RSC Advances

RSC Publishing

REVIEW

Nano-structure and property transformations of carbon systems under γ-ray irradiation: a review

Cite this: *RSC Advances*, 2013, **3**, 10579

Zhiwei Xu,* Lei Chen, Baoming Zhou, Yinglin Li, Baodong Li, Jiarong Niu, Mingjing Shan, Qiwei Guo, Zhen Wang and Xiaoming Qian

Received 11th January 2013,
Accepted 14th March 2013

DOI: 10.1039/c3ra00154g

www.rsc.org/advances

Carbon-based materials have been used quite successfully for decades within industry sectors. Especially, the application of them in the field of aerospace has been paid lots of attention. The severe environment such as γ-rays in space, which may give rise to the formation of atomic defects, may deteriorate the performance of carbon-based devices significantly. However, in addition to the well-known cases of destroying the properties of carbon systems, recent experiments show that γ-ray irradiation can also be employed as an attractive tool for the fabrication, modification and manipulation of carbon materials. In this article, we briefly review the recent progress in our understanding of γ-ray irradiation-induced phenomena in some carbon systems with experimental results and theoretical analysis. Particular emphasis is put on the discussion of the effects of γ-rays on nanostructure and morphology of carbon fibers, graphite, carbon nanotubes, graphene and diamond, as well as the methods for tailoring their mechanical, chemical and electronic properties. Finally, we attempt to identify the future directions in which the irradiation-induced modification field is likely to develop.

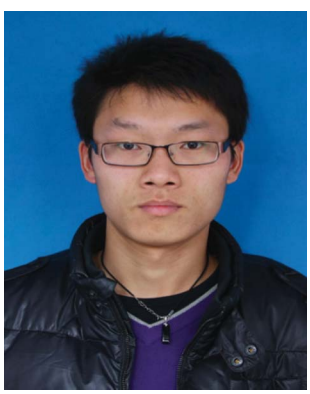
1. Introduction

Carbon is a unique element because a simple variation in its local bonding configuration (sp^3 *versus* sp^2) gives rise to a variety of materials as diverse as diamond, graphite, fullerenes, disordered, and nanostructured carbons including nanocrystalline diamond and carbon nanotubes (CNTs). For over a decade, carbon-based nanomaterials created interest both in view of the obvious academic importance and technological relevance, especially in the field of aerospace.[1,2] Severe environmental tolerability is the prime factor in the development in novel space materials and it is believed that across the main radiation environments (such as γ-rays), carbon materials may outperform their conventional counterparts, where the improvement is attributed to perfect structures.[2,3] Except for the deterioration of carbon materials, in recent years, irradiation-induced grafting is being extensively investigated as a new technique to alter properties of various materials, such as films, fibers, powders and molded objects.[4–6]

Key Laboratory of Advanced Braided Composites, Ministry of Education, School of Textiles, Tianjin Polytechnic University, Tianjin 300160, P. R. China.
E-mail: xuzhiwei@tjpu.edu.cn; Fax: +86 022 83955231; Tel: +86 022 83955231

Zhiwei Xu

Zhiwei Xu graduated in 2007 from Herbin Institute of Technology with a PhD degree. Since December 2007, he has been a group leader. His current scientific interests include the irradiation modification of carbon nanomaterials, structure of multi-scale composites and preparation of hybrid ultrafiltration membranes.



Lei Chen

Lei Chen received his Bachelor's degree in textile engineering from Yancheng Institute of Technology in 2008, and then joined the group of associate Prof. Zhiwei Xu at Tianjin Polytechnic University, recieving his Master's degree in 2011. Now he is a PhD candidate. His primary interests are in the areas of the effects of irradiation on carbon materials, and the interface design of carbon fiber reinforced composites.

And γ-radiation has been applied extensively in initiating polymeric backbones, modifying polymer blends, and in preparing interpenetrating polymer networks.[7] It can induce chemical reactions at any temperature in the solid, liquid and gas phase without any catalyst[8,9] and may give rise to quite unexpected and even counter-intuitive results. In addition, γ-ray irradiation is a safe method that could protect the environment against pollution, reduce maintenance cost and save energy consumption. Large and thick three-dimensional objects could also be treated by irradiation without consideration of the shape of the samples, which is convenient for industrialization.[10,11]

The aim of this review is to summarize the most recent experimental results on γ-irradiation effects in various carbon systems, such as carbon fibers, graphite, fullerenes, diamonds, CNTs, graphene and their composites. We reviewed the alternations of microstructure and morphology of carbon systems induced by γ-rays. The modifications of mechanical, electrical and chemical properties caused by irradiation were also investigated. We restricted our consideration to selected papers reporting results of irradiation with γ-rays without reviewing the effects of ion and electron beams irradiation which have been summarized impressively in A. V. Krasheninnikov's work.[12]

2. Carbon fibers

Carbon fibers have superior properties in strength, modulus, stiffness and lightness and thus are widely used as reinforcement in carbon fiber reinforced plastics, metals, ceramics and C–C composites.[13] Many works have been conducted to improve the mechanical properties of the single fibers for stretching their applications in carbon fiber reinforced polymer (CFRP) composites. In addition, the interface between carbon fibers and resin matrix also plays a critical role in controlling the overall properties of the composites, while the smooth and inertness characteristics of carbon fiber surface usually result in inferior wettability and weak adhesion between the fibers and resin.[14–16] With regard to these reasons, extensive research has been devoted to the surface treatment of carbon fibers in order to improve their bonding to the resin matrix.[17–20] In the predecessors' works and our previous papers, modifications of single fibers and interface of CFRP induced by γ-ray irradiation were both investigated exhaustively.[10,21–27] The exact alterations are illustrated in detail in the following parts.

2.1. Fiber surface topography

The change of fiber surface topography after γ-ray irradiation is shown in Fig. 1. Compared with the original carbon fiber, the treated carbon fiber surface was rougher and the grooves of fiber surface became wider and deeper (see Fig. 1). It could be interpreted by γ photons etching process on carbon fiber surface.[22] Moreover, Increase in roughness was observed with increase in treatment dose. Therefore, interfacial adhesion between grafted fibers and matrix resin may be enhanced by increasing the surface area (increasing roughness) which may provide more points of contact between the fiber and the matrix. The Compton scattering effect is mostly responsible for the interaction of γ-rays with carbon fibers. The predominant interaction mechanism is ionization.[30] The electron and scattered photon are produced after the incident photon interacts with carbon atom of carbon fibers and graphite. Then the carbon free radical is created by anion or cation radical mechanisms. The amount of first class flaws is decreased and the graphitization of carbon fibers is improved. It is highly likely that gamma irradiation causes the significant heating in carbon fibers and graphite.[21]

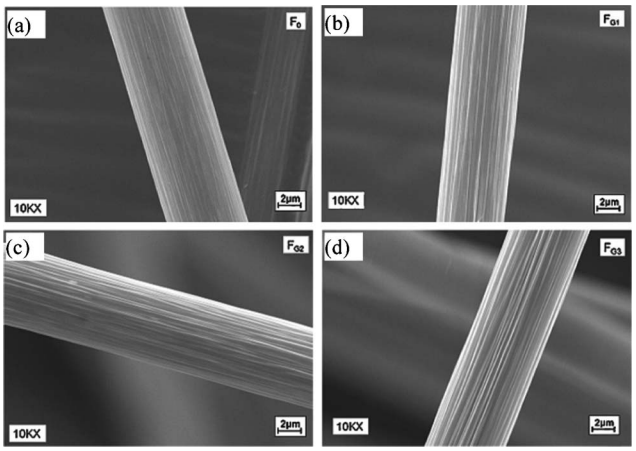


Fig. 1 Scanning electron microscope (SEM) images of the surface of (a) pristine carbon fiber surface and γ-ray-treated carbon fibers with the dose of (b)100 kGy, (c) 200 kGy and (d) 300 kGy (Reprinted with permission from ref. 30 and 31, copyright from Elsevier).

2.2. Surface elements

The SEM images of pristine, epoxy co-irradiation treated, chloroepoxy propane (ECP) co-irradiation treated and acrylic acid pre-irradiation treated carbon fibers are shown in Fig. 2. After irradiation and grafting, more pieces of tiny fragments stuck to the fiber surface, which suggested that the absorbability of treated fibers might be enhanced to some extent. The alterations of surface elements and functional groups of carbon fibers were investigated in our previous works and the results are listed in Tables 1 and 2 respectively.[22,23] Carbon and oxygen were the major surface elements and small amounts of nitrogen amounting to less than 0.6% on the surface of the untreated carbon fiber samples were observed. As shown in Table 1, the amount of surface oxygen was increased and the amount of surface carbon was decreased after irradiation and grafting. An about two-fold increase in oxygen content occurred after irradiation grafting. The large variation of oxygen groups may be attributed to the grafting of monomers onto carbon fiber surface and the oxidation of carbon fibers by γ-ray irradiation.

C–C (graphitic carbon and amorphous carbon) were the major carbon functional components on the surface of carbon fiber samples. From Table 2, it is clear that the carbonyl carbon in ketones and quinines (C=O) and carboxyl or ester

 This journal is © The Royal Society of Chemistry 2013

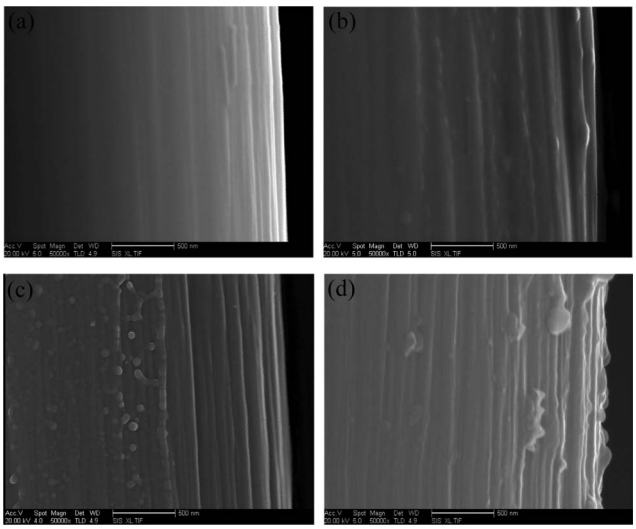


Fig. 2 SEM micrographs of carbon fiber surface: (a) as-received; (b) epoxy co-irradiation treated; (c) ECP co-irradiation treated; (d) acrylic acid pre-irradiation treated (Copyright from Elsevier).[24]

(COOH/COOR) functional groups increased, and the graphitic carbon (C–C) and carbon bonded phenolic or alcoholic hydroxyl or ether oxygen (C–OH/C–O–C) functional groups decreased after treatment. The oxygen group is the main contribution on the surface of carbon fiber, which was obtained from γ-ray irradiation process, compared to the virgin carbon fiber sample. Furthermore, the carboxyl or ester functional group percentage of carbon fibers treated by acrylic acid is greater than that of carbon fibers treated by epoxy and ECP. These results may be attributed to the γ-ray irradiation inducing free radical reaction between carbon fiber surface and monomers.[23]

2.3. Fiber surface energy

In Table 3, the surface free energy, its dispersive component and its polar component of carbon fibers are summarized. It can be seen that both the dispersive and polar components of surface free energy, γ_f^d and γ_f^P, increased after treatments. We have also found that the irradiation treatments of carbon fibers gave an increase in surface functionality in the context of XPS studies, which may take chief responsibility for the improved polar component. The increase in dispersive component was attributed to the possible presence of deep grooves in fiber surface, which were generated by pre-irradiation and co-irradiation etching.

Table 1 Variation of surface composition of the carbon fibers before and after treatment[24] (Copyright from Elsevier)

Elements	C (%)	O (%)	Cl (%)	O/C
As-received	87.39	12.61	0	0.14
Epoxy co-irradiation	72.47	27.53	0	0.38
ECP co-irradiation	69.29	30.12	0.59	0.43
Acrylic acid pre-irradiation	72.75	27.25	0	0.37

Due to the improvement in the fiber surface energy, the wetting performance of carbon fiber was improved after irradiation. The weight of wetting was increased and the complete wetting time of the treated sample was reduced compared with the untreated sample. The increased functional group concentration and the enhanced polarity of the fiber surface should be the main reasons for these alterations.[23] In addition, the new synthesis method of fluorinated carbon nanofibers assisted by gamma irradiation was evaluated in Zhang's work.[31] It was found that γ-irradiation resulted in structural disorder and hyperfluorination occuring for those reaction routes. γ-Irradiation is too energetic under F_2 atmosphere, the fluorination being effective but in majority due to CF_2 groups.

2.4. Microstructure of carbon fiber

X-Ray diffraction (XRD) is an efficient method to characterize the microstructure of carbon materials. The main peak can be seen to occur at approximately $2\theta = 25.5^\circ$, corresponding to the (002) reflections of the pseudo-graphite structure.[32] There is also a much weaker band at $\sim 44^\circ$ 2θ, which is usually assigned to the (10) turbostratic band of disordered carbon materials. The weakest band at $\sim 53^\circ$ 2θ corresponds to the (004) reflections of the pseudo-graphite structure.

The γ-ray irradiation was an effective method for improving the graphitization degree of polyacrylonitrile based carbon fibers. It can be seen from Fig. 3 and Table 4 that the average d002 interlayer spacing, indicative of the degree of graphitization, decreases gradually from 0.352 nm for the untreated fibers to 0.345 nm for the fibers irradiated at the dose of 2.0 MGy. Compared to that of untreated fibers, the value of treated fibers is closer to the ideal value of the spacing of graphite layers in a perfect graphite crystal (0.335 nm), therefore indicating the improvement of average graphitization of the treated fibers. Large decrease in the d002 interlayer spacing of carbon fibers has been achieved by γ-ray irradiation and an approximately linear dependence on absorbed dose has been suggested. The intensity of (002) peak in carbon fibers decreased and the carbon content of carbon fibers surface layer was improved by irradiation. Compton scattering effect and heating caused by γ-rays are proposed to be responsible for the graphitization of carbon fibers and graphite.[10,21] In addition, the decrease of flaws and microstructural parameters such as d002 interlayer spacing can be closely related to the variations of density, tensile strength and Young's modulus.[10]

The influence of absorbed dose of γ rays on the fiber density is evident from Fig. 4.[10] The curve shows that the density increased with the absorbed dose. The main reason for this alteration should be the increased crystallinity, which can be further proved by the irradiation induced alterations in graphite and multi-walled carbon nanotubes (MWCNTs) in the latter sections. In addition, it may be seen from Fig. 4 that the main density increase occurred in the first 0–0.5 MGy dose and there was an approximately linear relationship between density and absorbed dose (0–0.5 MGy). Then this density increase was less pronounced above 0.5 MGy, which may due to the approaching of threshold under 0.5 MGy γ-rays. However, the density of irradiated fibers was much far away from the density of perfect graphite (2266 kg m^{-3}) though the

Table 2 Relative content of functional groups in C1s spectra of carbon fibers from X-ray photoelectron spectroscopy analysis (XPS)[24] (Copyright from Elsevier)

Groups	C–C (%)	C–OH/C–O–C (%)	C=O (%)	COOR/COOH (%)
Binding energy (eV)	284.7–284.9	285.5–285.8	286.5–286.8	288.5–288.9
As-received	49.7	31.9	12.9	5.5
Epoxy mutual treated	38.4	26.0	21.4	14.1
ECP mutual treated	40.2	26.2	20.1	13.5
Acrylic acid pre-irradiation	40.3	25.6	19.1	15.0

packing fraction of fibers was increased from 77.4% for the as-received fiber to 79.5% for the fiber irradiated at 2 MGy dose.[10] The difference of the density change between carbon fibers and graphite or MWCNTs (as illustrated in the later sections) should be caused by highly porous nature of carbon fibers. It is expected that γ irradiation, like hot stretching and temperature, affects the porosity of fibers.[33]

2.5. Fiber mechanical properties

The mechanical properties of single fibers have been investigated in our previous work.[10] Carbon fibers initially increase in strength, at low dose, but reduction in strength occurs at high dose (Fig. 5(a)). The shape parameter was increased after irradiation grafting at each gauge length. Young's modulus is substantially increased with the increase in absorbed dose (see Fig. 5(b)). These results are probably attributed to the reduction of flaws and decrease of interlayer spacing by γ-ray irradiation. Additionally, Compton scattering effect caused by γ-ray is proposed to be responsible for the structural and mechanical changes of fibers. These results indicated that γ-ray irradiation was expected to be an effective method for improving the mechanical properties and graphitization degree of carbon fibers.[10,22] However, Tiwari *et al.* have got an opposite result in their works.[28,29] They tested the untreated and treated fiber tows in tension, which was different from the single-fiber method according to ASTMD3379M standard in our report[10,11] and found that irradiated fibers showed lower tensile strength as compared with the untreated one. Higher the dose, higher was the roughness and pitting on the surface of fibers, higher was the reduction. They believed that the reduction may be due to the increment in pits and grooves on the surface after treatment. These two opposite results may be due to the difference in testing method and need be further investigated to make sure the main mechanisms for these differences.

2.6. Composites reinforced by carbon fibers

The unique combination of physical and chemical properties of CFRP has led to their widespread application in different fields of industry, machine and sport. With improved in-plane mechanical properties, CFRP laminates have been widely used in many structural engineering fields, such as aerospace engineering, automotive industry, *etc.* However, their weak interlaminar mechanical properties, *e.g.* low interface strength and fracture toughness, may easily lead to formation of internal interfacial delaminations under various transverse loadings, and limit their applications in more expansive fields.[34,35] Recently, irradiation-induced grafting is being extensively investigated as a new technique to alter surface properties of carbon fibers in order to improve the mechanical and thermal properties of CFRP. It is indicated that γ-ray irradiation grafting treatment is not only convenient and environment-friendly but high efficient in modification of carbon fibers. It is expected to be employed in the industrialized treatment.[36]

In our previous work,[22] the interlaminar shear strength (ILSS) results of composites reinforced by carbon fibers treated in different methods are shown in Fig. 6. After irradiation grafting, the ILSS of treated samples increased significantly. A maximum ILSS value can be found after epoxy co-irradiation

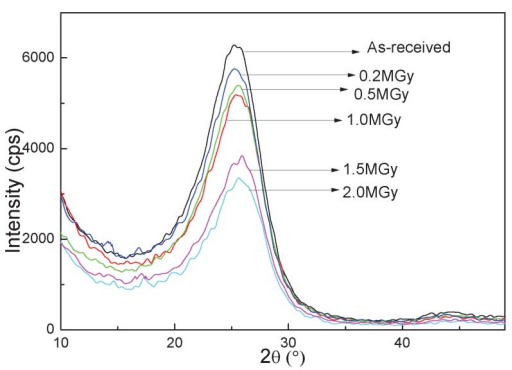


Fig. 3 X-Ray diffraction intensity distribution for the carbon fibers irradiated at different doses (Copyright from Elsevier).[23]

Table 3 Surface free energy of carbon fibers[24] (Copyright from Elsevier)

	γ_f^d (mJ m^{-2})	γ_f^p (mJ m^{-2})	γ_T^f (mJ m^{-2})
As-received	39.8 ± 1.6	2.4 ± 0.3	42.2 ± 2.0
Epoxy co-irradiation	44.6 ± 1.9	6.2 ± 0.5	50.8 ± 2.3
ECP co-irradiation	46.8 ± 2.4	7.8 ± 0.6	54.6 ± 2.6
Acrylic acid pre-irradiation	45.1 ± 2.5	8.4 ± 0.5	53.5 ± 2.1

Table 4 X-Ray diffraction structural parameters of carbon fibers[23] (Copyright from Elsevier)

	2θ [002] (°)	d002 (nm)
As-received	25.3	0.3520
0.2 MGy	25.32	0.3517
0.5 MGy	25.44	0.3501
1.0 MGy	25.62	0.3477
1.5 MGy	25.74	0.3460
2.0 MGy	25.79	0.3454

This journal is © The Royal Society of Chemistry 2013

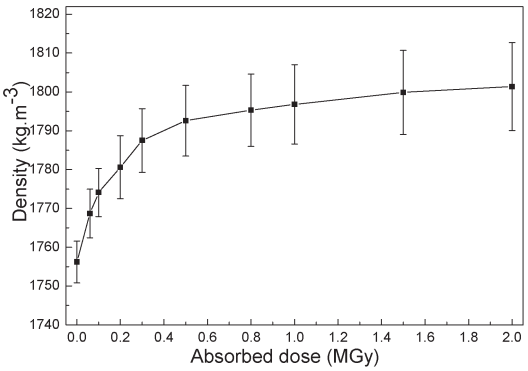


Fig. 4 Effect of γ-ray irradiation on the density of carbon fibers (Copyright from Elsevier).[10]

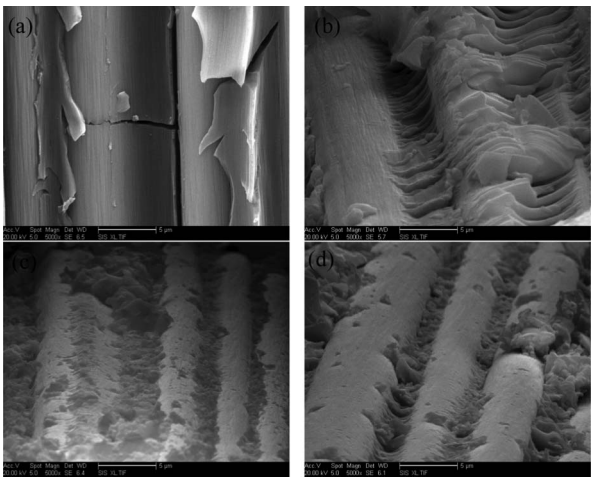


Fig. 6 SEM micrographs of fracture surface of composites: (a) untreated fiber composites; (b) epoxy co-irradiation treated fiber composites; (c) ECP co-irradiation treated fiber composites; (d) acrylic acid pre-irradiation treated fiber composites. (Copyright from Elsevier).[24]

grafting, *i.e.* 94.1 MPa, about 21.8% improvement compared with that of untreated one. The ECP co-irradiation and acrylic acid pre-irradiation grafting carbon fiber/epoxy composites performed marginally better (18.1% and 17.5%) than those manufactured using untreated carbon fiber/epoxy composites, respectively (see Fig. 7). The improvement on ILSS of carbon fiber/epoxy composites could be attributed to the enhancement of the interfacial adhesion strength of the fiber and matrix after irradiation grafting.

There are several mechanisms for the fiber-matrix bonding, which involve mechanical interlocking, chemical bonding, adsorption interaction and diffusion of polymer chain segments.[37–39] As far as irradiation-treated samples are concerned, it can be inferred that surface roughening and polar functionality, both factors generated by irradiation grafting, mainly contribute to the interfacial adhesion. After irradiation grafting, the oxygen-containing functional groups increased and the increasing of amounts of oxygen-containing functional groups on the fibers played an important role in improving the ILSS of the resulting composites due to higher electronegativity and polar characteristics at the interface between the carbon fiber surface and the composite matrix.[23] However, the relative roles of mechanical interlocking due to surface roughness and surface chemical bonding in fiber/matrix adhesion are difficult to separate. The enhancement of the surface roughness was beneficial for the wettability between fiber and matrix, resulting in mechanical anchor and chemical bonds. Generally, the improvement of ILSS should be attributed to the increase of surface roughness, surface free energy and the active chemical functional group and the decrease of surface microcrystal of carbon fiber, which were induced by γ-irradiation.[22,23]

Moreover, it should be noted that the enhancement of the interfacial bonding is concerned with the grafting reagent. Interlaminar shear testing has indicated that the epoxy co-irradiation carbon fiber/epoxy composites perform marginally better than those manufactured using ECP co-irradiation carbon fiber/epoxy composites. This result can be attributed to the fact that the grafting coating of the former is the same as matrix resin and thus the functional groups on fiber surface react with the matrix resin easily.[22]

Absorbed dose and dose rates were proved to influence the ILSS of CFRP in varying degrees in our work.[23] After surface treatment, the ILSS values of the CFRP were enhanced by 37.1% (30 kGy) and 31.2% (250 kGy), respectively compared with the untreated one. The better adhesion strength of the CFRP is due to the high density of surface carbon oxygen functional groups induced by γ-ray irradiation process. The increasing degree of the ILSS treated by 250 kGy γ-rays was less than the one treated by 30 kGy γ-rays. It may be due to being

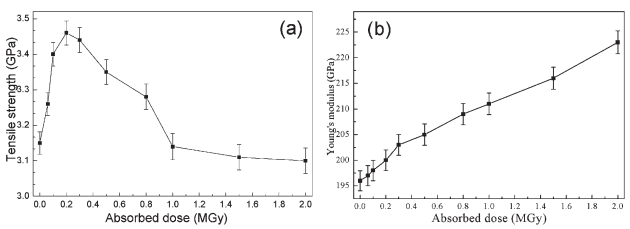


Fig. 5 Effect of γ-ray irradiation on the (a) tensile strength and (b) Young's modulus of carbon fibers (Copyright from Elsevier).[10]

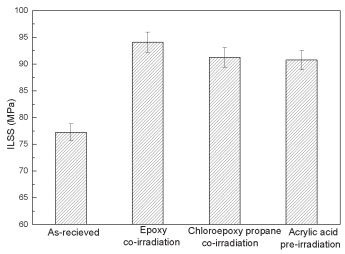


Fig. 7 Effect of γ-ray irradiation grafting on ILSS of carbon fiber/epoxy composites (Copyright from Elsevier).[24]

severely corroded by excessive irradiation. Thus, irradiation at proper absorbed dose are a benefit for enhancing the ILSS of CFRP and excessive irradiation would not achieve better interface between carbon fibers and epoxy by this method. In addition, it could be found that ILSS of carbon fiber/epoxy composites slightly changed if the absorbed dose is a fixed value. It can be concluded that irradiation dose rate was not a major factor for modifying the surface of carbon fiber. In other words, if the industrialized modification of the carbon fiber surface by irradiation method was realized, high absorbed dose rate could be used in order to save treating time.[23]

Except for ILSS, some other properties of CFRP were also studied after the irradiation treatment of carbon fibers. In Tiwari's work, the treated composites showed higher wear resistance, lower wear rates and lower friction coefficient than that of the pristine CFRP due to the improved adhesion between the fibers and matrix.[28,29] Thermal properties of CFRP were also found to be improved by γ-irradiation. The glass transition peak of the specimen, determined from torsional braid analysis, shifts towards a higher temperature compared with an unirradiated specimen in the work of Ma *et al.*[36] The value of the glass transition temperature (T_g) is increased from 416.8 to 424.3 K. The increase of T_g may also be attributed to the improvement of interfacial bonding, which brings the increasing of heat conductivity between carbon fibers and the matrix.[36] The surface modification of the fiber by γ irradiation also led to better dispersion in the rubber matrix. This in turn gave rise to further improvements in mechanical and dynamic mechanical properties of composites. The thermal conductivity also exhibited improvements from that of the neat elastomer, although thermal stability of the composites was not significantly altered by the functionalization of carbon nanofibers.[40,41]

3. Graphite

3.1. Graphite microstructure

Martin Hulman *et al.* have studied the Raman spectra of graphite at various doses of γ-ray irradiation and the results are shown in Fig. 8.[3] For graphite, the intensity as well as the position of the G line does not change upon irradiation. On the other hand, the intensity of the D line increases significantly, confirming the defect-based mechanism for Raman scattering from this particular phonon mode. In Cataldo's work, the interpretation of the Raman spectrum suggests that the radiation causes the formation of domains of hexagonal diamond, amorphous 'glassy' carbon and of onion-like carbon. He thought that the results are not surprising because it has already been shown that electron irradiation causes the formation of onion-like carbon[42,43] which can be reversibly transformed into ultradisperse diamond.[44,45] The new aspect covered by this letter regards the formation of hexagonal diamond and glassy carbon domains by irradiating graphite with γ-quanta.[30] Telling *et al.*[46] have theoretically discussed the stabilization of the products of γ-irradiation on a graphite lattice, suggesting that vacancies produced by γ-rays are stabilized by creating pentagon-heptagon defects and pushing one carbon atom out of the graphene plane. Galvan *et al.* also observed several structures after irradiation, while the two most important ones were onion layers with fullerene like structure and graphitic like structure with rotational and translational displacements.[47]

However, the results in our works were seen to show great contradictions compared with that mentioned above. Fig. 9 shows XRD intensity distribution of graphite untreated and irradiated at dose of 2.0 MGy.[21] After irradiation, no new peak from graphite powder appeared. The peak of the (002) plane becomes sharper after irradiation. It can be calculated from the Bragg equation that the d002 interlayer spacing, indicative of the degree of graphitization, decreases from 0.33756 nm for untreated graphite powder to 0.33706 nm for the irradiated graphite powder, therefore indicating the high level of graphitization of graphite powder irradiated at 2.0 MGy. The main reason for this contradiction should be due to the different irradiation conditions. It has been proved that the self-organization phenomenon could occur at high doses and an open and highly dissipative environment, which were successfully explained by Seeger as self-organized phenomena.[48,49]

3.2. Defective sites

It was concluded by Cataldo[50] that at least for the radiation dosages used, and for the particles energy involved, similar type of defective micro-domains are formed in both cases with electron or γ-ray irradiation: hexagonal diamond, fullerene-like structures (multiwall onion-like carbon and carbon nanotubes) as well as glassy carbon. Their conclusions are in line with the conclusions of other researchers,[51] who have

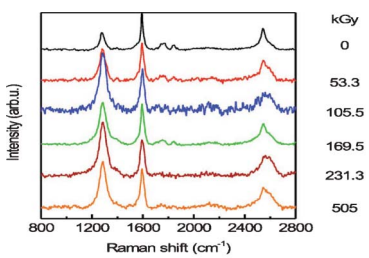


Fig. 8 Raman spectra of graphite for various stages of irradiation as indicated in the figure (Reprinted with permission from ref. 3, copyright from American Institute of Physics).

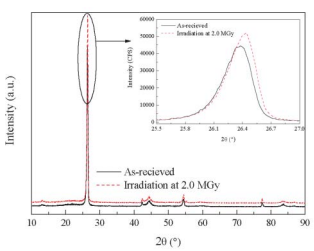


Fig. 9 XRD intensity distribution for graphite powder (Copyright from Elsevier).[23]

This journal is © The Royal Society of Chemistry 2013

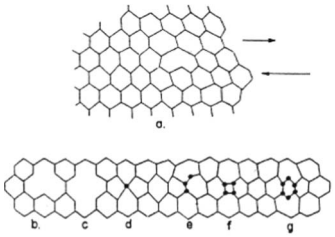


Fig. 10 Examples of defective structures caused by radiation-damage in graphene sheets of sp^2-hybridized carbon. (a) Two-dimensional strain, (b) single vacancy, (c) double vacancy, (d) double vacancy plus one atom, (e) double vacancy plus three atoms, (f) double vacancy plus four atoms, (g) double vacancy plus six atoms (Reprinted with permission from ref. 52, copyright from Taylor & Francis Online).

shown that curled surfaces (fullerene-like structures) are formed by both electron and ion-irradiation treatment of graphite. The formation of pentagonal, heptagonal and other more complex kind of defects in the graphene sheet of graphite has been proposed and discussed for a long time. The γ-radiation damage was significant, and comparable to that caused by electron bombardment especially in terms of introduction of fullerene-like sites, like the onion-like carbon, but other fullerene-like sites can be expected. The formation of these sites implies necessarily a C–C bond rupture in the solid, followed by graphene sheet curling as a consequence of the introduction of pentagonal, heptagonal or other sites (called fullerene-like sites). These kinds of defects are illustrated in Fig. 10. C–C bond rupture is a consequence of ionization and ionization decay processes rather than the physical impact of electrons on carbon atoms. Moreover, trapped electrons and holes in the solid may be expected, as it happens in other semiconductors treated with radiation. These trapped defects may be concentrated in the amorphous and glassy domains of carbon black and at the edges of the graphene sheets.

In composites, radiation defects to fillers such as carbon black and graphite induced by γ-radiation or neutrons dramatically increases their ability to adsorb resin irreversibly. The increased adsorption power of radiation-damaged fillers has been attributed to the formation of higher concentration surface defects in the form of trapped free radicals, fullerene-like structures and other kinds of defects. The mechanical properties of rubber compounds filled with radiation treated carbon blacks show a significant increase in their reinforcing effects, in line with the increased ability to form ''bound rubber''.[52] Furthermore, γ-irradiation can also be used to immobilize the polymer on the graphite surface by cross-linking the water-soluble polymer into an insoluble network.[53]

4. Diamond

Diamond is renowned among scientists and technologists for its impressive combination of exceptional physical (mechanical, thermal, electrical, electrochemical, and biological) properties offering multifunctionality that qualifies it to become the 21st century engineering material for multiple applications.[54,55] Diamond has a reputation for being radiation-hard material, therefore it is being suggested as a suitable semiconductor for detectors in high irradiation environments.[56–58]

4.1. Damage

Gamma irradiation causes damage by the indirect process of generating electrons (by Compton scattering and pair production) which then displace atoms (or ionise the material). The knock-on may cause further damage by displacing further atoms. The intrinsic defects (vacancies and interstitials) which are created by radiation damage are immobile at room temperature in diamond. Therefore, once the mechanisms of damage are understood for one type and energy of the particle, the dose and energy dependence of irradiation by other particles at a range of energies can be extrapolated. γ-Rays form predominantly isolated vacancies and interstitial pairs (Frenkel pairs). The range of 1 MeV electrons in diamond is about 1.3 mm with a nearly constant damage profile up to this cut-off. The range of gamma photons is much greater, with about 85% of 1 MeV photons passing through a 5 mm diamond without causing any damage. The total damage rates were calculated to vary between 0.01 and 5.15 vacancies per incident electron and between 0.02 and 6.10 vacancies per photon over the energy ranges investigated. In Campbell's work, the radiation damage of diamond caused by γ-irradiation can be predicted by taking into account the mechanisms of interactions of γ-radiation with matter.[59] Table 5 shows the vacancy production per millimeter as a function of the irradiation energy, and the total vacancies were found to be increased with the increase of the energy.

Diamond showed a dramatic change in structural properties after a cumulative dose of 260 kGy. It was indicated that diamond tends to reach a state of insensitive radiation phase after a cumulative dose of 26 kGy, suggesting the possibility of fabricating radiation buffer materials protecting the device/material underneath.[60,61]

However, as the irradiation proceeds, some of the carbon atoms displaced from their lattice sites may relax back into the vacant site, and the damage event will not be observed in the later measurement.[62] The annealing of damage is an additional factor reducing the vacancy populations that are detected experimentally and this is strongly dependent on temperature and radiation flux. All these processes can be modeled and extrapolated to other energies and particles. The atoms displaced by the radiation usually have quite small energies. Therefore they cannot move very far from the vacancy before they come to rest. Many of the knock-on atoms are

Table 5 Vacancies produced by gamma irradiation (Reprinted with permission from ref. 61, Copyright from Wiley)

Gamma energy (MeV)	(Vacancies/gamma)/cm
1	0.03
2	0.09
5	0.19
10	0.48
15	0.84

displaced less than 0.5 nm. At the displacement site, much of the energy is deposited as phonons, which cause a local heating of diamond. This may allow the interstitials to migrate, even if the nominal irradiation temperature is too low for their nominal migration.[62] In addition, it was found that annealing of the γ-irradiated type diamonds differed substantially from that for the electron irradiated samples; 60% of the monovacancies were removed between 350 and 525 K. Monovacancies were introduced either by 2.3 MeV electron irradiation or by ^{60}Co irradiation, where the latter type of irradiation causes damage due to Compton scattered electrons with a maximum energy of only 1.1 MeV.[63]

4.2. Electrical properties

In Gupta's work, microcrystalline diamond was submitted to gamma radiation with radiation doses of 10, 50, and 200 kGy.[64] It showed a dramatic improvement in the emission properties only after a cumulative dose of 260 kGy. The enhancement in emission characteristics shows the critical role of defects with their associated electronic defect states, and of sp^2-bonded carbon channels in the electron field emission mechanism of diamonds. Though it is still lacking an investigation concerning the alteration of electrical properties of diamond, Bruzzi *et al.* have found that the surface electrical conductivity was increased by ion bombardment by many orders of magnitude, which was induced by the production of carbon vacancies that can be also generated with γ-irradiation.[58]

In addition, different types of diamonds may have different response on the γ-irradiation. It was shown that the effect of gamma irradiation on boron-doped diamond thin films was distinctive compared to those of undoped diamond films with changes in electronic behavior from metallic to semiconducting, especially in the case of heavily boron-doped diamond films demonstrated by micro-Raman spectroscopy and electrical property characteristics.[54] In addition, the results also indicate that almost all of the boron-doped diamond thin films studied hereby tend to reach a state of damage saturation when submitted to gamma irradiation of 10^3 kGy.[54]

5. Fullerenes

The presence of fullerene species in the extraterrestrial samples found on Earth implies that these compounds are able to survive very long passages through diverse space environments. The most energetic known events in the Universe are supernovae and gamma ray bursts.[65,66] In the present work we wish to review earlier experimental data of fullerene stability toward high energy γ-irradiation. It was found by Basiuk *et al.*[67,68] and Cataldo[69] that the degree of C_{60} decomposition withstanding prolonged γ-irradiation, both in the presence and absence of liquid water, was less than 15%, demonstrating its extreme stability. Through Raman spectroscopy it was possible to observe that γ irradiation induces C_{60} dimerization and trimerization. The similar fullerene stability can be expected in different space environments, where the large carbon clusters are formed, incorporated into interstellar dust particles and subsequently into comets, and travel through the Universe. Cataldo *et al.*[70] have also shown that a dose of 2.6 MGy causes partial oligomerization of both C_{60} and C_{70} fullerenes (see Fig. 11). Oligomers are made by fullerene cages chemically connected each other which can yield back free fullerenes by a thermal treatment.

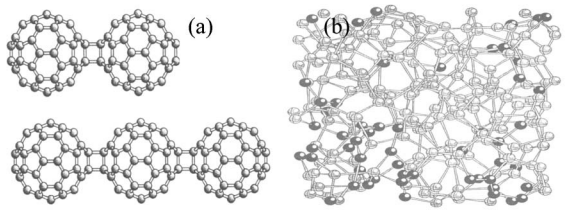


Fig. 11 (a) Structures of C_{60} fullerene oligomers: the dimer (top) and the trimer (bottom), and (b) a representation of collapsed (amorphized) fullerene cages after irradiation. Dark dots represent sp^2 hybridized carbon atoms and light dots represent sp^3 hybridized carbon atoms (Reprinted with permission from ref. 72, copyright from Oxford University Press).

Irradiation dose was also suggested to have significant effect on the graft of functional groups on fullerenes. Angelini *et al.* have found that bare silica surface is able to graft C_{60} both in vacuum and in presence of air. As determined by TGA, the amount of C_{60} grafted on silica surface was dependent from the radiation dose administered and independent from the C_{60} concentration and the nature of the organic solvent. In absence of air, a dose of 48 kGy was sufficient to ensure a grafting level of 30% by weight of C_{60} in the hybrid material. The fullerene/silica hybrid material shows a remarkable thermal stability.[71]

C_{60} fullerene is considered a free radical sponge. In fact, it reacts with a number of different types of radicals and normally it undergoes multiple addition reactions, leading to adducts with different stability.[72–75] When they were irradiated in molecularly dispersed forms, the behavior of fullerenes was investigated by Cataldo *et al.*[76] In presence of air the interference of oxygen is evident and the radiolysis should be conducted in high vacuum to avoid the interference of oxygen. A detailed analysis of the kinetics of the multiple additions of benzyl radicals to the fullerene cage was made spectrophotometrically with the determination of the addition rate constants at the each addition step and the average number of benzyl groups added to the fullerene cage as function of the radiation dose. Under the irradiation in toluene, multiple additions of benzyl radicals on fullerene cage occurred, which was depended from the conditions adopted, *i.e.*, fullerene concentration and radiation dose. Radiolysis causes also the precipitation of a fraction of fullerene products which are insoluble in toluene. Moreover, it has been shown that fullerene can be grafted onto polyisoprene chains by γ-radiation either in n-hexane where C_{60} has low solubility or in toluene where C_{60} is much more soluble.[77,78]

 This journal is © The Royal Society of Chemistry 2013

6. CNTs

CNTs, which can be divided into two main categories: single-walled carbon nanotubes (SWCNTs) and MWCNTs depending upon the number of rolled up layers, have been the subject of extensive research experimentally and theoretically for a wide range of applications including sensors, nano-electronic composites, displays, biomaterials and energy storage devices.[79–84] Recently, γ-ray irradiation, as a controlled method for modifying the physical and chemical properties of CNTs, has attracted much attention.

6.1. Defects

The treatments of CNTs by γ-ray irradiation seems to increase the number of defects such as carbon dangling bonds and γ-irradiation can cause perforation of the sidewalls of MWCNTs. Focused irradiation knock out carbon atoms from the nanotube walls, leading to defect formation on the surface of the nanotubes. In the Raman spectroscopy of CNTs, the D line is due to the formation of the defects and its intensity benefits strongly from the presence of the defects. Bellucci *et al.* have already shown that the sample irradiated by γ-rays reveals a significant increase in the D band intensity. This phenomenon can be related to the fact that exposure to γ-rays quickly destroys germs, although also altering the exposed material by producing defects in CNTs.[85] In addition, defects created by irradiation destroy the coherent motion of atoms on the nanotube circumference. As a result, the intensity of the radial breathing mode decreases.[3] Besides, Jovanovic *et al.*[86] and Guo *et al.*'s[87] data (see Fig. 12) obtained by Raman spectroscopy are consistent with the ability of γ-irradiation to form defects on the sidewalls of CNTs.[86]

In V. Skakalova's work, it was suggested that the defect concentration of irradiated-CNTs was saturated at a dose of approximately 170 kGy. As an important consequence, a maximum at 170 kGy was observed in the dose dependencies of both Young modulus and electrical conductivity as well. A large redistribution in electronic structure led also to a remarkable enhancement of electrical conductivity.[88] In addition, due to the formation of defects on CNT walls, the diameter of CNTs decreased according to the absorbed dose of irradiation. Larger specific area and pore volume as compared with the pristine CNTs were formed due to the increase of microporosity in CNTs.[89]

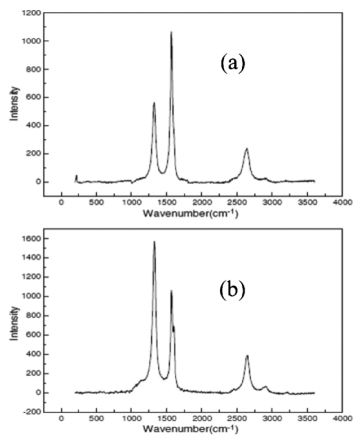


Fig. 12 Raman spectra of unirradiated MWCNTs (a) and γ-irradiated MWCNTs (b) (Reprinted with permission from ref. 89, copyright from IOP Science).

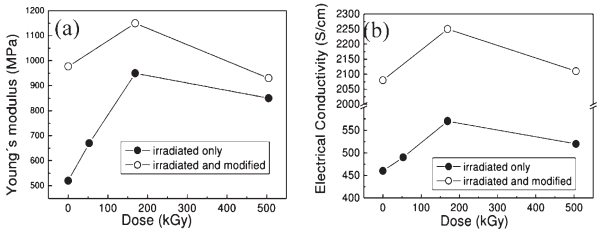


Fig. 13 (a) Young modulus and (b) electrical conductivity of SWCNTs *vs.* dose of γ-irradiation (●) and then functionalized (○) SWCNT-paper (Reprinted with permission from ref. 90, copyright from Elsevier).

6.2. Different alternations in SWCNTs and MWCNTs

It was found that MWCNTs seem to be more robust than SWCNTs, which showed an apparent collapse on prolonged exposure.[60,61] Skakalova *et al.* have pointed out that both Young modulus and electrical conductivity for SWCNT-paper are sensitive to the dose of γ irradiation. The Young modulus and electrical conductivity reach the maximum at a dose of 170 kGy (see Fig. 13), suggesting the saturation of the defect concentration at the dose of approximately 170 kGy.[88,90] In contrast to their work on SWNTs, Guo *et al.*'s results supported the view that the concentration of functionalization groups attached to MWCNTs increases continuously as γ-irradiation dose increases. No saturation of the defect concentration was found within the dose domain up to 250 kGy (see Fig. 14).[87] They thought that the difference in dependence of defect concentration on irradiation dose might be related to the CNT species. The SWCNTs used by Skakalova *et al.*[88,90] have only one shell. Excessive defects on the shell would lead to the collapse of SWCNTs. Thus there is a critical defect concentration at a dose of 170 kGy. However, MWCNTs that have many shells are much more resistant to γ-radiation. Radiation damage of a part of the external layers on the MWCNTs results in the production of new external layers and new defects, including defects between two layers. Therefore defect concentration on the MWCNTs increases continuously with γ-irradiation dose within the dose range under the study.[86,87]

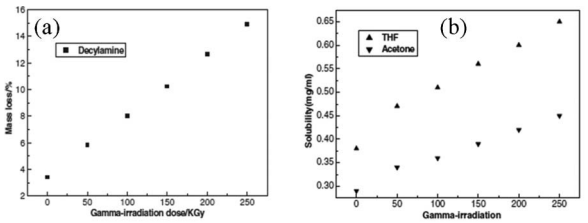


Fig. 14 (a) The mass loss of MWCNTs *versus* dose of γ irradiation and (b) the solubility of MWCNTs in tetrahydrofuran (THF) and acetone *versus* γ-irradiation dose (Reprinted with permission from ref. 89, copyright from IOP Science).

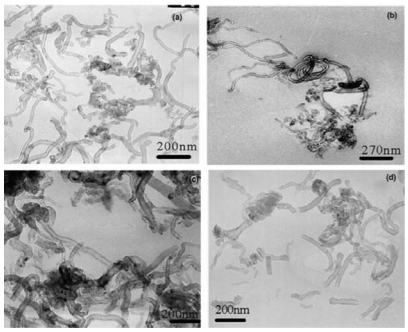


Fig. 15 Transmission electron microscope (TEM) microphotograph of (a) raw MWCNTs, (b) irradiated MWCNTs at an absorbed dose of 78 kGy, (c) a sample acid treated with 0.5 mol L^{-1} H_2SO_4 for a week at room temperature, (d) irradiated MWCNTs at dose of 78 kGy in the presence of 0.5 mol L^{-1} H_2SO_4 (Reprinted with permission from ref. 103, copyright 2004 from Elsevier).

6.3. Cutting of the CNTs

Typical CNTs are long and entangled, which makes it difficult to manipulate these CNTs for such applications, especially for nano-electronics and drug delivery.[91,92] Thus, controlling the length of CNTs has recently become an intriguing subject. In order to cut CNTs to shorter and operable length, various approaches including chemical etching,[93,94] ultrasonic treatment,[95] and mechanical treatment[96,97] have been developed. Cutting of CNTs by high energy rays such as γ-rays and electron-beams has also been reported.[98,99]

Jung *et al.*[100] found that MWCNTs were effectively cut with a facile and mild cutting method by using γ-irradiation in the presence of hydrogen peroxide. The results confirmed that the structural integrity of the cut MWCNTs was preserved with a negligible surface damage. Water soluble and short MWCNTs could also be prepared by using simple gamma irradiation with dilute sulfuric acid as a sensitizer (see Fig. 15).[101] In Jovanovic's work, the atomic force microscope (AFM) study has shown that γ-irradiation reduces the length and diameter of the SWCNT bundles obtained after subsequent functionalization with DNA.[86] The D/G ratios of the irradiated MWCNTs slightly increased after the irradiation. This increase in the D/G ratios should be attributed to the increase in defects induced by γ-irradiation. These defects on the MWCNTs could be formed through the interaction between MWCNTs and highly-energetic photons during γ-irradiation.[87,99] The radicals also will be generated through the radiolysis of agent by γ-irradiation. These radicals can attack the defects on the MWCNTs because of their high oxidizing potential and thus cut MWCNTs into shorter ones.[102]

6.4. Different media

Functionalization of CNTs under γ-rays was thought to shorten and damage the structure of CNTs in a fixed manner. However, it was found that CNTs showed an opposite behavior in structural change when irradiated in the different media.[103,104] In our work, γ-ray irradiation decreased the inter-wall distance of MWCNTs and improved their graphitic order in air, while irradiation in ECP increased the inter-wall distance of MWCNTs and disordered the structure (see Fig. 16 and

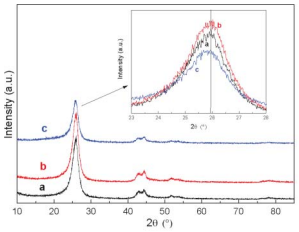


Fig. 16 X-Ray diffraction patterns of MWCNTs, (a) pristine, (b) irradiated in air and (c) irradiated in ECP (Copyright from Elsevier).[105]

17.).[103,105] Also these results are not surprising because it had already been shown that γ-rays caused the improvement in graphitic order of graphite and carbon fibers[21] in air and damaged and shortened the nanotube structure[87,106] in polar liquid. Due to great penetrating power of γ-rays, MWCNTs irradiated in air show a significant rearrangement and the defect concentration can be decreased. As a result, the inter-wall spacing decreases because the defective graphenes typically have large interlayer spacing.[107] Another possible mechanism is that the irradiation can push one carbon atom out of the graphene plane and then a cross-link between neighboring graphene layers is formed.[48,108] However, besides the above changes, γ-ray irradiation in ECP can shorten tubes,[101] and ECP might be strongly bonded to dangling bonds of tubes to form grafting chains. The distance of graphene in MWCNTs increases, as the defective structure increases.[103]

Skakalova *et al.* also found that the effect of irradiation was much stronger for samples irradiated in air in comparison to those in vacuum.[90] For samples irradiated in air, changes in Young modulus and electrical conductivity of SWCNT-paper were observed with maximum value for a dose of 170 kGy. Under vacuum there was only a small effect of irradiation. Oh found that the CNTs were easily cut when using cyclodextrin as a grinding reagent or when using a H_2SO_4/HNO_3 mixture.[109] Jovanovic suggested that CNTs irradiated in ammonia interact more efficiently with ssDNA compared to other samples which were irradiated in water and air.[86]

6.5. Chemical modification

Since the discovery of the CNTs by Ijima,[110] their insolubility in most solvents and matrices has limited their applications and the functionalization of CNTs has been extensively

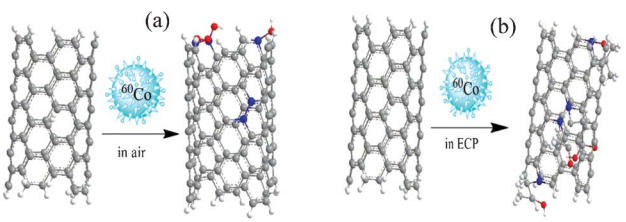


Fig. 17 Illustrations of structural changes in MWCNTs in media of (a) air and (b) ECP (Copyright from American Institute of Physics).[107]

 This journal is © The Royal Society of Chemistry 2013

studied. Combining γ-irradiation with chemical doping showed sensitivity of the doping affinity to the number of defects created by irradiation. Among them, a covalent reaction of CNTs with polymers is widely used because the long polymer chains help to disperse the nanotubes into a wide range of solvents even at a low degree of functionalization.[88,111–113] The major advantages of radiation grafting are (a) the reaction is carried out at room temperature and more controllable than in chemical operation, (b) the grafting can be carried out in gaseous and liquid phase of the monomer, and (c) the modified material is free from residuals of initiator or catalyst.[106]

In Guo's work, MWCNTs irradiated with γ-rays were subjected to chemical modification with thionyl chloride and decylamine. Elemental analysis (EA) and thermogravimetric analysis (TGA) for the modified MWCNTs indicated that γ-radiation increased the concentration of functional groups bound to MWCNTs, which arose due to the increasing number of defect sites created on the MWCNTs by γ-photons. Compared with untreated MWCNTs, γ-irradiation significantly enhanced the solubility of MWCNTs in acetone and THF. In addition, the concentration of functional groups attached to the MWCNTs was found to increase monotonically with increasing radiation dose due to the increase of defects created on the MWCNTs by γ-photons. We therefore conclude that γ-irradiation provides a novel approach to prepare various functionalized modifications of CNTs.[87] Chen *et al.* developed a facile strategy to prepare water-soluble MWCNTs by two steps of γ-radiation and the whole procedures are illustrated in Fig. 18. Results showed that poly(acrylic acid) (PAA) chains were successfully grafted onto the surface of MWCNTs. A core-shell structure was proved to be formed, and the external diameter of resultant MWCNTs was increased remarkably. The PAA-grafted MWCNTs showed very good solubility in water and some polar solvents.[106] Polystyrene-grafted MWCNTs were successfully synthesized by a simultaneous radiation-induced graft polymerization process. The results showed that polystyrene was successfully grafted onto the surface of MWCNTs. The synthesized polystyrene-grafted MWCNTs exhibited a good solubility in organic solvents.[111,114]

The degree of grafting was found to be strongly dependent on the grafting conditions such as the absorbed dose and the initial monomer concentration in the grafting solution. It was found that the degree of grafting at a fixed dose of 20 kGy showed the tendency to increase with increasing concentration of styrene up to 50 vol% beyond which it decreased.[111,114] When the styrene concentration increases further, homopolymerization is more pronounced and the diffusion of styrene is hindered. As a result, the final degree of grafting decreases.[115,116] In addition, the intensity of the D-band further increased with the functionalization of γ-irradiated nanotubes, indicating that the polymer backbone is wrapped around nanotubes rather than inserted into defects in the nanotube wall.[86]

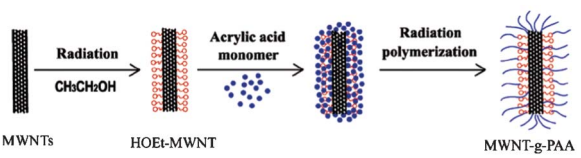


Fig. 18 The preparation of PAA-grafted MWCNTs (Reprinted with permission from ref. 108, copyright from American Chemical Society).

Besides improving the solubility of CNTs, functionalization of CNTs can be used in many other fields of technology. The poly(4-vinylphenyl-boronic acid)-grafted MWCNTs were used as sensing sites in enzyme-free glucose sensors for the detection of glucose without enzymes.[117] An improved hydrogen adsorption capacity was obtained for commercial MWCNT sample by γ-ray irradiation due to the increasing number of defects created by γ-photons. The capacity would reach the maximum when defect concentration achieves saturation. Hydrogen adsorption on γ-ray irradiated MWCNTs was by both physisorption and chemisorption. However, only treatment with γ-ray irradiation was not an effective method to sufficiently improve the hydrogen adsorption capacity of CNTs.[118] Jovanovic used γ-irradiation as a pre-treatment in the process of functionalization of SWCNTs with DNA in order to attach different polar functional groups to the sidewalls of SWCNTs. After γ-irradiation, dried SWCNTs were functionalized with DNA. The greatest advantage of this novel process for the production of SWCNT/DNA dispersion was the use of DNA in a significantly smaller quantity.[86]

6.6. Dispersion of gold nanoparticles on CNTs

CNTs find applications as a support for metal catalysts.[119–121] The catalytic activities of CNTs could be augmented by incorporating suitable metallic nanoparticles into the walls/side of CNTs. However, the metallic alloy nanoparticles were aggregated onto the surface of the carbon supports because of the hydrophobic nature of the supports. In order to change from hydrophobic to hydrophilic properties on the surface of MWCNTs, the interactions between metal particles and specific functional groups can be utilized for anchoring metal nanoparticles onto CNTs with the method of γ-rays.[122,123]

In Showkat's work, gold nanoparticles were dispersed into thiol-functionalized multi-wall carbon nanotubes (MWCNTs). The thiol groups were utilized as linker to hold the gold nanoparticles without agglomeration. γ-Radiation was used as source to reduce gold metal ions without having any additional reducing agents. The method provides formation of gold nanoparticles without being contaminated by the by-products from the normal reducing agents.[122]

Surface modification of SWCNTs with γ-irradiation was proved to bring carboxyl and hydroxyl groups and provide support for the dispersion of nanoparticles on the surface of SWCNTs in Oh *et al.*'s work. Of interest, the attachment of the nanoparticles onto SWCNTs was strong enough to be present even after chemical cleaning and ultra-sonication.[124] Wu tried to decorate MWCNTs with Ag nanoparticles relying on covalently bonded polymers, *via* one-step covalent grafting of the polymer to the surface of MWCNTs, and simultaneous reducing of Ag^+ ions to Ag which were then efficiently anchored onto the MWCNTs. The procedures are shown in Fig. 19.[125]

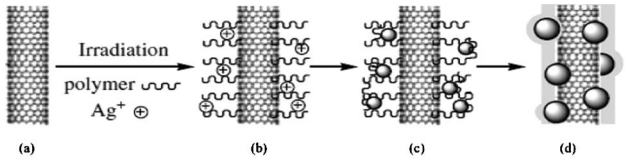


Fig. 19 Illustration of the formation mechanism of Ag-polymer-grafted-MWCNTs under γ-ray irradiation. (a) Dispersing MWCNTs into water and the association of Ag^+ ions with polymer. (b) Irradiation-induced grafting of polymer to the surface of MWCNTs. (c) Formation of Ag nanoclusters stabilized by entangled polymer chains. (d) The confined growth of Ag nanoclusters in the cross-linked polymer networks results in the higher stability of Ag nanoparticles in a gel matrix (Reproduced with permission from ref. 127, copyright from IOP Science).

Different irradiation conditions would have various effects on deposition of metal nanoparticles on CNTs. Cveticanin *et al.* showed that one-step synthesis, dispersion and decoration of CNTs with Ag nanoparticles using γ-irradiation method is more efficient when the γ-irradiation Ag/poly(vinyl alcohol)/CNTs synthesis is performed with poly(vinyl alcohol) radicals only as a reduction species, both for SWCNTs and MWCNTs.[126] Zhang *et al.* suggested that the surfactant additive makes the deposition more homogeneous and the optimum irradiation dose is 40 kGy.[127]

6.7. Composites reinforced by nano-fillers

Many nano-fillers (CNTs, nanoclays, *etc.*) have been considered to be applied as the modifiers of the traditional polymers in order to enhance the mechanical, thermal, electric, and gas/liquid barrier properties or to add multi-functionality.[128–132] Two crucial factors to develop advanced CNTs–polymer composites are: (1) uniform dispersion of CNTs in polymer matrix and (2) strong interfacial interactions for efficient load transfer from the polymer matrix to the CNTs.[133] Using a γ-irradiation is beneficial to promote crosslinking in the matrix and potentially enhance the interaction between nanotubes and matrix.[134]

In Yu's work,[135] purified-MWCNTs (*p*-MWCNTs) and grafted *p*-MWCNTs (g-MWCNTs) were incorporated into nylon-6 system. After irradiation, some functional groups were covalently bonded to CNTs and the bonding was proved by improvement of I_D/I_G from 1.34 to 1.36. Comparing with un-grafted MWCNTs, the number of CNTs in per unit area is larger for nylon-6/g-MWCNT composite, thus g-MWCNTs should have better interfacial adhesion than un-grafted MWCNTs. After the incorporation of 0.2 wt% MWCNTs, the tensile strength of nylon-6 has an increase of 10% for *p*-MNCNTs and 14% for grafted g-MWCNTs. In the meantime, the notched impact strength decreases accordingly. However, the notched impact strength of g-MWCNTs/nylon-6 composites was higher than that of *p*-MWCNTs/nylon-6 composites. In addition, the flexural strength, flexural modulus and heat distortion temperature (HDT) of g-MWCNTs/nylon-6 composites were higher than those of *p*-MWCNTs/nylon-6 composites and neat nylon-6. Since both epoxy group and carboxyl group on *p*-MWCNTs can react with –CONH– groups along the polymer chains in nylon-6,[133] the grafted polymer on *p*-MWCNTs can act as compatibilizer and strengthen the interfacial interactions which lead to better mechanical properties as well as higher HDT of nylon-6/g-MWCNTs composite.[135] In Lee's work, a one pot synthesis of a composite comprising of SWNT, polyaniline and Au nanoparticles was successfully established by γ-irradiation. These composites are expected to find applications as catalysts, sensors and in microelectronic devices.[7] In Cataldo's work, the γ-irradiation of polyisoprene and C_{60} solutions in decalin was employed to prepare polyisoprene/C_{60} composites. The thermal stability was found to be enhanced by the presence of C_{60} fullerene and crosslinks induced by the irradiation.[78]

Compared with mechanical properties, electric properties of composites were found to be more labile to radiation effects.[133] Srivastava showed that a significant increase in the conductivity of composite was observed in consequence of irradiation. The breaking and homogenous distribution of the nanofillers and the production of free radicals in polymer due to crosslinking after irradiation have been found to be responsible for the increase in the conductivity of the composite. The improvement of the conductivity is also correlated with the morphological changes. In addition, a decrease in the positive temperature coefficient of resistance effect and elimination of the negative temperature coefficient of resistance effect of the composite has been observed after irradiation. These results are explained on the basis of morphological changes in the composites after γ-ray irradiation. This effect of irradiation on negative temperature coefficient of resistance effect has been attributed to the prevention of re-agglomeration of the smaller conducting graphite particles to form the conducting pathways because of the reduction in the filler particle size, the increase in surface area of the expanded polymer particles and high viscosity of the molten polymer at higher temperature. No significant change in the hardness has been observed after γ-ray irradiation at room temperature.[136] In Lee's work, activation energy of the samples reduced as the irradiation dose increased. This is believed to have been caused by more polymer peroxides being created by an irradiation and oxidation. In the second chemoluminescence experiment, the chemoluminescence intensity rapidly declined as the temperature, irradiation dose and the CNT content increased. Finally, examination of the fracture surfaces indicated that the lamella structure of the polymer changed as the irradiation dose increased.[137]

7. Graphene

Graphene, a single atomic layer of sp^2-hybridized carbon, has attracted tremendous attention owing to its strictly two-dimensional structure and a wide range of unusual properties. It has rapidly changed its status from being an unexpected and sometimes unwelcome newcomer to a rising star and to a reigning champion.[138–141] Graphene oxide (GO) is single- or few-layer graphite oxide which exhibits excellent performance. The tunable oxygenous functional groups of GO facilitate the modification on the surface and make it a promising material

 This journal is © The Royal Society of Chemistry 2013

for composites with other materials.[142] It also works as the mediator to produce graphene. A literature survey shows that some irradiation techniques have been applied to modify the properties of graphene, such as electron irradiation,[143–149] ion irradiation[150,151] and *et al.* In our previous work, alterations of the structure and functional groups of graphene and GO induced by electron beam irradiation were investigated.[152,153] γ-Rays have been proved to be more effective than electron and ion beams and irradiation with γ-rays should have great potential for produce unimaginable functionalizations on graphene and GO. In addition, for devices used in the aerospace or nuclear industry, where the radiation characteristics may be a major concern, it is essential to ascertain the radiation effect on the properties of graphene and GO. Effects of γ-ray irradiation on micromechanical exfoliated mono-, bi- and tri-layer graphene samples have been successfully studied in Liu's work.[154] Defects are produced and induce crystal lattice deformation, which is confirmed by the blue shift of the G band, and the increase in the D and D′ bands after irradiation. However, bi-layer graphene exhibits greater stability under irradiation, which has more potential applications in the radiation environments. Moreover, the carrier density of mono-layer graphene was found to be increased by the investigation of the electrical property.

7.1. Reduction of graphene oxide

γ-Ray irradiation has also been known as a widely used method to prepare nanoparticles in aqueous solution by the reduction of their precursor by the as-formed aqueous electrons and hydrogen radicals.[155,156] Reduction of graphene oxide (GO) could be implemented by γ-ray irradiation in alcohol/water in the absence of oxygen.[157,158] According to the radiation chemistry of water,[159] γ-ray irradiation can decompose the water molecules to both oxidative (hydroxyl radical, OH) and reductive (hydrogen radical and hydrated electron, $H^{\bullet}$ and e^{-} aq) species. Whilst alcohols can eliminate the oxidative OH as radical scavengers and transform into reductive radicals,[160] which can be used to create a reducing medium for chemical reaction under the γ-ray irradiation in the absence of oxygen. After irradiation, the color of GO dispersion turns from yellow to black as shown in the insert of Fig. 20 (a). UV-Vis spectra show that the shoulder peak of GO around 290 nm disappears and the sharp absorption peak around 230 nm is red-shifted to 270 nm after γ-ray irradiation in Fig. 20 (a), which is consistent with the characters of reduced GO. From the FT-IR spectra in Fig. 20 (b), we can see the decarboxylation effect of γ-ray irradiation on GO sheets, as the peak at 1731 cm^{-1} assigned to carboxyl groups disappeared in the spectrum for reduced GO. Oxygen absence and alcoholic addition are proved to be the essential factors for reduction process, which correlated the production of reductive radicals with GO's reduction. The investigation of resultant reduced GO papers' electrical conductivity indicates that this method is favorable to build up graphene-based composites for the application in the field of electricity. In addition, a facile and environmentally friendly approach to prepare well-dispersed graphene sheets by γ-ray induced reduction of a GO suspension in *N,N*-dimethyl formamide (DMF) at room temperature was

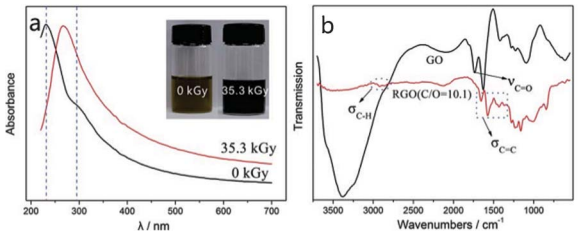


Fig. 20 (a) UV-Vis spectra of GO dispersion before and after irradiation. The insert shows the photographs of GO dispersion in an ethanol/water (50 v/v%) before (0 kGy) and after (35.3 kGy) the irradiation; (b) Fourier transform infrared spectroscopy (FT-IR) spectra of starting GO and reduced GO measured on transmission mode (Reprinted with permission from ref. 160, copyright from Royal Society of Chemistry).

demonstrated in Zhang's work.[161] GO is reduced by the electrons generated from the radiolysis of DMF under γ-ray irradiation.[161] As shown in Fig. 21, the high resolution TEM (HR-TEM) image of reduced GO shows an ordered graphite lattice. The reduced GO can be re-dispersed in many organic solvents, and the resulting suspensions are stable for two weeks due to the stabilization of $N(CH_3)^{2+}$ groups on the sheets.

7.2 Preparation of functionalized graphene

Considering the graphene-based composites, in fact, the excellent performance of them rests not only with the inherent properties of graphene, but more importantly with the compatibility between graphene and its matrix or other functional components. As to solution processing, the stability of graphene dispersions in aqueous or organic systems is obviously critical for the preparation of composites. Thereby, one of the tasks of preparing graphene-based nanomaterials is to enhance the stability of graphene or GO dispersions in solution.

A facile method of successive intercalation, grafting and exfoliation of graphite oxide in monomers by γ-ray irradiation to obtain functionalized graphene nanosheets was reported in our previous work.[162] The schematic comparison of our strategy and the traditional method to prepare functionalized graphene nanosheets is given in Fig. 22. Obviously, due to the

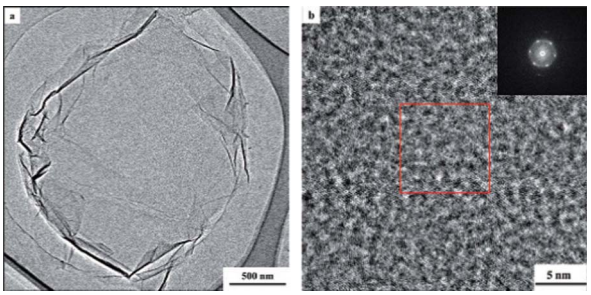


Fig. 21 (a) TEM and (b) high-resolution TEM (HR-TEM) images of reduced graphene oxide. The insert in (b) is a fast Fourier transform pattern of the HR-TEM image (Reprinted with permission from ref. 163, copyright from Royal Society of Chemistry).

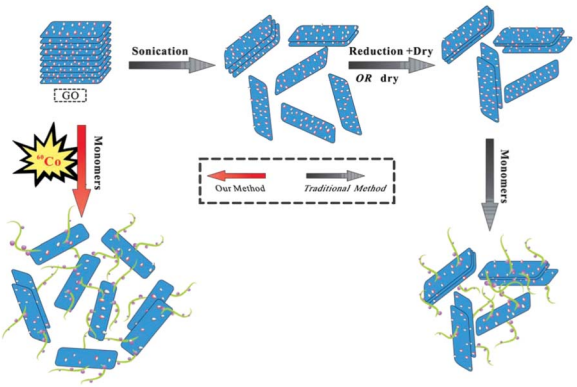


Fig. 22 Schematic drawing of a comparison of the functionalization of graphene nanosheets by our strategy and the traditional method (Copyright from Royal Society of Chemistry).[164]

extensive exfoliation, the functionalized graphene nanosheets with a high percentage of single-layer graphene are evidenced to be prepared by γ-ray irradiation. In addition, our strategy is a way for the preparation of functionalized graphene nanosheets with much less agglomeration than the traditional method. It should be attributed to the fact that interlayer functionalization of GO in our experiment is designed to be achieved *via* high energy γ-rays before exfoliation. The aggregation and the restacking through van der Waals interactions are reduced significantly owing to the bonding of long polystyrene chains on the planes.[163] Moreover, the elimination of the drying procedure also plays a significant role in preventing agglomeration. These mechanisms can be supported well by the AFM and TEM results in Fig. 23 and 24. It is noteworthy that the height value may be higher than that of the pristine GO monolayers but lower than bilayers due to

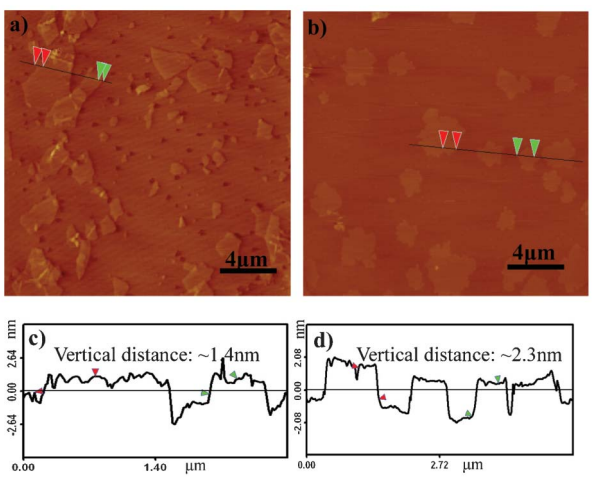


Fig. 23 Tapping mode AFM topographic images of (a) graphene nanosheets from the GO sonicated for 2 h, (b) graphene nanosheets from the dispersed irradiated GO in THF, (c) cross-section of graphene nanosheets from the sonicated GO and (d) cross-section of graphene nanosheets from the dispersed irradiated GO in THF (Copyright from Royal Society of Chemistry).[164]

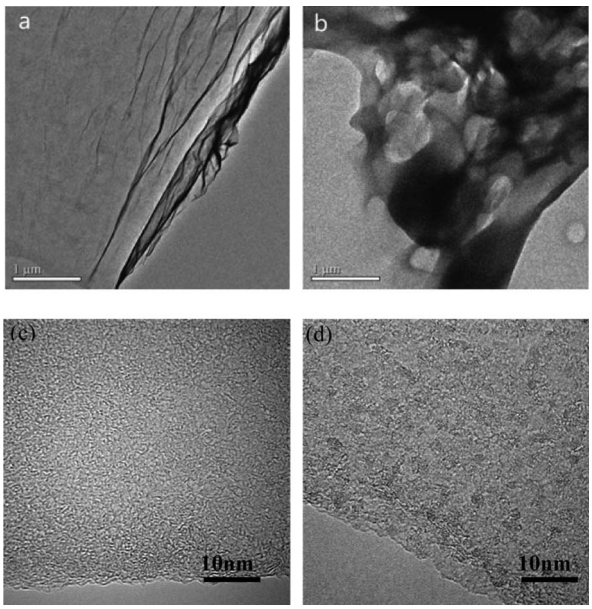


Fig. 24 TEM images for (a) GO and (b) functionalized GO[167] and HR-TEM images for (c) GO and (d) irradiated GO[164] (Reprinted with permission from ref. 167, copyright from Royal Society of Chemistry).

the PS chains grafted on the nanosheet surfaces or trapped underneath the drop-dried graphene flake 'coffee rings'.[164] Moreover, in Zhang's work,[165] the excellent dispersibility and stability of GO-*g*-poly(vinyl acetate) in common organic solvents are also readily rationalized in terms of the full coverage of poly(vinyl acetate) chains and solvated layer formation on graphene oxide sheets surface, which weakens the interlaminar attraction of GO sheets.

7.3. Formation of nanopores on graphene

In contrast to pristine graphene (Fig. 25), the irregular nanopore appeared in plane, and the trim edge was cut so that graphene with notched edges was prepared owing to the radiolysis promoting C–C bond breaking in the nanosheets under γ-rays.[2,166] Therefore, γ-ray irradiation is capable of

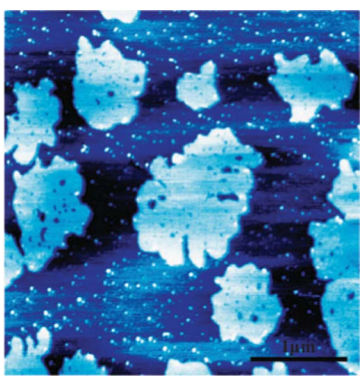


Fig. 25 The strengthened image of the AFM topographic images of graphene from the irradiated GO (Copyright from Elsevier).[168]

 This journal is © The Royal Society of Chemistry 2013

creating radiation defects at certain points. Spontaneously interlocking between the etching graphene and polymer matrix will be arisen with the formation of these nanostructures. The development of an interlocking microstructure of graphene-based composites makes graphene potentially more favorable for altering the matrix properties, such as the mechanical, rheological and permeability properties, and degradation stability.[167]

Though some attentions have been devoted to the radiation effect of graphene caused by γ-rays, the investigations concerning the exact mechanisms are very limited. In our future study, we will focus on this field and it is hoped that the properties of graphene and other carbon systems can be modified in a tailored fashion by employing the γ-ray irradiation and the modification mechanisms of γ-irradiation induced alterations can be understood further in the future.

8. Other carbon materials

Ercin[168] presented the results of the treatment of activated carbons with γ-irradiation. They found that specific surface areas of irradiated samples are measured to be greater than those of non-irradiated samples. This might be considered as an indication to some loss of material from the surface by γ-irradiation. The effect of irradiation was more severe in the loss of the functional groups present in the structure. The main difference between irradiated and non-irradiated carbons is the loss of the most of the functional groups of the irradiated carbons. In Zhang's work,[169] viscose-based activated carbon fiber (VACF) was modified with acrylonitrile by γ-irradiation-induced grafting polymerization. The grafting yield is higher than 12% according to TGA results. However, after grafting modification, VACF shows a small decrease in the specific surface area. In addition, Romanenko found that the conductivity of onion-like carbon was directly affected by the low energy γ-irradiation, which caused the reduction of the defects in the graphite-like conducting layers.[170] Novel nanocarbon hybrids of SWCNTs and ultradispersed diamond (UDD) were irradiated by various dose of γ-irradiation in Gupta's work.[2] It was shown that γ-irradiation generates microscopic defects albeit marginal as compared with E-beam considering the energy scale difference as well as the mechanism. This result is due to the fact that for gamma irradiation, a larger fraction of the deposited energy goes into bond breaking rather than atomic displacement. A concentration of 0.25 wt% UDD increased the radiation resilience of SWCNTs by enhancing the amorphization threshold energy and maintained their vibrational properties while only slightly changing for individual component elucidated through intensity and position variation of prominent Raman spectroscopy signatures. The dangling bonds at the interface can trap electrons and suppress conductivity through the interface. Therefore for electronic applications, models of hybrid structures with all bonds saturated should be considered. It can be either surface reconstruction or hydrogen passivation. Pre-existing atomic scale defects are affected due to excitation induced by γ-photons allowing recombination and helping to improve the structure or limit the damage. In their later work,[171] the MWCNTs when combined with nanodiamond showed a slight decrease in their conductance further affected by irradiation pointing at relatively good interfacial contact. They recommended that tailoring defects artificially allows more thermal channels for thermal packaging in microelectronics and electrical conduction pathways and available sites for electrochemical and electron field emission applications.

9. Conclusions and outlook

A review of the structural transformations of carbon materials by γ-rays is presented in this paper based on a wealth of experimental and theoretical data. It can be concluded that γ-irradiation of carbon materials may result in many fascinating and unexpected phenomena that can be readily used for engineering carbon materials and tailoring their properties instead of destroying them completely. The Compton scattering effect is mostly responsible for the interaction of γ-ray with carbon materials.

The grafting of reactive functional groups by γ-ray irradiation was expected to be an effective method for modifying the physicochemical properties of carbon fibers and improving the interfacial adhesion of composites. The roughness, amount of containing-oxygen functional groups and surface energy were all found to increase significantly after irradiation grafting. Compared with graphite, diamond is more resistant to the γ-ray irradiation so that it is being suggested as a suitable material in high irradiation environments. With regard to CNTs and graphene, γ-ray also works as a controlled method for modifying their physical and chemical properties. The tailoring and functionalization of CNTs and graphene induced by γ-ray irradiation modified the interlayer nanostructures and enhanced their solubility. CNTs can be successfully cut by using γ-ray irradiation with a sensitizer to improve their homogeneity in the solvent as well. Moreover, γ-irradiation technique can be regarded as a facile method for the preparation of organic and inorganic composites, such as CNTs or graphene/polymer and CNTs/gold nanoparticle composites. Structures and properties of the other carbon materials such as fullerenes, activated carbons and nanocarbon hybrids can also be decorated by γ-rays.

This review has clearly shown that the understanding of γ-radiation effects in carbon systems is pretty good, thanks to extensive and systematic experimental and theoretical works preformed by the predecessors. A few key aspects such as the structure changes and property alternation start to be already well understood. However, the understanding of the response mechanisms is still not very complete, due to the relatively little experimental and practically no theoretical work on the system of graphene, which works as a basic building block for graphitic carbon materials. On the other hand, the effects of the multi-factors like temperature and electricity fields in the irradiation environment on the structures and properties of

carbon systems is worthy of further investigation for fulfilling the irradiation mechanisms. Overall, this review has shown that there are numerous exciting scientific issues to study, such as organic and inorganic functionalization of carbon material surface; modification of properties by introducing defects and optimization of the degree of carbon system graphitization under certain γ-ray irradiation environments.

Acknowledgements

The authors acknowledge support from the National Natural Science Foundation of China (11175130), Natural Science Foundation of Tianjin, China (10JCYBJC02300) and China Postdoctoral Science Foundation (2012M520578).

Notes and references

1 R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787–792.
2 S. Gupta, A. M. Scuttler and J. Farmer, *J. Appl. Phys.*, 2010, **107**, 104308.
3 M. Hulman, V. Skakalova, S. Roth and H. Kuzmany, *J. Appl. Phys.*, 2005, **98**, 024311.
4 T. Zaharescu, S. Jipa, R. Setnescu, E. S. Dragan and M. V. Dinu, *Mater. Chem. Phys.*, 2008, **112**, 612–616.
5 H. G. Park, T. Li and S. H. Choi, *Mater. Chem. Phys.*, 2007, **105**, 325–330.
6 A. Hiroki, H. T. Tran, N. Nagasawa, T. Yagi and M. Tamada, *Radiat. Phys. Chem.*, 2009, **78**, 1076–1080.
7 K. P. Lee, A. Y. Gopalan, P. Santhosh, S. H. Lee and Y. C. Nho, *Compos. Sci. Technol.*, 2007, **67**, 811–816.
8 N. Salah, S. S. Habib, Z. H. Khan, S. Al-Hamedi and F. Djouider, *Radiat. Phys. Chem.*, 2009, **78**, 910–913.
9 R. L. Clough, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2001, **185**, 8–33.
10 Z. W. Xu, Y. D. Huang, C. Y. Min and L. Chen, *Radiat. Phys. Chem.*, 2010, **79**, 839–843.
11 J. Akhavan, E. Kronfli and S. C. Waring, *Polymer*, 2004, **45**, 2119–2126.
12 A. V. Krasheninnikov and K. Nordlund, *J. Appl. Phys.*, 2010, **107**, 071301.
13 M. G. Sung, K. Sassa, T. Tagawa, T. Miyata, H. Ogawa, M. Doyama, S. Yamada and S. Asai, *Carbon*, 2002, **40**, 2013–2020.
14 K. E. Atkinson and C. Kiely, *Compos. Sci. Technol.*, 1998, **58**, 1917–1922.
15 C. Ageorges, K. Friedrich and L. Ye, *Compos. Sci. Technol.*, 1999, **59**, 2101–2113.
16 R. B. Yallee and R. J. Young, *Compos. Sci. Technol.*, 1998, **58**, 1907–1916.
17 A. Bismarck, C. Wuertz and J. Springer, *Carbon*, 1999, **37**, 1019–1027.
18 Z. Q. Zhang, Y. W. Liu, Y. D. Huang, L. Liu and J. W. Bao, *Compos. Sci. Technol.*, 2002, **62**, 331–337.
19 A. Fukunaga and S. Ueda, *Compos. Sci. Technol.*, 2000, **60**, 249–254.
20 M. A. Montes-Moran, A. Martinez-Alonso, J. M. D. Tascon and R. J. Young, *Composites, Part A*, 2001, **32**, 361–371.
21 Z. W. Xu, L. S. Liu, Y. D. Huang, Y. Sun, X. Q. Wu and J. L. Li, *Mater. Lett.*, 2009, **63**, 1814–1816.
22 Z. W. Xu, Y. D. Huang, C. H. Zhang, L. Liu, Y. H. Zhang and L. Wang, *Compos. Sci. Technol.*, 2007, **67**, 3261–3270.
23 J. Q. Li, Y. D. Huang, Z. W. Xu and Z. Wang, *Mater. Chem. Phys.*, 2005, **94**, 315–321.
24 Z. W. Xu, Y. D. Huang, C. H. Zhang and G. Chen, *Mater. Sci. Eng., A*, 2007, **444**, 170–177.
25 Z. W. Xu, Y. D. Huang, Y. J. Song, C. H. Zhang and L. Li, *J. Rare Earths*, 2007, **25**, 462–468.
26 Z. W. Xu, L. Chen, Y. D. Huang, J. L. Li, X. Q. Wu, X. M. Li and Y. Jiao, *Eur. Polym. J.*, 2008, **44**, 494–503.
27 Z. W. Xu, L. Chen, L. S. Liu, G. W. Chen and X. Q. Wu, *Polym. Polym. Compos.*, 2010, **18**, 31–35.
28 S. Tiwari, J. Bijwe and S. Panier, *Wear*, 2011, **270**, 688–694.
29 S. Tiwari, J. Bijwe and S. Panier, *Wear*, 2011, **271**, 2184–2192.
30 F. Cataldo, *Carbon*, 2000, **38**, 634–636.
31 W. Zhang, L. Spinelle, M. Dubois, K. Guerin, H. Kharbache, F. Masin, A. P. Kharitonov, A. Hamwi, J. Brunet, C. Varenne, A. Pauly, P. Thomas, D. Himmel and J. L. Mansot, *J. Fluorine Chem.*, 2010, **131**, 676–683.
32 Y. Huang and R. J. Young, *Carbon*, 1995, **33**, 97–107.
33 S. Ozbek and D. H. Isaac, *Carbon*, 2000, **38**, 2007–2016.
34 N. Hu, Y. Li, N. Hori, M. Arai, Y. L. Liu and H. Fukunaga, *Composites, Part A*, 2009, **40**, 2004–2012.
35 N. Sela and O. Ishai, *Composites*, 1989, **20**, 423–435.
36 H. Y. Ma, Y. D. Huang, Z. Q. Zhang and L. Shao, *Mater. Sci. Technol.*, 2002, **18**, 1585–1588.
37 H. Zhang, Z. Zhang and C. Breidt, *Compos. Sci. Technol.*, 2004, **64**, 2021–2029.
38 J. Kalantar and L. T. Drzal, *J. Mater. Sci.*, 1990, **25**, 4186–4193.
39 J. Kalantar and L. T. Drzal, *J. Mater. Sci.*, 1990, **25**, 4194–4202.
40 J. J. George and A. K. Bhowmick, *Nanoscale Res. Lett.*, 2008, **3**, 508–515.
41 D. R. Sekulic, M. V. Gordic, I. M. Djordjevic, Z. S. Petrovic and M. M. Stevanovic, *J. Nucl. Mater.*, 2009, **383**, 209–214.
42 D. Ugarte, *Nature*, 1992, **359**, 707–709.
43 T. Hata, Y. Imamura, E. Kobayashi, K. Yamane and K. Kikuchi, *J. Wood Sci.*, 2000, **46**, 89–92.
44 F. Banhart and P. M. Ajayan, *Nature*, 1996, **382**, 433–435.
45 F. Banhart, T. Fuller, P. Redlich and P. M. Ajayan, *Chem. Phys. Lett.*, 1997, **269**, 349–355.
46 R. H. Telling, C. P. Ewels, A. A. El-Barbary and M. I. Heggie, *Nat. Mater.*, 2003, **2**, 333–337.
47 D. H. Galvan, I. L. Garzon, P. Santiago and M. Jose-Yacaman, *Fullerene Sci. Technol.*, 1998, **6**, 867–883.
48 F. Banhart, *Rep. Prog. Phys.*, 1999, **62**, 1181–1221.
49 A. Seeger, *Radiat. Eff. Defects Solids*, 1989, **111–112**, 355–368.
50 F. Cataldo, *Fullerene Sci. Technol.*, 2001, **9**, 409–424.
51 M. Takeuchi, S. Muto, T. Tanabe, H. Kurata and K. Hojou, *J. Nucl. Mater.*, 1999, **271–272**, 280–284.
52 F. Cataldo, *Polym. Int.*, 2001, **50**, 828–834.
53 M. Maizels, W. R. Heineman and C. J. Seliskar, *Electroanalysis*, 2000, **12**, 241–247.
54 S. Gupta, M. Muralikiran, J. Farmer, L. R. Cao and R. G. Downing, *J. Mater. Res.*, 2009, **24**, 1498–1512.

 This journal is © The Royal Society of Chemistry 2013

55 J. A. Garrido, C. E. Nebel, M. Stutzmann, E. Gheeraert, N. Casanova, E. Bustarret and A. Deneuville, *Diamond Relat. Mater.*, 2002, **11**, 347–350.

56 W. Adam, C. Bauer, E. Berdermann, P. Bergonzo, F. Bogani, E. Borchi, A. Brambilla, M. Bruzzi, C. Colledani, J. Conway, W. Dabrowski, P. Delpierre, A. Deneuville, W. Dulinski, B. van Eijk, A. Fallou, F. Fizzotti, F. Foulon, M. Friedl, K. K. Gan, E. Gheeraert, E. Grigoriev, G. Hallewell, R. Hall-Wilton, S. Han, F. Hartjes, J. Hrubec, D. Husson, H. Kagan, D. Kania, J. Kaplon, C. Karl, R. Kass, K. T. Knopfle, M. Krammer, A. Logiudice, R. Lu, P. F. Manfredi, C. Manfredotti, R. D. Marshall, D. Meier, M. Mishina, A. Oh, L. S. Pan, V. G. Palmieri, M. Pernicka, A. Peitz, S. Pirollo, P. Polesello, K. Pretzl, V. Re, J. L. Riester, S. Roe, D. Roff, A. Rudge, S. Schnetzer, S. Sciortino, V. Speziali, H. Stelzer, R. Stone, R. J. Tapper, R. Tesarek, G. B. Thomson, M. Trawick, W. Trischuk, E. Vittone, A. M. Walsh, R. Wedenig, P. Weilhammer, H. Ziock, M. Zoeller and R. D. Collaboration, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 1999, **434**, 131–145.

57 M. J. Guerrero, D. Tromson, C. Descamps and P. Bergonzo, *Diamond Relat. Mater.*, 2006, **15**, 811–814.

58 M. Bruzzi, M. Bucciolini, M. Casati, C. DeAngelis, S. Lagomarsino, I. Lovik, S. Onori and S. Sciortino, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2004, **518**, 421–422.

59 B. Campbell and A. Mainwood, *Phys. Status Solidi A*, 2000, **181**, 99–107.

60 S. Gupta, *Mater. Res. Soc. Symp. Proc.*, 2007, **956**, 235–241.

61 S. Gupta, R. J. Patel and N. D. Smith, Advanced carbon-based material as space radiation shields, Boston, MA, 2004.

62 B. Campbell, W. Choudhury, A. Mainwood, M. Newton and G. Davies, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2002, **476**, 680–685.

63 S. Dannefaer, A. Pu, V. Avalos and D. Kerr, *Phys. B*, 2001, **308–310**, 569–572.

64 S. Gupta, B. L. Weiss, B. R. Weiner, L. Pilione, A. Badzian and G. Morell, *J. Appl. Phys.*, 2002, **92**, 3311–3317.

65 P. A. Karam, *Health Phys.*, 2002, **82**, 491–499.

66 P. A. Karam, *Radiat. Phys. Chem.*, 2002, **64**, 77–87.

67 V. A. Basiuk, G. Albarran, E. V. Basiuk and J. M. Saniger, Stability of interstellar fullerenes under high-dose gamma-irradiation: new data, Paris, France, 2004.

68 V. A. Basiuk, G. Albarran, E. V. Basiuk and J. M. Saniger, in *Space Life Sciences: Astrobiology: Steps toward Origin of Life and Titan before Cassini*, ed. M. Bernstein, R. NavarroGonzalez and R. Raulin, Elsevier Science Ltd, Oxford, 2005, vol. 36, pp. 173–177.

69 F. Cataldo, *Fullerene Sci. Technol.*, 2000, **8**, 577–593.

70 F. Cataldo, G. Strazzulla and S. Iglesias-Groth, *Mon. Not. R. Astron. Soc.*, 2009, **394**, 615–623.

71 G. Angelini, O. Ursini and F. Cataldo, *J. Radioanal. Nucl. Chem.*, 2010, **284**, 179–187.

72 S. Sato, M. Yamada, T. Wakahara, T. Tsuchiya, M. O. Ishitsuka, T. Akasaka and M. T. H. Liu, *Tetrahedron Lett.*, 2007, **48**, 6290–6293.

73 M. Orfanopoulos and M. D. Tzirakis, *Org. Lett.*, 2008, **10**, 873–876.

74 B. L. Tumanskii, O. G. Kalina, V. I. Sokolov, A. L. Chistyakov, I. V. Stankevich, A. Han, Y. Murata and K. Komatsu, *Chem. Phys. Lett.*, 2004, **395**, 157–160.

75 C. H. Lee, T. S. Lin and C. Y. Mou, *Phys. Chem. Chem. Phys.*, 2002, **4**, 3106–3111.

76 F. Cataldo, E. Lilla, O. Ursini and G. Angelini, *J. Radioanal. Nucl. Chem.*, 2009, **279**, 31–41.

77 F. Cataldo, O. Ursini and G. Angelini, *Radiat. Phys. Chem.*, 2008, **77**, 734–741.

78 F. Cataldo, O. Ursini and G. Angelini, *Radiat. Phys. Chem.*, 2008, **77**, 742–750.

79 M. Dimaki and P. Boggild, *Nanotechnology*, 2004, **15**, 1095–1102.

80 K. Gjerde, T. Schurmann, I. Bu, K. B. K. Teo, W. I. Milne and P. Boggild, *Carbon*, 2006, **44**, 3030–3036.

81 A. F. Ismail, P. S. Goh, S. M. Sanip and M. Aziz, *Sep. Purif. Technol.*, 2009, **70**, 12–26.

82 Z.-P. Sun, X.-G. Zhang, Y.-Y. Liang and H.-L. Li, *J. Power Sources*, 2009, **191**, 366–370.

83 M. Naffakh, M. Remskar, C. Marco, M. A. Gomez-Fatou and I. Jimenez, *J. Mater. Chem.*, 2011, **21**, 3574–3578.

84 A. L. Martinez-Hernandez, C. Velasco-Santos and V. M. Castano, *Curr. Nanosci.*, 2010, **6**, 12–39.

85 S. Bellucci, M. Chiaretti, P. Onorato, F. Rossella, M. S. Grandi, P. Galinetto, I. Sacco and F. Micciulla, *Nanomedicine*, 2010, **5**, 209–215.

86 S. P. Jovanovic, Z. M. Markovic, D. N. Kleut, N. Z. Romcevic, V. S. Trajkovic, M. D. Dramicanin and B. M. T. Markovic, *Nanotechnology*, 2009, **20**, 445602.

87 J. X. Guo, Y. G. Li, S. W. Wu and W. X. Li, *Nanotechnology*, 2005, **16**, 2385–2388.

88 V. Skakalova, U. Dettlaff-Weglikowska and S. Roth, *Diamond Relat. Mater.*, 2004, **13**, 296–298.

89 B. Safibonab, A. Reyhani, A. Nozad Golikand, S. Z. Mortazavi, S. Mirershadi and M. Ghoranneviss, *Appl. Surf. Sci.*, 2011, **258**, 766–773.

90 V. Skakalova, A. Hulman, P. Fedorko, P. Lukac and S. Roth, *AIP Conf. Proc.*, 2003, **685**, 143–147.

91 T. Saito, K. Matsushige and K. Tanaka, *Phys. B*, 2002, **323**, 280–283.

92 Z. Y. Chen, K. J. Ziegler, J. Shaver, R. H. Hauge and R. E. Smalley, *J. Phys. Chem. B*, 2006, **110**, 11624–11627.

93 J. Y. Li and Y. F. Zhang, *Appl. Surf. Sci.*, 2006, **252**, 2944–2948.

94 A. Bismarck, M. Q. Tran, C. Tridech, A. Alfrey and M. S. P. Shaffer, *Carbon*, 2007, **45**, 2341–2350.

95 M. Yudasaka, M. Zhang, C. Jabs and S. Iijima, *Appl. Phys. A: Mater. Sci. Process.*, 2000, **71**, 449–451.

96 A. Kukovecz, T. Kanyo, Z. Konya and I. Kiricsi, *Carbon*, 2005, **43**, 994–1000.

97 A. Eftekhari, S. Manafi and F. Moztarzadeh, *Chem. Lett.*, 2006, **35**, 138–139.

98 T. D. Yuzvinsky, A. M. Fennimore, W. Mickelson, C. Esquivias and A. Zettl, *Appl. Phys. Lett.*, 2005, **86**, 053109.

99 D. Yang, X. H. Zhang, C. C. Wang, Y. C. Tang, J. J. Li and J. H. Hu, *Prog. Nat. Sci.*, 2009, **19**, 991–996.

100 J. H. Choi, C. H. Jung, D. K. Kim, Y. C. Nho, K. Shin and D. H. Suh, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2008, **266**, 3491–3494.

101 J. Peng, X. X. Qu, G. S. Wei, J. Q. Li and J. L. Qiao, *Carbon*, 2004, **42**, 2741–2744.
102 E. Bekyarova, K. Kaneko, M. Yudasaka, D. Kasuya, S. Iijima, A. Huidobro and F. Rodriguez-Reinoso, *J. Phys. Chem. B*, 2003, **107**, 4479–4484.
103 Z. Xu, L. Chen, L. Liu, X. Wu and L. Chen, *Carbon*, 2011, **49**, 350–351.
104 D. Kleut, S. Jovanovic, Z. Markovic, D. Kepic, D. Tosic, N. Romcevic, M. Marinovic-Cincovic, M. Dramicanin, I. Holclajtner-Antunovic, V. Pavlovic, G. Drazic, M. Milosavljevic and B. T. Markovic, *Mater. Charact.*, 2012, **72**, 37–45.
105 Z. Xu, C. Min, L. Chen, L. Liu, G. Chen and N. Wu, *J. Appl. Phys.*, 2011, **109**, 054303.
106 S. M. Chen, G. Z. Wu, Y. D. Liu and D. W. Long, *Macromolecules*, 2006, **39**, 330–334.
107 M. Yoon, J. Howe, G. Tibbetts, G. Eres and Z. Zhang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **75**, 165402.
108 A. V. Krasheninnikov and K. Nordlund, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2004, **216**, 355–366.
109 S. D. Oh, S. H. Choi, B. Y. Lee, A. Gopalan, K. P. Lee and S. H. Kim, *J. Ind. Eng. Chem.*, 2006, **12**, 156–160.
110 S. Iijima, *Nature*, 1991, **354**, 56–58.
111 C. H. Jung, D. K. Kim and J. H. Choi, *Curr. Appl. Phys.*, 2009, **9**, S85–S87.
112 L. L. E. Kranksith, A. Negron-Mendoza, F. G. Mosqueira and S. Ramos-Bernal, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2010, **619**, 51–54.
113 J. A. Fagan, N. J. Lin, R. Zeisler and A. R. H. Walker, *Nano Res.*, 2011, **4**, 393–404.
114 H. X. Xu, X. B. Wang, Y. F. Zhang and S. Y. Liu, *Chem. Mater.*, 2006, **18**, 2929–2934.
115 M. M. Nasef, H. Saidi, A. M. Dessouki and E. M. El-Nesr, *Polym. Int.*, 2000, **49**, 399–406.
116 M. Khayet, M. M. Nasef and J. I. Mengual, *J. Membr. Sci.*, 2005, **263**, 77–95.
117 D. S. Yang, D. J. Jung and S. H. Choi, *Radiat. Phys. Chem.*, 2010, **79**, 434–440.
118 W. Qian, J. F. Chen, L. Z. Wei, L. S. Wu and Q. W. Chen, *Nano*, 2009, **4**, 7–11.
119 H. W. C. Postma, T. Teepen, Z. Yao, M. Grifoni and C. Dekker, *Science*, 2001, **293**, 76–79.
120 A. Bachtold, P. Hadley, T. Nakanishi and C. Dekker, *Science*, 2001, **294**, 1317–1320.
121 J. Kong, M. G. Chapline and H. J. Dai, *Adv. Mater.*, 2001, **13**, 1384–1386.
122 A. M. Showkat, K. P. Lee, A. I. Gopalan, S. H. Choi and Y. C. Nho, *Diamond Relat. Mater.*, 2007, **16**, 1688–1692.
123 H. T. Zhao, X. J. Han, M. F. Han, L. F. Zhang and P. Xu, *Mater. Sci. Eng., B*, 2010, **167**, 1–5.
124 S. D. Oh, B. K. So, S. H. Choi, A. Gopalan, K. P. Lee, K. R. Yoon and I. S. Choi, *Mater. Lett.*, 2005, **59**, 1121–1124.
125 W. T. Wu, L. Shi, Y. S. Wang, W. M. Pang and Q. R. Zhu, *Nanotechnology*, 2008, **19**, 125607.
126 J. Cveticanin, A. Krkljes, Z. Kacarevic-Popovic, M. Mitric, Z. Rakocevic, D. Trpkov and O. Neskovic, *Appl. Surf. Sci.*, 2010, **256**, 7048–7055.
127 X. Y. Zhang, Y. Ye, H. D. Wang and S. D. Yao, *Radiat. Phys. Chem.*, 2010, **79**, 1058–1062.
128 F. H. Gojny, M. H. G. Wichmann, B. Fiedler and K. Schulte, *Compos. Sci. Technol.*, 2005, **65**, 2300–2313.
129 E. T. Thostenson, Z. F. Ren and T. W. Chou, *Compos. Sci. Technol.*, 2001, **61**, 1899–1912.
130 T. Ogasawara, Y. Ishida, T. Ishikawa, T. Aoki and T. Ogura, *Composites, Part A*, 2006, **37**, 2236–2240.
131 T. Yokozeki, Y. Iwahori, M. Ishibashi, T. Yanagisawa, K. Imai, M. Arai, T. Takahashi and K. Enomoto, *Compos. Sci. Technol.*, 2009, **69**, 2268–2273.
132 P. A. O'Rourke Muisener, L. Clayton, J. D'Angelo, J. P. Harmon, A. K. Sikder, A. Kumar, A. M. Cassell and M. Meyyappan, *J. Mater. Res.*, 2002, **17**, 2507–2513.
133 T. X. Liu, I. Y. Phang, L. Shen, S. Y. Chow and W. D. Zhang, *Macromolecules*, 2004, **40**, 7214–7222.
134 P. Castell, F. J. Medel, M. T. Martinez and J. A. Puertolas, *J. Nanosci. Nanotechnol.*, 2009, **9**, 6055–6063.
135 H. B. Yu, X. Y. Mo, J. Peng, M. L. Zhai, J. Q. Lia, G. S. Wei, X. H. Zhang and J. L. Qiao, *Radiat. Phys. Chem.*, 2008, **77**, 656–662.
136 N. K. Srivastava, S. Rattan and R. M. Mehra, *Polym. Eng. Sci.*, 2009, **49**, 1136–1141.
137 K. Y. Lee and K. Y. Kim, *Polym. Degrad. Stab.*, 2008, **93**, 1290–1299.
138 L. Wang, L. Sun, C. Tian, T. Tan, G. Mu, H. Zhang and H. Fu, *RSC Adv.*, 2012, **2**, 8359–8367.
139 A. K. Geim, *Science*, 2009, **324**, 1530–1534.
140 P. Rani and V. K. Jindal, *RSC Adv.*, 2013, **3**, 802–812.
141 Q. Zheng, Z. Li and J. Yang, *RSC Adv.*, 2013, **3**, 923–929.
142 W. Ai, J.-Q. Liu, Z.-Z. Du, X.-X. Liu, J.-Z. Shang, M.-D. Yi, L.-H. Xie, J.-J. Zhang, H.-F. Lin, T. Yu and W. Huang, *RSC Adv.*, 2013, **3**, 45–49.
143 J. D. Jones, P. A. Ecton, Y. Mo and J. M. Perez, *Appl. Phys. Lett.*, 2009, **95**, 013101.
144 D. Teweldebrhan and A. A. Balandin, *Appl. Phys. Lett.*, 2009, **94**, 013101.
145 D. Teweldebrhan and A. A. Balandin, *Appl. Phys. Lett.*, 2009, **95**, 246102.
146 I. Childres, L. A. Jauregui, M. Foxe, J. F. Tian, R. Jalilian, I. Jovanovic and Y. P. Chen, *Appl. Phys. Lett.*, 2010, **97**, 173109.
147 J. H. Warner, M. H. Rummeli, A. Bachmatiuk and B. Buchner, *Nanotechnology*, 2010, **21**, 325702.
148 M. Xu, D. Fujita and N. Hanagata, *Nanotechnology*, 2010, **21**, 265705.
149 J. H. Warner, M. H. Rummeli, L. Ge, T. Gemming, B. Montanari, N. M. Harrison, B. Buchner and G. A. D. Briggs, *Nat. Nanotechnol.*, 2009, **4**, 500–504.
150 L. Tapaszto, G. Dobrik, P. Nemes-Incze, G. Vertesy, P. Lambin and L. P. Biro, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 233407.
151 T. Kim, H. C. Kang, T. Tran Thanh, J. D. Lee, H. Kim, W. S. Yang, H. G. Yoon and K. S. Suh, *RSC Adv.*, 2012, **2**, 8808–8812.
152 L. Chen, Z. Xu, J. Li, C. Min, L. Liu, X. Song, G. Chen and X. Meng, *Mater. Lett.*, 2011, **65**, 1229–1230.
153 Z. W. Xu, L. Chen, J. L. Li, R. Wang, X. M. Qian, X. Y. Song, L. S. Liu and G. W. Chen, *Appl. Phys. Lett.*, 2011, **98**, 183112.
154 M. X. Han, Z. Y. Ji, L. W. Shang, Y. P. Chen, H. Wang, X. Liu, D. M. Li and M. Liu, *Chin. Phys. B*, 2011, **20**, 086102.
155 S. Egusa, M. A. Kirk, R. C. Birtcher and M. Hagiwara, *J. Nucl. Mater.*, 1985, **133–134**, 795–799.

 This journal is © The Royal Society of Chemistry 2013

156 J. L. Marignier, J. Belloni, M. O. Delcourt and J. P. Chevalier, *Nature*, 1985, **317**, 344–345.
157 W. F. Chen, Z. Y. Zhu, S. R. Li, C. H. Chen and L. F. Yan, *Nanoscale*, 2012, **4**, 2124–2129.
158 B. W. Zhang, L. F. Li, Z. Q. Wang, S. Y. Xie, Y. J. Zhang, Y. Shen, M. Yu, B. Deng, Q. Huang, C. H. Fan and J. Y. Li, *J. Mater. Chem.*, 2012, **22**, 7775–7781.
159 A. R. Anderson and E. J. Hart, *J. Phys. Chem.*, 1962, **66**, 70–75.
160 M. Simic, P. Neta and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794–3800.
161 Y. Zhang, H.-L. Ma, Q. Zhang, J. Peng, J. Li, M. Zhai and Z.-Z. Yu, *J. Mater. Chem.*, 2012, **22**, 13064–13069.
162 L. Chen, Z. W. Xu, J. L. Li, Y. L. Li, M. J. Shan, C. H. Wang, Z. Wang, Q. W. Guo, L. S. Liu, G. W. Chen and X. M. Qian, *J. Mater. Chem.*, 2012, **22**, 13460–13463.
163 K. Jo, T. Lee, H. J. Choi, J. H. Park, D. J. Lee, D. W. Lee and B. S. Kim, *Langmuir*, 2011, **27**, 2014–2018.
164 Z. Jin, T. P. McNicholas, C. J. Shih, Q. H. Wang, G. L. C. Paulus, A. Hilmer, S. Shimizu and M. S. Strano, *Chem. Mater.*, 2011, **23**, 3362–3370.
165 B. W. Zhang, Y. J. Zhang, C. Peng, M. Yu, L. F. Li, B. Deng, P. F. Hu, C. H. Fan, J. Y. Li and Q. Huang, *Nanoscale*, 2012, **4**, 1742–1748.
166 Y. Zhang, L. Chen, Z. Xu, Y. Li, B. Zhou, M. Shan, Z. Wang, Q. Guo and X. Qian, *Mater. Lett.*, 2012, **89**, 226–228.
167 S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature*, 2006, **442**, 282–286.
168 D. Ercin, M. Eken, Z. Aktas, S. Cetinkaya, B. Sakintuna and Y. Yurum, *Radiat. Phys. Chem.*, 2005, **73**, 263–271.
169 S. J. Zhang, Q. K. Zhang, S. X. Chen, Q. Y. Yuan and P. Y. Li, *Polym. Adv. Technol.*, 2009, **20**, 1168–1173.
170 A. I. Romanenko, O. B. Anikeeva, V. L. Kuznetsov, T. I. Buryakov, E. N. Tkacev, S. I. Moseenkov and A. V. Arzhannikov, *J. Optoelectronics Adv. Mater.*, 2008, **10**, 1745–1748.
171 S. Gupta and J. Farmer, *J. Appl. Phys.*, 2011, **109**, 014314.

This journal is © The Royal Society of Chemistry 2013