Synthesis of graphene using gamma radiations

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Abstract. Considering the advantages of radiolytic synthesis such as the absence of toxic chemical as a reducing agent, uniform distribution of reducing agent and high purity of product, the synthesis of graphene (rGO) from graphene oxide (GO) by the gamma irradiation technique using a relatively low dose rate of 0.24 kGy h^{-1} has been described. Structural and physicochemical properties of GO and rGO were investigated with the help of various characterization techniques. The presence of peak at 271 nm in ultraviolet–visible spectrum, C=C aromatic stretching vibrations between 1450 and 1600 cm^{-1} in the Fourier transform infrared spectrum and significant decrease in photoluminescence peak intensity at 470 and 567 nm wavelengths represent the reduction of GO to graphene by gamma irradiation. The decrease in stacking height from 7.71 nm in GO to 3.52 nm in rGO as observed from the X-ray powder diffraction analysis further confirms the same. Raman spectra show significantly lower D to G band ratio for rGO compared with GO. Also, the cyclic voltammograms obtained using GO- and rGO-modified electrodes (working electrode) in standard redox system show enhanced peak intensities together with decrease in potential difference between oxidation and reduction peaks in case of graphene.

Keywords. Graphene oxide; gamma radiations; reduction; graphene.

1. Introduction

Graphene is a two-dimensional single layer of carbon arranged in a honeycomb network. It received incredible attention in diverse areas of research because of its extraordinary electrical and thermal conductivities,^{1,2} high mechanical strength,³ large specific surface area, good biocompatibility and low manufacturing cost.⁴ The high electrical and thermal conductivities of graphene originate from the extended long-range π -conjugation. The biocompatibility, high conductivity and the large surface area of graphene have made it an ideal candidate in the development of bioelectronic devices. The outstanding properties of graphene have been a subject in the development of ultrafast electronic and optical devices, energy storage, photo-catalysis, electrochemical sensors and biosensors.^{5–10} Research has been focused to a large extent on developing routes to obtain large sheets of monolayer or bi-layer graphene. Graphene was initially isolated by mechanical exfoliation, peeling off the top surface of small mesas of pyrolytic graphite,^{11,12} which is not appropriate for large-scale applications. At later stages, single sheets of graphene oxide (GO) were chemically reduced to graphene (rGO) after deposition on a silicon substrate;^{13,14} this method also has limited applications. In recent times, large sheets of graphene have been synthesized by chemical vapour deposition (CVD) of CH_4 or C_2H_2 gases on copper or nickel substrates.^{15,16} However, the CVD method also

involves limitations due to the use of gaseous raw materials. Another approach to synthesize GO in bulk is exfoliation of graphite oxidized with strong acids either by rapid thermal expansion¹⁷ or by ultrasonic dispersion.^{18,19} However, these methods yield graphene sheets with higher degree of defects. Numerous reducing agents including hydrazine,²⁰ sodium borohydride²¹ and hydroquinone²² have been used for the chemical reduction of GO. However, they are highly poisonous, explosive and cause more defects on graphene sheets.²⁰ Thus, a novel route to synthesize graphene is still a challenge.

Gamma (γ)-rays are electromagnetic radiations with high energy and short wavelength. For the past two decades, the use of γ -radiations in the preparation of colloidal metal nanoparticles, composites and in the studies of redox processes occurring on these particles has been found to be highly advantageous.^{23–25} Important advantages of γ -ray synthesis compared with other methods such as chemical are: (1) reduction can be carried out without using excess reducing agent or producing undesired oxidation products of the reductant, (2) the reducing agent is uniformly generated in the solution, (3) radiation is absorbed regardless of the presence of light-absorbing solutes and products, (4) simplicity and (5) cost effective. Also, in radiolytic method it is easier to control the size, shape and size distribution of nanoparticles by optimizing parameters such as dose and dose rate. The results of γ -irradiation reaction strongly depend on irradiation conditions, the material type and irradiation medium.^{26–29} The dose rate has significant effect on the above-mentioned features of the product.³⁰ It has been reported that the interaction between the γ -radiations and

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the multi-walled carbon nanotubes with the absorbed dose of 150 kGy destroyed the nanostructure of carbons, leading to the formation of diamond-like structures and carbon oxides. In addition, γ -irradiation with an absorbed dose of 100 kGy improved graphitization and surface properties of multi-walled carbon nanotubes while at higher absorbed dose (150 kGy), it resulted in damaged structures.²⁷ Zhang *et al*^{28,29} have reported for the first time the synthesis of graphene using a dose rate of 0.88 kGy h⁻¹ and a total absorbed dose of 35.3 kGy. In addition, the effect of γ -irradiation at a higher dose rate of 3 kGy h⁻¹ and absorbed dose of 60–150 kGy on graphene with few layers have been investigated recently.²⁶

In the present paper, attempts were made to check the feasibility of formation of graphene (rGO) using a relatively low dose rate of 0.24 kGy h⁻¹ for a total absorbed dose between 2.88 and 14.40 kGy. The analysis of the products revealed that complete reduction of GO to rGO occurs at a total dose of 11.52 kGy by irradiating the solution of GO in 1:1 water–alcohol mixture which is significantly lower than previous reports. A comparison between our results with those of others^{26,28,29} reveals that reduction of GO occurs at a lower dose rate as well as lower absorbed dose. Also, the electrocatalytic activity of samples before and after irradiation has been investigated. The electrochemical analysis indicates an enhancement in the electrocatalytic activity of rGO.

2. Experimental

2.1 Chemicals and reagents

Graphite powder, H₂SO₄, NaNO₃, NaOH, H₂O₂ (30%), K₃Fe(CN)₆ and KMnO₄ were purchased from Sigma-Aldrich (USA). Methanol, ethanol, isopropanol and *tert*-butanol were obtained from SD-Fine Chemical (SDFCL, India). All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in Milli-Q water (18 M Ω cm⁻¹).

2.2 Instrumentation

The ⁶⁰Co γ -source was from the Department of Chemistry, University of Pune, supplied by BARC (Bhabha Atomic Research Center), Mumbai, India, with a dose rate of 0.24 kGy h⁻¹. The solutions were sonicated using an IMECO 34 KHz frequency, 500 W sonicator. The cyclic voltammetric (CV) measurements were performed on CHI 1100 Electrochemical Analyzer using a conventional three-electrode system. All the electrochemical measurements were carried out in an air-tight borosilicate jacket glass cell with B-14 standard glass joints to fix the electrodes. The electrochemical cell consisted of a glassy carbon (GC) electrode (3 mm diameter) modified with GO and rGO as working electrode, Ag/AgCl/sat. KCl as a reference electrode and Pt as a counter electrode. For measurement of resistance, pellets of the samples (1 cm² and 500 μ m in thickness) were prepared by

placing 50 mg of each powder between two iron plates of a die and compressed at a pressure of 78 kN.

2.3 Synthesis of GO

GO was synthesized from graphite powder using modified Hummer's method.³¹ In brief, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 ml of conc. sulphuric acid under constant stirring. After 1 h, 3 g of KMnO₄ was added gradually to the above solution while keeping the temperature less than 20°C to prevent overheating and explosion. The mixture was stirred at 35°C for 1 h and the resulting solution was diluted by adding 500 ml of water under vigorous stirring. To ensure the completion of reaction with KMnO₄, the suspension was further treated with 30% H₂O₂ solution (5 ml). The resulting mixture was washed with HCl and H₂O followed by filtration and drying, the GO sheets were thus obtained.

2.4 Synthesis of graphene (rGO)

GO (5 mg) was dispersed in 10 ml of ethanol–water (1 : 1) mixture using ultrasonic bath for 30 min. The dispersion was transferred into a glass bottle fitted with a septum. The dissolved oxygen was removed by bubbling nitrogen gas for 10 min. The samples were irradiated in a ⁶⁰Co γ -ray source at a dose rate of 0.24 kGy h⁻¹ for different doses (2.88–14.40 kGy). The product so obtained was collected and washed with Milli-Q water and dried under vacuum. Similar procedure was adopted for other alcohols.

2.5 Preparation of electrodes

GC electrode (3.0 mm diameter) was polished with alumina nano-powder and rinsed with Milli-Q water. Fresh dispersion of samples (GO and rGO) were prepared for each experiment by dispersing 1.0 mg of each sample in 1.0 ml of Milli-Q water with sonication. From this, 10 μ l of solution was drop-casted on the pre-cleaned GC disk electrode and dried under vacuum at room temperature. Bare GC and GC modified with GO and rGO were used for the electrochemical measurements.

2.6 Characterization techniques

Fourier transform infrared (FTIR) spectra of the samples were recorded on a Thermo Scientific NICOLET 6700 spectrophotometer using KBr as the mulling agent. Ultraviolet–Visible (UV–Vis) spectra of the samples were collected on a UV–Vis spectrophotometer (Perkin-Elmer LAMBDA 950). Photoluminescence (PL) spectra of the samples were recorded on a spectrofluorometer (JASCO, FP8300) and X-ray diffraction (XRD) analysis of powders were carried out on Bruker AXSD-8 Advance X-ray diffractometer with monochromatic CuK α radiation (λ = 1.5406 Å). Data were collected from 10° to 60° at a scan rate of 0.1° min⁻¹. The morphologies of the samples were observed under scanning electron microscope (SEM, JEOL JSM-6360). Raman spectra of the samples were recorded by Horiba JobinYvon,

France at $\lambda = 532$ nm laser power 1.7 mW, 100 $\times$ objective lens, 0.9 NA.

3. Results and discussion

Graphene was synthesized by γ -irradiation of dispersion of GO powder in 1 : 1 (V/V) ethanol–water mixture by irradiating the samples for different doses between 2.88 and 14.40 kGy at a dose rate of 0.24 kGy h⁻¹. Preliminary investigations were carried out by recording the UV–Vis spectra of irradiated samples. Figure 1 shows the UV–Vis spectra of the samples obtained after irradiation along with un-irradiated GO dispersion. From the figure, it is observed that GO shows maximum absorption peak at ~ 237 nm attributable to π – π^* transition of the atomic C–C bonds and shoulder peak at ~ 300 nm due to n – π^* transitions of aromatic C–C bonds.^{28,29,32,33} Similar spectrum was obtained for sample after irradiation for 2.88 kGy. However, after irradiation for a dose of 5.76 kGy the spectrum shows a decrease in the intensity of peak as well as a shoulder corresponding to GO along with a red shift in the peak of ~ 4 nm (237–241 nm), indicating partial reduction of GO to graphene. An additional peak observed in rGO at ~ 208 nm represents the absorbance due to the formation of C–H bonds during reduction simultaneous to C–C bond breaking.³⁴ Further irradiation of sample to a dose of 11.52 kGy shows a sharp decrease in the absorbance with a drastic red shift in the peak from 237 to 271 nm which can be attributed to complete reduction of GO to rGO, and the restoration of C=C bonds,^{28,29} the decrease in the intensity of absorbance additionally indicates the complete reduction since rGO has lower solubility compared with GO. The red shift is related to the enhanced electron concentration and structural ordering, thereby confirming the restoration of sp² carbon atoms and formation of graphene with better quality. The spectrum of the sample irradiated for a dose of 14.40 kGy shows an overlap with

the spectrum obtained after 11.52 kGy indicating saturation. These results led us to conclude that 11.52 kGy is an optimum dose for efficient conversion of GO to rGO. Therefore, further analyses were carried out for the sample irradiated for a dose of 11.52 kGy.

Water on γ -irradiation is known to undergo radiolysis (decomposition) forming both, oxidative as well as reductive species. When alcohol is added to water, it scavenges the $\cdot\text{OH}$ radicals, forming water together with alcohol radicals.^{35–37} These alcohol radicals provide a reducing medium for chemical reaction to occur under γ -irradiation in the absence of oxygen (oxygen supports formation of strong oxidative products such as H₂O₂, $\cdot\text{O}_2\text{H}$ and O₂⁻)

where RH corresponds to methanol, ethanol, isopropanol and *tert*-butanol. The effect of different alcohol radicals was investigated by irradiating the dispersion of GO in a series of 1 : 1 (V/V) water–alcohol (methanol, ethanol, isopropanol and *tert*-butanol) mixtures. The UV–Vis spectra of the samples are shown in figure 2. As noted from the figure, the maxima of the absorption peak for rGO appears at 245, 240, 260 and 271 nm for methanol, *tert*-butanol, isopropanol and ethanol, respectively. These results imply that ethanol–water system serves as the best medium, resulting in efficient conversion of GO to rGO. This can be attributed to the differences in the rate constants of alcohols for scavenging hydroxyl radicals where ethanol exhibits the highest rate constant compared with other alcohols as reported by Janata,³⁸ for aqueous solutions of water and alcohols by pulse radiolysis. The FTIR spectra for GO and irradiated sample are depicted in figure 3. The FTIR spectrum of GO represents

Figure 1. UV–Vis spectra of un-irradiated GO and rGO obtained after irradiation of GO + 1 : 1 water–ethanol solutions for different gamma doses.

Figure 2. UV–Vis spectra of rGO obtained after irradiation of GO + 1 : 1 water–alcohol mixtures for a total dose of 11.52 kGy.

two peaks at ~ 1630 and ~ 1740 cm^{-1} attributable to C=C and C=O stretching vibrations, respectively, and a broad peak at ~ 3300 cm^{-1} can be assigned to stretching mode of O–H bond.³⁹ In contrast with this, disappearance of all the above-mentioned peaks simultaneous to the appearance of two new peaks between 1450 and 1600 cm^{-1} associated with the C=C of aromatic ring confirms the reduction of functional groups of GO and formation of graphene (figure 3).

The PL spectra of GO and rGO were recorded using an excitation wavelength of 240 nm as shown in figure 4. The emission peak at 307 nm is due to oxidation of graphite and formation of crystalline graphitic sp^2 in GO. Additionally, a strong peak at ~ 470 nm is attributable to the π – π^* transitions of GO. The remarkable sharp emission peak at ~ 567 nm (visible range) in GO arise due to the CO, C=O and O=C–OH functionalized groups present on the GO. Contrary to this, significant decrease in the intensity of the PL

Figure 3. FTIR spectra of GO and rGO (from bottom to top).

Figure 4. PL spectra of GO (solid line) and rGO (dotted line) obtained at an excitation wavelength of 240 nm.

spectrum in case of irradiated sample correspond to quenching of PL due to removal of functional groups and restoration of greater number of sp^2 clusters, further confirming the formation of rGO.⁴⁰

The morphologies of the samples could be observed with the help of SEM analysis (figure 5). The SEM images of GO (figure 5a and b) show randomly aggregated wrinkled sheets associated with each other, while, the SEM images of graphene (figure 5c and d) exhibit thinner, wrinkled sheets and fluffy structure.

The X-ray diffractograms of GO and rGO (figure 6), reveal the presence of graphitic peaks at $2\theta = 12.05^\circ$ for GO and $2\theta = 25.88^\circ$ for rGO. The d -spacing⁴¹ were calculated by Bragg's law (3) and are found to be 7.27 Å for GO and 3.44 Å for rGO.⁴²

$$\lambda = 2d \sin \theta, \quad (3)$$

where λ is the wavelength of the X-ray beam (0.154 nm), d the distance between the adjacent GO sheets or layers and θ the diffraction angle.⁴¹

The thickness of crystallites (stacking heights) computed by Debye–Scherrer equation (4) for GO, and rGO are found to be 7.71 and 3.52 nm, respectively.

$$l_a = \frac{0.89\lambda}{\beta \cos \theta}, \quad (4)$$

where l_a is the stacking height, 0.89 is a constant dependent on the crystallite shape, λ the X-ray wavelength, β and θ the full-width at half-maxima (FWHM).^{43–45} The variation in stacking height between GO and rGO reflects the influence of irradiation on the structure as well as morphology of the GO.

In addition, the reduction of GO to rGO has also been verified by Raman spectroscopy. This characterization gives useful information related to the electronic and structural properties of graphene. The representative Raman peaks of graphene are reported to be as D (~ 1348 cm^{-1}), G (~ 1592 cm^{-1}) and 2D (~ 2704 cm^{-1}) bands. The G band represents the E_{2g} mode that is in-plane optical vibration of aromatic carbon rings and depicts the relative degree of graphitization. The D band corresponds to the degree of disorder and its intensity shows the level of edge chirality. Therefore, the intensity ratio of G : D bands of rGO represents the various types of disorders such as defects, ripples and edges.^{46,47} Figure 7 shows the Raman spectra of GO and rGO samples. The I_D/I_G and I_{2D}/I_{D+G} ratio of GO (1.02 and 1.32) are remarkably lower than that of rGO (1.24 and 1.50), respectively, indicating less topological disorder, defect density and higher degree of crystallinity in the rGO structure.⁴² Also, the widths of D and 2D peaks for GO are greater compared with that of rGO.^{46,47} These results indicate that rGO has more perfect conjugated structure that leads to enhanced electron transfer.

The electrochemical properties of the samples were studied with reference to $\text{K}_3\text{Fe}(\text{CN})_6$ redox system because of its sensitivity to the surface chemistry and microstructure

Figure 5. SEM micrographs of (a and b) GO and (c and d) rGO samples.

Figure 6. X-ray diffractograms of GO and rGO samples.

as well as the density of electronic states near the Fermi potential.⁴⁸ Figure 8a shows the electrochemical response of $K_3Fe(CN)_6$ [5 mM], KCl [0.5 mM] at bare GC-, GO- and rGO-modified electrodes at a scan rate of 100 mV s^{-1} . The cyclic voltammogram of $K_3Fe(CN)_6$ is apparently enhanced at rGO-modified electrode (solid line) compared with GO (dashed line), as reflected by the increase in the peak current (I_p) together with decrease in the peak to peak potential [$\Delta E_p = 0.11$ for rGO and $\Delta E_p = 0.15$ for GO]. The peak currents are observed to increase linearly as a function of square root of the scan rate ($50\text{--}500 \text{ mV s}^{-1}$), for both, GO and rGO (figure 8b and c). This indicates that the

Figure 7. Raman spectra of GO and rGO (top to bottom).

electrochemical reaction occurring at the electrode surface is diffusion controlled. The linear regression equation (figure 8d) is expressed as: $I_{pa} (\mu A) = 20v (\text{V s}^{-1})^{1/2} - 40$ ($R^2 = 0.9982$), $I_{pc} (\mu A) = 20v (\text{V s}^{-1})^{1/2} - 10$ ($R^2 = 0.9986$), for rGO and $I_{pa} (\mu A) = 4v (\text{V s}^{-1})^{1/2} - 9$ ($R^2 = 0.9676$), $I_{pc} (\mu A) = 5v (\text{V s}^{-1})^{1/2} + 2$ ($R^2 = 0.9885$), for GO. Thus, electrochemical response of rGO is seen to exhibit excellent reversibility, suggesting the easier electron transfer and enhancement in electrocatalytic activity.

To evaluate the conductivity of rGO and GO the electrical resistances of the samples were measured, results show a sharp decrease in resistance of rGO (182Ω) compared

Figure 8. Cyclic voltammograms of samples recorded in 5.0 mM $K_3[Fe(CN)_6]$ + 1.0 M KCl solution vs. Ag/AgCl reference electrode: (a) bare GC and GC electrode modified with GO and rGO at a scan rate of 100 mV s^{-1} , (b) GO (c) rGO electrode recorded as a function of scan rate and (d) plot of I_p (oxidation and reduction peak) vs. square root of scan rate.

with that of GO (600 k Ω). Therefore, the above mentioned analyses clearly reveal that GO is reduced to graphene by γ -irradiation.

4. Conclusions

rGO has been obtained by γ -irradiation of GO in 1 : 1 water-ethanol mixture for a total dose of 11.52 kGy at a relatively low dose rate of 0.24 kGy h^{-1} . The reduction of GO to rGO was evaluated by FTIR, UV-Vis, PL, micro-Raman spectroscopy and XRD analysis and the morphology of products were studied using SEM. The synthesized product exhibits high conductivity and enhanced electrocatalytic activity.

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References

- Kim K S, Zhao Y, Jang H, Lee S Y, Kim J M, Kim K S, Ahn J H, Kim P, Choi J Y and Hong B H 2009 *Nature* **457** 706
- Balandin A A, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F and Lau C N 2008 *Nano Lett.* **8** 902
- Li D, Mülleri M B, Gilje S, Kaner R B and Wallace G G 2008 *Nat. Nanotechnol.* **3** 101
- Segal M 2009 *Nat. Nanotechnol.* **4** 612
- Jo G, Choe M, Lee S, Park W, Kahng Y H and Lee T 2012 *Nanotechnology* **23** 112001
- Li Q, Guo B, Yu J, Ran J, Zhang B and Yan H 2011 *J. Am. Chem. Soc.* **133** 10878
- Qian W, Hao R, Zhou J, Eastman M, Manhat B A, Sun Q, Goforth A M and Jiao J 2013 *Carbon* **52** 595
- Yang J and Gunasekaran S 2013 *Carbon* **51** 36
- Shao Y, Wang J, Wu H, Liu J and Aksay I A 2010 *Electroanalysis* **22** 1027
- Liu F, Piao Y, Choi K and Seo T S 2012 *Carbon* **50** 123
- Ponomarenko L A, Schedin F, Katsnelson M I, Yang R, Hill E W, Novoselov K S and Geim A K 2008 *Science* **320** 356
- Geim A K and Novoselov K S 2007 *Nat. Mater.* **6** 183
- Winterlin J and Bocquet M L 2009 *Surf. Sci.* **603** 1841
- Eizenberg M and Blakely J M 1979 *Surf. Sci.* **82** 228
- Gilje S, Han S, Wang M, Kang K L and Kaner R B 2007 *Nano Lett.* **7** 3394
- Gomez-Navarro C, Weitz R T, Bittner A M, Scolari M, Mews A, Burghard M and Kern K 2007 *Nano Lett.* **7** 3499
- Schniepp H C, Li J L, McAllister M J, Sai H, Herrera-Alonso M, Adamson D H, Prud'homme R K, Car R, Saville D A and Aksay I A 2006 *J. Phys. Chem. B* **110** 8535
- Niyogi S, Bekyarova E, Itikis M E, McWilliams J L, Hammon M A and Haddon R C 2006 *J. Am. Chem. Soc.* **128** 7720
- Stankovich S, Piner R D, Chen X, Wu N, Nguyen S T and Ruoff R S 2006 *J. Mater. Chem.* **16** 155
- Stankovich S, Dikin D A, Piner R D, Kohlhaas K A, Kleinhammes A, Jia Y, Wu Y, Nguyen S T and Ruoff R S 2007 *Carbon* **45** 1558

21. Si Y and Samulski E T 2008 *Nano Lett.* **8** 1679
22. Wang G, Yang J, Park J, Gou X, Wang B, Liu H and Yao J 2008 *J. Phys. Chem. C* **12** 8192
23. Henglein A and Meisel D 1998 *Langmuir* **14** 7392
24. Rao V M, Castano C H, Rojas J and Abdulghani A J 2013 *Radiat. Phys. Chem.* **84** 39
25. Rojas J V and Castano C H 2012 *Radiat. Phys. Chem.* **81** 16
26. Casaos A A, Puértolas J A, Pascual F J, Hernández-Ferrer J, Castell P, Benito A M, Maser W K and Martínez M T 2014 *Appl. Surf. Sci.* **301** 264
27. Safibonaba B, Reyhanib A, Nozad Golikandb A, Mortazavib S Z, Mirershadib S and Ghorannevissa M 2011 *Appl. Surf. Sci.* **258** 766
28. Zhang B, Li L, Wang Z, Xie S, Zhang Y, Shen Y, Yu M, Deng B, Huang Q, Fan C and Li J 2012 *J. Mater. Chem.* **22** 7775
29. Zhang Y, Ma H, Zhang Q, Peng J, Li J, Zha M and Yu Z 2012 *J. Mater. Chem.* **22** 13064
30. Remita H, Lampre I, Mostafavi M, Balanzat E and Bouffard S 2005 *Radiat. Phys. Chem.* **72** 575
31. Krishnamoorthy K, Mohan R and Kim S J 2011 *Appl. Phys. Lett.* **98** 244101
32. Xu Sh, Yong L and Wu P 2013 *ACS Appl. Mater. Interfaces* **5** 654
33. Vasu K S, Chakraborty B, Sampath S and Sood A K 2010 *Solid State Commun.* **150** 1295
34. Qian W, Chen J, Wei L, Wu L and Chen Q A 2009 *Nano* **4** 7
35. Alam M S, Rao B S M and Janata E 2003 *Radiat. Phys. Chem.* **67** 723
36. Alam M S, Rao B S M and Janata E 2001 *Phys. Chem. Chem. Phys.* **3** 2622
37. Belloni J, Mostafavi M, Remita H, Marignier J L and Delcourt M O 1998 *N. J. Chem.* **22** 1239
38. Janata E 2002 *Indian Acad. Sci.* **114** 731
39. Guo H, Wang X, Qian Q, Wang F and Xia X 2009 *ACS Nano* **3** 2653
40. Shang J, Ma L, Li J, Ai W, Yu T and Gurzadyan G G 2012 *Sci. Rep.* **2** 792
41. Sheng Y, Tang X, Peng E and Xue J 2013 *J. Mater. Chem. B* **1** 512
42. Zhang L, Liang J, Huang Y, Ma Y, Wang Y and Chen Y 2009 *Carbon* **47** 3365
43. Hun Huh S 2011 Physics and applications of graphene – experiments, Mikhailov S (ed) Thermal reduction of graphene oxide (InTech) ISBN: 978-953-307-217-3
44. Saner S, Okyay F and Yürüm Y 2011 *Fuel* **90** 2609
45. Sakika B K, Boruah R K and Gogo P K 2007 *J. Chem. Sci.* **121** 103
46. Dong X, Li B, Wei A, Cao X, Chan-Park M B, Zhang H, Li L J, Huang W and Chen P 2011 *Carbon* **49** 2944
47. Dong X, Xing G, Chan-Park M B, Shi W, Xiao N, Wang J, Yan Q, Sum T C, Huang W and Chen P 2011 *Carbon* **49** 5071
48. Lin W J, Liao C S, Jhang J H and Tsai Y C 2009 *Electrochem. Commun.* **11** 2153