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Synthesis and characterization of graphene nano structure and investigation of its application in fire retardant properties

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Abstract: *The development of advanced materials with enhanced flame-retardant properties has become a critical area of research, driven by the need for safer and more sustainable solutions. This study focuses on the synthesis, characterization, and evaluation of graphene oxide (GO) and reduced graphene oxide (rGO) as flame-retardant materials. GO and rGO were synthesized using a chemical reduction method, and their structural, morphological, and thermal properties were thoroughly characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and Raman spectroscopy. The results revealed that the reduction process significantly altered the structural and morphological properties of GO, leading to a more compact and thermally stable rGO with reduced oxygen content and fewer structural defects. The flame-retardant performance of GO and rGO was evaluated using limiting oxygen index (LOI), UL-94, and heat release rate (HRR) tests. The findings demonstrated that rGO exhibited superior flame-retardant properties compared to GO, with a higher LOI value (24.2%) and a significantly lower HRR (271.3 W/g). The improved performance of rGO is attributed to its reduced oxygen content, which minimizes fuel availability during combustion, and its compact structure, which enhances thermal stability. These results highlight the potential of rGO as an effective flame-retardant material for applications in polymers, coatings, and composites. As a result, this study provides valuable insights into the relationship between the structural properties of graphene-based materials and their flame-retardant performance.*

Keywords: Graphene oxide (GO), Reduced graphene oxide (rGO), Fire-resistant materials, Thermal stability, Limiting oxygen index (LOI)

1. Introduction

The growing need for advanced materials with superior fire-retardant capabilities has spurred extensive research into nanomaterials, particularly those based on graphene [1, 2]. Graphene, a two-dimensional carbon-based material, has garnered widespread interest due to its remarkable mechanical strength, thermal conductivity, and electrical properties. Its versatility has led to applications in diverse fields such as materials science, electronics, and energy storage [3, 4]. In recent years, the use of graphene-based materials in flame retardancy has emerged as a promising area of research. These materials offer a sustainable and eco-friendly alternative to traditional halogenated flame retardants, which are often associated with environmental and health concerns [5, 6]. Graphene oxide (GO) and reduced graphene oxide (rGO), in particular, have shown significant potential in improving the fire resistance of polymer composites, owing to their unique structural properties and high thermal stability [1, 7].

The flame-retardant capabilities of graphene-based materials stem from their ability to act as effective barriers, limiting the diffusion of oxygen and volatile decomposition products during combustion. This barrier effect reduces the heat release rate and delays ignition, thereby enhancing fire safety [2]. Furthermore, during combustion, these materials can form a protective char layer that shields the underlying polymer from heat and flames, further improving their performance [8]. However, the effectiveness of graphene-based flame retardants is highly dependent on factors such as the synthesis process, the extent of reduction (in the case of rGO), and their uniform dispersion within the polymer matrix. As a result, a detailed understanding of the structural properties and interaction mechanisms of these materials is crucial for optimizing their flame-retardant performance.

Hence, Graphene-based materials, particularly GO and rGO, have gained attention as environmentally friendly alternatives to traditional halogenated flame retardants. Their high thermal stability and unique structural properties make them highly effective in improving the fire resistance of polymer composites [5, 7]. The flame-retardant performance of these materials is largely attributed to their excellent barrier properties, which inhibit the diffusion of oxygen and volatile decomposition products during combustion. This, in turn, reduces the heat release rate and delays ignition [1]. Additionally, graphene-based materials can form a protective char layer during combustion, further enhancing their fire-retardant capabilities [2]. However, the effectiveness of these materials depends on factors such as their synthesis methods, degree of reduction, and dispersion within polymer matrices. Therefore, a comprehensive understanding of their structural characteristics and interaction mechanisms is crucial for optimizing their performance.

This study focuses on the synthesis and characterization of graphene nanostructures, specifically GO and rGO, and their application in flame retardancy. The synthesis process plays a critical role in determining the structural integrity and functional properties of graphene-based materials. Advanced structural and physicochemical characterization techniques offer comprehensive insights into the crystallinity, surface functionalization, morphology, and defect density of the synthesized materials. These properties play a critical role in determining their flame-retardant performance [8, 9]. To assess the fire-retardant properties of GO and rGO, several tests were conducted, including limiting oxygen index (LOI), UL-94, and heat release rate (HRR) measurements. The LOI test determines the minimum oxygen concentration required to sustain combustion, while the UL-94 test evaluates the material's resistance to dripping and flame propagation [6, 10]. HRR analysis offers critical insights into the heat release characteristics, which are essential for understanding the material's combustion behavior [11].

The findings of this research contribute to the expanding body of knowledge on graphene-based flame retardants and provide valuable insights into their practical applications in enhancing the fire safety of polymeric materials. As the demand for sustainable and high-performance flame retardants continues to grow, graphene and its derivatives represent a promising avenue for future advancements in fire-resistant coatings and composite materials.

2. Experimental Section

2-1. Synthesis of Graphene Oxide (GO) via Modified Hummers Method

Graphene oxide (GO) was synthesized using the modified Hummers method, which involves the oxidation of graphite in the presence of strong oxidizing agents. Initially, 2 g of natural graphite powder was added to a mixture of concentrated sulfuric acid (H_2SO_4, 98%) and sodium nitrate ($NaNO_3$) in an ice bath under continuous stirring. Potassium permanganate ($KMnO_4$) was then gradually added to the mixture while maintaining the temperature below 20°C to prevent overheating. The reaction was allowed to proceed for 2 hours under vigorous stirring. Afterward, the mixture was diluted with deionized water, and hydrogen peroxide (H_2O_2, 30%) was added to terminate the reaction, resulting in a bright yellow suspension. The suspension was then washed repeatedly with deionized water and hydrochloric acid (HCl, 5%) to remove residual ions and by-products. Finally, the GO was collected by centrifugation, dried at 60°C, and stored for further use.

2-2. Synthesis of Reduced Graphene Oxide (rGO) via Chemical Reduction

Reduced graphene oxide (rGO) was synthesized through a chemical reduction process using hydrazine hydrate as the reducing agent. In a typical procedure, 100 mg of GO was dispersed in 100 mL of deionized water and sonicated for 1 hour to obtain a homogeneous suspension. Hydrazine hydrate (1 mL) was then added to the GO suspension, and the mixture was heated to 95°C under continuous stirring for 24 hours. During this process, the color of the suspension changed from brown to black, indicating the reduction of GO to rGO. The reduced product was washed several times with deionized water and ethanol to remove excess hydrazine hydrate and other impurities. The resulting rGO was collected by filtration, dried at 60°C, and stored for further characterization and application.

2-3. Production of Fireproof Fabric

To produce fireproof fabric, GO and rGO were incorporated into a polymer matrix to enhance its flame-retardant properties. Initially, GO and rGO were dispersed in acetone using an ultrasonic bath to ensure uniform dispersion. An epoxy prepolymer glue was then added to the suspension, and the mixture was stirred for 1 hour to achieve a homogeneous coating solution. The solution was applied to a piece of glass fabric using a dip-coating method, ensuring even coverage. The coated fabric was heated in an oven at 80°C for 2 hours to remove the solvent and cure the epoxy resin. After curing, the fabric was cut into smaller pieces and subjected to compression molding to enhance adhesion between the coating and the fabric. The final product was dried at room temperature for 24 hours, resulting in a fireproof fabric ready for flame-retardancy testing.

3. Results and discussion

3.1. Characterization tests

Figure 1 demonstrates the X-ray diffraction (XRD) patterns of GO and rGO. XRD analysis is one of the most highly-used characterization tests, which is typically adopted to examine crystallographic structure of the prepared GO and rGO. Moreover, it can provide information on their interplanar spacing. According to XRD pattern of GO represented by Figure 1, a well-defined sharp diffraction peak can be found at 2θ of 10.56°. The aforementioned peak is attributed to crystal plane of (001), which is the characteristic of graphene oxide [3, 4]. Reduction of GO has resulted in the change of its XRD pattern. Based on Figure 1 exhibiting the XRD pattern of reduced graphene oxide, a pronounced broad peak can be seen at 2θ of approximately 24.5°, which is ascribed to crystal plane of (002) and is an indication of rGO. Another diffraction peak can be detected at roughly 43°, which is imputed to lattice plane of (102) [8].

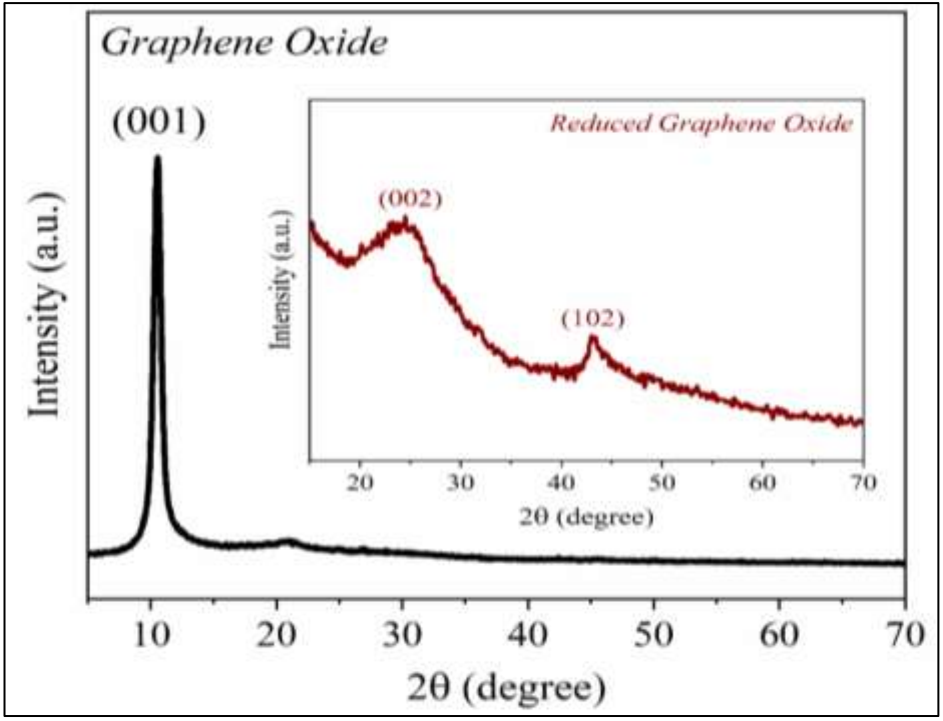

Figure 1. XRD patterns of GO and rGO in the 2θ range from 5 to 70 degrees.

In order to calculate interplanar spacing of GO and rGO, the following equation was used, known as Bragg equation [12]:

$$2d_{hkl}sin\theta = n\lambda \qquad (1)$$

Where d_{hkl} denotes the interplanar spacing, θ indicates the diffraction angle, n is relevant to the order of diffraction, and λ signifies the X-ray wavelength equals to 1.541 Å. By means of the Bragg equation, interplanar spacing values of 0.79 and 0.37 nm are respectively obtained for GO and rGO, implying that reduction of graphene oxide gave rise to a decrement in its interplanar spacing.

Fourier-transform infrared spectroscopy (FTIR) was another characterization test utilized to structurally investigate the fabricated GO and rGO. FTIR is useful owing of its capability to detect the functional groups exist within the prepared samples.

In accordance with Figure 2 showing the FTIR spectrum of graphene oxide, the absorption bands related to oxygen-containing groups, including hydroxyl, carbonyl, and carboxyl are distinguishable. Accordingly, a broad peak is observed at the wavenumber of 3363 cm^{-1}, which corresponds to stretching vibration of hydroxyl (O-H) group [5]. In addition, the absorption bands found at 1374 and 1224 cm^{-1} are assigned to hydroxyl group [5]. The peaks seen at 1729 and 1623 cm^{-1} are respectively attributed to stretching vibrations of C=O and C=C groups [7]. The peak located at 1054 cm^{-1} is ascribed to absorption band of C-O [9]. The peak at 590 cm^{-1} is relevant to the out-of-plane bending vibration of C-H in the benzene ring [9]. The absorption band found at 2279 cm^{-1} is pertinent to physisorbed carbon dioxide (CO_2) molecules present in air during measurements [13]. As evidenced by FTIR spectrum of rGO (Figure 2), reduction of GO has led to disappearance of some absorption bands related to oxygen-containing groups from the spectrum of graphene oxide. Accordingly, the peak relevant to O-H group at 3430 cm^{-1}, the peak showing C=O at 1718 cm^{-1}, the peak pertinent to C=C at 1571 cm^{-1} and the peak demonstrating C-O at 1149 cm^{-1} are detectable in the FTIR spectrum of rGO.

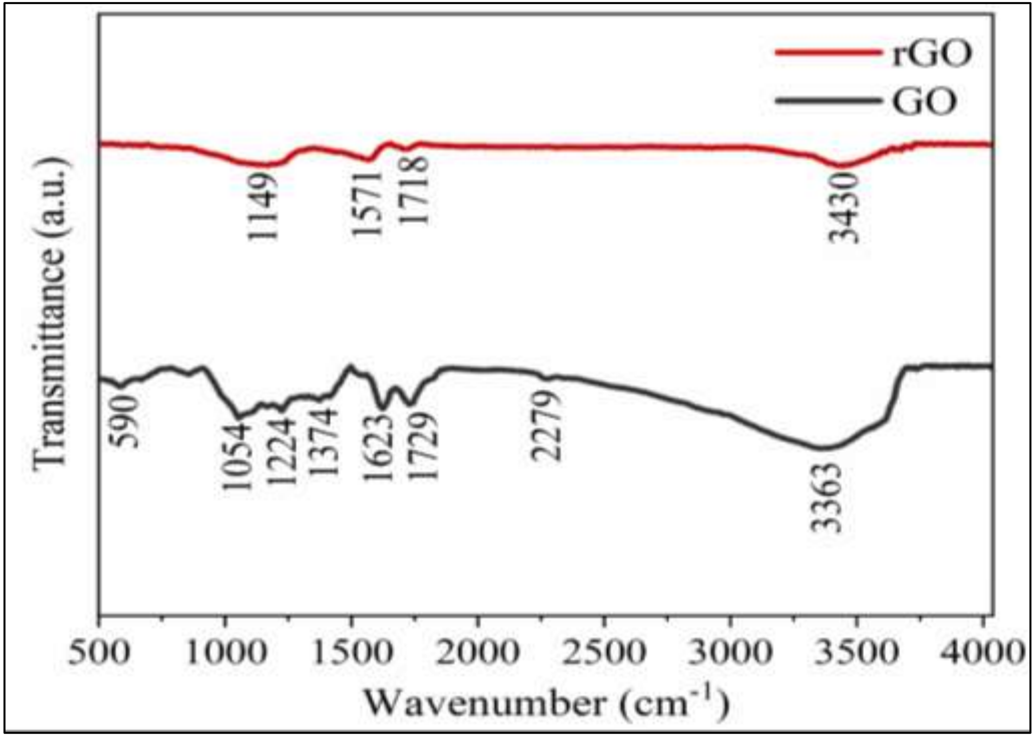

Figure 2. FTIR spectra of GO and rGO recorded from 500 to roughly 4000 cm^{-1}.

Figures 3a-d illustrate field emission scanning electron microscopy (FESEM) images taken from synthesized GO and rGO. FESEM is a powerful and advantageous characterization means for acquiring information on the morphology of GO and rGO. According to Figures 3a,b, rigid, ultrathin layered sheets with full of wrinkles and folded regions appear in the FESEM images of graphene oxide. According to literature, such those regions can be arisen from the presence of oxygen-containing functional groups, like the ones detected in the FTIR spectroscopy, on the surface of GO. The covalently attachment of those functional groups with carbon atoms caused disruption of extended sp^2 conjugated system of the graphene sheets in the honeycomb-lattice shape [6, 7].

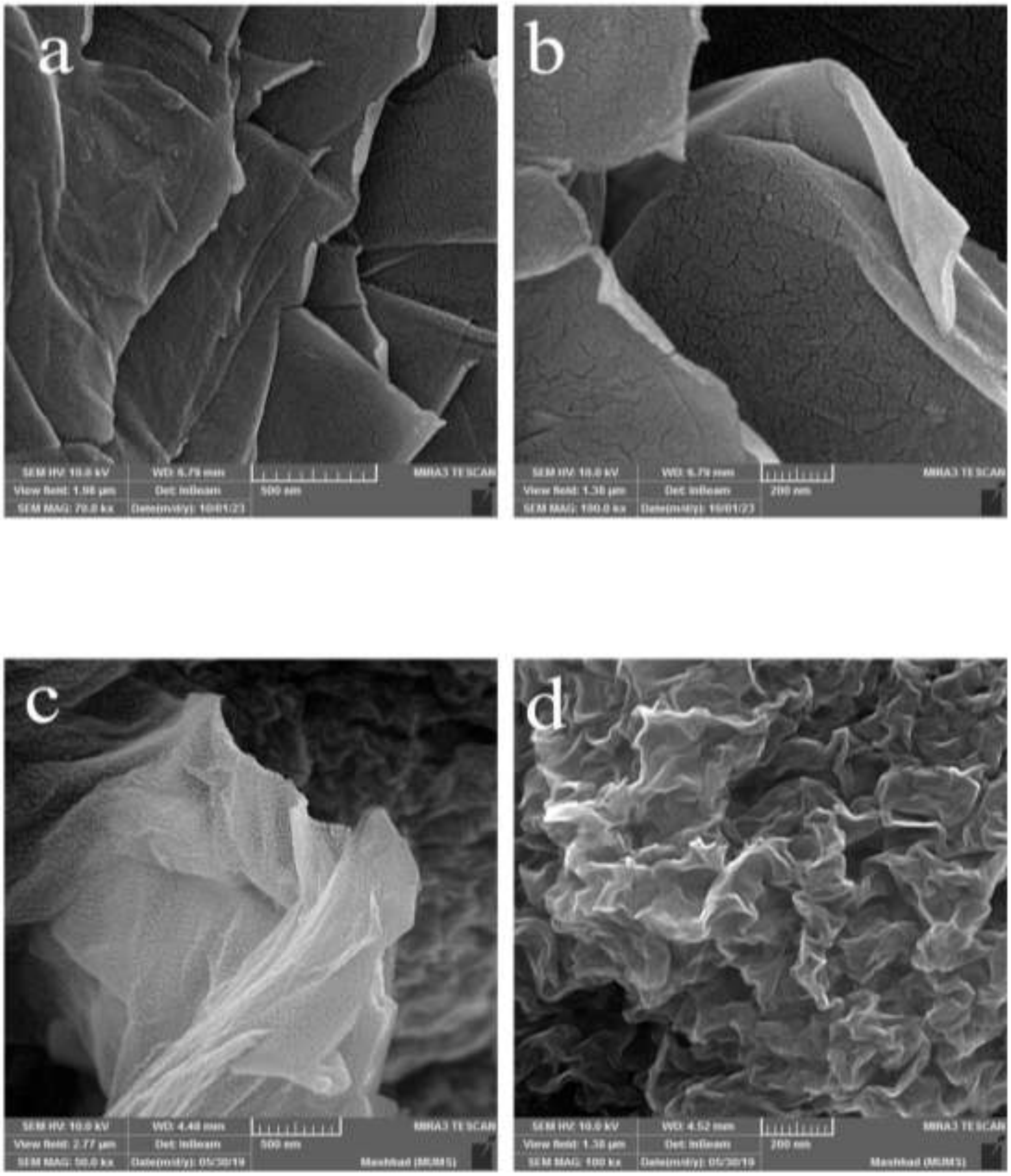

Figure 3. FESEM images of (a,b) GO, and (c,d) rGO obtained at different magnifications.

Reduction of graphene oxide sheets has brought about the change of their morphology. As the FESEM image of reduced graphene oxide demonstrates (Figure 3d), a more compact structure is visible for rGO, compared to one observed for GO. The reason behind it is that the reduction process removed the majority of oxygenated functional groups, which subsequently resulted in coming close of the layers to each other by π-π interaction [6]. Moreover, compared to GO, the sheets for rGO are smoother and reveal minimum folding (Figure 3c).

The morphology of synthesized GO and rGO was further investigated by means of transmission electron microscopy (TEM).

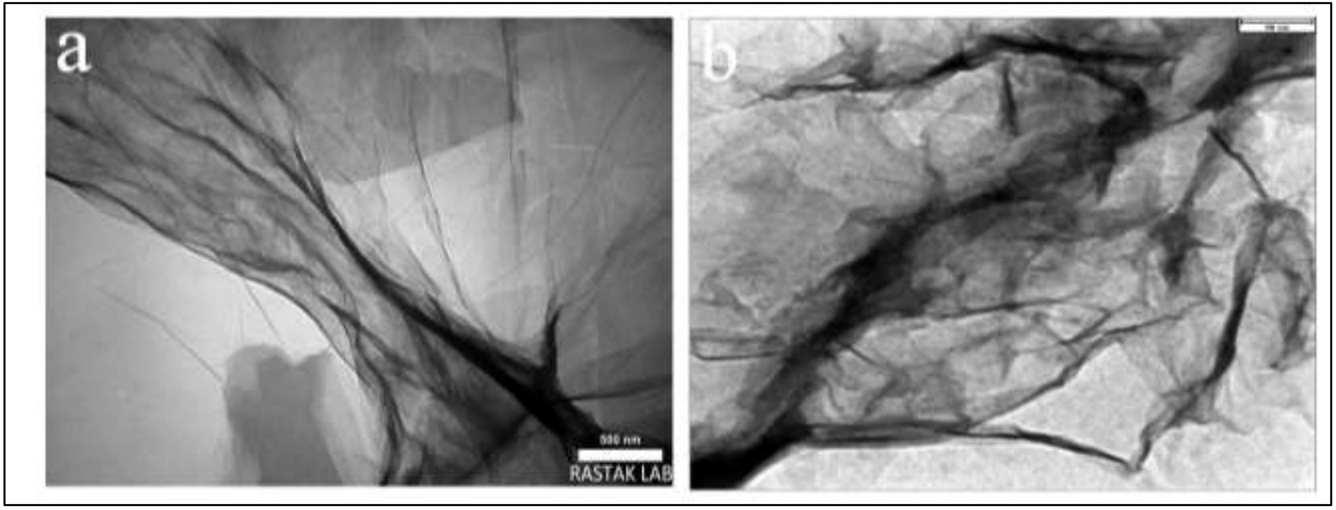

Figure 4. TEM images of (a) GO, and (b) rGO.

In accordance with Figure 4a, the semi-transparent, wrinkled and folded sheets are detectable for GO. On the other hand, the transparency of the sheets for rGO is less than the one seen for GO (Figure 4b). It seems that the layers to be closely stuck together, as also observed in the FESEM image of rGO (Figure 3d).

Energy dispersive X-ray spectroscopy (EDXS) was used to probe the elemental composition of the synthesized GO and rGO. Figure 5a exhibits the EDXS pattern of graphene oxide. Accordingly, the characteristic peaks of carbon (C) and oxygen (O) elements are respectively found at approximately 0.25 and 0.5 keV. The peak related to oxygen element is associated with the oxygenated functional groups. Like GO, the peaks demonstrating C and O elements are evident for rGO (Figure 5b). However, the intensity of the peak of oxygen element in EDXS of rGO is less than the one for GO, which can be attributed to removal of oxygen-containing functional groups.

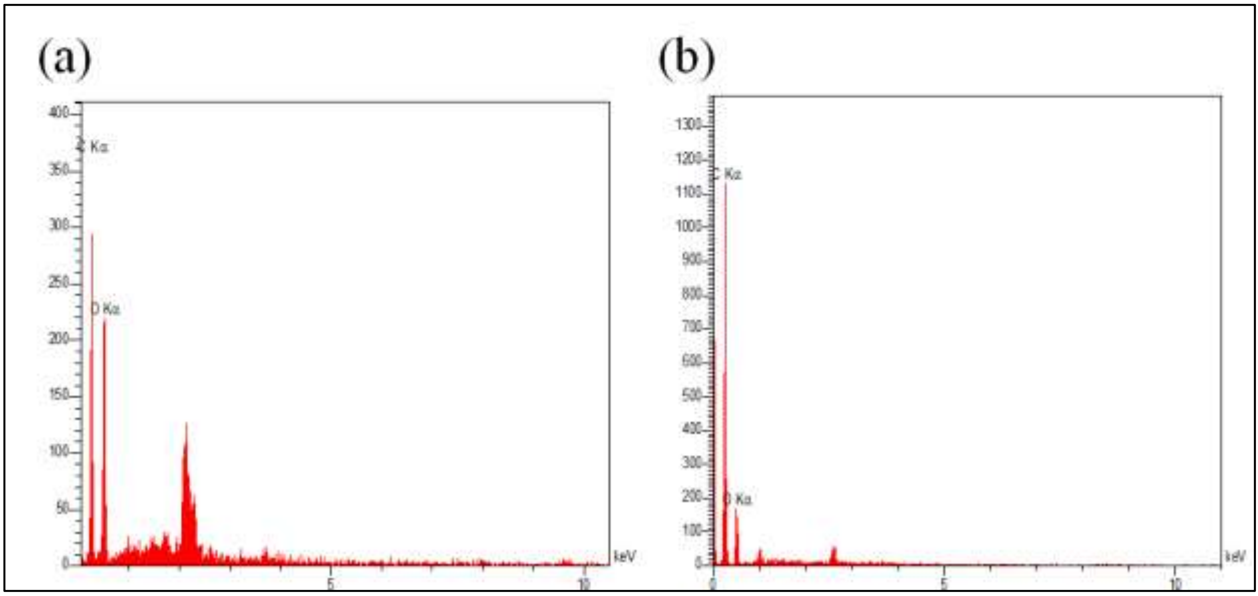

Figure 5. EDXS patterns of (a) GO and (b) rGO.

Raman spectroscopy was employed to scrutinize structural defects for instance ordered, disordered, and impurities inside GO and rGO. The Raman spectrum of GO shows two indicative peaks (Figure 6), including D-band and G-band. The former is located at about 1362 cm^{-1}, which shows sp^3 defects in the graphitic structure. In other words, with the aid of D-band, valuable information on surface defects and also structural imperfections originating from attached oxygenated functional groups with carbon atoms can be attained. D band possesses A_{1g} symmetry and is ascribed to breathing mode of k point phonons.

The latter peak is situated at approximately 1588 cm^{-1}, which signifies in-plane vibration of sp^2 carbon atoms and is imputed to vibrational mode of E_{2g}. G band accounts a fingerprint for revealing the symmetry and crystallizability of carbon. In addition to aforementioned prominent peaks, another peak can be detected at about 2825 cm^{-1}, which is pertinent to 2D band [3, 6, 10, 11].

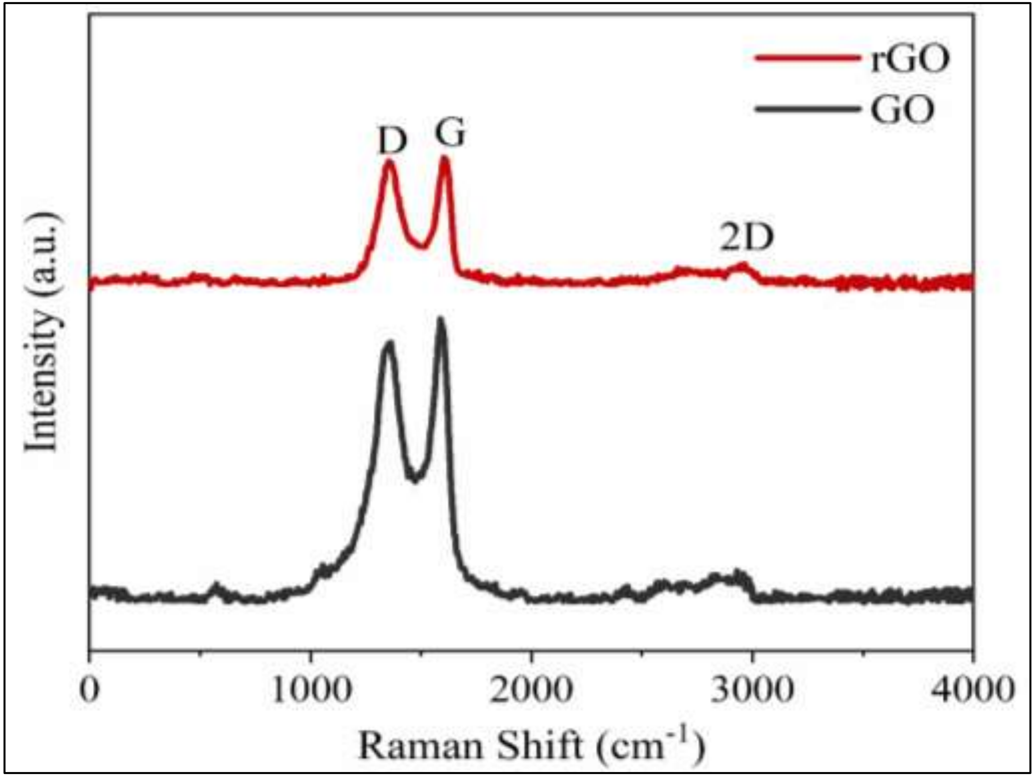

Figure 6. Raman spectra of GO and rGO recorded from 0 to 4000 cm^{-1}.

Like GO, the characteristic peaks of D-band and G-band can be found for rGO (Figure 6), which are respectively centered at about 1356 and 1603 cm^{-1}. Besides, the peak related to 2D band is detectable at approximately 2949 cm^{-1}. The ratio between intensity of D-band to G-band (I_D/I_G) is a good parameter for measuring structural disorder in GO and rGO [1]. Accordingly, I_D/I_G values of 0.86 and 0.84 respectively calculated for GO and rGO, meaning that reduction of graphene oxide has resulted in a reduction in its structural disorder associated with oxygen-containing groups. These results are in a well agreement with FESEM images. In this regard, sheets with minimum folding and high smoothness were observed for rGO, which was attributed to efficient role of reduction process in removal of oxygenated functional groups.

3.2. Combustion properties

The combustion properties of synthesized GO and rGO were examined as follows. Limiting oxygen index (LOI) and UL-94 tests are typically adopted for evaluation of the flammability of materials. The results obtained from the measurements are listed in Table 1.

Table 1. Flame-retardancy factors obtained from the LOI and UL-94 measurements.

Sample	LOI (%)	Dripping	UL-94
GO	21.3	No	Not rating
rGO	24.2	No	Not rating

Based on Table 1, the synthesized GO demonstrates LOI value of 21.3%. However, reduction of graphene oxide has resulted in a betterment in LOI. Accordingly, the reduced graphene oxide reaches LOI value of 24.2%. The aforementioned results corroborated that the flame retardancy of GO can be efficiently enhanced through reduction process. The better performance of rGO with respect to GO can be attributed to its negligible amounts of oxygenated functional groups, which could play an important role in combustion process. No dripping was occurred for both GO and rGO after ignition. None of the prepared GO and rGO had a classification in the UL-94 measurements. It may be due to their insufficient amounts, which were not able to protect them from decomposition [2].

In addition to LOI and UL-94 tests, heat release rate (HRR) measurements were conducted to probe the combustion characteristics of GO and rGO. Figure 7 illustrates the HRR curves of GO and rGO. The main heat release peak found at the temperature of 511 °C was considered for obtaining the HRR values.

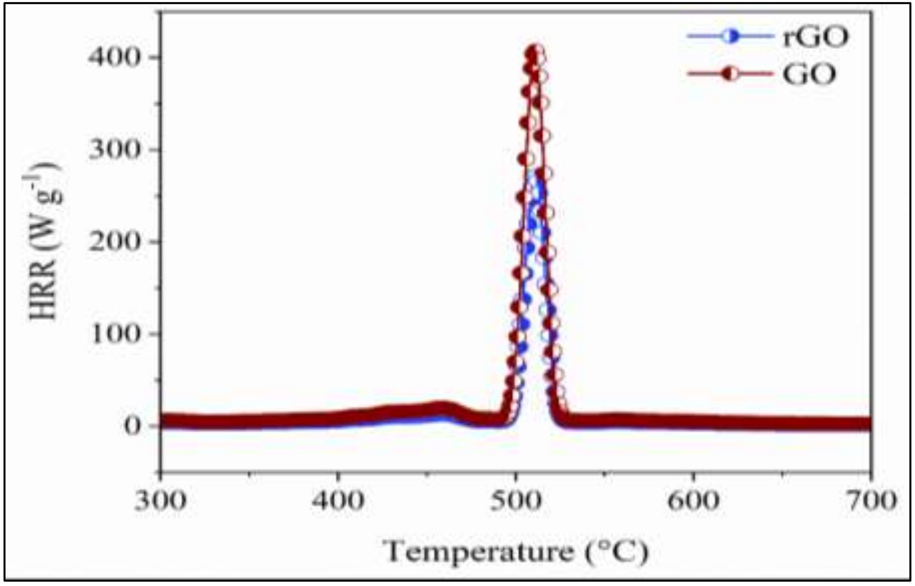

Figure 7. HRR curves for the flame retardants of GO and rGO.

In this regard, the HRR value delivered by graphene oxide sheets was about 407 W/g. However, reduction of GO has gave rise to a considerable reduction in HRR. Accordingly, the HRR value attained for reduced graphene oxide was 271.3 W/g, indicating its lower fuel consumption rate in comparison with GO. As a consequence and by taking the results obtained from LOI, UL-94, and HRR measurements into account, rGO is a better flame-retardant material compared to GO (Figure 8) [2].

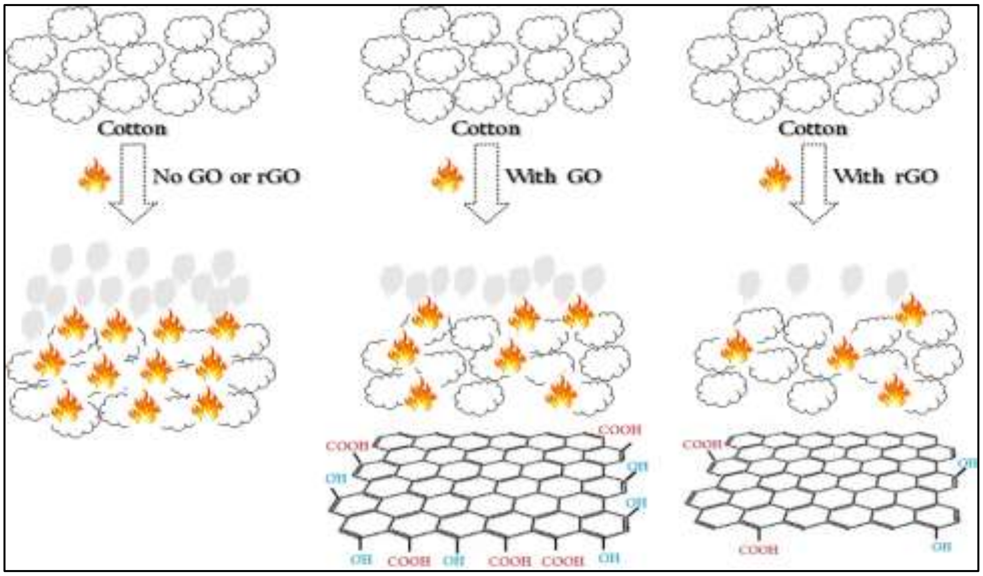

Figure 8. A schematic for better flame-retardancy of rGO with respect to GO.

4. Conclusions

In the present study, GO and rGO were synthesized to examine their flame-retardancy properties. Various characterization tests were employed to structurally scrutinize the prepared samples, one of which was XRD analysis, which demonstrated the characteristic diffraction peaks related to GO and rGO. In evidenced by this test, reduction of graphene oxide resulted in a decrement in its interplanar spacing. FTIR spectrum and also EDXS pattern of rGO exhibited less oxygen-containing functional groups compared to GO.

FESEM images of both GO and rGO showed different morphology. Compared to GO, rGO sheets revealed more smoothness and less wrinkles and folded regions. Moreover, a more compact morphology was shown by rGO, which also verified by TEM microscopy. Better morphology of rGO and its less structural defects, as corroborated by Raman spectroscopy, were arisen from the removal of oxygenated functional groups, which subsequently resulted in its better flame-retardancy properties. Accordingly, rGO reached more LOI and less HRR values in comparison with GO, which could make it an ideal flame-retardant material for reducing the fire hazards.

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