

Effects of Peroxide and Persulfate Oxidizing Agents on the Texture of Graphene Oxide

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ABSTRACT

In this research, the effects of peroxide and persulfate oxidizing agents such as hydrogen peroxide (H_2O_2), potassium persulfate ($K_2S_2O_8$), ammonium persulfate ($(NH_4)_2S_2O_8$) and meta-chloroperoxybenzoic acid (mCPBA) on the texture of graphene oxide (GO) are considered by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and elemental mapping *via* energy dispersive X-ray spectroscopy (EDX). According to FT-IR results, GO and GO treated by oxidizing agents contain a layer of carbon atoms that decorated by oxygen-containing groups. Based on XRD data, a phase transition from more crystalline graphene oxide to more amorphous state is observed where GO is treated by oxidizing agents. It seems that oxidizing agents can create and enlarge the hole defects in graphene oxide. Significant changes in the morphology of the GO after treatment by oxidizing agents are observed *via* the FESEM micrographs. The value of the C/O atomic ratio for the GO treated by mCPBA is 1.23. This compound show the higher degree of oxidation than GO and GO treated by other oxidants. The corresponding value for the prepared GO is 1.94.

Keywords: Graphene oxide, Oxidation, Oxidizing agent, Peroxide, Persulfate

INTRODUCTION

Oxidation reactions have an important role in organic chemistry, so that significant progress has been achieved within this area in recent decades [1]. There are several different definitions for oxidation, i.e. loss of electrons, increase in oxidation state, loss of hydrogen, or gain of oxygen [2]. An oxidizing agent is a substance that is capable of causing oxidation [3]. Oxidizing agents are important in many chemical processes including combustion, metabolism and corrosion [3]. They are also commonly used in industrial processes such as in the production of fuels, purification of water, bleaching of fabrics, vulcanization of rubber and storage of energy in batteries [3, 4].



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Hydrogen peroxide (H_2O_2) is an oxidizing agent which is commonly found in cosmetics, bleaching agents, toothpaste and detergents [5]. It is medically used as an antiseptic and antibacterial agent for disinfection and wound irrigation [5]. Also, it has been used in dentistry as a mouth wash to reduce plaque and to improve recovery after oral surgery [5, 6]. This compound reacts on contact with oxidizable organic materials, metals and in alkaline solutions by producing free hydroxyl radicals, which react with lipids, proteins and DNA [5]. Aromatic aldehydes can be transformed to phenols by oxidizing with H_2O_2 in acidic methanol [7]. Alkenes and α,β -unsaturated acids have been epoxidized with H_2O_2 in a catalytic system [7]. Vicinal diols have been prepared from alkenes by oxidizing with H_2O_2 in the presence of catalysts [7]. H_2O_2 has also been used to oxidize alcohols and amines by employing catalysts [7].

Peroxy-carboxylic acids such as meta-chloroperoxybenzoic acid (mCPBA) are among the most powerful organic peroxide oxidizing agents [8]. The main industrial uses of these compounds are in the manufacture of epoxides, synthetic glycerol and epoxy resins [8]. They also have been used as disinfectants, fungicides, bleaching agents and for shrink-proofing wool [8]. Typical reactions include epoxidation and hydroxylation of alkenes, oxidation of sulfides to sulfoxides or sulfones, transformation of ketones to esters or lactones, conversion of aldehydes to carboxylic acids and oxidation amines to amine oxides [7, 8].

Persulfates such as potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) are often used in environmental applications such as soil and groundwater remediation [9], but also in other applications such as chemical syntheses, electronics, and as hair dyes and bleaching agents in pharmaceuticals and cosmetics [10]. They are powerful oxidants capable of oxidizing almost all organic compounds [11]. As they have the capacity to degrade a wide range of organic pollutants, there are reports that promote persulfate-based oxidation process as a viable alternative to hydrogen peroxide-based processes in water treatment [12–14].

Graphene oxide (GO) is a single layer of graphite oxide which is exfoliated from this compound [15]. Graphite oxide can be prepared by the intercalation and oxidation of graphite powder [16]. For this purpose, graphite powder is chemically reacted with acids (HCl , H_2SO_4 and HNO_3 etc.) followed by the intercalation of alkali metals (KClO_3 , KMnO_4 , NaNO_3 etc.) [16]. So many methods have been widely developed in the past decades for the preparation of GO, but the Hummers' method is the most widely used one nowadays [17]. The Hummers' method involves treatment of graphite with potassium permanganate (KMnO_4) and sulfuric acid (H_2SO_4) [18]. Also, this method has been modified to improve the yielded GO (oxidation degree) and/or to speed up the process [17]. The modified Hummers' method requires H_2SO_4 , KMnO_4 , H_2O and H_2O_2 for GO formation [17]. The prepared GO mainly consists of individual sheets of graphene with attachments of oxygen functional groups (hydroxyl, epoxy, carbonyl and carboxyl) [16].

GO has been explored in a wide range of applications such as energy generation/storage, electronic and photonic devices, optical devices, clean energy, chemical/bio sensors and drug delivery [16]. Moreover, the chemical functionalization of GO by noncovalent and covalent approaches is very attractive for synthetic chemists [15]. Using oxidizing agents as oxidant [19, 20], initiator [21], cross-linker [22], matrix modifier [23] and catalyst [24] in many of synthetic reactions is unavoidable. Therefore, it is important to investigate the effects of oxidizing agents on the texture of graphene oxide which is the subject of this study. To clarify the importance of this issue, some recent publications are mentioned in the following.

El-Sheikh reported the effect of oxidation of multi-walled carbon nanotubes (MWCNTs) with various oxidizing agents such as HNO_3 , H_2O_2 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ [25]. Peng and Liu studied the effects of H_2O_2 oxidation on morphology and structure of the MWCNTs [26]. Teoh et al. investigated the evaluation of various oxidizing agents include HNO_3 , H_2SO_4 , $\text{HNO}_3/\text{H}_2\text{SO}_4$ and KMnO_4 to assess their effectiveness on covalent functionalization of MWCNTs [27]. Zhang et al. reported the systematic investigation of the effect of chemical oxidation on the structure of single-walled carbon nanotubes (SWCNTs) by using different oxidants including HNO_3 , $\text{HNO}_3/\text{H}_2\text{SO}_4$ and KMnO_4 [28]. Kashif et al. investigated the effect of KMnO_4 on graphene oxide (GO) morphological and structural properties [29].

In the current research, the effects of H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and mCPBA on the functional groups, crystallinity, morphology and degree of oxidation of GO are considered by FT-IR, XRD, FESEM, EDX and elemental mapping techniques. We report the first comparison between GO and GO treated by peroxide and persulfate oxidizing

agents. The findings of this manuscript help researchers to choose the appropriate oxidizing agent and use it to optimize the performance of GO in organic synthesis.

MATERIALS AND METHODS

Materials and Characterization

The fine powder of extra pure graphite and all other chemicals used in this study (sulfuric acid 98%, potassium permanganate, sodium chloride, hydrochloric acid 37%, dichloromethane, sodium bicarbonate, hydrogen peroxide 30%, potassium persulfate, ammonium persulfate and meta-chloroperoxybenzoic acid 75%) were obtained from Merck.

The FT-IR spectra were recorded using KBr pellets on PerkinElmer (RXI model) Fourier transform infrared spectrophotometer. The XRD measurements were performed using Bruker (D8-Advance) X-ray diffractometer with CuK α radiation. The FESEM images and elemental mapping patterns were taken by TESCAN MIRA III Field Emission Microscope equipped with EDS system for elemental analysis.

Experimental

GO was prepared by oxidation of graphite in modified Hummers method [30] with minor changes. First, graphite (0.5 g) was ground with NaCl (2.5 g, 42.779 mmol). Then, NaCl was dissolved in deionized water and removed by filtration. The remaining graphite was stirred in H₂SO₄ 98% (11.5 mL) for 12 h. Thereafter, KMnO₄ (2.5 g, 15.819 mmol) was gradually added while keeping the temperature below 20 °C by an ice-bath. The resulting mixture was stirred at 40 °C for 1.5 h. Next, deionized H₂O (22.5 mL) was added and the mixture heated at 55 °C for 0.5 h. The reaction was terminated by addition of deionized H₂O (70 mL) and H₂O₂ 30% solution (5 mL). The mixture was filtrated and washed several times by HCl aqueous solution 5% and deionized water. The final product was exfoliated by ultrasonication and dried at room temperature for 24 h.

For treatment of GO with hydrogen peroxide, GO (0.01 g) was added to H₂O₂ solution 30% (10 mL) and stirred in an oil bath at a pre-set temperature of 80 °C for 24 h. After cooling, the resulting mixture was filtrated and washed several times by deionized water. The final product was dried at room temperature for 24 h.

For treatment of GO with potassium persulfate, GO (0.01 g) was added to the solution of K₂S₂O₈ (0.125 mmol) in deionized water (5 mL) and stirred in an oil bath at a pre-set temperature of 80 °C for 24 h. After cooling, the resulting mixture was filtrated and washed several times by deionized water. The final product was dried at room temperature for 24 h.

For treatment of GO with ammonium persulfate, GO (0.01 g) was added to the solution of (NH₄)₂S₂O₈ (0.125 mmol) in deionized water (5 mL) and stirred in an oil bath at a pre-set temperature of 80 °C for 24 h. After cooling, the resulting mixture was filtrated and washed several times with deionized water. The final product was dried at room temperature for 24 h.

For treatment of GO with meta-chloroperoxybenzoic acid, GO (0.01 g) was added to the solution of mCPBA (0.125 mmol) in dichloromethane (5 mL) and stirred at room temperature for 24 h. The resulting mixture was filtrated and washed several times with dichloromethane, aqueous solution of sodium bicarbonate 10% and deionized water. The final product was dried at room temperature for 24 h.

RESULTS AND DISCUSSION

For the preparation of GO in Hummers' method, NaNO₃ and KMnO₄ dissolved in concentrated H₂SO₄ have been used to oxidize graphite [31]. This method suffers from several defects including toxic gas generation (NO₂ and N₂O₄), residual nitrate and low yield [32]. In this research, GO is prepared by oxidation of graphite in modified Hummers' method [30]. In this method, KMnO₄ and concentrated H₂SO₄ are used for oxidation of graphite. The sulfuric acid is the concentrated acidic medium that intercalates the graphite and expands it, and potassium permanganate is the oxidant [17]. The main role of H₂O₂ in modified Hummers' method is to remove the excessive KMnO₄ or in other words to stop the reaction [33, 34].

In the following, the effects of peroxide and persulfate oxidizing agents on the texture of GO are considered by FT-IR, XRD, FE-SEM, EDX and elemental mapping techniques. For this purpose, a specific amount of GO is treated by the aqueous solution of H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ at $80\text{ }^\circ\text{C}$. This temperature for treatment of GO is chosen in order to work with a temperature higher than the routine temperatures of GO preparation (i.e. $25\text{--}60\text{ }^\circ\text{C}$ [35]). As mCPBA is insoluble in water and sensitive to heat, the treatment of GO by this oxidizing agent is performed in dichloromethane at room temperature.

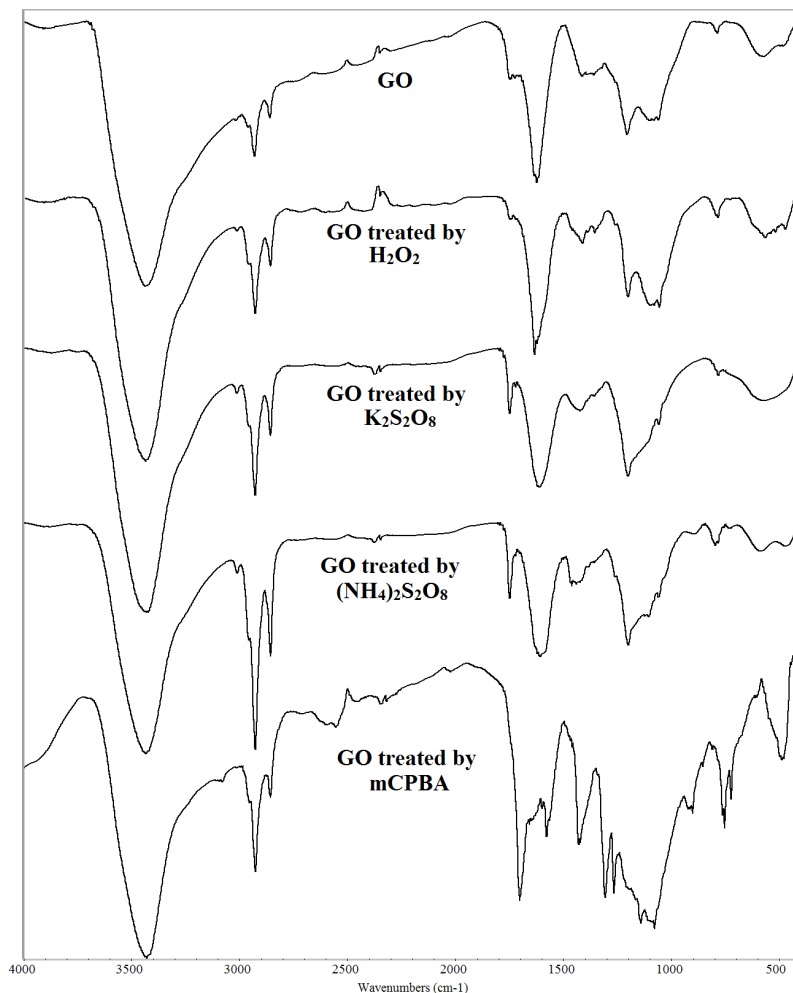


Figure 1. FT-IR spectra of GO and GO treated by oxidizing agents.

FT-IR spectra of GO and GO treated by oxidizing agents are depicted in Figure 1. Also, frequencies for various modes of vibrations are collected in Table 1. GO contains a layer of carbon atoms that decorated by oxygen-containing groups such as C-O, C-O-C, C = O and -OH. This result agrees with that reported in the literature for GO [36, 37]. The broad bands observed at $3000\text{--}3700\text{ cm}^{-1}$ with the maxima at 3434 cm^{-1} for GO and around $3420\text{--}3434\text{ cm}^{-1}$ for other oxidized samples are attributed to the O-H stretching vibrations. The bands appeared at 1358 cm^{-1} for GO and around $1352\text{--}1354\text{ cm}^{-1}$ for other oxidized samples are assigned to the O-H bending vibrations. These bands are the result of the presence of hydroxyl groups within the structures. The bands located at 1742 cm^{-1} for GO and around $1700\text{--}1742\text{ cm}^{-1}$ for other oxidized samples are assigned to the C = O stretching vibrations, corresponding to the carboxyl groups on the edges of the layer planes or conjugated carbonyl groups. The bands seen at 1406 and 1618 cm^{-1} for GO and around $1410\text{--}1458$ and $1576\text{--}1630\text{ cm}^{-1}$ for other oxidized samples are ascribed to the C = C stretching vibrations, confirming that the C = C bonds still remain after treatment of GO by oxidizing agents. The bands found at 2854 , 2926 and 3006 cm^{-1} for GO and around $2854\text{--}3078\text{ cm}^{-1}$ for other oxidized samples are assigned to the C-H stretching vibrations, suggesting the presence of both sp^3 and sp^2

carbon atoms that are created during the oxidation process. The bands centered at 1054, 1096 and 1202 cm^{-1} for GO are assigned to the stretching vibrations of C-OH, C-O and C-O-C groups due to phenol, carboxylic acid, ether and epoxide functionalities. These bands can be observed in the more oxidized samples at around 1052–1138 cm^{-1} .

Table 1. FT-IR frequencies (in cm^{-1}) for various modes of vibrations (stretching (S) and bending (B) modes) of GO and GO treated by oxidizing agents.

Vibration mode	GO	GO treated by H_2O_2	GO treated by $\text{K}_2\text{S}_2\text{O}_8$	GO treated by $(\text{NH}_4)_2\text{S}_2\text{O}_8$	GO treated by mCPBA
S(O-H)	3434	3434	3420	3434	3426
S(C-H)	3006, 2926, 2854	3008, 2924, 2854	3010, 2926, 2854	3008, 2924, 2854	3078, 2924, 2854
S(C = O)	1742	1742	1746	1746	1700
S(C = C)	1618, 1406	1630, 1410	1608, 1420	1604, 1458	1576, 1426
B(O-H)	1358	1352	1354	1354	1354
S(C-O-C)	1202	1198	1198	1198	1194
S(C-OH)	1096, 1054	1096, 1052	1122, 1054	1102, 1056	1138, 1074

The XRD pattern of the prepared GO shows (001) and (100) diffraction peaks at $2\theta = 10.7$ and 42.1° with d-spacing of 8.25 and 2.14 Å, respectively. This result agrees with that reported in the literature for GO [38, 39], confirming the successful preparation of this compound. The effect of oxidizing agents such as H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and mCPBA on the XRD pattern of GO is shown in Figure 2. Moreover, Table 2 compares the variation of diffraction peaks position (2θ), intensity and d-spacing before and after treatment of GO. It can be seen that the intensity of the diffraction peaks for GO after treatment by oxidizing agents decreases drastically. Also, a phase transition from more crystalline graphene oxide to more amorphous state is observed where GO is treated by oxidizing agents. It seems that oxidizing agents can create and enlarge the hole defects in graphene oxide. The amorphous carbon has a broad diffraction peak at about $2\theta = 20^\circ$ [40–42]. Therefore, the broad peaks observed at 26.6, 24.2, 28.2 and 30.6° for GO treated by H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and mCPBA, respectively, confirm the amorphous nature of these compounds. The change from ordered GO to an amorphous phase in different conditions has been previously stated [43–45].

Table 2. The diffraction peaks position (2θ , in degree) intensity and d-spacing (in Å) before and after treatment of GO by oxidizing agents.

Compound	GO phase	Amorphous phase
	2θ (intensity, d-spacing)	2θ (intensity)
GO	10.7 (1171.4, 8.25), 42.1 (395.2, 2.14)	29.3 (43.0)
GO treated by H_2O_2	11.0 (71.6, 8.01), 42.5 (75.1, 2.13)	26.6 (191.3)
GO treated by $\text{K}_2\text{S}_2\text{O}_8$	42.8 (87.1, 2.11)	24.2 (146.3)
GO treated by $(\text{NH}_4)_2\text{S}_2\text{O}_8$	7.1 (79.7, 12.51), 42.4 (92.5, 2.13)	28.2 (57.7)
GO treated by mCPBA	9.8 (395, 9.02), 42.5 (119.1, 2.12)	30.6 (45.7)

According to XRD patterns, the GO treated by mCPBA at room temperature has a more ordered structure (similar to GO) compared to the GO treated by other oxidizing agents at 80°C , which is due to the formation of larger hole defects at higher temperature. It has been reported that during the low-temperature and mid-temperature stages of graphene oxide preparation, the hole defects of graphene oxide would diminish significantly [35]. When the

reaction temperature is over 50 °C, the graphene oxide became unstable and many holes in the graphene oxide due to excessive oxidation are formed [35].

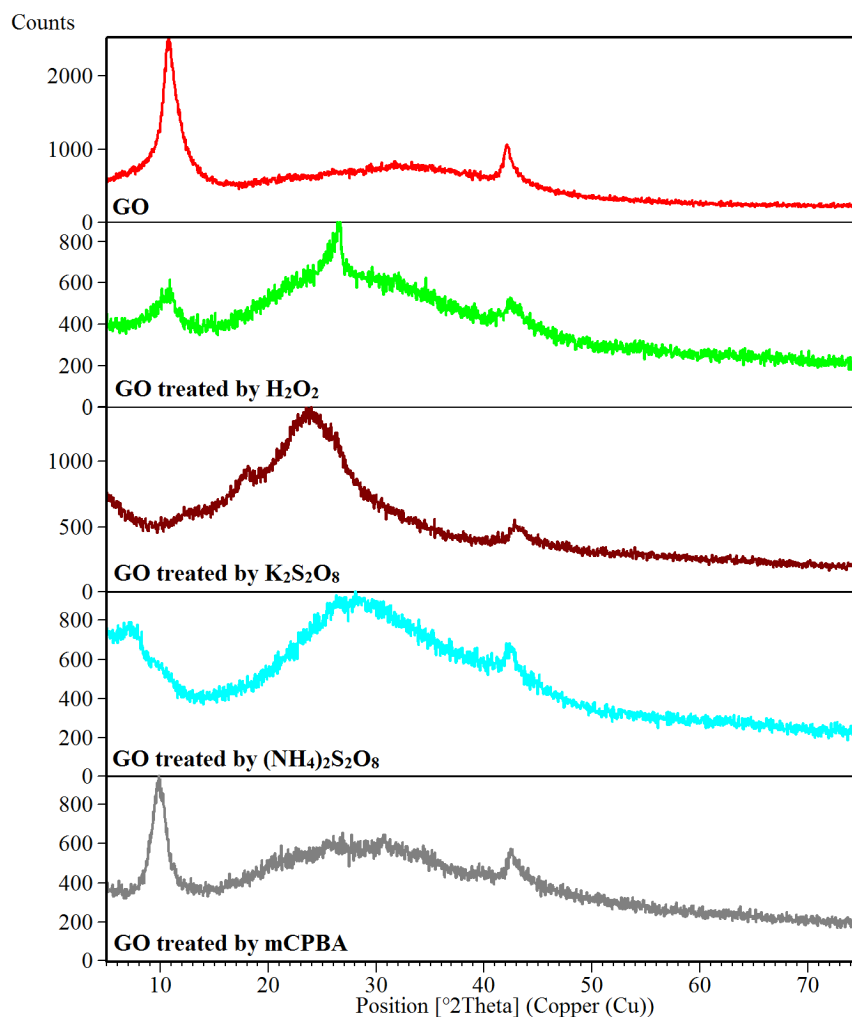


Figure 2. XRD patterns of GO and GO treated by oxidizing agents.

For the GO treated by mCPBA, the XRD peak of GO (001) from 10.7° shifts to a lower 2θ angle (9.8°) with increasing d-spacing from 8.25 to 9.02 Å. Similarly for GO treated by (NH₄)₂S₂O₈, this peak shifts to a lower 2θ angle (7.1°) with increasing d-spacing (12.51 Å). The highest deformation is belongs to GO treated by K₂S₂O₈ in which this peak shifts below 5°, and therefore is not observed in the recorded 2θ range. For GO treated by H₂O₂, the GO (001) peak shifts to a higher 2θ angle (11.0°) with decreasing d-spacing (8.01 Å). Both of H₂O₂ and mCPBA add epoxy groups within the oxidized structure of GO. But since mCPBA is much larger than H₂O₂, the layer spacing expands. Persulfates moreover the epoxy groups, introduce carboxyl and hydroxyl functional groups to the surface, which is in associated with increasing the interlayer spacing.

The FESEM micrographs of the GO prepared by modified Hummers' method in this study are shown in Figure 3. It can be seen that the flakes of GO are tightly packed together in a sponge like structure (due to the H-bonds between layers). The FE-SEM micrographs of GO treated by (NH₄)₂S₂O₈ and mCPBA are compared in Figs. 4 and 5, respectively. Significant changes due to the formation of hole defects in the morphology of the GO after treatment by oxidizing agents are observed *via* the FE-SEM micrographs.

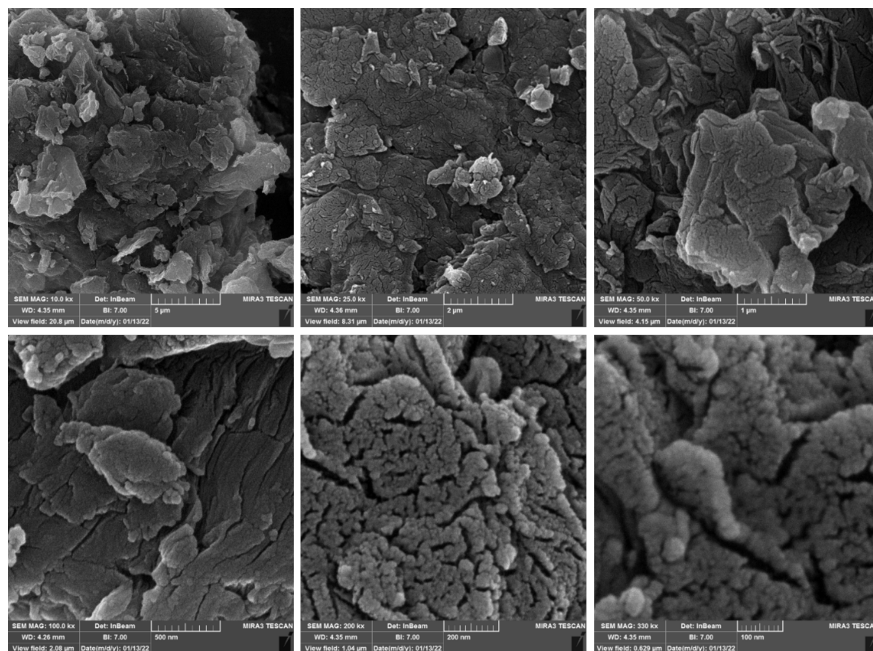


Figure 3. FESEM micrographs of the prepared GO.

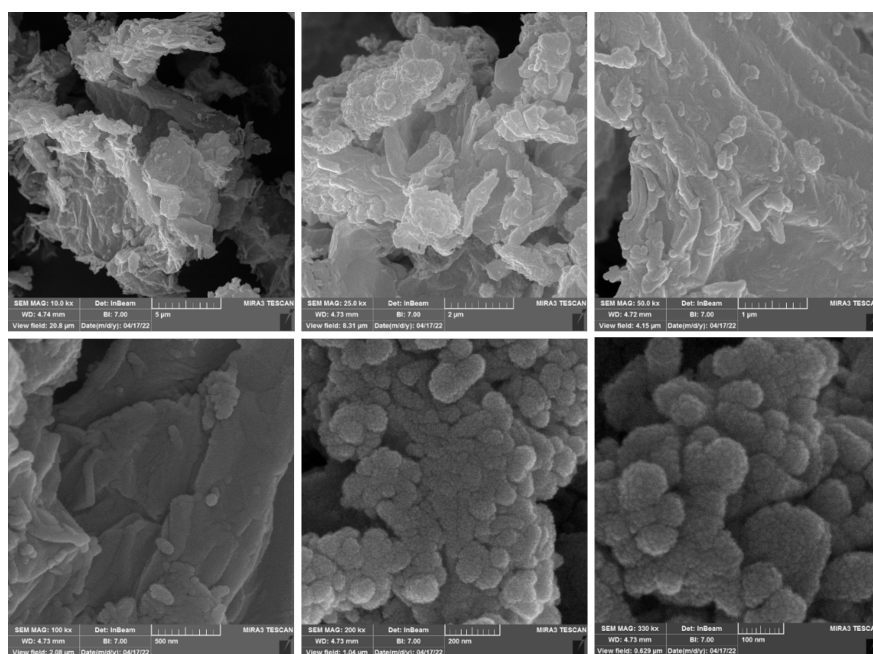


Figure 4. FESEM micrographs of GO treated by $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

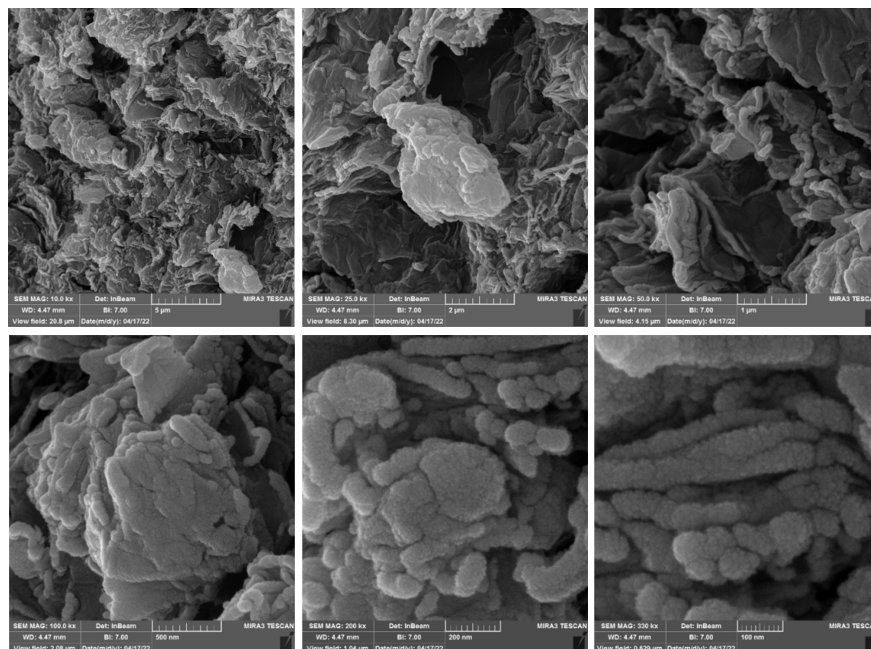


Figure 5. FESEM micrographs of GO treated by mCPBA.

The base SEM images, elemental maps and elemental compositions (weight (W) and atomic (A) percentages) according to EDX line scan analysis for GO and GO treated by oxidizing agents are indicated in Figure 6. The GO contains 66.00 A% (59.33 W%) C and 34.00 A% (40.67 W%) O. The high A% (or W%) of oxygen in GO confirms successful oxidation and the presence of oxygen-containing groups within the carbon layers. The carbon to oxygen atomic ratio is used to compare the relative levels of oxidation. This value decreases with increasing oxidation. The value of the C/O atomic ratio for GO is 1.94. Based on the EDX results, the highest % of O is found for GO treated by mCPBA (44.82 A%). The value of the C/O atomic ratio for this compound is 1.23. The GO treated by H_2O_2 contains 33.70 A% O. The value of the C/O atomic ratio for this compound is 1.97. The % of O for GO treated by $\text{K}_2\text{S}_2\text{O}_8$ is 32.24 A%. The value of the C/O atomic ratio for this compound is 2.10. This value for GO treated by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is determined 34.59 A%. The value of the C/O atomic ratio for this compound is 1.89. Therefore, GO treated by mCPBA show the higher degree of oxidation than GO and GO treated by other oxidants.

CONCLUSIONS

GO was prepared by oxidation of graphite in modified Hummers' method. The effects of peroxide and persulfate oxidizing agents (H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and mCPBA) on the texture of GO were considered by FT-IR, XRD, FE-SEM, EDX and elemental mapping techniques. According to FT-IR results, GO and GO treated by oxidizing agents contain a layer of carbon atoms that decorated by oxygen-containing groups (i.e. hydroxyl, epoxy, carbonyl and carboxyl). Based on XRD data, a phase transition from more crystalline graphene oxide to more amorphous state is observed where GO is treated by oxidizing agents. It seems that oxidizing agents can create and enlarge the hole defects in graphene oxide. The XRD pattern of GO treated by mCPBA at room temperature has a more ordered structure (similar to GO) compared to the GO treated by other oxidizing agents at 80 °C, which is due to the formation of larger hole defects at higher temperature. Significant changes due to the formation of hole defects in the morphology of the GO after treatment by oxidizing agents are observed by the FE-SEM micrographs. The highest degree of oxidation is predicted for the GO treated by mCPBA.

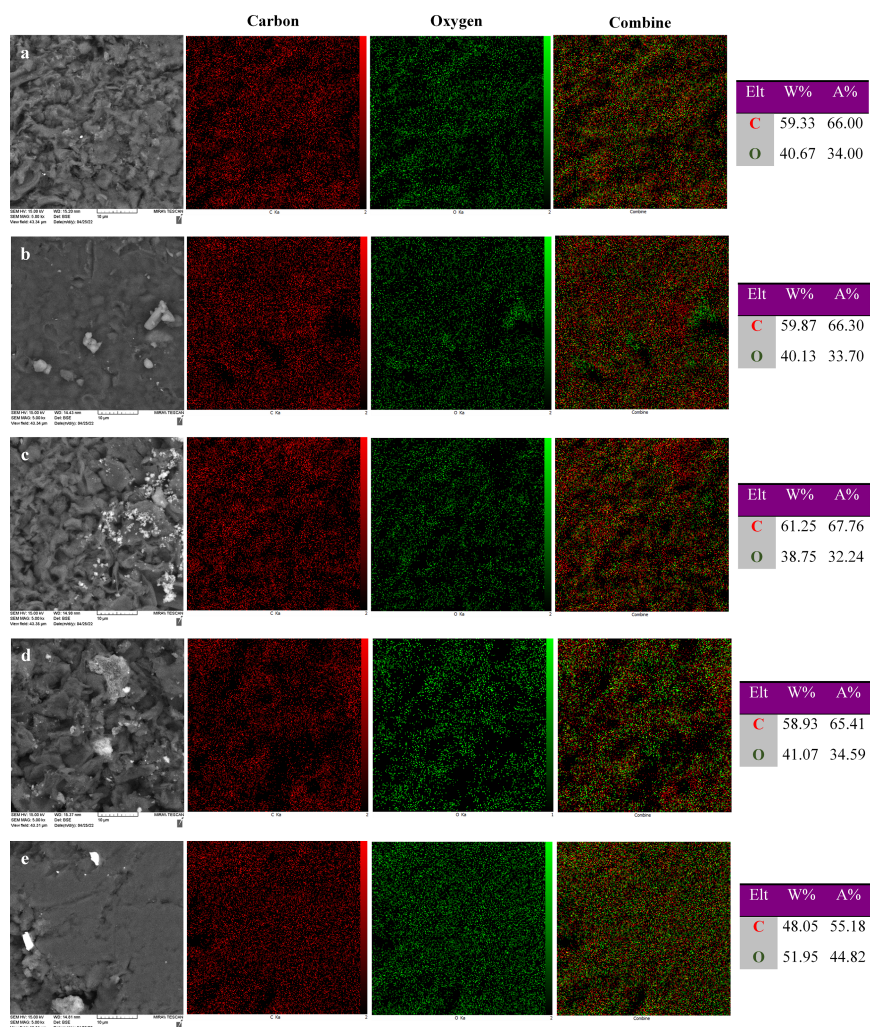


Figure 6. The base SEM images, elemental maps and elemental compositions according to EDX line scan analysis (the average of 5 data points) for GO (a) and GO treated by H_2O_2 (b), $\text{K}_2\text{S}_2\text{O}_8$ (c), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (d), and mCPBA (e).

STATEMENTS AND DECLARATIONS

Authors' Contributions

Y. Mahdavi: Investigation.

M. Zamani: Conceptualization, Methodology, Validation, Formal analysis, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

Conflicts of Interest/Competing Interests

The authors declare that they have no competing interests.

Ethics Approval

Not applicable.

Data and Code Availability

All data generated or analyzed during this study are included in this published article.

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