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REGULAR ARTICLE

Tuning of Graphene Oxide Thin Films Synthesis and Characterization with Electronic Behaviour

A. Mondal[1,3], A.K. Kundu[1,2], H.S. Biswas[1,*] ✉ iD, D.K. Maiti[4,†]

[1] *Department of Chemistry, Surendranath College, 24/2, Mahatma Gandhi Road, Kolkata-700009 India*
[2] *Department of Chemistry, Sripat Singh College, Jiaganj, Murshidabad, 742123 India*
[3] *Harindanga High School, Falta-743504 India*
[4] *Department of Chemistry, University of Calcutta, University College of Science, 92, A.P.C. Road, Kolkata-700009 India*

Graphene oxide (GO), a graphene derivative, is synthesized through an improved Hummers method, enhancing its solubility, dispersibility, and reactivity by introducing oxygen-functional groups. The process involves oxidizing purified natural graphite flakes, followed by solvothermal treatment. Exfoliation of graphite oxide in distilled water using ultrasonic waves results in the formation of a graphene oxide thin film. This method optimizes the production of GO, harnessing its unique properties for various applications in materials science and nanotechnology. The structural and physicochemical characteristics of the materials were analyzed through X-ray powder diffraction (XRD), Fourier transformation (FTIR), Scanning electron microscopy (SEM), and ultraviolet-visible spectroscopy (UV-Vis). XRD peak indicated a $2\theta^0 = 10.05^0$ corresponding to an interlayer spacing of 0.83 nm. FTIR and Raman analyses revealed the introduction of oxygen atoms into the graphite layer, forming various chemical bonds such as C-H, OH, C=O, C-O-C, and COOH with graphene. SEM images illustrated the formation of ultrathin and homogeneous graphene films. The UV-vis spectra of GO exhibited a prominent absorption peak at approximately 239 nm, corresponding to the $\pi - \pi *$ transition of atomic C-C bond and at 301 nm, corresponding to the n-π* transition of aromatic C-C bonds. The electrochemical behavior of a glassy carbon electrode modified with GO was explored using the $K_3[Fe(CN)_6]$ redox couple system. The results indicated that the electron transfer process controlled the electrochemical behavior.

Keywords: Graphene oxide, Solvothermal, XRD, FTIR, SEM, UV-Vis spectroscopy, Raman spectra.

1. INTRODUCTION

Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, has gained widespread attention due to its outstanding electrical, mechanical, and thermal properties [1]. However, the pristine form of graphene exhibits challenges in terms of processability and compatibility with certain applications due to its hydrophobic nature and limited functionalization [2, 3]. This led to the development of graphene oxide (GO) which stands out as a fascinating material with unique thermal, electrical and optical characteristics [4]. In recent years, graphene and its derivatives have emerged as pivotal materials in the realm of nanotechnology, owing to their exceptional properties and versatile technological applications, spanning from electronics to biomedicine [5, 6]. This paper delves into the synthesis and characterization of graphene oxide, aiming to provide a comprehensive overview of the current state of research in this field and the potential applications that arise from the distinctive properties of GO.

The synthesis of graphene oxide typically involves the oxidation of graphite, the precursor of graphene. The most widely employed method for GO synthesis is the Hummers' method [7, 8]. Other methods, such as the Staudenmaier and Brodie methods, offer variations in the synthesis process, each with its advantages and limitations [6, 7]. It is essential to emphasize the significance of controlling reaction parameters during the synthesis process to achieve tunable properties of graphene oxide. The choice of oxidizing agents, reaction time, and temperature play a crucial role in determining the extent of oxidation and the functional groups present on the GO surface.

As a two-dimensional nanomaterial, GO exhibits exceptional surface area, high conductivity, and tunable functional groups, rendering it versatile for applications in electronics, energy storage, and beyond. In this context, a thorough understanding of the structural, optical, morphological, and electrochemical characteristics of GO thin films becomes crucial for harnessing their full potential in practical applications. In this study, we present a comprehensive analysis of GO thin films using a combination of advanced characterization techniques, including X-ray Diffraction (XRD), UV-Vis spectroscopy, Fourier Transform Infrared (FTIR), Raman spectroscopy, scanning electron microscopy (SEM), and electrochemical studies. The purpose of this multi-faceted approach is to gain insights into the intricate details of GO thin films, laying the groundwork for their targeted utilization in various technological advancements. The

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* Correspondence e-mail: harishankarb7@gmail.com
† dkmchem@caluniv.ac.in

multi-faceted characterizations presented in this study establish a solid foundation for the understanding and utilization of GO thin film. Moreover, the scalability of production processes becomes a crucial consideration, paving the way for the practical implementation of graphene oxide in diverse technological advancements.

2. EXPERIMENTAL

2.1 Preparation of Graphene Oxide

The preparation of graphene oxide (GO) involved an advanced modification of the Hummer technique followed by solvothermal [11, 12]. In a meticulous procedure, 4 grams of graphite flake and 2.5 grams of potassium nitrate (KNO_3) were combined in a 1000 ml round bottom flask with 110 ml of 98% sulfuric acid (H_2SO_4).

This amalgamation was subjected to an ice bath, maintained between 0℃ and 6℃, while continuously stirred for 2 hours. Following this initial phase, 8 grams of $KMnO_4$ were gradually introduced to the mixture to ensure the temperature remained below 5 ℃. The resulting suspension underwent a 2-hour reaction period in the ice bath, followed by an additional 60 minutes of stirring. Subsequent to this, another round of stirring took place in a 40℃ water bath for an additional 60 minutes. The temperature of the mixture was then elevated and maintained at 98℃ for an additional 60 minutes. The resulting suspension, totaling 400 mL, was diluted with deionized water, reaching a temperature of 25 ℃ after five minutes. At this point, 10 mL of H_2O_2 was judiciously introduced. The ensuing reaction product underwent centrifugation and underwent multiple washing cycles using deionized water and a 5% HCl solution. A small amount of ethanol was then added to the mixture. After filtration, the resulting solution was transferred to a Petri dish and mica foil, where it underwent drying within a vacuum chamber and achieved a distinctive brown substance.

2.2 Preparation of Electrodes

The Glassy carbon electrode has a diameter of 5.0 mm. Aluminium nano-powder was used to polish the electrode and water was used to rinse the electrode. For every experiment, a fresh dispersion of the sample (GO) was created by dispersing 1.0 mg of each sample in 1.0 mL of Milli-Q water using sonication. A solution of 10 μL was applied onto the GC disk electrode, which had been pre-cleaned, and then dried under vacuum at room temperature. The electrochemical measurements were conducted using both unmodified GC and GC that had been modified with GO.

2.3 Instrumental

Ultrasonic Waves were applied during the exfoliation process in milli-Q water to promote the separation of graphene layers. Glassy Carbon Electrode was used for the deposition of graphene oxide. In the present work, the powder x-ray diffraction technique was carried out using a RigakuMiniFlex 600 instrument. Solid powder samples were analyzed by monochromatic X-ray from Cu Kα radiation and short wavelength, λ = 1.5418 Å. The scanning rate and 2θ range of the operating system were typically 0.02^0 per second and 5^0 to 80^0. Ultraviolet and visible spectrophotometry

(UV-Vis) was used to take the absorption spectral within the region (190 to 800 nm) at room temperature by using a Specord-200 (Analytik Jena, Germany) spectrophotometer. Raman spectra were acquired employing a confocal micro-Raman spectrometer (LabRAM HR Vis., Horiba JobinYvon S.A.S). The spectrometer features an 800 mm focal length Czerny-Turner-type spectrograph equipped with reflective optics and spectral resolution of 0.1 cm^{-1}/pixel when utilizing a wavelength of 488 nm facilitated by an 1800 gr/mm grating. FTIR spectrum of the material was attained using an Infrared Fourier Vacuum prism spectroscope, specifically the Vertex 70v model manufactured by Bruker Optik GmbH in Germany. The analysis utilized an Attenuated Total Reflectance (ATR) crystal made of Zn-Se, specifications of the Vertex 70v instrument include a KBr beam splitter, a DLaTGS detector, a Mid-Infrared (MIR) source, a Rock-Solid measuring device system, a spectral resolution surpassing 0.4 cm^{-1}, and a contamination-free vacuum environment maintained at less than 0.2 mbar. Cyclic voltammetry experiments were conducted using a hybrid setup comprising a potentiostat/galvanostat coupled with an EC-AFM system (Agilent AFM 5500 series with PicoScan software, USA). Glassy carbon modified by graphene oxide and reduced graphene oxide served as the working electrode, connected through an *L*-shaped pogo electrode. The counter electrode (CE), crafted from platinum-iridium, maximally covered the inner rim of the liquid cell. The reference electrode (RE) was positioned within the electrolyte without direct contact with the working electrode. The electrochemical cyclic voltammetry experiments involved applying a potential range of -1.0 V to $+1.0$ V using different scan rates (mVs^{-1}). The redox couple $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in a 1 mM ferricyanide solution dissolved in 0.1 M H_2SO_4 served as the probe on the working electrode.

3. RESULT AND DISCUSSION

X-ray Diffraction (XRD) analysis of graphene oxide thin films revealed a distinct peak at a 2θ value of 10.05°, signifying a characteristic inter-layer spacing of 0.83 nm. The prominent peak observed in the XRD pattern at 10.05° indicates the presence of well-defined crystallographic planes within the graphene oxide thin films (Fig. 1). This peak corresponds to the (001) plane reflection, suggesting a preferential alignment of the graphene layers [13, 14]. The calculated inter-layer spacing of 0.83 nm is consistent with the typical range reported for graphene oxide, indicating a significant expansion compared to pristine graphene. The expansion in inter-layer distance can be linked to the insertion of oxygen-containing groups, such as hydroxyl, epoxy, and carboxyl groups causing repulsion between adjacent layers and resulting in the expansion of the inter-layer spacing. The expansion of inter-layer spacing implies a less compact stacking arrangement, influencing the overall electronic and mechanical properties of the thin films.

The UV-Vis spectroscopy analysis of the Graphene Oxide (GO) thin films revealed distinctive absorption peaks at approximately and shoulder at 239 nm and 301 nm. The absorption peak at 239 nm corresponds to
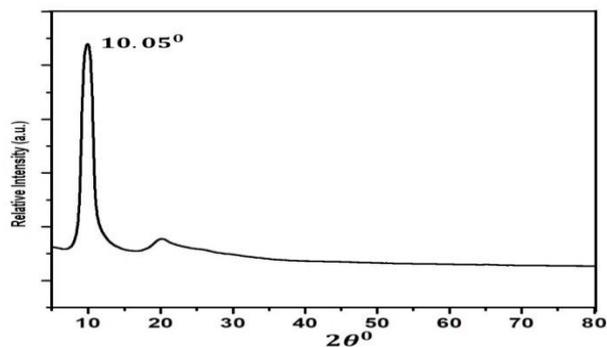
Fig. 1 – X-ray pattern of graphene oxide

the π-π^* transition of the atomic C-C bond, indicating the presence of conjugated pi-electron systems in the graphene oxide structure [15], while the peak at 301 nm is attributed to the n-π^* transition of aromatic C-C bonds (Fig. 2). This transition is characteristic of sp^2 hybridized carbon atoms, confirming the formation of graphene oxide with a high degree of oxidation. It suggests the presence of oxygen-containing functional groups, such as epoxide and hydroxyl groups, within the graphene oxide structure. These spectroscopic features serve as clear indicators of the successful formation of graphene oxide in the thin film samples. The π-π^* and n-π^* transitions play a significant role in the material's behaviour and response to light, making graphene oxide a promising candidate for various optoelectronic applications.
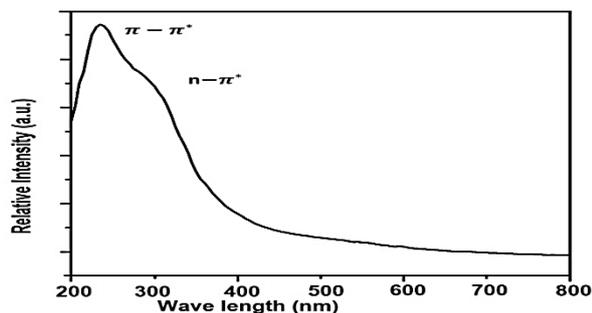
Fig. 2 – UV-Vis spectra of prepared graphene oxide

The Fourier Transform Infrared (FTIR) spectra of graphene oxide (GO) reveal several distinctive peak positions, providing crucial insights into the successful functionalization of graphene through the introduction of oxygen atoms [16]. The identified peaks include a broad band in the range of $2700 - 3500$ cm^{-1}, along with specific peaks at 1725 cm^{-1}, 1631 cm^{-1}, 1417 cm^{-1}, and 1050 cm^{-1} (Fig. 3). The broad peak observed in the region of $2700 - 3500$ cm^{-1} is indicative of the presence of O-H stretching vibrations, suggesting the incorporation of hydroxyl and carboxyl groups such as hydroxyl (-OH) and carboxyl (-COOH) moieties in the graphene oxide structure. The peak at 1725 cm^{-1} corresponds to the C=O stretching vibration, the peak at 1631 cm^{-1} is associated with C=C stretching vibrations, indicating the presence of residual sp^2 carbon domains in the graphene oxide structure. The preservation of sp^2 carbon domains suggests that the oxidation process did not lead to complete graphitic carbon destruction, and the material retains some graphene-like characteristics. The peak at

1417 cm^{-1} can be attributed to the C-O stretching vibration, indicating the presence of epoxy (C-O-C) and alkoxy (C-O) groups, 1050 cm^{-1} corresponds to the C-O stretching vibration of epoxy groups. The appearance of this peak further supports the successful incorporation of oxygen-containing functional groups.

The Raman spectra of graphene oxide (GO) exhibit distinct peaks that provide valuable information about its structural properties [17]. The prominent peaks observed in the spectra are the D-peak at 1570 cm^{-1}, the G-peak at 1356 cm^{-1}, the 2D peak at 2690 cm^{-1}, and the defect-activated peak (D+G) at 2920 cm^{-1}. The D-peak in the Raman spectrum of GO is indicative of structural defects and disorder in the graphene lattice. This peak arises due to the presence of sp^3 carbon bonds, which may result from the introduction of oxygen-containing functional groups during the oxidation process. The G-peak represents the in-plane vibration of sp^2 carbon atoms in the graphene lattice.
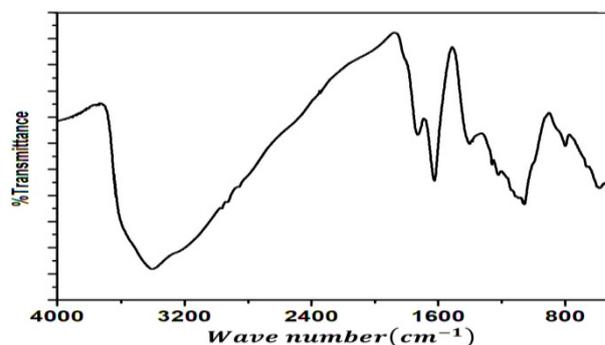
Fig. 3 – FTIR spectrum of graphene oxide

A shift in the G-peak position or changes in its intensity can provide insights into the extent of oxidation and the presence of functional groups on the graphene sheets. The 2D peak is associated with the second-order overtone of the D and G peaks and is a signature of the graphitic nature of the material. The defect-activated peak (D+G) is a combined peak that arises from the interaction between the D and G modes (Fig. 4).
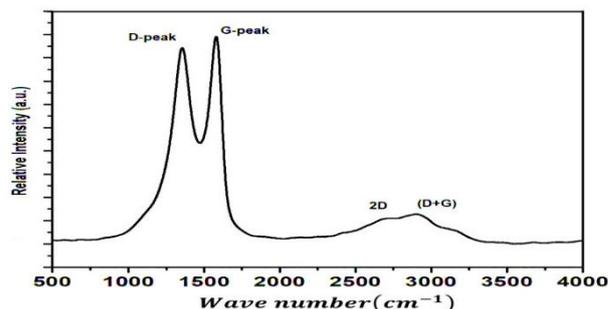
Fig. 4 – Raman spectrum of graphene oxide

Overall, the Raman Spectra of graphene oxide reveals valuable information about its structural characteristics, degree of disorder, and the impact of oxidation [18].

SEM images (Fig. 5) illustrated the successful formation of ultrathin and homogeneous graphene films.

The enhanced Hummers method, coupled with ultrasonic exfoliation, produced uniform and well-defined

structures, essential for assessing stability and suitability for diverse applications [19]. The uniform and well-defined structures observed in SEM images contribute to the understanding of film stability. Morphological characteristics are essential for applications like sensors, where surface interactions play a crucial role [20].
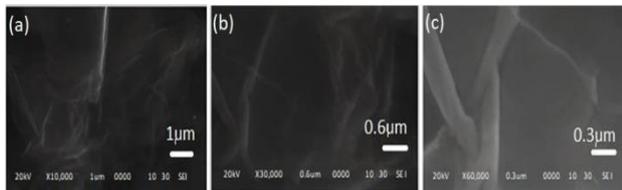
Fig. 5 – SEM morphology of synthesized graphene oxide (a) 1 μm, (b) 0.6 μm, (c) 0.3 μm

Glassy carbon electrodes modified with GO were investigated using the $K_3[Fe(CN)_6]$ redox couple system. Results indicated that the electron transfer process controlled the electrochemical behavior, emphasizing the potential of GO thin films in energy storage applications. This electrochemical analysis provides valuable data for designing and optimizing graphene-based electrodes with enhanced performance for various electrochemical devices and stability for batteries or supercapacitors. Further research can focus on optimizing these properties for specific applications and scaling up production processes.

Fig. 6 – Cyclic voltammograms of graphene oxide-modified glassy carbon in different scan rates using 1 mM $K_3[Fe(CN)_6]$ in 0.1 M H_2SO_4

4. CONCLUSION

The analysis of graphene oxide (GO) thin films through X-ray Diffraction (XRD), UV-Vis spectroscopy, Fourier Transform Infrared (FTIR), Raman spectroscopy, scanning electron microscopy (SEM), and electrochemical studies have provided valuable insights into the structural, optical, morphological, and electrochemical characteristics of the material. The XRD analysis revealed a distinct peak at $2\theta = 10.05°$, indicative of a characteristic inter-layer spacing of 0.83 nm, suggesting a preferential alignment of graphene layers. UV-Vis spectroscopy confirmed the successful formation of graphene oxide with absorption peaks at 239 nm and 301 nm, corresponding to π-π^* and n-π^* transitions, providing insights into the electronic structure of the thin films. FTIR spectra further supported the functionalization of graphene with oxygen-containing groups, while Raman spectroscopy provided information on structural defects and disorder. SEM images illustrated the successful formation of ultrathin and homogeneous graphene films, crucial for applications requiring stability and specific surface interactions. The investigation of GO-modified glassy carbon electrodes in the $K_3[Fe(CN)_6]$ redox couple system highlighted the control of electrochemical behaviour by the electron transfer process, emphasizing the potential of GO thin films in electronic applications. These multi-faceted characterizations of GO thin are aimed at optimizing properties for specific applications and scaling up production processes, paving the way for the practical implementation of graphene oxide in diverse technological advancements.

5. CONFLICTS OF INTEREST

There are no conflicts to declare.

6. ACKNOWLEDGMENTS

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Синтез та характеристики оксиду оксиду графену з електронною поведінкою

A. Mondal[1,3], A.K. Kundu[1,2], H.S. Biswas[1], D.K. Maiti[4]

[1] *Department of Chemistry, Surendranath College, 24/2, Mahatma Gandhi Road, Kolkata-700009 India*
[2] *Department of Chemistry, Sripat Singh College, Jiaganj, Murshidabad, 742123 India*
[3] *Harindanga High School, Falta-743504 India*
[4] *Department of Chemistry, University of Calcutta, University College of Science, 92, A.P.C. Road, Kolkata-700009 India*

Оксид графену (GO) синтезується за допомогою вдосконаленого методу Хаммерса, підвищуючи його розчинність, дисперсність та реакційну здатність, вводячи кисневі функціональні групи. Процес передбачає окислення очищених природних графітових пластівців з подальшим сольвотермальним лікуванням. Відлущування оксиду графіту в дистильованій воді за допомогою ультразвукових хвиль призводить до утворення тонкої плівки оксиду графену. Цей метод оптимізує виробництво GO, використовуючи його унікальні властивості для різних застосувань у матеріалознавстві та нанотехнології. Структурні та фізико-хімічні характеристики матеріалів аналізували за допомогою рентгенівської порошкової дифракції (XRD), трансформації Фур'є (FTIR), скануючої електронної мікроскопії (SEM) та ультрафіолетової спектроскопії (УФ-ВІЗ). XRD Peak вказав $2\theta^0 = 10.05^0$ на міжшаровий інтервал 0,83 нм. Аналізи FTIR та Рамана виявили введення атомів кисню в графітовий шар, утворюючи різні хімічні зв'язки, такі як C-H, OH, C = O, C-O-C та COOH з графеном. Зображення SEM проілюстрували утворення ультратонких та однорідних графенових плівок. Ультрафіолетові спектри GO демонстрували чіткий пік поглинання приблизно на 239 нм, що відповідає $\pi - \pi*$ переходу атомного зв'язку C-C та при 301 нм, який відповідає переходу $n - \pi*$ ароматичних зв'язків C-C. Електрохімічна поведінка склоподібного вуглецевого електрода, модифікованого з GO, була досліджена за допомогою системи окислювально -відновної пари $K_3[Fe(CN)_6]$. Результати показали, що процес передачі електронів контролював електрохімічну поведінку.

Ключові слова: Оксид графену, Сольвотермальна, XRD, FTIR, SEM, УФ-ВІС Спектроскопія, Спектри Рамана.