PREPARATION AND CHARACTERISTICS OF REDUCED GRAPHENE OXIDE IN ETHANOL/WATER SOLUTION BY γ-RAY IRRADIATION

Presented by Mr. Doan Binh (PhD.)
R & D Center for Radiation Technology, VINATOM, Vietnam
Email: doanbinh192@yahoo.com

Content

ICARST 2017
1st International Conference on Applications
of Radiation Science and Technology

1. Summary

- Reduction of graphene oxide (GO) in ethanol/water solution in the presence of oxygen with γ–ray irradiation in the dose range of 0-250 kGy was studied;
- GO suspension dispersed in the ethanol/water solution at a concentration of 1 mg/ml under ultrasonic, and then irradiated by γ–ray in absorbed dose range of 0 – 250 kGy;
- The characteristic properties of GO and rGO samples were analyzed by UV-vis, FTIR, XRD, Raman spectra, TEM, TGA, measurement of contact angle and electrical conductivity;
- The electrical conductivity of rGO was increased from 2.4×10^{-2} to 2.58 S/cm with a increase of the absorbed doses from 25 to 250 kGy, respectively;
- This study could be performed to produce a large quantity of the rGO from GO with a simple reduction process by gamma irradiation.

2. Background

General information

- Graphene can be defined as a two-dimentional mono-layer of carbon atoms.
- There are lots of reduction routes of GO sheets to produce rGO with good improvement of the mechanical, electrical, optical and thermal properties and its characterization (Zhu, 2010; Hanifah, 2015).
- The reduction of GO sheets has been performed by the following ways such as chemical, chemico-physical, mechanical, solvothermal, electrochemical ones and so on (Stankovic,2007; Singh, 2011; Li, 2011; Loryuenyong, 2013; Wang, 2014; Shang, 2015,).
- Optimizing the preparation parameters of GO and rGO for large-scale production is evaluated and tested (Lee, 2013; Fathy, 2016).

Chemical reduction methods

- GO is usually synthesized via a oxidizing process of graphite using oxidants based on Hummers'method and modified Hummers'approach (Hummer, 1958; Si, 2008; Shahriary, 2014);
- The chemically selective reduction of GO in ethanol, ethyleneglycol, glycerol, and hydrazine hydrate is reported (Xu, 2014).
- Reduced graphene oxide paper is yielded by super-critical ethanol treatment (Liu, 2012).
- The radiation-induced oxidation of ethanol and methanol by hydrogen peroxide in aqueous solution is discussed previously (Burchill, 1970).

2. Background (cont.)

Chemico-physical reduction methods in combination with irradiation

Gamma-ray irradiation

- The reduced GO in the presence of silver nanoparticle and exposure to gamma irradiation is synthesized in an ionic liquid (Wang, 2013).
- Gamma ray irradiation effects on GO in an ethylenediamine aqueous solution is investigated (Li, 2014).
- Single-step preparation of meso-porous and reduced GO by gamma ray irradiation in gaseous phase is studied;and tuning the grade of graphene: Gamma ray irradiation of free-standing GO films in gaseous phase is also published from the authors' group (Dumee, 2014).
- A study on Raman spectroscopy is applied for few-layer graphene films with gamma-ray assisted irradiation (Kleut, 2014).
- The reduced GO in alcohol/water mixture under exposure to gamma ray in the absence of oxygen is considered as an effective and clean route to synthesize functionalized graphene (Zhang, 2012).

Electron beam irradiation

- Some studies on ion and electron irradiation induced effects in nano-structured materials, graphene oxide, graphite, graphene, carbon nanotubes, amorphous carbon have been carried out (Krasheninnikov, 2010; Chen, 2011; Cretu, 2012; Park, 2013; Iqbal, 2013; Kwon, 2014).

2. Background (cont.)

Thermal reduction methods in combination with ultrasonic or laser irradiation

- GO can be reduced by microwaves in combination with thermal reduction (Chen, 2010; Hojati-Talemi, 2010), with solvothermal method (Tran, 2013).
- Reduction of GO with laser irradiation (Trusovas, 2013), rGO from graphite oxide under ultraviolet irradiation (Ji, 2013), ultra-violet laser irradiation on graphene (Wakaya, 2012).

Doping nanoparticles

- Doping nanoparticles onto graphene or GO has been done for the following works (Brenner, 2012; Bi, 2013; Ortega-Amaya, 2015).

Nano-composites

A lot of research works have been reported on graphene or rGO and/or GO mixed with acrylic resins (Fabbri, 2012), polymer-nanocomposites (Potts, 2011; Young, 2012), polymer-composites (Fryczkowski, 2013), conductive polymer composite thin films (Xie, 2013), CMC nanocomposite superabsorbent hydrogels (Sung, 2016), end-functional polymers (Choi, 2010), filled polyethyleneterephthalate composites (Zhang, 2011

2. Background (cont.)

Some applications of rGO

Some applications from graphene, GO or rGO have been extensively studied and developed as presented on

- A sample support in TEM (Pantelic, 2012);
- Highly efficient supports for metal nanocatalysts (He, 2014);
- Drug delivery system and tissue engineering (Goenka, 2014);
- Super-capacitor electrodes (Li, 2012);
- Chemical functionalization of graphene;
- And other applications (Kuila, 2012).

Objective of the presentation

The reduction of GO to rGO by γ- ray irradiation in ethanol/water solution in order to improve the electrical conductivity aiming at development and production of highly capable energy storage devices.

3. Experimental

1. Chemicals and materials

- Pure graphite flake
- 99.5% ethanol (EtOH)
- $NaNO_3$, H_2SO_4, $KMnO_4$, HCl, H_2O_2, and acetone, distilled water

All chemicals were analytical reagents and used without further purification.

- An alpha-cellulose membrane with 8-12 μm pore-size of Sartorius AG Company

2. Preparation of rGO

- The modified Hummer's method was used for the preparation of GO from graphite powder;

3. Experimental (cont.)

rGO was prepared according to the following flow chart:

GO in EtOH/water
1 mg/1 ml

→ Mixture dispersed by ultrasonic, 1 hr

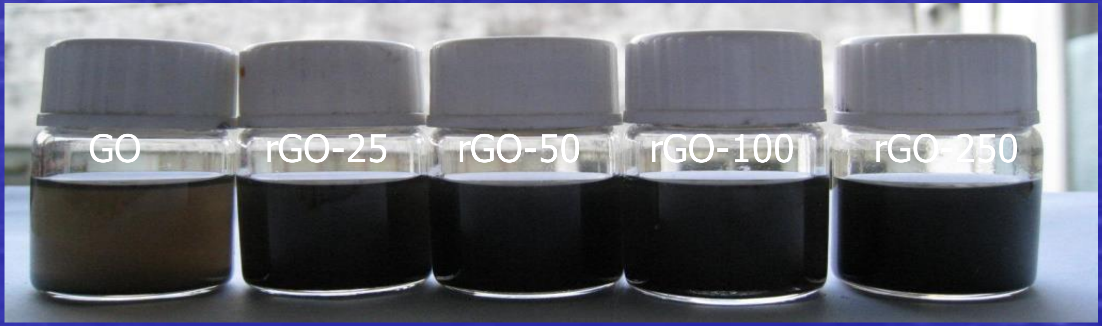
→ Mixture standed overnight

→ GO suspension γ-irradiated at doses 0-250 kGy, 1 kGy/hr

→ Irr. GO suspention filtered, washed

→ obtained rGO dried 70 ^{0}C, ground

→ rGO powder



Photographs of GO and rGO samples

3. Experimental (cont.)

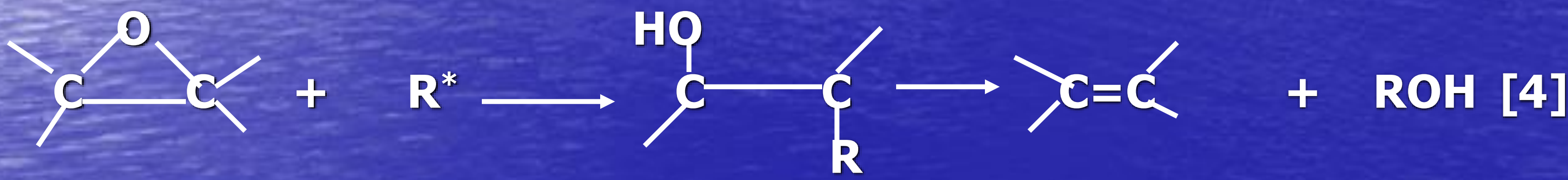
An proposed pathway of γ-irradiated reduction of GO to rGO in EtOH/water

$$H_2O \rightsquigarrow e^-_{aq}, H^*, HO^*, H_2O_2, H_2 \longrightarrow H_3O^+ \quad [3]$$

$$e^-_{aq} + H_2O_2 \longrightarrow HO^- + HO^*, \quad HO^- \longrightarrow HO^* + e^-_{aq} \quad [33]$$

$$H^* + CH_3CH_2OH \longrightarrow H_2 + CH_3C^*HOH\,(C^*H_2CH_2OH)\ (R^*) \quad [3]$$

$$HO^* + CH_3CH_2OH \longrightarrow H_2O + CH_3C^*HOH\,(C^*H_2CH_2OH)\ (R^*) \quad [3]$$



(GO) (rGO)

3. Experimental (cont.)

Determination of GO reduction reaction into rGO by γ-irradiation in ethanol/water solution via analysis of their characteristic properties

- UV-vis curves
- FTIR spectra
- XRD patterns
- Raman spectra
- TEM images
- TGA plots
- Measurement of contact angle and electrical conductivity.

4. RESULTS AND DISCUSSION

1. Analysis of UV-vis curves

- The UV-vis spectra of GO and rGO at 25 kGy with the shoulder peak around 290 nm due to n→π* transition of C=O bonds;

- This peak disappeared after γ-irradiated from 50 to 250 kGy. The strong absorption peak around 230 nm regarding to π →π* transition of aromatic C – C bonds red-shifted to 264, 266, 268, 282 nm corresponding to the absorbed doses of 25, 50, 100, and 250 kGy, respectively;

- The sharply reduced GO was in the presence of ethanol/water in combination to the gamma ray irradiation at high absorbed dose;

- This meant that the electronic conjugation in the graphene sheets was re-arranged and partially retored.

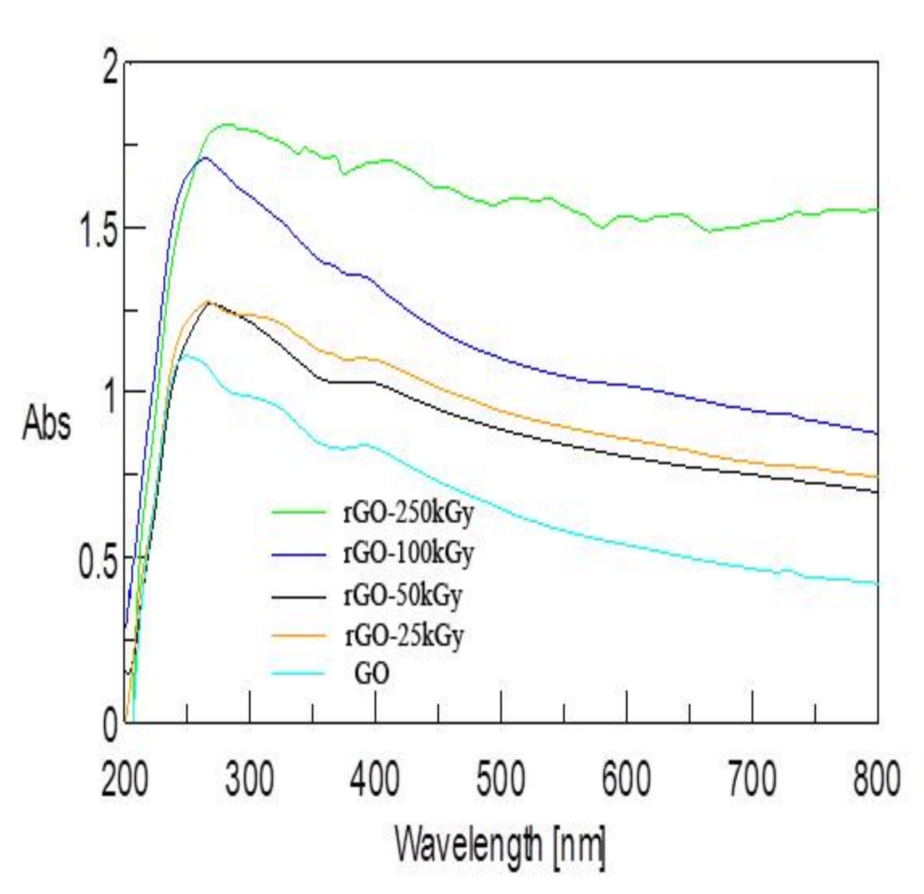


Fig.1. UV-vis curves of GO, rGO-25 kGy, rGO-50 kGy, rGO-100 kGy, and 250 kGy

4. RESULTS AND DISCUSSION (cont.)
2. Analysis of FT-IR spectra

- The stretching vibration band of C=O at 1732 cm^{-1} and of C-O of epoxy groups at 1124 - 1142 cm^{-1} and OH at 3,450 cm^{-1} in the GO spectrum was due to the high oxygen contained groups;

- As for rGO spectrum, the intensity of absorption bands involving in the oxygen containing groups decreased remarkably with the increasing the absorbed doses from 25 to 250 kGy;

- The absorption bands with a strong intensity appeared at 1615 cm^{-1} attributed to the vibration of C=C band

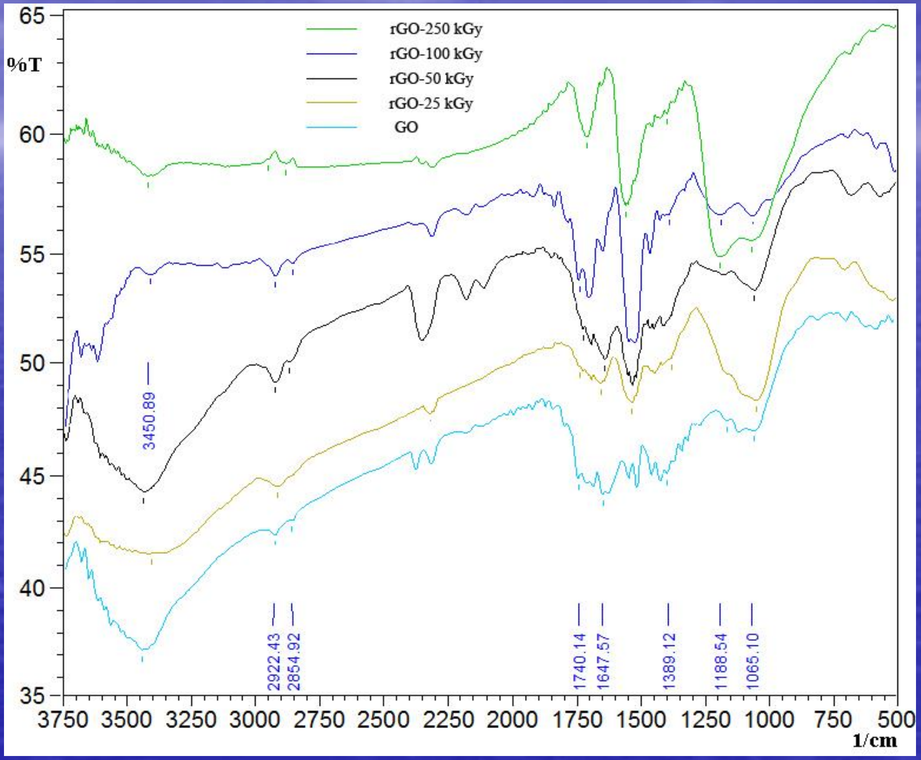


Fig.2. FT-IR spectra of GO, rGO-25 kGy, rGO-50 kGy, rGO-100 kGy and rGO-250 kGy

4. RESULTS AND DISCUSSION (cont.)
3. Analysis of XRD patterns

- The bulk crystalline structure of rGO with a new broaden diffraction peak assigned to d-spacing 7.20 Å. $2\theta=12.30^0$ for irradiating at 25 100 kGy; if increasing the absorbed dose to 250 kGy, a new peak rGO attributed to d-spacing 3.76 Å. $2\theta=23.64^0$ appeared approximately to the XRD peak for the pristine graphite;

- The XRD peak of GO was found at d-spacing 8.13 Å. $2\theta=10,87^0$, indicating the rGO had an inhomogeneous crystalline structure for rGO exposed to gamma ray irradiation in the ethanol/water.

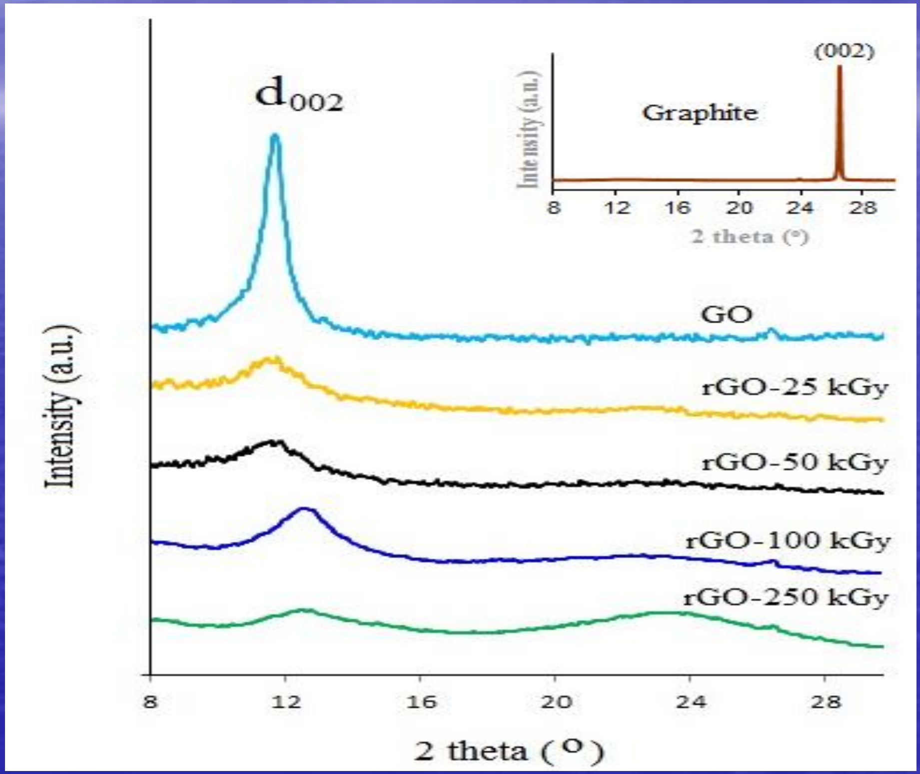


Fig.3. XRD patterns of GO, rGO-25 kGy, rGO-50 kGy, rGO-100 kGy, and 250 kGy

4. RESULTS AND DISCUSSION (cont.)

4. Analysis of Raman spectra

- The Raman spectrum of the graphite displayed a G peak featured at 1581 cm^{-1};

- The Raman spectrum of the GO in the presence of the G band enlarged and shifted to 1594 cm-1, and appearance of the D band at 1340 cm^{-1} with a stronger intensity, indicating there was a size decrease of the in-plane sp^2 domains caused by an oxidation;

- The Raman spectra of rGO also had both G and D bands at 1584 and 1352 cm^{-1}, respectively. But there was an increased D/G intensity ratio of the graphite compared to GO and rGO formed from γ-ray irradiation with upward absorbed doses from 0 to 250 kGy;

- There was a decrease in the average size of the sp^2 domains upon a remarkable reduction of the GO exposed to gamma ray at high absorbed doses and a formation of the new graphitic domains.

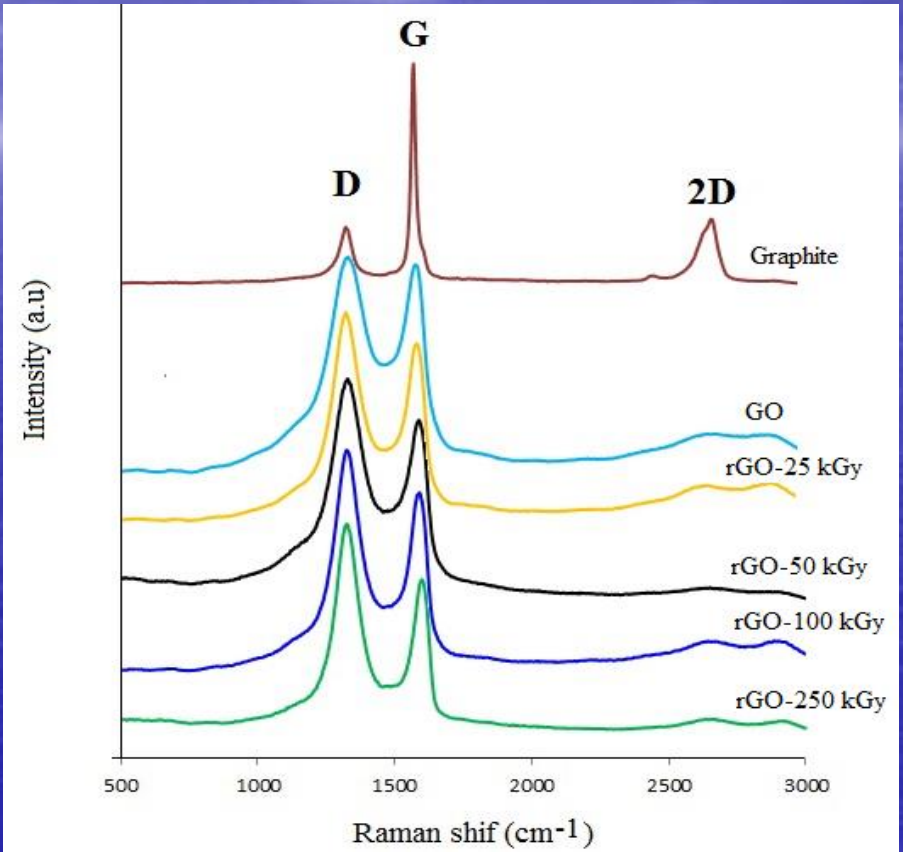


Fig.4. Raman spectra of GO, rGO-25 kGy, rGO-50 kGy, rGO-100 kGy, and rGO-250 kGy

4. RESULTS AND DISCUSSION (cont.)

5. Analysis of Raman spectra (cont.)

Table 1. I_D/I_G intensity ratio of D and G band for GO and various reduced GO in Raman spectra

No.Sample	Abs. dose, kGy	D band, cm^{-1}	G band, cm^{-1}	I_D/I_G ratio
Graphite	0	1,331.6	1,581.6	0.346
GO	0	1,339.5	1,590.8	1.036
rGO-25	25	1,331.6	1,596.0	1.181
rGO-50	50	1,327.6	1,588.1	1.177
rGO-100	100	1,324.2	1,590.5	1.172
rGO-250	250	1,324.2	1,599.2	1.238

4. RESULTS AND DISCUSSION (cont.)

6. Analysis of TEM images

- GO suspension with a structure of stacked layers by a lot of GO layers in solutions observed in Fig. 5a.
- rGO suspension on highly exfoliated graphite observed in Fig. 5b & 5c. The higher transparent areas indicated the creation of thinner layer structure by a few exfoliated GO layers after γ–ray irradiation-induced reduction.

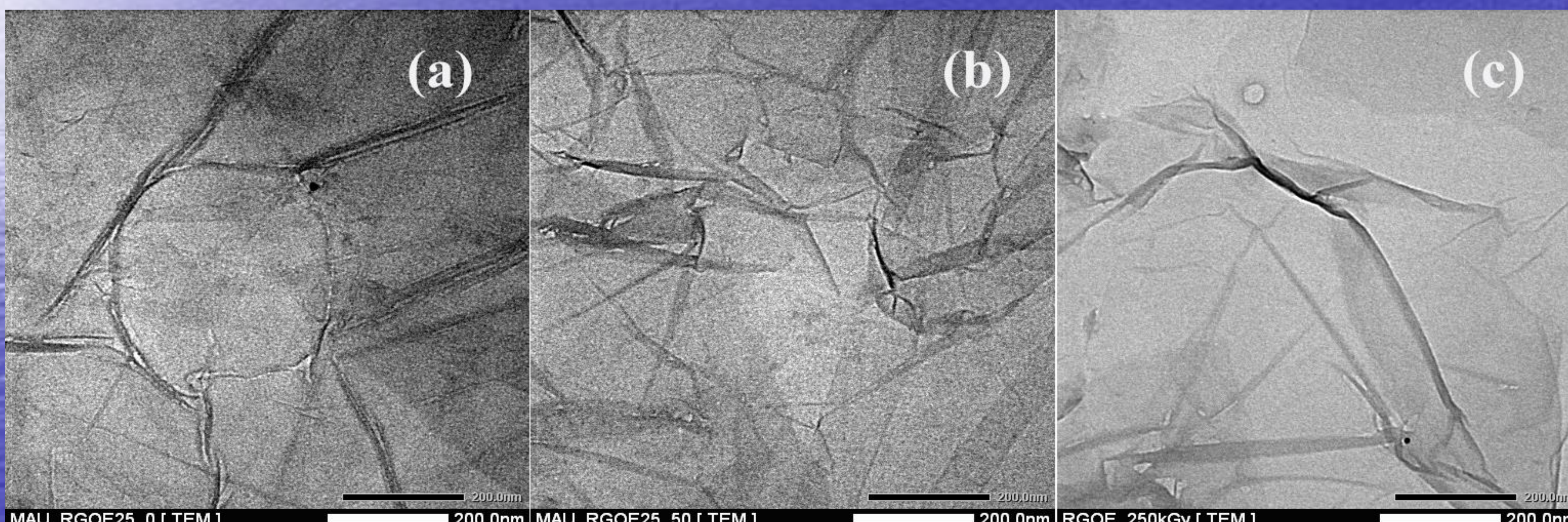


Fig.5. TEM images of GO (a) and rGO at 50 kGy (b) and 250 kGy γ-irradiation (c)

4. RESULTS AND DISCUSSION (cont.)

7. Analysis of TEM images

- A slight mass loss below 100 ^{0}C, the loss of absorbed water in both GO and rGO.

- Increased heating from 100 to 300 ^{0}C, a pyrolysis of labile oxygen-containing functional groups to produce CO, CO_2 and the other products. A vigorous gas release was resulted in large and rapid mass loss of GO;

- rGOs' were more thermally stable than GO. While graphite was very durable to the thermal impact to 600 ^{0}C;

- The incremental rGO with an increase of absorbed dose could made them more thermally stable. Their slow mass loss was detected when rGOs' were heated up to 600 0C, which only cracked carbon-structural network.

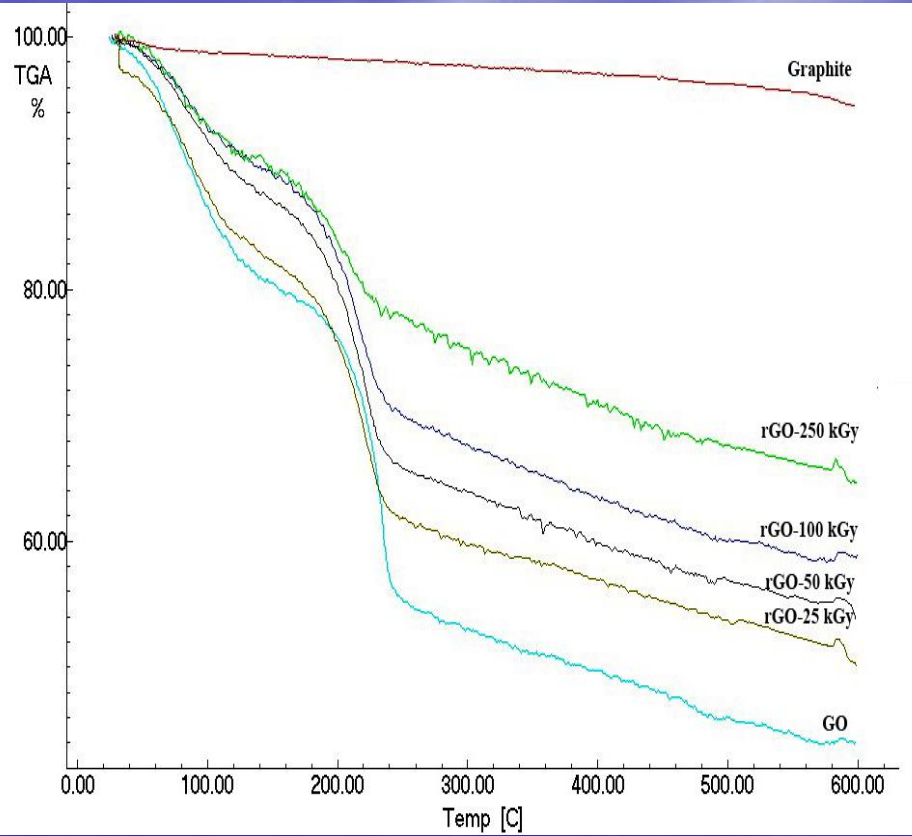


Fig.6. TGA plot of GO, rGO-25 kGy, rGO-50 kGy, rGO-100 kGy, and rGO-250 kGy

4. RESULTS AND DISCUSSION (cont.)

8. Measurement of contact angle

Table 2. Results of measuring contact angle of GO and rGO

No.	Sample	Abs. dose, kGy	Contact angle, degree
1	GO	0	58.2 ± 0.7
2	rGO-25	25	58.3 ± 0.7
3	rGO-50	50	61.2 ± 0.8
4	rGO-100	100	74.2 ± 0.8
5	rGO-250	250	106.4 ± 1.3

- The water droplet was dropped on the GO or rGO film, resulting in the contact angle of 58.2 ± 0.7^{o} for GO film and 106.4 ± 1.3^{o} for irradiation-reduced GO one at 250 kGy;

- The absorbed doses for irradiating GO increased with an increase in their contact angles. It meant that the GO was reduced remarkably to form rGO;

- As-resulted rGO films were non-wetting with water and became more hydrophobic than GO films .

4. RESULTS AND DISCUSSION (cont.)

9. Measurement of electrical conductivity

Table 3. Results of measuring electrical conductivity of GO and rGO

Sample	Abs. dose, kGy	Resistivity, kΩ/sq	Elect. conductivity, S/cm
GO	0	-	0
rGO-25	25	210.0	0.02
rGO-50	50	20.0	0.22
rGO-100	100	8.5	1.23
rGO-250	250	2.0	2.58

- The electrical conductivity of reduced GO films according to the increased absorbed doses.

- The oxygen-containing functional groups in GO were possibly removed and partially restored defects in graphitic lattice structures of rGO

5. Conclusion

- GO can be simply reduced and exfoliated by gamma irradiation in alcohol/water solution to form rGO, which was less defected than that prepared by other method;

- The more transparent solution of rGO was obtained after γ-irradiation-induced reduction proved by TEM. In addition, the formation of rGO was confirmed by analysis of spectral records of UV-vis, FT-IR, and Raman; building up XRD pattern; plotting TGA; and measuring contact angle and electrical conductivity;

- This method is a promising way to reduce GO into rGO in an environmentally friendly solution by γ-ray irradiation for potential large-scale applications.

Acknowledgements

- The authors would like to thank the RCA Regional Office, in the Republic of Korea for a grant in order to participate in ICARST-2017 in Vienna, Austria;

- We are also thankful to R & D Center for Radiation Technology (VINAGAMMA), Ho Chi Minh city for supports of γ–irradiation and administrative procedures;

- We would like to express our gratitude to the IAEA organizing committee of ICARST-2017 for us to have this good opportunity in joining the conference.

References

[1] Hummers, W.S., Offeman, R.E., Preparation of graphitic oxide. *J Am Chem. Soc.* 80 (6) (1958), 1339.

[2] Zisman, W.A., Relation of the equilibrium contact angle to liquid and solid constitution. *Advances in Chemistry, American Chemical Society, USA*, 1964

[3] Burchill, C.E., and Ginns, I.S., The radiation-induced oxidation of ethanol and methanol by hydrogen peroxide in aqueous solution. *Canadian J. Chem.*, 48(1970) 2628-2632

[4] Stankovic, S., Dikin, D. A., Piner, R. D., Kohlhaas, K.A., Kleinhammes, R., Jia, Y., Wu, Y., Nguyen, S.B.T., Ruoff, R.S., Synthesis of graphene – based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, 45 (2007), 1558-1565

[5] Si, Y., and Samalski, E.T., Synthesis of water-soluble graphene. *Nano. Lett.*, 8(6) (2008), 1679-1687

[6] Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J.S., Potts, J.R., and Ruoff, R.S., Graphene and graphene oxide: Synthesis, properties and applications. *Adv. Mat.* (2010), 1-19

[7] Choi, E.Y., Han, T.H., Hong, J., Kim, J.E., Lee, S.H., Kim, H.W., and Kim, S.O., Non-covalent functionalization of graphene with end-functional polymers. *J. Mater. Chem.*, (2010), 1-4

[8] Krasheninnikov, A.V., and Nordlund, K., Ion and electron irradiation-induced effects in nanostructured materials. *J. Appl. Phys.*, 107 (2010)

[9] Chen, W., Yan, Li., and Bangal, P.R., Preparation of graphene by the rapid and mild thermal reduction of grapheme oxide induced by microwaves. *Carbon*, 48(2010), 1146-1152

[10] Hojati-Talemi, P., Simon, G.p., Preparation of graphene nanowalls by a single microwave-based method. *Carbon*, 48(2010), 3993-4000

[11] Li, Q., Wang, L., Zhu, Y., Qian, Y., Solvothermal synthesis of graphene sheets at 300 0C. *Mat. Lett.*, 65 (2011), 2410-2412

[12] Singh, V., Joung, D., Zhai, L., Das, S., Khondaker, S. I., Seal, S., Graphene based materials: past, present and future. *Prog. in Mater. Sci.*, 56 (2011), 1178-1271

[13] Zhang, H., He, S., Chen, C., Zheng, W., and Yan, Q., Electrical conductivity of melt compounded functionalized graphene sheets filled polyethyleneterephthalate composites. *Phys. Appl. of Graphene Experiments,* (2011), 409-420

[14] Chen, I., Xu, Z., Li, J., Min, C., Liu, L., Song, X., Chen, G., Meng, X., Reduction and disorder in graphene oxide induced by electron beam irradiation. *Mater. Lett.*, 65(2011), 1229-1230

[15] Potts, J.R., Dreyer, D.R., Bielawski, C.W., and Rloch, I. A., Gong, L., Novoselov, T., Ruoff, R.S., Graphene-based polymer – nanocomposites. *Polymer*, 52 (2011), 5-25

[16] Zhang, B., Li, L., Wang, Z., Xie, S., Zhang, Y., Shen, Y., Yu, M., Deng, B., Huang, Q., Fan, C., and Li, J., Radiation induced reduction: An effective and clean route to synthesize functionalized graphene. *J. Mater. Chem.,* 22 (2012), 7775-7781

[17] Cretu, O., Rodriguez-Manzo, J.A., Demortiere, A., and Banhart, f., Electron beam-induced formation and displacement of metal clusters and amorphous carbon. *Carbon*, 50(2012), 259-264

[18] Wakaya, F., Taraoka, T., Kisa, T., Manabe, T., Abo, S., and Takai, M., Effects of ultra-violet laser irradiation on graphene. *Microelectronic Eng.*, 97(2012), 144-146

[19] Brenmer, K., Yang, Y., Murali, R., Edge doping of graphene sheets. *Carbon*, 50 (2012), 637-645

[20] Li, Z.J., Yang, B.C., Zhang, S.R., Zhao, C.M., Graphene oxide with improved electrical conductivity for super-capacitor electrodes. *Appl. Surf. Sci.*, 258 (2012), 3726-3731

[21] Bose, T.K.S., Mishra, A.K., Khanra, P., Kim, N.H., Lee, J. H., Chemical functionalization of graphene and its applications. *Prog. Mater. Sci.*, 57 (2012), 1061-1105

[22] Fabbri, P., Valentini, L., Bon, S.B., Foix, D., Pasquali, L., Montecchi, M., and Sangermano, M., In-situ graphene oxide reduction during UV-photopolymerization of graphene oxide/acrylic resins mixture. *Polymer*, 53 (2012), 6039-6044

[23] Young, R.J., Kinloch, I.A., Gong, L., Novoselov, K.S., The mechanisms of graphene nanocomposites: A review. *Comp. Sci. Tech.*, 72 (2012), 1459-1476

[24] Liu, S., Chen, K., Fu, Y., Yu, S., Bao, Z., Reduced graphene oxide paper by super- critical alcohol treatment and its electro-chemical properties. Appl. Surf. Sci., 258 (2012), 5299-5303

[25] Loryuenyong, V., Totepvimara, K., Eimburanapravat, P., Boonchompoo, W., and Buasri, A., Preparation and characterization of reduced grapheme oxide sheets via water-based exfoliation and reduction methods. *Adv. Mat. Sci. Eng.*, (2013), 1-5

References (cont.)

[26] Lee, S., Eom, S.H., Chung, J.S., Hur, S. H., Large-scale production of high-quality reduced graphene oxide. *J. Chem. Eng.*, 233 (2013), 297-304

[27] Wang, S., Zhang, Y., Ma, H., Zhang, Q., Xu, W., Peng, J., Li, T., Yu, Z., Zhai, M. , Ionic-liquid assisted facile synthesis of silver nanoparticle-reduced graphene oxide hybrids by gamma irradiation. *Carbon*, 55 (2013), 245-252

[28] Park, M., Shin, H.K., Kim, B.S, Pant, B., Barakat, N.A.M., Kim, H.Y., Facile preparation of graphene induced from electron beam irradiated graphite. *Mater. Lett.*, 105 (2013), 236-238

[29] Iqbal, M.Z., Kelekci, O., Iqbal, M.W., and Eom, J., The structural and electrical evolution of chemical vapor deposition grown graphene by electron beam irradiation induced disorder. *Carbon* 59 (2013), 366-371

[30]] Trani, V.K., Kwak, D.S., Kwon, Y. J., Cho, H. Y., Tran, N.H., Chung, H., Ham, H., Lee, C., Nguyen, V.D., Ngo, T.T., Kim, H.W., Direct production of highly conductive graphene with a low oxygen content by a microwave-assisted solvothermal method. *Chem. Eng.*, 232(2013), 346-355

[31] Trusovas, R., Ratautas, K., Kaitis, G.R., Barkauskas, J., Stankeviciene, I., Niaura, G., Mazeikiene, R., Reduction of graphite oxide to graphene with laser irradiation. *Carbon*, 52(2013), 574-582

[32] Fryczkowski, R., Gorczowska, M., Shcsarczyk, C., Fryczkinska, B., and Janicki, J., The possibility of obtaining graphene/polymer composites from graphene oxide by a one step process. *Comp. Sci. Tech.*, 80 (2013), 87-92

[33] Ji, T., Hua, Y., Sun, M., Ma, N., The mechanism of the reaction of graphite oxide to reduced graphene oxide under ultraviolet irradiation. *Carbon,* 54 (2013), 412-418

[34] Bi, H., Zhao, W., Sun, S., Cui, H., Lin, T., Huang, F., Xie, X., and Jiang M., Graphene films decorated with mental sulfide nanoparticles for use as counter electrodes of dye-sensitized solar cells. *Carbon*, 61 (2013), 116-123

[35] Xie, S., Zhang, B., Wang, C., Wang, Z., Li., L., and Li, J., Building up graphene-based conductive polymer composite thin films using reduced GO prepared by gamma ray irradiation. *J. Sci. World*, (2013), 1-7

[36] Shahriary, L., Athawale, A. A., GO synthesized by using modified Hummers' approach. *Intl.J. Renewable Energy and Environmental Engineering*, 2(1) (2014), 58-63

[37] Xu, C., Yuan, R.S., Wang, X., Selective reduction of graphene oxide. *New Carb. Mat.,* 29(1) (2014), 61-66

[38] Li, J., Zhang, B., Li, L., Ma, H., Yu, M., Li., J., Gamma ray irradiation of effects on graphene oxide in an ethylenediamine aqueous solution. *Rad. Phys. Chem.*, 94 (2014), 80-83

[39] Dumee, L.F., Feng, C., He, L., Yi, Z., She, F., Peng, Z., Gao, W., Banos, C., Davies, J.B., Huynh, C., Hawkins, S., Duke, C. M., Gray, S., Hodgson, P.D., Kong, L., Single-step preparation of meso-porous and reduced graphene oxides by gamma ray irradiation in gaseous phase. *Carbon,* 8675 (2014)

[40] Dumee, L.F., Feng, C., He, L., Allioux, F.M., Yi, Z., Gao,W., Banos, C., Davies, J.B., Kong, L., Tuning the grade of graphene: Gamma ray irradiation of free-standing graphene oxide films in gaseous phase. *Appl. Surf. Sci.,* 322 (2014), 126-135

[41] Kleut, D.N., Markovic, Z.M., Antanovic H. I.D., Dramicanin, M.D., Kepic, D.P., and Markovic, B.M.T., Gamma ray-assisted irradiation of few-layer graphene films; A Raman spectroscopy study. *Phys. Sci.*, T162 (2014), 1-4

[42] Kwon, Y.J., Cho, H.Y., Na, H.G., Lee, B.C., Kim, S.S., and Kim, H.W., Improvement of gas sensing behaviour induced graphene oxides by electron-beam irradiation. *Sensors and Actuators B: Chemical,* 203(2014), 143-149

[43] He, D., Kou, Z., Xiong, Y., Cheng, K., Chen, X., Pan, M., Mu, S., Simultaneous sulfonation and reduction of graphene oxide as highly efficient supports for metal nanocatalysts. *Carbon*, 66 (2014), 312-319

[44] Goenka, S., Sant, V., Sant., S., Graphene-based nanomaterials for drug delivery and tissue-engineering. *J. Controlled Release*, 173(2014), 75-88

[45] Stobinski, L., Lesiak, B., Malolepszy, A., Mazurkiewicz, M., Mierzwa, B., Zemek, J., Jiricek, P., Bieloshapka, I., Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods. *J. Electron Spectrosc. Relat. Phenom.*, 195 (2014), 145–154.

[46] Huang, Y., Chen, X., Zhang, M. Q., Reversible surface wettability conversion of graphene films: optically controlled mechanism. *J. Mater. Sci.* 49 (2014), 3025–3033.

[45] Wang, N., Zhang, Y., Zhu, F., Li, J., Liu, S., Na, P., Adsorption of soluble oil from water to graphene. *Environ Sci Pollut Res.* 21 (2014), 6495–6505.

[47] Shang, Y., Zhang, D., Liu, Y., Gui, C., Preliminary comparison of different reduction methods of GO. *Bull. Mater. Sci.*, 38(10) (2015), 7-12

[48] Hanifah, M.F,R., Jaafar, J., Aziz, M., Ismail, A.F., Othman, M.H.D., and Rahman, M.A., Effects of reduction time on the structural, electrical and thermal properties of synthesized reduced grapheme oxide nanosheets. *Bull. Mater. Sci.*, 38(6) (2015), 1569-1576

[49] Li, X., Tang, T., Li, M., He, X., Photochemical doping of graphene oxide thin films with nitrogen for electrical conductivity improvement. *J. Mater. Sci. Mater. Electron.* 26, (2015),1770–1775.

[50] Ortega-Amaya, R., Matsumoto, Y., Perez-Guzman, M.A., and Ortega-Lopez, M., In-situ synthesis of Cu2O and Cu nanoparticles during the thermal reduction of copper foil-supported GO. *J. Nanoparticles Res.,* (2015), 1-8

[51] Fathy, M., Gomaa, A., Taher, F.A., El-Fass, M.M., and Kashyput, E.B., Optimizing the preparation parameters of GO and rGO for large-scale production. *J. Mater. Sci.*, 51 (2016), 5664-5675

THANK YOU FOR YOUR KIND ATTENTION!