A Sustainable Modified Hummers Method for Synthesizing Graphene Oxide Nanosheets

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In this study, graphite oxide (GO) nanosheets were prepared using a new modified Hummer method. This method takes less time than previous modified Hummer methods. The method requires only 6 hours to complete and still achieves a high yield of GO. Morphological and structural characteristics were investigated. GO exhibits good morphological and structural characteristics, including valuable defects (such as functional groups containing OH, COOH, and C=O) and a good graphitic structure. This modified Hummer method demonstrably mitigated waste generation and the potential for decreased time and cost requirements.

Keywords: Nanosheets; EDX mapping; Graphene oxide; Hummer method
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1. Introduction

The conversion of graphene to graphene oxide (GO) currently offers the most promising avenue for large-scale production. However, this seemingly straightforward transformation carries structural and compositional defects [1]. GO has either a multilayer or single-layer structure with the introduction of oxygen-containing functional groups (e.g. -COOH, =O, -OH) onto the sp^2 hybridized carbon lattice of graphene breaking sp^2 bonds and introducing sp^3 hybridization [2]. These oxygenated groups decorate both surfaces and edges of the GO sheets, influencing their electronic properties, interlayer spacing, and overall morphology. The defects in GO lead to high surface area, selective binding, (functionalization groups in GO enable targeted removal of specific contaminants), and hydrophilicity (oxygen groups make GO water-loving and facilitate water permeation while repelling pollutants or simple to prepare water based suspensions) [3]. The introduction of oxygenated defects in GO might unlock a plethora of exciting applications across various fields, such as water purification (filtration membranes) [2], super capacitors (electrode material) [4], biosensors [5,6], energy storage devices [7], and batteries [8]. Hummer's method is a wide chemical process that produces GO from graphite. The chemicals used in this method were $NaNO_3$ (50g), graphite (100g), H_2SO_4 (2.3 Liter), and $KMnO_4$ (300g). The reaction is carefully quenched with ice and water due to this reaction is exothermic [9]. Hummer's method produces more amount of oxygen and a high yield of GO, and its scalability makes it suitable for industrial applications. The process of exfoliation, which involves the introduction of oxygen functional groups, disrupts the graphitic order and reduces the number of layers. Exfoliation of graphite into GO can be completed by a higher concentration and amount of H_2SO_4. $KMnO_4$ is a very strong oxidizing agent (readily donating oxygen) that reacts with H_2SO_4 generating the oxidant Mn_2O_7 (Mn(II)) (Fig. 1) [10,11]

$$H_2SO_4 + 2KMnO_4 \rightarrow H_2O + K_2SO_4 + Mn_2O_7$$

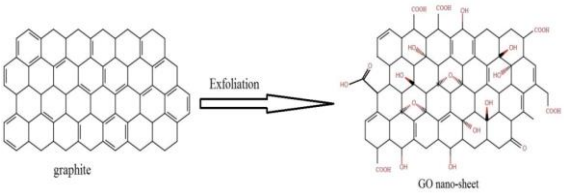


Fig. (1) Scheme of exfoliation of graphite into GO

The main role of $NaNO_3$ is for further oxidation of graphite layers and increased interlayer distance. The absence of $NaNO_3$ achieves GO with less oxidation [12]. H_2O_2 is required to remove the excessive $KMnO_4$ and to stop the reaction. The role of water was to quench the reaction after the graphite had oxidized. This study aims to modify the classic Hummers method for GO synthesis by using less amount of H_2SO_4 and other reagents reducing waste generation, lowering the synthesis cost, and significantly reducing the reaction time to 6 hours (from the typical 12-24 hours).

2. Experimental Part

Graphite native (B.D.H), $NaNO_3$ (Merck, 99.0%), $KMnO_4$ (Merck, 99.0%), H_2O_2 (B.D.H, 97.0%), HCl (B.D.H, 37%), H_2SO_4 (B.D.H, 99.0%) were supplied and used as start materials. A PerkinElmer, Lambda 25 Raman spectrophotometer, a JEIO BS-11 digital water bath, a Philips PW1730 x-ray diffraction analyzer, a HV-295 single-beam UV-Visible spectrophotometer, a JEOL JSM-6510 LV field-emission scanning electron microscope equipped by

an energy-dispersive x-ray spectrometer were used to characterize and evaluate the surface properties of the GO. The modified Hummer's method was effectively employed for the synthesis of graphene oxide (GO) nanosheets. Initially, a solution comprising 2g of graphite powder and 1g of $NaNO_3$ was mixed with 150mL of 98% H_2SO_4. This mixture was vigorously stirred for 30 minutes while being placed in an ice bath in order to maintain a temperature below 5°C. Subsequently, 8g of $KMnO_4$ was gradually added over a period of 6 hours, with continuous stirring using a magnetic stirrer. The reaction was terminated by the addition of 1 L of distilled water, followed by 20 mL of 32% H_2O_2 with thorough mixing. The resulting product was then purified through successive immersion in distilled water and a 20% HCl solution. Finally, the black and brown-colored product was air-dried overnight at room temperature to obtain GO nanosheets (Fig. 2).

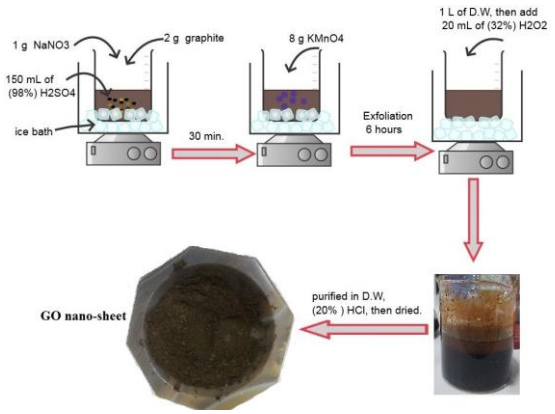


Fig. (2) Scheme of synthesis steps of GO nanosheets

3. Results and Discussion

Two sharp diffraction peaks were observed during the XRD analysis of graphene oxide (GO) at 2θ of 42.53° (100) and 12.15° (001) (Fig. 3). The (100) peak signifies the ordered stacking of GO sheets in the (100) plane, while the (001) peak indicates the presence of interlayer spacing between the GO sheets, which is typically larger than the interlayer spacing in pristine graphene [13,14]. This interlayer spacing is typically larger than that of pristine graphene due to the presence of oxygen-containing functional groups in GO.

The grain size of GO was calculated to be 10.49nm using the Scherrer's equation ($D=0.9\lambda/\beta\cos\theta$), where D is the grain size, 0.9 is the K constant, λ=1.54Å is x-ray beam wavelength, θ is the diffraction angle, and β is the full-width at half maximum (FWHM) of the diffraction peak. EDX analysis provides valuable insights into the elemental composition of a sample surface. Each element manifests a distinct peak that corresponds to its unique atomic signature (Fig. 4). Moreover, EDX mapping is a potent technique utilized to visually depict the spatial distribution and diffusion of elements within a given sample. In this study, the weight percentage (wt.%) corresponds to the GO formula (Fig. 5). The presence of oxygen in the EDX spectrum indicates the presence of functional groups on the surface of the GO nanosheets.

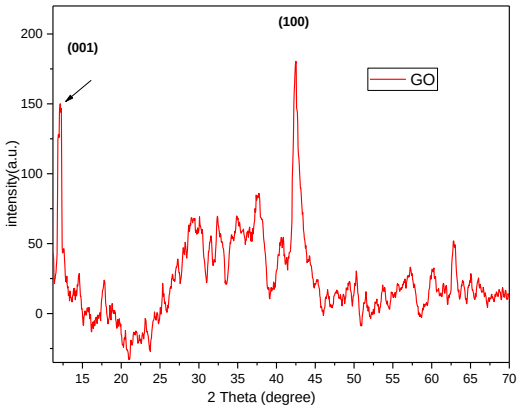


Fig. (3) XRD pattern of GO prepared in this work

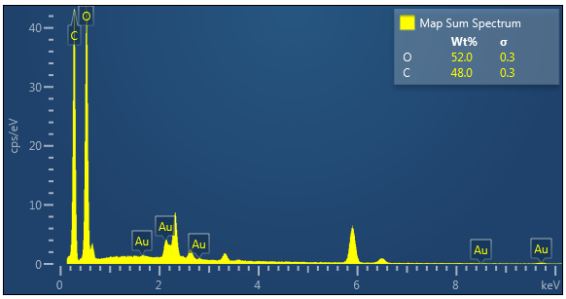


Fig. (4) EDX spectrum of GO prepared in this work

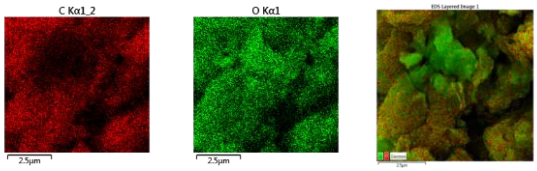


Fig. (5) EDX mapping of GO prepared in this work

Raman spectroscopy is used to analyze the chemical and physical characteristics of carbon materials. During Raman spectroscopy, the D, G, and 2D peaks are used as distinctive identifiers for carbon materials. The G band represents the crystalline structure of the sample and indicates the vibrational mode of sp^2 hybridized carbon atoms in graphene sheets. The 2D band, which is a result of the second-order Raman scattering process, is used to determine the thickness of graphene layers. The D band provides information about defects and its intensity is directly related to the extent of defects [15]. In the case of GO, changes that occur during various treatments can be monitored using the G and D bands. The G band is around 1589 cm^{-1} and the D band of GO is approximately 1355 cm^{-1} (Fig. 6a). The 2D band appears at 2685.13 cm^{-1}. The low-intensity ratio of I_G/I_D, measured at 0.957, indicates exfoliation. For a defect-free single-layer graphene (high-quality), the ratio of I_{2D}/I_G bands is expected to be 2. The measured

ratio of I_{2D}/I_G is 0.126, a value commonly used to confirm the presence of a defect in the graphene sample (such as functional groups containing OH, COOH, and C=O) and a good graphitic structure [16]. Peak deconvolution techniques are frequently utilized to extract information concerning individual peaks in intricate mixtures and separate the original signals from a convoluted signal. Weak intense modes in Raman spectroscopy often overlap with neighboring prominent modes, leading to broadening. Consequently, peak deconvolution is employed to isolate the contribution of each Raman mode from the broadened Raman peak (Fig. 6b). FE-SEM images offer insights into the surface of GO nanosheets at different magnifications (Fig. 7). The surface of GO displays a distinct texture characterized by abundant wrinkles and folds. These textures arise from the presence of oxygen-containing functional groups, such as -OH and -COO groups, which disrupt the pristine honeycomb lattice of graphene. The diverse morphology of the GO surface plays a pivotal role in determining its exceptional mechanical and electrical properties, reactivity, and surface area. TEM delves deeper into the inner of GO nanosheets, showcasing depicting uniformly thin sheets with a wrinkled appearance (Fig. 8).

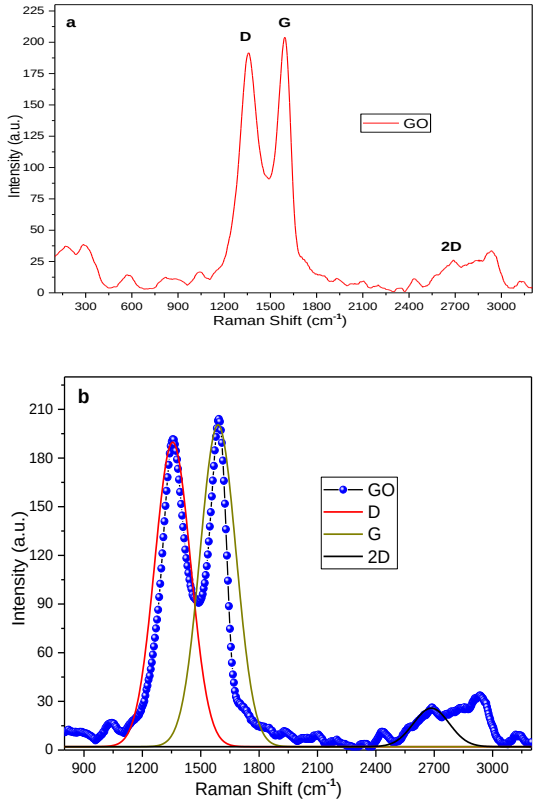


Fig. (6) Raman spectra of (a) GO and (b) deconvoluted spectra

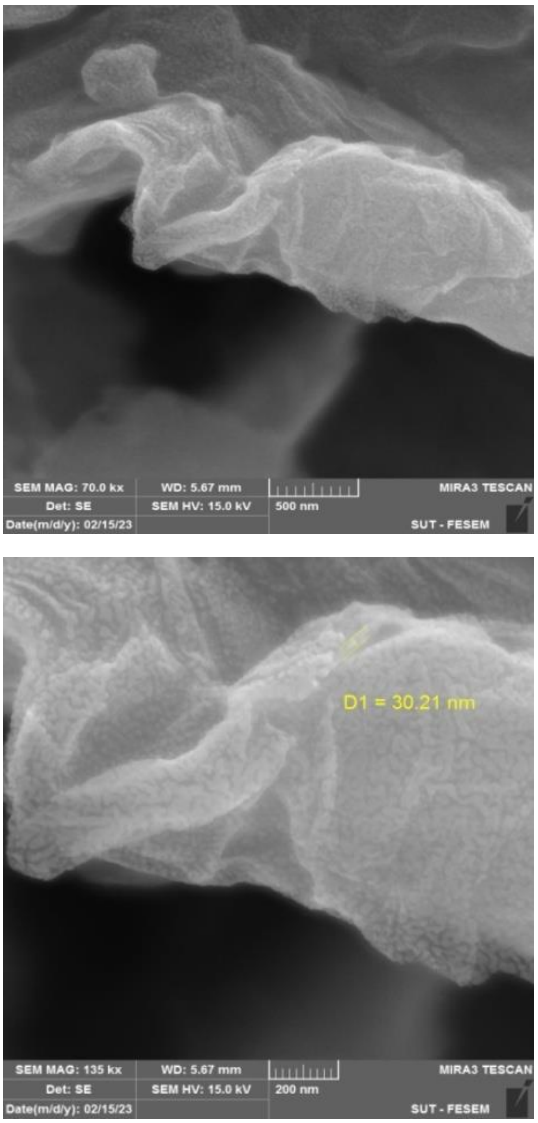
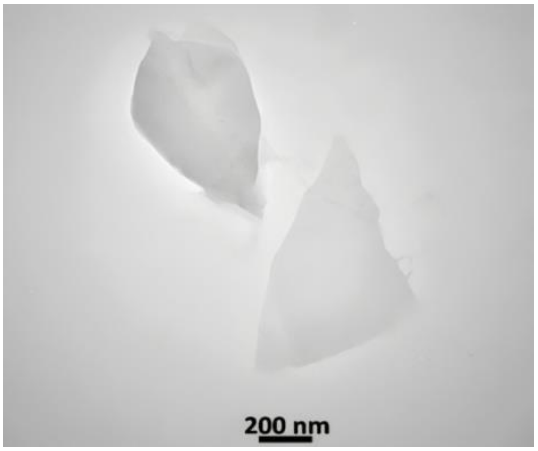


Fig. (7) FE-SEM images of the GO nanosheets prepared in this work



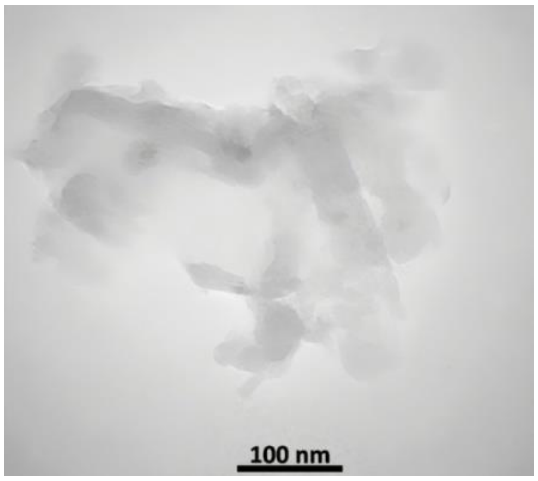


Fig. (8) TEM images of the GO nanosheets prepared in this work

4. Conclusion

This study presents a modified Hummer's method for rapid, sustainable synthesis of high-quality GO nanosheets. This method dramatically reduces synthesis time to 6 hours, compared to 12-24 hours for traditional modified Hummer's approaches, without compromising yield. Advanced characterization reveals valuable defects (functional groups) and a well-preserved graphitic structure in the obtained GO. Significantly, the method minimizes waste generation by using less H_2SO_4 and other reagents, promoting a more eco-friendly synthesis. This approach offers a promising, efficient, and sustainable route for producing high-quality GO nanosheets with great potential for diverse applications in the future.

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