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Synthesis and Characterization of Graphene Oxide Flakes for Transparent Thin Films

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We have synthesized large scale, thin, transparent graphene oxide (GO) flakes by Hummer's method and investigated their suitability for fabrication of transparent nanocomposites. The GO flakes were comprehensively characterized by X-ray diffraction, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), Raman spectroscopy and Differential Scanning Calorimetry (DSC). X-ray diffraction displayed the peak of graphene oxide at 9°degree, which is characteristic peak of GO in agreement with the literature results. Scanning Electron Microscopy images revealed that thin, transparent, flake form GO with 14.8 μm lateral size and 0.31μm thickness were synthesized. In literature materials have shown that, the average lateral sizes of GO flakes change between 0.4 - 12.4μm. The comparison with literature results show that for the first time, our group could synthesize large scale, thin and more transparent GO flakes by simple Hummer's method using simple dispersed graphite. EDX measurements indicate the formation of layered structure with oxygen containing functional groups. The intensity ratio between D and G peaks in the Raman spectra proves that less defective GO flakes have been synthesized. The solution ability of the synthesized material indicate that high quality GO flakes were synthesized, which make them effective soluble material due to oxygen containing groups formed on the graphene plane during synthesis process.DSC results shows that these flakes are thermally stable till 200 °C.

Due to high solubility properties, large scale and transparency they can be very useful in fabrication of high optical transparent nanocompoties for replacement indium tin oxide transparent conductors in solar panels, biomedical applications and microwave absorbers for electromagnetic interference (EMI) environmental protection.

Keywords: graphene oxide, SEM, DSC, Raman analysis, XRD.

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Introduction

Nanomaterials play an important role in fabrication of new generation devices due to their high surface to volume ratio, reduced size effects, extraordinary properties. Particularly, carbon nanomaterials play an important role in improvement of nanotechnology. For example, graphene is very good semiconductor material with large surface area, high stiffness, good optical transmittance and high thermal conductivity properties [1-7].

Chemical exfoliation method is considered as an easy and cost-effective synthesis method for mass production of graphene. GO can be considered as a new "bridge" material for mass production of graphene. Graphene oxide is graphene sheet decorated with oxygen containing

groups. The advantage of this material is that this material can be synthesized by oxidizing graphite crystals in large quantities with cost-effective way. Due to these oxygen containing groups, this material is hydrophilic and can be dissolved in many solvents. This property makes it useful for uniformly deposition on different substrates and form thin films and networks, which are very potential for microelectronics, transparent conductive film, composite materials, solar energy and biomedical applications [8, 9].

We have prepared high quality, large scale, thin, transparent GO flakes by Hummer's method. The crystal structure, morphology, element analysis and thermal stability were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), EDX and DSC analysis.

I. Experimental Method

1.1. Synthesis of GO

There are three methods for synthesis of GO- the Brodie method [10], Staudenmaier method [11] and Hummer's method [12].

In this research work GO was synthesized by Hummer's method [11]. Initially, 96 % H_2SO_4 (10 ml) was taken in a beaker. As source material 1 gram of 99.9995 % dispersed graphite was used. 1 gram of dispersed graphite was stirred in Petri cup with 0.5 g of $NaNO_3$ and added to sulfuric acid. Residue sulfuric acid (13 ml) also added and the system stirred using magnetic stirrer. During 2 hours KMnO4 (3 g) was slowly added to the system. During this process the system is located in ice bath and the temperature was controlled and not to exceed 20 ^{0}C. After stirring process the system was located to warm bath to control the temperature 35 ^{0}C. Brownish gray paste was obtained after this process. 46 ml distilled water was added to the system and immidetly boiled after an hour 250 ml distilled water was added and stirred. After a while 100ml 30 % H_2O_2 was added and stirred. The colour of system changed during this process. The brownish yellow colour is the sign of synthesis of GO. The final product was filtred. The obtained material was dried at 50 ^{0}C for 2 hours in vacuum box. The picture of the synthesized GO was shown in Figure 1 a.

The solution ability of the synthesized GO is the first sign that the high qualitative GO was synthesized, since GO is very effective soluble material due to oxygen containing groups formed on the graphene plane during synthesis process (Figure 1 (b),(c)). In comparison with another allotropes of carbon, like carbon nanotubes, GO is soluble in all solvents including deionized water. For example, CNTs can form only suspension in different solvents and are not soluble. This property makes this material very useful for fabrication of thin, transparent and optical transmittance polymer nanocomposites.

1.2. Characterization

The X-Ray Diffraction analysis of the synthesized GO was performed using D2 Phaser diffractometer (Bruker 5000, Germany), used with CuK_α radiation with wavelength 1.5406 Å and 2θ = 05° - 80° range. The surface morphology and element alaysis of the GO were carried out using Scanning Electron Microscope (SEM) by JEOL (Oxford Instruments,15kv SEI, WD - 4,5mm)

a)

b)

c)

Fig. 1. Images of synthesized GO flakes (a), GO solution in DMF for 30 min (b) and 2 hours (c).

with energy dispersive X-ray spectroscope facility attached to it. Raman spectra was utilized to detect the quality-possible structural defects in graphene flakes. The measurements were carried out by a Raman scattering between 500 and 9000 cm^{-1} ranges using Nanofinder 30 Confocal Laser Microspectrometer working with 532 nm laser line (laser power 8 mW, a 100 grooves/mm grating, exposure time 10 s). Differential scanning calorimetry (NETZSCH DSC 204F1 Phoenix) was performed under a flowing gaseous argon atmosphere in (-100 to 500 °C) temperature range.

II. Results and Discussion

2.1 X-Ray Diffraction

The structural properties of the synthesized GO were characterized using the XRD analysis, as shown in Fig. 2. The XRD analysis was recorded in the 2θ range of 5 - 80^0.

The result confirms the formation of GO flakes by the presence of a characteristic 2θ peak at 9°, which is characteristic peak of GO in agreement with the literature results [13, 14]. Based on literature materials, this peak corresponds to a d-spacing (8.546 Å), which suits to the inter layer space of graphene oxide sheets decorated by oxygen-rich groups on both sides of the sheets and water molecules trapped between the sheets. The second broad peak can be explained with incomplete oxidation of graphite and the significant indicator of amorphous material.

2.2. Raman analysis of GO flakes

Raman spectroscopy is a non-destructive technique to characterize graphite materials, in particular to determine the defects and the ordered and disordered structures of graphene [15-17]. Fig. 3 shows the Raman spectra of the synthesized GO flakes. The Raman spectra of the GO flakes shows two prominent peaks at 1340 and 1596 cm^{-1},

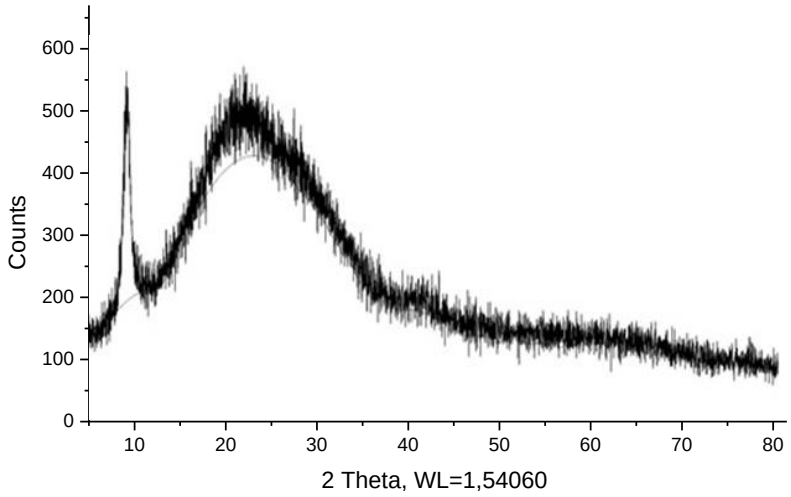


Fig. 2. X-Ray diffraction pattern of the GO nanoflakes.

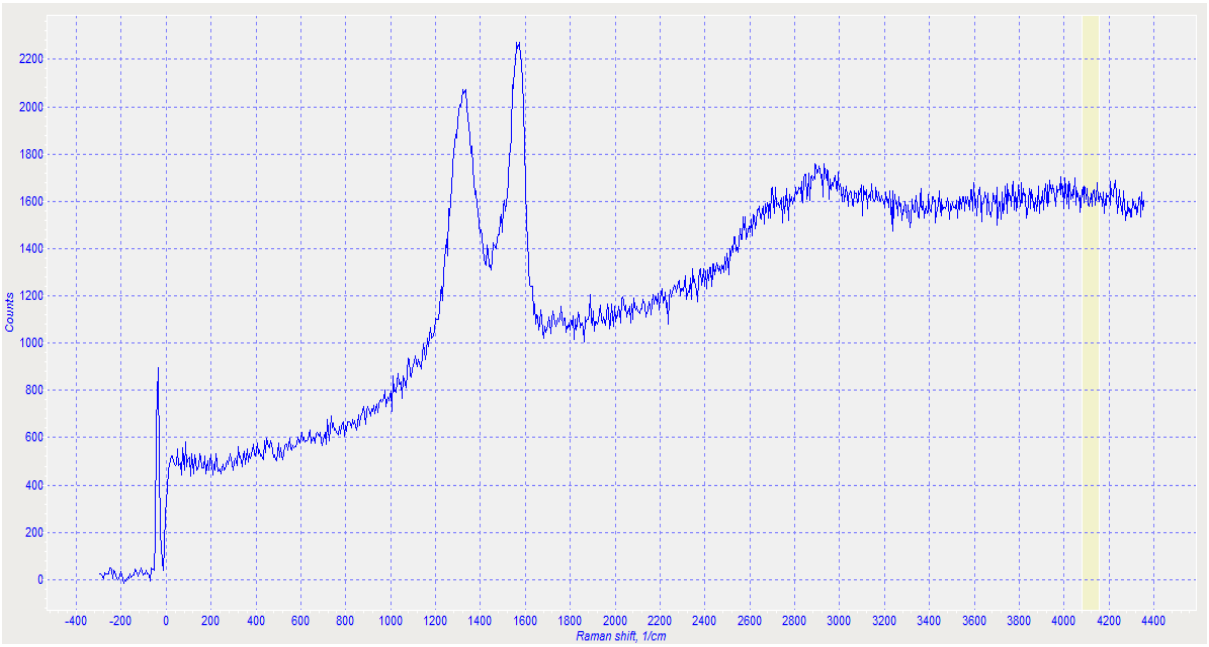
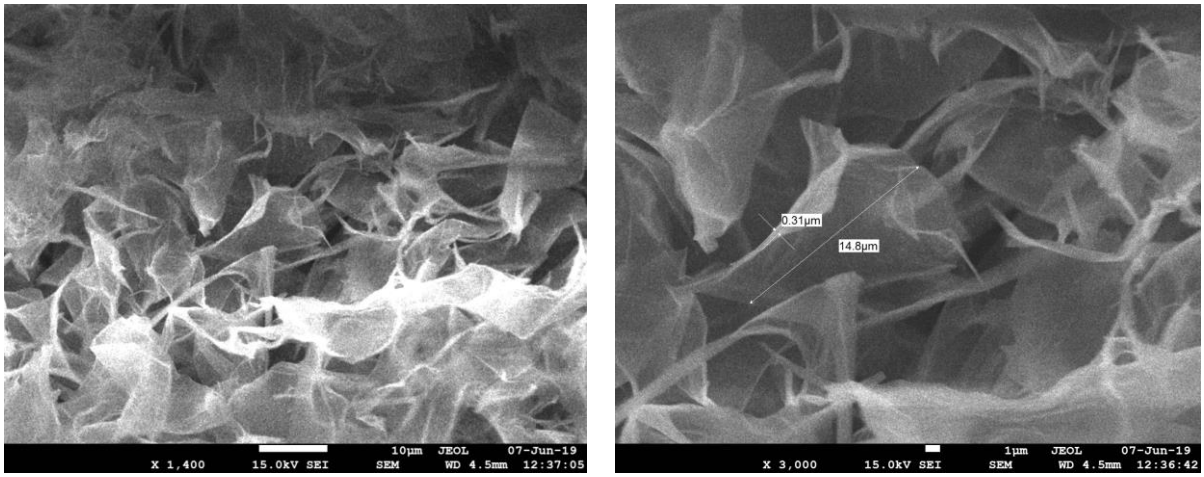


Fig. 3. Raman spectroscopy of the GO flakes.



a) b)

Fig. 4. Scanning Electron Microscopy (SEM) images of graphene oxide flakes (a), Size distribution and thickness of the GO flakes (b).

corresponding to the D- and G-bands. Usually, the graphene powders synthesized by chemical approach show a strong D band in the Raman spectrum with the intensity ratio of $I_D/I_G > 1$ due to the defects and partially disordered crystal structure of graphene sheets. The Raman analysis result proves that the synthesized GO flakes are less defective based on the results of intensity ratio of the G and D bands.

The GO flakes I_D/I_G ratio (0.93) significantly shows the sp^2 domains of carbon networks and decreases in edge planes and disorders. It proves that high qualitative GO flakes have been synthesized using simple Hummer's method using dispersed graphite as carbon source material.

2.3. SEM analysis of GO

For improvement the application ability of GO flakes as transparent nanocomposite thin films, a key factor and challenge to increase a size of the flakes and their transparency degree. Currently, most graphene oxide flakes available in the market are less than 10 micrometres in size [18, 19]. The size of the synthesized GO flakes depends on the type of carbon sources as well as their sizes and synthesis methods.

Scanning Electron Microscopy measurements were carried out to study the surface morphology of the synthesized graphene oxide in detail. Fig. 4 displays the shape and size distribution analysis results of the synthesized GO, taken at different magnifications. SEM images of the Graphene Oxide (GO) shows that during synthesis process flake form wrinkle GO layers have been formed. The GO flakes are observed clearly on the SEM picture. Since, the main properties of GO strongly depend on the mean size of the flakes, the size distribution of the flakes were measured.The main purpose of our research, to synthesize large size and transparent GO flakes.

The SEM images show that flake shape layers with 14.8 μm lateral size and 0.31 μm thickness were synthesized. The shape and size of the flakes confirm that the synthesized GO is not a single layer, however it has the multiple layers. In literature, the average lateral sizes of GO change between 0.4 - 12.4μm [20]. The size and transparency of the GO flakes play an important role in nanocomposite technology. It is clear from the figure 4 that, the synthesized GO flakes are very transparent which is very useful for fabrication of transparent polymer composites. The thickness of our synthesized GO flake bundle is nearly 0.31 μm. Based on Tang [21] and his group analysis results, if the lateral size of GO flakes less than 20 μm, probable this material have less than 5 layers. According to another literature results [22] it is possible to synthesize three type of GO material. GO with lateral dimension 3 ~ 4 μm which can be considered large and thin and the sheet layer number is 5, if the thickness is around 0.2 ~ 0.4μm the GO layer can be considered thin and small and will be consist of 5 layers and GO with lateral size 0.2 ~ 0.4μm thick and small and about 40 layers. In comparison with other research works our results prove that it could be possible to synthesize effective GO flakes which makes them very useful for successful application in composite technology. Based on these results, we can say that our synthesized GO flakes do not belong to one of these groups as its lateral size is 14.8 μm, therefore based on literature materials we can consider that our GO has less than five layers. However, to determine the exact number of layers, TEM and high resolution AFM analysis will be very useful.

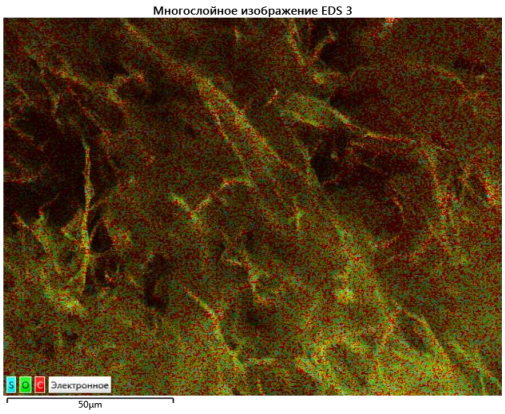
2.4. EDX analysis

Figure 5(a, b) shows the EDX spectrum for the synthesized GO flakes. The spectrum showed peaks (Fig.5 (b)) corresponding to C, O and S elements. Figure 5(b) shows the highest EDX spectrum which corresponds to carbon. The presence of oxygen and sulfur can be seen as a result of H_2SO_4, H_3PO_4 and $KMnO_4$ used as oxidizing agent. This is a confirmation that graphene oxide was actually formed as it is graphene layer decorated with oxygen containing groups.

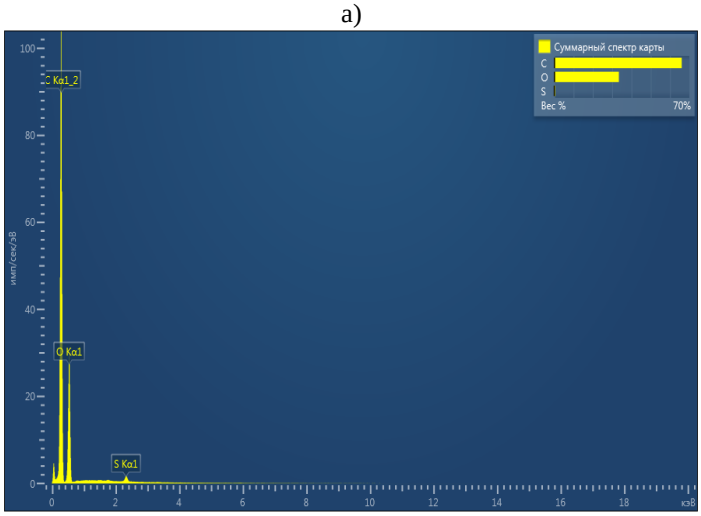
The detail information about distribution of consisting elements (C, O, S) of the synthesized GO flakes was shown in Figure 6.

2.5. DSC analysis of the GO flakes

The DSC curve shows thermal properties of the GO flakes. The GO flakes stability and thermal decomposition results are presented in Figure 7. As



a)



b)

Fig. 5. EDX spectrum of the synthesized GO flakes.

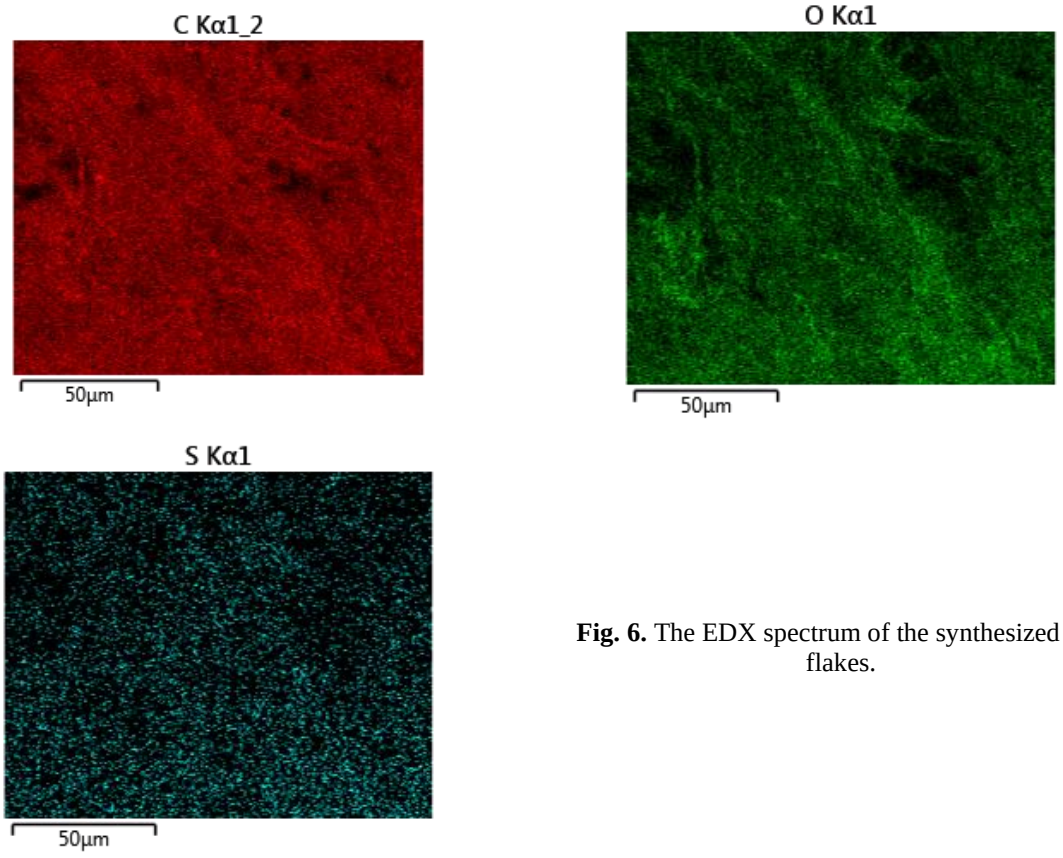


Fig. 6. The EDX spectrum of the synthesized GO flakes.

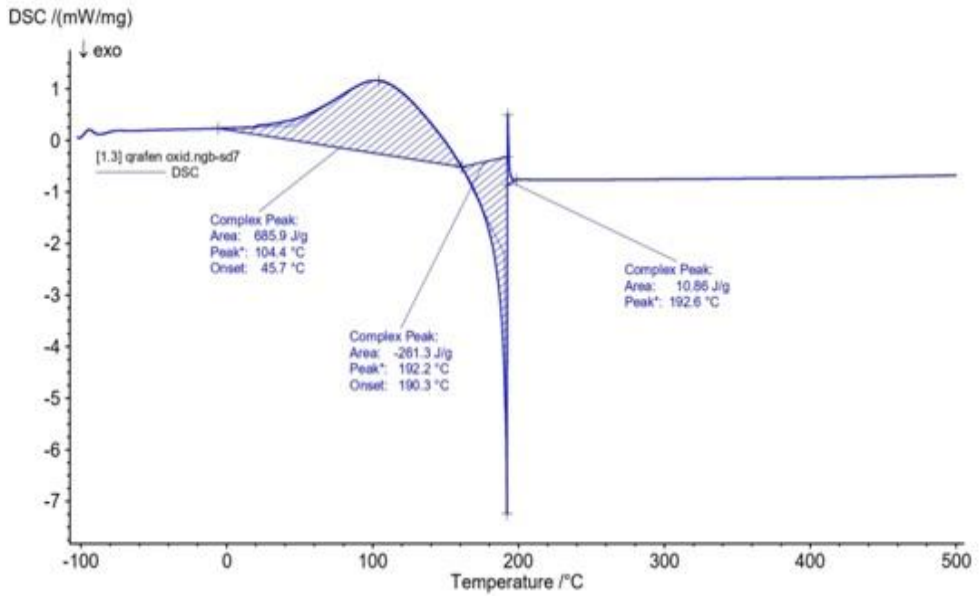


Fig. 7. DSC analysis of graphene oxide flakes.

starting material 10 mg of GO flakes were taken. The experiment was carried out in Argon atmosphere. The thermal study of the material was measured in -100 and 500 °C temperature ranges. The exothermic peak, observed at 104 °C is attributed to the reduction of GO flakes.

The results show that with increasing temperature the DSC curve of the GO flakes shows two peaks. The crystallization temperature is represented by an exothermic peak at 104.4 °C. This gives rise to heat generation. From 192.2 °C total decomposition of GO flakes was observed. The investigation thermal analysis of the synthesized GO flakes is very important [23], as these properties plays important role in preparation of nanocomposites based on GO flakes.

Conclusion

We have synthesized large scale, transparent, thin graphene oxide flakes by modified Hummer's method, using dispersed graphite as carbon source material. SEM analysis present that flake form GO with 14.8 μm lateral size and 0.31μm thickness was synthesized. The Raman analysis results prove that less defective GO flakes were synthesized and these flakes are easily soluble in DMF which is main factor for fabrication of nanocomposites. The EDX spectrum showed peaks corresponding to C, O elements and the presence of O element is a confirmation that graphene oxide was actually formed as it is graphene layer decorated with oxygen containing groups.

These properties could qualify the GO flakes for use in thin films and networks for potential applications in transparent nanocomposite technology, biomedical applications, microwave absorbers for electromagnetic interference environmental protection.

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Синтез і властивості пластіців оксиду графену для створення прозорих тонких плівок

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В роботі були синтезовані пластівці оксиду графену (GO) великого розміру за методом Хаммера та досліджували їх придатність для виготовлення прозорих нанокомпозитів. Отримані тонкі GO-пластівці всебічно досліджувалися за допомогою рентгенівської дифрактометрії, скануючої електронної мікроскопії (SEM), методами енергодисперсійного рентгенівського аналізу (EDX), комбінаційного розсіювання світла (КРС) та диференційної скануючої калориметрії (DSC). Дифракція рентгенівських променів показала пік оксиду графена при 9°, що є характерним піком GO і узгоджується з літературними даними. Розміри синтезованих пластинок, згідно дослідженння SEM, складають: 14,8 мкм - бічні частини та 0.31 мкм - товщина, а отже вдалося синтезувати масштабні, тонкі та прозорі GO-сруктури методом Хаммера, використовуючи звичайний дисперсний графіт. Вимірювання EDX вказують на утворення шаруватої структури з кисневмісними функціональними групами. Співвідношення інтенсивності між піками D та G у спектрах КРС доводить, що синтезовано малодефектні GO-структури. Розчинна здатність синтезованого матеріалу свідчить про високу якість отриманих структур та робить його ефективним розчинним матеріалом завдяки кисневмісним групам, що утворюються на площині графена в процесі синтезу. На високу термостійкість отриманих GO-структур (аж до2000 °C) вказують результати аналізу даних диференційної скануючої калориметрії.

Завдяки високим розчинним властивостям, великим латеральним розмірам та прозорості отримані GO-пластівці можуть бути використані у виробництві прозорих нанокомпозитів для заміни провідників типу ITO у сонячних панелях, біомедичних застосувань та мікрохвильових поглиначів (EMI) для захисту середовища від електромагнітних перешкод.

Ключові слова: оксид графену, SEM, ДСК, раманівський аналіз, рентгенівська діагностика.