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Controlled synthesis, characterization and reduction of graphene oxide: A convenient method for large scale production

Tarko Fentaw Emiru^a, Delele Worku Ayele^{a,b,c,*}^a Material Science and Engineering Program, College of Science, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia^b Department of Chemistry, College of Science, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia^c Energy Research Center, Bahir Dar Institute of Technology, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia

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ABSTRACT

In this work, graphene oxide was synthesized by treating graphite powder with KMnO_4 and a mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ and reduced with ascorbic acid to produce reduced graphene oxide. The effects of reaction parameters such as reaction time, reaction temperature and amount of KMnO_4 on the degree of oxidation of graphite powder to graphene oxide were studied. The prepared graphene oxide and reduced graphene oxide were characterized by UV–Visible spectroscopy, FT–IR spectroscopy, and XRD. The results showed that treating graphite powder with KMnO_4 at 40 °C for 12 h resulted in better degree of oxidation. The designed synthesis strategy could be simple/convenient, easily controlled and an alternative approach for large scale production of graphene oxide (GO) and reduced graphene oxide (rGO).

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Introduction

Graphene related materials have so many potential applications such as light weight, thin, flexible, durable display screens and electric circuits, super capacitors [1], transistors [2], transparent conducting electrodes for the replacement of ITO, conductive polymer composite [3], energy storage materials due to having an extremely high surface area [4], and solar cells [5]. However, there is a challenge of producing high quality graphene in large quantity using low cost and environmental friendly method. Among graphene synthesizing mechanisms, mechanical exfoliation [6] can produce the pristine graphene. But, the process is complicated and the product is small size, which is limited for large scale quantities. CVD [7,8] also allows production of large area graphene films of single to few-layers. However, it requires high temperature up to 1000 °C along with a hydrocarbon gas flow as precursor and pure hydrogen as a carrier gas, which limits the application range. Epitaxial growth [9] can also produce graphene with perfect structure (defect free) and excellent properties but the products are small-size and are difficult to assemble into films. In addition, requirement of high energy limits its application for large scale production. Chemical method is the prominent method of producing graphene

based materials in large quantity [10]. However, the well-known chemical synthesis methods such as Brodie method [11], Staudenmaier method [12] and Hummer's method [13] were hazardous and toxic since ClO_2 and NO_2 evolves during the process. The Tour method (improved green synthesis method) is the one that is relatively safe (environmental friendly) [14]. In addition, the final yield is much higher than the former methods. This method describes that GO is synthesized by treating graphite powder with H_3PO_4 , H_2SO_4 and high quantity of KMnO_4 . However, the influence of the quantity of KMnO_4 , reaction time, and the temperature on graphite oxide preparation was not clear.

In this work, we prepared graphene oxide by easy, cost effective and convenient method via treating graphite powder with KMnO_4 and a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ as oxidant. Moreover, reduction of graphene oxide (GO) to produce reduced graphene oxide (rGO) was carried out using anon-toxic reducing agent, ascorbic acid (AA). To optimize the oxidation level, the effects of KMnO_4 , reaction time and reaction temperature were studied. Graphene oxide and reduced graphene oxide were characterized by visual inspection, UV–Visible spectroscopy, FT–IR spectroscopy, and XRD.

The route to prepare rGO involves three steps. Firstly, graphite powder is oxidized to graphite oxide, which can be dispersed in water or another polar solvent due to the presence of hydroxyl and epoxide groups across the basal planes of graphite oxide and carboxyl groups located at the edges [13]. Secondly, graphite oxide

* Corresponding author at: Material Science and Engineering Program, College of Science, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia.

E-mail addresses: delelew@bdu.edu.et, delelewwww@yahoo.com (D.W. Ayele).

can be exfoliated either by sonication or mechanical stirring to form few or single layer graphene oxide sheets [6]. Thirdly, graphene oxide is reduced by removing oxygen containing functional groups.

Experimental

Chemicals

Graphite powder and H₂SO₄ (98 wt%), Potassium Permanganate (KMnO₄), H₃PO₄ (85 wt%), Hydrochloric acid (HCl 35 wt%), barium chloride (BaCl₂), (C₆H₈O₆) and H₂O₂ (30%), CH₃CH₂OH (Assay; 97%). All reactants and solvents have been used without further purification.

Synthesis of graphite oxide

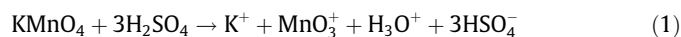
For a typical synthesis of graphite oxide, a mixture of 96 ml of concentrated H₂SO₄ and 10.7 ml of concentrated H₃PO₄ (9:1 volume ratio) was prepared. The mixture of these acids was poured slowly into the mixture of 0.6 g graphite powder and 4.8 g potassium permanganate (1:8) in a beaker under stirring with glass rod. The reaction was then heated to 40 °C controlled by water bath and stirred for 12 h. Then, the mixture was added into 250 ml of de-ionized water to stop the reaction. Following that 15 ml of H₂O₂ was added into the mixture. The addition of H₂O₂ resulted in yellow color, indicating high level of oxidation. The solution was then filtered to remove metal ions using filter paper and funnel. A yellow paste was produced. The paste was washed with 5% HCl aqueous solution using centrifuge until SO₄²⁻ was removed completely. The removal of SO₄²⁻ was detected by addition of barium chloride where the presence of sulfate ion showed a white precipitate when barium chloride was added to the supernatant. The supernatant was decanted away and the remaining solid material was collected. Then the mixture was washed multiple times with de-ionized water using centrifuge until the pH of the supernatant was neutral. Finally the material was dried at 50 °C for 24 h and a brown black sample was obtained.

Preparation of graphene oxide

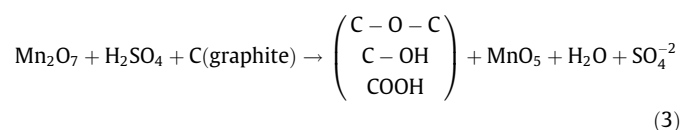
For a typical preparation of graphene oxide solution, 0.5 g of graphite oxide solid sample was grounded with mortar and pestle. The powder was dispersed in de-ionized water and stirred with magnetic stirrer at 60 °C for 12 h.

Formation mechanism of grapheneoxide

The active species to oxidize graphite is diamanganese heptoxide (Mn₂O₇) which is obtained via the reaction of monometallic tetra oxide and MnO₃⁺ as shown in the reaction 1 below [15].



The transformation of MnO₄⁻ into a more reactive form Mn₂O₇ will certainly help oxidize graphite powder as shown in the reaction below [16].



But the bimetallic form of manganese oxide has been reported to detonate when heated up to 55 °C temperature or when reacted with organic compounds [15].

Reduction of graphene oxide

Graphene oxide was reduced by using ascorbic acid (C₆H₈O₆). 5 g ascorbic acid was added to the GO solution and stirred with magnetic stirrer for 30 min at 60 °C. The product was centrifuged to remove the supernatant. Then, excess H₂O₂ was added to the black paste to oxidize the unreacted ascorbic acid by stirring for 30 min at 60 °C. After stirring, the resulted black product was collected by centrifugation and washed with ethanol and water 3 times respectively and then dried at 100 °C for 24 h.

The proposed mechanism for reduction of GO by ascorbic acid

The epoxy groups of GO can be easily attacked by nucleophilic reagents, resulting in a nucleophilic substitution reaction to open the epoxy rings [17]. It is supposed that ascorbic acid donates proton and electron to graphene oxide. It opens the epoxide rings and converts to easily leaving group (OH) and finally dehydrates, leaving a graphene sheet. To remove the OH group it is believed that ascorbic acid donates one proton to the OH group and finally dehydrates.

Designation of the prepared samples

GO1, GO2, GO3 and GO4 were graphite oxide samples. These samples were synthesized by taking the same amount of graphite powder, for the same reaction time and at the same reaction temperature. But, the concentration of KMnO₄ was varied.

GO5 and GO6 were graphite oxide samples. These samples were synthesized by taking the same amount of graphite powder, the same amount of KMnO₄ and for the same reaction time. But the reaction temperature was varied.

GO7, GO8, GO9 and GO10 were graphite oxide samples synthesized by taking the same amount of graphite powder, the same amount of KMnO₄ and at the same reaction temperature. But the reaction time was varied. The parameters and designations of the prepared samples are shown in the Table 1 below.

Characterization techniques

UV–Visible spectroscopy was used in detection of the conjugation network and absorption of GO and rGO. Double beam Lambda 35 UV–Vis spectrophotometer (Perkin Elmer, USA) was used to obtain the absorption spectra of GO and rGO. The GO and rGO solution samples were scanned for wavelength range from 200 to 800 nm. FTIR (Perkin Elmer, USA) was employed to analyze the presence/absence of functional groups on GO and rGO sheets. GO and rGO pellets were prepared using KBr and the samples were scanned in the range from 400 cm⁻¹ to 4000 cm⁻¹ to obtain the FTIR spectra. The X-ray diffraction (XRD) patterns of graphite, GTO and rGO powders were recorded with a scanning rate of 1° per minute in a 2θ range from 10° to 80° with Cu Kα radiation (λ = 1.5418 Å) to characterize the inter layer spacing. It was done at 40 keV and 30 mA.

Result and discussion

Visual observations

Formation of graphite oxide was preliminarily well known by changing of color as shown in Fig. 1(E). Initially, when the mixture of acids was added slowly into the mixture of graphite powder and potassium permanganate, it produced a dark green color with a slight exothermic to 30–40 °C as shown in the Fig. 1(A). The dark green color seems to indicate that Mn₂O₇ was formed. As the

Table 1Synthesis parameters (reaction time, reaction temperature and concentration of KMnO_4) and designations of the prepared samples.

Sample	Graphite (g)	KMnO_4 (g)	$\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ ratio	H_2O_2 (ml)	Temperature ($^{\circ}\text{C}$)	Time (h)
GO1	0.6	3.6	9:1	15	50	12
GO2	0.6	4.2	9:1	15	50	12
GO3	0.6	4.8	9:1	15	50	12
GO4	0.6	5.4	9:1	15	50	12
GO5	0.6	4.8	9:1	15	40	12
GO6	0.6	4.8	9:1	15	50	12
GO7	0.6	4.8	9:1	15	40	8
GO8	0.6	4.8	9:1	15	40	10
GO9	0.6	4.8	9:1	15	40	12
GO10	0.6	4.8	9:1	15	40	14

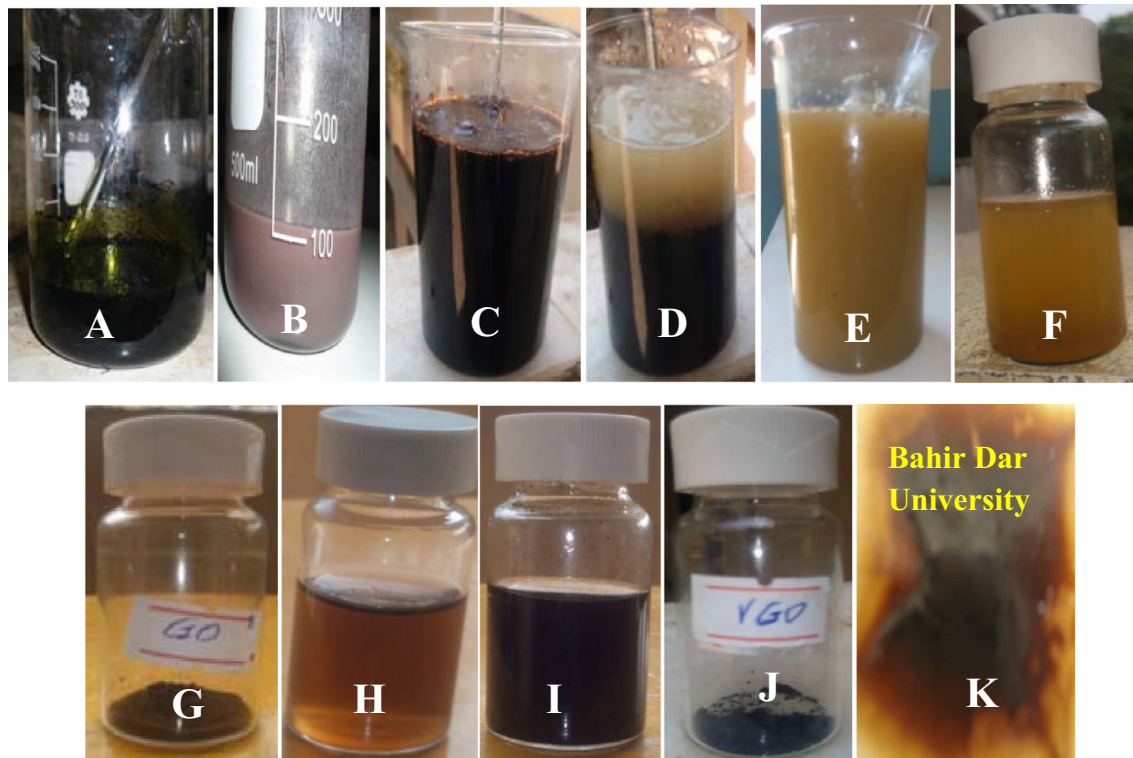


Fig. 1. Digital images taken (A) when the mixture of acids was poured into the mixture of graphite powder and KMnO_4 , (B) slurry obtained at the end of 12 h of heating and stirring, (C) after the slurry was added into 250 ml de-ionized water, (D) after H_2O_2 was added without stirring, (E) when stirred after adding H_2O_2 , (F) graphite oxide dispersion in de-ionized water, (G) graphene oxide powder after dried in oven and grounded, (H) graphene oxide solution in de-ionized water, (I) reduced graphene oxide solution in de-ionized water, (J) reduced graphene oxide (rGO) powder, (K) graphene oxide (GO) film.

reaction continued, the mixture turned to slurry as seen in the Fig. 1(B). When the slurry was added to 250 ml of de-ionized water, after cooling at room temperature, it releases heat and a dark purple color was observed as shown in the Fig. 1(C). This color indicates there might be unreacted KMnO_4 since the solution of KMnO_4 gives purple color. The addition of H_2O_2 into the mixture also releases heat and effervesces (evolution of steam and oxygen gas) as shown in the Fig. 1(D) and a bright yellow color was observed as shown in the Fig. 1(E). The purpose of H_2O_2 was to consume the residue KMnO_4 [18]. The color change indicated the high level oxidation of graphite powder [19]. The obtained graphite oxide was dispersed in H_2O upon mechanical stirring. This might be through the introduction of functional groups which are responsible for hydrophilic nature of graphite oxide.

The filtration of the mixture resulted in a brown paste, which was graphite oxide product. The washing process of graphite oxide paste with 5% HCl aqueous solution was done using centrifuge until SO_4^{2-} was removed. During this process the removal of SO_4^{2-} was detected by barium chloride (BaCl_2). The addition of BaCl_2 into

the supernatant resulted in white precipitate (formation of barite or BaSO_4) indicating the presence of sulfate ions and no change was observed when there was no SO_4^{2-} .

The graphite oxide powder dispersions in de-ionized water resulted in non-homogeneous suspension. Aggregated graphite oxide particles were observed. When graphite oxide powder was treated with heat under magnetic stirring in distilled water, the inhomogeneous graphite oxide suspension turned into yellow-brown homogenous dispersion as shown in Fig. 1(H), resulted in the exfoliation of graphite oxide. When the heat treatment continued the water released large amount of heat. As the treatment of magnetic stirring and heating further continued, the functional groups on the graphene oxide layers in graphite oxide particles may gradually ionize, resulted in growing negatively charged graphene oxide layers and increasing electrostatic repulsion among them [20]. This might increase the interlayer distance of graphite oxide layers and reduced the van der Waals forces which resulted in exfoliation of graphite oxide into single or few layers graphene oxide nanosheets.

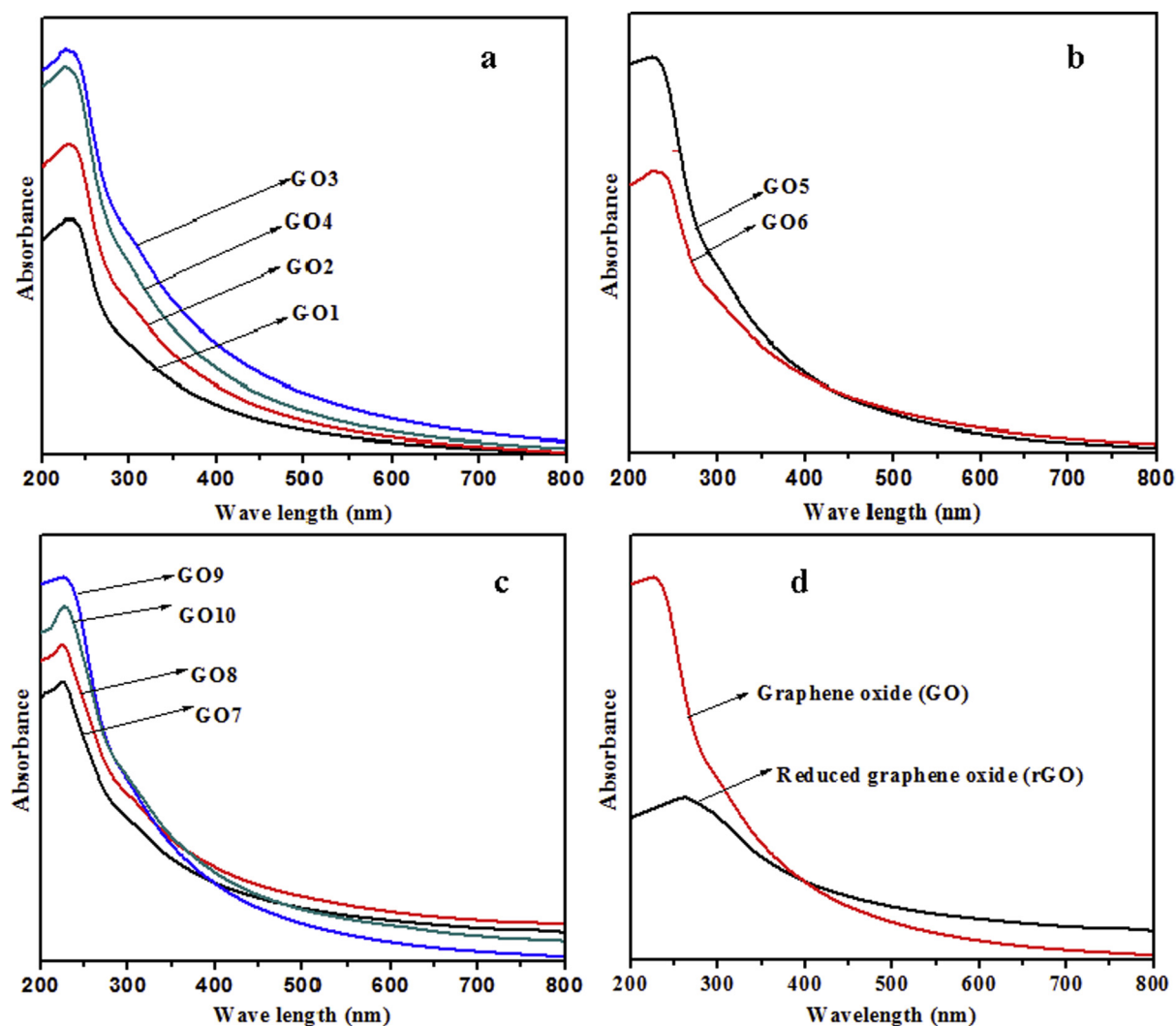


Fig. 2. UV-Visible spectra recorded in aqueous solutions (0.4 g/L) of GO at different (a) concentration of KMnO_4 , (b) reaction temperature, and (c) reaction time (d) Comparison of UV-Visible spectra recorded in aqueous solutions of graphene oxide and reduced graphene oxide.

The reduction of GO was also monitored by visual observation. As shown in Fig. 1(H), the GO dispersion was brownish yellow while the reduction of GO with ascorbic acid resulted in a black dispersion (Fig. 1(I)). This was probably a result of an increase in the hydrophobicity of the material caused by a decrease in oxygen containing functional groups (removal of the majority of functional groups) on the surface of the sheets [21]. The color change or the black color of rGO can also be assigned to the partial restoration of the π -network between the sheets due to removal of oxygen-containing functional groups resulted in electronic conjugation with in reduced sheets [22].

The amount of oxidizing agent, reaction temperature and reaction time were the most determinant factors of graphene oxide synthesis. The effect of these parameters on the oxidation level of graphene oxide was studied using UV-Visible spectra. To study the effect of the oxidizing agent (KMnO_4) on the oxidation degree of graphite powder, equal concentration of graphite oxide powder from four samples (GO1, GO2, GO3 and GO4) were first grounded with a mortar and pestle, and dispersed in one liter of de-ionized water to make graphene oxide solution. The dispersions with the same concentration were characterized by UV-Visible spectroscopy. The spectra for each sample were recorded as shown in the Fig. 2(a). The absorption peak was at 230 nm for GO1, 228 nm for GO2, and 226 nm for GO3 and GO4. These peaks are

corresponding to $\pi \rightarrow \pi^*$ transitions for the $\text{C}=\text{C}$ bonding, which is similar to the reported value in the literature [23,24]. A similar shoulder was also observed around 300 nm for all four samples, which is attributed to $n \rightarrow \pi^*$ transition of the carbonyl groups ($\text{C}=\text{O}$) [14].

The degree of oxidation (or the degree of remaining conjugation in graphene oxide sheets) can be determined by λ_{max} of UV-Visible spectrum [14]. The more $\pi-\pi^*$ transitions (conjugation), the less energy needs to be used for the electronic transition, which results in a higher λ_{max} [14]. The absorption peak for sample GO3 and GO4 is the lowest wavelength (226 nm) compared to others. There might be a decrease of the delocalized electrons and it is believed that higher energy was required for the electronic transition as compared with the other two samples, GO1 and GO2. This indicates that the samples were more oxidized with more functional groups on the basal planes.

As seen from the Fig. 2(a), the intensity of the peak of each sample is different. The higher the intensity at around 300 nm, the larger the degree of oxidation of GO whereas the less intensity is for less degree of oxidation [25]. Thus the absorption band around 300 nm indicated the degree of oxidation. Here, the intensity at around 300 nm for GO3 was highest suggests that the degree of oxidation was highest for it. This might be the effect of high concentration of the oxidizing agent (KMnO_4) which found to increase

the oxidation level of GO. However, the intensity at around 300 nm for GO4 is relatively low as compared to GOC3. This seems to indicate that more potassium permanganate will over oxidize graphite.

To study the effect of reaction temperature on the degree of oxidation two samples (GO4 and GO5) were taken. Their ratio of graphite powder to KMnO_4 was 1:8 and temperatures were fixed at 40 °C and 50 °C. As seen from Fig. 2(b), the intensity of the absorption peaks at 40 °C (GO5) was higher than the absorption peak at 50 °C (GO6). This suggests that GO5 was more oxidized and high temperature might reduce the oxidation level of graphite. The reason seems that the increasing temperature leads to a decrease in the degree of oxidation due to this may be only a few exfoliated layers get oxidized [26]. It has also been reported that high temperature during the oxidation process reduces the size of the graphene oxide produced [27].

Reaction time was also one of the determinant factors of degree of oxidation. Four samples (GO7, GO8, GO9 and GTO10) were taken for this study. The reaction temperature was fixed at 40 °C for all samples since the oxidation level was better at this temperature and the reactions were performed for 8, 10, 12 and 14 h. As depicted from Fig. 2(c), the peak intensity of GO increased with increasing reaction time from 8 to 12 h. This suggests that enough time is required for higher degree of oxidation. However, as the reaction time further increased from 12 to 14 h, the absorption peak intensity decreased. This might be the result of over oxidation. The successful reduction of graphene oxide was also confirmed by UV–Visible spectroscopy as shown in the Fig. 2(d). The UV–Visible spectrum of graphene oxide showed an absorption peak at 226 nm. After reduction by ascorbic acid, the peak of reduced graphene oxide was observed at 262 nm. The absorption of reduced graphene oxide red shifted to 262 nm suggests that the electronic conjugation within graphene sheets was restored (increased electron concentration after the reduction) [22].

FT-IR spectroscopy is a powerful technique to characterize the presence of different functional groups in graphene oxide including oxygen containing functional groups. FT-IR spectrum was recorded and the spectrum of GO obtained confirmed the successful oxidation of the graphite (Fig. 3). Some functional groups such as O–H, C–OH, COOH and C=O were observed. A broad peak between 3500 cm^{-1} and 2500 cm^{-1} in the IR spectrum of GO is due to the carboxyl O–H stretching mode [28,29,18,30,31]. The absorption peaks corresponding to O–H stretching (a peak $\sim 3400\text{ cm}^{-1}$) which is superimposed on the OH stretch of carboxylic acid, is due to the presence of

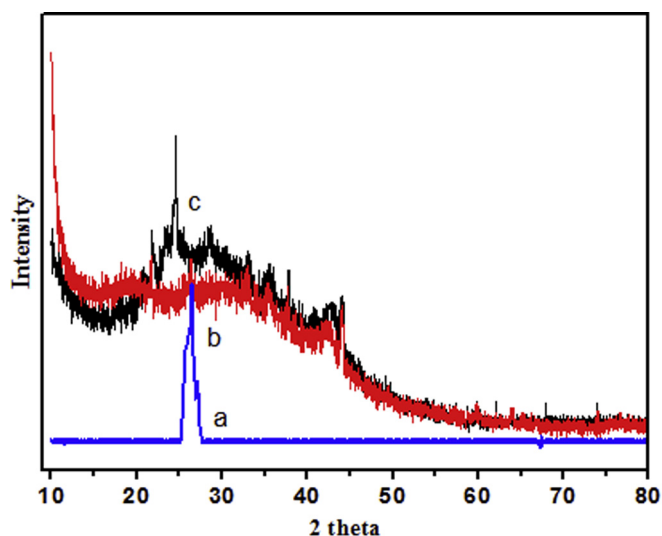


Fig. 4. X-ray diffraction patterns of (a) graphite (b) graphene oxide and (c) reduced graphene oxide.

absorbed water molecules and alcohol groups [28]. The IR peaks corresponding to 2927 cm^{-1} and 2849 cm^{-1} are due to the asymmetric and symmetric CH_2 stretching of GO respectively while the peak around 1619 cm^{-1} is attributed to C=C stretches from unoxidized graphitic domain [29]. The peak at around 1720 cm^{-1} is attributed to C=O stretch of carboxyl group [18], 1224 cm^{-1} corresponds to C–OH stretch of alcohol group [30], 1080 cm^{-1} is attributed to C–O stretching vibrations of C–O–C [31].

The reduction of GO was also characterized by FT-IR spectroscopy. As seen from the Fig. 3, all the intensities of the peaks corresponding to the oxygen containing functionalities of reduced graphene oxide were decreased as compared to the intensities of peaks of graphene oxide and even some were disappeared. This showed the successful reduction of graphene oxide by ascorbic acid. But all the peaks were not disappeared which seems to indicate that GO was not completely reduced by ascorbic acid and indicating the presence of some functional groups.

X-ray diffraction patterns for graphite, graphene oxide and reduced graphene oxide are shown in Fig. 4. The diffraction peak for graphite powder was at $2\theta = 26.4^\circ$ with a corresponding layer to layer distance of 0.34 nm, which is similar in the literature [32]. After oxidation of graphite powder, the diffraction peak for graphene oxide was at around $2\theta = 10^\circ$ corresponding to a layer-to-layer distance of 0.88 nm which is close to in the literature [16]. The patterns showed a larger interlayer spacing of graphene oxide than graphite powder layers due to the insertion of oxygen containing functional groups between the layers [33]. In addition, the diffraction peak appeared at around $2\theta = 43^\circ$ in XRD pattern of graphene oxide, indicates that graphene oxide exhibits turbostratic disorder [34]. XRD analysis also confirmed the reduction of graphene oxide. As seen from the Fig. 4, the diffraction peak of graphene oxide ($2\theta = 10^\circ$) shifted to $2\theta = 23.8^\circ$ (diffraction peak of reduced graphene oxide) corresponding to a layer to layer distance of 0.37 nm. This indicates that when graphene oxide is reduced to reduced graphene oxide the inter layer distance was decreased due to the removal of oxygen containing functional groups, resulted in restacking of the reduced graphene oxide sheets.

Conclusion

In this study graphene oxide was synthesized and then reduced to reduced graphene oxide (rGO) by easy and convenient method. Graphene oxide was obtained by treating graphite powder with

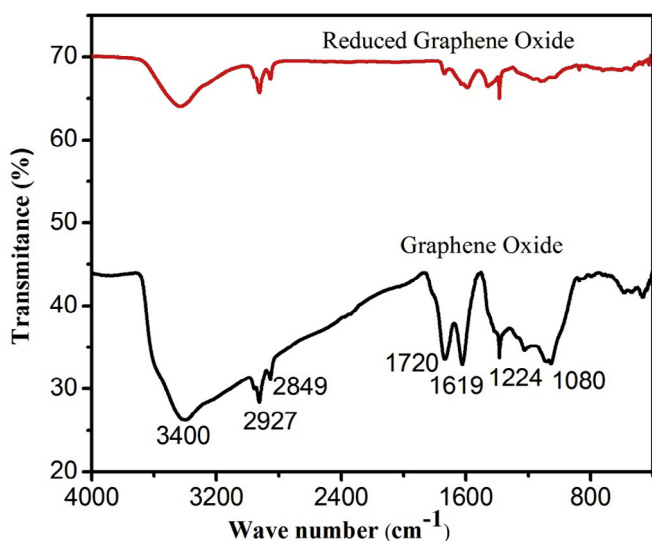


Fig. 3. FT-IR spectra of graphene oxide (GO) and reduced graphene oxide (rGO) powder.

KMnO₄ and a 9:1 mixture of H₂SO₄ to H₃PO₄. The obtained graphene oxide was reduced to reduced graphene oxide by ascorbic acid. The preparation of graphene oxide was controlled by reaction temperature, reaction time and concentration of KMnO₄. Both graphene oxide and reduced graphene oxide were characterized by UV–Visible spectroscopy, FT-IR spectroscopy, and XRD techniques. The result showed that better oxidation degree of graphite powder was obtained by treating 0.6 g graphite powder with 4.8 g of KMnO₄ (1:8) for 12 h of reaction time and at 40 °C reaction temperature with UV–Vis maximum absorption at 226 nm. The developed synthesis method for graphene oxide and reduced graphene oxide is an alternative approach and could be advantageous for large scale production.

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