REDUCTION OF GRAPHENE OXIDE IN ETHANOL SOLUTION BY GAMMA IRRADIATION FOR PREPARING REDUCED GRAPHENE OXIDE MATERIAL WITH WATER DESALINATION

Nguyen Thanh Duoc[1*], Doan Binh[1], Pham Thi Thu Hong[1], Ha Thuc Huy[2]
[1]*Research and Development Center for Radiation Technology, 202A street 11, Linh Xuan ward, Thu Duc district, Ho Chi Minh city, Vietnam*
[2]*University of Science – Ho Chi Minh city, 227 Nguyen Van Cu street, HCM. city, Vietnam*
[*]*Email: duoc153@gmail.com*

Abstract: Reduction of graphene oxide (GO) for preparing the reduced graphene oxide (rGO) by γ–ray irradiation was investigated. GO was dispersed in the ethanol solution with the GO concentration of 1 mg/ml, then irradiated with γ–ray in presence of oxigen at dose range of 0 – 100 kGy for preparation of rGO product. The characteristic properties of GO and rGO were determined by UV-Vis spectroscopy, X–ray diffraction (XRD), Transmision Electron Microscopy (TEM) and contact angle measurement. The result showed that water desalination efficiency of rGO was about 46 – 48%.

Key words: *graphene oxide, gamma, irradiation, desalination*

I. INTRODUCTION

Graphene can be defined as a mono-layer of carbon atoms connected by the sp^2 bonds forming the hexagonal lattice in structure [1] (Fig.1). It was discovered by two scientists of Novoselov and Gein (2014) with its attractive properties including good thermal conductivity, large theoretical specific surface area, high electron mobility, good optical transmittance; in addition, it is so thin and harder than diamonds [1,2]. Until now, graphene has been studied for application in many high-technique fields such as bio-sensor, solar cells, energy storage and so on [1,2].

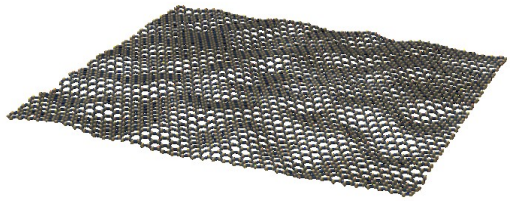

Fig.1. *Structure of graphene material*

In recent years, graphene material was prepared by reduction process of graphene oxide (GO) through many different methods: chemical, solvothermal, electrochemical method; ultrasonic irradiation, gamma ray or electron beam irradiation and so on [3-11]. And GO is usually synthesized via an oxidizing process of graphite using oxidants based on Hummers'method and modified Hummers'approach [5]. There are lots of reduction routes of GO sheets to produce rGO with a good improvement of its properties as graphene's ones. One of useful properties of graphene and GO is its ability of water desalination [12-14].

In this paper, we focus on the reduction of GO to prepare reduced GO (rGO) by gamma ray irradiation in ethanol/water medium to improve the ability of desalination aiming at the development and production of membrane filter applied in treatment of salt water or brackish water.

II. EXPERIMENTAL

II.1. Sample irradiation to prepare rGO

Graphite oxide was synthesized from graphite powder by the modified Hummer's method [5,11]. GO suspension was prepared by adding an amount of 0.01g of graphite oxide in 10ml of ethanol/water solution (25%, v/v) and dispersed under ultrasonic for 1 hour in an ultrasonic bath (Elma Elmasonic S40H, Germany). The prepared suspension was sealed and irradiated at a room temperature by gamma rays in the range of absorbed doses from 0 to 100 kGy with the dose rate of 1.0 kGy/h. Irradiated GO (or rGO) was filtrated and washed by distilled water several times, dried at 70^{o}C and ground into a fine powder for next experiments.

II.2. Preparation of rGO films

The rGO films were prepared by dispersing 0.04g of rGO in 200ml of ethanol solvent under ultrasonic for 2 hours in the ultrasonic bath. Then, the suspension was centrifuged at 2000 rpm by a centrifuge (EBA 12, Hettich, Germany) and decanted the supernatant. rGO films were obtained by vacuum filtration of the prepared supernatant with an 8-12μm alpha-cellulose membrane, washing with distilled water several times, dried at 80^{o}C for 48 hours and kept in a desiccator before use.

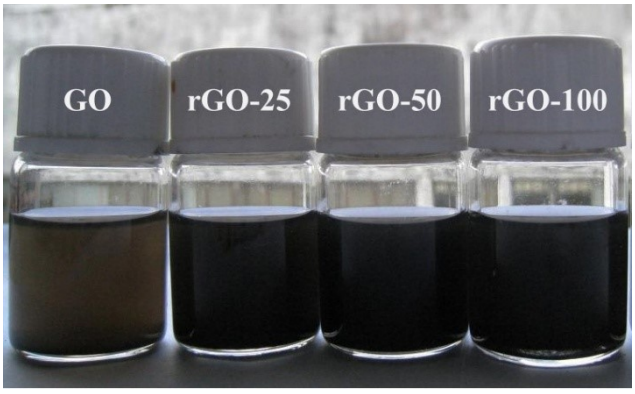

Fig. 2*. Suspensions of GO and rGO irradiated at doses of 25 kGy, 50 kGy and 100 kGy*

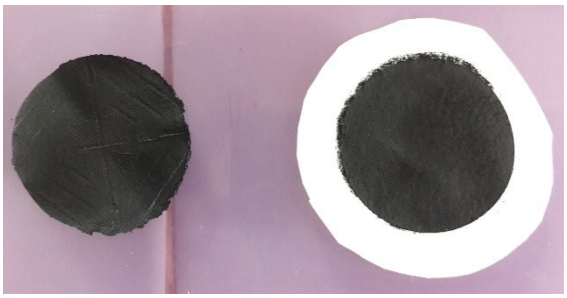

Fig.3. *rGO films*

II.3. Determination of characteristic properties of rGO

II.3.1. Ultra-Violet Visible (UV-vis) spectroscopy

UV-vis absorption spectra were measured with a JASCO V630 spectrophotometer, Japan in the wavelength region of 200 – 800 nm. Gamma ray pre-irradiated and post-irradiated GO samples in ethanol/water solution were prepared at a concentration of 0.025 mg/ml.

II.3.2. X–ray diffraction (XRD) pattern

X-ray diffraction patterns of the samples were taken on a XRD D8 Advance diffractometer, Bruker, Germany with monochromatized Cu-Kα radiation (λ= 1.5406Å) at a scanning rate of 0.04^{o}/s in a wide angle range (2θ = 5 - 30^{o}) at ambient temperature.

II.3.3. Transmission Electron Microscopy (TEM)

The TEM measurements of all samples were performed on a JEM 1010 instrument, Jeol, Japan with the high resolution scanning electron micro-scope plus a transmission mode.

II.3.4. Contact angle measurement

Surface wettability of all sample films was measured on a OCA 20L instrument (Germany) using distilled water as a wettable solvent in condition of room temperature.

II.3.5. Test of water desalination

NaCl solution was prepared at the concentration of 4% (like the salt concentration in seawater) and 1% (like the salt concentration in brackish water). Then NaCl solutions were filtered through rGO films by vacuum filtration. NaCl concentration in filtered solution was measured by indirect potentiometric method determining electrical conductivity [15] at temperature of 30°C, in which a standard line showing the effect of NaCl concentration on the electrical conductivity at room temperature was prepared. Water desalination efficiency (DE) of rGO films were evaluated by the following formula:

$$\text{DE } (\%) = \frac{C_0 - C_1}{C_0} \times 100$$

Where C_0 is the initial concentration of NaCl solution and C_1 is the concentration of filtered NaCl solution through rGO film.

III. RESULTS AND DISCUSSION

III.1. UV-vis spectra

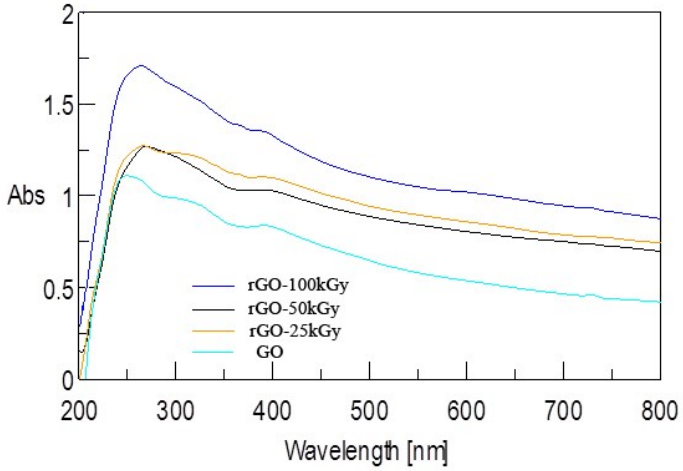

Fig.4. *The UV-vis spectra of GO and rGO irradiated at different absorbed doses*

Fig. 4 shows UV-vis spectra GO and resulted rGO at dose of 0, 25, 50 and 100 kGy. As indicated in Fig. 4, the UV-vis spectrum of GO with the shoulder peak around 240 nm due to n→π* transition of C=O bonds but this peak was changed after gamma rays irradiation with doses from 25 to 100 kGy. It was characterized with the strong absorption peak of GO at around 240 nm regarding to π →π* transition of aromatic C – C bonds red-shifted to 264, 266 and 268 nm corresponding to the absorbed doses of 25, 50 and 100 kGy, respectively. It was suggested that the reduced GO was formed in the presence of ethanol/water by the gamma ray irradiation at high absorbed dose. This meant that the electronic conjugation in the graphene sheets was re-arranged and partially restored.

III.2. XRD pattern

XRD patterns of graphite and GO are shown in Fig.5a. It can be observed a sharp peak with high intensity at $2\theta = 26.3^o$, corresponding to $d_{002} = 3{,}395$Å. It implied that graphite has an orderly crystalline structure. Meanwhile, GO's XRD pattern appeared a larger peaks with low

intensity at 2θ = 11.6°, corresponding to d_{002} = 7,617Å. This result indicated that orderly crystalline structure of graphite was changed and the gap between the graphite layers has been widened because the oxidation of Hummer's method prepared the polar functional groups such as hydroxyl, carboxyl on the carbon layers.

Fig.5b shows the XRD patterns of GO and rGO irradiated at 25, 50 and 100 kGy. The result indicated that rGO irradiated in the dose range of 25-100 kGy had diffraction peak at 2θ ~ 12 – 13°, which was the characteristic one of GO. It suggested a few hydrophilic functional groups still existed in the structure of rGO after γ-gamma irradiation in the ethanol/water. And the intensity decreased with the increase of absorbed doses for irradiating GO. Thus, the obtained result proved that the crystalline structure of GO had changed thanks to gamma ray irradiation in the ethanol/water.

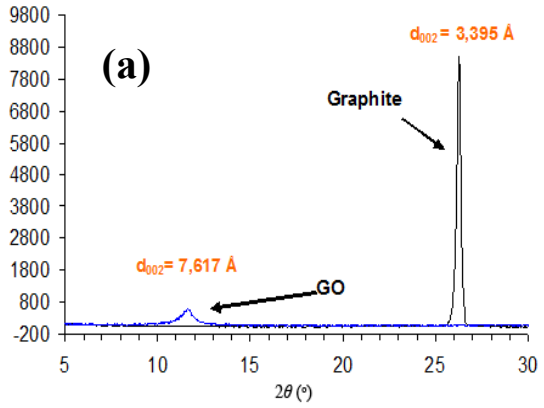

Fig.5a. *XRD patterns of Graphite and GO*

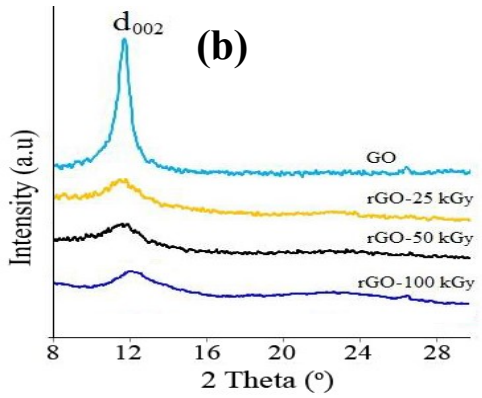

Fig.5b. *XRD patterns of rGO at different absorbed doses*

III.3. TEM images

TEM images of non-irradiated and irradiated GO suspensions at 50 kGy are shown in Fig.6. The non-irradiated suspension of GO with a structure of stacked layers by a lot of GO layers in solutions were observed in Fig.6a. The image of rGO was observed on highly exfoliated graphite as shown in Fig.6b. The higher transparent areas indicated the creation of thinner layer structure by a few exfoliated GO layers after γ–ray irradiation-induced reduction in the solutions [16].

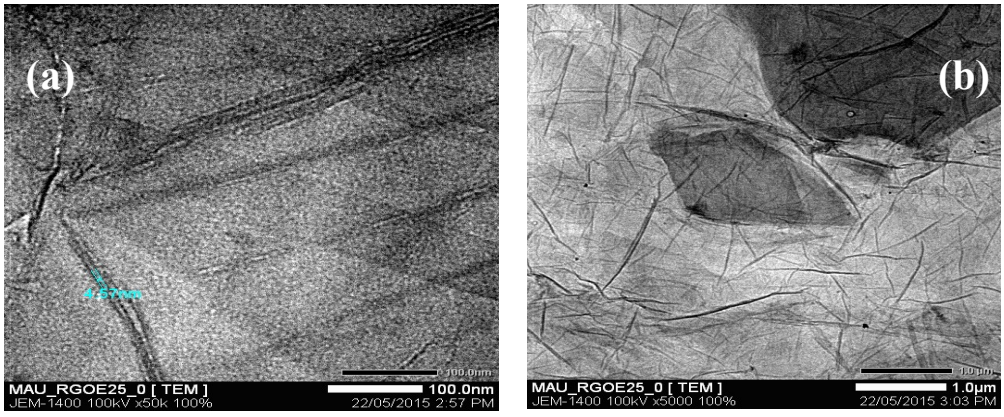

Fig.6. *TEM images of GO sheet (a), of rGO-50 kGy (b)*

III.4. Contact angle measurement

Table 2 and Fig 8 showed the differences in the contact angles of GO and rGO films for the water drops formed on their surface, which was used to evaluate the various surface wettability of these films [9]. It observed that the water droplet was dropped on the GO or rGO film, resulting in the contact angle of 58.2 ± 0.7^{o} for GO and 74.2 ± 0.9^{o} for irradiation-reduced GO one at 100 kGy. However, contact angle increased with increase of the absorbed doses for irradiating GO. It meant that the GO was reduced remarkably to form rGO due to the resulted rGO films were non-wetting with water and became more hydrophobility than GO films [17].

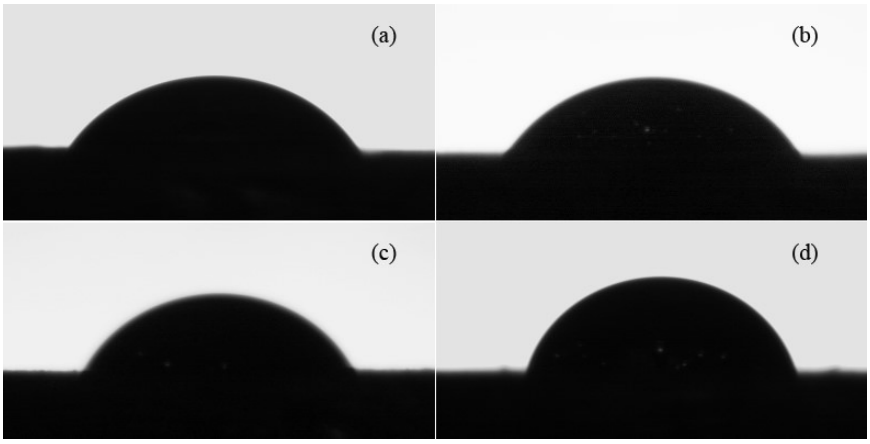

Fig.7. *Photos for contact angle measurement of GO (a), rGO-25 kGy (b), rGO-50 kGy (c) and rGO-100 kGy (d).*

Table 1. *The results of contact angle of GO and rGO films*

Sample	Dose, kGy	Contact angle, degree
GO	0	58.2 ± 0.7
rGO-25	25	58.3 ± 0.5
rGO-50	50	61.2 ± 1.1
rGO-100	100	74.2 ± 0.9

III.5. Test of water desalination

Table 3 shows the filtration efficiency of saline solution in GO and rGO films at a pressure of 2 psi in vacuum filtration at temperature 30 °C. The results showed that rGO gave better desalination efficiency than GO, for example the salt filtering efficiency of GO and rGO-25 in NaCl 4% solution was 15.4% and 19.6%, respectively. The dose does not significantly affect the salt filtration efficiency of rGO membrane, particularly the filtration efficiency of rGO-25 and rGO-100 in NaCl 4% solution is 19.6% and 20.3%, respectively. In addition, the concentration of salt in the initial solution also affects the salt filtration ability of the film. The higher the salt concentration, the lower the salt filtration efficiency of the film. The ability of the voids of the membrane to be filled with molecular ions leads to the saturation of the membrane being lost.

Table 2. *The results of water desalination of GO and rGO films*

	Desalination efficiency, %	
Sample	4% NaCl solution	1% NaCl solution
GO	15.4 ± 0.9	33.4 ± 0.6
rGO-25 kGy	19.6 ± 0.6	46.0 ± 1.2
rGO-100 kGy	20.3 ± 0.8	48.0 ± 0.7

IV. CONCLUSION

Graphene oxide can be simply reduced and exfoliated by gamma irradiation in alcohol/water solution, which was less defected than that prepared by other method. The more transparent solution of rGO was obtained after gamma irradiation-induced reduction, which was confirmed by analysis of rGO through the evaluation of their characteristic properties supported by spectral records of UV-vis, XRD pattern, TEM images. Hydrophobic properties of rGO increased steadily with the increase of absorbed dose. Desalination ability of rGO film was better than GO one. Further research should be carried out to analyze the effect of filtration pressure, number of rGO layers on desalination ability of rGO film.

References

1. Royal Swedish Academy of Sciences, Scientific Background on the Nobel Prize in Physics 2010 GRAPHENE*,* 2010.
2. Y. Zhu, "Graphene and graphene oxide: Synthesis, properties, and application", Advanced Materials, 22, 1-19, 2010.
3. D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W.L., and J.M. Tour, "Improved synthesis of graphene oxide", ACS Nano, 4, 4806-4814, 2010.
4. W.S. Haummers, Jr., and R.E. Offeman, "Preparation of graphitic oxide", Journal of the American Chemical Society, 80 (6), 1958.
5. Tam T. Mai, Chi Nhan Ha Thuc and Huy Ha Thuc, "Preparation of Graphene Nano-Layer by Chemical Graphitization of Graphite Oxide from Exfoliation and Preliminary Reduction", Fullerenes, Nanotubes and Carbon Nanostructures, 23, 742-749, 2015.
6. C. Xu, R. Yuan, and X. Wang, "Selective reduction of graphene oxide", New Carbon Materials, 29, 61-66, 2014.
7. X. Li, T. Tang, M. Li, and X. He, "Photochemical doping of graphene oxide thin films with nitrogen for electrical conductivity improvement", Journal of Material Science: Materials in Electronics, 26, 1770-1775, 2015.
8. V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker, and S. Seal, "Graphene based materials: Past, present and future", Progress in Materials Science, 56, 1178-1271, 2011.
9. Z. Wang, P. Li, Y. Chen, J. He, B. Zheng, J. Liu, and F. Qi, "The green synthesis of reduced graphene oxide by the ethanol-thermal reaction and its electrical properties", Materials Letters, 116, 416-419, 2014.
10. M. Park, H.K. Shin, B.S. Kim, B. Pant, N.A.M. Bakakat, and H.Y. Kim, "Facile preparation of graphene induced from electron-beam irradiated graphite", Materials Letters, 105, 236-238, 2013.
11. P. T. T. Hồng, "Nghiên cứu tổng hợp tấm nano grapheme từ oxít graphene bằng phương pháp chiếu xạ gamma Co-60", *Luận văn Thạc Sĩ,* Chuyên ngành vật liệu và linh kiện nano, PTN Công nghệ Nano, ĐHQG Tp. HCM, 2015.

12. H. M. Hegab and L. Zou, “Graphene oxide-assisted membranes: Fabrication and potential applications in desalination and water purification”, Journal of Membrane Science, 484m 95-106, 2013.

13. E. Y. M. Ang, T. Y. Ng, J. Yeo, Z. Liu and K. R. Geethalakshmi, “Free-standing graphene slit membrane for enhanced desalination”, Carbon, 110, 350-355, 2016.

14. S. M. Ghaseminezhad, M. Barikani, M. Salehirad, “Development of graphene oxide-cellulose acetate nanocomposite reverse osmosis membrane for seawater desalination”, Composites Part B, 161, 320-327, 2019.

15. A. Aghigh, V. Alizadeh, H. Y. Wong, Md. S. Islam, N. Amin and M. Zaman, “Recent advances in utilization of graphene for filtration and desalination of water: A review”, Desalination, 365, 389-397, 2015.

16. L. Stobinski and et al., “Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods”. Journal of Electron Spectroscopy and Related Phenomena, 195, 145-154, 2014.

17. W. A. Zisman, “Relation of the equilibrium contact angle to liquid and solid constitution”, Advances in Chemistry, 43, 1-51, 1964.

NGHIÊN CỨU KHỬ OXIT GRAPHEN TRONG DUNG DỊCH ETHANOL BẰNG PHƯƠNG PHÁP CHIẾU XẠ GAMMA NHẰM CHẾ TẠO VẬT LIỆU RGO CÓ KHẢ NĂNG KHỬ MUỐI TRONG NƯỚC CAO

Nguyễn Thành Được[1*], Đoàn Bình[1], Phạm Thị Thu Hồng[1], Hà Thúc Huy[2]

[1]Research Trung tâm Nghiên cứu và Triển khai Công nghệ Bức xạ

202A Đường 11, P. Linh Xuân, Q. Thủ Đức, Tp.HCM

[2]Đại học Khoa Học Tự Nhiên – TpHCM, 227 Nguyễn Văn Cừ, Quận 5, Tp.HCM

[*]Email: duoc153@gmail.com

Tóm tắt: Oxit graphen (GO) được khử bằng phương pháp chiếu xạ gamma nhằm chế tạo vật liệu oxit graphen khử (rGO). Oxit graphen được phân tán trong dung dịch ethanol tạo hệ huyền phù ở nồng độ 1mg/ml, sau đó được chiếu xạ bằng tia gamma (25 – 100 kGy) trong điều kiện có oxi. Các tính chất đặc trưng của rGO được xác định bằng phổ UV-vis, nhiễu xạ tia X, chụp ảnh TEM và đo góc tiếp xúc. Hiệu suất khử muối của màng rGO được khảo sát đối với dung dịch NaCl. Kết quả cho thấy hiệu suất khử muối trong nước của rGO tốt hơn của GO và đạt 46 – 48% đối với nồng độ muối ban đầu là 1%.

Từ khóa: *Oxit graphene, gamma, chiếu xạ, khử muối.*