layers of graphene sheets to fabricate high quality thin films, exhibiting high transparency, as well as conductivity. Many of graphene's unique properties are best utilized in the thin films, but composite materials can also take advantage of graphene incorporation.

Pristine graphene has an electron mobility of  $10^3 \text{ cm}^2/\text{V}\cdot\text{s}$  [5], a film of  $\sim 10$  nm thick has electrical conductivity of  $1250 \text{ S/cm}$  with a transparency of more than 70% over the wavelength range of 1000-3000 nm [6]. The extremely high conductivity (low resistivity) is due to the ballistic transport within one plane of graphene, which arises due to the delocalization of charges over the entire sheet [4]. A single sheet of graphene possesses high mechanical strength due to the strong  $\pi$ -bond in its honeycomb crystal lattice, for instance a graphene paper exhibits a tensile strength up to 35 GPa [7].

Solution processed graphene nanosheets may contain lattice defects and grain boundaries acting as trap centers that negatively affect the conductivity. To overcome this obstacle, graphene films are usually made thicker than a single layer. Moreover, graphene can be formed with two different edge configurations: zigzag and armchair [8]. Zigzag graphene is always metallic while armchair 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, which allows graphene to be soluble in many solvents and can be further attached with many functional groups depending upon different applications. Graphene oxide can be viewed as a graphene sheet with many defects on its basal plane: mainly oxygen containing functionalities, such as carbonyl, ether, and/or hydroxyl groups. The oxidized form of graphene also provides route for functionalization and other unique chemistry methods to be performed and hence further enhance its application potential. While the functionalization improves solubility and processing parameters, it also affects its aforementioned desirable optical and electrical properties. These can be tuned depending upon the application and in some instances subsequent reduction of graphene oxide can result in the same 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 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 on the electrode to accelerate the electrolysis. Using

photovoltaic (PV) panel as a source of power can turn the method into green technique. Moreover, graphite electrode is relatively expensive. Using inexpensive pencils of high graphite content can be a good substitute. In this work, graphene nanosheets were synthesized using a green and ecofriendly electrochemical method by using PV panel as a source of electric power. 5B pencil in saline medium is used as electrode to turn the method into a very inexpensive technique. The method can produce a high quantity of graphene in a very short time.

## 2. Experimental Procedure

Graphene nanosheets were synthesized using electrochemical exfoliation technique. Two electrodes of high content graphite pencil (5B) were immersed in Epsom salt electrolyte consisting of 2% of magnesium sulfate ( $\text{MgSO}_4$ ) 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). The amount of current passing through the circuit can be controlled by three factors: the distance between electrodes, the applied voltage, and/or the electrolyte concentration. In the current experiment, 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 dispersion was obtained as shown in Figure (1-f). Fluorescent properties of the dispersion were studied using spectrofluorometer (type RF-5301PC). Optical transmission of graphene samples dropcast on glass slides was investigated using Shimadzu double beam UV-VIS-IR spectrophotometer. Crystal structure was studied using X-ray diffraction (type Angstrom AD2700). Fourier-Transform Infrared (FTIR) analysis was performed on graphene using FTIR spectroscopy

(type Nicolet™ iSTM 10 FTIR Spectrometer) from Thermo Fisher Scientific company.

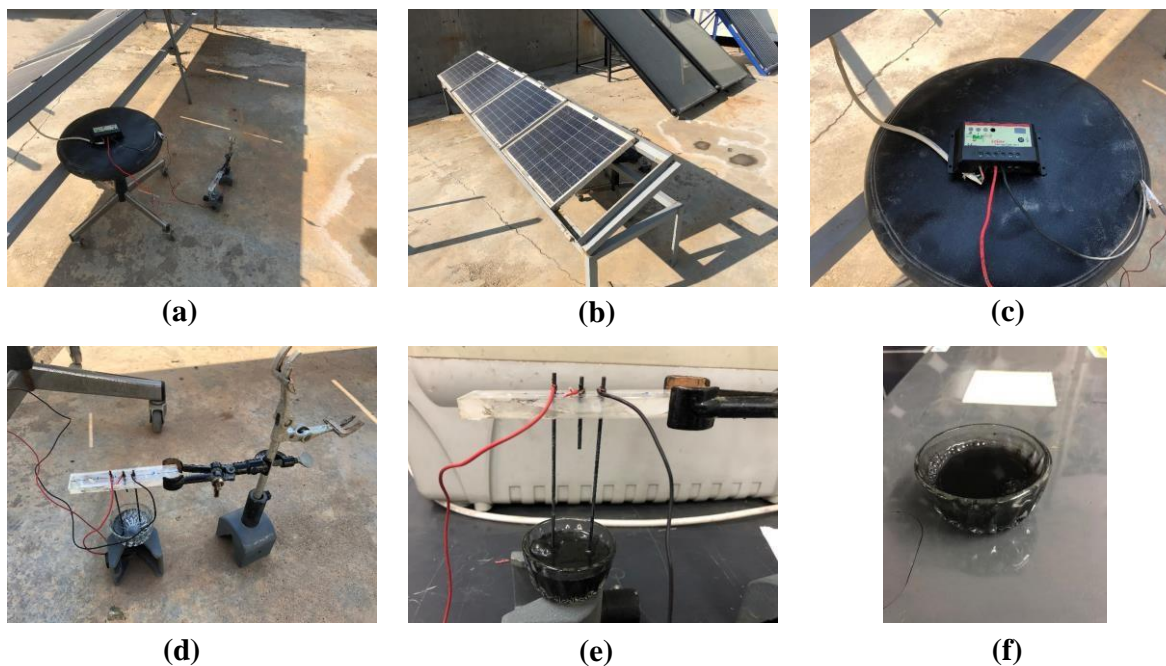


Figure (1). (a) The experimental setup, (b) the PV panel used, (c) the charge controller, (d) the electrochemical setup, (e) a close-up look of the electrochemical setup, and (f) the graphene dispersion.

### 3. Results and Discussion

The XRD spectrum of graphene films deposited on glass substrate in  $2\theta$  range of ( $5^\circ$  to  $60^\circ$ ) is displayed in Figure (2). Several peaks are shown in the spectral pattern. Some of them are for electrolyte residues and the impurities of the pencil. However, graphene 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 graphene nanosheets [11]. This can indicate that the obtained graphene is a multilayer graphene sheets. The diffraction peak at  $2\theta = 26.25^\circ$  corresponds to the short range interplanar spacing [12].

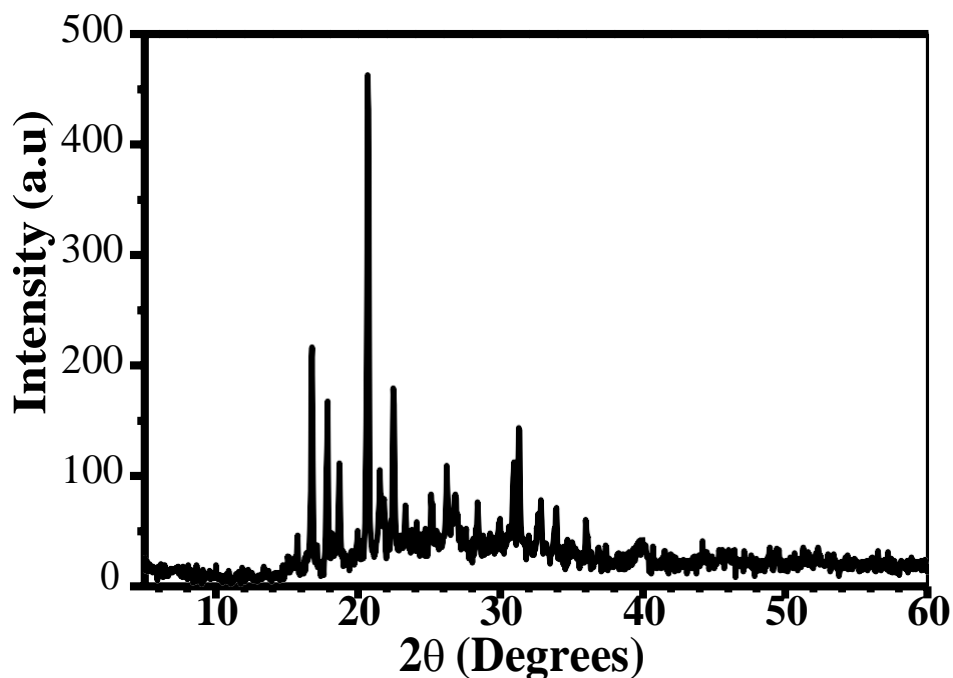


Figure (2). XRD diffraction pattern of graphene nanosheets.

The photoluminescence (PL) of graphene suspension is illustrated in Figure (3). Excitation wavelength used is 350nm and the PL signal is integrated from 350nm to 800nm. Photoluminescence in graphene is arising from oxygen-based functional groups. In these groups, the emission is occurred from the transition of  $\pi$ - $\pi^*$  transition [13]. Because of the existence of wide size of  $sp^2$  hybridization distribution in graphene, the bandgap is varied along wide range (from UV to Near IR region) [13]. Therefore, we can see two peaks of PL emission (at wavelengths 355nm and 701nm).

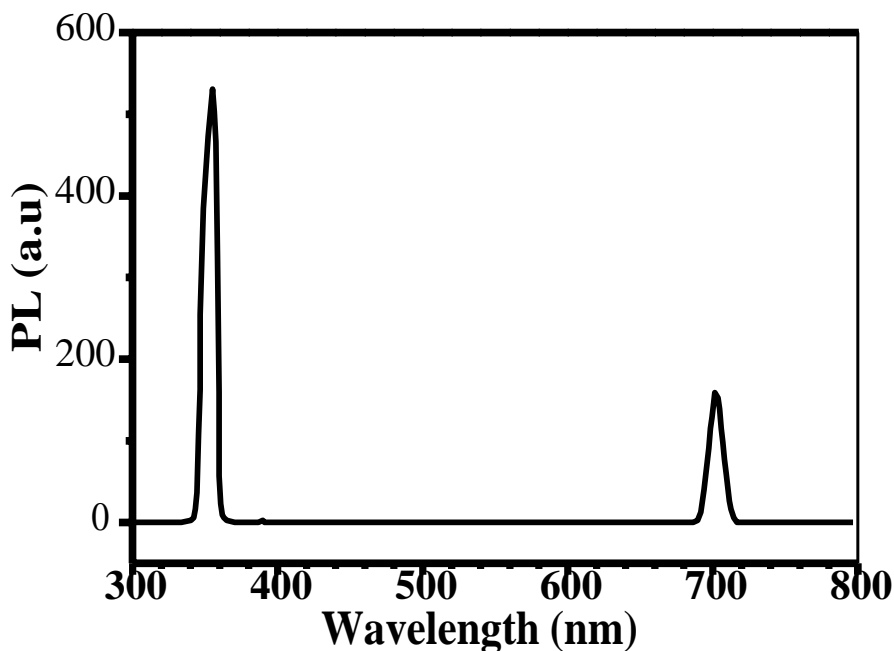


Figure (3). Photoluminescence of 2% graphene aqueous solution.

Spectral absorbance shown in Figure (4) reveals 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 [10]. This result shows the fingerprint of graphene nanosheets.

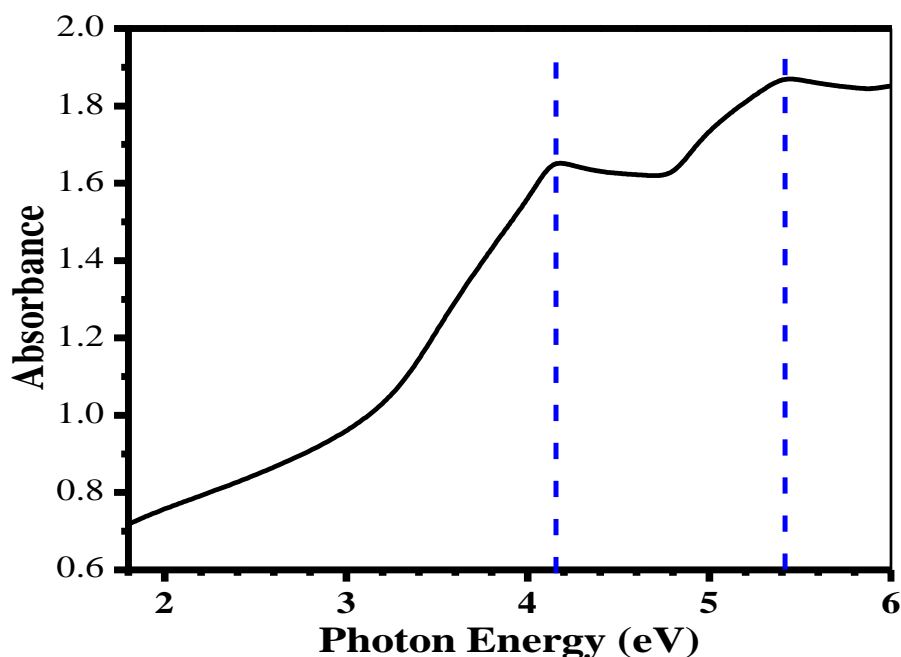


Figure (4). UV-VIS-NIR spectroscopy of graphene thin film dropcast onto glass substrates.

FTIR transmittance spectrum of graphene is presented in Figure (5). The broadband transmittance peak at  $3430\text{ cm}^{-1}$  is attributed to the stretching vibrations of hydroxyl groups, which maybe from the remaining water in graphene [14]. The two adjacent peaks ( $2928$  &  $2846\text{ cm}^{-1}$ ) are corresponding to the hydrogen bonded OH groups of COOH [14]. The bands at  $1735\text{ cm}^{-1}$  and  $1614\text{ cm}^{-1}$  are corresponding to the C=O stretching vibrations [14]. Functional groups such as C-OH ( $1375\text{ cm}^{-1}$ ), and C-O ( $1039\text{ cm}^{-1}$ ) can be observed at the low frequency region. The results of FTIR show that graphene nanosheets are functionalized and they can rather be considered as graphene oxide nanosheets.

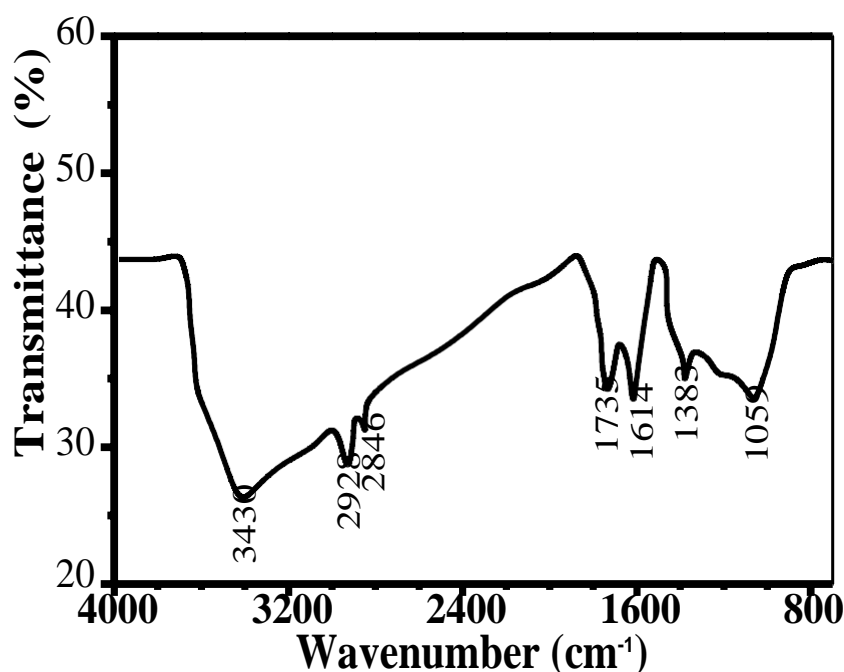


Figure (5). FTIR spectrum of graphene nanosheets deposited on glass slide.

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 CO<sub>2</sub> 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 used. 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 0.5g of CO<sub>2</sub>, therefore, the reduction of CO<sub>2</sub>



in this microscale experiment is 0.75g. This small amount can 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 graphene 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 CO<sub>2</sub> 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.

#### **5. Acknowledgement**

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