

Review on the green synthesis of reduced graphene oxide

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Carbon-based material, *i.e.*, reduced graphene oxide (RGO), is a chemical substance obtained from graphite powder, which is of great interest since the last two decades. It is used in a large number of fields, like heterogeneous catalysis, bio-sensing, energy storage, drug delivery, etc. Graphite powder is oxidized and exfoliated to generate graphene oxide (GO) by using the traditional modified Hummer's method, which after reduction generates the RGO. Synthesis of RGO from GO can be done by using chemical reduction methods, as well as by using green methods. Due to their environmentally friendly and less hazardous nature, green methods are preferred over chemical reduction methods to prepare the RGO from GO. The RGO and GO synthesized were characterized using XRD, UV-visible, TGA, FESEM and FTIR techniques.

Keywords- Graphene oxide, Reduced graphene oxide, Graphite oxide, Green synthesis.

INTRODUCTION

Graphene has a hexagonal network structure of sp² hybrid carbon atoms arranged with each other to construct a one-atom-thick sheet [1]. In this one-atom-thick sheet of graphene all the carbon-carbon bond lengths are 1.42 Å, intermediate with respect to C-C and C=C bond lengths. Graphene was discovered in 2004 by researchers at Manchester University. For this great discovery, they won the Nobel prize in physics in 2010 [2]. Over the recent years graphene has been focused as a good research material due to its large surface area and high conductivity-based technological applications [3]. Due to its excellent outcomes from various experiments, it is used in a large number of fields like bio-sensing [4], drug delivery [5], catalysis [6], and energy storage [7].

This makes it suitable for a wide range of applications, like Li-ion batteries [8], thin film transistors [9], and solar cells [10, 11]. Till now, a large number of methods have been developed for the large-scale production of graphene and these methods include chemical vapor deposition [8], [12, 13], mechanical exfoliation [14, 15], aerosol pyrolysis [16], solvothermal methods [17] and chemical reduction methods [18, 19]. By the reason of cost-effective nature and good yield of RGO obtained from GO, the chemical reduction method is considered as the best method [20].

To prepare RGO from GO reducing agents like hydrazine, dimethyl hydrazine, hydroquinone, or sodium borohydride can be used. Still, due to these reducing agents' poisonous, non-environmentally friendly nature, they can exert some harmful effects during bio-related applications [21, 22]. Synthesis of RGO can also be done by using green methods. Among the green methods, phytoextracts like green tea [23], carrot roots [24], bacteria (*Escherichia coli*) [25], orange (*C.Sinensis peel*), cloves (*S. Aromaticum*), cherry (*P.Serrulate*) [26], salvia spinosa [27], *Hibiscus Sabdariffa L* [28], rose water [29], etc. can be used to synthesize reduced RGO. Synthesis of RGO can also be done by using the environmentally friendly method, in which RGO is prepared by UV irradiation of exfoliated GO nanosheets [30]. Aqueous phytoextracts like mango (*Mangifera indica L*) leaves extract and potato (*Solanum tuberosum L*) extract are good reducing agents to produce RGO from GO [31]. These phytoextracts are easily available, environmentally friendly, non-hazardous reducing agents to prepare RGO [25]. Mango and potato phytoextracts containing phenolic compounds like caffeic acid, chlorogenic acid, gallic acid, protocatechuric acid, salicylic acid, vanillic acid [32-36], etc., which have hydroxyl groups, use the reduction of oxygen functionality present in GO as a mild reducing agent [37, 38].

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Green methods are environmentally friendly and less hazardous in comparison to the chemical methods to prepare RGO from GO. However, still, there are some limitations of green methods like high time consumption [39], and poor stability [40-42] which are not favorable for obtaining a good yield of RGO.

EXPERIMENTAL

Synthesis of graphene oxide (GO) by modified Hummer's method

GO can be synthesized from graphite powder by using modified Hummer's method [43, 44]. Modified Hummer's method does not involve NaNO_3 but gives the yield of GO approx. equal to the usual Hummer method. The modified Hummer's method is eco-friendly because it eliminates the evolution of toxic gases like NO_2 , N_2O_4 [45], etc. In this method, 2 g of graphite powder is mixed with 50 ml of concentrated sulfuric acid while stirring constantly. The mixture is then cooled in an ice bath, which makes a suspension. Below 100°C , 6 g of KMnO_4 , which is an oxidizing agent, is slowly added to this suspension (caution: blast can occur if KMnO_4 is added quickly). Now the suspension is stirred at 25°C for 25 minutes followed by sonication in an ultrasonic bath for 8 minutes.

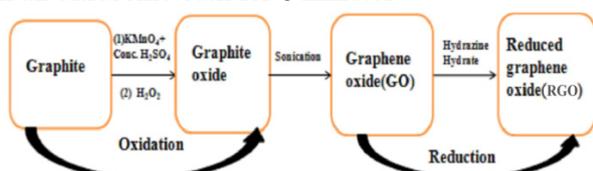


Fig. 1. General path for the synthesis of GO and RGO

After ultrasonication 250 ml of distilled water is introduced to the mixture with 10-fold repetition of the stirring and sonication process. Now 30 ml of H_2O_2 is introduced into the exfoliated graphite oxide obtained after ultrasonication of the dispersed solution for 1 hour. Ultrasonication of this content at 10000 rpm GO is prepared, which is washed by 2M HCl and distilled water until pH 7. The graphene oxide obtained in this way is dried at room temperature for 24 hours [46]. The general pathway for synthesizing GO and RGO from graphite powder is represented in Fig. 1 [46].

Preparation of reduced graphene oxide (RGO) through graphene oxide (GO)

Green synthesis to prepare RGO from GO is an environmentally friendly method, such as using various plant materials or bio-molecules as reducing

agent. These are eco-friendly and non-hazardous methods to prepare RGO from GO. For the green synthesis of RGO firstly a reducing agent containing phytoextract is prepared. Now, this phytoextract is mixed with GO prepared by a customized Hummer's method, by which the reducing agent present in the phytoextract causes the reduction of GO into RGO.

Green synthesis of reduced graphene oxide (RGO) from graphene oxide (GO) by using mango leave extract

For this purpose, fresh mango leaves (*Mangifera indica L.*) are washed and dried and then ground to obtain the powder form. This powder is placed in a conical flask and 100 ml of Millipore water is added, followed by stirring for 1 hour at 50°C by a magnetic stirrer until a homogenous mixture is obtained. This mixture is centrifuged and filtered by using Whatman 42 filter paper. Mango leaves extract prepared is added to the GO dispersion obtained from the ultrasonicated mixture of GO prepared by modified Hummer's method and deionized water (maintaining a 1:1 volume ratio of GO and phytoextract) and stirring is done for 12 hours at 60°C by using a magnetic stirrer. This reaction mixture is refluxed in an oil bath at $70\text{-}80^\circ\text{C}$ for 8 hours, as a result of which the brownish color of GO is converted into dark black color. After centrifuging and washing with deionized water and acetone, this black solution gives RGO, which is dried in a vacuum desiccator for 48 hours [31].

Green synthesis of reduced graphene oxide (RGO) from graphene oxide (GO) by using potato extract

For this purpose, at first thinly sliced potatoes are washed with hot distilled water, then sliced potato is taken in 100 ml of Millipore water and ground to convert it into potato paste. Now the mixture is centrifuged, and the supernatant liquid is collected as potato extract. Potato extract prepared is added to the GO dispersion obtained from the ultrasonicated mixture of GO prepared by the modified Hummer's method and deionized water (maintaining a 1:1 volume ratio of GO and phytoextract) and stirring is done for 12 hours at 60°C by using a magnetic stirrer. This reaction mixture is refluxed in an oil bath at $70\text{-}80^\circ\text{C}$ for 8 hours, as a result of which the brownish color of GO is converted into dark black color. At last, this dark-colored solution is centrifuged, washed with deionized water, and then cleaned with acetone to produce RGO, which is then dried for 48 hours in a vacuum desiccator [31].

Green synthesis of reduced graphene oxide (RGO) from graphene oxide (GO) by using S. Spinosa leaf extract

To prepare *S. Spinosa* leaf extract, *S. Spinosa* leaves are washed with distilled water and dried for five days in the shade. Now the dried leaves of *S. Spinosa* are ground with double distilled water in the grinder. Finally, this ground mixture is extracted using a Soxhlet extracting apparatus, as a result of which *S. Spinosa* leaf extract is obtained and stored at 4°C. The *S. Spinosa* leaf extract is mixed with GO suspension (which is made by mixing graphene oxide made by a modified version of Hummer's method and distilled water in a mixer) This mixture is stirred for 12 hours in an oil bath at 95°C. This changes the color of the solution and shows that RGO has formed. Now on centrifuging (at 10000 rpm for 10 minutes) and washing the top layer containing an aqueous solution of GO by de-ionized water, solid reduced RGO is obtained, which is dried and stored [27, 47].

Green synthesis of reduced graphene oxide (RGO) from graphene oxide (GO) by using Hibiscus Sabdarriffa L. extract

To obtain the *Hibiscus Sabdarriffa L.* extract, the powder form of the flower of *Hibiscus Sabdarriffa L.* plant is mixed with deionized water, heated and stirred on a magnetically stirred hot plate for 30 minutes. Now the mixture is filtered, and the filtrate is cooled at 25°C. to obtain *Hibiscus Sabdarriffa L.* extract which is mixed with a suspension of GO obtained from an ultrasonicated mixture of GO and deionized water. This mixture is stirred for 150 minutes using a mechanical stirrer under sonication by which the brown color of GO is changed into black which conforms to the formation of RGO [28].

Green synthesis of reduced graphene oxide (RGO) from graphene oxide (GO) by using green tea extract

In this method, about 1.5 g of GO powder is added to 150 ml of green tea extract and stirred for 72 hours. Now the sample mixture is diluted using deionized water and centrifuged twice at 5000 rpm for 15 minutes. Finally, solid RGO is obtained on filtration, which is dried in an oven at 80°C for 24 hours [45].

Green synthesis of reduced graphene oxide (RGO) from graphene oxide (GO) by using lemon juice

For this synthesis, lemon juice is extracted by squeezing a yellow lemon and centrifugation at

13000 rpm for 10 minutes. Now after filtration, the filtrate is obtained as lemon juice which is stored at 4°C for further use. The lemon juice is mixed with GO with sonication and the pH of the mixture is maintained at 12.3 with the help of 4 ml of aqueous NaOH solution. Now on stirring the mixture in an oil bath at 80°C for 2 hours, a black-colored mass is collected. This black-colored mass on centrifugation and washing by deionized water gives pure RGO after drying at 50°C for 24 hours, which is stored at 25°C [48].

Green synthesis of reduced graphene oxide (RGO) from graphene oxide (GO) using Plectranthus amboinicus leaf extract

First, *Plectranthus amboinicus* leaves are washed through running tap water, then with deionized water. The *Plectranthus amboinicus* leaves are dried at 50°C using a hot air oven and converted into powder form using mortar and pestle. Now the *Plectranthus amboinicus* leaf powder is mixed with deionized water and the mixture is refluxed for 2 hours. Finally, on filtration using Whatman No 1 filter paper, the leaf extract of *Plectranthus amboinicus* is obtained. The GO prepared previously is mixed with *Plectranthus amboinicus* leaf extract in 2:1 ratio and ultrasonicated for 1 hour. This mixture is placed in a stainless-steel autoclave for 12 hours at 100°C. The color change from brown to black indicates the reduction process to produce RGO from GO. This solution is washed by sonication at 9000 rpm, initially using deionized water and then ethyl alcohol. This sample is dried at 60°C in a vacuum oven to obtain RGO [49].

Green method for reduction of GO into RGO by hydrothermal treatment

For the purpose of preparing RGO from GO, at first GO with de-ionized water is sonicated with the help of ultrasonic bath cleaner about 30 minutes by which a homogenous yellow-brown dispersion is obtained. This yellowish-brown mixture is heated in an autoclave for 4 hours at 150°C, and then RGO is obtained by filtering and washing it with deionized water and then drying it in a vacuum oven at 60°C for one night [50].

Other than the above green synthesis to prepare RGO from GO, some other plant extracts like leaf extract, fruit extract, flower extract, peel extract, bark/stem extract, seed extract, root extract, and pollen grain extract are also used as reducing agents to make RGO from GO using green methods. Table 1 [51] lists all of these plant extracts as green reducing agents (1.1 to 1.8).

Table 1. Leaf extracts for the reduction of GO into RGO

S.No	Botanical Name	Reduction Method	S.No	Botanical Name	Reduction Method
1	<i>Colocasia esculenta</i>	Stir, reflux	21	<i>Ocimum sanctum</i>	Reflux
2	<i>Mesua ferrea L.</i>	Stir, reflux	22	<i>Anacardium occidentale Linn</i>	Stir
3	<i>Spinacia oleracea</i>	Stir	23	<i>Eucalyptus</i>	Reflux
4	<i>Ginkgo biloba</i>	Stir	24	<i>Ocimum sanctum L.</i>	Stir
5	<i>Eichhornia crassipes</i>	Reflux	25	<i>Stigma phyllonovatum</i>	Stir
6	<i>Pulicaria glutinosa Prunus serrulate Magnolia Kobus Platanus orientalis</i>	Reflux	26	<i>Euphorbia cheiradenia Boiss</i>	Reflux
7	<i>Diopyros kaki Pinus desiflora Acer palmatum Ginkgo biloba</i>	Reflux	27	<i>Mentha arvensis</i>	Reflux
8	<i>Azadirachta indica</i>	Stir, reflux	28	<i>Tribulus terrestris Mentha piperita</i>	Autoclave
9	<i>Euphorbia wallichii</i>	Reflux	29	<i>Urtica dioica L.</i>	Stir
10	<i>Spinacia oleracea Ficus religiosa</i>	Reflux	30	<i>Euphorbia milli</i>	Stir
11	<i>Artemisia vulgaris</i>	Reflux	31	<i>Thymbra spicata</i>	Reflux
12	<i>Paederia foetide L.</i>	Stir	32	<i>Euphorbia heterophylla (L.)</i>	Reflux
13	<i>Platanus orientalis</i>	Reflux	33	<i>Memecylonedule</i>	Water bath
14	<i>Oleae uropaea</i>	Water bath	34	<i>Elaeis guineensis</i>	Reflux
15	<i>Melissa officinalis L.</i>	Stir	35	<i>Zataria multiflora</i>	Reflux
16	<i>Annonas quamosa</i>	Reflux	36	<i>Azadirachta indica</i>	Stir
17	<i>Eucalyptus</i>	Water bath	37	<i>Telfairia occidentalis</i>	Stir
18	<i>Camellia sinensis</i>	Reflux	38	<i>Murray akoenigii</i>	Autoclave
19	<i>Aloe vera</i>	Reflux	39	<i>Acalypha indica</i>	Autoclave
20	<i>Aloe vera (L.) Burm.f.</i>	Reflux	40	<i>Erythrina senegalensis</i>	Reflux

Table 2. Fruit extracts for the reduction of GO into RGO

S.No	Botanical Name	Reduction Method	S.No	Botanical Name	Reduction Method
1	<i>Cocos nucifera L.</i>	Oil bath	6	<i>Zante currants</i>	Water bath
2	<i>Punica granatum</i>	Stir	7	<i>Phyllanthus emblica</i>	Reflux
3	<i>Ficu scarica</i>	Stir	8	<i>Phyllanthus emblica</i>	Autoclave
4	<i>Vitis vinifera</i>	Reflux	9	<i>Fragaria ananassa</i>	Reflux
5	<i>Terminalia bellirica</i>	Water bath	10	<i>Helicteres isora</i>	Sonication

Table 3. Flower extracts for the reduction of GO into RGO

S. No	Botanical Name	Reduction Method
1	<i>Tagetes erecta</i>	Stir
2	<i>Rosa damascena</i>	Autoclave
3	<i>Syzygium aromaticum</i>	Reflux
4	<i>Chrysanthemum morifolium</i>	Water bath

Table 4. Peel extracts for the reduction of GO into RGO

S. No	Botanical Name	Reduction Method
1	<i>Citrus sinensis</i>	Stir
2	<i>Sugar cane bagasse</i>	Stir
3	<i>Citrus hystrix</i>	Stir

Table 5. Bark / stem extracts for the reduction of GO into RGO

S. No	Botanical Name	Reduction Method
1	<i>Cinnamomum verum</i>	Reflux
2	<i>Saccharum officinarum</i>	Autoclave
3	<i>Cinnamomum zeylanicum</i>	Reflux
4	<i>Alstonia scholaris</i>	Stir

Table 6. Seed extracts for the reduction of GO into RGO

S. No	Botanical Name	Reduction Method
1	<i>Phaseolus aureus L.</i>	Stir
2	<i>Glycine max (L.) Merr.</i>	Stir
3	<i>Vitis vinifera</i>	Stir
4	<i>Terminalia chebula</i>	Reflux

Table 7. Root extracts for the reduction of GO into RGO

S. No	Botanical Name	Reduction Method
1	<i>Daucus carota subsp. sativus</i>	Stir
2	<i>Salvadora persica L. (miswak)</i>	Stir
3	<i>Allium cepa (onion)</i>	Stir
4	<i>Daucus carota</i>	Stir
5	<i>Zingiber officinale Roscoe</i>	Reflux

Table 8. Pollen grain extract for the reduction of GO into RGO

S. No	Botanical Name	Reduction Method
1	<i>Peltophorum pterocarpum</i>	Stir heat-treated in Ar gas

Characterization of graphene oxide (GO) and reduced graphene oxide (RGO)

With the help of XRD, UV-VIS, FTIR, TGA, and FESEM analysis the formation of GO and RGO was confirmed in the following way.

X-ray diffraction analysis

When the XRD patterns of GO and RGO are taken with an x-pert powder diffractometer using a copper rotating anode and an incident beam with a wavelength of 154 nm, the d-spacing (according to Bragg's equation $n\lambda = 2d\sin\theta$) of the most intense peak from the (001) plane is 1.45 nm for GO and 379 nm for RGO (Fig. 2) [46]. This occurs by reason of hydroxyl, epoxy, and carbonyl groups present in GO [44] and in RGO d-spacing is decreased due to the smaller number of oxygen containing functionalities

[52]. This observation will indicate the reconstitution of the sp^2 framework on reduction [46].

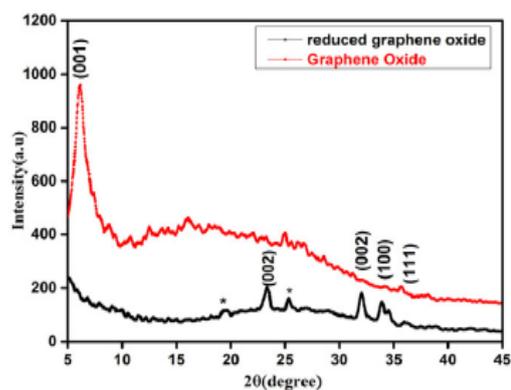


Fig. 2. X-ray diffraction pattern of GO and RGO

UV-visible spectroscopy analysis

When GO is obtained after the reduction of graphite, then oxygen atoms are attached to the graphene layer. Because of this, polarity is increased. This results in water's increasing solubility, which can be observed by a color change from yellow to brown. The brown-colored solution (GO solution) exhibits absorption maxima of different intensity according to the concentration of GO formed [53]. The absorption maximum for GO is 225 nm in the oxidized material. When UV-visible absorption spectra were analyzed, GO and RGO exhibited absorption peaks at 226 nm and 257 nm, respectively (Fig. 3) [53]. This shift in UV-visible absorption maxima conforms to the formation of RGO, as well as the recovery of the π -conjugated structure of graphene after the reduction process of GO into RGO. This result also matches with the other reported literature [54].

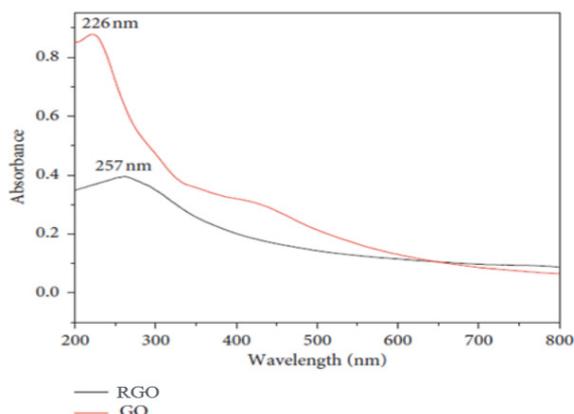


Fig. 3. UV-visible spectra of GO and RGO.

Fourier transform infrared spectroscopy analysis

Fig. 4 [55] represents the FTIR spectra of graphite oxide (GrO) and GO. Both GrO and GO exhibit the FTIR spectral peaks at 1050 cm^{-1} (stretching peak of C-O bond), 1310 cm^{-1} (peak of C-OH bond), 1630 cm^{-1} (stretching peak of C=C), 1740 cm^{-1} (stretching peak of C=O) and 3320 cm^{-1} (stretching peak of -OH group). All these peaks indicate the presence of alkene, hydroxyl, and carbonyl functional groups in the GrO and GO, which conform to the synthesis of GO [54]. Both GrO and GO exhibiting the same FTIR spectra means that both these have the same skeleton. There is only one difference that GO is the exfoliated sheet of GrO.

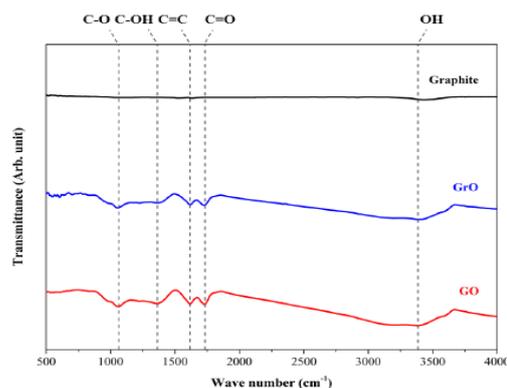


Fig. 4. FTIR spectra of graphite, GrO, and GO

RGO is prepared from GO by a reduction process. Fig. 5 [55] represents the FTIR spectra of RGO, as well as the effect of the functional groups on the annealing process of GO in the oven.

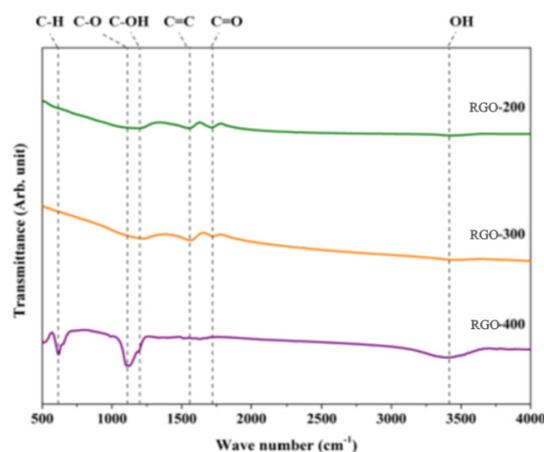


Fig. 5. FTIR spectra of RGO under annealing conditions of GO

The absorbance of oxygen-related functional groups is higher in Fig. 4 compared to Fig. 5. This indicates the formation of RGO by the reduction process of GO [45, 55].

Thermogravimetric analysis

For the measurement of thermal stability of GO and RGO, TGA measurement was used in the temperature range between 0°C and 800°C in nitrogen atmosphere, as shown in Fig. 6 [48]. This TGA of GO and RGO shows that weight loss in RGO is less than in GO under different temperature conditions (Fig. 6). This will indicate the smaller number of oxygen containing functionalities in RGO with respect to GO. This type of result in weight loss for GO and RGO agrees with the reported work of Gan *et al.* [56].

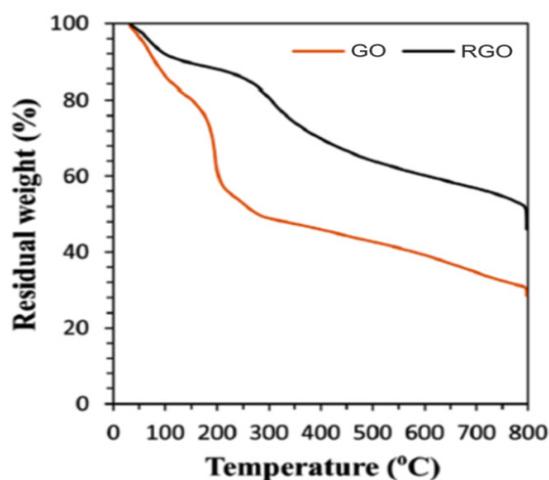


Fig. 6. TGA spectra of GO and RGO

Field emission scanning electron microscope analysis

This analysis is used to study the surface morphology of GO and RGO. This is observed in Fig. 7 [46]. It indicates the highly wrinkled structure of RGO in comparison to GO, which concludes that the surface of GO gets crimped on converting into RGO because of eliminating oxygen-containing functional groups from the surface.

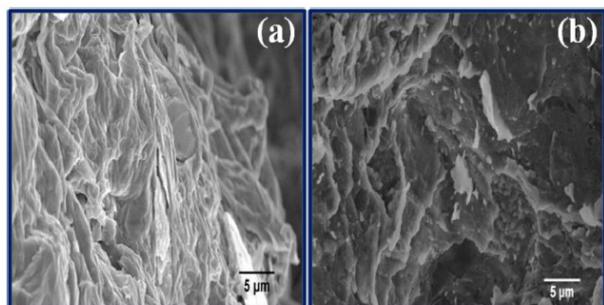


Fig. 7. FESEM image of GO (a) and RGO (b)

CONCLUSIONS

GO obtained from graphite powder by modified Hummer's method can be reduced by using chemical processes, as well as green methods to prepare the RGO, but from the different reported results, green methods using different plant extracts are preferred over the chemical methods due to the environmentally friendly nature of green methods. Green methods are preferred, particularly during the biologically related application of RGO, because poisonous or hazardous chemicals involved or generated by using chemical methods cause harmful effects. Since the yield of RGO prepared using chemical reduction methods is higher than the yield obtained using green methods, in this respect, green methods are not considered suitable for preparing RGO.

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