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Original Article

Synthesis of Graphene Oxide and its Physicochemical Study

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Abstract *- In this research work, graphene oxide was synthesized in different mole ratios and at different temperatures as well in different time intervals, and the optimal conditions of the process were determined. As a result, based on the physical and chemical properties of graphene oxide, aspects of its use as a component for electron transport in new third-generation solar cells were studied. Moreover, based on the results of IR-spectrum, SEM, and X-ray spatial and thermal analysis of the synthesized graphene oxide, its analysis data is presented.*

Keywords *- Graphite, Graphene oxide, Semiconductor, Optics, Thermal analysis, Solar cells.*

1. Introduction

Graphene oxide is one of the electrically conductive materials with many electrons. Materials based on graphene oxide and its derivatives are used as the main component of organic solar cells due to their large surface area and low electrical resistance [1,2]. The electrical conductivity of dielectric polymer nanocomposites treated with graphene oxide improves several times. [3]. Today, organic perovskite-based solar cells are used in the production of non-composite polymers modified with graphene oxide due to the intensive increase in electron transport layers. Also, the dye increases the efficiency of photocatalytic reactions for TiO_2 composites of titanium dioxide and graphene oxide, which are used as photoanodes in sensitive solar cells [4, 5]. Graphene-based nanocomposites have been the focus of many researchers in recent years due to their excellent mechanical, electrical, and thermal properties. Transparent graphene oxide electrodes with a large surface area can become an integral part of solar cells based on inexpensive organic polymer materials. Recently, graphene oxide and modified graphene oxide have been used as components for electron transport in new, rapidly developing solar cells based on organic perovskite [6, 7]. The basic principle of operation of a graphene-based solar cell is essentially the same as that of conventionally produced inorganic silicon solar cells. Some of the currently used materials will be replaced by graphene derivatives.

Today, due to the intensive increase in electron transport layers of non-composite polymers modified with graphene oxide, organic dye-sensitized solar cells are used in the production of solar cells. Also, TiO_2, which is used as a photoanode in dye-sensitized solar cells, increases the efficiency of photocatalytic reactions for composites of titanium dioxide and graphene oxide [8, 9].

As with any device or material, materials based on graphene oxide derivatives have parameters that can be improved to improve performance. In particular, a number of properties, such as heat resistance, electrical conductivity, mechanical stability, and adaptability to aggressive environments, allow us to open a new stage of our scientific research directions in the future [10].

It is also possible to obtain superconducting composites from graphene and graphene oxide-based products. When small amounts of graphene or graphene oxide-based materials are added to non-electrically conductive polymer resins, a superconducting mixture is produced.

When the properties based on graphene oxide added to the composition are increased, the electrically conductive fillers begin to contact each other, and free electrons can easily move, creating a dielectric path that conducts electric current. These superconducting composites are lightweight, corrosion resistant, and can be easily tailored to meet specific manufacturing needs [11, 12].

2. Experimental Part

2.1. Material and Methods

The following chemicals and equipment are needed for the preparation of materials: graphite powder sifted through a fine mesh sieve, potassium permanganate, hydrogen peroxide 40%, concentrated sulfuric acid 96%, hydrochloric acid solution, distilled water and a magnetic flask with a thermometer and a water bath.

Graphene oxide was synthesized from graphite powder by low-temperature oxidative polymerization method. This modernized synthesis method involves oxidation of graphite layers and delamination by heat treatment of the solution.

2.2. Synthesis of Graphene Oxide

3 grams of graphite powder and 2 grams of $NaNO_3$ salt were weighed and placed in a 400 ml conical flask in an ice bath (0-5 °C) with constant stirring. Then, 50 ml of concentrated H_2SO_4 (96%) solution was added and mixed with a magnetic stirrer at a low temperature. Stirring was continued at this temperature for 3 hours, and 18 g of potassium permanganate was added very slowly to the resulting suspension. The addition rate and reaction temperature were carefully controlled to be below 15 °C. The ice bath was then removed and the mixture was stirred at 35 °C until a brown mass was formed and stirred for another 3h. Then, 100 ml of water was gradually added to it. The reaction temperature rapidly increased to 98 °C, and then the color of the solution turned dark brown. This solution was then diluted by adding an additional 200 ml of water with constant stirring. Finally, the solution was treated with 10 ml of H_2O_2 to stop the reaction when the color changed to dark black. For purification, the mixture was first washed repeatedly with 10% HCl and then several times with distilled water. After filtration and vacuum drying at room temperature, graphene oxide (GO) powder was obtained. The dried pitch black graphene oxide (GO) powder is soluble in organic solvents.

2.3. Factors Affecting the Synthesis of Graphene Oxide

Analytical data on the influence of the mass ratio of graphite and potassium permanganate on the yield of the product formed during the synthesis of graphene oxide in the presence of graphite, potassium permanganate, concentrated sulfuric acid, hydrogen peroxide, and ammonia solution for neutralization, the duration of the reaction, and the difference in the reaction temperatures are detailed in Table 1.

During the experiment, reactions were carried out by taking graphite and potassium permanganate in different mass ratios. In the process, the results of the reactions performed by taking different mass ratios of potassium permanganate to graphite were presented. In the reaction of graphite and potassium permanganate in a mass ratio of 1:6, the yield of the process was found to be 80% (Figure 1).

Table 1. Study of the effect of concentration, time and temperature of reactants on the yield of the product.

Ass ratio of initial products	Duration of the reaction (hours)	Temperature dependence of the reaction,ºC	Reaction yield %
GRAPHITE-POTASSIUM PERMANGANATE			
1:1	2	30	40
1:2	3	20	50
1:3	4	10	60
1:4	4,5	5	70
1:5	5	0	75
1:6	6	-5	80
1:9	8	-10	80

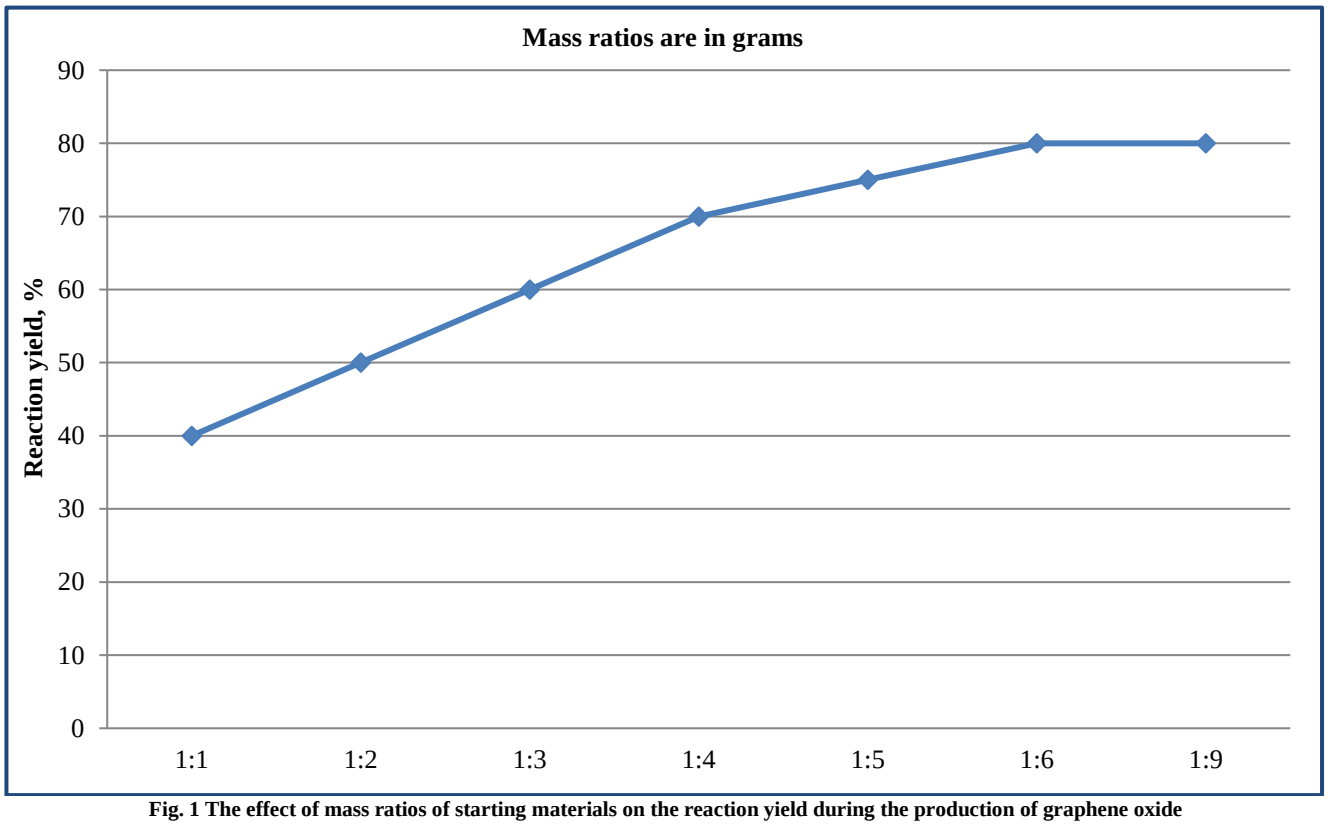


Fig. 1 The effect of mass ratios of starting materials on the reaction yield during the production of graphene oxide

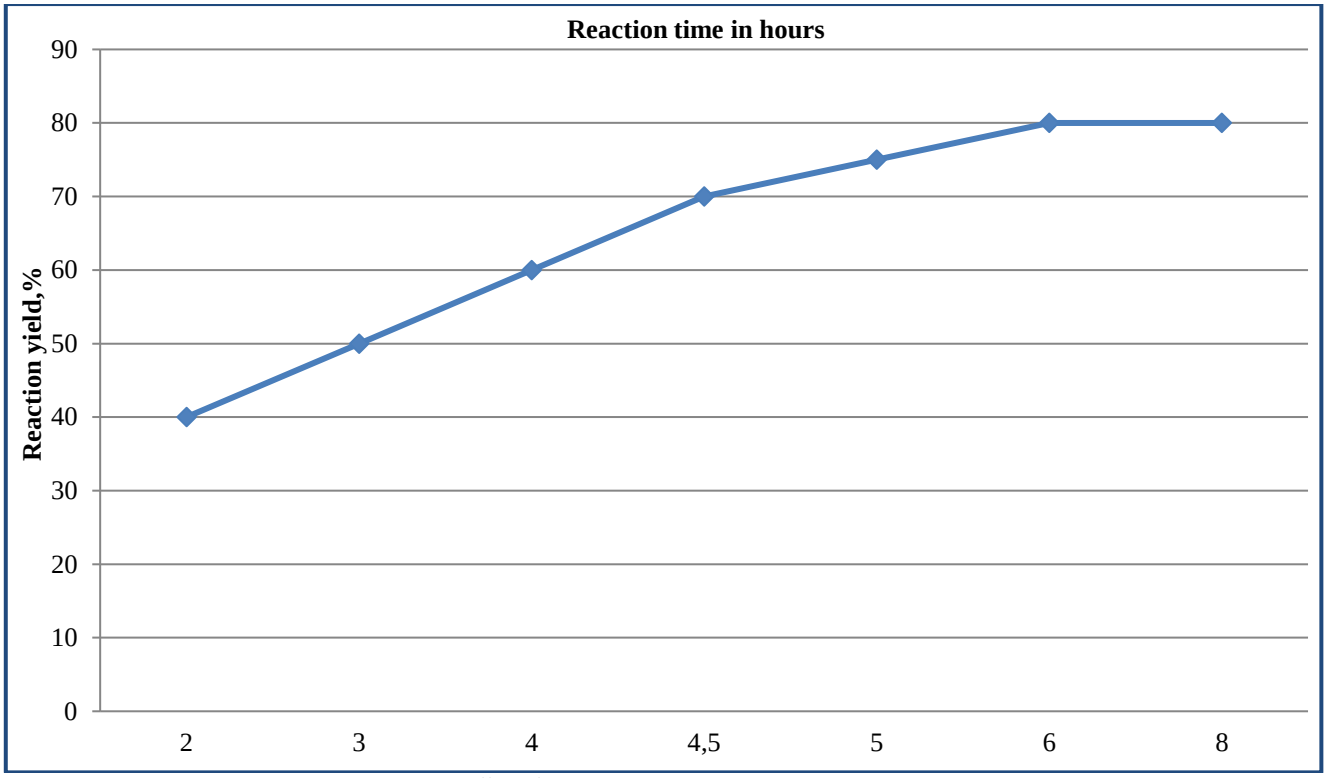


Fig. 2 Effect of time on reaction yield in graphene oxide production

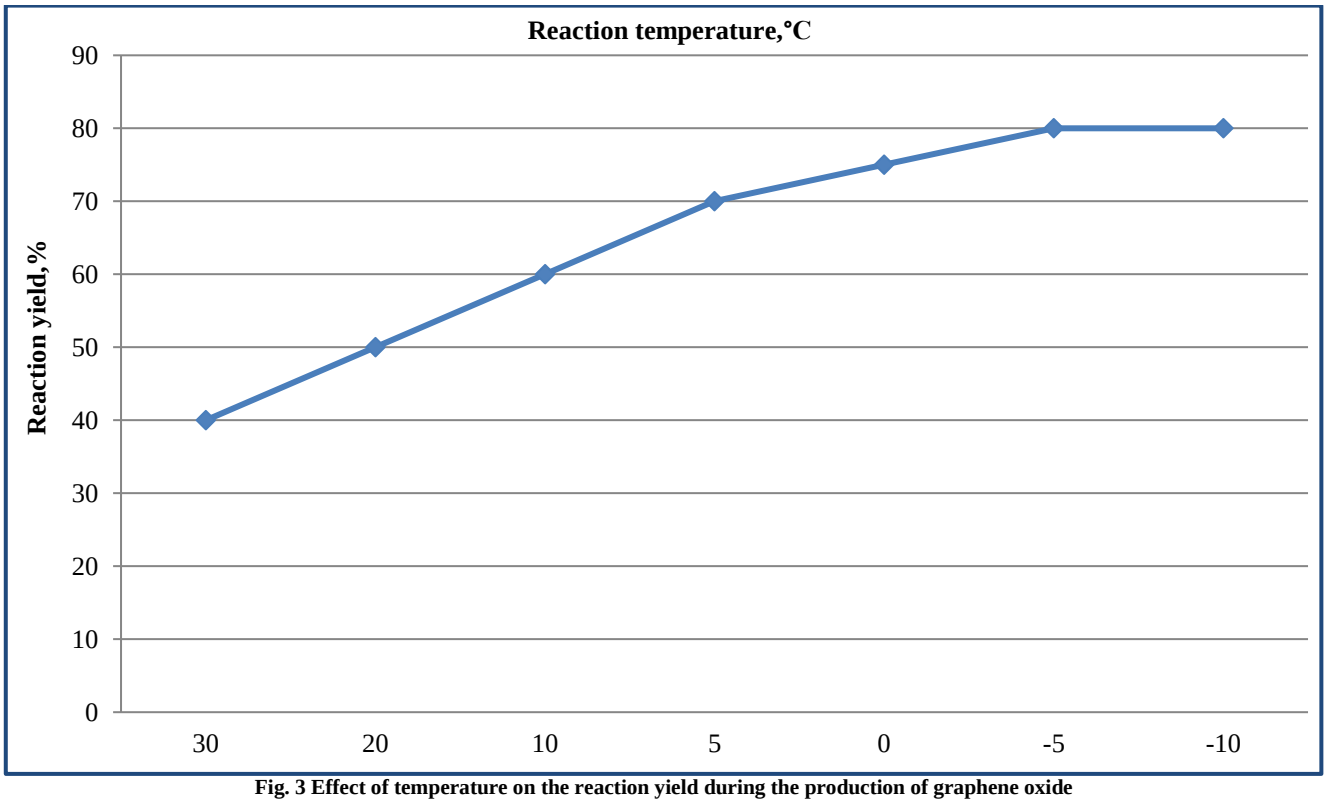


Fig. 3 Effect of temperature on the reaction yield during the production of graphene oxide

Experiments were conducted at different times. The yield of the product obtained at different time intervals during the reaction, i.e., from 2h to 8h, was tested, and the results are shown in Figure 2. It was found that the yield of the product obtained during the reaction of graphite and calcium permanganate for 6 hours is higher than 80%. Experiments were conducted at different temperatures. In the process, the performance of the reactions performed at different temperatures was tested at both low and high temperatures, and the results are shown in Figure 3.

It was found that the yield of the product obtained in the reaction of graphene with potassium permanganate in the temperature range from 0 °C to -5 °C is higher than 80%.

3. Obtained Results and their Discussion

3.1. Study of Physical and Chemical Properties of Synthesized Graphene Oxide

Based on the results of infrared spectroscopy (IR), Scanning Electron Microscopy (SEM) and X-ray spatial (RF) analysis of graphene oxide synthesized by oxidative polymerization, their analysis was presented.

This infrared spectroscopy (IR) technique is used to obtain absorption, emission, and phototransmission spectra of solids, liquids, or gases using infrared light. It can also be used to determine the composition of unknown compounds [13]. In our study, infrared spectroscopy (IR) analysis was used to study the bond interactions in the graphene oxide formed by the reaction before and after the graphite oxidation process.

Figures 4a) and b) show infrared spectroscopic images of graphite and synthesized graphene oxide (GO). Graphene oxide shows absorption peaks confirming the presence of C-O functional groups with vibrational frequencies of 1047 cm^{-1} [14]. The absorption peaks between 1593cm^{-1} and 1705cm^{-1} indicate that this C=C bond is preserved before and after the oxidation process. A broad peak from 588 cm^{-1} to 3750 cm^{-1} due to the O-H region of water H_2O molecules adsorbed on graphene oxide (GO) is reported to belong to the valence vibrational frequencies of hydroxyl groups [15].

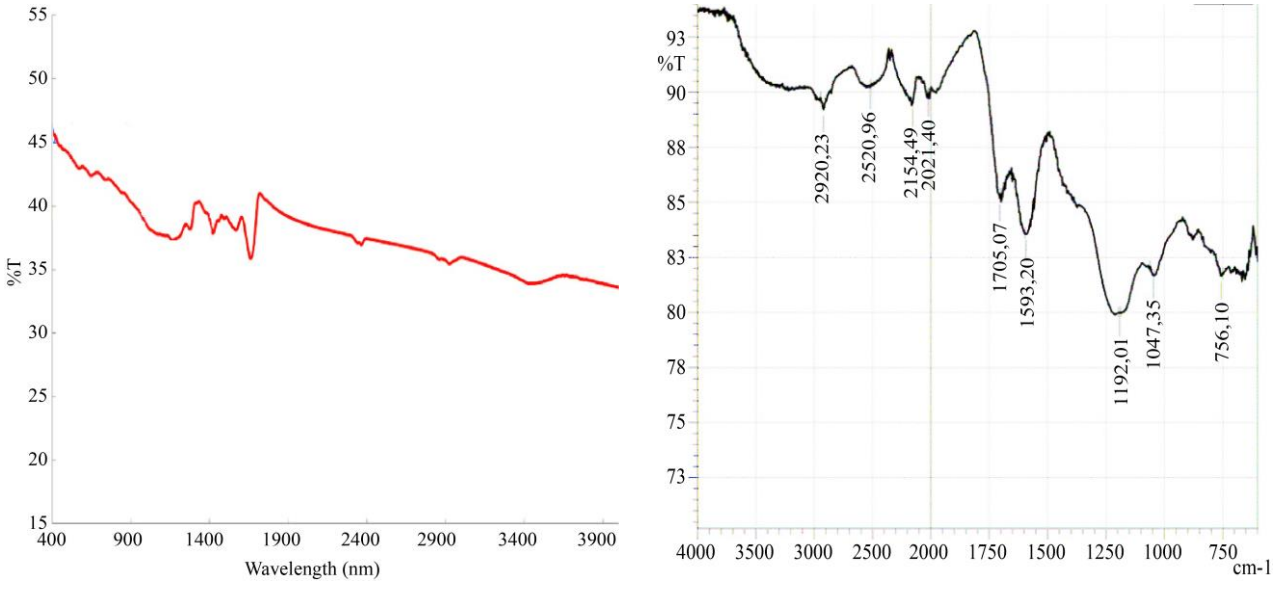
The high electron conductivity, transparency, and flexibility of graphene oxide make it suitable for use in dye-sensitized solar cells [16, 17]. Here, they can be used in different ways, such as electrodes (anodes and cathodes), acceptor layers, donor layers, buffer layers and active layers [18]. Many applications within a solar cell depend on the inherent tunable parameters of graphene oxide, including thickness, thermal annealing temperature, dopant concentration in the layer, and its photovoltaic performance [19, 20]. Organic polymer solar cells are the most studied and used graphene oxide-based solar cells to date [21].

Due to the diversity of organic polymer solar cells and how to incorporate graphene oxide derivatives into them, including the transparent electrode, the composition, structure and properties of the photoactive layers, their useful performance coefficients differ from each other.

The morphology and structure of the nanomaterials were analyzed using a scanning electron microscope. Figure 5 (a) shows the SEM image of typical graphite. The SEM image shows how the sheets cross in Figure 5 (a). 2 (b, c, d) shows SEM images of layered graphene oxide (GO) [8].

Originally, graphene oxide (GO) layered crystalline graphite was considered as a result of chemical exfoliation and oxidation [22]. Surprisingly, under certain conditions of graphite oxidation, carbon atoms retain the integrity of the two-dimensional structure of the layers with oxygen-containing functional groups attached to both sides and edges of the carbon plane. However, very recent results have shown that the same structure can be obtained using an alternative (bottom-up) hydrothermal glucose treatment or even Chemical Vapor Deposition (CVD). Therefore, today, it is worth giving a more general definition based on its structure: a monoatomic carbon layer modified by oxygen functional groups on both surfaces.

Like any 2d carbon graphene oxide (GO), it can have a monolayer or multilayer structure. The carbon layers in multilayer GO are characterized by functional groups attached to each layer of carbon atoms. Although GO, like graphene, is a two-dimensional carbon material, its properties are far from those of graphene. It does not absorb visible light, has very low electrical conductivity compared to graphene, and significantly increases reactivity [23]. Due to the pores and large surface area in the graphene oxide layers, the semiconductor TiO_2-treated composite increases the absorbance of visible light-sensitive dyes. As a result, due to the above properties, the paint is allowed to be used in sensitive solar cells [24].



(a) **(b)**

Fig. 4 Infrared spectrum of a) graphite and b) graphene oxide

Table 2. Diffractogram data of graphene oxide

№	2theta- scanning angle [°2θ]	Peaks [cts]	FWHM integral width [°2θ]	d- interplanar distance [Å]	I- density of peaks
1	10.98	13.15	0.2000	8.0515	33.18
2	26.60	41.60	0.2400	3.3484	87.47
3	37.74	19.35	0.1600	2.3817	61.03
4	43.98	396.31	0.2000	2.0572	1000.00
5	64.32	327.47	0.2800	1.4472	590.21
6	77.42	237.02	0.2400	1.2317	498.38

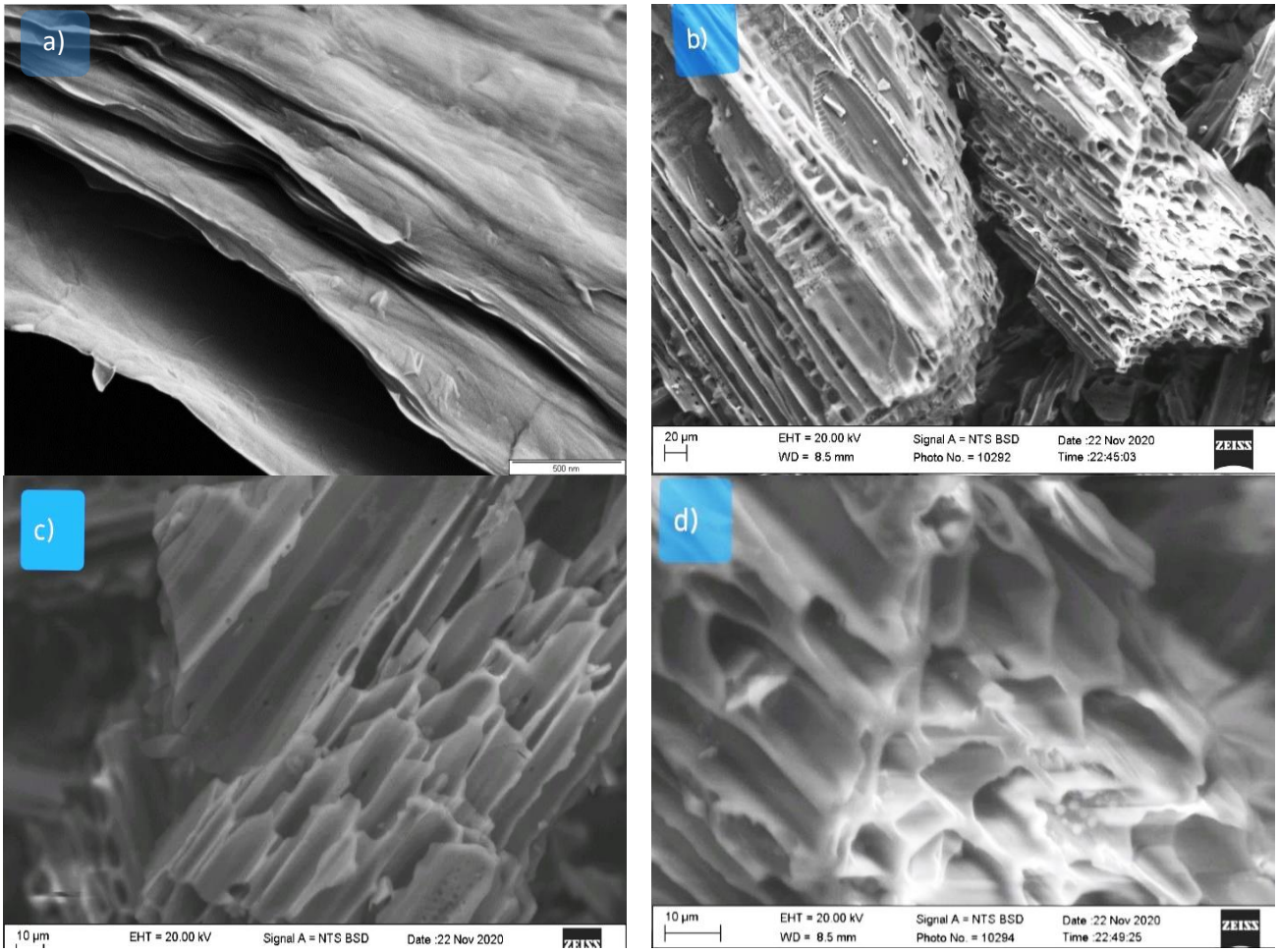


Fig. 5 SEM images of (a) graphite and (b, c, d) graphene oxides

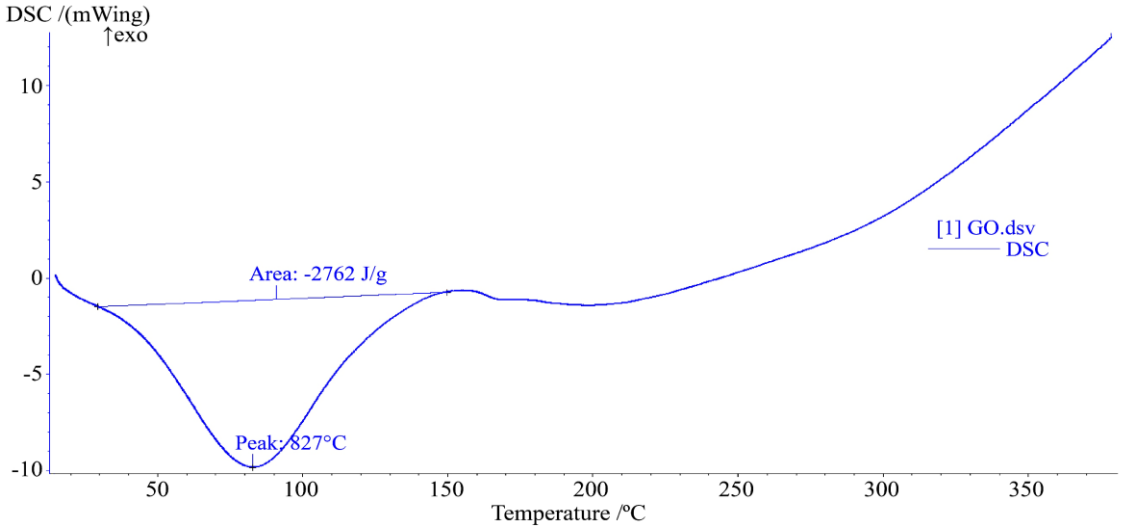


Fig. 6 Thermogram of graphene oxide in a differential scanning calorimeter

Table. 3 X-ray phase analysis of synthesized graphene oxide

Profile area	Counts	Weight %
Total area	167271	100.00 %
Diffraction peaks	170776	102.10 %
Background	0	0.00 %
Instrumental background	0	0.00 %
Amorphous phases	0	0.00 %
Degree of crystallinity (DOC) = 100.00 %	Amorphous content (weight %) = 0.00 %	

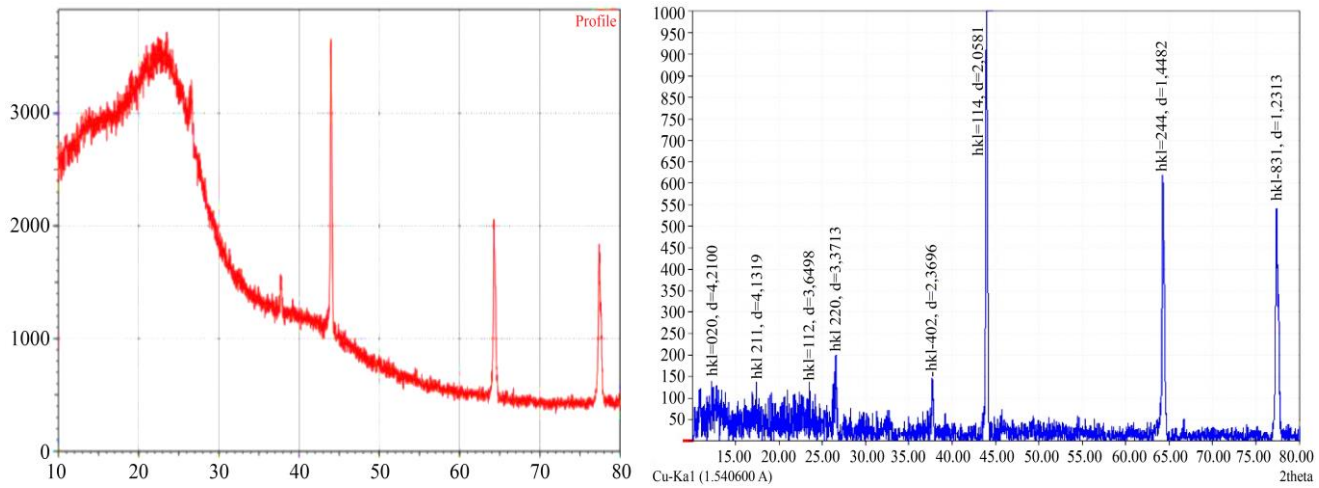


Fig. 7 An X-ray phase analysis study of synthesized graphene oxide.

3.2. Study of the Thermal Analysis of the Synthesized Graphene Oxide

Figure 6 shows the differential scanning calorimeter thermogram of the synthesized graphene oxide. Moisture loss was observed in the thermogram range of 50-120 ºC. In the range of 150-200 ºC, no thermal changes occurred in the obtained substance, which indicates that graphene oxide is heat resistant and thermally stable.

From 250 ºC to 400 ºC, decomposition occurred in the substance. The direction we use, that is, if we take organic dyes as a light-absorbing paint pigment for solar elements, then the temperature will not be so high. We can use this substance without any obstacles, considering its corrosion resistance.

3.3. Study of X-ray Phase Analysis of Synthesized Graphene Oxide

Analyzes were carried out in X-ray spatial analysis equipment of the synthesized graphene oxide (XRD-6100 SHIMADZU X-RAY Defractometer). Measuring the average distance between the layers or rows of atoms of the obtained polymer material, determining the direction of a single crystal or molecule, finding the crystalline or amorphous structure of an unknown material and how much it is, measuring the size, shape and internal structure of small crystalline regions, and analyzing the qualitative and quantitative composition of the substance allowed to get. Graphene oxide molecule was found to have a 100% crystal arrangement Table 2. Coherent scattering field (CFT) sizes (nanocrystal sizes) are classically calculated by the Williamson-Hull formula [25].

$$B(2\theta) = \frac{K\lambda}{L\,Cos\theta}$$

Where V (2th) is the average size of crystals (nm)

K- dimensionless particle coefficient form (Williamson-Hull) The value of K is from 0.68 to 2.08. For spherical crystallites with cubic symmetry,

K = 0.94.

L- FWHM (Full Width at Half Maximum) is the reflection of the integral width in the diffractogram. (in 2nd radian and unit) [26]

λ-X-ray wavelength is Cu Ka = 1.540600 Å.

cost is the X-ray radiation cosine of the diffraction angle. (Breggovsky Corner). cost=0.2 value is taken.

Graphene oxide is calculated according to the values given in the formula when calculating the particle size according to the Williamson-Hull equation [27].

Example:

$$B(2\theta) = \frac{K\lambda}{L\,Cos\theta}$$

B (2θ) =0,94•1.540600/ 0.2200•0,2=33,91

Table. 4 Calculation of the particle size of graphene oxide according to the Williamson-Hull equation

№	2theta- scanning angle [°2θ]	FWHM integral width [°2θ]	*d* (nm)- the average size of crystals	*d* (nm) average
1	10.98	0.2000	36.2041	37,72
2	26.60	0.2400	30.1701	
3	37.74	0.1600	48.2721	
4	43.98	0.2000	36.2041	
5	64.32	0.2800	25.8601	
6	77.42	0.2400	30.1701	
7	10.98	0.2000	36.2041	

According to the Williamson-Hull equation, the average size (nm) of graphene oxide was calculated to be 37.72, and the size of the obtained graphene oxide particles was proved to be nanoparticles. As a result of the addition of nanoparticle graphene oxide to the composition of the composite, electrically conductive fillers begin to communicate well with each other, as a result, free electrons move easily and form a permanent path that transports electrons. Due to the pores in the layers of graphene oxide and the large surface area, the composite treated with semiconductor TiO_2 increases the absorption of dyes sensitive to visible light. As a result, due to their above properties, it is possible to use them in dye-sensitized solar cells.

4. Conclusion

Graphene oxide was synthesized from graphite powder by the method of oxidative polymerization. The effects of temperature, concentration and time on the reaction yield of synthesized graphene oxide were studied. As a result, it was determined that the yield of the product obtained in the processes carried out with graphite and potassium permanganate in a mass ratio of 1:6 for 6 hours at temperatures from 0 ºC to -5 ºC is higher than 80%.

Morphology, surface area and porosity (SEM) of the synthesized graphene oxide nanolayer at 100 nm in a scanning electron microscope, the bonding nature of the atoms in it, the absorption frequencies (IR) in infrared spectroscopy, as well as the average crystal size and shape of graphene oxide particles, their distribution patterns in X-ray phase was analyzed by analysis methods. As a result, the average crystal size of graphene oxide particles was calculated to be 37.72 d (nm) according to the Williamson-Hull equation. Also, it was found that the graphene oxide molecule has a 100% crystal structure, and it was proved that the size of the particles is nanoparticles.

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