Engineering of nanostructured carbon materials with electron or ion beams

Irradiating solids with energetic particles is usually thought to introduce disorder, normally an undesirable phenomenon. But recent experiments on electron or ion irradiation of various nanostructures demonstrate that it can have beneficial effects and that electron or ion beams may be used to tailor the structure and properties of nanosystems with high precision. Moreover, in many cases irradiation can lead to self-organization or self-assembly in nanostructures. In this review we survey recent advances in the rapidly evolving area of irradiation effects in nanostructured materials, with particular emphasis on carbon systems because of their technological importance and the unique ability of graphitic networks to reconstruct under irradiation. We dwell not only on the physics behind irradiation of nanostructures but also on the technical applicability of irradiation for nanoengineering of carbon and other systems.

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The experience gained during decades of irradiation studies tells us that bombardment of solids with energetic particles creates defects and thus deteriorates the materials. Indeed, the first motivation for studying how irradiation changes the structure and properties of solid targets was the necessity of understanding the irradiation-induced degradation of components of nuclear fission or fusion reactors[1]. The problem of disorder appeared also in another technologically important area: ion implantation into semiconductors[2], as the implanted atoms create a large number of lattice defects in the devices.

One might expect that irradiation should have the same effects on nanosystems as on bulk solids. But it has recently been demonstrated that irradiation, especially when combined with heat treatment, can sometimes have beneficial effects on nanostructured materials. Examples are irradiation-mediated engineering, self-assembly or self-organization in carbon nanosystems. The atomic structure and morphology of carbon nanotubes or related structures can be tailored by irradiation[3–9] and they can be interconnected or merged in a controllable way[5,8,10,11]. Irradiation can give rise to extreme pressure inside nanotubes[12] or fullerene-like 'onions'[4], so that these systems can be used as compression cells to induce high-pressure transformations of materials on the nanometre scale. Even diamond crystals can be nucleated and grown under an intense electron or ion beam inside onions[4,13] or thin amorphous carbon films[14,15]. Moreover, irradiation can be used to tailor the mechanical[6], electronic[7,16–18] and even magnetic[19,20] properties of nanostructured carbon.

Impressive examples of irradiation-assisted manipulation of non-carbon nanoscale materials are the patterning or ordering of the magnetic properties of ultrathin ferromagnetic films[21,22], fabrication of nanodots[23] and silicon dioxide clusters[24], the self-organization of ensembles of embedded nanoclusters caused by the inverse Ostwald ripening effect[25], the transformation of spherical nanocolloids into ellipsoids with the aim of building a photonic crystal[26], or the creation of metallic nanoparticles in dielectric matrices[26], just to mention a few. Overall, during the past decade the number of papers containing the words 'irradiation' and 'nanostructures' has increased by a factor of 50 and the number of citations by nearly three orders of magnitude.

Here we summarize the key experimental findings and the current theoretical understanding of irradiation effects in nanostructured materials. We focus mainly on carbon systems because of their exciting properties and unique ability to reconstruct under irradiation. We further restrict our consideration to selected work reporting results of irradiation with ions or electrons and do not review effects of photon irradiation.

ENGINEERING OF NANOSYSTEMS BY PARTICLE IRRADIATION

The development of nanosystems for technological applications relies on techniques to modify the systems with almost atomic precision. Obviously this cannot be achieved with conventional macroscopic tools. Nanostructures can be modified by the tips of scanning tunnelling/atomic force microscopes (STM/AFM), but these techniques can't be used at the moment for mass production.

Treating nanostructures with particle beams can circumvent many difficulties, as irradiation has two main advantages. First, ion beams can be focused onto spots of a few nanometres in diameter, and electron beams from field emission guns onto areas as small as 1 Å in diameter, which is less than the distance between atoms in molecules or solids. Particle beams can be scanned over the structures orders

of magnitude faster than mechanical tips and thus offer much better chances to treat a large number of structures within a reasonable time. Second, the response of some structures to the particle beam can be such that the restructuring of the systems is governed by principles of self-organization. Then, the desired modification of the nanosystems can be achieved even without the need to focus the beam. Furthermore, bombardment with energetic ions or electrons can cause chemical reactions locally or the sputtering of atoms from one part of the structure into another part, and remove or mix the atoms in pre-defined areas.

WHAT IS SPECIAL ABOUT CARBON NANOSTRUCTURES?

The reason for intensive research on irradiation effects in carbon nanostructures such as fullerenes[27], single- or multi-walled nanotubes (SWNTs and MWNTs)[28], or nanodiamonds[19], is the high technological importance of these systems owing to their unique mechanical and electronic properties, which can be tailored by irradiation. However, and even more importantly, the rich physics and intriguing behaviour of nanostructured carbon under irradiation comes from the ability of graphenic networks to reorganize their structures like no other material. New bonds around defects restructure the lattice by creating a modified but coherent network that retains many of its original properties. In addition to sp^2-hybridized graphitic structures including graphene[29], carbon also exists in sp^3 (diamond) and sp^1 (linear carbene chain) forms, as well as in hybrid structures[30]. The difference in cohesive energy between the different phases is very small. By using energetic particle beams the system can be driven away from equilibrium and, under certain conditions, quenched into a metastable atomic configuration.

PRODUCTION OF DEFECTS UNDER ION OR ELECTRON IRRADIATION

When an energetic particle (ion or electron) penetrates a solid, it collides with the nuclei and the electrons of the target so that the projectile energy is transferred to the target atoms, as described in Box 1. If the target recoil atom acquires enough kinetic energy to leave its original position, various atomic-scale defects appear. Although most point defects disappear on a submicrosecond timescale after the impact (for example, because of annihilation of vacancy–interstitial pairs), some defects may remain in the system.

Owing to different mechanisms of conversion of electronic excitations into heat, the electronic structure of the target strongly affects the result of an electron or ion impact. In metals electronic excitations are delocalized because of the presence of conduction electrons. This makes electronic excitations less important, so that radiation damage in metals comes mostly from knock-on atom displacements. In insulators, however, excitations may result in local bond-breaking. Different responses of the systems to irradiation can be used to change the structure of composite materials selectively.

NANOSCALE MATERIALS UNDER IRRADIATION

The irradiation-induced generation of defects in nanosystems is different from bulk materials because of the limited size of the system in one or more directions. Many electrons or ions traverse these tiny objects without inelastic interaction so that little energy is deposited, contrary to bulk systems where all the energy is eventually absorbed. This also means that the probability for energy loss of an impinging particle is low in small targets and decreases with increasing electron[31] or ion[32] energy. Correspondingly, the amount of damage in

Box 1 Stopping of energetic particles in solids

The slowing down of an energetic ion moving in a solid target can be separated into two different channels[2,104]: electronic and nuclear stopping. The nuclear stopping originates from collisions between the ion and the nuclei of atoms in the target, so that the ion's kinetic energy is partly transmitted to a target atom as a whole resulting in its translatory motion. The energy loss is determined by screened Coulomb interactions. A common feature for all ions is that the nuclear stopping is important only for relatively slow and heavy ions. The electronic stopping is governed by inelastic collisions between the moving ion and the electrons in the target, which can be either bound or free. Many different physical processes contribute to the electronic stopping: ionization of the target atoms, generation of phonons through the electron–phonon coupling, collective electronic excitations such as plasmons, and so on. Electronic stopping dominates at high ion energies. The crossover between the nuclear and electron stopping depends on the ion mass (in the case of a carbon target, 100 keV for Ar ions, and 1 MeV for Xe). For hydrogen ions (protons), electronic stopping always prevails.

Energetic electrons interact with the nuclei and the electron system in the target[31]. For reasons of momentum conservation, only a tiny fraction of the impinging electron energy can be transferred to a nucleus, so a rather high electron energy ('threshold energy') is needed to displace an atom (this occurs via electron–nucleus scattering). For example, an electron energy of 100 keV is needed to transfer approximately 20 eV to a carbon atom; this is the threshold for displacing the atom permanently in a graphitic structure. Electron–electron scattering, on the other hand, is possible at low electron energies and may cause ionization or bond breaking. This kind of energy transfer normally does not lead to atom displacements but may damage the target because of local reactions. The cross-section of both nuclear and electron scattering decreases with increasing electron energy; however, electron–nucleus scattering only leads to observable effects if the displacement threshold energy is exceeded.

Many structural modifications of nanosystems were first carried out in electron microscopes where the irradiation of specimens with energetic electrons is unavoidable and radiation effects were often seen accidentally as a by-product of structural characterization. For defect generation the most important mechanism of energy transfer from electrons to the target atoms is the ballistic collisions of the electrons with the nuclei. The electron energies in TEMs range typically between 100 and 300 keV and in a few high-voltage instruments may exceed 1 MeV. Hence, the electrons may have enough momentum to displace atoms permanently from their positions[31,105]. The advantage of carrying out irradiation experiments in a TEM is that all structural modifications under the electron beam can be monitored in real time and at the full lateral resolution of the instrument. Modern electron microscopes achieve point resolutions of 1 Å or even better and can focus the electron beams onto spots of less than 1 nm diameter (in some instruments 1 Å spots are achievable). Enormous beam current densities can be achieved when the electron beams are focused onto a spot (approximately 300 A cm^{-2} in beams from thermal electron guns and up to 10^5 A cm^{-2} from field emission guns). Because irradiation effects are governed by the temperature of the material under the beam, high-temperature specimen stages (with an adjustable specimen temperature up to 1,000 °C or more) have to be used in such *in situ* experiments.

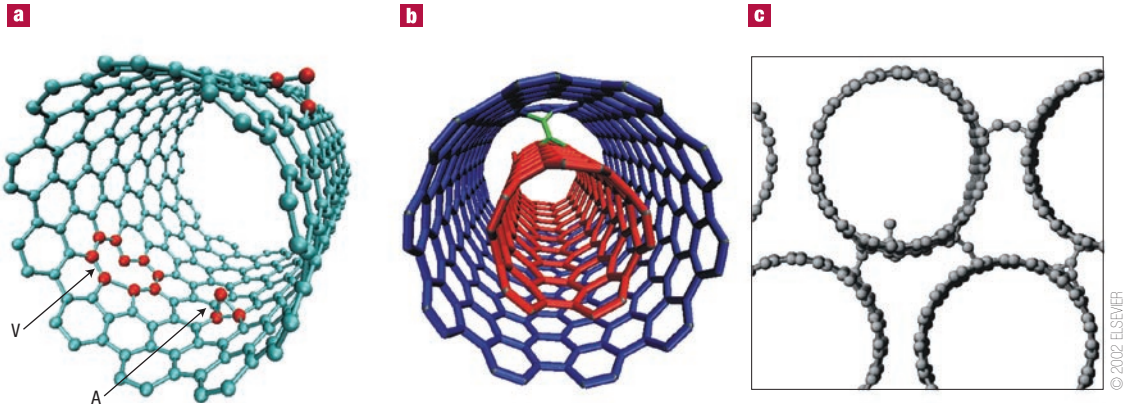

Figure 1 Molecular models of carbon nanotubes with typical point defects. **a**, Short fragment of an SWNT with a vacancy (V) and double-coordinated carbon atoms (A) adsorbed onto the outer and inner surfaces of the tube. **b**, Covalent bond between the shells of a MWNT formed by two atoms with dangling bonds at vacancies in adjacent shells. **c**, Irradiation-induced covalent links between the tubes in a bundle (reprinted with permission from ref. 106).

a nanoscale object is low when the particle energy is high, provided that displacement cascades do not play a considerable role.

On the other hand, the reduced dimensionality may give rise to a different temperature profile after the impact so that the local temperature may exceed the melting temperature of the material. This is particularly important for ion irradiation of zero-dimensional objects. For example, just 30 eV transferred to an isolated fullerene C_{60}, which is an amount of energy that can easily be transferred by a single ion impact, will raise the 'temperature' in the fullerene to about 2,000 K, as can easily be evaluated by dividing the transferred energy by the number of atoms and taking into account that half of this value should be taken, owing to the equipartition theorem. Furthermore, the large fraction of surface atoms in nanosystems results in a high sputtering yield (removal of atoms from the system). The finite size of the system also affects the electronic structure and thus the mechanisms of conversion of electronic excitations to kinetic energy of the atoms[33].

RADIATION DEFECTS IN CARBON NANOSTRUCTURES

Similar to bulk materials, irradiation-induced defects in carbon nanostructures can conventionally be divided into point defects, such as interstitial–vacancy pairs, and defects of higher dimensions. Examples of the latter are dislocations in graphene sheets[9] or mechanically strained nanotubes[34]. Native and irradiation-induced defects in carbon nanostructures can be detected by various experimental techniques. Defects can be directly observed by STM[35] or transmission electron microscopy (TEM)[9,36], or identified by Raman scattering[37–39] as the intensity ratio of the 'D-band' to the 'G-band'[38], or X-ray photoelectron spectroscopy[40–42] by monitoring changes in the C1s peak shape, which is very sensitive to the type of carbon bonding.

The most prolific irradiation-induced defects in graphenic carbon nanostructures are vacancies (single or multi-vacancies, as shown in Figs 1 and 2) and adatoms, which play the role of interstitials in isolated SWNTs[43]. Unlike metals where the structure of a vacancy is essentially a missing atom in the lattice, carbon sp^2 nanostructures develop an extended reconstruction of the atomic network near the vacancy[44–46] by saturating two dangling bonds and forming a pentagon as shown in Fig. 1. In graphene, single vacancies reconstruct as well[47–49], but in nanotubes the reconstruction is much stronger owing to the curvature and inherent nanoscale size of the system. It is easier for a nanotube to contract locally to 'heal' the hole and thus saturate energetically unfavourable dangling bonds. Di-vacancies[46] and multi-vacancies[50] also reconstruct as shown in Fig. 2. Thus, curved graphitic structures such as carbon nanotubes can be referred to as self-healing materials under irradiation[51].

Along with vacancies and interstitials, defects of another type may exist in nanotubes: these are the pentagon/heptagon Stone–Wales (SW) defects[52] associated with a rotation of a bond in the nanotube atomic network (Fig. 2a). SW defects normally appear because of an 'incomplete' annealing of the atomic structure after annihilation of a Frenkel pair.

A number of more complex defects can be formed in MWNTs and bundles of SWNTs. An example is inter-shell covalent bonds (formed, for example, by two dangling bonds at the vacancies in the adjacent shells) in MWNTs[53]. Likewise, defect-mediated covalent bonds between adjacent SWNTs in the bundle can appear (Fig. 1b). The bonds can be due to vacancies or to 'Wigner defects'[54], a metastable atom configuration formed by a vacancy and a nearby interstitial. As shown below, these defects heavily affect the mechanical properties of nanotubes.

Experiments on irradiation of nanostructured carbon materials[31] indicate that much of the irradiation-induced damage can be annealed when the irradiation is carried out at temperatures higher than 300 °C through dangling bond saturation[43] and an increased mobility of point defects[46,55]. Thus, severe radiation damage in graphitic systems that could destroy the structure can be minimized at moderately high temperatures, and the engineering of carbon nanostructures with energetic particle beams becomes possible.

DISPLACEMENT THRESHOLD ENERGY

The displacement threshold energy T_d is a fundamental characteristic describing the radiation hardness of a material. It can be defined as the minimum energy acquired by an atom through the impact of an energetic particle that enables it to leave its position in the atomic network. The atom can either take a metastable (interstitial) position in the lattice or leave the system. The value of T_d is different for different carbon allotropes[14,31], as it is related not only to bond energy but also to local chemical bonding and the availability of open space in the structure. It is smaller in sp^2-bonded carbon (15–20 eV) than in diamond-like structures (30–48 eV), so that the ratio of sp^2 to sp^3 carbon can be changed by irradiation[14,31]. Moreover, T_d may depend on the system geometry, for example on the diameter of a nanotube[55]. All

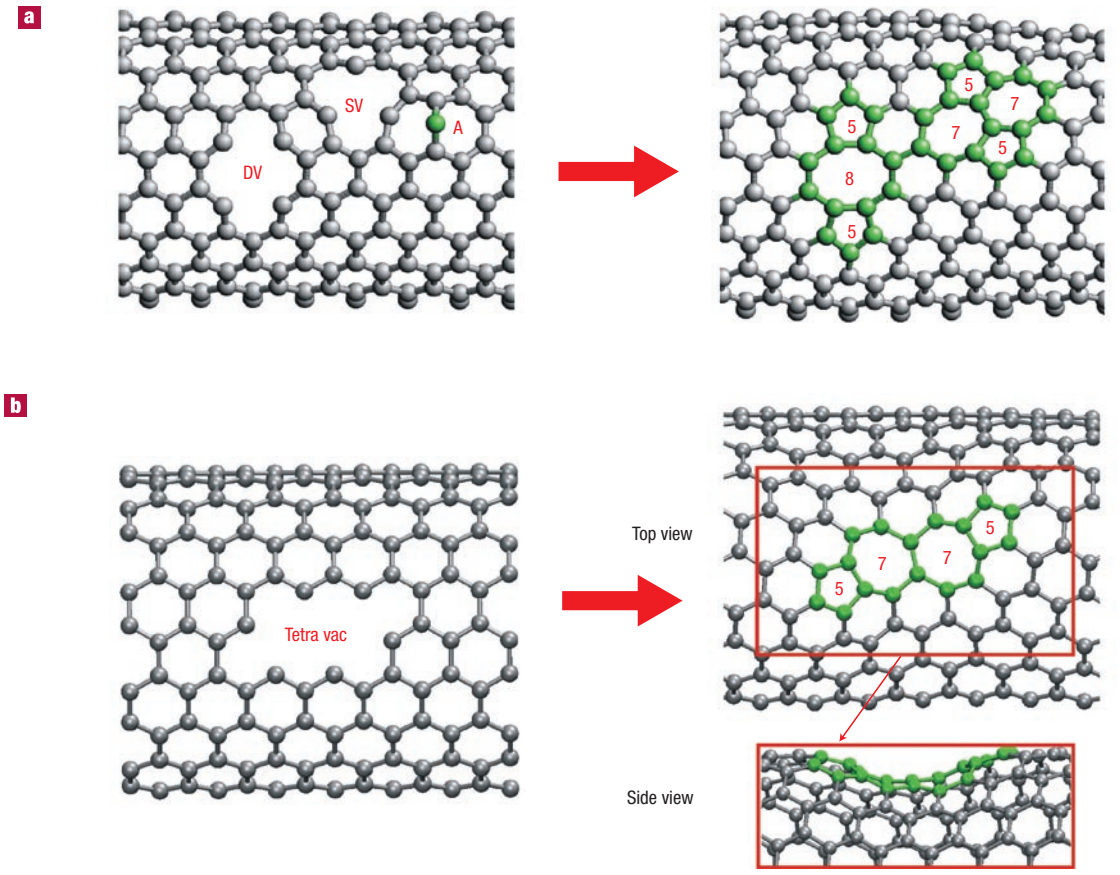

Figure 2 Reconstructions of the atomic network of a carbon nanotube near point defects as predicted by atomistic computer simulations[43,50]. **a**, A double vacancy (DV) transforms to an agglomeration of five- and eight-membered rings. A single vacancy (SV) and an adatom may form a metastable Stone–Wales (5–7–7–5) defect. **b**, Reconstruction of a tetra-vacancy. Note that the effective size of the 'hole' decreases at the expense of local diameter reduction, so that carbon nanotubes can be referred to as self-healing materials.

of these can be used to displace atoms selectively by setting the beam energy just above the threshold and thus alter the structure of the material locally.

ELECTRON-BEAM ENGINEERING OF CARBON NANOTUBES

The removal of carbon atoms from a SWNT or MWNT leads to a reconstruction of the network from a purely hexagonal to a coherent structure containing also non-six-membered rings. This changes the curvature of the graphene cylinders locally (positive curvature around pentagons and negative curvature around heptagons). Furthermore, the cylinders shrink because of the continuous loss of atoms[56]. Thus, irradiation with an electron beam of variable diameter can be used to perforate the outer shell of tubes by removing a few atoms (Fig. 3a), to bend the tubes (Fig. 3b–d)[57], or to adjust their diameter, both on a desired scale with a precision of less than the diameter of the tube. Sustained irradiation of nanotubes leads to shrinkage[55,56] until the lower stability limit of a SWNT, which is at a diameter of 0.4 nm, is reached (Fig. 3e). It is apparent that the stability of the tubes decreases with decreasing diameter, that is, the displacement threshold is lower when the tube is thinner. This can be seen in Fig. 3e where the innermost tube in the centre of the image broke and closed its open ends by fullerenic caps. MWNTs can be transformed into SWNTs and, conversely, bundles of SWNTs to MWNTs. This is shown in Fig. 3e where a SWNT bundle (still visible at the diagonal edges of the image) has been collapsed to form a MWNT which, again, transforms to single graphenic cylinders (seen in the centre of Fig. 3e) when exposed to sustained irradiation.

SWNTs can be cut by moving a focused electron beam across the tube[58] (this is shown for bundles in Fig. 3f–h). After cutting, the open ends of the tube were observed to close immediately with hemispherical caps. Atoms trapped inside the tubes are available for annealing so that new cuts require a higher dose. Nanotubes can also be cut by a low-energy electron beam (under the threshold for ballistic atom displacement) owing to irradiation-stimulated chemical etching of the tube by reactive species like water radicals[59].

The coalescence of two parallel SWNTs under electron irradiation was demonstrated[8] at 600–800 °C. These transformations were found to proceed by means of vacancies via a zipper-like mechanism, imposing a continuous reorganization of atoms in individual tube lattices along adjacent tubes[60]. Thus, a combination of electron-beam-stimulated coalescence and shrinkage of nanotubes can be used to control the diameter of individual nanotubes, while cutting nanotubes should make it possible to study quantization-related phenomena in short nanotubes, halfway between zero- and one-dimensional objects.

ION IRRADIATION OF CARBON NANOSTRUCTURES

Early experiments[42] on bombardment of carbon nanotubes and fullerenes with ions reported essentially destructive effects, but recent work has provided convincing evidence that ion irradiation

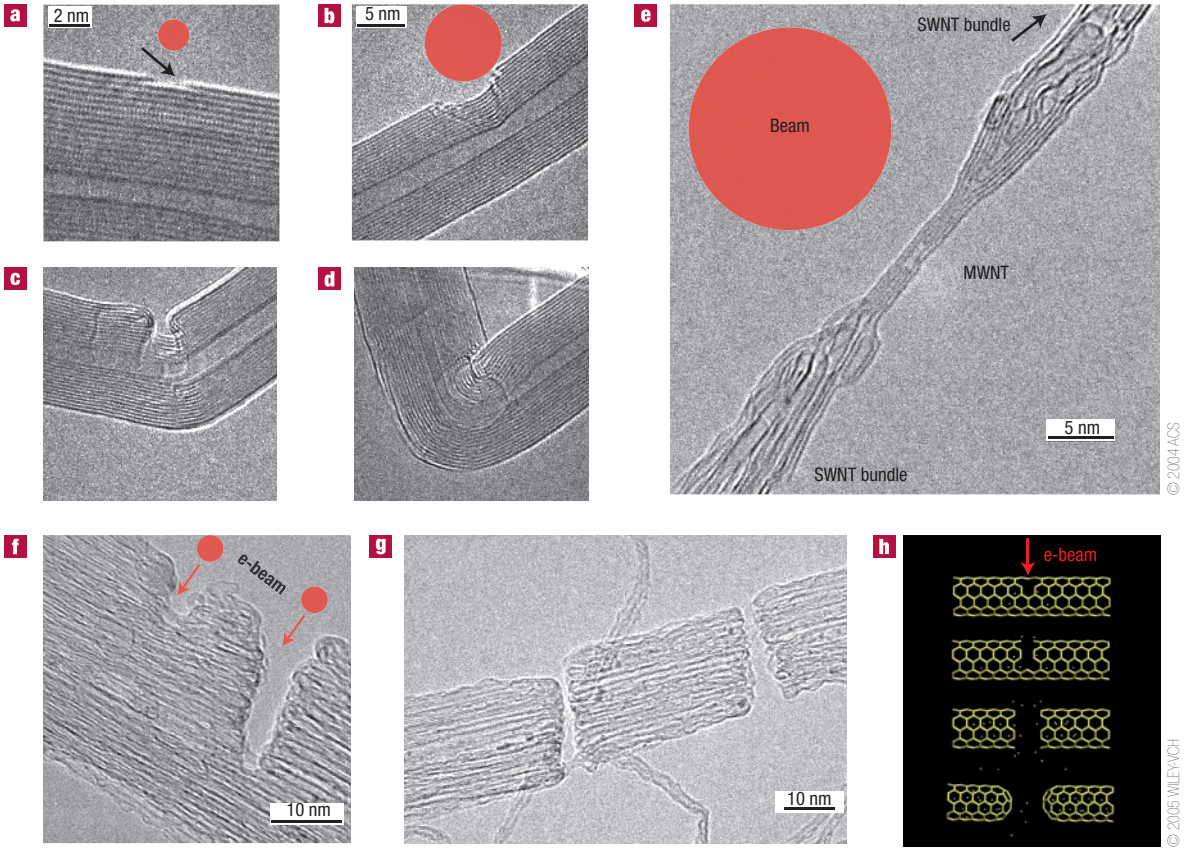

Figure 3 Electron-beam engineering of carbon nanostructures: effects of electron irradiation on carbon nanotubes. The circle in each figure indicates the diameter of the beam. **a**, When the electron beam in a field-emission TEM is fully focused onto a spot of 1-nm diameter or less, single graphene layers can be locally peeled from a MWNT[57]. **b–d**, When the electron beam diameter is approximately half the size of a nanotube diameter, the irradiation of one wall can be used for controlled bending of the tube. **e**, Irradiation of a bundle of SWNTs transforms the bundle to a MWNT which, in turn, can be gradually transformed to a double- (shown here) or single-walled tube[57]. The collapse of a MWNT happens from the inside: that is, it is always the innermost tube (which has the lowest stability) that breaks first. **f**, A bundle of SWNTs can be cut by a focused electron beam[58]. Repeated cutting needs higher doses because carbon interstitials are trapped inside the tubes and anneal defects at the new cuts. **g**, Complete sectioning of a nanotube bundle. **h**, Model of electron-beam-induced cutting. Parts a–e reprinted with permission from ref. 57. Parts f–h reproduced with permission from ref. 58.

can be used in a creative way. Spatially localized ion irradiation of individual MWNTs[61] and SWNTs[62] deposited on SiO_2 substrates was used to create defective regions that worked as tunnel barriers for electrons in the nanotubes (Fig. 4) so that quantum dots[61,62] and single-electron inverters[63] were formed. Much insight into the effects of individual defects on conductance was obtained from low-dose irradiation of individual SWNTs with 120-eV Ar ions combined with electronic transport measurements[7]. Ion irradiation of bundles of SWNTs[16] was shown to give rise to current redistribution between the damaged and undamaged tubes in the same bundle, which can be interpreted as evidence for the formation of irradiation-mediated links between individual SWNTs in the bundle, similar to the links that appear in electron-irradiated nanotube bundles[6,64].

Irradiation of MWNTs with 30-keV and 50-keV Ga ions resulted in peculiar structural transformations in the nanotubes[17]: the outer shells of the MWNTs remained intact, while the inner layers reorganized into highly ordered pillbox-like nano-compartments with diameters of about 5 nm and of varying lengths between 2 and 20 nm. The formation of similar bamboo-like structures in MWNTs irradiated with 4-MeV Cl_2^+ ions was also reported[65]. Self-irradiation with 100-eV C^+ ions was used for making nanotube-'amorphous diamond' nanocomposites[66] in which conducting mats of SWNTs were protected against wear by 50-nm 'amorphous diamond' films.

Focused ion beams have been used[18] to thin, slice and alter the structure and composition of MWNTs at precise locations along the nanotube axis. This strategy of harnessing ion-beam-induced defect generation and doping could be attractive for modulating chemical and electrical properties along the nanotube length to fabricate nanotube heterostructures or networks for device applications.

In a promising demonstration[38] of an irradiation-assisted way for manufacturing nanotube networks consisting of perfectly straight and suspended structures, SWNTs grown suspended between pillars of Si/SiO_2 structures were irradiated with 30-keV Ga^+ ions, and the nanotubes were straightened by ion beam scans. Argon ion irradiation also straightened as-grown curly nanotubes[39] as seen in Fig. 5. As a result, the field-emission properties of nanotubes were enhanced because of the increased aspect ratio and reduced mutual shielding. An additional contribution may have come from irradiation-induced defects, which made the nanotube surfaces more active, thus emitting more electrons. As irradiation-induced defects normally increase the reactivity of nanotubes (for example, owing to dangling bonds at surface defects), focused ion irradiation followed by mild chemical treatment was used to functionalize nanotubes in pre-selected

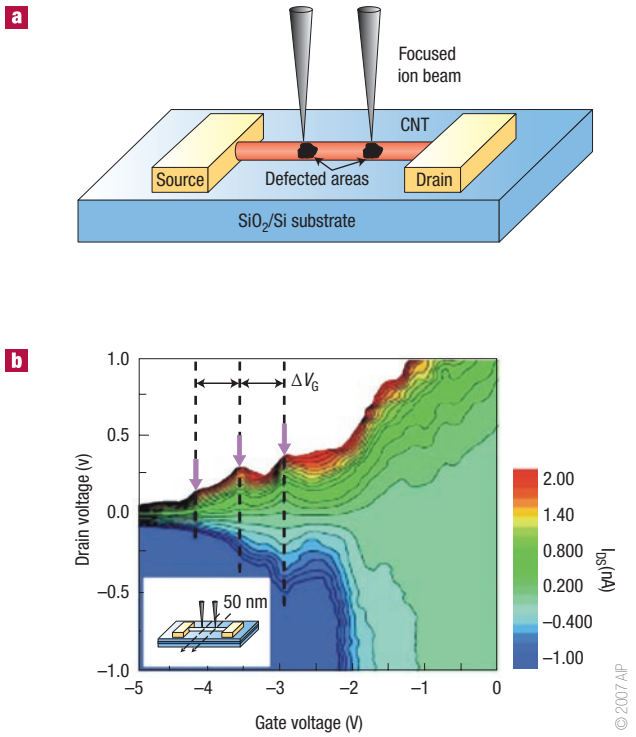

Figure 4 Using ion irradiation for making nanotube-based electronic devices. **a**, Schematic illustration of the fabrication of a quantum dot in a carbon nanotube by using focused ion beams. **b**, Contour plots of source–drain currents for the system shown in **a** at room temperature as functions of source–drain voltage after ion bombardment. The arrows indicate the irradiation-induced features corresponding to the Coulomb blockade regime. Reprinted with permission from ref. 62.

locations[37,41] (Fig. 5). Such functionalizations are important prerequisites for tailoring nanotubes in biochemical applications.

High-energy ion irradiation of semiconducting fullerene crystals resulted in the formation of conducting 'tracks', which are amorphous regions appearing along the trajectory of the ion[67]. Normally the tracks are well aligned with respect to the beam directions and can themselves be regarded as nanostructures inside bulk materials. Irradiation with Ar and Si (non-magnetic) ions gave rise to magnetism in fullerene films[68], a phenomenon that is still not fully understood. The response of nanotubes to high-energy proton irradiation was studied as well, motivated by the possible use of nanotubes as electronic component in space applications[69,70]. It was reported that nanotube-based devices should be extremely durable in space applications[70], but more work is required to assess the stability of nanotubes in the space environment.

INTERCONNECTING CARBON NANOSTRUCTURES

The tendency of irradiation-induced dangling bonds to saturate in carbon nanostructures, combined with the inherent ability of carbon to form structures with different coordination of the atoms, opens new ways for electron-beam-assisted engineering of carbon nanostructures at high temperatures. Electron irradiation of crossing SWNTs in the TEM was shown[11] to result in the welding of the tubes. Various stable junctions were created (Fig. 6a). Two crossing pristine tubes would not normally join, even at high temperatures, as the structure of the junction containing non-hexagonal rings and strongly distorted bonds is less stable than the two perfect tubes. However, irradiation-induced vacancies and energy gain by dangling bond saturation made it possible to weld the tubes together. These results suggest that it may now be possible to fabricate nanotube networks by growing crossed nanotubes or moving them mechanically followed by controlled electron irradiation at high temperatures. Simulations[71] showed that the welded nanotube structures should be mechanically stable in spite of many defects at the junction. As atomistic simulations[72] pointed out, ion beams can also be used for nanotube welding. The theoretical predictions were corroborated later by experiments. Irradiation of overlapping nanotubes with 10-keV Ga ions resulted in the welding of nanotubes[18] (Fig. 6b).

Electron irradiation can be used to fuse fullerene cages inside carbon nanotubes ('peapods')[73,74]. The resulting structures consist of corrugated tubules nested inside the original SWNT. Irradiation-mediated fusion of fullerenes was also implemented inside boron–nitrogen nanotubes[10]. As a result, a carbon nanotube was obtained inside the BN nanotube (Fig. 6c). Because BN nanotubes are insulating, the use of the electron beam for producing such structures (a conductive inside an insulating wire) opens new ways for making complex nano-cables with predetermined electrical properties.

NANOTUBES AND ONIONS AS HIGH-PRESSURE CELLS

The irradiation-induced removal of carbon atoms from closed graphitic cages such as nanotubes or fullerene-like spherical onions causes the shrinkage of the cages. Because of the annealing of defects and restructuring, these cages remain coherent with a high tensile strength[55]. Several electron- and ion-irradiation experiments have shown that the self-contraction of these structures, once they are filled with carbon or other materials, can build up extreme pressure in the interior (Fig. 7). The irradiation of carbon onions with intense electron[4] or ion[13] beams leads to such a heavy contraction of the onions that the pressure in their centres is high enough for the nucleation of diamond crystals (Fig. 7e). These were the first experiments that enabled observation of the nucleation of diamonds with atomic resolution.

When carbon nanotubes or onions are filled with other (non-carbon) materials, the compression of the graphitic shells under irradiation sets the encapsulated material under high pressure. This results in several interesting phenomena[12]. The collapse of nanotubes filled with transition metals such as Fe, Co or Ni deforms the crystals and eventually extrudes them from the tube as shown in Fig. 7a–d. The pressure inside the tubes is of the order of 20–40 GPa as measured from the lattice spacings of the elastically compressed metal cores[75] and estimated from atomistic simulations[12].

The self-compression of carbon onions has been made use of in several experiments where metal crystals were encapsulated by the spherically closed graphitic shells. The restructuring of the shells during contraction deforms the encapsulated crystals considerably so that the formation of crystal defects in the metals can now be monitored in real time and at atomic resolution in the electron microscope[76]. The pressure from the shells and the firm coverage of the surface can also lead to considerable superheating and supercooling of the metal crystals inside the shells. A melting hysteresis of almost 400 K has been observed for encapsulated Sn crystals[77]. Furthermore, reactions between metal crystals and the carbon shells can be induced by irradiation and monitored *in situ* at high resolution[75].

Self-compression of carbon onions and nanotubes encapsulating nanocrystals under irradiation provides a unique opportunity to study the response of individual nanocrystals to mechanical deformation, as the extrusion process can be monitored in real time at atomic resolution in the TEM. Moreover, such a set-up can be used for making new materials or unique phases that can exist at high pressure and at the nanoscale only.

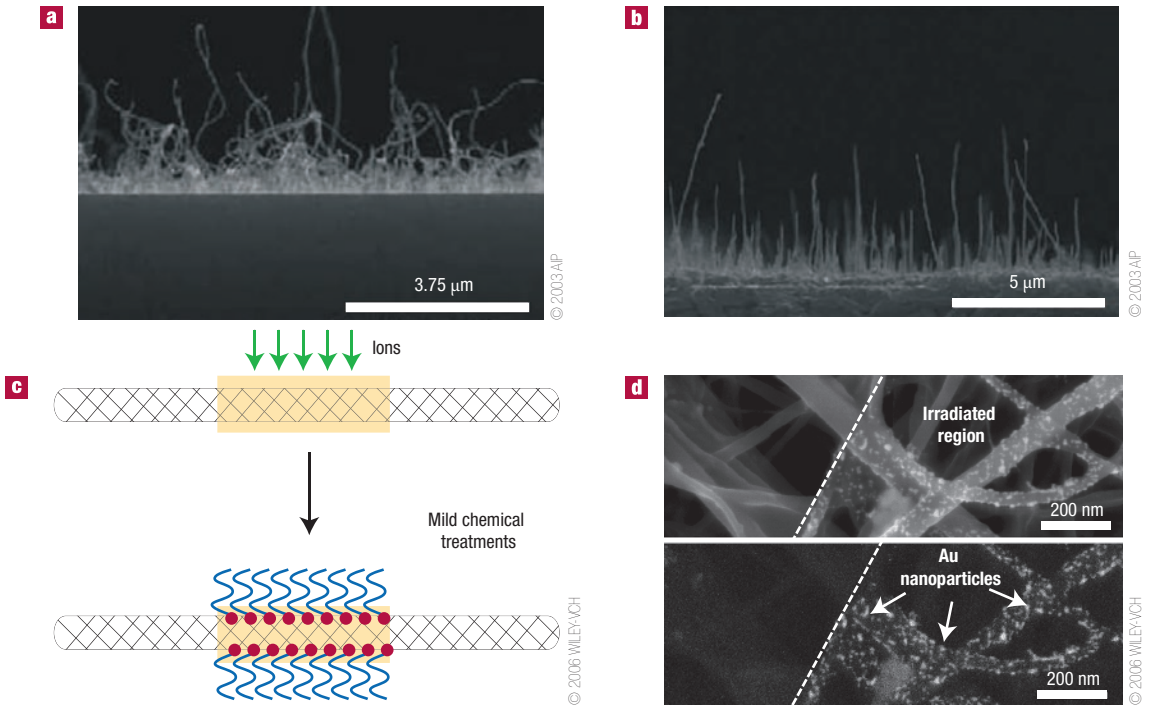

Figure 5 Ion-beam-assisted engineering of carbon nanotubes. **a**, **b**, Scanning electron microscopy images of nanotubes before (**a**) and after (**b**) irradiation illustrating the straightening of nanotubes by Ar ion beams to improve the field-emission effect because of an increased aspect ratio and reduced mutual shielding. **c**, **d**, Site-selective functionalization of carbon nanotubes. **c**, Schematic illustration of the experimental set-up. **d**, Immobilization of Au nanoparticles on ion-irradiated regions of carbon nanotubes. Parts a,b reprinted with permission from ref. 39; parts c,d reprinted with permission from ref. 37.

INFLUENCE OF DEFECTS ON NANOTUBE PROPERTIES

Carbon nanotubes are the most important members of the nanocarbon family because of their excellent mechanical and electronic properties. The effects of irradiation on these properties can be summarized as follows.

MECHANICAL PROPERTIES

Irradiation has a deleterious effect[53,78,79] on the axial mechanical properties of nanotubes because it creates vacancies. However, the mechanical properties of macroscopic structures such as networks and fibres made from nanotubes may be improved by irradiation. The reason for this is the strengthening of the interaction between the tubes by irradiation-induced crosslinks. Normally, the van der Waals interaction between tubes allows them to slide against each other, and the strength of macroscopic materials is accordingly low. As irradiation gives rise to covalent bonds between the tubes, the overall strength of the nanotube material may increase. Indeed, a considerable increase in the bending modulus of nanotube bundles was seen[6] after electron irradiation. Irradiation should also increase the tensile strength of macroscopic nanotube products. Simulations[80] demonstrated that the stiffness and tensile strength of 'bucky paper' (a material made from a network of interwoven nanotubes) and nanotube fibres can be increased by several orders of magnitude owing to covalent bonds at the bundle contact areas. First experiments[81] confirm this trend, so that irradiation may indeed be a viable way for making strong nanotube-based materials.

ELECTRONIC PROPERTIES

Irradiation-induced defects have strong influence on the electronic structure of sp^2-bonded carbon. New states near the Fermi energy and localized at vacancies have been predicted[49,82,83], followed by experimental STM observations[35] of the states that can, in principle, be used for engineering the local electronic structure of nanotubes. The defects also affect the electron transport in nanotubes because of the quasi-one-dimensional geometry. Under irradiation the resistivity of the samples normally increases by several orders of magnitude[7,16], depending on the original sample perfection and the conductivity regime. For macroscopic SWNT ropes the effect of irradiation proved to be more complicated[64]. A minimum in resistivity as a function of irradiation dose was found, which was interpreted as a result of a twofold effect of the irradiation: the domination of covalent bond formation between tubes in a bundle owing to broken bonds in the tube walls, and the amorphization of the sample at a high dose. Thus, irradiation with moderate doses may increase the conductivity of nanotube networks. As mentioned above, spatially localized irradiation can be used for creating functional electronic nanotube-based devices[61–63], so irradiation can also have a beneficial effect on the electronic properties.

ION IRRADIATION FOR CREATING MAGNETIC CARBON

Observations of magnetism in various metal-free carbon systems have stimulated much research work[84] on the magnetic properties of pure carbon systems. The driving force behind these studies was to create technologically important, light, non-metallic bio-compatible magnets with a Curie point well above room temperature. Irradiation of graphite with protons[20] resulted in a significant magnetic signal, which was explained in terms of complexes formed between vacancies and hydrogen interstitial atoms[47]. High-energy (100 keV) nitrogen ion irradiation of nano-sized diamond (which is graphitized at high irradiation dose) followed by magnetic measurements on the

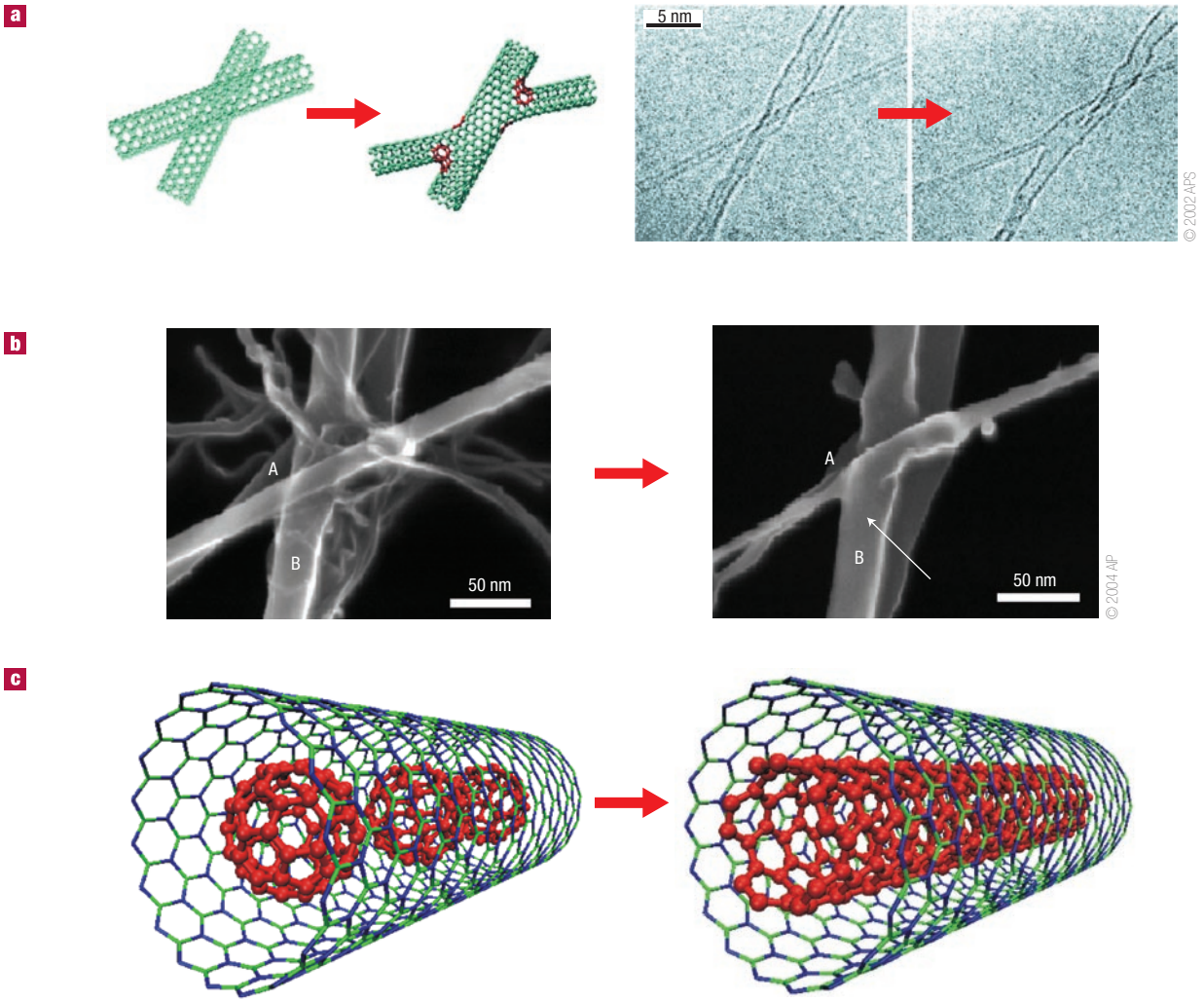

Figure 6 Welding of carbon nanostructures by electron and ion beams. **a**, Molecular model and TEM pictures of two crossed single-walled carbon nanotubes before irradiation and when the tubes were welded by the electron beam. Reprinted with permission from ref. 11. **b**, Scanning electron microscope pictures of MWNTs welded by ion irradiation. Reprinted with permission from ref. 18.**c**, Molecular model illustrating how fullerenes can be fused together and transformed into a SWNT inside carbon and boron nitride nanotubes[10]. Such a set-up can be used to make conducting carbon cores sheathed by insulating BN tubes.

doped samples showed ferromagnetic order at room temperature[19]. The appearance of magnetism after heavy-ion irradiation was also reported for fullerene films[68], which could originate from defects in the graphitic network such as under-coordinated atoms, for example vacancies[85,86]. However, the experimental proofs for the occurrence of magnetism in pure carbon systems are not undisputed and further experiments are necessary to clarify the picture.

IRRADIATION-INDUCED SELF-ORGANIZATION PHENOMENA

Nowadays, the term 'self-organization' is always used when a system develops some kind of structuring by itself, that is, without selective intervention from outside. In its original meaning, however, self-organization described the appearance of spontaneous ordering in dissipative systems. Nanoparticles under intense electron or ion irradiation are far from thermal equilibrium. Defects are continuously generated and heat is released from the particles. Because only a minor fraction of the transferred energy is stored in persistent defects (most defects anneal immediately), there is a considerable energy flux through the particles and the conditions for self-organization in dissipative systems might be fulfilled. The transformation of graphite to diamond under electron or ion irradiation is an example of such a process where a system is driven to a state (diamond) that is energetically less favourable but has a higher degree of order[87]. Electron irradiation of a graphite–diamond interface at high temperature but vanishing pressure has been shown to lead to the growth of diamond at the expense of graphite[88]. Conversely, heating without irradiation leads to the relaxation towards equilibrium — that is, to the transformation of diamond to graphite. The treatment of such a system with the principles of non-equilibrium thermodynamics has resulted in the development of phase diagrams of carbon under particle irradiation where diamond is the most stable phase in a certain range of irradiation intensity and temperature[87,89].

If we consider self-organization in a less strict and wider context, we can also describe structural transformations of nanoparticles under irradiation when they develop new morphologies or certain defect structures. For example, the bending or curling of graphene layers caused by the introduction of non-six-membered rings is a process that works by itself and leads to the formation of interesting

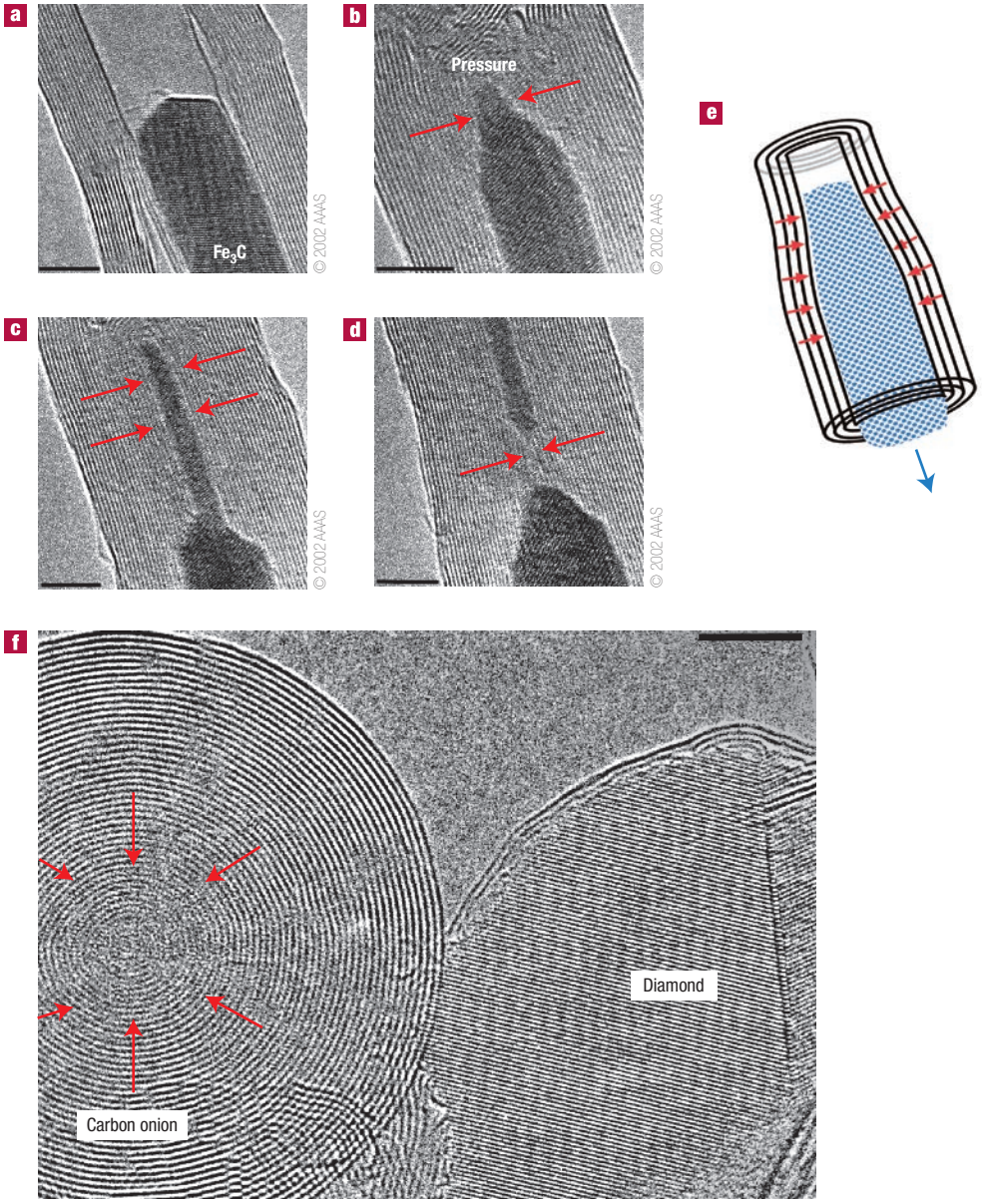

Figure 7 Pressure build-up inside nanotubes and onions. Electron irradiation leads to the shrinkage and collapse of cylindrically or spherically closed graphitic structures. **a**–**d**, Effect of electron irradiation on a carbon nanotube filled with a crystalline Fe_3C wire. Reprinted with permission from ref. 12. **e**, The contraction of the tube deforms and extrudes the Fe_3C crystal as depicted here. **f**, Carbon onions (left) self-compress under electron irradiation[4] until, under favourable geometrical conditions, a diamond crystal nucleates in their core. The diamond continues to grow until the onion has wholly transformed to diamond, even when pressure no longer prevails. The result of an almost complete transformation of an onion to diamond is seen on the right-hand side. All scale bars are 5 nm.

morphologies such as the perfectly spherical carbon onions[3]. Here, surface tension on removal of carbon atoms is the driving force that tends to make closed graphene cages spherical. Because the shells of carbon onions consist of an arrangement of pentagons, hexagons and heptagons[90], they are in an energetically higher state than planar graphite but local ordering is also decreased. The same argument may be applied to the formation of SWNT junctions[11,18] or the straightening of nanotubes[38,39] under irradiation. New and more complicated structures with a large number of defects form. Although local entropy increases, new morphologies self-assemble on a larger scale.

Irradiation can result in the growth of carbon nanotubes from catalytically active metal crystals, a phenomenon that can also be interpreted as self-organization. Recently, an irradiation experiment in the TEM allowed the monitoring of the birth of nanotubes and observation of their growth at high resolution and high temperatures. MWNTs containing crystalline wires of transition metals (Fe, Co, Ni) were subjected to electron irradiation so that carbon atoms from the tube shells were ingested into the metals. The growth of new nanotubes from the end faces of the metal cores has been observed and interpreted in terms of bulk diffusion of carbon atoms[91]. Controlled growth-reversal of nanotubes under electron irradiation was also reported[92], and the results were understood as evidence for surface diffusion, contrary to ref. 91. As the growth mechanism of carbon nanotubes is still a subject of considerable debate, the *in situ* observations of irradiation-stimulated growth of nanotubes should help in fully understanding the catalytic growth mechanism of carbon nanotubes.

IRRADIATION EFFECTS IN NON-CARBON NANOSTRUCTURES

Many of the ideas of how electron and ion beams can be used for tailoring the properties of carbon nanostructures can be directly applied to non-carbon systems. For example, the morphology and properties of BN systems, which also form tubular or fullerene-like structures, can be tuned by electron irradiation: octahedral BN fullerenes and other curled structures have been formed under electron irradiation (ref. 93 and references therein), and selective removal of atoms from BN nanotubes[94] can further be used for structural engineering at the nanoscale.

Spatially localized electron beams can create nano-holes in silicon and metal nanowires, and can be used to cut and weld them[95]. The same technique can also be applied for making ultrathin (1 nm thick or less) nanobridges in ZnO wires[96].

As for ion irradiation, extensive work demonstrates that ordered nanostructures can be fabricated by self-organization[25] originating from an interplay between disorder, sputtering[97] and self-assembly due to irradiation-stimulated diffusion. A delicate balance between different processes can result in the formation of nanoclusters or quantum dots with unique electronic[98,99] or magnetic[21,22] properties and in the creation of metallic nanoparticles in dielectric matrices[26].

CONCLUSIONS AND OUTLOOK

Based on a wealth of experimental and theoretical data, it can be concluded that irradiation of nanostructures does not necessarily destroy them but may result in many fascinating and unexpected phenomena that can be readily used for engineering nanosystems and tailoring their properties.

One can envisage that one of the most immediate applications would be the use of electron or ion beams as 'cutting and welding tools' on the nanoscale. Various nano-objects can be shaped by the beams and welded to each other or to macroscopic systems. In particular, arrays of inter-connected carbon nanotubes with different electronic properties can be manufactured by using spatially localized irradiation, which could be fundamental for carbon-based electronics[100]. The main obstacle here is that defects may unintentionally be created in other parts of the system, but the damage can be minimized after making a device by high-temperature annealing or, in principle, by photoexcitation-mediated healing of defects[101]. At the same time, the nanotube-based circuitry can gain from defected areas deliberately created to work as electron tunnelling barriers and thus provide the desired functionality of the device.

Irradiation should also be a useful tool for engineering graphene-based devices. Graphene has just emerged as a new material and has already shown many interesting properties[29]. The close relationship between graphene and carbon nanotubes suggests that electron or ion irradiation should have great potential for making graphene-based components of devices by, for example, doping pre-selected areas of graphene sheets and cutting nanoribbons with high spatial precision. As for making nanoribbons, strips with a width of several nanometres can be cut out, but the structures may curl[3,93] under irradiation, which would complicate the use of this technique. On the other hand, the introduction of defects such as pentagons or heptagons into graphene could be used to create new morphologies or topologies of graphitic nanoparticles with subnanometre precision.

Another enticing possibility is to use beams of energetic particles for functionalization of graphitic nanostructures, as irradiation-induced defects at the surface should increase the chemical reactivity of the structures. This is important because a pristine basal plane of graphite is chemically almost inert. Thus, functional groups can be attached to graphene or nanotubes in pre-selected areas, which should be important for biological or other applications. Another plausible application of irradiation, which has been discussed in the literature[40], is to improve mechanical properties and conductivity of nanotube–polymer composite materials by enhancing the adhesion between polymers and nanotubes through defects. In macroscopic samples made from nanotubes only, improvements in the mechanical properties are also expected from irradiation-induced covalent bonds between the tubes. Thus irradiation may help to create nanotube-based macroscopic ropes with excellent tensile strength and flexibility.

In a biological context, in addition to defect-mediated functionalization, another interesting application may be creation of magnetic biocompatible systems by irradiating fullerenes, nanodiamonds or nanotubes with non-magnetic ions.

The reversal of the graphite–diamond phase equilibrium under particle irradiation promises many possible applications. Although the energy needed to transform graphite to diamond via irradiation is extremely high, the production of diamond on a small scale could be an interesting perspective for developing nanodevices on the basis of diamond. Likewise, high-pressure effects in graphitic encapsulates may be used to create or transform individual nanoparticles.

Many other applications such as the use of nanotubes as masks against irradiation to make ultra-narrow metal nanowires[102] and as conduits for channelling of energetic ions[103] have been discussed. The ongoing research is likely to open up more new avenues for harnessing irradiation on the nanoscale.

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