Raman spectroscopy and X-ray photo-spectroscopy analysis of graphite media irradiated at low doses

D.A. Bradleya,b,∗, Z. Siti Rozailac, M.U. Khandakera, K.S. Almugrend, Worawat Meevasanae, S.F. Abdul Sanic

a Sunway University, Centre for Biomedical Physics, Jalan Universiti, 47500, Subang Jaya, Malaysia
b Department of Physics, University of Surrey, Guildford, GU2 7XH, United Kingdom
c Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur, 50603, Malaysia
d Dept. of Physics, Princess Nourah Bint Abdulrahman University, Riyadh, Saudi Arabia
e Synchrotron Light Research Institute of Thailand and Suranaree University of Technology, 111 University Ave, Muang, Nakhon Ratchasima, 30000, Thailand

HIGHLIGHTS
• Low-dose photon irradiations used in initiating structural alteration in carbon-rich materials.
• Analysed via Raman and X-ray photo-spectroscopy, providing analysis of dose dependence.
• Disorder via defect creation and annealing as competing dominant effects across dose range.
• O1s/C1s ratio a potential parameter for dose dependent damage analysis in graphite.

ARTICLE INFO
Keywords: Carbon Dosimetry Spectroscopy Structural alterations

ABSTRACT
We explore the utility of controlled low-doses (0.2–100 Gy) of photon irradiation as initiators of structural alteration in carbon-rich materials. To-date our work on carbon has focused on β-, x- and γ-irradiations and the monitoring of radiotherapeutic doses (from a few Gy up to some tens of Gy) on the basis of the thermoluminescence (TL) signal, also via Raman and X-ray photo-spectroscopy (XPS), providing analysis of the dose dependence of single-walled carbon nanotubes (SWCNT). The work has been extended herein to investigate possibilities for analysis of structural alterations in graphite-rich mixtures, use being made of two grades of graphite-rich pencil lead, 8H and 2B, both being in the form produced for mechanical pencils (propelling or clutch pencils). 2B has the greater graphite content (approaching 98 wt%), 8H being a mixture of C, O, Al and Si (with respective weight percentages 39.2, 38.2, 9.8 and 12.8). Working on media pre-annealed at 400 °C, both have subsequently been irradiated to penetrating photon-mediated doses. Raman spectroscopy analysis has been carried out using a 532 nm laser Raman spectrometer, while for samples irradiated to doses from 1 to 40 Gy, XPS spectra were acquired using Al Kα sources (hv ∼1400 eV); carbon KLL Auger peaks were acquired using 50 eV Pass Energy. At these relatively low doses, alterations in order-disorder are clearly observed, defect generation and internal annealing competing as dominating effects across the dose range.

1. Introduction
The considerable versatility of carbon materials arises in great part from the strong dependence of their physical properties on the ratio of sp2 (graphite-like) to sp3 (diamond-like) bonds. In regard to graphite itself, it is to be appreciated that this is made of up of planar arrangements of covalently bonded carbon atoms, Van der Waals bonding providing the weak interplanar link; the utility of the common graphite-rich pencil depends upon this. In investigation of structural alterations brought about by extrinsic effects, Raman spectroscopy is currently perhaps the most used non-destructive and high-resolution technique for carbon structural studies, providing valuable information of defects, stacking of graphene layers, crystallite size in- and out-of-plane of graphite and edge states. Conversely, and as used herein, X-ray photo-spectroscopy (XPS) can explore the distribution of oxygen-containing functional groups, C-OH being a particular example.
et al., 2018).

Interest concerns order–disorder alterations brought about by relatively low dose irradiations, use being made of x- and gamma-ray sources. As alluded to, the primary means of analysis herein is Raman microspectrometry and XPS, the latter concerning chemical shifts, electron binding energy depending on the oxidation state of the atom as well as the level from which photoemission occurs. Such shifts, readily observed in XPS spectra, are: (i) of high intrinsic resolution (core levels are discrete and generally of a well-defined energy) and are; (ii) described within a one-electron process (simplifying interpretation). Atoms of higher positive oxidation state exhibit greater binding energy, a result of the additional coulombic interaction between the photoemitted electron and the ion core. The situation is one providing the ability to discriminate between different oxidation states and chemical environments.

Present work is distinct from the many defect study alterations in graphite and graphene conducted using neutron, gamma-mediated and electron/ion irradiation dose values from 10s to several hundred kGy and more (Uğur Akbaba et al., 2018; IAEA-TECDOC-901, 1996, the latter reflecting in part the work of Professor B.T. Kelly and his reviews encompassing more than five decades of studies on the irradiation behaviour of graphite). Instead, in present work use is made of photon-mediated electron dose deposition (acknowledging photolelectrons and Auger electrons to deliver the dose while photons provide the means of transport) and direct electron doses, with values from a fraction of a Gy through to 100 Gy. The arrangement followed allows for well-controlled irradiations delivered in periods of relatively short duration (minutes to hours), typically maintaining stable dose-rates. The intention is to demonstrate that x-ray irradiations create structural alterations in carbon-rich materials at much lower doses than previously determined, also pointing to a convenient means by which analyses of structural changes in carboniferous media can be made.

Prior work by members of this group have been on single-wall carbon nanotubes (SWCNT) and doses in the range 0.2–6 Gy, Bardi et al. (2017) using Raman analysis of x-ray irradiated samples in demonstrating evidence of structural alterations, while Abdulaziz et al. (2016, 2017, 2019) have used a relatively low activity (95 MBq) 90Sr/90Y beta source, $E_{B} = 0.546$ MeV/2.28 MeV, providing XPS analyses revealing regularity in change of the sp2 to sp3 hybridization. Noted in regard to high dose studies is that a good fraction of these have involved bulk measurements of change, as in for instance concerning electrical resistance, as exemplified by Abbe et al. (2017) on single-walled carbon nanotubes (SWNT) and MWNT and multi-walled carbon nanotubes/resin composites (ME), combining the electrical measurements with Raman analysis to demonstrate a firm link between damage causation and bulk change in electrical conductivity. Similarly, mechanical property alterations have also been investigated, strength in particular, forming yet another area of considerable interest (see for instance, Filleter and Espinosa, 2013), firmly associating stress-strain accommodation with cross-linking of CNT fibres. Importantly, in regard to bulk property alterations of nuclear graphitades and other carbon materials, McEnaney and Wickham (1996) have observed degradation of a wide range of properties, thermal or radiolytic oxidation (also in this context see, Ram Krishna et al., 2015), fractional weight loss, strength, elastic modulus and thermal conductivity, to all be capable of being fitted to simple exponential relationships of the form: $S = S_{0} \exp (-bx)$, with $S_{0}$ and b experimental parameters. In this same context, Abdulaziz et al. (2019) have reported such fitting to also be applicable in rationalising changes in sp2 to sp3 hybridization in SWCNT with dose.

### 2. Experimental details

Irradiation studies were made of two grades of graphite-rich pencil lead, 8H and 2B, both morphologically in a regular form consistent with their use in mechanical pencils (propelling or clutch). Each was of diameter 0.5 mm. 2B has the greater graphite content (approaching 98 wt %), 8H being a mixture of C, O, Al and Si (with respective weight percentages 39.2, 38.2, 9.8 and 12.8). Our interest here has been to look at what influence the predominant clay binder additive (Al2O3) might have on the otherwise graphite results. Working on media pre-annealed at 400 °C (mitigating against the influence of defects mechano-chemically induced prior to irradiation), both have subsequently been irradiated to penetrating photon-mediated doses, either through use of an ERESOC model 200 MF4-RW X-ray machine or otherwise a 60Co gamma-rays irradiator, access to both sources being provided at the Physics Department of the University of Malaya. Both systems have been calibrated so that the dose results are to be considered accurate assessments. The X-ray set was operated at 150 kVp to deliver doses ranging from 10 mGy to 6 Gy; conversely, gamma-ray irradiations provided for an extended upper limit to dose, the range extending from 1 to 100 Gy.

Spectroscopic analyses were only made some days and more after irradiation, a matter of importance in allowing for relaxation phenomena and with that identification of stable defects generation. Raman spectroscopy analysis of the irradiated samples was carried out using a 532 nm laser Raman spectrometer. X-ray Photoelectron Spectroscopy (XPS) of gamma irradiated samples for doses ranging from 0 to 40 Gy were acquired using an Al Kα source (hv ∼1400eV), with facilities located at the Synchrotron Light Research Institute (SLRI), Thailand and University Teknologi Petronas (UTP), Malaysia; carbon KLL Auger peaks were acquired using 50 eV Pass Energy, the sample D-parameter being determined.

### 3. Results and discussion

#### 3.1. Effective atomic number

Across the range of photon energies used herein the likelihood of photon interactions in a given material is strongly influenced by its effective atomic number, a single-valued representation of the multi-element composition (Table 1). At lower energies dose deposition is dominated by the photoelectric (pe) process; at more elevated energies the domination of pe gives way to the Klein Nishina cross-section of the inelastic process albeit remaining important. A further influencing factor is the material density. Through use of an energy dispersive x-ray facility attached to a scanning electron microscope (SEM/EDX), 2B is seen to provide by far the greater graphite content, with C approaching 98 wt %, while 8H comprises a mixture of the elements C, O, Al and Si, with C approaching 40 wt %.

For a mixture of elements, and within the regime dominated by the pe process, the effective atomic number $Z_{eff}$ is conventionally calculated using the Mayneord equation (Khan, 2010), as follows:

$$Z_{eff} = (a_{1}Z_{1}^{2.94} + a_{2}Z_{2}^{2.94} + a_{3}Z_{3}^{2.94} + ... + a_{n}Z_{n}^{2.94})^{1/n}$$

(1)

with $a_{1}, a_{2}, ... a_{n}$ the fractional contribution of each element to the total number of electrons in the mixture (Table 2).

#### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>8H</th>
<th>2B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td>Atomic (%)</td>
<td>Weight (%)</td>
</tr>
<tr>
<td>C</td>
<td>39.19</td>
<td>50.35</td>
</tr>
<tr>
<td>O</td>
<td>38.18</td>
<td>36.96</td>
</tr>
<tr>
<td>Al</td>
<td>9.80</td>
<td>5.62</td>
</tr>
<tr>
<td>Si</td>
<td>12.83</td>
<td>7.07</td>
</tr>
</tbody>
</table>
3.2. Raman spectroscopy

The Raman signals arising from lattice vibration (phonons) of graphitic materials consisting of stacked graphene layers are known to be highly sensitive to the degree of structural disorder (defects). As shown in Fig. 1, the most prominent feature in the Raman spectra is the so-called G band, assigned to the in-plane vibration of the C-C band and appearing at 1570 cm$^{-1}$. The D-band, at $\sim 1350$ cm$^{-1}$ (D refers to the disordered band) and the G’ band at $\sim 2700$ cm$^{-1}$ (considered to be an overtone of the D band) are prominent features. The G band exhibits a high frequency shoulder at $\sim 1620$ cm$^{-1}$ (the so-called D’) that is typical of defective graphite-like materials. These components are clearly evidenced in the deconvolution curve of the Raman spectra of 2B and 8H samples, as shown in Fig. 2 (a) and (b), focusing on first-order Raman spectroscopy ranging from 1000 to 2000 cm$^{-1}$. Two other bands to be taken into account are located at 1188 and 1489 cm$^{-1}$ in the fitting curve to the spectrum, being respectively assigned to the C-C and C=C stretching vibration modes of amorphous carbon ([Jawhari et al., 1995], and polyene-like structure ([Dippel et al., 1999]). In Fig. 1, evidence is also found of a number of minor peaks, one at 2330 cm$^{-1}$ arising from the N$_2$ present in air ([Pimenta et al., 2007]), those at 2270 - 2280 cm$^{-1}$ due to isocyanate vibrations (N=C=O) and a shoulder peak at 2340 cm$^{-1}$ corresponding to the C=N=O asymmetric stretch vibration. Weak Raman peaks at around 1100 cm$^{-1}$ have previously been attributed to the perpendicular Si-O vibrations of kaolinite clay (clay being the binding agent in graphite pencils), observable at 1020, 1043 and 1110 cm$^{-1}$ ([Frost, 1995]).

The Raman spectra were taken at three different points on each sample (noting the values at each point to be close to their mean value), interest being in the integrated intensity ratio of the baseline subtracted D to G band. The G-band position, the D-band width and $I_D/I_G$ intensity ratio describe graphitic order in the material ([Jawhari et al., 1995]). In Figs. 3 and 4, it is seen that the $I_D/I_G$ intensity ratio for samples irradiated to 10 mGy to 6 Gy of 150 kVp x-rays and to 1–100 Gy of 60Co γ-rays is in both cases sensitive to small change in lattice structure. For both curves fluctuations in the $I_D/I_G$ intensity ratio are noted across the entire range of investigated dose. Fig. 3 concerns 2B samples, relating to 98 wt % carbon, Fig. 3a showing the range of fluctuations across the entire dose range, while Fig. 3b shows the situation for the x-ray irradiations across the more restricted dose range up to 6 Gy. Fig. 4 shows the counterpart situation for 8H samples, the medium being a mixture of C, O, Al and Si (with respective weight percentages 39.2, 38.2, 9.8 and 12.8). In regard to the range of fluctuations, that of 8H is less, the relative change in the $I_D/I_G$ intensity ratio being much greater in the case of the graphite rich 2B by a factor of the order of 2 when compared with that for 8H samples. Working on carbon structural alterations at doses very much lower than previously investigated, the results offer surprise. While it is clear that more extensive measurements are going to be required, on the basis of current Raman spectrometry observations we suggest the following:

(i) photo-, Auger- and Compton electron energy deposition, localized on the nm scale due to multiple scattering, are creating the basis for structural alterations and their annealing in competition;
(ii) linear energy transfer (LET) differences between the x- and γ-ray irradiations are being expressed;
(iii) suppression of effects in 8H resulting from the presence of additional molecular oxygen, Al and Si.

![Fig. 1. Wide Raman spectra of 2B and 8H samples irradiated to a 10 Gy dose of 60Co γ-rays.](image)

![Fig. 2. Deconvolution of Fig. 1 spectra of a: (a) 2B sample and: (b) 8H sample.](image)

![Table 2. Effective atomic number of 2B and 8H samples.](table)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effective atomic number, $Z_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2B</td>
<td>6.13</td>
</tr>
<tr>
<td>8H</td>
<td>9.41</td>
</tr>
</tbody>
</table>

![Fig. 3.](image)

![Fig. 4.](image)
3.3. X-ray Photoelectron Spectroscopy (XPS)

Fig. 5 shows XPS spectra results for the 2B and 8H samples, irradiated using $^{60}$Co γ-rays to a dose of 40 Gy. The upper panel shows results for irradiated 2B, the spectrum showing a sharp and intense C1s peak together with an appreciably smaller O1s peak. In contrast, for similarly irradiated 8H (39 wt % of C, 38 wt % of O), observation is made of a relatively lower intensity C1s peak, an intense O1s peak and smaller but nevertheless well-defined expressions of O2s and of molecular Al and Si.

C1s XPS spectra deconvolution peaks are shown in Fig. 6 for both 2B and 8H, clearly indicating two peaks, their origin corresponding to C-C sp$_2$ bonds (284.6 eV) and C-C sp$_3$ bonds (285.6 eV); together with C = O (286.7 eV) they relate to defect structure. The appreciable C = O peak is entirely apparent, an overt expression of the 38 wt % of O in 8H media. Fig. 7 shows an expanded view of the C1s peak for the graphite rich 2B samples, accompanied by a plot of peak intensity as a function of dose. For doses up to 30 Gy a noticeable trend is the chemical shift towards larger binding energies. As noted previously, atoms of higher positive oxidation state exhibit greater binding energy, a result of the additional coulombic interaction between the photo-emitted electron and the ion core. Such variation is not accompanied by similar well-behaved change in relative intensity, as seen in Fig. 7b. This is presumably a complexity introduced by the dose dependent change in the sp2 to sp3 hybridization in graphite rich media, a feature also being noted by Abdulaziz et al. (2019) for SWCNT over the same dose levels, as well as by others for graphite albeit at other dose levels. Even greater, more intractable changes are seen in the 8H samples, a result of the more complex mixture in this particular medium. Also of note is the lack of any discernible dose dependent trend in change of the full-width at half maximum (FWHM) value of the C1s peak, either for 2B or 8H.

Fig. 8 shows the intensity ratio of O1s to C1s for 2B samples irradiated for doses up to 40 Gy using $^{60}$Co γ-rays. With normalization based on results from the same irradiated sample a clearer trend is observed, the ratio decreasing with dose. Distinct from the 2B results, Fig. 9 shows the more irregular change in C1s intensity of similarly irradiated 8H samples, finding no parallel with that of 2B samples, with similar lack of perceivable trend in the intensity ratio of O1s to C1s with dose for the same 8H samples.

X-ray induced Auger features, shown in Figs. 10 and 11 for the present samples, present at around 260 eV (kinetic energy), resulting from initial x-ray photo-ionisation followed by relaxation and subsequent ejection of valence electron from carbon atoms, denoted as C KLL (Barlow et al., 2016). The shape of the C KLL feature depends on...
the in-surface arrangement of C atoms (Mizokawa et al., 1987). In order to extract such information a common approach is called for, as detailed by Mezzi and Kaciulis (2010) in taking the first differential of the C KLL Auger spectrum, from this defining a so-called D-parameter. The approach has been used to good effect by Alanazi et al. (2016, 2017, 2019) as an analytical tool in investigation of the dose-dependent sp2 to sp3 hybridization ratio of SWCNT. For current samples, the dose dependency of the D-parameter varies considerably, reflecting changes in the sp2 to sp3 hybridization ratio (Figs. 12 and 13. The contention parallels rationalization of the Raman results, with competition between structural alterations and annealing of those alterations. To highlight this, Fig. 14 shows a combined graph of the $I_D/I_G$ and D-parameter over the dose range 0–60 Gy, with 150 kVp x-rays used to deliver doses from 10 mGy to 6 Gy and 60Co γ-rays extending irradiation to the higher doses. A marked parallel is observed between variations in $I_D/I_G$ and the D-parameter.

4. Conclusion

Present work concerns stable defects generation in irradiated graphite-rich media of a bulky nature (mm thickness), with results highly suggestive of competition between defects generation and annealing of structural alterations by the same photon-driven causation, one obtaining domination over the other within particular dose brackets. Thus in regard to the Raman data, for the very lowest doses one first sees an initial radiation-driven increase in the $I_D$ (defects) peak, followed subsequently by domination of the radiation-driven annealing which...
occurs simultaneously so that a dip then arises. The pattern is repeated at greater doses. Also, in use of 150 kVp x-rays and $^{60}$Co $\gamma$-rays, evidence is obtained of LET dependence. Through use of photon-mediated electron dose deposition, the work has been conducted at unprecedentedly low values of dose, from 10 mGy through to 100 Gy, with analyses subsequently carried out using two well-established spectroscopies, Raman and XPS. The work points to a rich area of investigation, present results at 100 Gy and below certainly not representing anything like an exhaustive exposition; the Raman spectra are a case in point, open to very much wider analyses than space provides for herein. Similarly, for XPS studies, depth-dose variations are of importance, being a manifestly surface technique; use of varying diameter pencil leads could be of assistance here, the surface to volume ratio increasing inversely with rod diameter.

Continuing within the same theme as above and reflecting on work conducted by others, while use could have been made herein of SEM imaging, as done by others in seeking evidence of alterations in structure, that previous work was carried out at much greater dose values. In present circumstance SEM deposited dose would have contributed at appreciable levels (see for instance, Galloway and Roitman, 1977), differing with SEM exposure duration, a situation not open to well-controlled dose delivery. The demonstration of damage causation in irradiated carbon is a

occurs simultaneously so that a dip then arises. The pattern is repeated at greater doses. Also, in use of 150 kVp x-rays and $^{60}$Co $\gamma$-rays, evidence is obtained of LET dependence. Through use of photon-mediated electron dose deposition, the work has been conducted at unprecedentedly low values of dose, from 10 mGy through to 100 Gy, with

analyses subsequently carried out using two well-established spectroscopies, Raman and XPS. The work points to a rich area of investigation, present results at 100 Gy and below certainly not representing anything like an exhaustive exposition; the Raman spectra are a case in point, open to very much wider analyses than space provides for herein. Similarly, for XPS studies, depth-dose variations are of importance, being a manifestly surface technique; use of varying diameter pencil leads could be of assistance here, the surface to volume ratio increasing inversely with rod diameter.

Continuing within the same theme as above and reflecting on work conducted by others, while use could have been made herein of SEM imaging, as done by others in seeking evidence of alterations in structure, that previous work was carried out at much greater dose values. In present circumstance SEM deposited dose would have contributed at appreciable levels (see for instance, Galloway and Roitman, 1977), differing with SEM exposure duration, a situation not open to well-controlled dose delivery.

The demonstration of damage causation in irradiated carbon is a

Fig. 8. Intensity ratio of O1s to C1s for 2B samples irradiated to 0–40 Gy of using $^{60}$Co $\gamma$-rays.

Fig. 9. C1s intensity of 8H samples irradiated to 0–40 Gy of using $^{60}$Co $\gamma$-rays.

Fig. 10. 2B for $^{60}$Co doses upto 40 Gy: (a) C KLL Auger spectra; (b) 1st derivative of C KLL spectra and D value.
Fig. 11. 8H samples irradiated to doses from 1 to 40 Gy using $^{60}$Co $\gamma$-rays: (a) C KLL Auger spectra; (b) use made of first derivative of C KLL Auger spectra to determine values of the D-parameter.

Fig. 12. Relationship between dose and D-parameter for 2B and 8H samples.

Fig. 13a. % sp2 and D-parameter for 8H samples, using diamond (100% sp2) and graphite (100% sp3) as references. A similar situation is seen for the 2B samples, as below.

Fig. 13b. % sp2 and D-parameter for 2B samples, using diamond (100% sp2) and graphite (100% sp3) as references. A similar situation is seen for the 8H samples in Fig. 13a above.
connected with the same dissociation energy could well be simply conjecture or could perhaps have underpinning relevance that is yet to be determined.

Acknowledgements

The authors express gratitude for the following sources of funding: Bantuan Kecil Penyelidikan (BKP) from the University of Malaya - BK093-2016, also from the Fundamental Research Grant Scheme (FRGS) of the Ministry of Education Malaysia - FP032-2017A.

References


