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GREEN SYNTHESIS AND CHARACTERIZATION OF REDUCED GRAPHENE OXIDE

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The distinctive chemical, physical, thermal and mechanical properties of graphene made it widely recognized material in wide-ranging field of science and technology. Generally, the synthesis of graphene or reduced graphene oxide (rGO) requires two main steps. The first step involves the oxidation of graphite to graphene oxide (GO) and in the second step, reducing agents or reductants contribute to the reduction of GO to form rGO. A large number of reducing agents have been applied to synthesize rGO such as hydrazine, hydroxyl amine, sodium borohydride, etc. However, the hazardous nature of such reducers created a space for the research on green reducing agents for rGO synthesis. This study introduces the low-cost green synthesis of rGO via green reducing agents such as eucalyptus hybrid extract, thiourea, lemon extract and starch. Among all the green reductants, eucalyptus hybrid extract exhibited the remarkable reduction of GO, as confirmed by VU-visible spectroscopy, Fourier transform infrared spectroscopy, and X-ray diffraction results. The absorption peak of rGO-eucalyptus is appeared at 272 nm, whereas the d-spacing between layers is determined to be 0.364 nm. The obtained band gap of rGO-eucalyptus (2 eV) is found less as compared with other reducing agents such as thiourea, lemon extract and starch. The stretching vibration of oxygen functionalities appeared in FTIR of GO, is disappeared after reduction with eucalyptus extract. The flavonoid components of eucalyptus extracts are antioxidant in nature and hence, work as reducing agents.

Keywords: eucalyptus hybrid extract, flavonoid, graphene oxide, green reduction, reductant, starch.

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Introduction

Graphene oxide (GO) is an exceptional material, which can be regarded as a sole monomolecular layer of graphite having several oxygenated functionalities such as carboxyl, carbonyl, hydroxyl and epoxide groups [1,2]. The reduction of GO results in the formation of reduced graphene oxide (rGO) [3]. In general, rGO looks like graphene, however the presence of some heteroatoms, residual oxygen and structural defects, differentiates it from GO. Both materials have been applied in energy storage, polymer composite materials, nanocomposite

materials, catalysis, water treatment, biomedical applications, as a surfactant and with some intersections among these areas [4–6]. As the graphene based materials have a wide range of applications, their demand is too high. Therefore, the high quality and low-cost production of graphene based material is a challenging issue [7].

A number of techniques have been introduced to synthesis graphene from graphite including thermal exfoliation, liquid phase exfoliation, micromechanical cleavage, non-catalytic synthesis, epitaxial growth, scotch tape method, vacuum thermal annealing, chemical vapor deposition, direct ultrasound sonication, carbon nanotubes cutting, and reduction of GO [2,6]. Generally, the reduction of GO involves different chemical reducing agents such as hydroxylamine, sodium borohydride, hydroquinone, hydrazine, etc. [3]. Although the chemical reduction is a widely adopted method, the toxic nature of the reductants is a major disadvantage of this method. The traces of these hazardous reductants could have an adverse impact, predominantly during biological applications including drug delivery and catalysis.

Other alternative methods include the thermal and microwave reduction of GO [3]. Although thermal treatment is found effective to eliminate the oxygen-containing functionalities, this method involves the complex operational setup and consumes the higher amount of energy. Electrochemical reduction of GO is also a quick and harmless method as compared with chemical reduction. In this method, the reduction is achieved in an electrochemical cell by means of potential, which directs the reduction progression with electrons as reductants [3]. However, this method is incapable of healing the vacancies and defects came from the precursor GO.

The objective of this study is to synthesize the low-cost green synthesis of rGO using green reducing agents including eucalyptus hybrid extract, thiourea, lemon extract and starch. Application of green reductants has a great potential to eliminate the environmental and health threats as they are free of toxicity, carcinogenicity, and corrosion. The synthesized rGO material is characterized by several advanced techniques. This eco-friendly and cost-effective method offers a forthright reduction approach to synthesize rGO at large-scale. Furthermore, this study provides a pathway for the researches to explore the potential application of other phytoextracts in green synthesis of rGO. The combination of rGO with other inorganic materials can form hybrid materials with specific properties including high conductivity, planar geometry, large surface area, fascinating carrier transport possessions, and strong magnetism that can be used for wide range applications.

Material and methods

Chemicals and reagents

All the reagents and chemicals were of analytical grade and used without any further purification. Graphite powder, sulfuric acid (98%), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), sodium nitrate ($NaNO_3$), nitric acid (65%), hydrochloride acid (HCl) and thiourea (CH_4N_2S) were obtained from Merk Chemicals. Eucalyptus, lemon and starch were obtained from the domestic market.

Synthesis of GO and rGO

Primarily, GO is synthesized by oxidation of graphite powder in a mixture of concentrated $KMnO_4$ and H_2SO_4 solutions via modified Hummer's method. 250 mg GO powder is dispersed in 100 mL deionized water. The mixture is sonicated for 2 h and allowed to stir overnight on hot plate. Later, the mixture is centrifuged at 3000 rpm for 30 min. The obtained GO dispersed solution is used to prepare rGO. Four different reductants were used for the reduction of GO. Equal volume of lemon extract and GO solution are mixed together, allowed to stir for 5 min and then kept for two days to accomplish the reaction. Subsequently, the obtained product is washed thoroughly with ethanol and deionized water. The product is dried overnight at room temperature and termed as rGO-Lemon. Similar method is used for the synthesis of rGO-Eucalyptus hybrid using extract of eucalyptus leaves. To synthesize the rGO-Thiourea, 0.8 g of thiourea is added into the 20 mL of GO and the mixture is heated at 95^{0}C under continuous stirring. The obtained material is washed with deionized water and ethanol, and finally dried at room temperature. To obtain rGO-Starch, 15 mL of GO dispersed solution and 30 mL starch solution were mixed and sonicate for 150 min. Afterwards, the mixture is heated at 95^{0}C for 5 min until the thick dense shape is appeared. The product is dried at room temperature.

Instrumentation

The synthesized rGO material was characterized by number of characterization methods. UV-vis spectroscopic method was used to examine the bond transitions. The band gap energies were determined via Kubelka–Munk function. The Kubelka-Munk theory designated the behavior of light passing through a light scattering sample. The band gap was determined via plotting a graph of the square product of the energy and absorption coefficient versus energy. The band gap can be found by prolonging the straight

line from the straight part of the graph joining the x-axis. The crystalline structure of the synthesized rGO materials was examined with X-ray diffraction (XRD). The interlayer spacing was determined using Bragg's law. The functional groups in rGO were identified with Fourier transform infra-red (FTIR).

Results and discussion

XRD study

Figure 1 shows the XRD patterns of the GO synthesized via modified Hummer's method. The broad peak found at $2\theta=10.6^0$ corresponding to the 002 plane (d-spacing of 0.93 nm) was appeared in consistence with reported study [8]. The d-spacing (interlaying distance) of the sample is determined by Bragg's law. The interlayer distance and the peak position of the GO significantly depend on the extent of oxidation of graphite. As the oxidation introduces the oxygen functionalities (like epoxy and hydroxyl) within the GO, it increases the interlayer distance in GO [9]. A study also reported the intercalation of H_2O molecule as one of the reasons for large d-spacing when the GO is prepared with modified Hummers method [10].

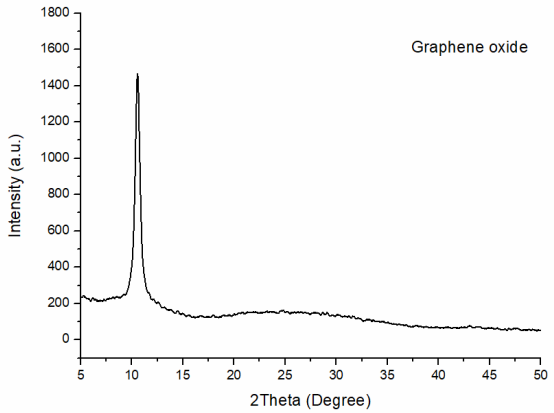

Fig. 1. XRD pattern of the GO

Followed by the reduction of GO using green reductants, a prominent change is recognized in the XRD pattern of rGO. A visible shift in the peak position is observed for all the rGO materials (Fig. 2). The characteristic peak of rGO is appeared at $2\theta=24.4^0$, 22.0^0, 18.8^0, and 16.8^0 when the GO samples are reduced by eucalyptus hybrid extract, thiourea, lemon extract and starch, respectively. Subsequently, the d-spacing is estimated 0.364, 0.403, 0.472, and 0.527 nm for the rGO-Eucalyptus hybrid, rGO-Thiourea, rGO-Lemon, and rGO-Starch, respectively. It is noteworthy that the angle of

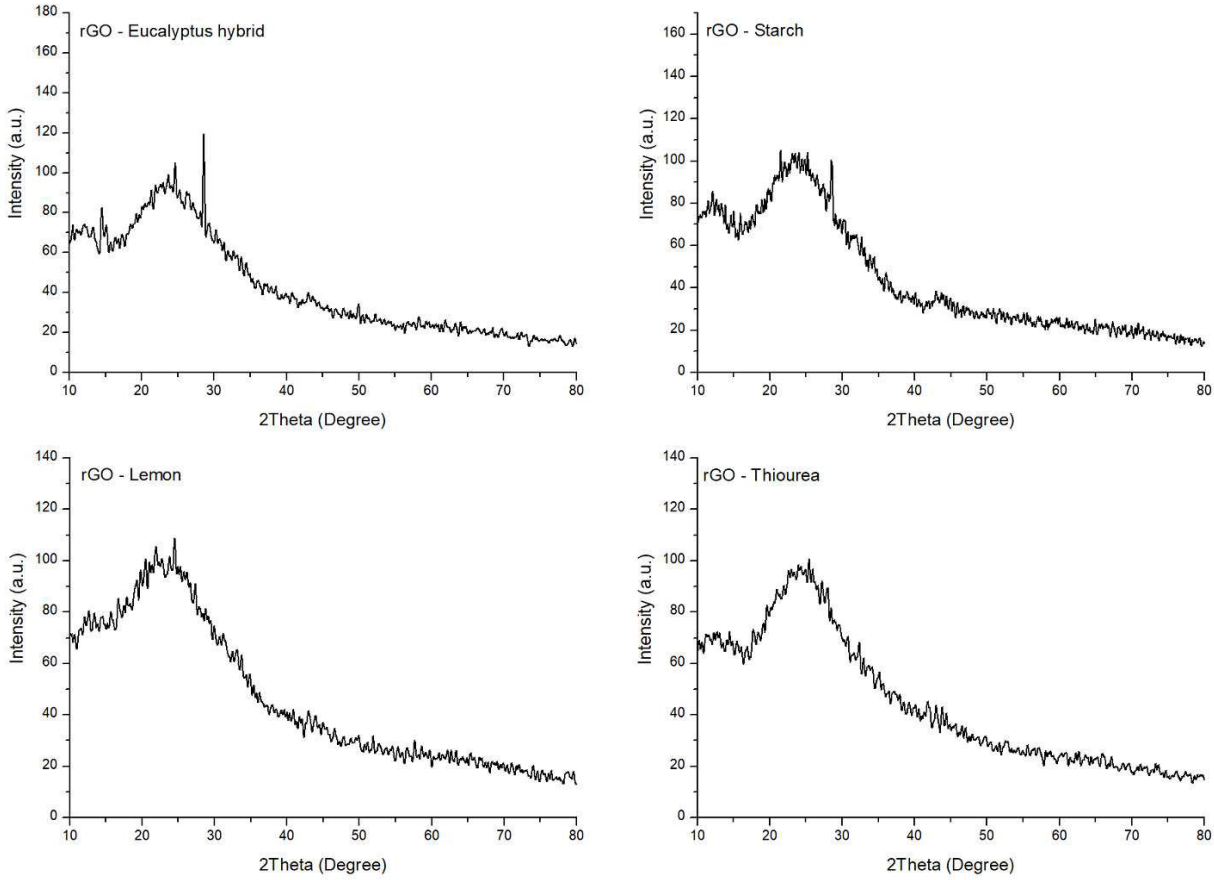

Fig. 2. XRD pattern of the all four types of rGO material

characteristic peaks is increased after reduction that incited a decrease in d-spacing between the GO layers. This is happened due to the exclusion of oxygen functional groups and the consequent reinstatement of the C=C bond within rGO. It is worth mentioning that no representative peak of GO at 10.6^0 can be found in the XRD spectra of rGO samples signifying that all of GO has changed to rGO.

UV-vis spectroscopic study

UV-vis spectroscopy is the reflectance spectroscopy or absorption spectroscopy that is active in ultraviolet to visible region. It results in the electron transition between ground and high energy states. UV region expands to the wavelength of 190–380 nm while visible region corresponds to the 380–750 nm. The UV-vis spectrum of GO and rGO materials are presented in Fig. 3. In case of GO, a broad absorption peak at 223 nm is observed that is subjected to the $\pi \rightarrow \pi^*$ transition of carbon–carbon double bond. The peak is originated due to the sp^2 hybridization of the material and associated units of carbon chain such as C–C, C–O and C=O bonds [11]. Furthermore, the shoulder from 302 nm, signifies the $\pi \rightarrow \pi^*$ transition due to the existence of oxygen functionalities [12].

In case of rGO, the adsorption peaks were identified at 272, 266, 262, and 256 nm for rGO-Eucalyptus hybrid, rGO-Thiourea, rGO-Lemon, and rGO-Starch, respectively. The peak of rGO materials is observed at higher region as compared with GO that refers to the higher absorbance of UV light due to the decreasing band gap. The significant shift in the UV-vis adsorption spectra also signifies the reinstatement of sp^2 hybridization and the high electron concentration [12]. Considering the higher shift in the UV-vis adsorption band of rGO samples, it can be stated that the eucalyptus hybrid extracts, thiourea, lemon extract and starch appeared fine for the reduction of GO [8].

Figure 4 shows the band gap energies of the synthesized GO and rGO as determined by applying Kubelka-Munk function. The estimated band gap energy for GO was 3.42 eV that is shifted to 2.00, 2.40, 2.63 and 2.78 eV after reduction with eucalyptus hybrid, thiourea, lemon, and starch, respectively. The observed shift in absorption peak is the sign of the GO reduction and the formation of rGO material. This finding is appeared in fine agreement with other studies on GO and rGO [1,2]. A study reported GO reduction using chemical agents including NH_4OH, fructose, glucose and ascorbic acid, and found substantial decrease in band gap [2]. Another study reported the direct proportionality between the concentration of epoxide functionalities on the surface and the band gap energies [13]. Other oxygen functionalities such as hydroxyl and carboxyl groups did not exhibit any significant effect on band gap energies.

FTIR study

The FTIR spectra of GO, rGO-Eucalyptus hybrid, rGO-Thiourea, rGO-Lemon, and rGO-Starch ares presented in Fig. 5. The peak at 3600 cm^{-1} indicates the stretching of the O–H bond due to the presence of hydroxyl group (phenol) in GO. The C–H bond is represented by a peak at 2972 cm^{-1}, whereas the peak at 2332 cm^{-1} is assigned to the stretching of the –C≡C– bond. The stretching mode of vibration for the –C=C– bond is signified by a peak at 1742 cm^{-1}. The peak at 1368 cm^{-1} corresponds to the carboxyl group (O=C–OH), and the peak at 1208 cm^{-1} shows the vibration mode of epoxide (C–O–C). Followed by reduction with eucalyptus hybrid, thiourea, lemon, and starch, a momentous change in FTIR spectra is observed for all the materials. A significant decrease is observed in the intensity of bond associated with hydroxyl group, which is the indication of active reduction of GO [7,14]. The FTIR pattern of rGO-Eucalyptus hybrid exhibited greater decline in stretching mode of vibrations for oxygen functionalities in of 2800 to 4000 cm^{-1} region as compared with other rGO materials. The higher magnification of FTIR pattern in the range of 3000 to 4000 cm^{-1} exhibited a prominent difference between GO and rGO samples. The stretching vibration of oxygen functionalities appeared in this region for GO, is disappeared or significantly decreased after reduction. It clearly confirms the reduction of GO in to rGO.

Role of active components of plant extract in reduction

Some other studies also reported the reduction of rGO using extracts of several plant extracts. It is noteworthy that the active components of plant extracts play a significant role in reduction. For instance, the citric acid is a main active component of lemon that plays a role of reducing agent. On the other hand, the leaves of eucalyptus contain several flavonoids such as tricetin (5,7,3',4',5'-pentahydroxyflavone), myricetin (3,5,7,3',4',5'-hexahydroxyflavone), quercetin (3,5,7,3',4'-pentahydroxyflavone), kaempferol (3,5,7,4'-tetrahydroxyflavone), and luteolin (5,7,3',4'-tetrahydroxyflavone). The flavonoid compounds act as antioxidants and the antioxidant properties of active components of eucalyptus leaves have been explored in earlier study [15]. As antioxidants are considered reducing agents, the active ingredients of eucalyptus contributed

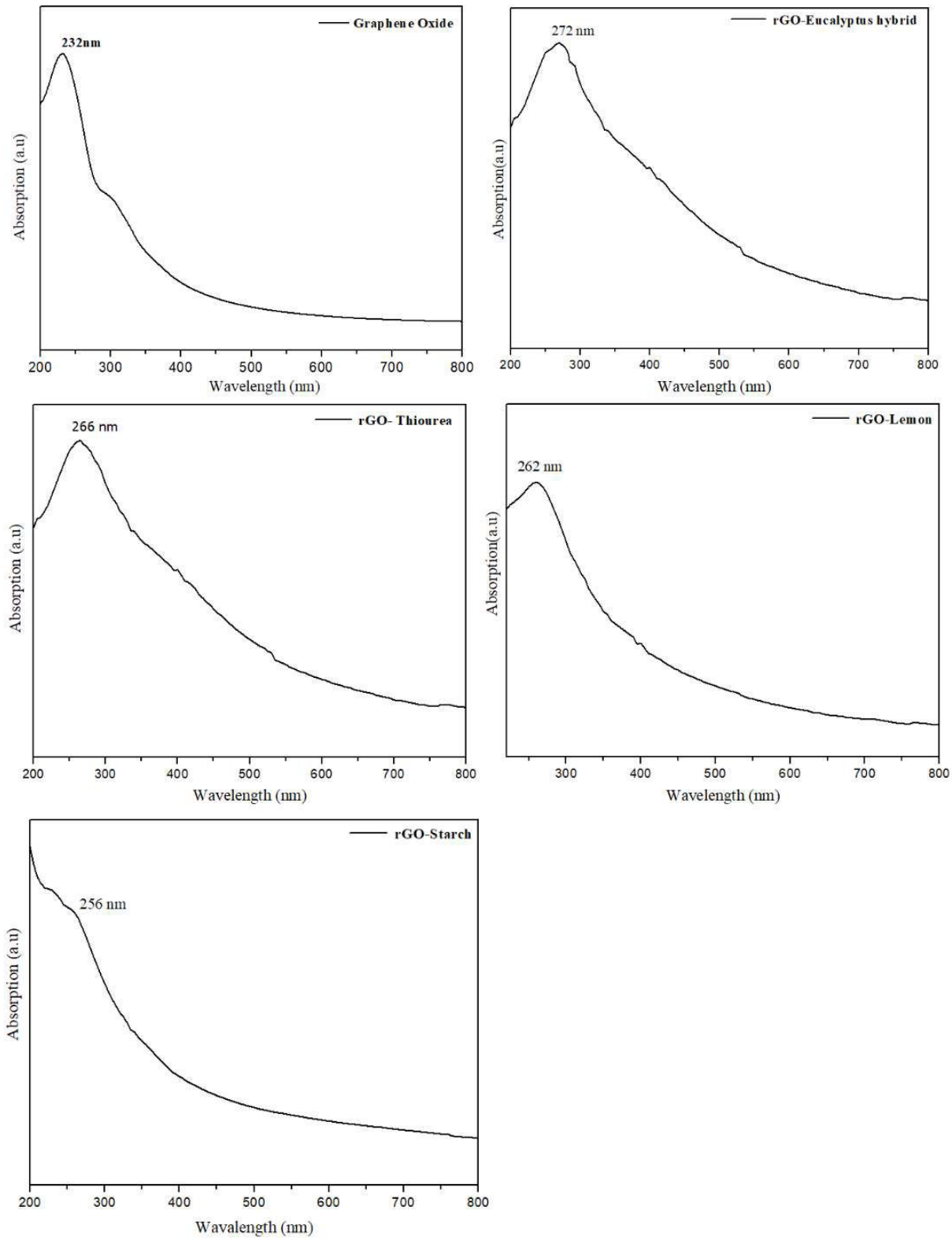

Fig. 3. The UV-Vis spectrum of GO, rGO-Eucalyptus hybrid, rGO-Thiourea, rGO-Lemon, and rGO-Starch

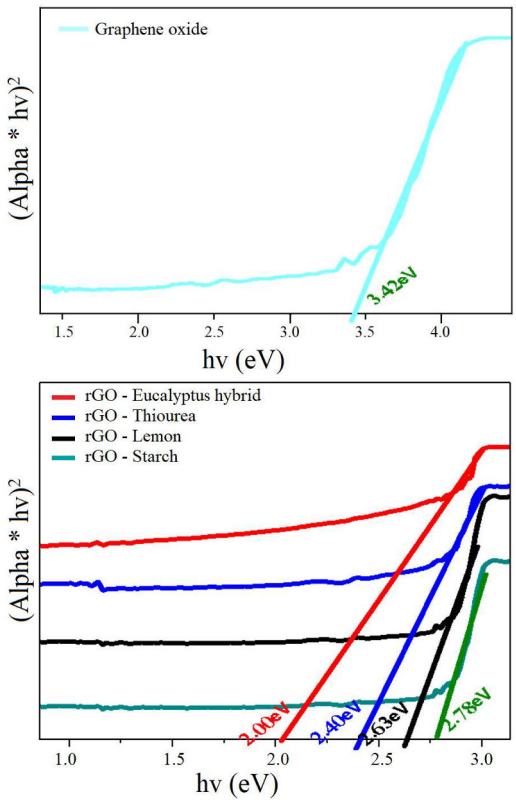

Fig. 4. Band gap energies of GO, rGO-Eucalyptus hybrid, rGO-Thiourea, rGO-Lemon, and rGO-Starch

significantly in reduction of GO.

Conclusions

In summary, eucalyptus hybrid extract, thiourea, lemon extract and starch extract exhibited significant potential as green reductants for the reduction of GO. As compared with other green reductants, the eucalyptus hybrid extract exhibited higher potential for the reduction of GO. The UV-vis absorption peak of rGO-Eucalyptus is found at 272 nm, which was the greater among all of other rGO materials. Moreover, the minimum value of d-spacing (0.364 nm) and band-gap (2 eV) were determined for the rGO-Eucalyptus. The flavonoid components of plant extracts are antioxidant in nature and hence, work as reducing agents. The excessive availability of ecofriendly and cost effective reducing agents makes them suitable for applying in large-scale production of rGO.

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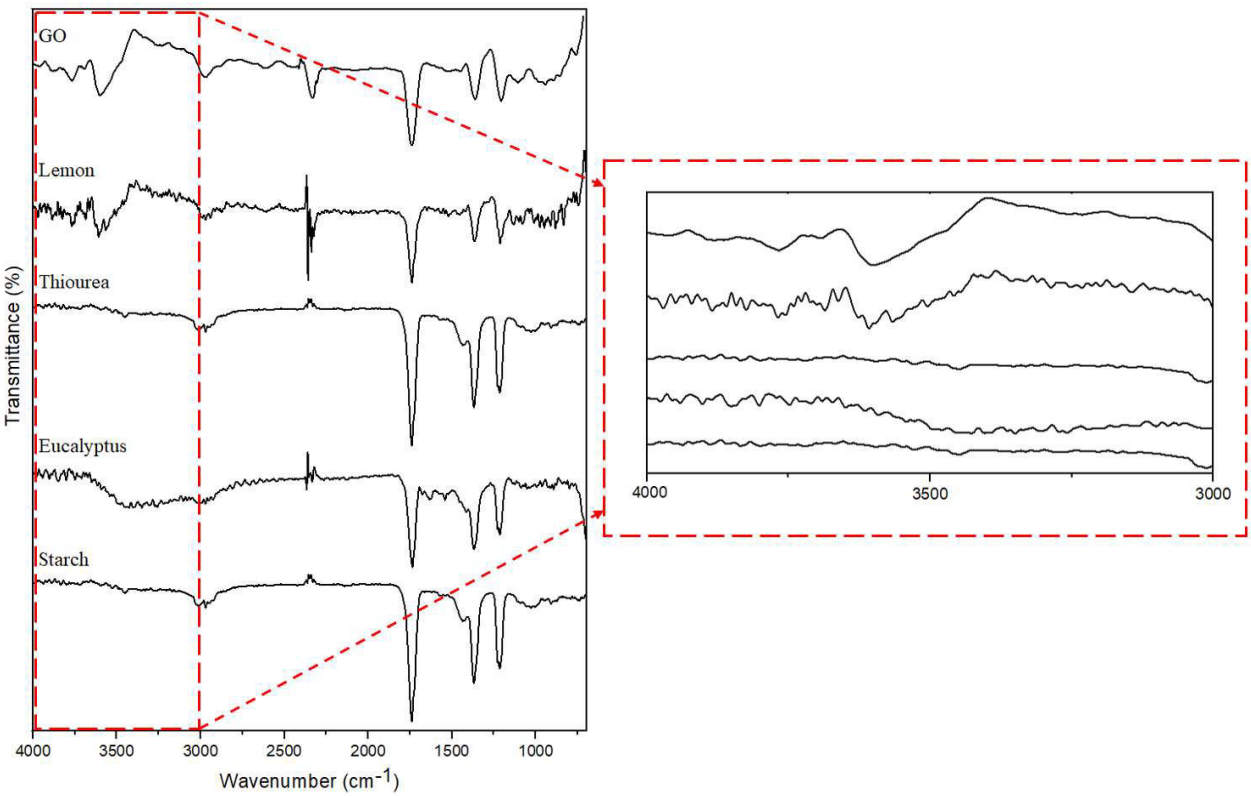

Fig. 5. FTIR spectra of GO, rGO-Eucalyptus hybrid, rGO-Thiourea, rGO-Lemon, and rGO-Starch

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ЗЕЛЕНИЙ СИНТЕЗ І ХАРАКТЕРИСТИКА ВІДНОВЛЕНОГО ОКСИДУ ГРАФЕНУ

Мухаммад Хак Наваз, Нафіс Ікбал, Рамла Рехман, Джун Вей Лім, Мухаммад Кашіф Шахід

Відмінні хімічні, фізичні, термічні та механічні властивості зробили графен широко визнаним матеріалом у різноманітних галузях науки й техніки. Як правило, синтез графену або відновленого оксиду графену (rGO) вимагає двох основних етапів. Перший етап включає окислення графіту до оксиду графену (GO), а на другому етапі відновники або відновники сприяють відновленню GO з утворенням rGO. Велика кількість відновників була застосована для синтезу rGO, такі як гідразин, гідроксиламін, борогідрид натрію тощо. Однак небезпечна природа таких відновників створила простір для дослідження зелених відновників для синтезу rGO. Це дослідження становить недорогий зелений синтез rGO за допомогою зелених відновників, таких як екстракт гібриду евкаліпта, тіосечовина, екстракт лимона та крохмаль. Серед усіх зелених відновників гібридний екстракт евкаліпта продемонстрував значне зниження GO, що підтверджено результатами УФ-видимої спектроскопії, інфрачервоної спектроскопії з перетворенням Фур'є та результатами рентгенівської дифракції. Пік поглинання rGO-евкаліпта спостерігається при 272 нм, тоді як d-відстань між шарами становить 0,364 нм. Отримана ширина забороненої зони rGO-евкаліпта (2 еВ) менша порівняно з іншими відновниками, такими як тіосечовина, екстракт лимона та крохмаль. Вібрація розтягування кисневих функціональних груп, яка з'явилася у інфрачервоних спектрах з перетворенням Фур'є GO, зникла після відновлення екстрактом евкаліпта. Флавоноїдні компоненти екстрактів евкаліпта є антиоксидантами за своєю природою і, отже, працюють як відновники.

Ключові слова: екстракт евкаліпта гібридного, флавоноїд, оксид графену, зелене відновлення, відновник, крохмаль.

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