Green Synthesis and Characterization of Reduced Graphene Oxide (RGO) using Sabdarriffa L extract and its Solubility Property

Hassan Abbas Alshamsi1, Sura K.Ali2, Salam H. Alwan Altaa3
1,2,3Department of Chemistry, College of Education, University of Al-Qadisiyah, Diwaniya 1753, Iraq
*Corresponding author E-mail: hasanchem70@gmail.com

Abstract
In this work, a synthesis of reduced graphene oxide using Hibiscus Sabdarriffa L extract was investigated. This way is operationally easy and environmentally friendly at compared with the reduction methods of graphene oxide using chemical agents. The prepared GO and reduced GO were characterized by Raman spectroscopy, UV-vis spectroscopy, Fourier Transform-Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Transition Electronic Microscope (TEM), Atomic Force Microscopy (AFM), Brunauer-Emmett-Teller (BET), Photoluminescence (PL), and Thermogravimetric analysis (TGA) provide a good indication of the removal of oxygen-containing groups from GO and the formation of RGO. It is found that the graphene sheets possess a frizzy morphology consisting of a thin wrinkled paper-like structure, fewer layers and large specific surface area (506.6 m² g⁻¹) and good thermal stability. Measurements show that the use of a natural agent is more likely to reduce functional aggregates in the graphene oxide than hydrazine. Moreover, it is less toxic, less volatile and safer than others.

Keywords: Green synthesis, RGO, Hibiscus Sabdarriffa L, characterizations, Solubility.

1-Introduction
Graphene a two-dimensional carbon material has been extensively studied in recent years due to its excellent, remarkable and exceptional mechanical, electrical, optical, thermal and surface properties[1]. Through the previous years, assorted techniques have been set up for creating graphene for example, mechanical or ultrasonic exfoliation, compound vapor deposition, epitaxial growth and chemical path by reduction graphene oxide[2]. More the now present strategies, solution-based chemical reduction of GO display the super ease of functionalization and possibility
for synthesis graphene on an industrial scope[3]. Because of the unique properties of graphene, it has been used in many applications such as electronic[4], photocatalysis[5], photovoltaic devices[6], gas sensors[7], drug delivery[8], clinical imaging[9] and antibacterial[10]. Regardless of the particular points of interest of the wet chemical technique, the greatest commonly used reductants, for example, hydrazine and NaBH₄. These reductants are greatly poisonous and have a detrimental effect on all applications. Therefore, the use of these reductants to dispose of sewage contaminants leads to increased noxious on the industrial scope[11, 12]. A group of researchers has treated the previous problems by using natural reductants instead of hazardous chemical reductants. For example Amaranthus dubius [13], Green tea leaves[2], Rose water[14], Wild carrot root[15], L-tryptophan [16], Fenugreek seeds[17], Grape seeds[18], Ginkgo biloba Paederiafeticide L. leaves[19] and L-Cysteine s[20]. Therefore, an active, low price and natural factor for the produce of graphene oxide in a large amount are still exceptionally attractive. Graphene oxide is the base material for the preparation of the reducing graphene oxide resulting from the oxidation reaction of the graphite using strong oxidative groups. Sheets are grafted with functional oxygen groups. This work makes the graphene oxide not only electrically insulated but also thermally unstable[21].

This work presents an environmentally friendly green synthesis of reduced graphene oxide via a nontoxic and commercially available Hibiscus Sabdarriffa Laqueous solution extract as a novel reductant model. Hibiscus Sabdarriffa L(English: Roselle; Arabic: karkade)is a species of Hibiscus grown widely in tropical and subtropical climates such as Sudan, India, South of Iraq, Egypt, Southern Asia, Northern Africa, Syria and many of other countries[22]. The chemical components of Hibiscus Sabdarriffa L include ascorbic acid, anthocyanins, hibiscus protocatechuic acid, anthocyanins, flavonoids, mucilage, pectin, polysaccharides, volatile compounds and quercetin[23, 24].

2-Experimental Section

2-1. Materials: Graphite fine powder was obtained from B.D.H., Sulphuric acid, sodium hydroxide and hydrochloric acid were purchased from Scharlau. Potassium permanganate was supplied by Fluka.

2-2. Characterization: UV-Visible(Double beam) spectrophotometer (UV-1650, Shimadzu) was used to recording the UV-visible absorption. FTIR spectra were recorded over the range 4000- 400 cm⁻¹ on a Shimadzu FTIR-8000 spectrometer using the KBr disc. X-ray diffraction (XRD) spectra were recorded on a D/max-2200/PC (Japan Rigaku Corporation) using Cu Ka radiation. AFM image was acquired with AA2000 atomic force microscopy (Angstrom advanced Inc.). SEM image was obtained using Model JSM 6390 from JOEL Company, Japan. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) was performed in nitrogen with a Perkin-Elmer
TGA2050 instrument at a heating rate of 10 °C/min. Raman spectroscopy (HR-800 Jobin-Yvon) was performed at room temperature using an Nd-YAG excitation source operating at a wavelength of 532 nm. The Brunauer-Emmett-Teller (BET) surface areas were measured from the N₂ adsorption using a Quadrasorb SIMP. The photoluminescence spectra were measured in a home-built laser induced luminescence spectrograph. The photoluminescence signal was collected with an ellipsoidal collecting mirror and focused onto a 320 mm monochromator (Jobin-Yvon Triax 320) by passing through a filter with a cutoff wavelength below 360 nm.

2-3. Preparation of Hibiscus Sabdarriffa L extract: 10g of plant flowers powder was added to 50ml of deionized water with heating and stirring on magnetic stirrer hot plate for 30 min till the temperature of boiling was achieved. Then, the mixture was filtered, and the filtrate was cooled to room temperature. Further diluted to 100ml with deionized achieve 10% extract solution.

2-4. Synthesis of GO and reduced graphene oxide using Hibiscus Sabdarriffa L extract: Graphene oxide was prepared from graphite powder by modified Hummer's method[25]. While the RGO is prepared by adding 0.1g graphene oxide to 100ml of distilled water under the ultrasound for 30min. Then transfer the suspended solution to a volumetric flask containing a known volume of the plant extract and stirring using mechanical stirrer for 150 min under sonication at adjusted temperature and pH. After the processing time is finished, the brown color of GO solution change to black. A sample of suspension was analyzed spectroscopy at 660 nm to study of RGO formation rate. In all cases, absorbance was recorded after centrifugation of suspension at 4000 rpm to remove aliquots and analysis of homogeneous dispersion, pH value was adjusted using 1M HCl and 1M NaOH. In addition, a uniform GO disperse was reduced adopting mixing treatment excluding sonication under the same set of effects mentioned above.

2-5. Study of Solubility: The study included determination of solubility of both graphene oxide and reduced graphene oxide using different organic solvents at the concentration of 0.5 mg/ml, 298 °C and pH = 7. Where the adsorption of these compounds was measured using UV-UV spectra at 660 nm. A calibration curve for GO and RGO was prepared in the ten solvents including water, ethanol, 2-propanol, n-hexane, benzene, xylene, chloroform, diethyl ether and toluene. The solubility of GO and RGO was analyzed by dissolving the largest quantity from the substance in solvents above was done separately. Using the slope obtained from the calibration curves, which was derived from the application of the Lambert beer's law, according to the coefficient of absorption for each calibration curve and then the absorption of the unknown compound was obtained as follows:

\[ A = \varepsilon b c \]  

(1)

Where A represents the absorption of an unknown concentration compound, \( \varepsilon \) represents the molar absorption coefficient, which is according to the calibration curve, b is the optical path length.
3-Results and Discussion

3-1. Characterization

Figure (1A) showed the UV-visible spectra of as synthesized GO and RGO were shown a $\pi-\pi^*$ absorption band at 229 nm and a shoulder $\pi-\pi^*$ absorption band at 296 nm. While $n-\pi^*$ absorption band at 272 nm return to RGO sheets, showing that a few oxygen groups on the GO sheet are elimination and obtained on the conjugated structure[26]. The FT-IR spectra exhibited in Figure (1B) GO demonstrates the epoxy groups relating to the epoxy (C- O- C) stretching vibrations (1050 cm$^{-1}$), phenolic hydroxyl groups (C- OH) stretching (1134 cm$^{-1}$) and carbonyl groups (C=O) of other carboxylic groups stretching frequency (1717 cm$^{-1}$). The peaks at 3544 and 1418 cm$^{-1}$ can be returned to the stretching and bending vibrations of -OH groups in GO and water molecules respectively. The reduce intensities of absorption bands for the rGO at 3564 cm$^{-1}$ result from the decrease of hydroxyl groups connected to the graphitic sheets[15].

The XRD patterns of G, GO and RGO are shown in Figure (2A). The XRD spectra of pure graphite shows a strong and sharp diffraction peak at $2\theta=26.53^0$ (d spacing =3.35) corresponding to layer structure. The strong diffraction peak at $2\theta=10.37^0$ (d spacing =8.52) correspond to graphene oxide. The increase of interlayer spacing in GO indicates formation of oxygen-containing groups between the layers during oxidation of graphite. The XRD patterns of RGO exhibits a weak peak at $2\theta=24.80^0$ (d spacing 3.52) indicate the formation of RGO[27]. Thermogravimetric analysis (TGA) was used to examine of thermal stability of G, GO and RGO in the temperature range 0-600$^0$C. Graphite exhibits a good thermal stability, while TGA of GO shows weight loss between 50-200$^0$C owing to evaporation of absorbed water molecules. The second weight loss (50%) is observed in the whole temperature range above200$^0$C that due to deoxygenating process. In the temperature above 440 $^0$C, further weight loss is observed can be ascribed to pyrolysis of CO and CO$_2$ groups in the unstable carbon remaining in the structure. The TGA of RGO shows more thermal stability compared to that of GO, due to low content of oxygen-containing groups[28].
Fig. 2. (A) XRD patterns, (B) TGA curves of G, GO and RGO

The surface morphology of the GO, RGO was observed by SEM, TEM and AFM. Figure (3A) show SEM image of GO wavy crimped appearance and the surface are hairy. In contrast, SEM image of RGO thin, crumpled sheets closely associated with each other[29].Figure (3B) show TEM image of GO transparent, uniform, silk and stable. While TEM image of RGO transparent nanosheets[30].

Fig. 3. (A) SEM, (B) TEM images of GO and RGO

Figure (4) show AFM image of GO that the thickness is 2.52nm, which is due to the hydrophilic property because of containing functional oxygen groups and structure a stable colloidal suspension in water, indicating they have a multilayer
structure. While FM image of RGO that the thickness 2.26 nm, showing that the sheets have a single layer of rGO[31].

![AFM images of GO and RGO](image_url)

**Fig. 4.** AFM images of GO and RGO

The specific surface area of RGO that calculated from multi-point BET plot is 506.686 m²/g. The adsorption/desorption isotherms of RGO and the pore size distributions are shown in Fig.5. The isotherms show the type IV curve with a H1 hysteresis loop (0.1<p/p₀<0.9), this mean that the surface includes a geometrical cylindrical pore with a high degree of pore size uniformity. The result indicated that surface has mesopores (diameter 2-50nm)[32].

**Table 1: surface area analysis of G, GO and RGO**

| Property                        | Graphite | GO     | RGO    |
|---------------------------------|----------|--------|--------|
| Surface area (m²/g), BET        | 143.083  | 318.060| 506.686|
| Pore volume (cm³/g), BJH ads    | 0.200    | 0.270  | 0.397  |
| Pore diameter (nm), BJH ads     | 2.454    | 1.937  | 1.934  |
| Pore volume (cm³/g), BJH des    | 0.197    | 0.265  | 0.391  |
| Pore diameter (nm), BJH des     | 2.460    | 2.185  | 1.924  |
| Isotherm type                   | 4        | 4      | 4      |
| Hysteresis(p/p₀)                | non      | 0.05<p/p₀<0.9 | 0.1<p/p₀<0.9 |
| Type of pore                    | Meso-porous | Meso-porous | Nano-porous |
Fig. 5. BET (BJH) analysis of GO and RGO

Photoluminescence (PL) spectra of graphene oxide, there is a decrease in the emission intensity, which is due to inter of oxygen molecules between the layers of graphite. When the reduction of graphene oxide at 10h and with the restoration of part of the conjugated system, there are two emission peaks for each spectrum in the ultraviolet region and the other located in the visible region of spectrum. There is also a decrease in the intensity of emission bands when the wavelength is increased, inducting to the studied carbon materials have multiple fluorescent colors[32]. Raman spectroscopy is a significant, non-destructive appliance used to study the structural variations of GO through the treatment process. The Raman spectrum of GO has two fundamental bands at 1353 and 1591 cm\(^{-1}\), identical to the D and G bands, respectively. The G peak of GO assigned to graphite (1591 cm\(^{-1}\)) can be due to the existence of double bonds. After treatment of the GO using green substance, the G peak of the RGO red-shifted toward the G peak of the graphite and the I(D)/I(G) ratio significantly increased[33].
Fig. 6. (A) PL and (B) Raman analysis of GO and rGO

3-2. Solubility Property

The results shown in Figure (5), summarized in Table 2, show a difference in the solubility, a high solubility of graphene oxide was observed in polar solvents such as water and ethanol. As for the reduced graphene oxide, it showed high solubility with non-polar solvents such as chloroform and toluene. The process of solubility of graphene oxide and reduce graphene oxide in polar and non-polarity solvents depends on several factors are the active groups in their composition and the solvent properties such as dipole moment and surface tension. In the practical part, GO and RGO solvent in ten solvents were irradiated with sonication bath for 30 min. The large particles were separated by a centrifuge at 4000 rpm for 30 min. The transparent solutions were then collected for analysis with UV and visible radiation after leaving for 10 days for ensuring their full solubility before analysis.

Table 2: The solubility values and the absorption coefficient of GO and RGO in a different solvents

| Solvent | S_{GO} (μg/mL) | S_{RGO} (μg/mL) | ε_{GO} L g^{-1} m^{-1} | ε_{RGO} L g^{-1} m^{-1} |
|---------|----------------|----------------|------------------------|------------------------|
| Water   | 5.85           | 3.22           | 3456                   | 2901                   |
|        |        |        |        |        |
|--------|--------|--------|--------|--------|
| Ethanol| 0.52   | 0.45   | 1500   | 1720   |
| Methanol| 0.14  | 0.44   | 1613   | 1713   |
| 2-propanol| 1.79 | 1.08   | 3165   | 1823   |
| n-hexane| 0.1    | 0.43   | 1513   | 1652   |
| Benzene| 0.8    | 1.06   | 1932   | 1962   |
| Xylene| 0.61   | 1.11   | 1884   | 1713   |
| Chloroform| 1.25 | 4.10   | 1818   | 3099   |
| Diethyl ether| 0.71 | 0.27   | 1670   | 1825   |
| Toluene| 1.37   | 4.02   | 1520   | 3019   |
| Tetrahydrofuran (THF)| 1.78 | 1.13   | 2400   | 1901   |
| Acetone| 0.67   | 0.83   | 1804   | 1835   |

4. Conclusions

A green and simplistic reduction method for reducing GO using Hibiscus Sabdarriffa L. aqueous extract is demonstrated. The route is environmentally friendly and can be used for cost-effective mass production. The RGO with a few-layers structure exhibited excellent thermal property and superior suspension stability, which made RGO a promising material for industry application. Hence, this method is an important alternative to the traditional chemical reduction routes to avoid usage of hazardous chemicals and to fulfill the high demand of graphene in near future.

References

1. W. Chen, L. Yan, P. R. Bangal, The Journal of Physical Chemistry C, 114(47)(2010)19885-19890.
2. Y. Wang, Z. Shi, J. Yin, ACS applied materials & interfaces, 3(4)(2011) 1127-1133.
3. H. Li, S. Pang, X. Feng, K. Müllen, C. Bubeck, Chemical Communications, 46(34)(2010) 6243-6245.
4. A. Akturk, N. Goldsman, Journal of Applied Physics, 103(5)(2008) 053702.
5. Z. D. Meng, L. Zhu, C. S. Lim, K. Ullah, S. Ye, K. Y. Cho, W. C. Oh., J. Ceram. Process. Res, 14 (2013) 349-354.
6. C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song, C. M. Li, Angewandte Chemie International Edition, 49(17) (2010) 3014-3017.
7. J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei, P. E. Sheehan, Nano letters, 8(10) (2008) 3137-3140.
8. K. Yang, L. Feng, Z. Liu, Expert opinion on drug delivery, 12(4)(2015) 601-612.
9. D. Kuzum, H. Takano, E. Shim, J. C. Reed, H. Juul, A. G. Richardson, J. de Vries, H. Bink, M. A. Dichter, T. H. Lucas, D. A. Coulter, E. Cubukcu, B. Litt, Nature communications, 5(2014) 5259.
10. J. Li, G. Wang, H. Zhu, M. Zhang, X. Zheng, Z. Di, X. Liu, X. Wang, Scientific reports, 4 (2014).
11. H. A. H. Alshamsi, S. K. Ali, International Journal of ChemTech Research, 9 (2016) 321-331.
12. J. I. Paredes, S. V. Rodil, M. J. F. Merino, L. Guardia, A. M. Alonso, J. M. D. Tascón, Journal of Materials Chemistry, 21(2)(2011) 298-306.
13. M. J. Firdhouse, P. Lalitha, Carbon: Science and Technology, 5(2)(2013) 253-259.
14. B. Haghighi, M. A. Tabrizi, RSC Advances, 3(32)(2013) 13365-13371.
15. T. Kuila, S. Bose, P. Khanra, A. K. Mishra, N. H. Kim, J. H. Lee, Carbon, 50(3)(2012) 914-921.
16. Salam H. Alwan Altaa, Hassan A. Habeeb Alshamsi, Layth S. Jasim Al-Hayder, Synthesis and characterization of rGO/Co₃O₄ composite as nanoadsorbent for Rhodamine 6G dye removal. Desalination and Water Treatment, 114 (2018) 320–331.
17. C. Singh, M. A. Ali, G. Sumana, ACS Sustainable Chemistry & Engineering, 4(3)(2016) 871-880.
18. S. Yaragalla, R. Rajendran, J. Jose, M. A. AlMaadeed, N. Kalarikkal, S. Thomas, Materials Science and Engineering: C, 65(2016) 345-353.
19. S. Gurunathan, J. W. Han, J. H. Park, V. Eppakayala, J. H. Kim, International journal of nanomedicine, 9 (2014) 363.
20. Hassan A. Alshamsi, Nuha A. Jaber, Green Synthesis of Reduced Graphene Oxide Using L-Cysteine as Reductant, Journal of Global Pharma Technology| 2018; 10(05):312-319.
21. W. Lv, D. M. Tang, Y. B. He, C. H. You, Z. Q. Shi, X. C. Chen, C. M. Chen, P. X. Hou, C. Liu, Q. H. Yang, ACS nano, 3(11)(2009) 3730-3736.
22. B. B. Mohamed, A. A. Sulaiman, A. A. Dahab, Bull. Environ. Pharmacol. Life Sci, 1(6) (2012) 48-54.
23. O. C. Zarrabal, D. M. B. Dermitz, Z. O. Flores, P. M. H. Jones, C. N. Hipólito, M. G. A. Uscanga, A. M. Medina, K. B. Bujang, Journal of experimental pharmacology, 4 (2012) 25.
24. I. D. C. Rocha, B. Bonnlaender, H. Sievers, I. Pischel, M. Heinrich, Food chemistry, 165(2014) 424-443.
25. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, (2010).
26. S. Yang, W. Yue, D. Huang, C. Chen, H. Lin, X. Yang, Rsc Advances,2(23)(2012) 8827-8832.
27. D. N. H. Tran, S. Kabiri, D. Losic, Carbon, 76 (2014)193-202.
28. H. Feng, R. Cheng, X. Zhao, X. Duan, J. Li, Nature communications, 4(2013) 1539.
29. S. H. A. Altaa, H. A. H. Alshamsi, L. S. J. Al-Hayder, Journal of Molecular Structure, (2017).
30. S. Y. Toh, K. S. Loh, S. K. Kamarudin, W. R. W. Daud, Chemical Engineering Journal, 251 (2014) 422-434.
31. R. S. Dey, S. Hajra, R. K. Sahu, C. R. Raj, M. K. Panigrahi, Chemical Communications, 48(12)(2012)1787-1789.
32. Nadia Hussain, Salam Alwan, Hassan Alshamsi, and Ibrahim Sahib, Green Synthesis of S- and N-Codoped Carbon Nanospheres and Application as Adsorbent of Pb (II) from Aqueous Solution, International Journal of Chemical Engineering, 2020, 2020, 9068358, 1-13.
33. Z. Luo, P. M. Vora, E. J. Mele, A. T. C. Johnson, J. M. Kikkawa, Applied physics letters, 94(11)(2009) 111909.
34. Viet H. P., H. D. Pham, T. T. Dang, S. H. Hur, E. J. Kim, B. Seon Kong, S. Kim, J. S. Chung, Journal of Materials Chemistry, 22(21)(2012) 10530-10536.