IOP Publishing Nanotechnology
Nanotechnology **20** (2009) 245607 (6pp) doi:10.1088/0957-4484/20/24/245607

Templated growth of graphenic materials

Nolan W Nicholas[1,2,7], **L Matthew Connors**[1], **Feng Ding**[3],
Boris I Yakobson[4], **Howard K Schmidt**[2,5] **and Robert H Hauge**[2,6]

[1] Department of Physics, Rice University, 6100 Main, Houston, TX, USA
[2] Richard E Smalley Institute for Nanoscale Science and Technology, Rice University, 6100 Main, Houston, TX, USA
[3] Institute of Textile and Clothing, Hong Kong Polytechnic University, Kowloon, Hong Kong
[4] Department of Mechanical Engineering and Materials Science, Rice University, 6100 Main, Houston, TX, USA
[5] Department of Chemical and Biomolecular Engineering, Rice University, 6100 Main, Houston, TX, USA
[6] Department of Chemistry, Rice University, 6100 Main, Houston, TX, USA

E-mail: nolan.nicholas@matricresearch.com

Received 6 March 2009, in final form 20 April 2009
Published 27 May 2009
Online at stacks.iop.org/Nano/20/245607

Abstract
A novel strategy is proposed for the topologically controlled synthesis of extended graphenic sheets by additively reacting carbon into a pre-existing graphene sheet which is on top of a templating substrate. This concept is implemented and demonstrated using chemical vapor deposition (CVD). Novel morphological features observed in this study suggest unusual aspects of the CVD growth process. CVD results demonstrate the basic soundness of the synthesis strategy but highlight the sensitivity of the process to certain types of disruption and the need for alternative forms of embodiment.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of carbon nanotubes the remarkable structural, thermal and electronic properties of graphenic lattice materials have become widely appreciated. Planar graphene has recently received a great deal of attention for potential use in a wide range of applications [1–3]. Planar graphene has many remarkable properties including extremely high sheet-strength and the largest diamagnetic response of any bulk room-temperature material [4], and has shown some indications of nanoscopically controllable ferromagnetism [5]. Graphene has attracted particular attention as being useful for high speed nanoelectronics applications and being potentially more easily integrated with existing microelectronics technology [6]. However, graphene suffers from a dearth of scalable sample preparation techniques. Commercially viable applications, particularly electronics, will require reliable large scale production of quality graphene; beyond the production capabilities of current technologies [7]. In graphenic lattice structures topology is critical to the physical properties of the structure. Electronic properties including metallicity [8], coherence length [9], and charge localization [10] are dictated by the topological characteristics of the graphene lattice.

Much of the experimental characterization of graphene has employed small graphene sheets extracted from larger graphite samples. Various methods have been used, such as rubbing planar graphite [11], lithographic etching with micromanipulation [12], and chemically solubilizing ‘platelets’ from graphite [13, 14]. This approach is also inherently size limited by the currently available graphite materials (generally 10 μ or smaller) [15] and provides no feasible route to precise topological control.

The most successful technique to date for producing graphene directly, and which has been widely used to study its promising electronic properties, has been the heteroepitaxial synthesis of graphene materials onto a 6H-SiC substrate by selective evaporation of silicon from the substrate so that the remaining excess carbon assembles into a graphene coating on the surface [16]. While this approach has demonstrated the potential for high quality electronics devices built from graphene, the inherent materials and UHV process limitations of this technique have led to the exploration of other techniques

---

[7] Author to whom any correspondence should be addressed. Present address: MATRIC Incorporated, 3200 Kanawha Turnpike, South Charleston, WV 25303, USA.

0957-4484/09/245607+06$30.00

for graphene synthesis for technological applications. Various other methods producing graphenic materials have been explored [17–22]; however, none of these methods is scalable to topologically controlled synthesis of graphenic materials on substrates suitable for technological applications. This provides significant motivation to better understand the basic physical mechanisms controling the growth of graphenic materials.

We propose and report here a new approach for synthesizing graphene structures. This method has been observed to grow sheets of graphene by additively reacting carbon molecules into a pre-existing graphene sheet resting on an inert templating substrate. It is shown that by reducing the degrees of freedom available to the system, graphenic materials with controlled topologies can be grown through simple CVD processes. Furthermore, this demonstration suggests that non-CVD methods may be utilized to synthesize graphenes with controlled topologies on various substrates.

2. Templated growth mechanism

Several factors contribute to the observed difficulty in synthesizing pristine graphene. Growing a sheet of graphene is essentially a process of epitaxy at a one-dimensional sheet edge to extend a two-dimensional planar lattice (in contrast to traditional epitaxy which occurs at a plane edge to form a three-dimensional lattice). This places particularly stringent requirements on the growth process. In order to create a single-crystal graphene lattice, nucleation of any other configuration must be suppressed; only additive growth of carbon atoms into the pre-existing graphene lattice will create arbitrarily large pristine graphene sheets.

Nucleation of new graphene lattices will tend to lead either to stacking of graphene sheets into bulk graphites or to co-planar graphene sheets and, ultimately, a polycrystalline material of orientationally mismatched graphene lattices. Such structures are commonly observed in CVD deposited graphites [23]. Incorporation of carbon feedstocks into graphitic lattice edges has been previously observed but has not been utilized to synthesize and extend graphenic lattices of controlled geometry [24].

Bond configuration defects can also disrupt the formation of pristine graphene lattices. Both sp1 and sp3 carbon bond structures can be formed and compete with the formation of a perfect hexagonal lattice of sp2 bonded carbon. Topological defects can also occur in completely sp2 bonded carbon lattices by the formation of pentagons or heptagons instead of hexagons. These factors dictate that defect structures at the graphene edge will dominate if the growth is rate limited by the reactivity of the graphene sheet edge. Once a defect has been enclosed in the lattice the activation energy and time required to anneal out the defect increases, so that enclosure around such a defect effectively seals it into the lattice.

These difficulties can be addressed by: (1) providing a template surface for growth; (2) delivering feedstock gas at a rate lower than the defect annealing rate; (3) suppressing the tendency of the system to nucleate extraneous carbonaceous materials—step-edge chemistry must dominate. While points 2 and 3 are typical of an epitaxial CVD process, the first point is unique to the two-dimensional lattice epitaxy required for topologically controlled synthesis of graphenic materials:

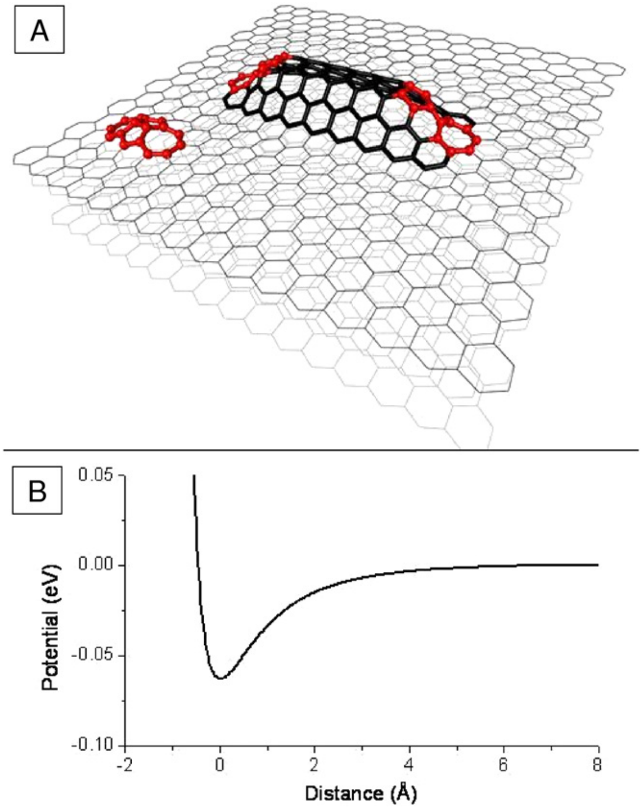

Figure 1. (A) The effects of templating are illustrated. A graphene lattice (shown in darker gray) rests on top of two lower graphene layers (shown in lighter gray) which act as a van der Waals template to the top layer. Solid features indicate extra atoms in the lattice as an linear edge dislocation and an added dimer. The edge dislocation has an associated energy cost of 16 eV and the added dimer has an energy cost of ∼4–5 eV with respect to an unstrained lattice. For the edge dislocation shown ∼13% of this is due to template interaction, for the added dimer only ∼4% of this energy is due to template interaction. These energies are calculated using the potential shown in (B). (B) The interaction of carbon atoms in this system was calculated using the Brenner [29] potential for intra-layer carbon atoms and with the Lennard-Jones (LJ) potential (parameter $\sigma = 0.337$ nm, $\varepsilon = 0.042\,038$ eV) for interlayer interactions.

(1) Templating surface: a non-reactive template such as a continuous sheet of graphene underlying the growing graphene layer applies a Lennard-Jones-like van der Waals potential [25] to the growing edge. This potential increases the energetic cost of all deviations from a pristine graphene sheet and geometrically reduces the space of favorable states available for growing materials to be included in the lattice. The non-reactive character of the substrate ensures that it does not stabilize non-sp2 bonds in the growing graphene. This idea is illustrated in figure 1. It is noteworthy that similar processes have previously been observed for various graphenic materials but have not been recognized as useful mechanisms in their own right [19, 26–28].

(2) Well-annealed carbon addition: carbon can be added to the graphene edge in a variety of different configurations. Furthermore, configurations not corresponding to the growth of pristine graphene are more kinetically reactive than those which do. Therefore if the carbon feedstock is supplied at a higher rate than defects can be annealed out of the edge [30] then growth will be dominated by reaction at defect sites forming a highly defective carbon lattice. This is accomplished through a combination of high graphene temperatures to speed annealing and low feedstock partial pressures. Etchants can also be selected to attack defects preferentially.

(3) Nucleation suppression: nucleation is suppressed by maintaining the system at a low sooting potential by keeping the feedstock at low partial pressures and low temperatures while maintaining the growing edge at high temperatures.

Together, these three elements provide a novel method suitable for the controlled growth of graphenic materials.

3. Experimental details

All experiments were performed on cleaved Highly ordered pyrolytic graphite (HOPG; Structure Probe Incorporated, SPI-1 grade) in a 1 inch diameter quartz tube furnace (Lindberg Blue) at temperatures from 800 to 1100 °C.

Hydrocarbon, alcohol and ketone species were provided as carbon feedstocks. Ethylene (Matheson Tri-Gas, Polymer Grade) was introduced through a standard gas flow controller. Alcohol (ethanol, 2-propanol and allyl alcohol) and ketone (acetone) species were drawn off as vapors from degassed liquid sources at low pressure; flow was regulated through a needle valve to maintain constant pressure (<150 mTorr) inside the furnace which was backed by a mechanical vacuum pump (Welch 1397, 500 $\mathrm{l\,min^{1}}$). Water was added to some tests with alcohol feedstocks to provide an etchant species in the growth environment; this was added by mixing water to the standard azeotropic composition for the alcohol followed by degassing the solution and evaporating off over half of the mixture at low pressure to achieve a steady state composition.

Graphene growth has been obtained using several classes of carbon feedstocks: hydrocarbon, alcohol and ketone species have all produced growth of graphene sheets. The best results have been obtained with ethanol. It is thought that the OH group carried by the ethanol reduces the sooting potential of the system and provides an etchant which reduces the tendency to grow defective material. Argon (Matheson Tri-Gas, UltraHigh Purity) was used as the diluent carrier gas for the feedstock. Trials were conducted in which nanopure water was included as an etchant in the system.

Grown materials were characterized by atomic force microscopy (AFM; Veeco Nanoscope IIIa). Figures depicted here are from AFM surface scans which measure the height of the grown material. All AFM characterization was performed in tapping mode using a silicon cantilever probe.

4. Results and discussion

This method has been observed to grow graphenic materials which are topologically templated over a graphite basal plane. Characterization of these results as growth features was confirmed by a series of before and after AFM observations of the same region which demonstrated that the features observed were the result of material addition rather than etching or other mechanisms. Both the extension of pre-existing graphenic sheets and the nucleation of new sheets has been observed, but the rate of nucleation has been maintained at very low levels (0.0015–0.0035 nucleations per square micrometer per minute on the free basal plane; edge driven nucleation can exhibit rates several orders of magnitude greater). A strong tendency toward higher quality graphene growth and fewer side products was observed with increasing temperature. Ethanol based feedstocks gave the best growth results; ethylene, 2-propanol and acetone also produced reasonable templated growth. Allyl alcohol based feedstocks (with and without water) produced only non-graphenic carbon features.

Ethanol feedstock partial pressures from 5 to 20 mTorr (0.1–0.3 mTorr background) have shown graphene sheet growth with low rates of nucleation. The process shows extreme sensitivity to low levels of contamination. Such contamination can be overwhelmed by using higher feedstock partial pressures with premixed etchant species (such as water) to dominate the reaction system; oxygen in particular is believed to be deleterious, possibly in relation to its ability to attack at non-step-edge sites in graphene and participate in non-hexagonal structures and out-of-plane bonding geometries [31]. Feedstocks containing water show graphenic growth at higher pressures but also show higher nucleation and may be prone to higher defect rates.

Graphene grown by this method shows several morphological features not observed in as-cleaved HOPG which help to elucidate the growth dynamics. In order to efficiently characterize the observations made, we introduce the following terminology: growth which extends a pre-existing step-edge outward without other superstructural feature is termed ‘sheet’ growth. Some growth conditions are observed to grow material which has a topographical roughness under AFM significantly greater than for as-cleaved HOPG, giving it a ‘crinkled’ appearance. In all cases of sheet growth, the number of graphenic layers in a sheet (as measured by AFM height profiles) was found to be the same as the number of layers in the step-edge from which it grew. Growth extending from a pre-existing edge will occasionally develop a spiral structure corresponding to growth around a screw dislocation. Growth of circular graphene structures which are not derived from a pre-existing graphene edge and which are single graphene layers in height (or occasionally double) has been observed; these are termed platelets. Structures resembling a circle with a wedge missing have been observed to form at growing edges, these are termed ‘Pacman’ morphologies. Non-graphenic carbon has also been observed to grow under certain conditions and is termed ‘nodular carbon’ due to the morphological shapes it takes.

Sheet growth is universally observed to grow rounded features from sharp corners in the pre-existing step-edge and

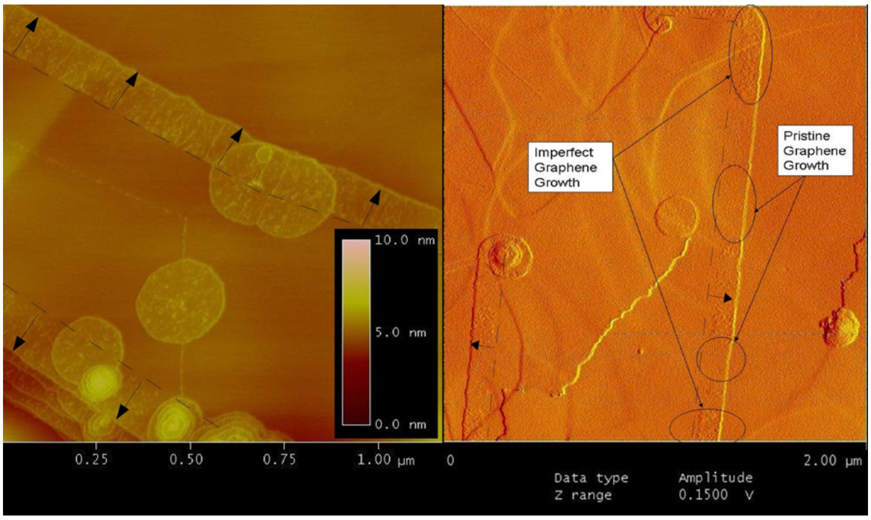

Figure 2. (A) Crinkled growth is seen extending from a pre-existing step-edge; the locations of the pre-existing step-edges are demarcated by dashed black lines and the direction of sheet growth is indicated by solid black arrows. Crinkled (imperfect) growth is clearly observed as a change in roughness of the surface relative to the native HOPG surface; the edges of this roughness clearly delineate sheet growths from the original HOPG material and allow measurement of linear growth. Platelet growth is also observed, notably all platelets formed at step-edge or other defect sites. This particularly highlights the competing processes of nucleation (which forms platelets), and sheet growth at step-edge sites. (B) Both crinkled and pristine growth are seen extending from the same step-edges as portions of the same sheet growth. The presence of both crinkled growth and pristine growth as different parts of the growth of the same sheet clearly demonstrates pristine growth but highlights the sensitivity of the conditions under which it is occurs.

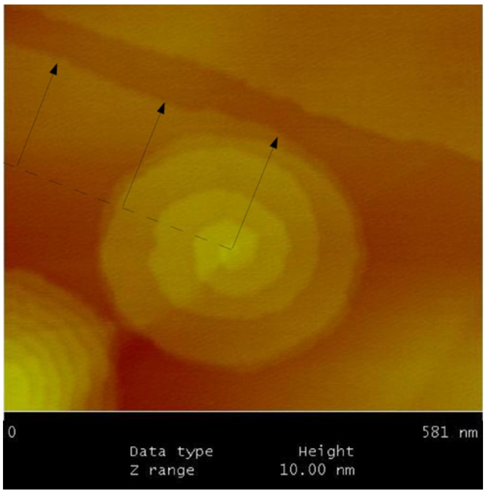

Figure 3. A spiral is observed in conjunction with pristine sheet growth.

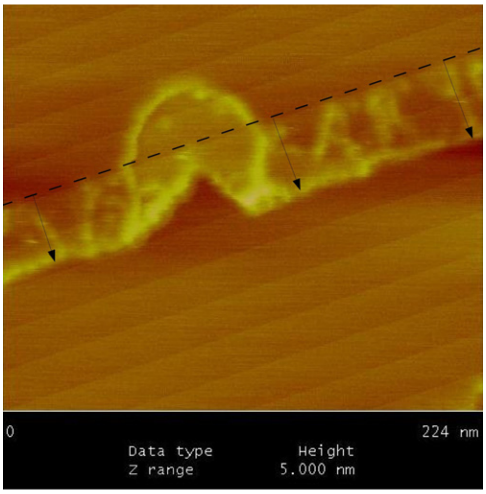

Figure 4. A Pacman structure is observed at a crinkled growth edge.

platelets universally form circular or nearly circular graphene sheets. These observations indicate that despite recent reports of the difference in crystallographic stability of various lattice edges [32, 33] this growth process shows very little selectivity of crystallographic axis under the growth conditions tested. Only in the growth of spirals have angular growth features been occasionally observed which may be indicative of some crystallographic selectivity.

Crinkled sheet growth is believed to be the result of the growth of graphene with a high density of structural defects, such as added dimers and edge dislocations, present in the sheet. Sheet defects of these types are illustrated in figure 1. These topological defects create strained regions in the lattice causing it to protrude upward (as it cannot protrude downward), as observed under AFM as seen in figure 2(A). However, the underlying template ensures that the growing material maintains an essentially planar morphology. These defects are observed to cluster in their formation, as indicated in figure 2(B) with crinkled and smooth regions forming spontaneously. It is known that topological defects exert mutual potentials within the lattice [34] but the exact physical basis for this clustering during growth remains unclear.

Growth of spiral morphologies is commonly observed, indicating the formation and growth of screw dislocations in the graphene lattice. A spiral growth structure is pictured in figure 3.

Pacman features, such as those seen in figure 4, are believed to be formed when a new sheet of graphene nucleates

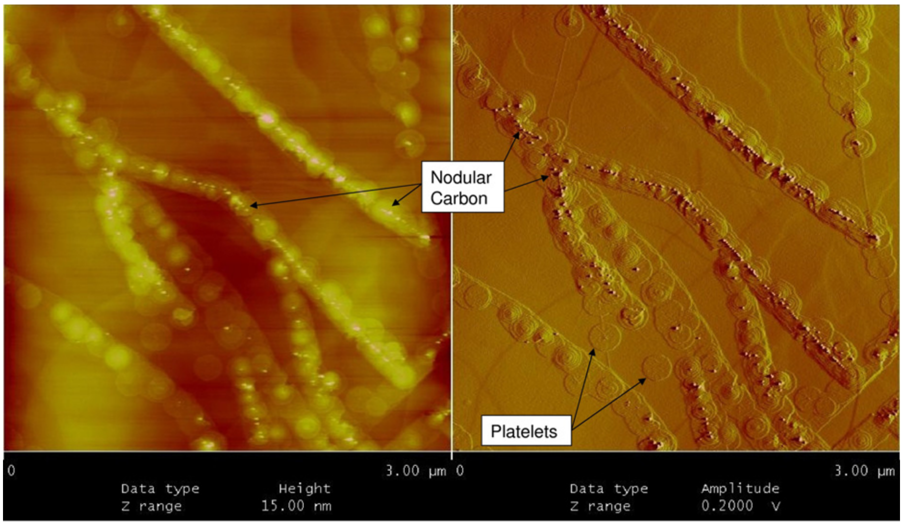

Figure 5. Nodular carbon is observed on top of many of the circular growth structures in this AFM image. Based on other observations it is likely that most of these structures show spiral morphologies which lead to the growth of nodular carbon in their centers due to the presence of a highly reactive site without the presence of an efficient templating geometry. However, the resolution of AFM images has so far been too low to observe this directly.

on top of a pre-existing sheet of graphene at a growing step-edge. When this occurs the growth can be retarded where the two step-edges are in contact and largely unaffected elsewhere. Therefore the nucleated sheet grows back away from the growing edge in a semicircular fashion just as it does during platelet growth, and the pre-existing edge not in contact with the nucleated layer grows linearly out unimpeded. However, the retardation of growth at the contact region leads to a wedge shaped region missing from the growth of both the platelet and the sheet graphene structures. The origin of this retardation is uncertain. Two mechanisms are immediately plausible: competition for carbon feedstock or lip–lip interactions between the edges which reduce the reactivity of the edges. Pacman features with various wedge angles have been observed, sometimes within a single sample; this may indicate that lip–lip interactions play some role in the retardation of the growing edge but further investigation will be required to fully elucidate this process.

Nodular carbon is typically observed to form at the tops of spirals and at features composed of many step-edges together; more rarely it can occur at a single step-edge or other structural defect. Presumably this morphology occurs when there are bond structures available to stabilize non-graphene growth of carbon and when pristine (without available bonds) substrates are not present to template the graphene growth. At multi-step features both of these conditions are met: there is no substrate present and lip–lip interactions [35–37] will allow for the stabilization of non-planar bonding configurations and lattice restructuring [38]. In figure 5 nodular carbon is observed at the tops of layered, circular growth structures.

Material grown from single step-edges or few step-edges together (up to four) tends to grow high quality planar material. In all cases the sheet growth is observed to retain the number of graphenic layers present at the original step-edge. The outgrowth of graphene layers from pre-existing step-edges has been conclusively observed in the alteration of the relative positions of step-edges before and after growth.

These initial observations suggest a number of directions by which this method could be extended. Lower temperature CVD conditions may be allowed through the judicial use of more reactive species [24]. It is coincidental that an edge of HOPG served as the nucleation site for the extended growth of graphene; graphene could also be grown by this same conceptual method using graphene seed sheets deposited on substrates other than HOPG which would support this type of growth. Highly inert substrates supporting van der Waals templating forces provide ideal candidates: inert ceramics or inherently planar materials like hexagonal boron nitride provide obvious choices. Furthermore, it should be recognized that the concept of templated growth naturally extends beyond the strictures of the gas-phase CVD process demonstrated here and could be applied to graphitic and polycyclic aromatic hydrocarbon-like syntheses in the liquid phase [39, 40] to grow extended graphene sheets onto substrates.

5. Conclusions

Graphene sheets have been grown over a template surface via CVD. These results demonstrate the validity of templated growth as a concept for graphenic synthesis while the unique morphologies developed by this process highlight the need to extend this concept to other materials to achieve technological application. The unique morphological features of this process are suggestive of the nature by which this growth occurs and the isotropic growth features observed indicates that this growth process is not strongly correlated to lattice direction.

Acknowledgments

This work was supported by US Department of Energy, Basic Energy Sciences, Division of Materials Science and Engineering under contract DE-AC05-00OR22725.

References

[1] Novoselov K S *et al* 2004 Electric field effect in atomically thin carbon films *Science* **306** 666–9

[2] Kane C 2005 Erasing electron mass *Nature* **438** 168–70

[3] Berger C *et al* 2006 Electronic confinement and coherence in patterned epitaxial graphene *Science* **312** 1191–6

[4] Flandrois S 2001 Magnetic properties of graphite and graphitic carbons *Graphite and Precursors* (*World of Carbon*) ed P Delhaes (Amsterdam: Gordon and Breach) pp 71–85

[5] Esquinazi P, Setzer A and Hoehne R 2002 Ferromagnetism in oriented graphite samples *Phys. Rev.* B **66** 024429

[6] Ball P 2004 Material witness: flat out C60 *Nat. Mater.* **5** 43

[7] Van Noorden R 2006 Moving towards a graphene world *Nature* **442** 228–9

[8] Mintmire J W, Dunlap B I and White C T 1992 Are fullerene tubules metallic? *Phys. Rev. Lett.* **68** 631–4

[9] Morpurgo A and Guinea F 2006 Intervalley scattering, long-range disorder, and effective time-reversal symmetry breaking in graphene *Phys. Rev. Lett.* **97** 196804

[10] Azevedo S, Furtado C and Moraes F 1998 Charge localization around disclinations in monolayer graphite *Phys. Status Solidi* b **207** 387–92

[11] Novoselov K S *et al* 2005 Two-dimensional atomic crystals *Proc. Natl Acad. Sci.* **102** 10451–3

[12] Lu X, Huang H, Nemchuk N and Ruoff R 1999 Patterning of highly oriented pyrolytic graphite by oxygen plasma etching *Appl. Phys. Lett.* **75** 193–5

[13] Si Y and Samulski E T 2008 Synthesis of water soluble graphene *Nano Lett.* **8** 1679–82

[14] Stankovich S, Piner R D, Chen X, Wu N, Nguyen S T and Ruoff R 2006 Stable aqueous dispersions of graphitic nanoplatelets via the reductionof exfoliated graphite oxide in the presence of poly(sodium4-styrenesulfonate) *J. Mater. Chem.* **1** 155–8

[15] Moore A W 1967 *Highly Oriented Pyrolitic Graphite* (*Chemistry and Physics of Carbon*) ed P L Walker (New York: Dekker) pp 69–176

[16] Berger C *et al* 2004 Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics *J. Phys. Chem.* B **108** 19912–6

[17] Wang J J *et al* 2004 Free-standing subnanometer graphite sheets *Appl. Phys. Lett.* **85** 1265–7

[18] Kastler M, Schmidt J, Pisula W, Sebastiani D and Muellen K 2006 From armchair to zigzag peripheries in nanographenes *J. Am. Chem. Soc.* **128** 9526–34

[19] Wellmann R, Bottcher A, Kappes M, Kohl U and Niehus H 2003 Growth of graphene layers on HOPG via exposure to methyl radicals *Surf. Sci.* **542** 81–93

[20] Nagashima A, Tejima N, Kawai T and Oshima C 1995 Electronic dispersion relations of monolayer hexagonal boron nitride formed on the Ni(111 surface) *Phys. Rev.* B **51** 4606

[21] Nakhmanson M S and Smirnov V P 1972 *Sov. Phys.—Solid State* **13** 2763 in Russian

[22] Malesevic A *et al* 2008 Synthesis of few-layer graphene via microwave plasma-enhanced chemical vapour deposition *Nanotechnology* **19** 305604

[23] Obraztov A, Obraztova E A, Tyurnina A V and Zolotukhin A A 2007 Chemical vapor deposition of thin graphite films of nanometer thickness *Carbon* **45** 2017–21

[24] Lee S Y, Kwak J H, Han G Y, Lee T J and Yoon K J 2008 Characterization of active sites for methane decomposition on carbon black through acetylene chemisorption *Carbon* **46** 342–8

[25] Girifalco L A, Hodak M and Lee R S 2000 Carbon nanotubes, ropes, buckyballs and a universal graphitic potential *Phys. Rev.* B **62** 13104–10

[26] Charlier J C and Iijima S 2001 *Growth Mechanisms of Carbon Nanotubes Carbon Nanotubes* (*Topics Applied Physics*) ed M Dresselhaus, G Dresselhaus and P Avouris (Berlin: Springer) pp 55–81

[27] Iijima S, Ajayan P and Ichihashi T 1992 Growth model for carbon nanotubes *Phys. Rev. Lett.* **69** 3100–3

[28] Louchev O and Sato Y 1999 Nanotube self-organization: formation by step-flow growth *Appl. Phys. Lett.* **74** 194–6

[29] Brenner D W 1990 Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films *Phys. Rev.* B **42** 9458–71

[30] Frenklach M and Ping J 2004 On the role of surface migration in the growth and structure of graphene layers *Carbon* **42** 1209–12

[31] Ajayan P and Yakobson B 2006 Material science: oxygen breaks into carbon world *Nature* **441** 818–9

[32] Girit C *et al* 2009 Graphene at the edge: stability and dynamics *Science* **323** 1705–8

[33] Jia X, Hofmann M, Meunier V, Sumpter B G, Campos-Delgado J and Romo-Herrera J M 2009 Controlled formation of sharp zigzag and armchair edges in graphitic nanoribbons *Science* **323** 1701–5

[34] Zhang X, Jiao K, Sharma P and Yakobson B I 2006 An atomistic andnon-classical continuum field theoretic perspective of elasticinteractions between defects (force dipoles) of various symmetries andapplication to graphene *J. Mech. Phys. Solids* **54** 2304–29

[35] Guo T, Nikolaev P, Rinzler A G, Tomanek D, Colbert D T and Smalley R E 1995 Self-assembly of tubular fullerenes *J. Phys. Chem.* **99** 10694–7

[36] Nardelli M B, Roland C and Bernholc J 1998 Theoretical bounds for multiwalled carbon nanotube growth *Chem. Phys. Lett.* **296** 471–6

[37] Choi Y, Park K A, Kim C and Lee Y H 2004 Oxygen gas-induced lip–lip interactions on a double-walled carbon nanotube edge *J. Am. Chem. Soc.* **126** 9433–8

[38] Rotkin S and Gogotsi Y 2002 Analysis of non-planar graphitic structures: from arched edge planes of graphite crystals to nanotubes *Mater. Res. Innov.* **5** 191–200

[39] Xiao Y *et al* 2006 Flower-like carbon materials prepared via a simple solvothermal route *Carbon* **44** 1589–91

[40] Weiss K, Beernink G, Dötz F, Birkner A, Müllen K and Wöll C H 1999 Template-mediated synthesis of polycyclic aromatic hydrocarbons: cyclodehydrogenation and planarization of a hexaphenylbenzene derivative at a copper surface *Angew. Chem. Int. Edn* **38** 3748–52