



Gamma Radiation Assisted Green Reduction of Graphene Oxide by Doum Palm (Hyphaene Thebaica) Fruit Powder.

Eman O. Taha^{1*}; H. A. Ashry²; H. Abdelsalam³; M. M. Atta²

¹Petroleum Applications Department, Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt.

²Radiation Physics Department, National Center for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority, Cairo, Egypt.

³Theoretical Physics Department, National Research Centre, Cairo, Egypt.



CrossMark

Abstract

Due to the wide range of graphene applications, there is still a need for a simple, low-cost, and scalable graphene synthesis technique. This work describes a facile, cost-effective, and green method for reducing graphene oxide (GO) using doum palm (Hyphaene thebaica) fruit powder. This method is based on the radiolysis of GO solution containing doum powder under γ -irradiation instead of alcohol essentially used in γ - derived reduced GO. As a natural antioxidant, doum powder acts as a scavenger to oxidative species produced during irradiation. Fourier transform infrared spectroscopy (FTIR) confirmed the removal of most oxygen functional groups from GO and conjugation between doum and derived reduced graphene oxide (DRRGO). From X-ray powder diffraction (XRD), the GO sharp peak disappeared and was replaced by a wide broad peak. X-ray photoelectron spectroscopy (XPS) outcomes revealed an increase in the (C/O) ratio in DRRGO compared to GO. Also, the C-C peak intensity ratio to the C-O peak intensity in the C1s region was increased from 0.58 in GO to 1.8 in DRRGO. The higher defect level of DRRGO compared to GO was deduced by Raman spectroscopy. Furthermore, the reduction effect on GO morphology was studied by High-resolution transmission electron microscopy (HRTEM) and Field emission scanning electron microscopy (FESEM). The thermal stability of DRRGO was higher than that of GO, as revealed by Thermogravimetric analysis (TGA). These findings illustrate that this method is promising for the eco-friendly and mass production of nanoscale bio-synthesized oxides conjugated to reduced GO for biological applications.

Keywords: Doum palm; Graphene oxide; Gamma radiation; green reduction;

1. Introduction

The stunning physical properties of graphene and its derivatives made them widely used in many industrial, medical, and environmental applications [1-4]. Reduced graphene oxide (RGO) is one of the graphene derivatives that have a great research interest due to its excellent optical, electrical, and chemical properties [5]. It has been used in huge numbers of applications such as sensors [6], supercapacitors [7], solar cells [8], drug delivery [9], batteries [10], and biomedical [11]. The preparation of RGO implies two steps: first, one converts graphite to graphene oxide (GO) by strong oxidation agents, then the second step is reduction GO [12]. There are different methods for graphene oxide (GO) reduction such as chemical [13], radiation [14], thermal [15], and electrochemical [16]. The chemical reduction of GO is the most common method due to

its easiness, large-scale production, and reliability [5]. Numerous reducing agents such as hydrazine [17], sodium hydrosulfite [18], sodium borohydride [19] were used for the chemical reduction of GO. The usage of such toxic agents implies harmful effects on the environment and in bio-applications such as drug delivery [5, 20]. Moreover, creating C-N bonds in RGO produced with hydrazine is difficult to eliminate and restricts the restoration of sp² conjugation. Additionally, microorganisms were employed for reduced GO, but these reducing agents cause contamination of produced reduced graphene; thus, further washing and purification are needed [21]. Thus, researchers recently have been focused on developing green and cost-effective methods for producing RGO.

Many researchers have investigated green nanotechnology, which serves plant and plant

*Corresponding author e-mail: eman.omar2006@gmail.com (Eman O. Taha)

Receive Date: 11 March 2022, Revise Date: 15 April 2022, Accept Date: 13 September 2022

DOI: 10.21608/EJCHEM.2022.126667.5617

©2022 National Information and Documentation Center (NIDOC)

extracts as a reducing agent to RGO preparation. In typical reduction, the green reducing agent mixed with GO aqueous solution then stirring or refluxing of the mixture is maintained at controlled temperature for certain times [22]. These methods is used to RGO preparation with various plant extract such as green tea [23], sugar cane juice[24], spinach[25], pomegranate juice[26], cinnamon [27], curcumin [28], Cherry [29], carrot roots[30], and Chrysanthemum[31]. Also, Azadirachta indica leaves and garlic were used for the green reduction of GO with the assistance of microwave and heating techniques [32, 33]. Doum palm (*Hyphaene thebaica*) is a desert palm native to the Nile valley, commonly called “African doum palm” [34]. The plant has brown ellipsoid fruits rich in polyphenolic compounds and antioxidants [35]. Doum fruit contains various nutritional compounds such as proteins, essential oils, carbohydrates, flavonoids, coumarins, hydroxycinnamates, and saponins.

The γ -Ray was used as a cheap and clean tool for GO reduction. It implies a reduction of GO in the solution mixture containing water and alcohol. The irradiation causes water radiolysis and produces oxidative and reductive species. The addition of alcohol as a scavenger of oxidative species while reductive species reduce is reported to be essential [7, 14, 36]. So it can deduce that GO reduction via γ -rays can't happen without alcohol.

In the present work, Doum fruit powder is used as a reducing agent for GO under gamma irradiation. The proposed reduction mechanism uses the Doum fruit powder as a natural antioxidant instead of alcohol used for scavenging the oxidative species produced upon γ -radiolysis of GO solution and permits the reductive species to reduce GO. The successful reduction process was verified via different characterization techniques.

2. Materials and Methods:

2.1. Materials:

Merck, Germany, supplied graphite with a thickness of around 50 μm . H_2SO_4 , H_3PO_4 (85%), and hydrazine hydrate were purchased from Sigma-Aldrich in the United States. El Nasr Pharmaceutical chemicals Company, Egypt, provided KMnO_4 , H_2O_2 , ethanol, and HCl. A local retailer provided the doum fruit powder.

2.2. Synthesis of Graphene Oxide:

The improved hummer method was employed for graphene oxide (GO) preparation [37].

Briefly, H_2SO_4 and H_3PO_4 (3:1) were mixed in an ice bath with 1 gm of graphite. The mixture was progressively supplemented with 6 gm of KMnO_4 while being stirred constantly for around 24 hours at a warm temperature. Deionized water was then added

to the mixture. Observed by one, the color of the mixture changed from dark green to dark brown. 30 mL of H_2O_2 solution was added to stop the oxidation process. After that, an aqueous HCl solution and deionized water were used to rinse the magnetic graphite oxide until the pH reached 3.

2.3. Synthesis of Doum Radiation Reduced Graphene Oxide (DRRGO):

The doum fruit was ground and washed with distilled water. GO (100 mg) dissolved in 100ml distilled water and then the solution was sonicated for about 30 minutes. Then 100 mg of doum powder was added to the GO solution, and further sonicated for 5 minutes. Then the mixture was irradiated with 80 kGy of γ -rays, the dose rate was $\approx 1 \text{ kGy h}^{-1}$. A ^{60}Co source at the National Center for Radiation Researches and Technology (NCRRT), Egyptian Atomic Energy Authority (EAEA), was used.

After the irradiation process, the GO solution turned brown into black, which endorses GO reduction. The derived complexes were precipitated and washed with distilled water. The derived sample was labeled as DRRGO. The schematic representation of DRRGO synthesis is given in Fig.1

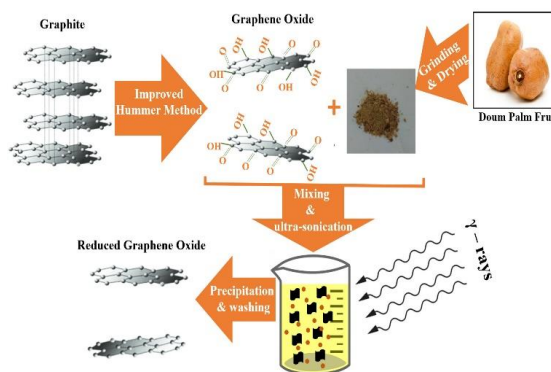


Fig.1. the schematic representation for the synthesis of Doum radiation reduced graphene oxide.

2.4 Characterization Techniques:

GO and DRRGO were studied using an X-ray diffractometer (XRD, Shimadzu) with CuK radiation ($= 1.5405\text{\AA}$). 40 kV of generator voltage and 30 mA of generator current were used in this experiment. The scan speed was set to 80 minutes, and the scan mode was continuous. The measurements were taken across the range of 4 to 80 degrees. Fourier Transform Infrared Spectroscopy (FT-IR) examines the samples' chemical structure (Shimadzu Prestige-21 spectrophotometer). It was in this range that the FT-IR spectra were collected.

Using a Field Emission Scanning Electron Microscope, the surface morphology is investigated (FESEM Sigma 300 VP, Carl Zeiss, Germany). For the jeol-jem2100 High-Resolution Transmission Electron Microscope (HRTEM, the operating voltage was 200 kV). Thermogravimetric Analysis (TGA; Shimadzu -50) was used to assess the thermal stability of GO and DRRGO in the range of 25–500 °C. Under a nitrogen environment, the heating rate was 10 °C min⁻¹. Analysis of materials' structural flaws at room temperature in the range of 200–2500 cm⁻¹ was performed using a Raman spectroscope with a Nd:Yag laser excitation source (532). The XPS equipment from Thermo Fisher ESCALAB 250i was used to analyze the chemical states of the constituent constituents of GO and DRRGO.

3. Results and Discussion:

FTIR spectroscopy was used to study the variation of functional groups of studied samples, which helps in the reduction verification of GO. Fig.2 represents the FTIR spectra of doum palm fruit, GO, and DRRGO samples. Doum palm fruit powder shows bands at 3310 and 2977 cm⁻¹ corresponding to OH of water molecules. Also, the bands located in the range 1000-1300 cm⁻¹ attributed to C-OH stretching and OH bending vibrations. The band at 1634 cm⁻¹ is due to C=C stretching vibrations [38].

GO shows various oxygen functional groups were detected in the FTIR spectrum. The strong broadband at 3190 cm⁻¹ is attributed to O-H vibrations. Also, the stretching vibrations of C=O were detected at 1721cm⁻¹, C–OH at 1390cm⁻¹, C-O at 1229, and 1056 cm⁻¹. The vibration of C=C at 1621cm⁻¹ was detected [39, 40]. Most GO bands showed severe intensity reduction, which advocates the effective reduction in DRRGO. While the new bands formed at 2977, 2891, 1466, 1383, 1250, 1155, and 1076 cm⁻¹ DRRGO attributed to doum palm fruit powder [38].

XRD was utilized to study the structural changes in samples and confirmation the reduction process of GO.

Fig. 3 depicts the XRD patterns of DRRGO and GO compounds. The (001) reflection plane of stacked graphite planes rich in oxygen groups is visible in the XRD pattern of the GO material, with distinctive diffraction peaks at 9.6° and a d-value of 9.2 Å. As shown in the DRRGO XRD pattern, a large broad peak at 23.7° is observed for the GO diffraction peak, demonstrating that DRRGO has a poorly ordered structure along the stacking direction and serves as a direct confirmation of successful GO reduction [21,

41]. Another weak peak at 11.4° in DRRGO indicates the presence of unreduced graphene oxide phases.

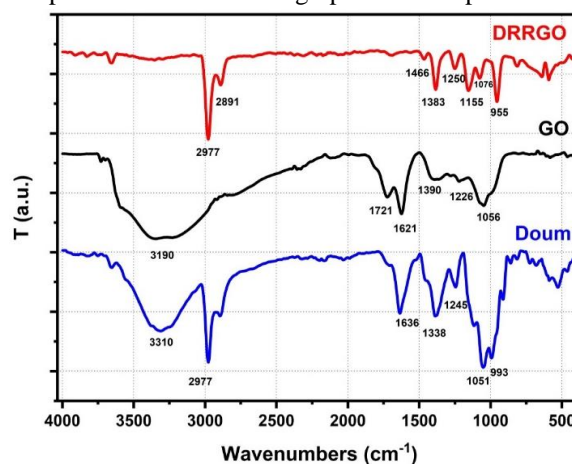


Fig.2. FTIR Spectra of Doum, GO, and DRRGO samples

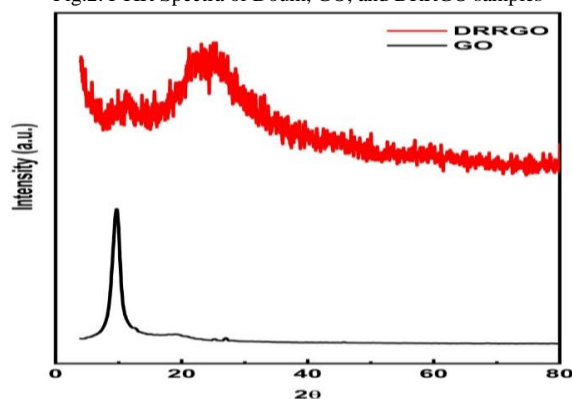


Fig.3. XRD of GO and DRRGO.

Raman spectroscopy is a well-reputed technique to study carbon-based materials' structural defects. Thus, Raman spectroscopy was utilized to study the structural defects of GO and DRRGO, and the results are sketched in Fig. 4 [31]. The GO spectrum represents two well-known bands: D at 1335 cm⁻¹ and G at 1579 cm⁻¹. The G band characterizes the crystalline graphite with E_{2g} zone center mode, but the D band describes the broken symmetry at edges or defects in the sample [42]. DRRGO has the same band with nearly the same position. But the relative increase of the D band to G band was observed, representing affective disorders compared to GO [43].

The graphitic materials' ratio of D to G bands intensities (I_D/I_G) is frequently used to measure their defects [44]. The calculated I_D /I_G equals 1.1 for DRRGO is higher than GO, which equals 0.9. This indicates a higher defect level of DRRGO and successful reduction, which is consistent with other reports [45].

The higher defects level in graphite causes broadening of the G and D bands and increased

relative intensity of the D band compared to the G band. Thus based on this quarrel & the detected narrower D and G bands of GO, it could be predicted that GO has more a regular and ordered structure than DRRGO [42].

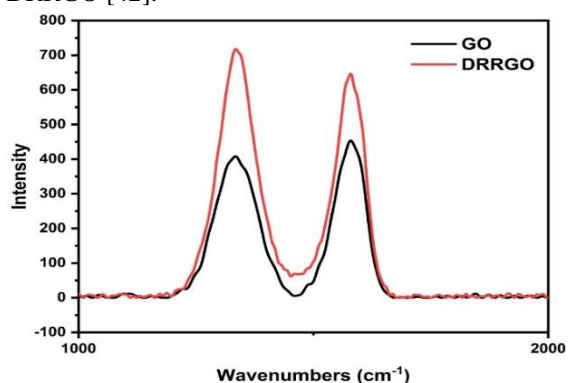


Fig.4. Raman spectra of GO and DRRGO.

X-ray Photoelectron Spectroscopy (XPS) is considered as the most important apparatus for an accurate evaluation of GO reduction energies of 287.1, 284.93, 285.33, 288.31 eV represent the C-O (33.9 at.%), C-C (31.12 at.%). Thus, XPS was used to evaluate the chemical composition of GO and DRRGO. The survey scan of GO and DRRGO revealed the dominant presence of carbon and oxygen in both samples with traces from nitrogen and sulfur, as shown in Fig.5 [46].

As shown in Fig. 6, the de-convoluted C1s peaks with binding C-HO (19.95 at.%) and C=O (5.03 at.%) of GO, respectively. In contrast, the reduction in DRRGO led to the dominance of C-C bonding. Further additional peaks observed at 286.08 eV, 288.1 eV and 289.0 eV represent C-O (3.65 at.%), C=O (2.73 at.%) and C-O-OH (1.77 at.%) respectively. The C-C peak intensity to intensity of C-O peak was increased from 0.58 in GO to 1.8 in DRRGO, confirming the successful reduction by doum palm fruit [22].

As shown in Fig.7, the O1s peak of GO was de-convoluted into three sections with binding energies of 532.03, 533.04, and 534.12 eV, which characterize C=O, C-O, and C-OH groups, respectively. These peaks were shifted to smaller binding energies to 531.8, 532.8, and 534.12 eV in DRRGO [47]. This means a larger electronic charge in oxygen atoms. Furthermore, DRRGO displays a decreasing intensity of C-O and C=O peaks compared to GO revealing the removal of such oxygen groups and successful reduction of GO[21].

Although some oxygen-containing functional groups peaks remain, this could be due to the adsorbed biomolecule of doum palm fruit on the DRRGO surface[32].

The Field Emission Scanning Electron Microscope (FESEM) was used to differentiate the surface

morphology of GO and DRRGO. As represented in Fig.8, GO exhibits a smooth structure with crimpy sheets. The DRRGO sheets were restacked and fractured upon reduction caused by self-assembly via Van der Waals' forces [31].

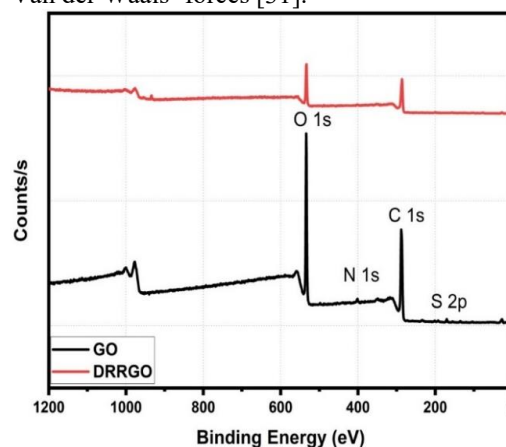


Fig.5. XPS survey scan of GO and DRRGO.

The High-Resolution Transmission Electron Microscope (HRTEM) was employed to study the reduction process on the surface morphology of GO. As shown in Fig.9, soft and transparent sheets of GO with limited crinkles have been exfoliated into several layers consistent with the former work [48]. The GRGO exhibited crinkly morphology and folded appearance upon reduction, confirming that the reduction process agrees with Raman's findings and the literature [31].

Thermogravimetric analysis was done for differentiating between the thermal behavior of GO and DRRGO, which is further beneficial for the reduction confirmation. TGA curves of GO and DRRGO are presented in Fig.10. The TGA curve of GO demonstrates three distinctive temperature spans. In the first one (from ambient up to 150 °C), the thermal degradation occurred due to adsorbed water, gas molecules, and loosely bonded. The second one (150 – 200 °C) is produced by the falloff of labile oxygen groups (anhydride, carboxylic, or lactone groups). The last one (284-600 °C) is ascribed to more thermally-stable oxygen functionalities [49]. Compared with GO, the DRRGO shows improved thermal stability, especially in the first two thermal degradation regions. The DRRGO exhibited weight loss of less than 12 % in the first region compared to nearly 18 % of GO. Also, the DDRO exhibited weight loss of 16 % and 21 % at the second and third weight loss regions, respectively, compared to 28 % and 7 % of GO. While the residual weights of GO and DRRGO were 44 and 46%, respectively [49].

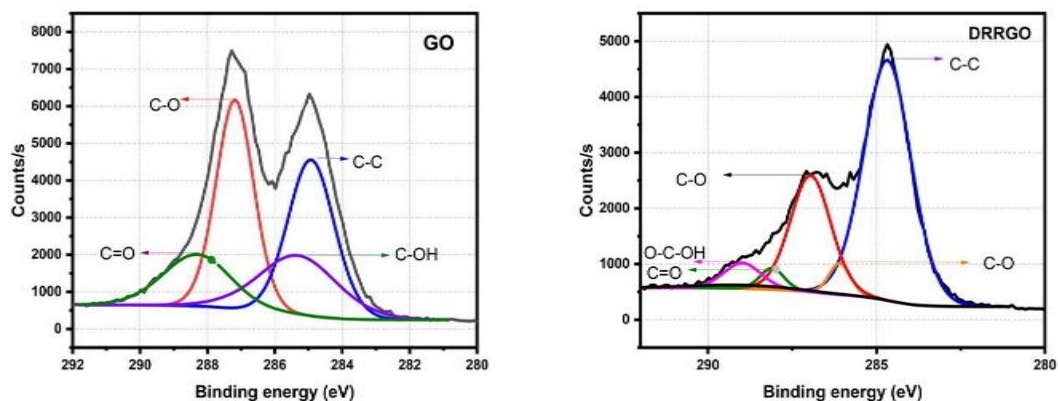


Fig.6: XPS spectra of C1s region of GO and DRRGO.

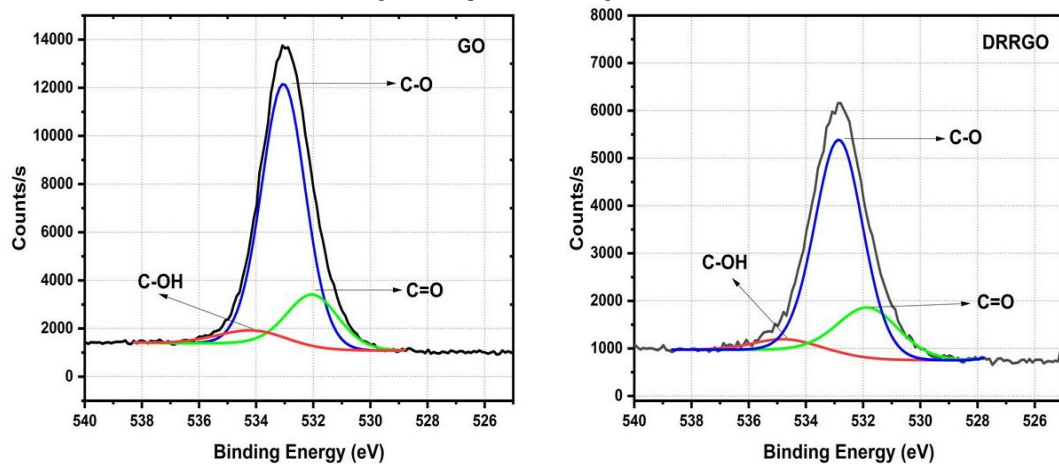


Fig.7: XPS spectra of O1s region of GO and DRRGO.

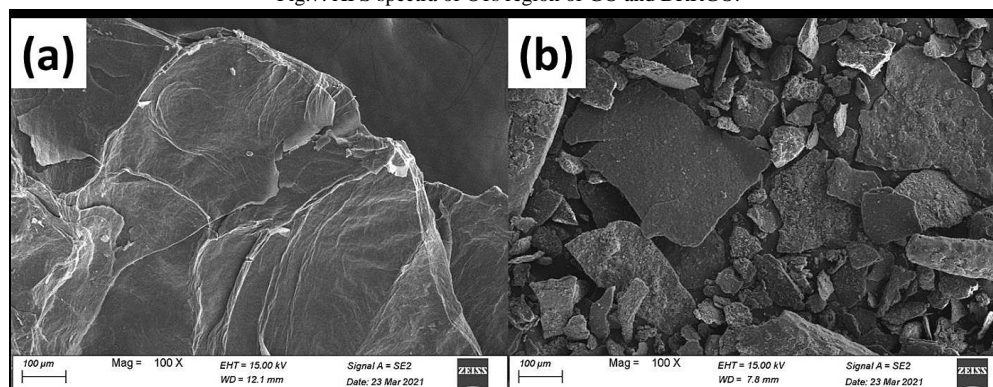


Fig. 8. FESEM images of (a) GO, and (b) DRRGO samples.

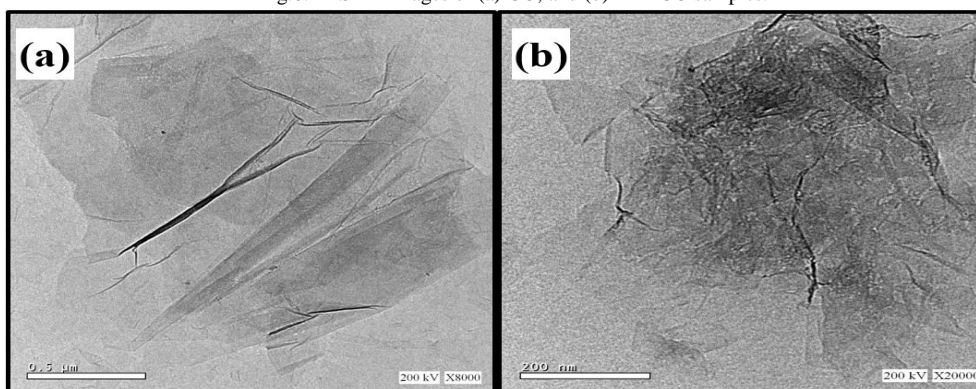


Fig. 9. HRTEM images of (a) GO, and (b) DRRGO samples.

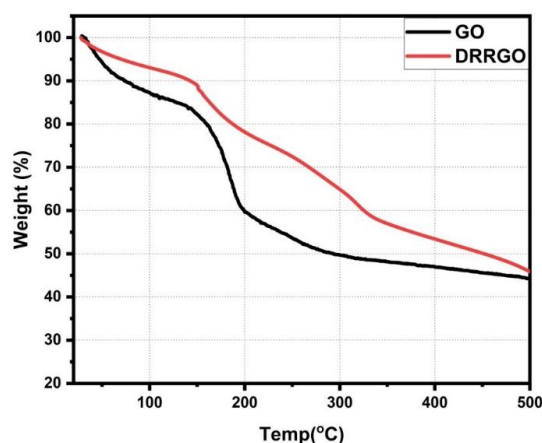


Fig.10: TGA curves for GO and DRRGO.

4. Conclusion

A novel reduction method for synthesizing reduced graphene oxide using Doum palm fruit powder is described. In this method, the radiolysis of GO solution induced by γ -rays produces oxidative and reductive species. Doum palm fruit powder as a natural antioxidant is used as a scavenger for oxidative species in the system, leading to GO reduction. The successful reduction process was verified with different characterization techniques. The FTIR technique confirms the removal of oxygen functional groups from GO. Replacing the high-intensity XRD peak of GO with the broad peak at 23.7° was further proof of reduction. The C-O bonding dominancy in GO compared to dominant C-C bonding in DRRGO was observed from XPS. The C-C peak intensity ratio to that of the C-O peak increased from 0.58 in GO to 1.8 in DRRGO, confirming the successful reduction by doum palm fruit.

Furthermore, DRRGO crinkly and folded morphology compared to the soft sheets of GO was observed by HRTEM. The soft structure of GO sheets compared with fractured DRRGO sheets was also observed by FESEM. Increased thermal stability of DRRGO compared with GO was recorded by TGA. These findings endorse using the γ -ray technique with the assistance of doum palm fruit as the green antioxidant as an efficient and eco-friendly method for GO reduction.

Acknowledgements:

This paper is based upon work supported by Science, Technology & Innovation Funding Authority (STDF) under grant (BARG Call7—Project ID 37200) to Egyptian Petroleum Research

Institute (EPRI), Cairo, Egypt. The authors greatly acknowledge this funding. The authors also would like to express their gratitude and appreciation to National Centre for Radiation Researches and Technology (NCRRT), Egyptian Atomic Energy Authority.

References:

- [1] E. Makhado, S. Pandey, J. Ramontja, Microwave assisted synthesis of xanthan gum-cl-poly (acrylic acid) based-reduced graphene oxide hydrogel composite for adsorption of methylene blue and methyl violet from aqueous solution, *International journal of biological macromolecules*, 119 (2018) 255-269.
- [2] R. Ahmed, A. Ibrahim, A. El-Bayoumi, M. Atta, Structural, mechanical, and dielectric properties of polyvinylchloride/graphene nano platelets composites, *International Journal of Polymer Analysis and Characterization*, 26 (2021) 68-83.
- [3] H. Abdelsalam, M.M. Atta, W. Osman, Q. Zhang, Two-dimensional quantum dots for highly efficient heterojunction solar cells, *Journal of Colloid and Interface Science*, 603 (2021) 48-57.
- [4] S. Samadi, M. Moradkhani, H. Beheshti, M. Irani, M. Aliabadi, Fabrication of chitosan/poly (lactic acid)/graphene oxide/TiO₂ composite nanofibrous scaffolds for sustained delivery of doxorubicin and treatment of lung cancer, *International journal of biological macromolecules*, 110 (2018) 416-424.
- [5] X. Jin, N. Li, X. Weng, C. Li, Z. Chen, Green reduction of graphene oxide using eucalyptus leaf extract and its application to remove dye, *Chemosphere*, 208 (2018) 417-424.
- [6] H. Shamkhalichenar, J.-W. Choi, Non-enzymatic hydrogen peroxide electrochemical sensors based on reduced graphene oxide, *Journal of the Electrochemical Society*, 167 (2020) 037531.
- [7] M. Atta, M.A. Maksoud, O. Sallam, A. Awed, Gamma irradiation synthesis of wearable supercapacitor based on reduced graphene oxide/cotton yarn electrode, *Journal of Materials Science: Materials in Electronics*, 32 (2020) 1-11.
- [8] M. Kashif, E. Jafaar, S.K. Sahari, F.W. Low, N.D. Hoa, A. Ahmad, A. Abbas, Z. Ngaini, M. Shafa, A. Qurashi, Organic sensitization of graphene oxide and reduced graphene oxide thin films for photovoltaic applications, *International Journal of Energy Research*, (2021).
- [9] X.J. Lee, H.N. Lim, N. Gowthaman, M.B.A. Rahman, C.A.C. Abdullah, K. Muthoosamy, In-situ surface functionalization of superparamagnetic reduced graphene oxide-Fe₃O₄ nanocomposite via *Ganoderma lucidum* extract for targeted cancer therapy application, *Applied Surface Science*, 512 (2020) 145738.

- [10] Y. Feng, H. Liu, One-step for in-situ etching and reduction to construct oxygen vacancy modified MoO₂/reduced graphene oxide nanotubes for high performance lithium-ion batteries, *Applied Surface Science*, 538 (2021) 147992.
- [11] M. M. Atta, M. E. Habieb, M. Mohamed, D. M. Lotfy, E. O. Taha, Radiation-assisted reduction of graphene oxide by aloe vera and ginger and their antioxidant and anti-inflammatory roles against male mice liver injury induced by gamma radiation, *New Journal Chemistry*, 46 (2022) 4406-4420.
- [12] A. Alkhouzaam, H. Qiblawey, M. Khraisheh, M. Atieh, M. Al-Ghouti, Synthesis of graphene oxides particle of high oxidation degree using a modified Hummers method, *Ceramics International*, 46 (2020) 23997-24007.
- [13] C.K. Chua, M. Pumera, Chemical reduction of graphene oxide: a synthetic chemistry viewpoint, *Chemical Society Reviews*, 43 (2014) 291-312.
- [14] P. Kumar, K. Subrahmanyam, C. Rao, Graphene produced by radiation-induced reduction of graphene oxide, *International Journal of Nanoscience*, 10 (2011) 559-566.
- [15] S.H. Huh, Thermal reduction of graphene oxide, *Physics and Applications of Graphene-Experiments*, (2011) 73-90.
- [16] M.A. Faiz, C.C. Azurahaman, S. Raba'ah, M. Ruzniza, Low cost and green approach in the reduction of graphene oxide (GO) using palm oil leaves extract for potential in industrial applications, *Results in Physics*, 16 (2020) 102954.
- [17] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*, 45 (2007) 1558-1565.
- [18] T. Zhou, F. Chen, K. Liu, H. Deng, Q. Zhang, J. Feng, Q. Fu, A simple and efficient method to prepare graphene by reduction of graphite oxide with sodium hydrosulfite, *Nanotechnology*, 22 (2010) 045704.
- [19] Z.-z. Yang, Q.-b. Zheng, H.-x. Qiu, L. Jing, J.-h. Yang, A simple method for the reduction of graphene oxide by sodium borohydride with CaCl₂ as a catalyst, *New Carbon Materials*, 30 (2015) 41-47.
- [20] S. Ramanathan, E. Elanthamilan, A. Obadiah, A. Durairaj, J.P. Merlin, S. Ramasundaram, S. Vasanthkumar, Aloe vera (*L.*) *Burm. f.* extract reduced graphene oxide for supercapacitor application, *Journal of Materials Science: Materials in Electronics*, 28 (2017) 16648-16657.
- [21] N. Díez, A. Śliwak, S. Gryglewicz, B. Grzyb, G. Gryglewicz, Enhanced reduction of graphene oxide by high-pressure hydrothermal treatment, *RSC Advances*, 5 (2015) 81831-81837.
- [22] Z. Ismail, Green reduction of graphene oxide by plant extracts: a short review, *Ceramics International*, 45 (2019) 23857-23868.
- [23] X. Weng, J. Wu, L. Ma, G. Owens, Z. Chen, Impact of synthesis conditions on Pb (II) removal efficiency from aqueous solution by green tea extract reduced graphene oxide, *Chemical Engineering Journal*, 359 (2019) 976-981.
- [24] A. Singh, B. Ahmed, A. Singh, A.K. Ojha, Photodegradation of phenanthrene catalyzed by rGO sheets and disk like structures synthesized using sugar cane juice as a reducing agent, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 204 (2018) 603-610.
- [25] D. Suresh, P. Nethravathi, H. Nagabhushana, S. Sharma, Spinach assisted green reduction of graphene oxide and its antioxidant and dye absorption properties, *Ceramics International*, 41 (2015) 4810-4813.
- [26] F. Tavakoli, M. Salavati-Niasari, F. Mohandes, Green synthesis and characterization of graphene nanosheets, *Materials Research Bulletin*, 63 (2015) 51-57.
- [27] D. Suresh, M.P. Kumar, H. Nagabhushana, S. Sharma, Cinnamon supported facile green reduction of graphene oxide, its dye elimination and antioxidant activities, *Materials Letters*, 151 (2015) 93-95.
- [28] S. Hatamie, O. Akhavan, S.K. Sadrnezhad, M.M. Ahadian, M.M. Shirolkar, H.Q. Wang, Curcumin-reduced graphene oxide sheets and their effects on human breast cancer cells, *Materials Science and Engineering: C*, 55 (2015) 482-489.
- [29] G. Lee, B.S. Kim, Biological reduction of graphene oxide using plant leaf extracts, *Biotechnology progress*, 30 (2014) 463-469.
- [30] T. Kuila, S. Bose, P. Khanra, A.K. Mishra, N.H. Kim, J.H. Lee, A green approach for the reduction of graphene oxide by wild carrot root, *Carbon*, 50 (2012) 914-921.
- [31] D. Hou, Q. Liu, H. Cheng, K. Li, D. Wang, H. Zhang, Chrysanthemum extract assisted green reduction of graphene oxide, *Materials Chemistry and Physics*, 183 (2016) 76-82.
- [32] C. Li, Z. Zhuang, X. Jin, Z. Chen, A facile and green preparation of reduced graphene oxide using Eucalyptus leaf extract, *Applied Surface Science*, 422 (2017) 469-474.
- [33] S.K. Srivastava, C. Ogino, A. Kondo, Green synthesis of thiolated graphene nanosheets by alliin (garlic) and its effect on the deposition of gold nanoparticles, *RSC Advances*, 4 (2014) 5986-5989.
- [34] A. Aremu, O. Fadele, Study of some properties of doum palm fruit (*Hyphaene thebaica* Mart.) in relation to moisture content, *African Journal of Agricultural Research*, 6 (2011) 3597-3602.
- [35] B. Hsu, I.M. Coupar, K. Ng, Antioxidant activity of hot water extract from the fruit of the Doum palm, *Hyphaene thebaica*, *Food chemistry*, 98 (2006) 317-328.
- [36] M. Atta, H. Ashry, G. Nasr, A. El-Rehim, Electrical, thermal and electrochemical properties of γ -ray-

- reduced graphene oxide, *International Journal of Minerals, Metallurgy and Materials*, 28 (2021) 1726-1734.
- [37] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J.M. Tour, Improved synthesis of graphene oxide, *ACS nano*, 4 (2010) 4806-4814.
- [38] A.A. Abdel-Khalek, R.A. Mohamed, M.M. Abdel-Hafeez, E.H. Gabrail, Surface and Intraparticle Diffusion of Crystal Violet Dye on Egyptian Doum Fruit from Aqueous Solutions, *International Journal of Engineering Research and Technology*, 13 (2020) 675-685
- [39] X. Meng, D. Geng, J. Liu, M.N. Banis, Y. Zhang, R. Li, X. Sun, Non-aqueous approach to synthesize amorphous/crystalline metal oxide-graphene nanosheet hybrid composites, *The Journal of Physical Chemistry C*, 114 (2010) 18330-18337.
- [40] M. Wojtoniszak, X. Chen, R.J. Kalenczuk, A. Wajda, J. Łapczuk, M. Kurzewski, M. Drozdziak, P.K. Chu, E. Borowiak-Palen, Synthesis, dispersion, and cytocompatibility of graphene oxide and reduced graphene oxide, *Colloids and Surfaces B: Biointerfaces*, 89 (2012) 79-85.
- [41] Y.-H. Wang, H.-H. Deng, Y.-H. Liu, X.-Q. Shi, A.-L. Liu, H.-P. Peng, G.-L. Hong, W. Chen, Partially reduced graphene oxide as highly efficient DNA nanoprobe, *Biosensors and Bioelectronics*, 80 (2016) 140-145.
- [42] V.B. Mohan, R. Brown, K. Jayaraman, D. Bhattacharyya, Characterisation of reduced graphene oxide: Effects of reduction variables on electrical conductivity, *Materials Science and Engineering: B*, 193 (2015) 49-60.
- [43] V.B. Mohan, M. Nieuwoudt, K. Jayaraman, D. Bhattacharyya, Quantification and analysis of Raman spectra of graphene materials, *Graphene Technology*, 2 (2017) 47-62.
- [44] F. Tuinstra, J.L. Koenig, Raman spectrum of graphite, *The Journal of chemical physics*, 53 (1970) 1126-1130.
- [45] J. Song, L. Xu, C. Zhou, R. Xing, Q. Dai, D. Liu, H. Song, Synthesis of graphene oxide based CuO nanoparticles composite electrode for highly enhanced nonenzymatic glucose detection, *ACS applied materials & interfaces*, 5 (2013) 12928-12934.
- [46] R. Al-Gaashani, A. Najjar, Y. Zakaria, S. Mansour, M. Atieh, XPS and structural studies of high quality graphene oxide and reduced graphene oxide prepared by different chemical oxidation methods, *Ceramics International*, 45 (2019) 14439-14448.
- [47] B. Gupta, N. Kumar, K. Panda, V. Kanan, S. Joshi, I. Visoly-Fisher, Role of oxygen functional groups in reduced graphene oxide for lubrication, *Scientific reports*, 7 (2017) 1-14.
- [48] C.-T. Hsieh, S.-M. Hsu, J.-Y. Lin, H. Teng, Electrochemical capacitors based on graphene oxide sheets using different aqueous electrolytes, *The Journal of Physical Chemistry C*, 115 (2011) 12367-12374.
- [49] A. Ganguly, S. Sharma, P. Papakonstantinou, J. Hamilton, Probing the thermal deoxygenation of graphene oxide using high-resolution in situ X-ray-based spectroscopies, *The Journal of Physical Chemistry C*, 115 (2011) 17009-17019.