An investigation of the Structural, Electrical and Optical Properties of Graphene-Oxide Thin Films Using Different Solvents

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Abstract: Graphene oxide (GO) thin films were prepared successfully using modified Hummer’s method, which includes oxidation of graphite and reduction to graphene oxide at room temperature. Then, the samples were deposited on glass substrates using the sol-gel technique. Different solutions have been used to obtain graphene oxide such as Ethanol, Acetone, and Deionized Water. The structural, optical and electrical properties of the prepared samples were diagnosed and studied using optical microscope and XRD diffraction, Fourier Transform Infrared Spectroscopy (FTIR) and UV-Vis spectrophotometer respectively. XRD pattern confirmed the formation of graphene oxide with a sharp peak at an angle of 2θ=11.42°. Thicknesses of (GO) samples using weight method have been calculated. In addition, the optical properties of the samples such as transmittance, reflectance, refractive index, extinction coefficient, and optical energy gap have been measured. The optical band gap of the samples dissolved in acetone, deionized water and ethanol has been measured of about 2.5, 2.45 and 2.35 eV respectively.

Keywords: Graphene oxide (GO), thin-film, XRD, different solvents, Hummer's method.

1. Introduction

The discovery of graphene has led to a lot of care in various fields of modern nanomaterial technology, and the reason for this is that most of its properties differ from graphite, which in turn has important applications in several fields such as: sensors, photovoltaics, energy storage and in electronics [1-3]. Graphene is a high-density, two-dimensional material that has strong transparency. It is made of carbon that has a shape similar to a bee house. Graphene possesses have unique properties that make it an interesting material in many industrial applications. The reason for this is that it is a little fish and it’s high elasticity makes it an important material in the manufacture of photovoltaic cells, billboards (lighting) and touch screens. There are several ways to prepare graphene, including the chemical exfoliation process [4]. Graphene oxide films are known for their mechanical strength, which makes them attractive to molecular separation and filtration applications. Although the nanofiltration process through graphene oxide membranes is limited only in aqueous solutions because organic solvents cannot permeate the graphene oxide membranes [5]. Rahul Raveendran Nair from the University of Manchester, (Manchester, UK) has developed high-coated graphene oxide films (highly
laminated GO-HLGO) that are thin enough to allow rapid penetration of both water and organic solvents through them [6]. The research team conducted filtration experiments using dyes containing methanol solutions. More than 99.9% of the pigment particles were not carried out [7].

There are many methods for preparing and producing of graphene oxide (GO), Hummer’s method, by adding potassium chlorate (KClO₃) to the mixture of graphite and sodium nitrate (NaNO₃) with sulfuric acid [8-12]. Modified Hummer’s method where 1 ml of concentrated sulfuric acid (H₂SO₄) is mixed and stirred in an ice bath for 2 hours with the addition of 1 gm of pure and fine graphite powder in addition to 1 gm of sodium nitrate (NaNO₃) and 5 gm of potassium permanganate (KMnO₄). Then, add 50 ml of hydrogen peroxide (H₂O₂) slowly drop by drop and 100 ml of distilled water (non-ionized) and notice the change of the colour of the mixture to a bright yellow colour [13]. Also, modified Staudenmair’s method and in the presence of strong reducing agents such as hydroquinone (C₆H₄(OH))₂) and hydrazine hydrate (NH₂NH₂.H₂O) as a reducing agent, as the use of hydrazine hydrate for the reduction process is more beneficial than using hydroquinone [14].

This paper aims to prepare graphene oxide using a different solution such as acetone; deionized water and ethanol, then demonstrate the formation of graphene oxide. The structural, optical and electrical properties of samples prepared have been investigated for use in photovoltaic applications.

2. Experimental

2.1. Film Fabrication

Graphene oxide films were prepared from graphite, using modified Hummer’s method, where 25 ml of concentrated sulfuric acid (H₂SO₄) were used in an ice bath for 2 h with the addition of 1 g of pure graphite powder, as well as 1 g of sodium nitrate (NaNO₃), and 5 g of potassium permanganate (KMnO₄). Then, put the mixture in an ice bath and stir the mixture using a magnetic stirrer for 2 days at room temperature. Then we will notice the change in the colour of the mixture from green to brown, then add 50 ml of hydrogen peroxide (H₂O₂) slowly; in addition to 100 ml of distilled water (free of ions). It is noticed that the colour of the mixture changes from to a bright yellow colour, and this indicates the formation of graphene oxide. Then, graphene oxide (GO) is separated using a centrifuge at 5000 RPM, and then graphene oxide is washed using dilute hydraulic acid (HCL) and distilled water (without ions) for several times until an acid neutral function is obtained for the resulting filtrate. It is indicated pure graphene was produced using an electric dryer. All materials were purchased from (Sigma-Aldrich) company. Then the solutions have been deposited on glass substrates (Microscope Slides) type RS with (1.1 mm) thick and (2×2.5) cm². Glass slides were cleaned carefully in an ultrasonic bath treatment type (BRANSON Ultrasonic-CAMDA 19 SPC) with ethanol, acetone, deionized water and dichloromethane (CH₂Cl₂), each one for 20 min and dried with nitrogen gas jet. The weight of the glass substrates was measured before and after the deposition of the solutions to measure the thickness of the samples using a sensitive balance of four digits (Analytical Balance). After that, the glass substrates were placed on the surface of the heater for some time 10 min to ensure the uniformity of their temperature, as a thermocouple was used in contact with the surface, where a thermocouple was used connected in contact with the glass surface and connected to a digital device to ensure the required temperature. The resulting solutions were deposited on the previously prepared glass substrates using sol-gel device, where speed of 3500 rpm was used for a period of 60 seconds for each case, and then the samples were placed in the laboratory oven to drying for 10 min at a temperature of 100 °C.
2.2. Film Thickness Measurements

To measure the thickness of the thin films prepared and deposited on glass substrates, the weight method was used to measure the thickness of the thin films due to the ease of this method and the availability of its devices. As this method only needs a sensitive electronic balance (4 digits) to measure the mass of the precipitated material on the substrate and through the product of the difference between the mass of the substrate before and after the deposition of thin films. With the help of the theoretical value of material density, whose thickness and the area of the film to be measured, the required thickness of the film can be found from the following relationship.

\[ d = \frac{\Delta w}{\rho \times A} = \frac{w_2 - w_1}{\rho \times (L \times W)} \]  

where: \( d \) is the film thickness \((\text{cm})\), \( \Delta w = w_2 - w_1 \) is the mass of the glass substrate before and after deposition, \( \rho \) is the theoretical density of the deposited material of about \((0.44, 0.9982, 0.719 \text{ and } 0.789) \text{ g/mL}\) for graphene, deionized water, acetone and ethanol, respectively, and \( A = L \times W \) is the area of the sample, in our case \( L \) is the length of the sample, \( W \) is the width of the sample (rectangle sample). It is a type of optical measurement.

2.3. Structural Properties

An X-ray diffraction device (D8 Advanced Brucker diffractometer) was used to identify the crystalline properties of the solid materials under study by using single-wavelength light \( \lambda = 1.5406 \text{ Å} \), from a standard source CuK\( \alpha \), with Voltage 40 kV, Current 30 mA and scanning speed 0.02 deg./min. The sample was scanned from \( 2\theta = (0 - 80) ^\circ \). Where the sample was examined by placing and fixing it on a very clean glass slide by preparing the material in the form of a thin film deposited on a glass substrate and fixed on an iron holder.

2.4. Optical Properties

Optical properties of thin films deposited by Hummer's method have been studied using a double beam spectrophotometer (PerkinElmer Lambda 950 (UV/Vis/NIR) spectrophotometer at room temperature. The results were performed at room temperature and a region from \((200 \text{ to } 1000) \text{ nm}\). The optical parameters of graphene oxide such as transmittance, reflectivity, refractive index, extinction coefficient have been recorded and calculated according to the following relations [15-20].

\[ T = \frac{I_t}{I_0} = (1 - R)^2 \times \exp(-\alpha d) \]  

\[ T + R + A = 1 \]  

where: \( T \) is transmittance, \( R \) is reflectance, \( \alpha \) is the absorption coefficient, \( d \) is the sample's thickness.

The extinction coefficient \( k \) is calculated using the following equation [17]

\[ k = \frac{(\alpha \times \lambda)}{(4 \times \pi)} \]  

While; the absorption coefficient \( \alpha \) can be calculated according to the following equation [18]

\[ \alpha = 2.303 \frac{A}{d} \]
Besides, the refractive index $n$ is found using equations based on the material's and is given by the following equation [19]

$$n = \left( (1 + \sqrt{R}) / (1 - \sqrt{R}) \right) \quad \text{(6)}$$

where: $R$ is the reflectance of the material.

2.5. Electrical Properties

The electrical properties of graphene oxide films depend on several factors. Electrical measurements were recorded using the planar structure to measure the electrical current–voltage. Data were recorded using a DC power supply of (0-30) V and the output current was recorded using Keithly Electrometer type 4830.

3. Results and Discussion

3.1. Chemistry

The importance of using X-rays lies in knowing the nature of the crystal structure of solids and thin films, as it proves to us that the films prepared in our work are pure and have a multi-crystalline structure.

The X-ray diffraction spectrum Figure 1, showed that the graphite sample has a sharp crystal peak of about ($2\theta=26.32^\circ$), which corresponds to Miller’s coefficients (002), thus, the intermediate distance of it is ($d=3.357 \text{ nm}$), see Eq. 2. Also, upon oxidation of graphite to graphene oxide, it’s X-ray diffraction characterizes by the appearance of a sharp peak at the angle ($2\theta= 11.42^\circ$), which corresponds to Miller’s coefficients (002), the intermediate distance has an amount of ($d=0.77 \text{ nm}$), as it is a result of the presence of oxygen, which has some functional groups that makeup graphene oxide. This result indicates the formation of graphene oxide. The peak at ($2\theta=10.48^\circ$) is due to incomplete oxidation of graphite, graphite cannot be oxidized 100%.

![Figure 1](image)

**Figure (1) X-ray diffraction spectrum of graphite powder and graphene oxide.**

By applying Eq. 1, the results obtained as shown in Table 1
Table (1) Thickness of (GO) samples using the weight method

| No.        | GO weight (g) | Solvent weight volume (mL) | Thickness before Deposition (µm) | Thickness After Deposition (µm) |
|------------|---------------|----------------------------|----------------------------------|---------------------------------|
| 2=Acetone  | 0.02          | 25                         | 3.459318                         | 3.51463                         |
| 3=deionized H$_2$O | 0.02          | 25                         | 2.877035                         | 2.796384                         |
| 5=Abs. Ethanol | 0.02          | 25                         | 2.306108                         | 2.210616                         |

It is evident from Figure 2 that the graphene oxide films prepared under normal (natural) light and dissolved in different solutions show that their colour tends to be dark brown and black concerning sample no. 2. Sample no. 3 we notice the formation of very thin and dense sheets of graphene oxide, while sample no. 5 differs from the previous two samples, where we notice the formation of a smooth film and the emergence of very fine (nanoscale) grains. In all the above cases, it is clearly noticed the formation of the graphene oxide when dissolved with three different organic solvents, but the sizes of the particles are differing in these different samples.

![Figure (2) Optical Micrographic images of the deposited graphene oxide films on glass substrates and dissolved with different solvents (2) acetone, (3) water and (5) ethanol, respectively.](image)

The infrared spectra of the graphene oxide composite are shown in Figure 3, which showed the presence of expansion and bending beams in the region of frequencies between (4000-400) cm$^{-1}$, where the infrared spectrum of graphene oxide showed the presence of a strong absorption beam at 1735 cm$^{-1}$ due to the organic carbonyl group (C=O) which is due to the carbonyl and carboxylic groups; which is by itself, evidence the formation of graphene oxide diffused between graphene oxide sheets.

Also, there is an expansion vibration at 3470 cm$^{-1}$ that returns to (O-H) in the (C-OH) group of the carboxylic acid with the possible presence of adsorbent water molecules on the surface.

In addition to the presence of an absorption beam at 1620 cm$^{-1}$ belonging to the group (C=C), as well as the presence of the epoxy (C-O) group and the laxoxy (C-O) group, as this confirms the presence of successful oxidation of graphite.
Figure (3) Infrared spectrum of graphene oxide dissolved in with different solvents (2) acetone, (3) water and (5) ethanol, respectively.
Optical analysis of samples deposited on glass was performed using UV-Vis spectroscopy. All-optical measurements were made of the spectral range (200-1100) nm. These two characterization techniques are generally used for bandgap determination and purity approximation respectively. The transmittance spectrum of films after adding graphene is shown in Figure 4. This Figure shows the transmittance as a function of the wavelength of graphene oxide samples dissolved in acetone, water, and pure ethanol. It is noticed that the transmittance increases with increasing wavelength and its average value at the visible region of the spectrum is (89%, 91% and 90%) and in the ultraviolet region, it is (76%, 77% and 79%) respectively.

Figure (2) Transmittance curves of graphene oxide dissolved in different solvents (2) acetone, (3) water and (5) ethanol, respectively.

Figure 5 shows the reflectivity as a function of the wavelength of the graphene oxide samples dissolved in the acetone, water and pure ethanol samples 2, 3, and 5, respectively. It is noticed from the figure the reflectivity decreases with increasing wavelength and the average value at the visible region of the spectrum is (8.9, 8.6 and 9) % and in the ultraviolet region is (15.8, 15 and 15.3) %, respectively.
Figure (3) Reflectance curves of graphene oxide dissolved in different solvents (2) acetone, (3) water and (5) ethanol, respectively.

The UV-visible spectra of aqueous solutions of graphene oxide were analyzed, and it was found that there is an absorption peak at 300 nm due to the electron transport n-π*, which belongs to the carbonyl group in graphene oxide. In addition to the presence of another absorption peak due to graphene oxide at the wavelength 230 nm, which indicates the electronic transmission π-π*, which results from the presence of a double carbon bond (C=C) in graphene oxide or the possibility that this bond is caused by some insoluble particles from the original graphite (this case is clear when sample 2, represented by graphene oxide dissolved in acetone. While; the rest of the two samples 3 and 5 dissolved in water and pure ethanol have only one absorption peak at 300 nm, as shown in Figure 6.

Figure (6) Absorptance curves of graphene oxide dissolved in different solvents (2) acetone, (3) water and (5) ethanol, respectively.

Figure 7 shows the extinction coefficient as a function of the wavelength of the graphene oxide samples dissolved in the acetone, water and pure ethanol samples 2, 3, and 5, respectively according to Eq. 4. It is noticed that the extinction coefficient increases with increasing the wavelength
due to the increase of the absorption coefficient at this range of wavelengths and that its average value at the visible region of the spectrum is (0.26, 0.23 and 0.24) % and in the ultraviolet region it is (0.30, 0.31 and 0.27) % respectively.

Figure (7) Extinction coefficient curves of graphene oxide dissolved in different solvents (2) acetone, (3) water and (5) ethanol, respectively.

Figure 8 shows the refractive index as a function of the wavelength of the graphene oxide samples dissolved in the acetone, water and pure ethanol samples 2, 3, and 5, respectively according to Eq. 6. It is noticed that the refractive index decreases with increasing the wavelength due to the decrease the reflectance at this range of wavelengths and that its average value at the visible region of the spectrum is (1.85, 1.83 and 1.86) % and in the ultraviolet region it is (2.2, 2.3 and 2.4) % respectively.

Figure (8) Refractive index curves of graphene oxide dissolved in different solvents (2) acetone, (3) water and (5) ethanol, respectively.

Figure 9 shows $(\alpha \nu)^2$ as a function of the photon energy $(\hbar \nu)$ of the samples 2, 3 and 5. The optical energy gap was calculated for the allowed indirect transmission of samples of graphene oxide.
at room temperature, by drawing the relationship between \((a\nu)^2\) and the photon energy, then a straight line (tangent to the curve) intersects the x-axis at the point where the value of it equals zero. It is noticed that the calculated energy gap value for the graphene oxide samples was \(E_g = 2.5\), \(2.45\) and \(2.35\) eV for samples 2, 3 and 5 respectively and based on Eq. 5.

3.2 Electrical Properties

Figure 10 presents the I-V curve for graphene oxide thin films dissolved in different solutions. One can see that increasing in current with applied voltage for the sample 5 is much greater than the other ones 2 and 3 indicate that the current at these solutions with graphene oxide is high because of many parameters such as grain boundary and size is greater compare with the others.
4. Conclusion

Graphene oxide (GO) thin films dissolved in three different solutions such as acetone, deionized water, and absolute ethanol have been prepared using modified Hummer's method and deposited onto glass substrates. After studying and analyzing the results of measurements, it was found that graphene oxide formation was established based on the X-ray diffraction spectrum, the absorbance spectrum and the optical energy gap value. For samples 2, 3 and 5 the absorption coefficient value of samples increases in the UV region and it's value decreases in the visible region. Also, the optical energy gap values of samples were close to each other, between (2.35-2.50) eV.

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