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Graphene Nano-Flakes and Nano-Dots: Theory, Experiment and Applications

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1. Introduction

The experimental isolation of graphene (Novoselov et al., 2004) was one of the greatest discoveries in materials physics for many years. The time between the prediction of the electronic structure of graphene (Wallace, 1947) and its experimental isolation was nearly 60 years (Novoselov et al., 2004) but, by contrast, since this experimental discovery 6 years ago there has been an enormous amount of theoretical and experimental interest in graphene membranes. This is because graphene has proved to have exceptional properties including very fast electron transport, room temperature quantum hall effect, the highest mechanical strength and greatest thermal conductivity yet measured (Castro Neto et al., 2009; Abergel et al., 2010). In particular its fascinating electrical properties have lead to the speculation that graphene may one day replace silicon as the material of choice for most electronic applications (van Norden, 2006).

From a physical perspective graphene is a large 2-D sheet or membrane of sp^2 bonded carbon atoms which we will term graphene membranes (GMBs), see figure 1. The basic structure of GMBs is that of fused heaxagonal rings of aromatic benzene so GMBs may be regarded as giant aromatic molecules. In chemistry they are often termed polycyclic aromatic hydrocarbons (PAH's) if the edges are hydrogenated (Wu et al., 2007; Zhi and Mullen, 2008). It may also be thought of as honeycomb lattice since, at least ideally, GMBs are large, flat structures consisting of hexagonal rings of carbon atoms with a nearest neighbour distance of 1.42 Å and bond angles of 120° (as shown in figure 1) just like the structure of a layer of honeycomb. As we shall see in section 4 another useful way of looking at these structures for some purposes is as two interpenetrating trigonal lattices, labeled A- and B-. But the important point here is that all of these descriptions and metaphors are referring to the same thing.

Despite having many exceptional properties GMBs have one very severe limitation from the point of view of electronics applications; they have no band-gap and a vanishingly small density of states at the Fermi level i.e. it is a semi-metal (Castro Neto et al., 2009; Abergel et al., 2010), (see section 4). Several methods have been suggested to induce a band gap in graphene and thus overcome this fundamental limitation. One method is to cut a GMB into nanoribbons (GNRs, see figure 1b) which may produce a band-gap, depending on the width (Castro Neto et al., 2009; Abergel et al., 2010). This observation has subsequently generated enormous research activity on GNRs. The reason for the appearance of a gap is
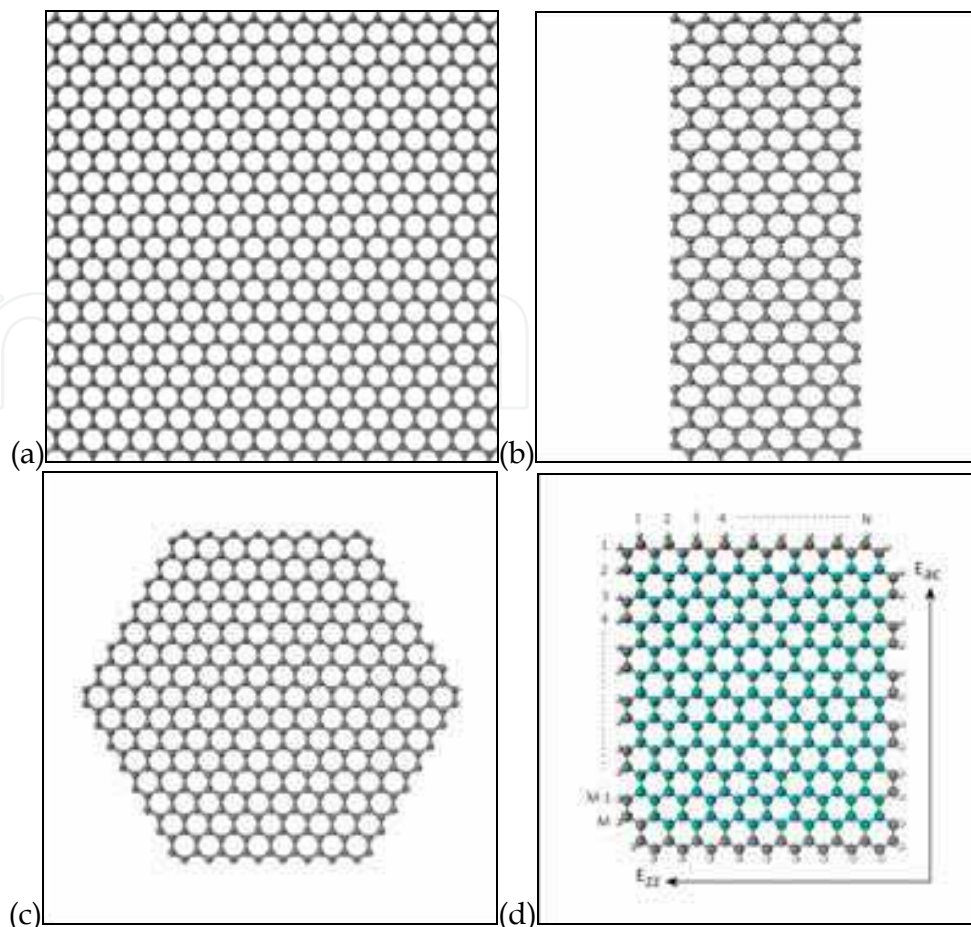
Fig. 1. The three basic type of graphene, (a) an infinite graphene sheet or membrane, 2-D graphene (b) a graphene nanoribbon, 1-D graphene, (c) a graphene nanoflake or graphene nanodot, 0-D graphene and (d) shows a GNF with a zigzag edge labeled by E_{zz}, an armchair edge labeled by E_{ac}.

that along with the finite width edge states begin to play a significant role in modifying the electronic properties since a significant number of atoms reside at the edges. Therefore, GNRs may be termed 1-D graphene and we may look at their production as adding one extra degree of engineering freedom to graphene as the fraction of edge atoms and hence edge states may be systematically controlled. There are two major types of idealized edge states, armchair and zigzag as can be seen on the sides and tops respectively of the structure represented in figure 1d. It has been shown that GNRs can be metals, semiconductors, half-metals, feromomagnets and antiferomagnets depending on their edge structures, width, shape and chemical termination (Castro Neto et al., 2009; Abergel et al., 2010; Son, et al, 2006a; Son et al., 2006b; Hod et al., 2007).

However, this critical dependence of their properties on their edge states also leads to new limitations in terms of fabrication (for use in electronic devices) because it is difficult to consistently and reliably produce GNRs with edge states of a particular type. Another limitation is that the cutting of GMBs into GNRs leads to electron mobility degradation and loss of performance in devices.

The zero-dimensional (0-D) form of graphene, which may be called graphene nano-flakes (GNFs) or graphene nano-dots (GNDs) (see figure 1c) also exists but has been much less extensively studied than GMBs or GNRs. This is surprising given that preliminary studies

suggest they show some very interesting properties which differ from those of 2-D and 1-D graphene and have great potential for a variety of applications principally as electronic and magnetic devices. These potential applications arise because GNFs not only have edge states, but also corner states, and may also be cut into a much larger variety of different shapes (see figure 2). The addition of these structural features may be regarded as giving GNFs yet another degree of engineering freedom over GMRs and twice as many degrees of freedom than GMBs. Examples of corner states can be seen where edge states meet in figure 1c and in figure 2 we see some examples of different shapes which are possible with GNFs, and the different types of corners that can be introduced.

Furthermore, in contrast to GNRs, GNFs can potentially range in size from molecular to semi-infinite 2-D structures, and consequently their electronic structures will vary from having discrete molecular levels to being band-like as their dimensions are made larger. This leads to the potential of spanning the range of electronic and magnetic properties from molecular-like to 2-D like by using GNFs of different dimensions. Of course, just as we see in GMBs and GNRs, GNFs also have their own inherent limitations, as we shall see in later sections.
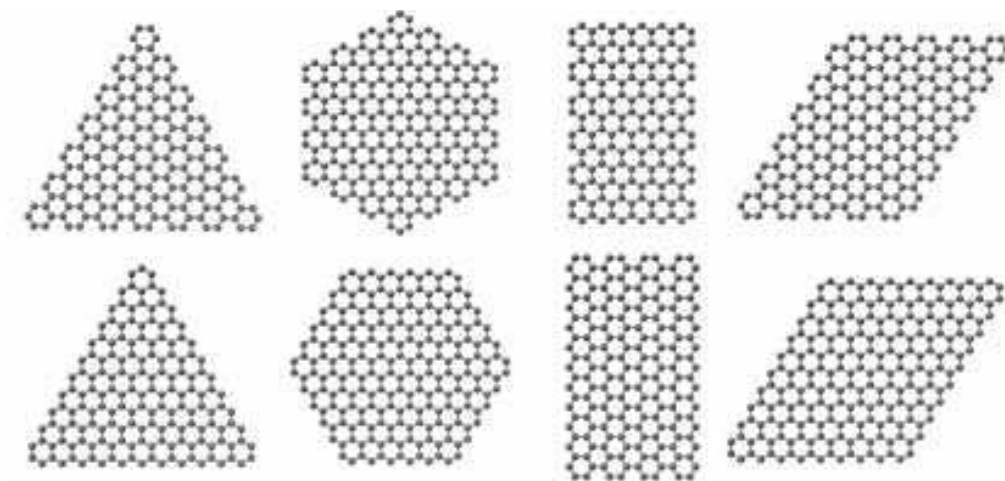

Fig. 2. This shows a variety of possible GNF shapes which might be produced with different geometries and corners, but always terminated with either zigzag or armchair edges.

In this chapter we give an outline of how GNF structures may be created, give a theoretical description of the structure and its stabilty, the electronic structure and basic characteristics. We then outline some of the potential applications of these nano-flakes in the areas of electronic and magnetic devices. Where there exists a large literature which is particularly the case for GMBs and GNRs but also in some areas on GNFs (particularly in the area of synthesis) we have attempted to reference comprehensive and up-to-date reviews in order to keep this chapter within reasonable limits.

2. The production of GNFs

As stated in the introduction graphenes consist of fused, combinations of sp^2 bonded carbon hexagons referred to as rings. Thus, at the one end of the size spectrum of graphenes we have a benzene radical or if terminated by hydrogen atoms we have benzene and at the other extreme an infinite 2-D graphene membrane. These limiting cases are usually treated by chemists or materials engineers, respectively, with materials physics spanning the sizes

in between. Depending of the perspective, there are two distinct classes of methods that have been generally used to make GNFs, partly because of this wide range of sizes of GNFs, and these are usually classified as bottom-up and top-down.

2.1 Bottom-up production of GNFs

As suggested above, these are essentially chemical method of production based on the chemistry of aromatic molecules. Small molecular units are "fused" to form large aromatic hydrocarbons by a large variety of chemical reactions some of which are shown in figure 3 below (Wu et al., 2007; Zhi and Mullen, 2008).
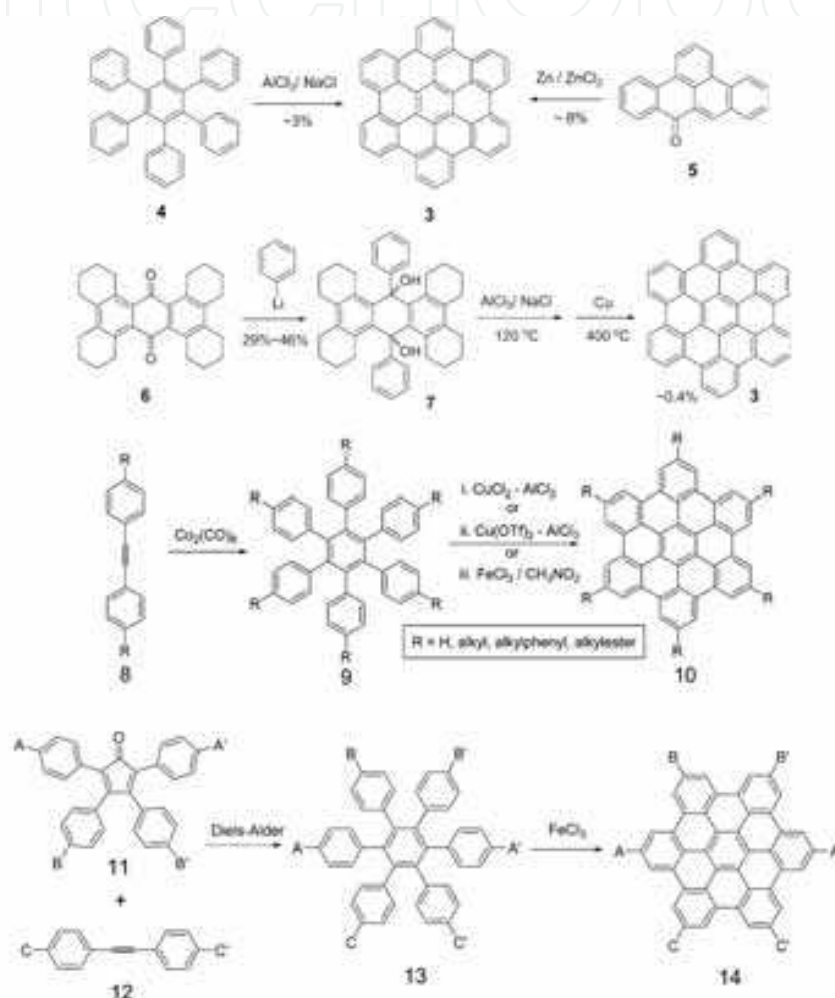
Fig. 3. Examples of various chemical reactions used to produce GNFs (Wu, et al., 2007).

The largest such structure produced by these methods reported to date is a 222 ring GNF. A variety of terminations of the benzene ring edges may be made by hydrogen, alkyl groups, etc (Wu et al., 2007; Zhi and Mullen, 2008).

Chemical methods, as well as producing nanoflakes can also be combined with other techniques to assemble these units into films. This is most commonly done in solution by mechanical extrusion, zone casting/refining, aligned substrate, magnetic field alignment and thermal annealing (Wu et al., 2007; Zhi and Mullen, 2008) but this can also be in vacuum by the use of soft-landing mass spectroscopy (Rader et al., 2006) as illustrated in the schematic diagram in figure 4.
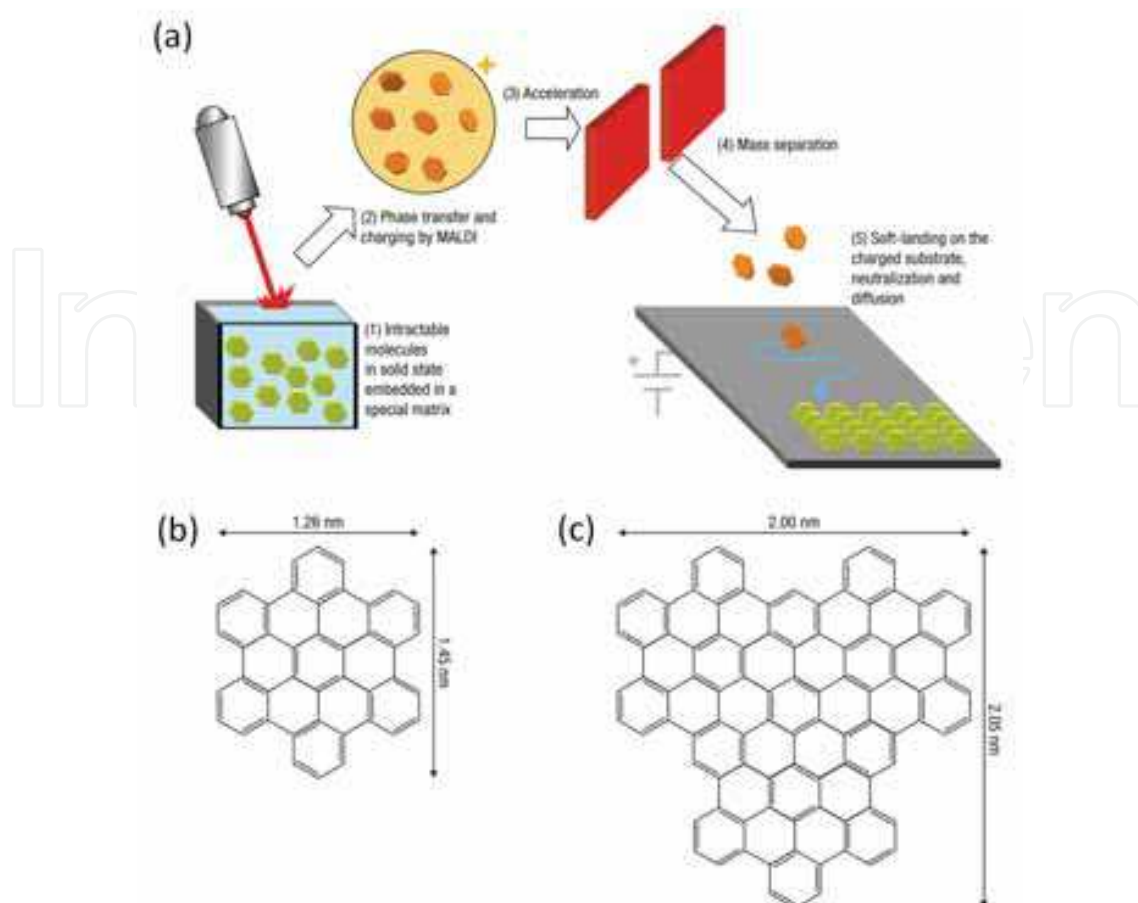
Fig. 4. Schematic diagram of the soft-landing set-up used with typical molecules shown as are the van der Waals dimensions of these molecule obtained by molecular modelling (Rader et al. , 2006).

2.2 Top-down production of GNFs
These methods start with a large piece of graphene sheet or graphene related material such as graphene oxide and cut GNFs directly from the sheets. These methods usually produce graphene islands in a membrane of graphene, which are effectively non-free standing GNFs that are often quite large. Such structures are then usually referred to as graphene quantum dots (GQDs).

Naturally, this method requires that one first produce large sheets (GMBs) and this has been done by a variety of methods, micromechanical cleavable of a graphite single crystal (Novoselov et al., 2004) by chemical means e.g. by starting from graphite oxide (Park & Ruoff, 2006) or by chemically "unzipping" carbon nanotubes (CNTs) (Terrones, 2009).

Presumably some or all of these techniques could be adapted to produce graphene GNFs. A possible adaption of the "unzipping" methods may be to directly "unroll" small fullerenes such as bucky-balls, nanohorns or small pieces of CNTs to produce free-standing GNFs. This does not seem to have been reported at the time of writing, but if such methods prove to be feasible it would open-up the possibility of transferring GNFs to a variety of substrates rather than just making them on graphene.

Graphene layers have also been produced on surfaces, either by removal of layers from a SiC crystal surface (Hass et al., 2008) or by chemical vapour deposition (Obraztov, 2009)

These methods might also be adaptable to the production of GNFs especially in light of recent work which showed that dome-shaped carbon nanoislands may be produced on the (111) surface of Ir (Lacovig et al., 2009).

Once sheets of 2-D graphene are produced, GNFs have to be "cut" from them which has currently been done by a variety of methods; combined e-beam lithography and plasma etching (Berger et al., 2006; Schedin et al., 2007; Stampfer et al., 2008; Neubeck el al., 2010), chemical stripping (Li et al., 2008), scanning tunneling microscope lithography (Tapaszto et al., 2008) and atomic force microscope lithography (Neubecket al., 2010), hydrocarbon lithography (Meyer et al., 2008) and catalytic cutting by atoms (Datta et al., 2008; Ci et al., 2008; Ci et al. 2009; Campos et al., 2009).
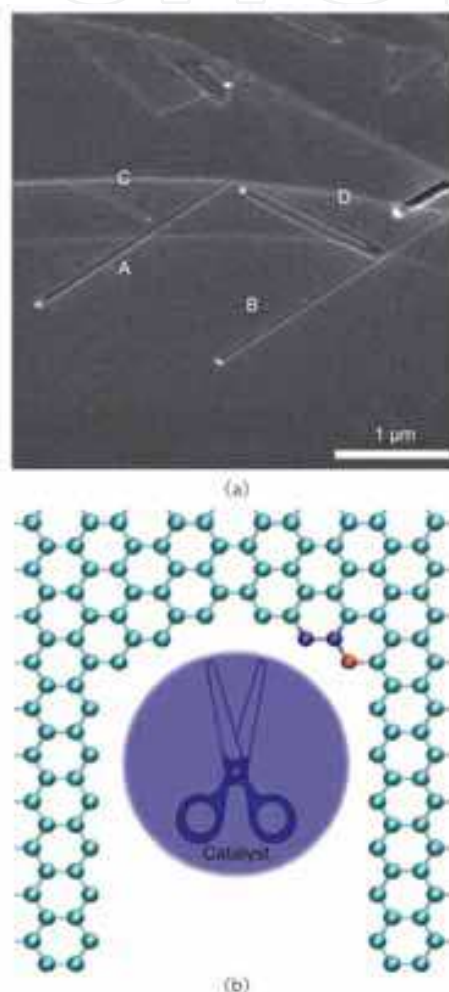

Fig. 5. An illustration of catalytic "cutting"of graphene. From Chi, L., Xu, Z., Wang, L., Gao, G., Ding, F., Kelly, F, Yakobso, I. & Ajayan, P (2008). Controlled nanocutting of graphene. *Nano Research*, Vol. 1 (2008) pp. 116-122

Standard e-beam lithography methods seem to be limited to producing features of greater than 10's of nanometers but scanning tunneling microscope lithography can produce much smaller features with pre-determined crystallographic orientations (Tapaszto et al., 2008).

Catalytic cutting seems particularly well suited to the production of GNFs as it can produce a variety of "cuts" giving very clean edges with definite edge geometries. This method was first developed using Fe atoms for multi-layered structures (Datta et al., 2008) and later

adapted (Ci et al., 2008; Ci et al., 2009; Campos et al., 2009) to produce single layer nanostructures (see figure 5). Being able to produce definite edge geometries is very important in determining the properties of GNFs so these techniques look very promising.

2.3 Functionalization

Graphene is hydrophobic and is therefore difficult to solubilize or disperse in most liquids, which limits their easy processability by many traditional methods. Thus, chemists have spent considerable effort in functionalizing graphenes so that they may be more readily solubilized or dispersed, especially in water. The bottom-up approach outlined in section 2.1 has the advantage that GNFs produced in this manner may be constructed from organic molecules which have solubilizing groups already attached before the GNF is synthesized. However, methods have been developed to make larger GNFs (as well as GMBs and GNRs) more soluble in a variety of solvents such as water and tetrahydrofurane (Loh et al., 2010). One study demonstrated that during the chemical production of graphenes one can avoid using graphene oxide (Salzmann et al., 2010). This is important as most chemical methods of producing GMBs are harsh, and often leave many defects and unwanted chemical groups attached. Groups such as carboxyl epoxy and hydroxyl are commonly used to solubilize in water and long alkyl chains make GNFs soluble in many organic solvents.

Unfortunately, many of these methods produce heterogeneous, non-stoichiometric functionalized products which contain defects. As a consequence of this is that, of course, their properties are modified by the attached chemical groups themselves. All these effects usually lead to a degradation of the properties of the graphenes produced in this way, but in some cases they may lead to the new and interesting behavior. For example, the optical properties of GNFs may be tailored by use of different attached groups, and this may open up the possibility of using graphene in optical applications (Loh et al., 2010).

2.4 Production of GNFs by confinement

As an alternative to producing regions of a material with actual physical boundaries as discussed in section 2.2, one of the standard methods of producing semiconducting nanodots is to confine a region of a bulk material by using an electrostatic potential (a gate potential) to produce a confined structure. This has been used for such system as GaAs. The confinement of electrons in such regions of graphene by use of potentials is not straightforward as the relativistic nature of the electronic excitations leads to Klein tunneling where these electrons can tunnel unimpeded through such barriers (Castro Neto et al., 2009; Abergel et al., 2010). Methods other than the straightforward use of "cutting" have been suggested to overcome this problem. This includes, creating a confinement potential within the graphene layer to trap an electron for a finite time, the introduction of a finite gap by coupling with the substrate or by using a bilayer, or the use of a magnetic confinement potential, the review by Abergel et al. gives an excellent and comprehensive summary and explanation of such methods (Abergel et al., 2010).

3. Structure and stability of GNFs in practice

In the introduction we discussed the idealized structures of GNFs, however, in practice real structures may differ considerable from these idealizations. In this section we will discuss some more realistic features of the structure of GNFs.
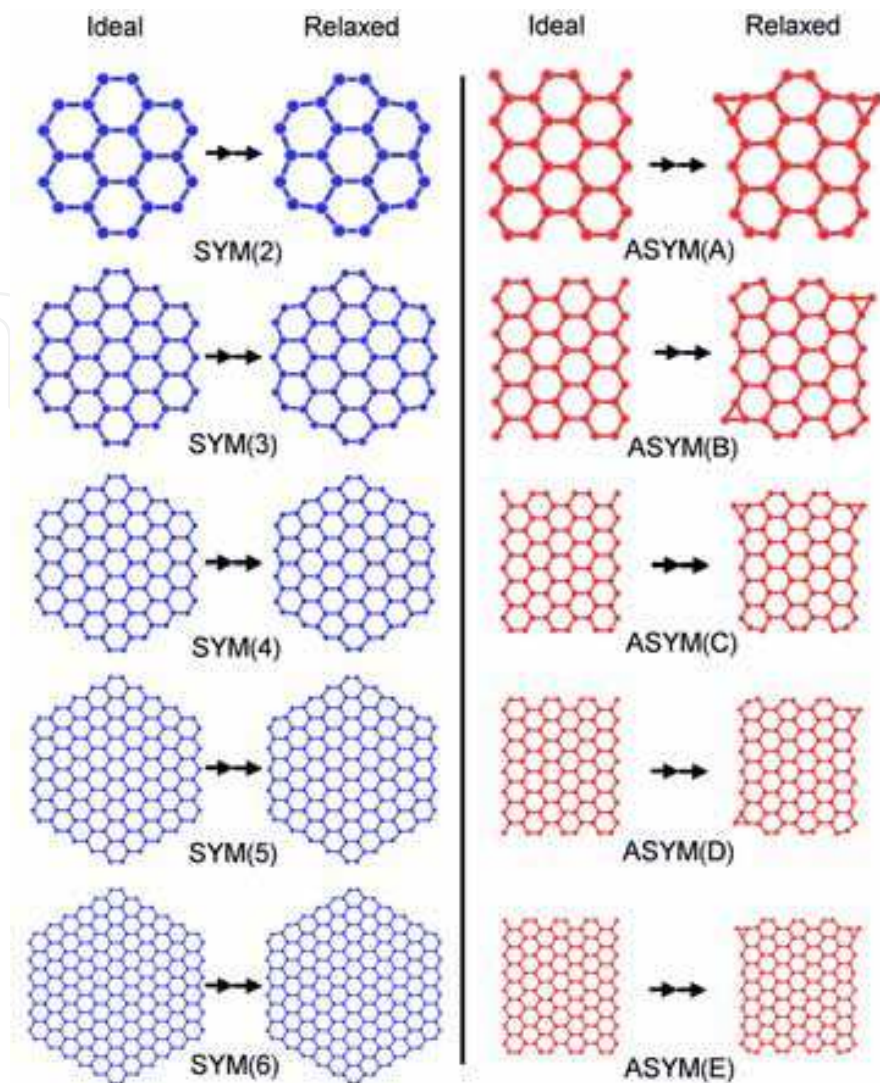
Fig. 6. The initial (ideal) structures on the left and final relaxed structures on the right for all symmetric (SYM) and asymmetric (ASYM) structures obtained by DFT (Barnard & Snook, 2008).

3.1 Edge reconstructions

The first factor one must consider when studying realistic GNFs is that, if the GNF is un-terminated then reconstructions at edges will occur, in order to break aromaticity, and lower the total energy of the flake. This is evident on the right-most structures in figure 6 where the edges of the relaxed structures of the asymmetric GNFs obtained by density functional theory (DFT) calculations (Barnard & Snook, 2008) show several types of reconstructions.

As we shall outline in section 4 the edges of GNFs (and of GNRs) play a very important role in determining their properties, and in particular their electronic and magnetic structure. As stated in the Introduction there are two basic types of edges in graphenes zigzag and armchair edges as illustrated in figures 1, 2 and 6. Note that the atoms on opposite zigzag edges belong to different A- and B- sub-lattices. However, other types of edge state are possible, if less numerous, such as reconstructed zigzags and armchairs (Gass et al., 2008; Koskinen et al., 2008; Koskinen et al., 2009) and those arising from unconventional "cuttings"(Wu & X.C. Zeng, 2008), as well as corner states which are formed where two

edges meet. Reconstructed corners can also be seen in the relaxed structure on the right hand side of figure 6. In fact as we mentioned in section 1, and shall see in section 4, GNFs offer the potential to tailor the edge states by cutting different shaped GNFs which is much more versatile than in GNRs and can lead to interesting advantages in using GNFs in electronic and magnetic applications.

3.2 Defects, adsorption, impurities and doping

In addition to edges and corners defects are another deviation from structural ideality. It was also recognized early on that defects can occur in GMBs, GNRs and GNFs and that they may have an important effect on the properties of these materials (Gass et al., 2008; Kraheninikov et al., 2009). In many cases the effect of defects may be detrimental as they often degrade the properties of graphene but in some cases may be useful, as they may introduce new properties such as magnetism, or may even increase the mechanical strength (Kraheninikov et al., 2009). Some of the earliest types of defects identified were point defects and Stone-Wales (SW) defects (Ma et al., 2009) consisting of two pentagons and two heptagons. Several types of defects have been subsequently predicted and/or observed in graphenes some of which are shown schematically in figure 7 (Carr & Lusk, 2010). One of the most interesting recent developments is the suggestion that an extended one-dimensional defect made of paired pentagons and octagons may function as a conducting nano-wire which would be of use in making graphene electronics (Carr & Lusk, 2010). Defects may also be of use in creating spintronic devices (see section 4), making microfluidic channels, forming porous membranes and offering active sites where controlled chemical reactions could take place. There is also theoretical and experimental evidence that SW-type represent preferred sites for atomic and molecular attachment and may be of benefit in modifying the properties of pure graphene structures. This may very well be a way of increasing the capacity of graphene to adsorb hydrogen and, thus, lead to a solution to the long standing question of providing a viable way of storing hydrogen to be used as a fuel. Defects may be deliberately produced by electron or ion beam irradiation as well as by their inadvertent introduction as a consequence of the fabrication processes, or through interaction with the substrate and with the environment.

Other related "defects" are adsorbed atoms and molecules (which, as mentioned above, may "decorate" defect sites) and dopants. There is a growing literature on defects, doping and adsorption in graphene but most of this is concerned with GMBs and GNRs and not with GNFs so there is a need and an opportunity for new research in this area. In particular, since GNFs are of finite size, the properties of a defect can dominate the structure, depending on the size and defect density. If the GNF is small, a high fraction of atoms will either participate in (or be in the vicinity of) a defect, and this may have a consequence for the thermal/chemical stability and structural integrity. In addition to this, while the opportunities for traditional defect patterning of GNFs (as per example in figure 7) may be limited by the finite size, new opportunities are introduced when one considers combinations of defects, edges and corners.

One may also regard the attachment of functional groups to the periphery (or to defect sites) of graphenes as an "impurity", particularly when they are non-functional, as they have the potential to quell the properties of pure graphene structures as mentioned in section 2.3. It should also be highlighted that adsorbates, defects and the attachment of functional groups to graphenes may change their structure and/or lead to non-planarity of the system. This will be particularly severe for small GNFs as is illustrated in figure 7d.
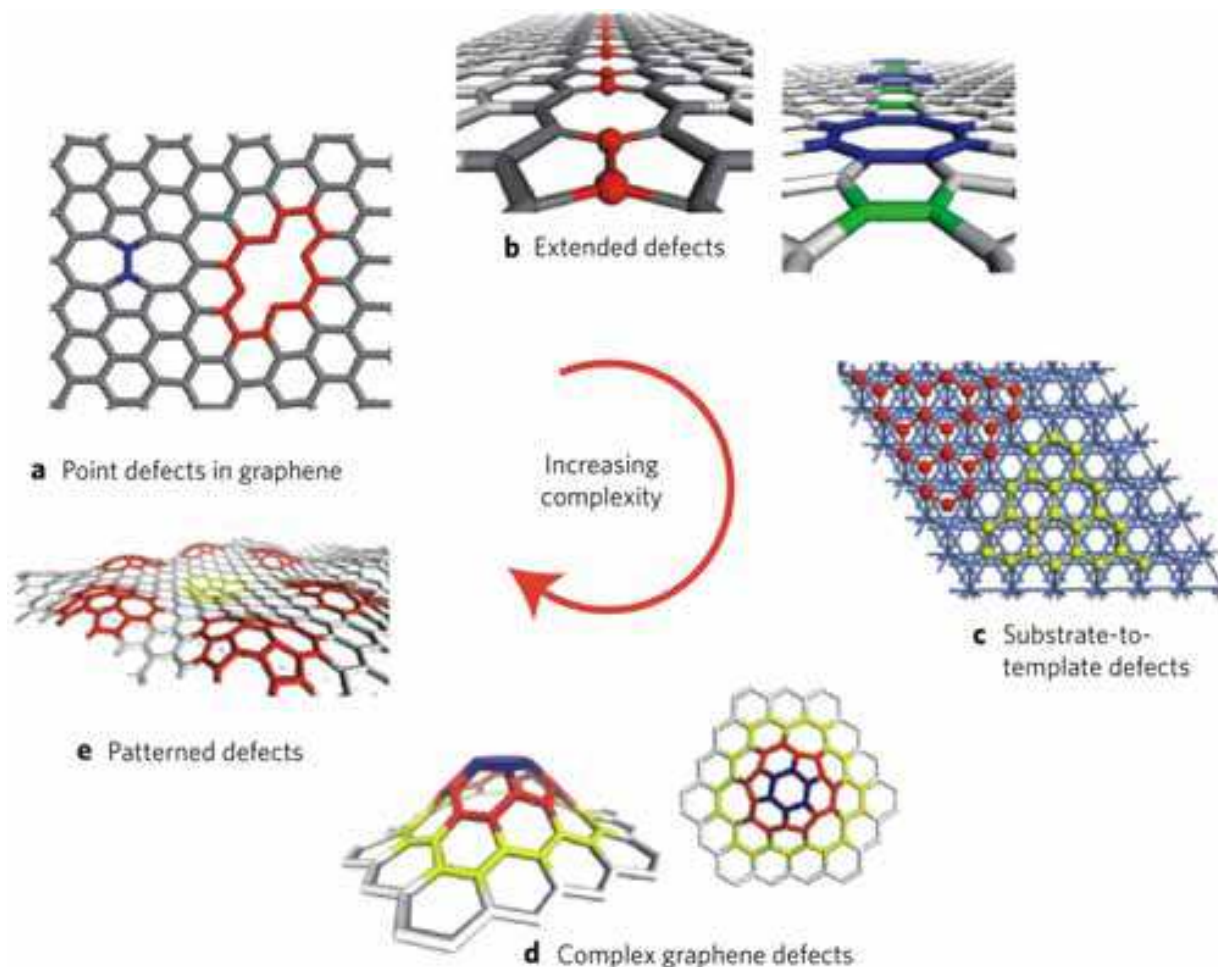
Fig. 7. A representation of defects which may occur in graphenes calculated by means of DFT (Carr & Lusk, 2010)

3.3 Vibrational states and ripples

When researching the properties and applications of graphenes, one must also remember that the structures outlined above are static, or represent a statistical average, and that vibrational states occur around these values. These states have been well studied in GMBs and in GNRs (Ferrari et al, 2006; Ni et al., 2008) but do not appear to have been extensively studied for GNFs. This is a problem that needs to be addressed as these vibrational states lead to Raman and/or infrared spectra which are very useful in identifying the structure of graphenes. The characteristic Raman G-band of graphene has been extensively used to differentiate single, double and multi-layer graphenes (Ferrari et al, 2006; Ni et al., 2008) as has the low frequency breathing modes of CNTs. These are considered signatures of these materials.

Another importance feature of vibrational effects is their contribution to the thermal conductivity of graphene. This is, possible, more important for GMBs as, because of their large thermal conductivity, they have been suggested as being useful for use as heat sinks. Nevertheless, the importance for GNFs remains largely unexplored.

Finally at finite temperature (T), not only do normal modes occur, but graphene structures develop ripples (Meyer et al., 2007; Castro Neto et al., 2009; Abergel et al., 2010). This was

first seen in GMBs, and is another departure from ideality. Now as has been shown theoretically (Mermin, 1968) that a truly 2-D crystal with harmonic forces is unstable for T > 0K, so this rippling is presumably the mechanism by which this instability is overcome. Although these structures are still composed of a single layer of C atoms, planarity is no longer preserved, and the structures are no longer mathematically 2-D. It has also been shown by ab initio molecular dynamics calculations that similar large scale vibrational modes occur in GNFs (Snook et al., 2005; Barnard & Snook, 2008) as shown in figure 8. More recently similar modes have been predicted theoretically in boron nitride nanoflakes (Topsakal et al., 2009) and boron nitride nanoribbons (Kan et al., 2008).
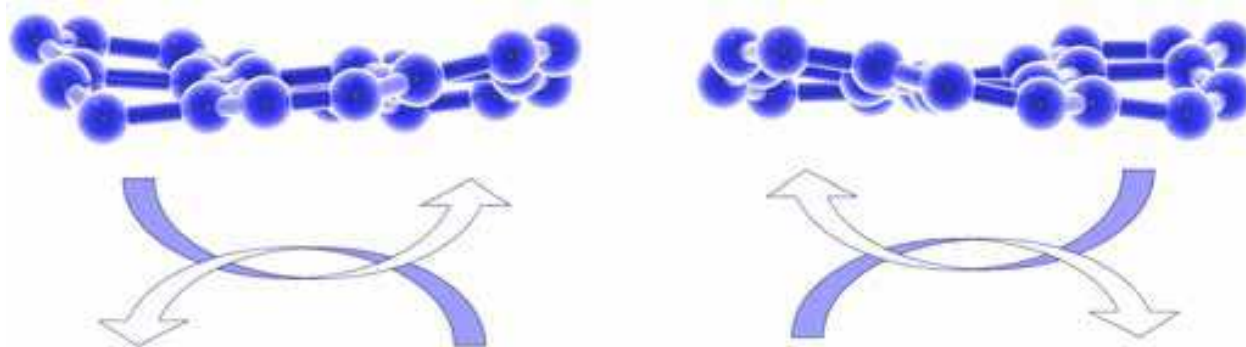
Fig. 8. Examples of the saddle-like distortions of the symmetric C_{24} flake, annealed at 900K. A dynamical rocking between these structures is observed following equilibration (Barnard & Snook, 2008)

4. Electronic structure and magnetic behavior of GNFs

One of the initial and, indeed, continuing interests with graphene membranes is in their fascinating electronic properties which we will only briefly outline here as there exists a large and growing literature on this topic (Castro Neto et al., 2009; Abergel et al., 2010). In fact because this literature is so vast and growing we will only give a brief outline of some of the fundamental aspects of electronic structure and their consequences for the particular case of GNFs.

4.1 The electronic structure of GMBs

As mentioned in section 1 the 2-D hexagonal lattice structure of GMBs may be looked on as two triangular lattices A- and B- , the reason for this is shown in figure 9. Wallace used a tight binding (or Huckel) model (Wallace, 1947) to show that the highest electronic states could be described by occupied π and unoccupied π* bands which meet only at the K and K* points in reciprocal space on the Fermi surface as shown in figure 11. This is why no band gap exists and as there is also a vanishing density of states at these points this makes 2-D graphene a semi-metal (or zero-bandgap semiconductor). The elementary excited electronic states show a linear dispersion relationship similar to massless, chiral, relativistic particles and are now termed "Dirac Fermions". This leads to the electron intrinsic mobility being much higher than in silicon (Castro Neto et al., 2009), and suggests that faster electronics can be made from graphene (than from Si). However, the zero-gap means that GMBs cannot be used for the construction of current types of Si-based electronic devices.
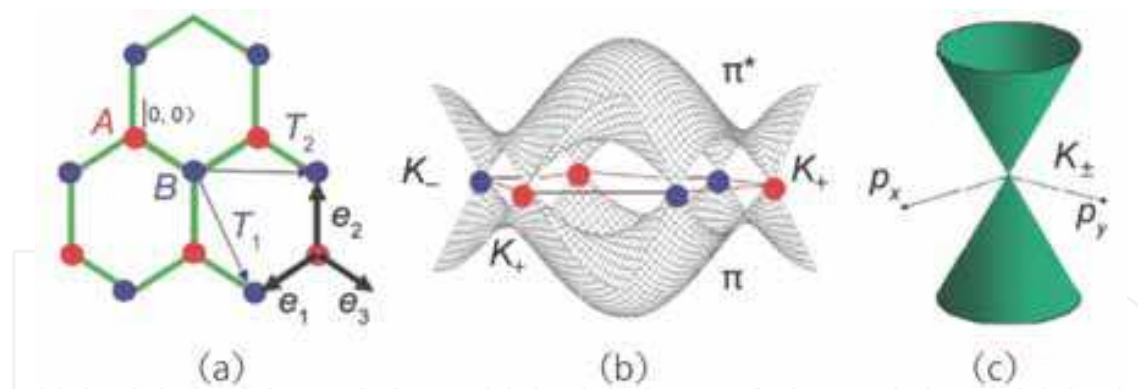
Fig. 9. (a) the graphene lattice (b) the π and π* bands and (c) the dispersion relation close to the $K_{\pm}$ points of the first Brillouin zone, a "Dirac cone" (from Cresti, A., Nemec, N., Biel, B., Neibler, G., Triozon, F., Cunerberti, G. & Roche, S. (2008). Charge transport in disordered graphene-based low dimensional materials. *Nano Research*, Vol. 1 (2008) pp. 361-394)

4.2 The effect of edges on the electronic structure of graphene

As previously outlined the simplest way to modify the electronic structure of GMBs is the introduction of edges and corners which has been most extensively studied in GNRs (Son, et al, 2006a; Son et al., 2006b; Hod et al., 2007; Castro Neto et al., 2009; Abergel et al., 2010). Although the properties of GNRs may be tailored using their edge states, edge states are actually even more important in GNFs than in GNRs as the fraction of atoms in edges can be made very large. In contrast, although corner states are unique to GNFs, and are likely to be invaluable for a variety of purposes, far fewer atoms reside at or near corners, and even in complicated shapes the corner-to-edge ratio is very low. Therefore, it is important to understand the effect of edges on electronic states of graphene nanostructures if we are to engineer designer GNFs in the near future.

As we know there are two basic types of edge structures, zigzag (ZZ) and armchair (AC) as displayed in figures 1 and 2, and that these edges contain dangling ("unsatisfied") bonds. This introduces a mixture of sp² and sp hybridization into the basic sp² graphene lattice unless the edges are chemically bonded to non-carbon atoms or functional groups (see figure 1d). Therefore, both un-terminated and terminated edge structures can alter the basic electronic structure of graphene and play a crucial role in determining the electronic and magnetic properties of finite structures. The effect of edge states on electronic and magnetic behaviour has been most extensively studied for GNRs, so at this stage we will selectively summarize some findings of relevance to GNFs (Son, et al, 2006a; Son et al., 2006b; Hod et al., 2007; Castro Neto et al., 2009; Abergel et al., 2010),

- GNRs with either ZZ edges or AC edges have a finite band gap and are semiconducting although the origin of the gap is different in each case.
- It has also been found theoretically that AC edged GNRs can be metallic but this has been suggested to be due to the limitations of the tight binding model used in these studies to describe their electronic structure.
- ZZ edges introduce localized states as is illustrated in figure 12. As opposite edges of such a GNR belong to different sublattices so the spin ordering is different on each edge.
- ZZ edges can create ferromagnetic (FM) or antiferromagnetic (AFM) phases.
- There are no localized states at AC edges which is illustrated in figure 12.

- Large magnetic moments occur at ZZ edges but there are none for AC edges.
- Functionalization ("passivation") of edges can significantly change the properties of GNRs with either AC or ZZ edges and in the latter case this can generate a fully spin polarized state.
- In an applied electric field ZZ terminated GNRs can produce a ½ metallic state.

An interesting consequence of the effect of edges on the spin state of GNRs is that ZZ terminated GNRs may be useful in the field of spintronics, whereas AC edges may not.
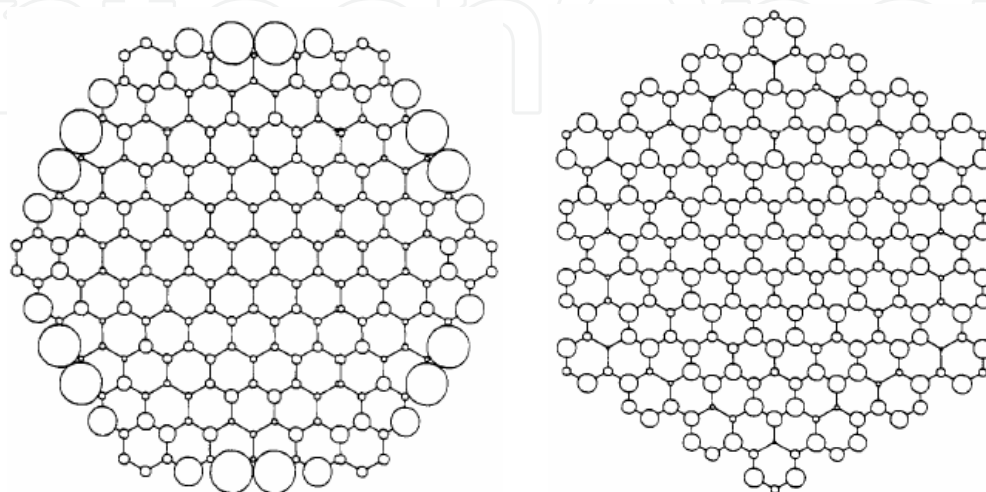

Fig. 10. The spatial distribution of populations of the HOMO level for GNFs having on the left zigzag edges and on the right having armchair edges (adapted from Stein & Brown, 1987).

4.3 The transition from discrete to band-like electronic states in GNFs
Small GNFs have discrete, molecular electronic energy levels, so the energy of the highest occupied molecular orbital (HOMO) takes the place of the Fermi Energy (E_f) and the difference in the energies of the HOMO and that of the lowest unoccupied molecular orbital (LUMO) corresponds to the energy gap (E_g). GNFs only have a continuous band structure when their dimensions are very large (see section 5) and a representation of this transition is shown in figure 11 (Chen & Tao, 2009). Along with this basic change in the nature of the electronic level, there is also a consequent change in electrical character from insulator to semiconductor, and then to a small or zero energy gap material (see figure 11).

Furthermore, for small GNFs the details of this discrete electronic structure can vary strongly with their shape and dimensions as illustrated in figure 12 and can be heavily influenced by termination i.e. passivation or functionalization.

4.4 Some general comments concerning the electronic states of GNFs
There have been a small but growing number of studies of the electronic states of GNFs using a variety of techniques such as tight binding models (TBMs), Hubbard models (HM), density functional theory (DFT) and the Dirac equation (DE). In these studies a variety of different shapes have been investigated including squares, rectangles, circles, triangles, disks, hexagons, polygons and non-symmetric shapes.

As outlined in section 4.2 it has been found that the electronic state and magnetic properties of GNFs are strongly influenced by the presence of edges and for small GNFs the effect is more pronounced than GMBs and GNRs.
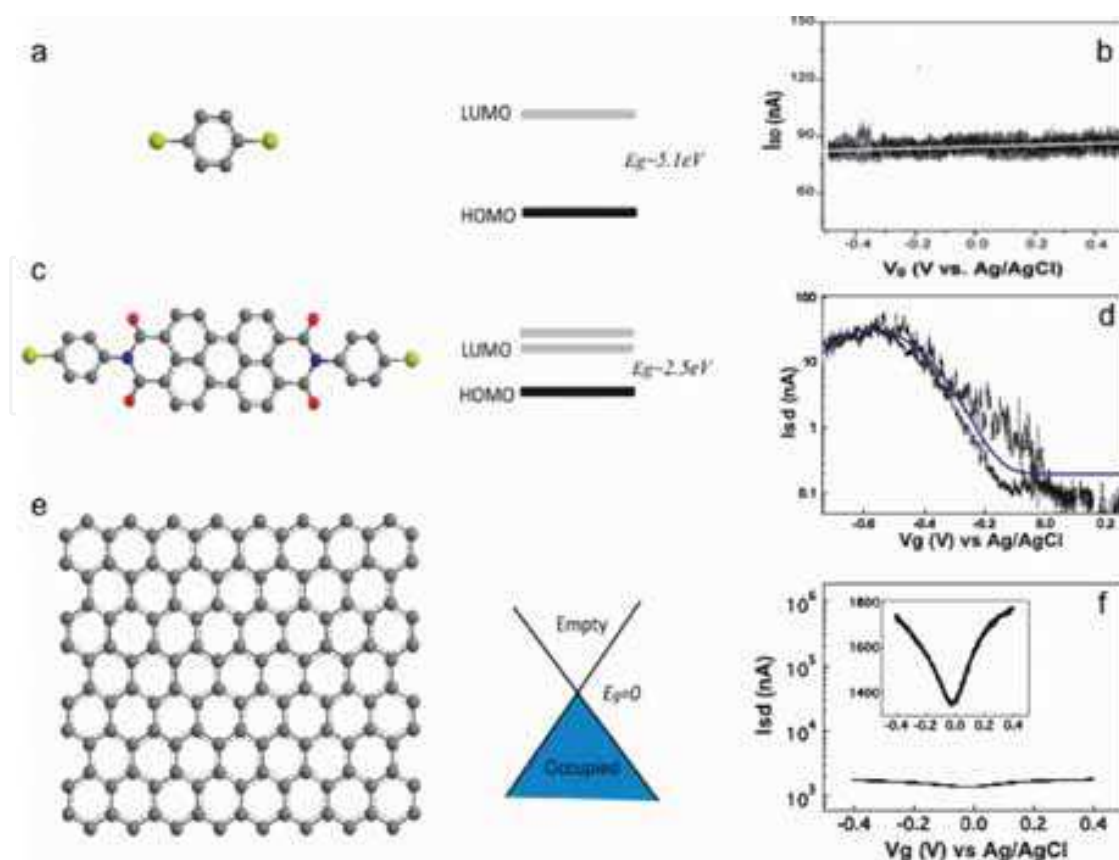
Fig. 11. Molecular structures, energy diagrams, and electrochemical gate effects of benzenedithiol, PTCDI, and a graphene sheet: (a) Benzenedithiol (containing a single benzene ring) has a large LUMO-HOMO gap (5.1 eV) and is "insulating" with a weak gate effect (b). (c) The LUMO-HOMO gap of PTCDI (containing seven rings) is ~2.5 eV, and the molecule is "semiconducting" with a large gate effect (d). (e) Graphene (containing a large number of rings) has a zero energy gap between the conduction and valence bands and shows semimetallic behavior with a weak gate effect (f)." (Chen & Tao, 2009).

4.5 Some interesting results for simple geometric shapes
4.5.1 Squares and rectangles
It has been shown for square and rectangular shaped GNFs (GNRs of finite length) that the band gap may be readily manipulated by altering the width of the GNF (Jing et al., 2007). The smallest rectangular GNFs consisting of a chain of n- fused single benzene rings (acenes) have been shown to have an AFM ground state for $n > 7$ (Jing & Sheng, 2008).

Interestingly a study GNFs with AC edges showed that unlike infinite GNRs they can be metallic (Shemella et al., 2007) and half-metallic states have also been predicted by DFT calculations with ZZ edges in the presence of an electric field (Hod et al., 2008; Zheng & Duley, 2008b).

The effect of functionalization and doping rectangular GNFs by the H, N, O, F, V atoms and by groups such as –OH, -CH$_3$ has also been studied by means of DFT calculations which showed that the electronic and magnetic properties of GNFs may be readily manipulated by these means (Zheng & Duley, 2008a; Sahin & Senger, 2008; Berashevich & Chakraborty, 2009; Olivi-Tran, 2010). This leads to the expectation that they may be extremely useful in areas such as spintropics, sensors and transistors.
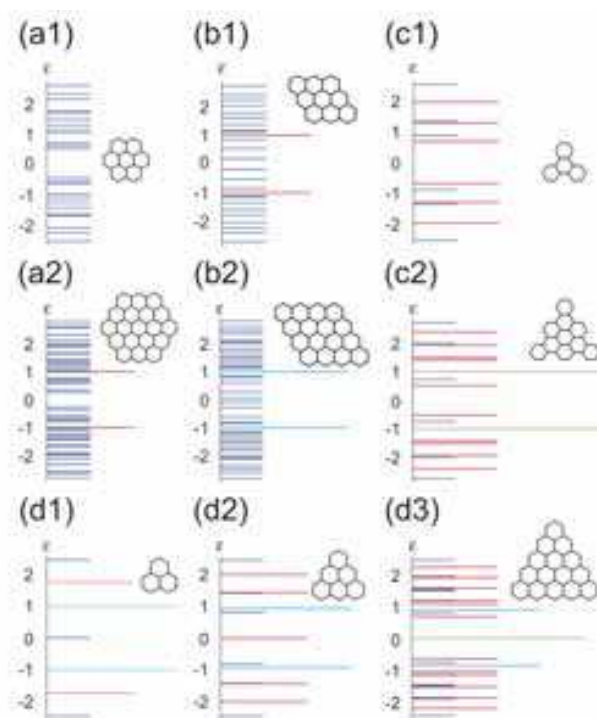
4.5.2 Nanodisks

Fig. 12. The electronic energy level diagrams for some GNFs whose shapes are shown beside the energy level diagram (Ezawa, 2008).

The electronic structure of a variety of compact structures based on highly symmetrical shapes such as large PAHs, triangular, hexagonal and other polygonal shapes, which are often termed nanodisks, have been studied by several groups (Stein & Brown, 1987; Banerjee & Bhattacharyya, 2008; Ezawa, 2007; Ezawa, 2008; Heiskanen et al., 2008; Kuc & Heine, 2010).
The results show that their electronic and magnetic structure may be varied considerably by changing the shape and size of the nanodisk and also by functionalizing them, once again suggesting that they may be extremely useful in fields such as spintronics. An example of the change in the electronic energy levels of some small graphene nanodisks with size and shape changes are shown in figure 12.

4.5.3 Some results for more complex shapes
The interesting magnetic properties of graphene arise from the properties of edge states which suggests the possibility to engineer materials with very interesting magnetic properties by using shapes other than the simple geometric ones mentioned above. Some research has begun into investigating the properties of more complicated shapes (Wang et al., 2008; Yazyev et al. , 2008 ; Yu et al. 2008) and because of the variety of shapes that GNFs can exist in they are ideal candidates for such studies.
A complication arises, however, as the relative energies of the various possible phases (AFM, FM, metal, semiconducting, ½ metal, non-magnetic) have to be worked out in order to find the most stable state. This is usually done by means of extensive and time consuming calculations so to try to circumvent this problem there have been various methods suggested to find simple rules to predict these stabilities (Yu et al. 2008; Dias, 2008; Potasz et al. 2010; Wang et al., 2009; Fernandez & Palacios, 2007). These methods are based on

considering the underlying geometry and topology of the graphene structures e.g. the fact that graphene may be pictured as two sublattices A- and B- as pointed out in the Introduction. Such methods should prove of great value in helping design GNF structures with the optimum magnetic behavior for applications such as spintropics (Trauzettel et al., 2007; Tombros, et al., 2007; Fal'ko, 2007; Rycerz et al, 2007). This prospect is enhanced by work that shows that the magnetic behavior of GNFs is very robust to disorder (Bhowmick & Shenoy, 2008; Wimmer et al., 2010).

5. Graphene and graphane nanoflakes

We have already introduced the simplest GNF; benzene, which is a planar six membered ring of C atoms each being terminated by a single H atom (monohydride). However, there is another stable six membered ring of C atoms; cyclohexane, which is a non-planar structure in which the C atoms are terminated by two H atoms (dihydride). If a GMB is completely hydrogenated on all carbon atoms on both sides of the sheet then the resulting structure, called graphane, is non-planar and consists entirely of sp^3 bonded carbon atoms and two sigma bonded hydrogen atoms per C atom. This structure was predicted theoretically by means of DFT calculations (Sofo et al., 2007) and discovered experimentally (Ryu et al., 2008; Elias et al., 2009) only quite recently. As graphane is an insulator it may be an ideal material to use in combination with graphene to form hybrid graphene/graphane integrated electronic devices and detectors. However, there remains the problem of how to "connect" these two materials together in an integrated hybrid device. Two recent theoretical studies have suggested ways that this might be achieved.

In one study (Barnard & Snook, 2010a), tight binding density functional theory (DFTB) was used to show that if a graphene nanoflake were anionically charged by adding excess electrons (for example by means of an electron beam) then beyond a certain level of added charge regions of the GNF would transform into hydrogen-less graphane. These results are shown in figure 13, where we can see that the graphene/graphane ratio, and the graphane distribution is dependent on the level of charge and the shape of the flake, but in each case this produces graphene/graphane boundaries and leaves the graphane regions ripe for functionalization by atoms or functional groups. Further work revealed that the charge-induced graphene to graphane can be predicted if the mass and the structure of the flake is known (or can be estimated) and identified by way of the shift in the Fermi level (Barnard & Snook, 2010 b). If this can be realized experimentally then it will enable structures consisting of co-existing regions of graphene and graphane to be produced spontaneously, and in the absence of volatile or expensive chemical environments.

As a follow-up to simulating "nanoroads" of graphene in graphane sheets (long strips of graphene in a graphane sheet) as an alternative to GNRs Yakobson et al. used DFT and DFTB methods to simulate graphene nanodots of various sizes embedded in a graphane sheet (Singh et al., 2010) as shown in figure 16 below. In this study it was found that the size n, shape and stability of the simulated dots were governed by the aromaticity of the dot and the interface between the two regions. Sizes corresponding to stable embedded aromatic molecules such as benzene and coronene were predicted to be stable and for larger dots hexagonal clusters are favoured i.e. structures congruent with the lattice hexagons which have armchair edges. Clusters had large band gaps of about $15/\sqrt{n}$ eV with the size dependence being characteristic of confined Dirac fermions (see figure 14). The largest dots have an electronic spectrum of GMBs (see section 4). The authors also simulated some arrays of dots and found that the band gaps of these structures are similar to that of isolated dots.
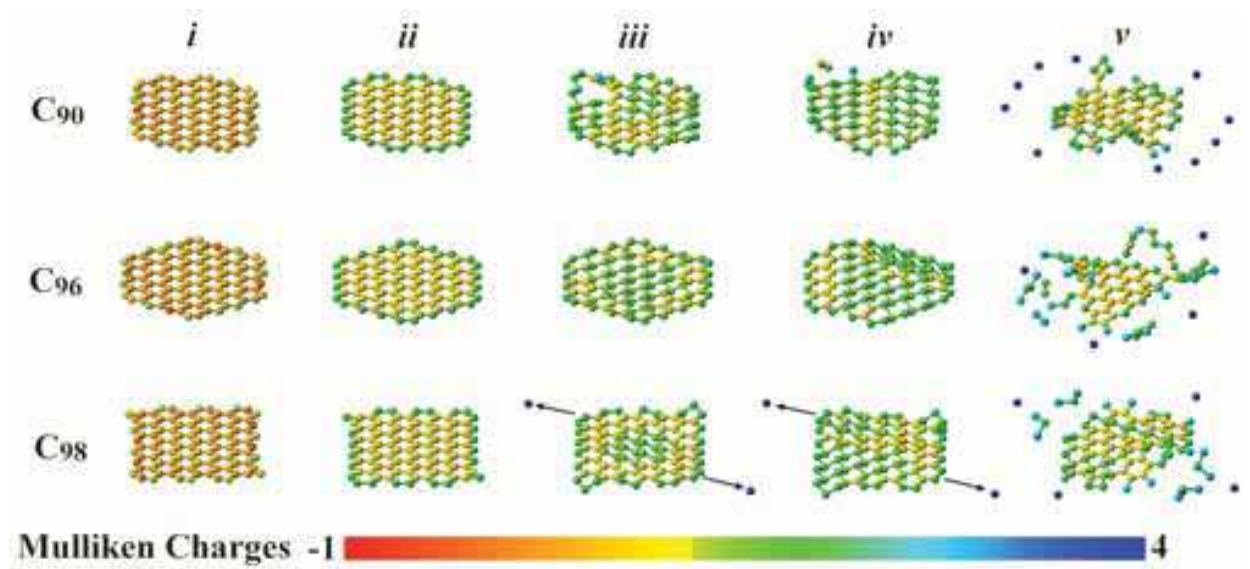
Mulliken Charges -1 ▮▮▮▮▮▮▮▮▮▮▮▮ **4**

Fig. 13. Structure and distribution of charges in C_{90} C_{96} and C_{98} anionic graphene nanoflakes at different stages of electron injection (Barnard & Snook, 2009).
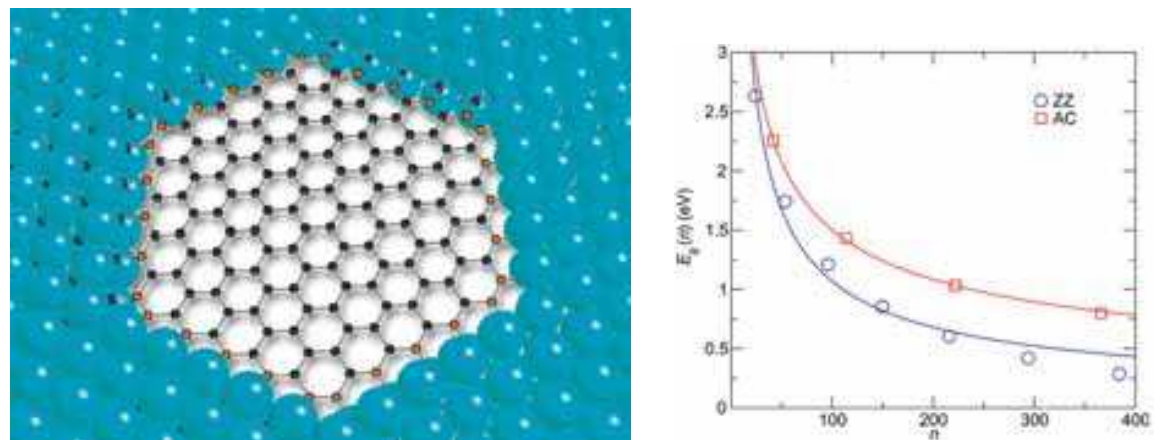

Fig. 14. Hexagonal GNF formed by removing atoms from a graphane sheet and the energy gap E_g as a function of the size of the GNF as a function of the size n (adapted from Singh et al, 2010).

6. Potential uses of graphene/graphane nanoflakes

Potential applications have been mentioned previously in this chapter particularly in section 4 but here we will review how some of these ideas have resulted in real device prototypes being made. Since GNFs may range in size from molecular to mesoscopic they have the potential to bridge the gap between molecular electronics and nano-electronics, and to integrate with existing technologies. Here we will give just two examples which will illustrate the extreme limits.

An example of the former class of devices is the use of coronenes to make a graphene field-effect transistor (FET) a "circuit diagram" of which is shown in figure 15. This device consists of a coronene molecule with wires to the source and drain electrodes consisting of linker molecules which behaved electrically as a FET and thus this is a molecular graphene transistor.
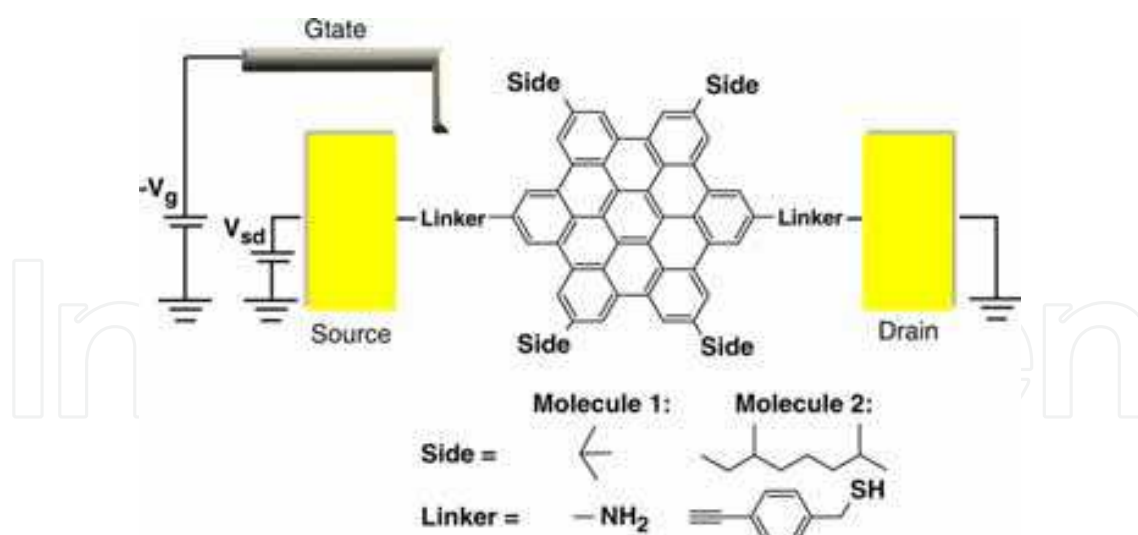
Fig. 15. Single HBC molecule FET (Diez-Perez et al., 2010).

At the other end of the size scale there has been considerable interest in building devices such as single electron transistors (Ponomarenko et al. 2008 and Stampfer et al., 2008). Figure 16 shows an SEM image and an artistic view of just such a transistor which was cut from GNRs to create a GQD by use of a combination of electron beam lithography and reactive plasma etching.
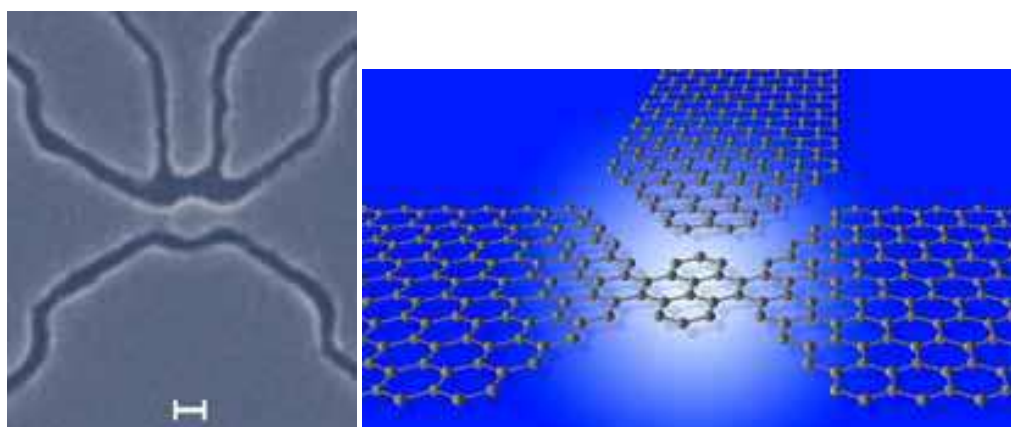

Fig. 16. An SEM image and an artistic impression of single electron transistor (Novoselov & Geim, http://www.condmat.physics.manchester.ac.uk/pictures/).

Currently the features of devices such as these are around 10 nm and so the GQD is quite large but it has been projected that dimensions should be able to be reduced to 1 nm in the future (Ponenmarkenov et al., 2008).

The work outlined above, and that of others (see for example Stampfer et al., 2008a and Stampfer et al., 2008b) shows that it is indeed possible to fabricate working electronic devices from graphene which contain GNFs and GQDs and this is set to become a growing area of research in the future.

7. Some other areas of future interest

Previous sections of this chapter have outlined what we belief have been the major areas of interest in GNFs up until the present and those that we believe will continue to be of major

interest in the future. However, there are several other areas which we feel deserve more attention in light of their potential for yielding new scientific discoveries and technological applications.

7.1 The role of GNFs in the synthesis of CNTs

CNTs continue to be of great importance particularly for many applications and occur in two forms (either semiconducting or metallic) which have quite different properties and uses. However, most syntheses produce a mixture of these different types of CNTs and it is very hard to separate them especially on the large scale needed for use in industrial applications. Recently it has been shown that GNFs may be directly converted to CNTs which involves GNFs containing between 60 and 100 atoms. This leads to the possibility of understanding at least one mechanism of formation of CNTs and it suggests that it may be possible to use this type of route to directly synthesis CNTs with specific chirality. This is potentially a very interesting area for increased activity combining scientific insight with practical applications.

7.2 The possible production of other nano-carbon flakes

The main thrust of research involving materials consisting of large aromatic carbon rings has been those where the rings are fused i.e. structures of the type shown in figures 1 and 2. However, the bottom-up methods which have been used to produce GNFs are also capable of producing nanoflakes of a different type.

For example it is already possible to combine small pieces of GNFs with various chemical groups (Wu et al., 2007; Zhi and Mullen, 2008) to produce interesting properties both similar and dissimilar to GNFs depending upon the mixing and configurations. An example might be to "hard-wire" together several different GNFs in much the same way that the single coronene molecule shown in figure 17 is hard-wired into a transistor circuit.

It may also be possible to make NFs of other aromatic molecules containing other atoms as well as carbon and from other planar systems containing no carbon atoms at all, such as boron nitride sheets. This could lead to even more interesting and versatile NF properties and applications.

7.3 Multiple layers and stacks of GNFs

In this review we have ignored few layered GNFs and large stacks of GNFs both of which have been the subject of theoretical and experimental interest. Such structures can have properties which differ from those of single GNFs, and of graphite nanocrystals, often in a beneficial way (Jackel et al., 2006; Abergel et al., 2010). An example of this is that bilayer GNDs have a different band gap than single layer GNDs and electrons in such structures may be confined with potential barriers in contrast to single layer GNFs (Abergel et al, 2010).

7.4 Optical properties

It has been shown experimentally that GMBs, graphene oxide and GNFs (Gokus, et al., 2009; Luo et al., 2009; Sun eta al., 2008; Loh, et al., 2010) have interesting optical properties when functionalized. This leads to the interesting possibility of developing graphenes with optical properties which may be tuned by changing the functional groups (Loh et al., 2010). Indeed it has been suggested that graphene composites may be used commercially for optical

applications such as saturable absorbers for laser applications before they are used for electronic ones. Thus it may well be a promising area to investigate the optical properties of GNFs both theoretically and experimentally. In fact it has already been shown theoretically that GNFs of different shapes can have a significant second hyperpolarizability which may be of use in non-linear optics applications (Nagai et al., 2010).

8. Conclusions

As we can see from the descriptions here, and throughout this book, graphene has already proved to be an extremely exciting new material which has many fascinating properties. Much of the research on graphene has been concerned with 2-D graphene (graphene membranes, GMBs) and 1-D graphene (graphene nanoribbons, GNRs), because of their interesting and potentially very useful properties have been relatively simple to isolate and address. Indeed it has already been shown that it is feasible to make working devices (albeit only at the laboratory level) using GMBs and GNRs for applications such as transistors, molecule detectors and flexible electrodes.

Less well studied is the 0-D form of graphene (graphene nanoflakes, GNFs or graphene nanodots, GNDs) which presents a greater degree of complexity, but offers a greater potential for flexibility and selectivity (both literally and figuratively). In this chapter we have attempted to show that GNFs share many useful features in common with these 2-D and 1-D forms of graphene, but also have unique additional properties such as interesting electronic and magnetic states and also many potential applications in electronics and detectors. Many of these additional features arise because GNFs may be engineered to form many more shapes than GMBs and GNRs and, as has been pointed out, GNFs can also span the dimensional scale from molecular to 2-D enabling potentially great versatility in many applications. A very promising area of future applications appears to lie in the area of spintronics and perhaps quantum computing as the magnetic properties of GNFs are not only comparable with those of GNRs which have previously been suggested for these applications but they may be manipulated and altered in a wide variety of ways.

Aside from the currently known features of GNFs, readers will undoubtedly be left with a range of questions. Far from being a failure, this serves to highlight that there is obviously great potential to further explore and exploit many of their properties, and so much more to be learned. The most obvious of these is their functional and optical properties which hold much promise for making optical devices.

Furthermore, GNFs also offer many challenges to refine existing scientific knowledge of their preparation and properties including, their improved synthesis and assembly by bottom-up and top-down methods, the refinement of confinement methods for GNDs and the exploration of their properties such as their vibrational spectra and magnetic behavior.

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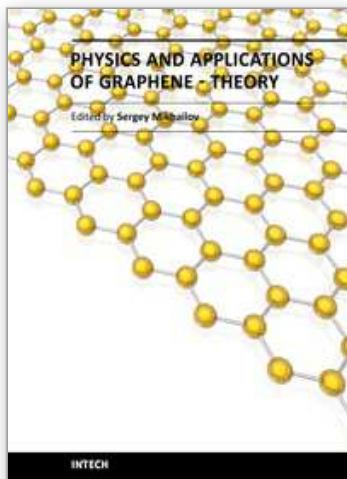
Physics and Applications of Graphene - Theory

Edited by Dr. Sergey Mikhailov

The Stone Age, the Bronze Age, the Iron Age... Every global epoch in the history of the mankind is characterized by materials used in it. In 2004 a new era in material science was opened: the era of graphene or, more generally, of two-dimensional materials. Graphene is the strongest and the most stretchable known material, it has the record thermal conductivity and the very high mobility of charge carriers. It demonstrates many interesting fundamental physical effects and promises a lot of applications, among which are conductive ink, terahertz transistors, ultrafast photodetectors and bendable touch screens. In 2010 Andre Geim and Konstantin Novoselov were awarded the Nobel Prize in Physics "for groundbreaking experiments regarding the two-dimensional material graphene". The two volumes Physics and Applications of Graphene - Experiments and Physics and Applications of Graphene - Theory contain a collection of research articles reporting on different aspects of experimental and theoretical studies of this new material.

How to reference

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Ian Snook and Amanda Barnard (2011). Graphene Nano-Flakes and Nano-Dots: Theory, Experiment and Applications, Physics and Applications of Graphene - Theory, Dr. Sergey Mikhailov (Ed.), ISBN: 978-953-307-152-7, InTech, Available from: http://www.intechopen.com/books/physics-and-applications-of-graphene-theory/graphene-nano-flakes-and-nano-dots-theory-experiment-and-applications

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