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**Ecole Doctorale**  
**3MPL**  
**Matière, Molécules, Matériaux**  
**en Pays de la Loire**

**Mémoire pour l'obtention de  
L'Habilitation à Diriger des Recherches**

Ecole doctoral 3MPL  
Matière, Molécules, Matériaux en Pays de la Loire

**Présenté par Christopher Ewels**

16 Février 2011

*“Computer Modelling of defects in carbon nanomaterials”*

**Composition du Jury**

Prof. Christian Colliex	LPS Orsay UMR8502	President du Jury
Prof. Malcolm Heggie	Sussex University	Rapporteur
Prof. Serge Lefrant	IMN Nantes UMR6502	Rapporteur
Prof. Kazu Suenaga	AIST, Tsukuba, Japan	Membre du Jury
Dr. Marc Monthioux	CEMES Toulouse UPR8011	Membre du Jury
Prof. Olivier Chauvet	IMN Nantes UMR6502	Membre du Jury
Dr. Jean-Luc Duvail	IMN Nantes UMR6502	Membre du Jury

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## Acknowledgements

It is difficult to write acknowledgements for a thesis which is intended to represent a snapshot of over fifteen years of work. Thus while I mention some names here I am very aware that there are many others who are not listed. Hopefully you know who you are!

Firstly I must thank all of my co-workers whom I've had the pleasure to work with. I've had that rare pleasure of a job which I wake up in the morning looking forward to, and for this I have you all to thank.

The results in this thesis do not represent my individual research but are collective work with my colleagues. In particular I must thank Malcolm Heggie for his guidance and insight on graphite defects (and getting me working on carbon in the first place amongst other things), and Irene Suarez for all the fun we had working together on metals, oxidation and making videos. Greg for sharing my passion for fullerenes (and being directly responsible for my first ever academic presentation with a hang over), and Bob Jones for his whole approach to life and science which has coloured my career from my first day as a PhD student in his group. It seems to me that my best collaborations start with friendship first, and science naturally follows: examples of that include but are certainly not limited to Carla Bittencourt, Denis Arçon, Kazu Suenaga, Nicole Grobert, Alberto Zobelli and Jean-Luc Duvail.

Special thanks are also due to Patrick (also Sven and Mark) for their great work developing and maintaining AIMPRO, the power house behind most of the results produced here.

Also to the friends I've worked with on science communication, notably Gill Watson but also Harry Kroto, Susana Trasobares, Irene, Xavier Rocquefelte and the others.

Those people who have provided guidance and help at critical stages of my career, particularly Christian Colliex, Alexandre Gloter and Odile Stephan, Olivier Chauvet and Serge Lefrant, but also many others.

I would also like to thank everyone in the IMN, and particularly within the PMN group, for making me so welcome since the arrival of the 'grand Breton' at the lab a few years ago. Thanks also to the HDR committee (and particularly the rapporteurs) for the time they have freely given to supporting, reading and examining this thesis.

Finally no acknowledgement is complete without thanks to my wife Flo and children Anna and Martin, who make all the rest of it worthwhile.

## Introduction

This thesis tracks a period of immense change for computational materials science. When I was working on my PhD in 1997, a calculation of a single point defect in a cluster of ~70 InP atoms took over 3 weeks on the most powerful machines we had in the laboratory. As I write this, I can run the same calculation in two or three hours on this desktop machine that I'm using as a word processor. Although examples like this are quoted frequently, the importance of this increase in calculationary power in just over a decade cannot be overstated.

The discipline of computational materials science has evolved into a completely different beast during this time, and continues to evolve. During my PhD we were barely able to run systems large enough to accurately model small individual point defects. Now we are able to turn our hand to entirely different problems – point defect interaction, clustering and aggregation, complex surface science problems, and extended defects such as dislocations in bulk materials. Extra levels of complexity can be added to the calculations to vastly improve precision and predictive capability. Temperature and time become accessible variables which could previously only be handled in very qualitative terms. Computational materials science is now a new discipline in its own right, sitting somewhere between traditional ‘pencil and paper’ theorists and experimental researchers.

This thesis explores some of the research breakthroughs made as a result of these changes. The importance of defect metastability and diffusion is shown, as well as interactions between point and line defects. These are not minor modifications to existing understanding; in many cases they rewrite the textbook on defect behaviour.

It is now possible for computation to make useful contributions to highly applied projects such as metal-nanotube gas sensors as described in Section 4; during the time period covered by this thesis we have seen computational modelling shift from being an unusual luxury in research grant applications into a necessary partner.

Throughout my research career I have looked at defects in materials. The Oxford English dictionary has multiple definitions of the term “defect”. The scientific sense of the term is given as ‘a discontinuity in the lattice of a crystal caused by missing or extra atoms or ions, or by dislocations’. However the word is also defined as ‘a shortcoming, fault, or imperfection : a lack or want, especially of something essential to perfection or completeness; deficiency’. It is a term with unavoidably negative connotations, and in a world sometimes obsessed with perfection it is maybe not obvious why anyone would find this an attractive area of study.

The behaviour of materials, like people, is often dominated by their defects. Defects are what make materials interesting, and despite the negative connotations of the word, defects can result in many of the most useful properties of any given material. In many cases, such as doped silicon, it is the defects which define its usefulness. So I hope therefore this thesis serves as a celebration of defects, imperfections, deformities and blemishes, and I will try to show that, at least in the field of carbon nanomaterials, there is an impeccable future for defects.

## Section 1 : Le Dossier Scientifique

### ***Curriculum Vitae : Christopher Ewels***

Date de naissance : 18 juin 1971 (Age 39)

Lieu de naissance : Harlow, Essex, UK

Nationalité : Anglais

Situation : Chercheur CNRS CR1 (Section 05) (Depuis 1/10/2005)

Adresse : Institut des Matériaux Jean Rouxel (CNRS UMR6502)

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44322 Nantes

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E-mail : chris.ewels@cnrs-imn.fr

**Refereed Publications to date :** 68

**Total Publications to date :** 97 (average of >9/year 2008-2010)

**Chapitres de Livres :** 6

**H-Factor :** 19 (total citations 1201)

#### **Autres responsabilités :**

Directeur, « Vega Science Trust » ([www.vega.org.uk](http://www.vega.org.uk)) (depuis mars 2006)

Vice-chair, reseau Europeen COST MP0901, « NanoTP » (2010-2014)

Membre de comité British Carbon Group

Membre de comité GDR-I ‘GNT Graphene Nanotubes’

Membre PhantomsNet ICT-Net steering committee for European graphene Roadmap (2011)

Membre editorial advisory board, “Materials Today” (2011)

Consultant communication de la science (ex : EU, CNRS)

#### **Autres expériences professionnelles :**

*(9.2003-6.2005) Bourse Européen Marie Curie Individuelle*

*Laboratoire de Physique des Solides, Groupe Christian Colliex, Université Paris Sud, Orsay*

Exploration des nouvelles nanostructures de carbone en couplant modélisation et spectroscopie de perte d'énergie des électrons : Etude des défauts intrinsèques, des défauts d'irradiation dans le graphite et les nanotubes, du dopage et de la fonctionnalisation chimique des nanotubes, des fullerènes et des nanostructures d'oxyde (dioxyde de titane).

*(9.2002-8.2003) Postdoctorant TMR, ONERA, Département des Matériaux Composites, Châtillon*

Synthèse de nouveaux matériaux composites à base de résine époxyde et de nanotubes de carbone. Tests mécaniques (micro durcissement, tension, etc.), extrusion, microscopies optique et électronique.

*(10.97-9.2002, 2 jours/semaine) CPES, Université de Sussex, UK*

Modélisation par ordinateur de matériaux à base de carbone (diamant, graphite, nanotubes, fullerènes). Défauts créés par irradiation dans le graphite, rôle des impuretés dans les matériaux, et dislocations.

*(5.99-9.2002, 3 jours/semaine) The Vega Science Trust <http://www.vega.org.uk/>*

Fondation créée par Sir Harry Kroto NL pour promouvoir les sciences dans les media. Participation au développement d'une chaîne scientifique diffusée par Internet, recherche pour les émissions télévisées (sur la BBC), production, relations publiques. Nommé dans les génériques de 12 émissions télévisées.

*(9.93-8.97) Doctorat, Statut de « Research Assistant », Dépt. Physique, Université d'Exeter*

Modélisation par ordinateur des impuretés et défauts dans les semi-conducteurs (surtout silicium).

*(10.89-7.93) Maîtrise, BA Hons 2:1, Matériaux et Métallurgie, Keble College, Oxford University*

**Prix, distinctions:****Prix**

Prix	<b>UE Prix d'Excellence de Marie Curie (2006)</b>
	Fonds International Wernaers pour diffusion des connaissances (EU projet nano <sup>2</sup> hybrids) 2008
Prix	CineGlobe Public Award for best science documentary (2010)
Joint Winner	2008 Open Laboratory Science Blog Awards
Finalist	2008 Foresight Institute Feynman Prize for theory.
Fellowship	Marie Curie Individual Fellowship, EU 5th Framework (2003-2005).
Fellowship	EPSRC Advanced Research Fellowship for young researchers (2005). (choisi poste CNRS)

**Current Contrats / financements**

Nanosim_graphene	ANR P'NANO (1/2010-1/2014) « <i>Simulation des Nano-matériaux et Nano-dispositifs à base Graphène : Approches multi-échelles</i> » <a href="http://www.nanosimgraphene.org">www.nanosimgraphene.org</a> Includes 1 PhD, 1 postdoc (15 months) + equipment My role: Participant in the theory workpackage WG1. IMN representative. Coordinator for project communication
NanoTP	EU COST Network (10/2009 – 10/2012) “ <i>Designing novel materials for nanodevices: From Theory to Practise</i> ”  My role: Project vice-chairman, management of theory section and project communication. Network of 150+ research groups across Europe (25 countries), examining nanoscale interfaces, notably carbon-metallic interfaces but extending later to consider also nanoscale oxide interfaces. From atomic scale modelling (incorporating new tool development), through spectroscopy and synthesis, to practical application.
SPRINT	ANR Blanche (1/2011 -1/2014) “ <i>Towards Selective Photo-induced Reactivity of Individual single walled Carbon NanoTubes</i> ” Includes 2 postdocs (1 with me, 12 months) My role: IMN representative, Theory WP leader
Nanormade	ANR Franco-Taiwan (1/2009-1/2012) « <i>Matériaux organiques nanostructurés pour la fabrication de diodes électroluminescentes</i> ” My role : Implication 20%, participant, Head of Theory workpackage

**Previously:**

Nano <sup>2</sup> hybrids	EU FP6 STREP 033311 (10/2006-3/2010) « <i>Interface design of metal nanocluster-carbon nanotube hybrids via control of structural and chemical defects in a plasma discharge</i> » <a href="http://www.nano2hybrids.net">www.nano2hybrids.net</a>
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My role: Workpackage Leader (Communication)  
 Theory Workpackage Member  
 Included 1 postdoc (36 months)

Proteus PHC « Proteus », Franco-Slovenian (2009-2010)  
 « *Système 1D de molécules magnétiques* »  
 My Role : Principal Investigator

Tournesol PHC “Tournesol”, Franco-Belgian (2009-2010)  
 « *Nanotube patterning via fluorine self-organisation for emulsions and high-end composites* »  
 My Role : Principal Investigator

Marie Curie Individuelle Fellowship, LPS Orsay (2003-2005)

EPSRC Fellowship (3 ans, annulé, j’ai pris le poste CNRS)

### **Principales collaborations (current) hors laboratoire IMN**

Malcolm Heggie Theoretical Chemistry, Sussex University, Brighton, UK  
*DFT Modelling of point and line defects in graphite*

Gregory Van Lier VUB Brussels, Belgium  
*“Gaussian” modelling of fluorination of carbons, fullerenes*

Alberto Zobelli,  
 Alexander Gloter LPS, Batiment 510, Orsay, Paris  
*STEM Microscopy of individual nanoobjects*

Kazu Suenaga AIST, Tsukuba, Japan  
*Electron microscopy of point defects in nanoscale carbons*  
 Visit to Japan for 2 months (2006)

Carla Bittencourt MateriaNova, Mons, Belgium  
*Plasma treatment of carbon nanomaterials*

Alexandr Okotrub Nikolaev Institute of Inorganic Chemistry RAS, Novosibirsk  
 Lyuba Bulusheva *Experimental and theoretical halogen treatment of C and BN*

Vojislav Krstic CRANN, Trinity College Dublin, Ireland  
*Experimental transport studies of individual nanoobjects*

Denis Arçon Josef Stephan Institut, Ljubljana, Slovenia  
 Polona Umek *Synthesis and EPR of nanoscale oxides*

Nicole Grobert Materials Science Department, Oxford University, Oxford  
*Synthesis of doped carbon nanotubes*

Nikos Tagmatarchis Chemistry, National Hellenic Research Foundation, Athens  
*Chemical functionalisation of fullerenes, nanotubes, nanocones*

Sven Öberg	Luleå Institute of Technology, Luleå, Sweden <i>Computer modelling of large defective nanosystems</i>
Gill Watson	Vega Science Trust, Brighton, UK <i>Science Communication strategies</i>

Other collaborators over the last fifteen years include Marc Monthoux, Marianne Glerup, Raul Arenal, Harry Kroto, Sylvain Latil, Alexis Vlandas, Odile Stephan, Susana Trasobares, Wahab Aallaf, Tiberiu Minea, Brigitte Bouchet-Fabre, Patrick Briddon, Jon Goss, Bob Jones, ... (apologies to those whose names I've accidentally forgotten!)

### **Conference Organisation**

NanoteC	Annual International carbon nanoscience conference First run in 1998, now in its 12th year (to be held in Nantes) Co-organiser annually with M. Heggie, G. Van Lier, N. Grobert
GraphITA 2011	European workshop on graphene (200 attendees), L'Aquila Italy May 2011, Scientific advisory committee
ICAMM 2010	International conference on advanced materials modelling July 2010, Nantes, France (130 attendees) Organising committee
NanoTP	Scientific Kick-Off meeting (100 attendees), Berlin March 2010, Co-Organiser
AIMPRO'08	International Workshop on DFT modelling December 2008, Nantes, France (40 attendees) Organiser
JNB2	National meeting, nanosciences in Brittany region Nantes, 120 participants, 2008 Member of local organising committee
ICAN09	International conference, Brazil, September 2009 Member of International advisory board.
Carbon	International Carbon Conference (~700 attendees) Aberdeen, Scotland, June 2006 Member of organising committee
EDS-2000	International conference on extended defects in semiconductors Brighton, 2000, Co-Organiser
Oxygen'96	International NATO conference on oxygen defects in Si, Exeter, June 1996, Co-Organiser

Also on advisory boards for JSI'2010 and various others.

## ***Animation et management de la recherche***

### Dans l'IMN / Nantes

1. *Communication Manager for the PMN Group.*

Organise group presentations, internal communication (publicity material for the group, contact point for journalists, etc)

2. *European representative/contact point for the IMN laboratory.*

Promote awareness of European funding and training possibilities within the lab.

3. *Committee Member, CCIPL (Centre de Calculs Intensif Pays de la Loire).*

Recently involved with procurement of a 200k€ supercomputer for the region.

### En Europe

1. Vice-chairman of COST network “NanoTP”.
2. Trustee (director) of the Vega Science Trust ([www.vega.org.uk](http://www.vega.org.uk)).
3. Committee Member of the British Carbon Group (2004- ).
4. Committee Member international GDR-I Graphene-Nanotubes
5. Member PhantomsNet ICT-NET committee for European graphene roadmap
6. Advisory Board Member for “Materials Today” journal (2011)

### ***Travaux d'expertise***

1. I am director of the Vega Science Trust ([www.vega.org.uk](http://www.vega.org.uk)), a science broadcast charity.
2. C’NAM touring exhibition “50 years of the transistor”, scientific expertise. (2008)
3. Expert advisory board for the EU Science and Society project “Nanologue” (2007)
4. Presented at EU meetings on science communication and training policy
5. Presentation and round table on science communication at CNRS ENCRE meeting.
6. Project reviewer for ANR, American NSF, also for journals (typically two or three per month) such as Physical Review, Carbon, ACS Nano, ...

### ***Science Communication***

Science communication is something I very much enjoy. While at Sussex University I took a partial career break from research for four years, working 1-2 days/week on research and the remaining 3-4 days/week for the science communication charity “The Vega Science Trust”. It became clear it was necessary to choose between the two, and while I chose to return to full-time science research I have nonetheless remained very active in science communication.

I feel strongly that it is important that we communicate our science with both the general public, and policy makers, and are able to engage them in active dialogue on the importance of scientific knowledge and understanding for the future of our society.

### ***Scientific Video and the Internet***

I am currently a trustee (director) of the Vega Science Trust ([www.vega.org.uk](http://www.vega.org.uk)). Vega is a charity established in the UK by the Nobel Laureate Sir Harry Kroto to provide a platform for scientists to communicate through science video, both on TV and the Internet. While it only has a small staff (two when I was there, now one full-time), Vega continues to produce programmes and innovative science outreach projects, and I am actively involved in future development of Vega, fundraising, project design and implementation. While working for Vega I developed Europe’s first ever online science video channel, with science videos streaming for free from the Vega website in 1998 when such things were almost unknown. I helped with programme development for joint projects with the BBC, and was involved in



recording (e.g. sound recordist for many archive recordings of Nobel prize winners). I created, promoted and organised the “Vega Science TV Awards” to promote high quality science in broadcasting, and we successfully lobbied for a “Science Night” on the BBC.



While at the IMN I was science communication workpackage leader for the EU nano<sup>2</sup>hybrids project, and designed and implemented its groundbreaking and award winning communication strategy. With guidance and training from an ex-BBC producer, we filmed video

diaries for the project website and YouTube throughout the project, in order to show the public how ‘real’ science projects work and provide a way for the public to become involved in a research project. We aimed to break some of the stereotypes of scientists, ideally present science as an interesting career choice, and try to transmit the excitement of genuine scientific discovery. The project won the 2008 Fonds International Wernaers prize for science communication and its videos have been watched nearly 300,000 times on [YouTube](#). One of our videos [“nanocheese”](#) (using cheese to explain the importance of surface area in nanoscience) won the CineGlobe 2009 public prize for best science documentary, and has been shown on the Roland Garros projection screens in Paris. The videos have been used by schools and universities for teaching, and received widespread coverage in amongst others: Nature blogs, New Scientist, Der Spiegel, Le Point, ...

### **Scientific Images**

I produce carbon nanoscience related artwork which is available in a gallery on my website. It has been exhibited at Florida State Art Gallery and is used regularly to illustrate nanotechnology articles in newspapers, journals and TV programmes around the world. (e.g. CNRS Editions, EU brochures, the Discovery Channel, Time Magazine...).

### **Schools and the General Public**

In 2008 with Philippe Deniard we began a successful annual visit for “La Perverie” lycée, with lectures, hands-on practical workshops for the students, and follow-up discussion (~35 students / visit). I also participate in [Passeport Recherche](#), as well as helping TIPE and TPE student projects.



I was also involved in the design of innovative schools outreach project [ES4FUN](#) at Cadiz University, Spain (including a visit to Cadiz, and a joint unsuccessful EU project proposal). The project used aerial photography combined with organisation of school-children to generate ‘life-sized’ simulations of atomic structures and processes. The project is ongoing and further events linking science and moving/visual arts are underway.

I participate actively each year in “Fête de la Science”, both for laboratory visits, and in the “Square des sciences” in the centre of Nantes, and developed with Xavier Rocquefelte a set of interactive webpages for the general public on our [laboratory website](#).

### **Expertise and Lecturing**

I have given invited talks and attended expert advisory meetings at the EU concerning science communication, and was an invited speaker on science communication at ENCRE, an event organised for new entrants to the CNRS. I have given public talks on nanotechnology and attended “Café Scientifique” on nanotechnology at the FNAC, Nantes. In 2006 I visited Panama where I gave two public lectures on nanotechnology.

## Section 2 : Activité d'encadrement

Since 1999 I have tutored or co-tutored 4 MR1 students, 5 MR2 (or equivalent) students, 4 PhD students, and 2 postdoctoral students (see details below). All of the completed MR2, PhD and postdoctoral students have peer-reviewed publications based on their work (the majority as first authors), and the majority have presented their work at national and international meetings. All the students have either gone on to take PhDs, become industry scientists, or academic lecturers, *i.e.* have continued their careers in science.

### Details of PhD Student Projects

#### Abu Yaya, IMN, Dec 2008-

*“Weak interactions in carbon nanosystems”*

Abu Yaya Sulley is in his third year of a PhD funded jointly by the CNRS and the region Pays de la Loire, via a BDI bursary. He studies weak interactions in carbon nanosystems, such as physisorption and hydrogen bonding between carbon nanotubes and neighbouring species ( $\text{Br}_2$  gas, conjugated polymers such as PPV, ...) Although his “directeur de these” is currently Professor Serge Lefrant the intention is to switch to me on obtention of my HDR.

#### Philipp Wagner, IMN, May 2010-

*“Modelling defects and their interaction in graphene”*

Philipp Wagner is in the first year of a PhD studying defects in graphene, funded by ANR nanosim\_graphene. Again, although his “directeur de these” is currently Professor Bernard Humbert, the intention is to switch to me on obtention of my HDR.

#### Nicolas Rousseau, IMN, Oct 2010-

*“Optimisation de l’architecture du réseau  $\text{TiO}_2$  pour le développement de cellules photovoltaïques de IIIème génération (MiBs)”*

I am a co-supervisor of Nicolas (along with Christophe) concerning modelling of –OH functional groups on nanooxide surfaces, coupling with Raman studies by Bernard Humbert (their other co-supervisor). The majority of their work will be within the CESES group.

#### Alberto Zobelli, LPS Orsay, 2005-Oct 2007

*“Electron beam generation and structure of defects in carbon and boron nitride nanotubes”*

Alberto Zobelli’s PhD was sponsored under a European contract and so he was officially based on three sites: LPS Orsay (where the majority of the work was performed), Dresden theoretical physics department (where he spent one year), and Uppsala, Sweden. His day to day supervision and project design was unofficially largely split between myself for the theoretical modelling and Alexander Gloter for the experimental microscopy (official supervisors were C. Colliex and G. Seifert). The project was a mixture of theoretical and experimental microscopy work studying defect formation under electron and ion irradiation in BN and C nanomaterials. Further details of the project are given elsewhere in this thesis.

#### Ahla El Barbary, Sussex, 2003-2005

*“First principles characterisation of defects in irradiated graphitic materials”*

Ahla El Barbary was a PhD student funded by British Energy to investigate point defect formation in nanoscale carbons using DFT calculations. She was supervised by Prof. Malcolm Heggie but I performed a significant co-tutoring role during her studies. Ahla’s work covered fundamental studies of intrinsic point defect centres in graphite (notably the isolated vacancy) with extensive simulation of experimental data such as STM and HRTEM images, and EELS spectra.

## Summary of Supervision Work with Postdocs, PhD and Masters Students

Nom	Niveau	Taux d'Encadrement	Dates	Laboratoire	Articles co-authored	Situation Actuelle	Titre du Projet
<b>Victor Lenader</b>	<b>Postdoc</b>	<b>50%</b>	<b>2011-</b>	<b>IMN</b>			<b>« Study of individual nanotubes by modelling and spectroscopy »</b>
<b>Vika Ivanovskaja</b>	<b>Postdoc</b>	<b>100%</b>	<b>2011-</b>	<b>IMN</b>			<b>« Defect behaviour in graphene »</b>
Irene Suarez-Martinez	Postdoc	100%	2007 - 2009	IMN	16 + 2 chapters	Research Fellowship Australie	<b>« Metallic nanoparticles on carbon nanotubes »</b>
Simon Scarle	Postdoc	~25%	2002-2003	Sussex	3	Research Assistant, UK	“Monte Carlo modelling of hydrogen in silicon”,
<b>Philipp Wagner</b>	<b>PhD</b>	<b>60%*</b>	<b>May 2010 -</b>	<b>IMN</b>	<b>5</b>		<b>“Modelling defects and their interaction in graphene”</b>
<b>Abu Yaya</b>	<b>PhD</b>	<b>60%*</b>	<b>Dec 2008 -</b>	<b>IMN</b>	<b>3</b>		<b>“Weak interactions in carbon nanosystems”</b>
<b>Nicolas Rousseau</b>	<b>PhD</b>	<b>30%</b>	<b>Oct 2011 -</b>	<b>IMN</b>			“Optimisation de l'architecture du réseau TiO <sub>2</sub> pour le développement de cellules photovoltaïques de 3 <sup>ème</sup> génération (MiBs)”
Alberto Zobelli	PhD	~50%	2005-Oct 2007	LPS Orsay	4	MdC, LPS Orsay	“Electron beam generation and structure of defects in carbon and boron nitride nanotubes”
Ahlam El Barbary	PhD	~25%	-Fev 2005	Sussex	4 + 1 chapter	Lecturer, Cairo Uni	“First principles characterisation of defects in irradiated graphitic materials”
Natalia Martsinovich	PhD	~10%	-Sep 2004	Sussex	4	Kings College, London	“Theory of defects arising from hydrogen in silicon and diamond”
<b>Lavin Ayazpour</b>	<b>MR2</b>	<b>50%</b>	<b>Fev-Juin 2011</b>	<b>IMN</b>			<b>“Ni nanoparticle interaction with carbon nanotubes using ionic liquid solvents”</b>

## Section 2 : Activité d'encadrement

## HDR Dr Chris Ewels

Amand Pateau	MR2	100%	Fev-Juin 2010	IMN In preparation	Sep 2010	Started PhD	<i>"Ripple effects in graphene ribbon edges"</i>
Vincent Guiot	MR2	100%	Fev-Juin 2008	IMN 2	Following a PhD		<i>"Molecular Magnets encapsulated in carbon nanotubes"</i>
Philippe Wagner	MR2	100%	Fev-Juin 2008	IMN 2 (see above)	Following a PhD		<i>"Effect of charging and bundling on nanotube radial breathing modes"</i>
Hussam El Cheikh	MR2	100%	Fev-Juin 2007	IMN 1	Following a PhD		<i>"Oxidation of heterofullerenes"</i>
Simona Leoni	MR2	~20%	1999	Sussex 1	Scientist in Industry		<i>"First principles computer modelling of effects of Ge and H on dislocations in Si"</i>
Brice Giraudet	MR1 Physique	100%	Avril-Juin 2010	IMN	Repeating MR1 year		<i>"Etude des défauts d'azote dans les nanotubes de carbone"</i>
Alexandre Garreau	MR1 Physique	100%	Avril-Juin 2009	IMN	PhD started Oct 2011		<i>"Etude de structure de dioxyde de titane par modélisation : Théorie de Fonction de Densité (DFT)"</i>
Julien Morin	MR1 Chimie	100%	Fev-Juin 2009	IMN	PhD started Oct 2011		<i>"Physical and Electronic structure of carbon nanoscrolls"</i>
François-Xavier Michaux	MR1 Physique	~80%	Fev-Juil 2004	LPS Orsay			<i>"Structure and bonding of TiO<sub>2</sub> based nanomaterials"</i>

**Bold** indicates currently working with me or completed this month.  
 \* : Intended to change to 100% should I receive my HDR.

## Awards for students working with me

<i>Abu Yaya (PhD)</i>	Poster prize, JSI'2010 (2010) Poster prize, Cargèse carbon summer school (2009)
<i>Irene Suarez-Martinez (post-doc)</i>	Oral presentation prize, JNB2, Nantes (2008) Poster presentation prize, NT'08, Montpellier (2008)
<i>Alberto Zobelli (PhD)</i>	Finalist, Foresight Institute Feynman Prize for theory (2008)
<i>Vincent Guiot (MR2)</i>	Best masters project in West France (2008) from the West France section of 'SF2M'

## Autres Activités d'Enseignement

### IMN Nantes

- 2010 Masters C'NANO, TP 'structure électronique' (20 heures)  
 2010 Ecole Doctorale, 'Modélisation pour les expérimentateurs, part 1', (4.5 heures)  
 2010 Ecole Doctorale, 'Modélisation pour les expérimentateurs, part 2', (10 heures)  
 2010 Masters C'NANO, TP 'structure électronique' (4 heures)  
 2009 Masters C'NANO, TP 'structure électronique' (16 heures)  
 2009 Ecole Doctorale, 'Modélisation pour les expérimentateurs, part 1', (4.5 heures)  
 2009 Ecole Doctorale, 'Modélisation pour les expérimentateurs, part 2', (20 heures)  
 2009 Masters C'NANO, TP 'structure électronique' (20 heures)  
 2008 Masters C'NANO, TP 'structure électronique' (4 heures)

### LPS Orsay

- 2007 Masters Nanoscience (Sussex University) given at Orsay, 'STM/AFM' (16 heures)  
 2006 Masters Nanoscience (Sussex University) given at Orsay, 'STM/AFM' (16 heures)

### ONERA Chatillon, Paris

- 2003 Cours en nanophysique en français (2 heures)  
 2002 Cours en nanophysique en français (2 heures)

### Sussex University, UK

- 2001 Problems classes in materials chemistry (4 hours)  
 2001 Tutorat en chimie de matériaux (4 heures)  
 1997 Practical classes in scientific computing (15 hours)  
 1997 Tutorat en informatique scientifique (15 heures)  
 1997 Introductory scientific computing for PhD students

### Exeter University, UK

- 1996 Problems classes in condensed matter physics (30 hours)  
 1996 Tutorat en matériaux condensés (30 heures)

## Jury de Thèse

1. *Chef de jury de thèse+rapporiteur* Mariam Ahmed, Newcastle University (2011)
2. *Rapporteur* Radouane Leghrib, URV Tarragona, Spain (2010)
3. *Rapporteur* Ngoc Nguyen Bich, ENSICAEN, CIMAP, Caen (2009)
4. *Membre de jury de thèse* Elie El Khoury, Ecole Centrale Nantes (2009)
5. *Chef de jury de thèse+rapporiteur* Richard Eyre, Newcastle University (2008)
6. *Membre de jury* Alberto Zobelli, LPS Orsay (2008)
7. *Chef de jury de these+rapporiteur* Mike Wardle, Newcastle University (2007)

## Section 3 : Research Career Summary

The following is a short summary of my previous research. To keep the size of the thesis manageable I have then followed by a more detailed description of just a few specific areas, focussing on topics I have worked on since arriving at the IMN.

### ***Early Work***

My PhD work concerned theoretical density functional (DFT) atomistic modelling of the behaviour of point defects in silicon, notably oxygen related electrically active defect centres<sup>1</sup>. I proposed a new model for shallow thermal donor defects based on NO<sub>2</sub> and CHO<sub>2</sub> cores, which has now become the standard model. These defects demonstrate a new mechanism for generating shallow donor levels involving electrostatic compression of an unbonded Si p-orbital by surrounding oxygen interstitials<sup>2</sup>. At Sussex University I extended this work to look at dislocations and dislocation-defect interaction, notably explaining hydrogen enhanced dislocation glide in terms of hydrogen catalysed kink formation<sup>3</sup>, and helped with the development of a Monte Carlo dislocation simulation to model hydrogen incorporation and interaction with dislocations. In addition I studied hydrogenated dipole formation, work which points towards possible mechanisms for the industrially important “Smart Cut™” process. At the same time I studied point and line defects in diamond, often drawing parallels and differences with similar defect species in silicon. This includes a possible sp<sup>2</sup>-based graphitic core structure for diamond dislocations which may play a role in generating the brown coloration in synthetic diamonds<sup>4</sup>.

### ***1. Intrinsic defects in carbon***

#### **Key Collaborations**

Prof. Malcolm Heggie, Sussex University  
 Prof. Kazu Suenaga, AIST, Tsukuba  
 Prof. Uschi Bangert, Manchester University  
 Prof. Sven Öberg, Luleå, Sweden  
 Dr Alberto Zobelli, LPS, Univ. Paris Sud

#### **Grants and Funding**

British Energy funding (Sussex)  
 AIST funded exchange (2 months Tsukuba)  
 JSPS student exchange 2011 for Ph. Wagner

My work in nanotechnology stems originally from calculations on nuclear graphites, which led to a wider interest in atomic-scale processes in carbon. While at Sussex I worked with Professor Heggie and developed several fundamental new principles concerning graphitic carbon behaviour, notably resolving the long standing question of Wigner energy storage in irradiated graphite. Wigner energy release was the cause of the Windscale nuclear fire in the 1950s, and although annealing techniques now allow safe energy release the fundamental processes of energy storage in graphites were still unexplained. I showed that surprisingly, vacancy and interstitial pairs do not automatically recombine but pass through a metastable intermediate state, where the interstitial carbon atom is trapped at the lip of the vacancy. The barrier to recombination corresponds to the 200°C energy release peak seen in irradiated graphites<sup>5</sup>. This result has profound implications for irradiated graphite behaviour, and may also have parallels in other materials.

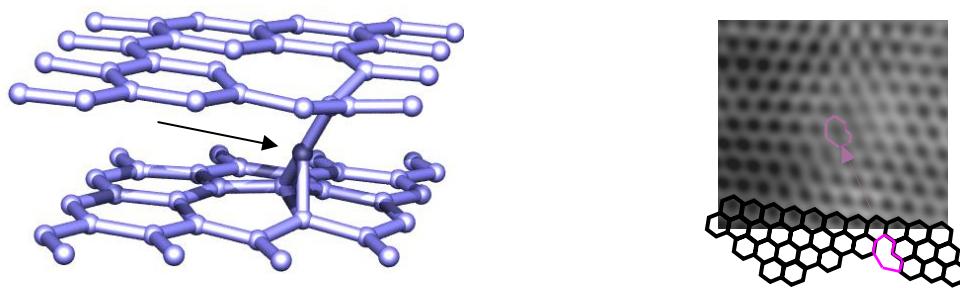
<sup>1</sup> Note that the references given here are clickable and take you to the relevant webpage.

<sup>2</sup> [C. P. Ewels, R. Jones, S. Oberg et al, Phys. Rev. Lett. 77 \(5\) 865 \(1996\)](#).

<sup>3</sup> [C. P. Ewels, S. Leoni, M. I. Heggie, et al, Phys. Rev. Lett. 84 \(4\) 690 \(2000\)](#).

<sup>4</sup> [C. P. Ewels, N. Wilson, M. Heggie, R. Jones, P. Briddon, J Phys Cond Matt 13 \(40\) 8965 \(2001\)](#).

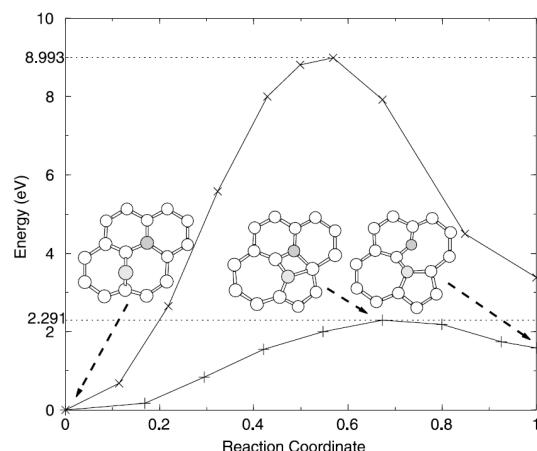
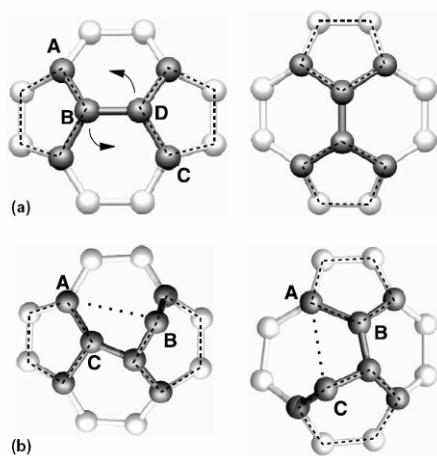
<sup>5</sup> [C. P. Ewels, R. H. Telling, A. A. El-Barbary, M. I. Heggie, P. R. Briddon, Phys. Rev. Lett. 91 025505 \(2003\)](#).



(left) The metastable interstitial-vacancy pair (arrow indicates the interstitial atom, vacancy sits above it) that can store energy in irradiated graphite. (right) Shuffle dislocation core seen in graphene confirming my prediction for vacancy dissociation under applied stress.

My understanding of the complexities of carbon bonding led me to propose, counter to intuition, that vacancy pairs could form bridging links between neighbouring graphite planes. This led to studies showing that many intrinsic defects in graphite and carbon nanotubes can form bridging defects of this kind. This acts to pin the defects, and plays a defining role in the mechanical, thermal and electronic properties of the host material. The work was published in *Nature Materials*<sup>6</sup> and has led to a surge of interest in using irradiation to strengthen nanotube based materials (113 citations).

Understanding of mechanical deformation of carbon nanosystems was further enhanced through my work on catalysed mechanisms for bond rotations in graphitic networks. These rotations control plastic in-plane deformation of graphite and nanotubes, and occur in fullerene and nanotube growth. Conventional models show high activation barriers corresponding to unphysical temperature regimes. I discovered a new mechanism, whereby an additional carbon atom can catalyse these rotations, leading to barriers over four times lower<sup>7</sup>. This has a major effect on in-plane yield strength, and is extremely important in explaining why only certain fullerene isomers are observed. It may yet prove key to explaining current work on nanotube and fullerene coalescence under irradiation.



Reaction mechanism for (a) uncatalysed carbon bond rotation on the surface of  $C_{60}$  and (b) my catalysed process<sup>7</sup>. Graph shows activation barriers for equivalent processes in graphite.

<sup>6</sup> R. H. Telling, C. P. Ewels, A. A. El-Barbary, M. I. Heggie, *Nature Materials* **2** 333 (2003).

<sup>7</sup> C. P. Ewels, M. I. Heggie, P. R. Briddon, *Chem. Phys. Lett.* **351** (3-4), 178 (2002).

We have since developed these ideas further and found other important metastable defect states, such as vacancy pairs which are stabilised at 3<sup>rd</sup> neighbour spacing through rehybridisation of the intervening carbon atoms. While not the most stable di-vacancy configuration they may nonetheless be the dominant vacancy species in irradiation damaged graphite over a range of temperatures<sup>8</sup>, and I suspect that metastable defect complexes play a far more critical role in carbon physics than previously realised. For example in 2010 I predicted the separation of vacancies into dislocation pairs under applied stress, leading to plasticity, and this has just been confirmed experimentally in graphene by Uschi Bangert using the Manchester ultra-STEM<sup>9</sup>.

In 2006 I spent two months visiting the group of Prof. Kazu Suenaga at the AIST, Tsukuba, Japan, in order to use their ultra-high resolution TEM equipment to search for intrinsic point defects in nanotubes. This has established an ongoing collaboration, and one of my PhD students has applied for a 2011 JSPS fellowship to visit them.

## **2. Chemical functionalisation of carbon**

### **Key Collaborations**

Dr G. Van Lier, VUB Brussels  
 Prof. A. Okotrob, L. Bulusheva, RAS Novosibirsk  
 Prof. J. -C. Charlier, LLN, Belgium  
 Dr. E. Flahaut, CEMES Toulouse  
 Dr. S. Latil, CEA Saclay

### **Grants and Funding**

PHC-EGIDE Tournesol (2009-2010)  
 Unfunded partner in 2011 Russian-French PICS  
 Support through COST network NanoTP

I have further explored my interest in fullerene isomers through a strong ongoing collaboration developed with Dr Van Lier at the VUB in Belgium. I have written a meta-code, SACHA,<sup>10</sup> which automates the process of exploring functionalised carbon isomers, allowing automatic detection and following of complex functional group addition pathways. This reduces by many orders of magnitude the complexity of problems such as the structural determination of stable chemically functionalised isomers.

Using SACHA I was able for the first time to derive the complete range of fluorination pathways from C<sub>60</sub> to C<sub>60</sub>F<sub>54</sub>, identifying all the major experimentally observed isomers and correcting some assumptions in the literature concerning their formation<sup>11</sup>. We have since applied it to other problems such as fullerene oxidation<sup>12</sup> and nanotube growth<sup>10</sup>. Notably I recently used it to show that metallic endofullerene chemistry differs from that of the parent host fullerene molecule. We compared chlorination of C<sub>70</sub> with that of K@C<sub>70</sub>, finding different stable ‘magic number’ isomers and functionalisation behaviour.<sup>13</sup> We hope this work will serve to launch a new exciting field of endofullerene chemistry.

<sup>8</sup> C. P. Ewels, M. I. Heggie, A. Zobelli, A. El-Barbary, P. R. Briddon, in preparation (2011)

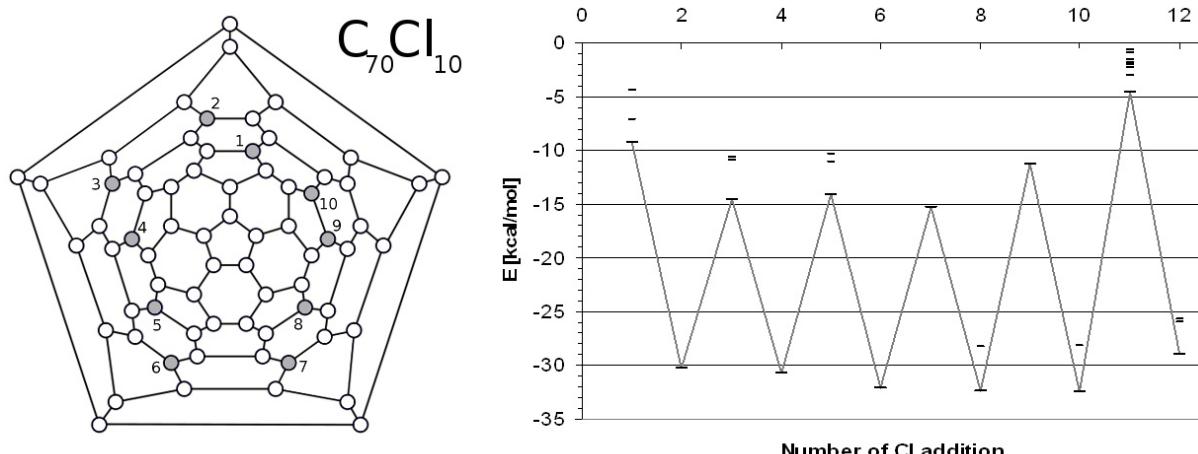
<sup>9</sup> C. P. Ewels, C. D. Latham, M. I. Heggie, U. Bangert, in preparation (2011)

<sup>10</sup> [C. P. Ewels, G. Van Lier, P. Geerlings, J. -C. Charlier, J. Chem. Inf. Model., 47 \(6\), 2208-2215 \(2007\).](#)

<sup>11</sup> [G. Van Lier, M. Cases, C. Ewels, R. Taylor, P. Geerlings, J. Org. Chem., 70, 1565-1579 \(2005\).](#)

<sup>12</sup> [G. Van Lier, C. P. Ewels, M. Cases-Amat, I. Suarez, P. Geerlings, J. Nanosci. Nanotech. 9, 6113-6119 \(2009\)](#)

<sup>13</sup> A. Vlandas, C. P. Ewels, G. Van Lier, JACS Submitted (2011)



Schlegel plot of the chlorine addition sequence to C<sub>70</sub> up to C<sub>70</sub>Cl<sub>10</sub> calculated with SACHA. The graph shows the binding energy of the most stable isomers for each addition step. The horizontal markers indicate other isomers within a 0.2 eV cut off energy. The low stability of n=11 addition explains the stability of C<sub>70</sub>Cl<sub>10</sub>. While n<11 are regioselective additions, n=11 has several isomer in a narrow energy range.

The detailed understanding of chemical functionalisation behaviour I have developed with fullerenes gives fresh insight into the surface chemistry of carbon nanotubes. Of particular interest is the fluorination of carbon nanotubes which changes their solubility and reactivity, and we have proposed, may serve as a route to nanotube separation and new behaviour for nanotubes at immiscible interfaces. With Dr Van Lier and Prof. Charlier I showed that fluorine spontaneously forms different surface patterns on carbon nanotubes depending on functionalisation conditions<sup>14</sup>, and we have recently confirmed this with new calculations coupled with experimental studies proposed and coordinated by myself and Dr Van Lier and performed in Russia<sup>15</sup>.

The direction of my research has also been influenced by the possibility for good collaboration within the Institute. For example, in collaboration with Dr Jean-Luc Duvail, Prof. Eric Faulques and others at the IMN we are starting to look at non-covalent functionalisation of carbon nanomaterials, and I have a PhD student in his third year on this subject. We have initially started with bromination of graphite, finding that a polar Br<sub>2</sub> transition state known for centuries by chemists is actually stabilised on graphene, potentially allowing its study for the first time.<sup>16</sup> We are now examining the interaction of conjugated polymers such as PPV with nanotubes and graphene.

### 3. Chemical light-element doping of carbon

#### Key Collaborations

Dr. V. Krstic, CRANN, Trinity College, Dublin  
 Dr. O. Stephan, LPS, Univ. Paris Sud  
 Dr. M. Glerup, Oslo University  
 Dr. T. Minea, LPGP, Univ. Paris Sud  
 Dr. B. Bouchet Fabre, CEA Saclay  
 Prof. Sir Harry Kroto NL, Florida State University

Dr. N. Tagmatarchis, Athens

Prof. D. Arcon and group, JSI, Ljubljana, Slovenia  
 Dr N. Grobert, Materials Dept, Oxford University

#### Grants and Funding

ANR P'NANO NANOSIM\_GRAPHENE (2010-13)  
 Marie Curie Individual Fellowship (2003-2005)

Besides post-growth functionalisation, another way to modify the behaviour of carbon nanomaterials is through the introduction of heteroatoms into the structure, the analogue of chemical doping of bulk materials. Of particular interest is nitrogen doping due to its relative

<sup>14</sup> C. P. Ewels, G. Van Lier, J. -C. Charlier, M. I. Heggie, P. R. Briddon, Phys. Rev. Lett., 96 216103 (2006).

<sup>15</sup> L. Bulusheva, Yu. Fedoseeva, A. Okotrub, E. Flahaut, I. Asanov, V. Koroteev, A. Yaya, C. P. Ewels, A. Chuvilin, A. Felten, G. Van Lier, D. Vyalikh, Chem. Mater. 22 (14), 4197 (2010)

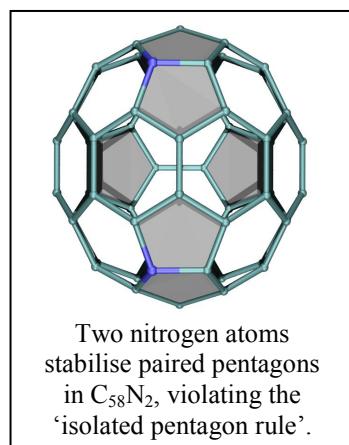
<sup>16</sup> A. Yaya, C. Ewels, et al, Phys. Rev. B, accepted (2011)

ease of introduction to fullerenes, nanotubes and graphene. In 2005 I co-authored a popular invited review on this subject<sup>17</sup>.

I have taken the approach of first studying nitrogen and phosphorus behaviour in fullerenes (primarily C<sub>60</sub>) and then transferred the knowledge to understand dopant behaviour in more complex nanotube systems. This has been performed with many experimental collaborative groups across France and Europe (listed above) and has been piloted by me.

There are a number of “traps” concerning doping of carbon nanomaterials which previous studies did not identify. One of these often found in the literature was that nitrogen doped fullerenes (azafullerenes) retain the same overall structure as their undoped counterparts. However I showed that nitrogen doping violates the isolated pentagon rule (first proposed by Kroto in the 1980s), stabilising lower symmetry fullerene isomers featuring paired pentagons (published in Nano Letters<sup>18</sup>). Multiple azafullerenes can cross-link and rebond in different arrangements depending on temperature, as evidenced through thermal ESR studies of crystalline C<sub>59</sub>HN, which were explained by my calculations (published in Chem. Commun.)<sup>19</sup>.

I have now extended this work to doping of carbon nanotubes (two book chapters and multiple articles). There is also a common literature assumption that higher nitrogen dopants in carbon materials will result in increased *n*-type doping due to the additional valence electron on each nitrogen atom. My calculations show this is not necessarily the case, since while substitutional nitrogen acts as a donor, nitrogen-vacancy complexes act as electron acceptors, and co-doping between these two species will result in charge compensation<sup>20</sup>. It is thus important to examine closely the chemical environment of the dopant atoms.



There has also been an assumption of similar dopant behaviour between phosphorus and nitrogen as they lie in the same chemical period.<sup>21</sup> We investigated heterofullerene oxidation, showing that while oxygen bonds to azafullerenes in much the same way as pristine fullerenes (primarily epoxide bonding with some annulene structures), phosphorus-doped fullerenes form phosphene-oxides, converting the doped fullerenes from donors to acceptors (a ‘hot paper’ in PCCP)<sup>22</sup>. We have recently had an article accepted concerning analogous phosphorus doped carbon nanotubes.<sup>23</sup> Steps in temperature dependent transport measurements of individual phosphorus doped nanotubes correspond to coupling between localised spins on the low density of defect sites. The doping behaviour is exactly explained via my calculations which predict substitutional high temperature doping followed by oxidation upon opening the furnace resulting in *p*-type substitutional P=O centres in the nanotube wall.

Collaborations with CEA Saclay and Oxford University Materials Science Department are underway to complete the characterisation of nitrogen doping in carbon nanotubes (notably their ability to detect gases).

<sup>17</sup> C. P. Ewels, M. Glerup, J. Nanosci. Nanotech. 5, 9, 1345 (2005).

<sup>18</sup> C. P. Ewels, Nano Letters 6 (5), 890 (2006), writeup in Nature Blogs

<sup>19</sup> D. Arcon, M. Pregelj, P. Cevc, G. Pagona, N. Tagmatarchis, C. P. Ewels, Chem. Commun. 3386 (2007)

<sup>20</sup> C. P. Ewels, Ph. Wagner, in preparation (2011)

<sup>21</sup> See for example I. O. Maciel, J. Campos-Delgado *et al*, Nano Letters 9 (6), 2267 (2009)

<sup>22</sup> C. P. Ewels, H. El Cheikh, I. Suarez-Martinez, G. Van Lier, Phys. Chem. Chem. Phys. 16, 2145 (2008)

<sup>23</sup> V. Krstic, C. P. Ewels, O. Stéphan, *et al*, ACS Nano, 4 (9), 5081 (2010).

#### 4. Controlled irradiation damage of carbon

##### Key Collaboration

Drs. A. Zobelli, A. Gloter, LPS, Univ-Paris Sud

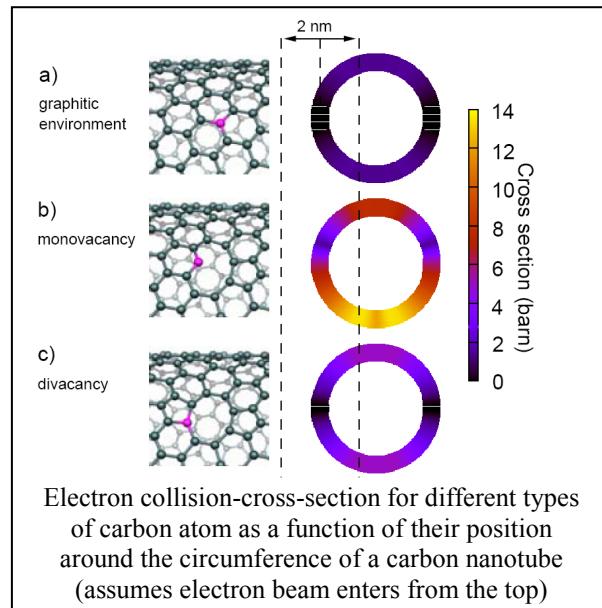
##### Awards and Funding

Finalists 2008 Foresight Institute Feynman Prize for theory  
Marie Curie Individual Fellowship (2003-2005)

The aim in this work was to precisely determine the absorption cross-section for different species and atomic environments from our calculations, and use this data to calibrate and control the electron beam in a scanning transmission electron microscope. This would allow image scanning with either no damage, or *controlled local* damage: for example ideally introducing single vacancies in specifically chosen locations in an individual nanotube. This allows use of the electron beam less as a microscopy / spectroscopy tool and more as an atomic scale top-down ‘carving’ tool for nanomaterials.

Using DFTB molecular dynamics simulations we derived full knock-on cross-sections for C and BN nanotubes<sup>24</sup>, as a function of the atom position within the tube wall, incoming electron energy, atom species, and also atom environment. Notably we showed that atoms neighbouring pre-existing defects have knock-on cross-sections an order of magnitude higher than those in pristine tubes, *i.e.* electron irradiation damage will tend to accumulate in regions of pre-existing damage. This was confirmed through a series of images of damaged tubes showing the formation of extended linear defects in BN nanotubes through atom knock-out (dislocation climb),<sup>25</sup> and we were able to produce controlled ‘notches’ (indentations) along BN nanotube walls at pre-defined locations, consisting of up to 3 primary vacancies and several tens of secondary neighbouring vacancies only<sup>26</sup>.

The work was in collaboration with the group of Christian Colliex, LPS Univ-Paris Sud, and formed the PhD of Alberto Zobelli (I was a co-encadrant, for the theoretical part of the study). While at the LPS on a Marie-Curie Individual Fellowship, I established the theoretical modelling section of the electron microscopy group, buying and installing a computing cluster, training Alberto Zobelli (now Maître de Conférences in modelling within the same group) and starting theory-experimental collaborations with other group members. The irradiation work was completed while I was in Nantes. Myself, Alberto Zobelli and Alexandre Gloter were finalists for this work for the **2008 Foresight Institute Feynman Prize for theory**.<sup>27</sup>



<sup>24</sup> A. Zobelli, A. Gloter, C. P. Ewels, G. Seifert, C. Colliex, Phys. Rev. B, **75**, 245402 (2007).

<sup>25</sup> A. Zobelli, C. P. Ewels, A. Gloter, G. Seifert, O. Stephan, S. Csillag, C. Colliex, Nano Lett. **6** (9), 1955 (2006)

<sup>26</sup> A. Zobelli, A. Gloter, C. P. Ewels, C. Colliex, Phys. Rev. B **77**, 045410 (2008).

<sup>27</sup> <http://www.foresight.org/about/2008Feynman.html>

## 5. Metal / Oxide interaction with Carbon

### Key Collaborations

Prof. J.-J. Pireaux, FUNDP, Namur (coordinator)  
 Prof. F. Reniers, ULB, Brussels  
 Dr. J. Guillot, CRPGL, Luxembourg  
 Prof. J.-C. Charlier, PCPM, Louvain-La-Neuve  
 Dr. E. Llobet, URV, Tarragona

Dr. Carla Bittencourt, Materianova, U. Mons  
 Marc Delgado, Sensotran, s.l., Barcelona  
 Gill Watson, Vega Science Trust  
 Ed Goldwyn, Goldwyn Productions

### Grants and Funding

FP6 STREP “nano<sup>2</sup>hybrids” (2006-2009)

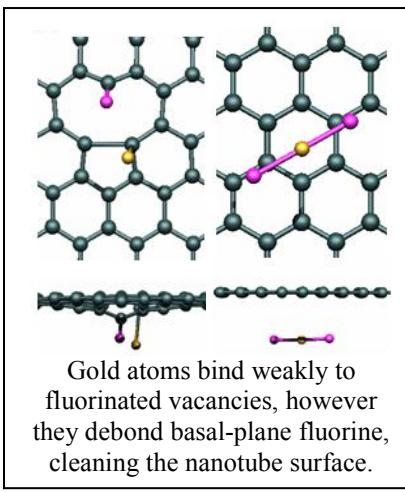
More recently I have extended my study of functionalised carbon systems to include metal decorated nanotubes for gas sensing, via the STREP project “nano<sup>2</sup>hybrids” (2006-2010). The project was driven by the industrial and applied partners developing new toxic gas (benzene) detectors based on metal decorated carbon nanotubes, and was unusual in the scientific range it covered (from my fundamental atomic-scale studies to prototype device design), requiring strong interdisciplinary ability to communicate between partners.

With my postdoc we studied individual metal atom deposition on graphene surfaces (as a model for large diameter nanotubes), looking at binding, clustering and surface diffusion behaviour.<sup>28</sup> However we rapidly expanded the study to include defects in the carbon network, notably vacancies and oxygenated vacancies. Our calculations show that species such as gold, while highly mobile on pristine surfaces, bind strongly at oxygenated defects which thus act as pinning sites<sup>29</sup>. Experimental groups within the project indeed found that pre-treatment of nanotubes using an oxygen plasma to create oxygenated vacancies gave a more uniform distribution of smaller nanoparticles on the nanotube surface, increasing the available surface area for gas absorption and hence detector sensitivity.

The close collaboration with experimental plasma treatment groups and spectroscopy (XPS and NEXAFS) has proved very productive. We have been able to address industrially important problems, for example showing why Ti forms sporadically poor nanotube contacts (due to oxygen poisoning)<sup>30</sup>, and we were able to propose Rh as a promising new nanotube contact metal<sup>31</sup>. The project has led to a prototype gas detector an order of magnitude more sensitive than those currently on the market (with additional advantages of cost and weight). The project was also unique for its science communication aspects detailed elsewhere.

The work has been very successful, and my postdoc and I have given invited talks on this at national and international meetings (JNB2, NT08, TRNM07,08, NanoteC, etc). The work has received awards (I. Suarez oral presentation prize JNB2, Poster prize NT08, Wernaer’s Science Communication Prize 2008, ...) and international press coverage.

While not currently a priority, I have nonetheless worked with experimental colleagues in the IMN and elsewhere on titanate TiO<sub>x</sub>-based nanoscrolls and nanorods<sup>32</sup> via interpretation and discussion of spectroscopic data, experiment design, and some modelling (1 MR1, 1 MR2 project).



<sup>28</sup> [I. Suarez-Martinez, A. Felten, J.-J. Pireaux, C. Bittencourt, C. P. Ewels, J. Nanosci. Nanotech. 9, 6171 \(2009\)](#)

<sup>29</sup> [J.-C. Charlier et al \(all nano<sup>2</sup>hybrids project partners\), Nanotechnology 20 375501 \(2009\).](#)

<sup>30</sup> [A. Felten, I. Suarez-Martinez, C. P. Ewels, et al, Chem. Phys. Chem. 10 \(11\), 1799-1804 \(2009\).](#)

<sup>31</sup> [I. Suarez-Martinez, C. P. Ewels, et al, ACS Nano, 4 \(3\), 1680 \(2010\).](#)

<sup>32</sup> [A. Gloter, C. Ewels, P. Umek, D. Arcon, C. Colliex, Phys. Rev. B 80, 035413 \(2009\); P. Umek, P. Cevc, A. Jesih, A. Gloter, C. P. Ewels, D. Arcon, Chem. Mater. 17 \(24\), 5945-5950 \(2005\).](#)

## 6. Carbon Nanomaterials : Some General Conclusions

### Key Collaborations

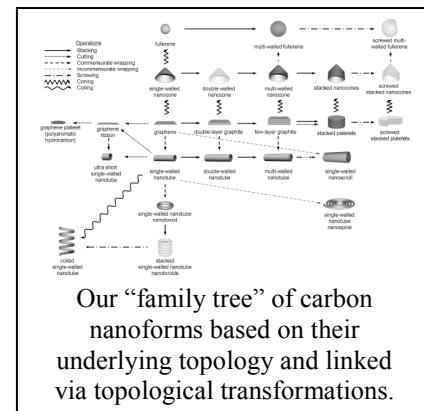
Prof. Marc Monthioux, CEMES Toulouse  
Dr. Irene Suarez-Martinez, Curtin University, Perth

### Grants and Funding

FP6 STREP “nano2hybrids” (2006-2009)

I have worked with a wide range of carbon materials (diamond, graphite, graphene, fullerenes, nanotubes and recently nanohorns<sup>33</sup>). In order to determine common trends in chemical behaviour, I launched a study on early stage oxidation of all of these. With my postdoc we derived a universal predictive law of the oxidation behaviour of any given carbon bond (both what sort of functional group will form, and what its formation energy will be) based only on the local geometry of the bond<sup>34</sup>. Thus for example while DFT calculations for oxidation of a carbon nanohorn with 300 atoms take us typically up to a week per bond considered, the geometric rule predicts the oxidation behaviour of all bonds in the system in a few seconds. There is potential to extend this to other chemical species, and we hope it will prove useful for understanding reactivity in other carbon nanomaterials and semi-amorphous carbons.

At the same time my overview of carbon nanomaterials has allowed me to write book chapters<sup>35</sup> and lecture on the “zoology” of these materials, since the majority of them are not widely known. In an attempt to introduce standardisation to the field we recently submitted a letter to Carbon proposing new standard nomenclature to describe the multiplicity of carbon nanoforms based on their underlying topology<sup>36</sup>. If the pages of discussion with the referees are any indication, I look forward to the debate this will launch within the carbon community!



## 7. Experimental Support and Work

Other side-projects include the theoretical identification of hydrogen behaviour in crystalline boron to support experimental muon-implantation studies<sup>37,38</sup>, characterisation and explanation of the formation of molecular vanadium oxohalide fragments  $\text{VOCl}_x\text{F}_y\text{Br}_z$  ( $x,y,z=0-3$ )<sup>39</sup>, and study of catalyst behaviour during nanotube growth<sup>40</sup>. I also have several experimental papers from my work on nanotube alignment in epoxide composites<sup>41</sup>, EELS of nitrogen doped tubes<sup>42</sup>, etc.

I have also initiated a project on hybrid magnetic-nanotube systems. With Alexis Vlandas in Oxford we successfully filled carbon nanotubes with high-spin molecular magnets, which I confirmed via EELS spectroscopy with Alexandre Gloter at the LPS, Orsay. With PHC-EGIDE support, this side project is now approaching completion with colleagues at the Josef Stefan Institute in Slovenia who have improved on our initial samples and are extending the project with other partners to test the magnetic behaviour of these exciting new hybrid materials. I had a MR2 project in 2007 DFT modelling crystals of such magnets which won the Ouest France prize 2009 for best Materials masters project.

<sup>33</sup> [I. Suarez-Martinez, M. Monthioux, C. P. Ewels, J. Nanosci. Nanotechnol. 9, 6144-6148 \(2009\)](#)

<sup>34</sup> I. Suarez-Martinez, C. P. Ewels, M. Monthioux, submitted (2011).

<sup>35</sup> I. Suarez-Martinez, N. Grobert, C. P. Ewels, « Handbook of Carbon Nanomaterials », Pan Stanford (2011)

<sup>36</sup> I. Suarez-Martinez, N. Grobert, C. P. Ewels, Carbon, submitted (2010)

<sup>37</sup> [S. F. J. Cox, J. S. Lord, A. D. Hillier, S. P. Cottrell, Ph. Wagner, C. P. Ewels, Physica B 404, 841-844 \(2009\)](#)

<sup>38</sup> Ph. Wagner, C. P. Ewels, I. Suarez, V. Guiot, S. Cox, J. S. Lord, P. Briddon, Phys. Rev. B, accepted (2011)

<sup>39</sup> [V. Guiot, I. Suarez, P. Wagner, J. Goss, P. Briddon, A. W. Allaf, C. P. Ewels, Inorg. Chem. 48, 3660 \(2009\).](#)

<sup>40</sup> [A. Gohier, C. P. Ewels, T.M. Minea, M.A. Djouadi, Carbon, 46, 1331-1338 \(2008\).](#)

<sup>41</sup> [C. P. Ewels, G. Desarmot, A. Foutel-Richard, F. Martin, AIP Conf. Proc. Vol. 685 \(1\) 99-102 \(2003\).](#)

<sup>42</sup> [C. P. Ewels, A. Gloter, T. Minea, B. Bouchet-Fabre, S. Point, C. Colliex, Eur. Phys. J. Appl. Phys., \(2008\).](#)

## Section 4 : Metal-Nanotube Interaction

The key step for integration of nanotubes into functional devices is the engineering of the electrical contact. Electronic devices based on CNTs have shown that their performance is influenced by a potential barrier existing at the metal-CNT contact that governs electron injection into the nanotubes<sup>43</sup>. To achieve low-resistance Ohmic contacts with nanotubes and thus advance their integration in new devices, investigation of the metal-CNT interaction is essential. In this context, metal nanoparticles supported on CNTs are important prototypes for understanding the nature of metal-CNT interaction.

Furthermore, these hybrid systems formed by two interacting structures whose electronic properties are affected by their dimension, open a vast and very exciting field for basic research. The electronic structure of CNTs is dependent on nanotube chirality and diameter. Moreover, the electronic properties of metal clusters are influenced by their dimension, i.e. by changes in their atomic coordination. The combination of these finite-size effects can impact on metal cluster-CNT interaction, having outstanding influence for future nanoscale devices.

For CNTs the critical importance of electrical contacts is quite well documented, but contradictory results have been reported on the dependence of the contact resistance upon the length of the contact region, and on the nature of the metal-nanotube interaction. Recently, Vitale et al. showed that in addition to the metal work function, the specific character of the chemical bond at the interface is an important factor determining the Schottky barrier height<sup>44</sup>.

Carbon nanotubes decorated with metal cluster nanostructures are proposed as prototype systems for molecular recognition at the nanoscale. The key concept is to use relatively small metallic clusters that donate or accept a significant amount of charge upon adsorption of a target molecule, so that electron transport in the nanotube is affected. We investigate here theoretically defective systems based on carbon nanotubes whose surfaces are randomly decorated with metal clusters.

Simulations of metal-nanotube interaction predict binding and diffusion energies of metal atoms at the tube surface, including realistic atomic models for defects potentially present at the nanotube surface. Specifically, we study here the interface between CNTs and surface deposited transition metals such as titanium, gold and rhodium, supported by experimental electron microscopy and photoemission spectroscopy.

Modelling provides a complete picture of surface binding, diffusion and aggregation properties for these metals, highlighting fundamental differences in their surface chemical and electronic behaviour. Oxygen in the interface between Ti and CNTs significantly weakens the Ti-CNT interaction. Ti atoms at the surface will preferentially bond to oxygenated sites. Potential sources of oxygen impurities are examined, namely oxygen from any residual atmosphere and pre-existing oxygen impurities on the nanotube surface, which we enhance through oxygen plasma surface pre-treatment. In contrast we find a less sensitive metal-CNT interface for Rh, and nanoparticle formation for metals such as Au and Pd.

Fully spin polarised AIMPOR calculations are performed using an 8×8 supercell of graphene, i.e. a monolayer of 128 carbon atoms unless specified otherwise. Since spin state is extremely

<sup>43</sup> J. Tersoff, *Nature* **424**, 6949 (2003)

<sup>44</sup> Vitale et al, *J. Am. Chem. Soc.* **130**, 5848, (2008)

important for small metal clusters, in each case we started with a high initial spin and allowed the calculation to optimise the spin state during geometrical optimisation.

The Brillouin zone was sampled using the Monkhorst and Pack scheme<sup>45</sup> with a sampling of  $1 \times 1 \times 1$  shifted by  $0.5a.u.$  in all directions. Single metal atoms were introduced and all atoms allowed to geometrically relax to the system ground-state structure. Multiple initial start structures were tested for each metal species. Gaussian-based basis functions are used to describe each atom type: 38 for C, 50 for Ti, Pt and Pd, 40 for Ni and Au. In the energetic analysis that follows, binding energies are defined as the difference in energy between the relaxed combined system and the isolated perfect graphite sheet and a single isolated metal atom unless stated otherwise. The diffusion barriers for the metal atoms were determined by constraining the system symmetry and was confirmed as a saddle point by subsequent symmetry breaking and structural optimization which led to the ground state structure.

### **Single Metal Atoms on pristine nanotube surfaces**

Theoretical studies on the interaction between metallic monolayers and an underlying graphene layer<sup>46</sup>, showed that the contact conductance varies as  $Ti > Pd > Pt > Cu > Au$ <sup>46</sup>. This order correlates with the distance between the first metal layer and the underlying graphene layer. However, this study does not address metal deposition at the earlier stage of the metal-CNT interface formation. In this context, Durgun et al.<sup>47</sup> addressed the interaction between one single atom with the carbon nanotube surface. While they examined many metal species, the interaction with point defects and metal diffusion at the surface was not considered.

Metal	Bulk cohesive energy (eV/atom)		
	Theoretical		Experimental
	Current work	Literature (DFT/LDA)	
Ti	6.44	6.29 <sup>48</sup>	4.85 <sup>48</sup>
Ni	5.71 (0.65)	5.98 <sup>48</sup>	4.44 (0.61) <sup>11</sup>
Pd	4.99	3.71 <sup>12</sup>	3.90 <sup>11</sup>
Pt	5.69	5.50 <sup>12</sup>	5.85 <sup>49</sup>
Cu	5.05	4.753 <sup>50</sup>	3.49 <sup>51</sup>
Rh	7.81	8.29 <sup>52</sup>	5.71 <sup>53</sup>
Au	4.43	3.05 <sup>12</sup>	3.99 <sup>11</sup>

*Bulk cohesive energies of the studied metals. The value of the magnetic moment per atom is shown between brackets in units of  $\mu_B$  where non-zero. Overestimation caused by use of the local density approximation is well known and matches other calculations in the literature.*

<sup>45</sup> H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976)

<sup>46</sup> Y. Matsuda, W. Deng, W.A.Goodard, *J. Phys. Chem C* **11**, 11113 (2007)

<sup>47</sup> E. Durgun, S. Dag, V.M.K. Bagci, O. Gülsen, T. Yıldırım, S. Ciraci, *Phys. Rev. B* **67**, 201401 (2003)

<sup>48</sup> P. H. T. Philipesen, E. J. Baerends, *Phys Rev B* **54**, 8, 5326 (1996)

<sup>49</sup> D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data, Suppl.*, 1982, **11**(2), 1.

<sup>50</sup> C. Domain, C. S. Becquart, *Phys. Rev. B* **65**, 024103 (2001)

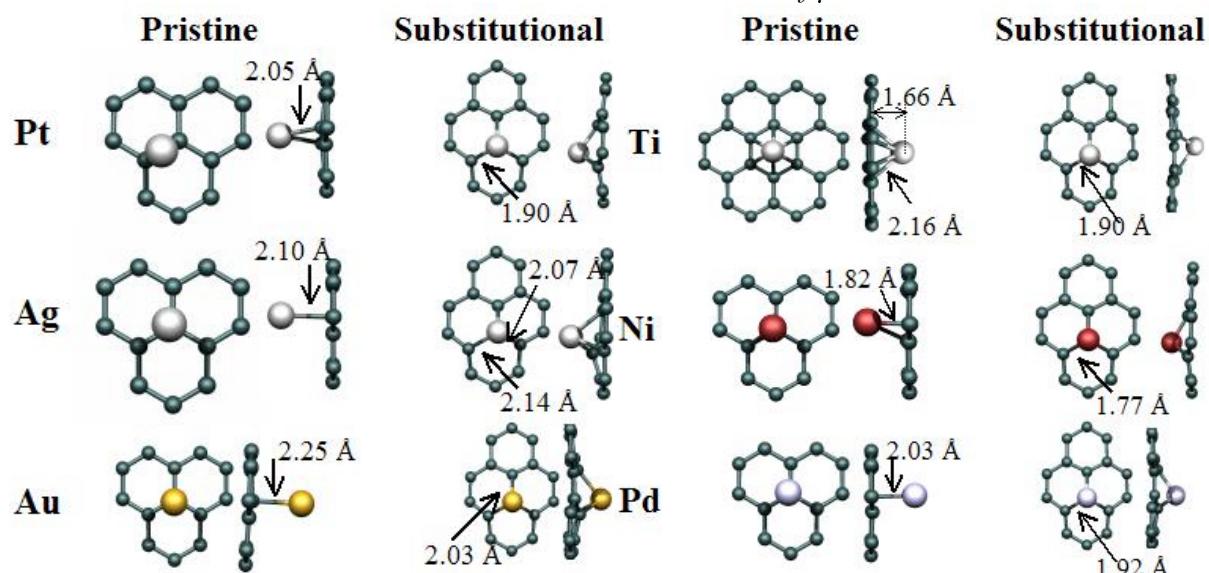
<sup>51</sup> C. Kittel, *Introduction to Solid State Physics*, 6th ed. Wiley, New York (1987)

<sup>52</sup> K. Stokbro, *Phys. Rev. B* **53** (11), 6869 (1996)

<sup>53</sup> CRC Handbook of Chemistry and Physics, 75th Ed., edited by D. R. Lide (CRC Press, Boca Raton, 1994).

Metal	Metal atom binding energy (eV) to	
	Pristine Graphene	Monovacancy
Rh	3.22 (1.0)	
Ti	2.64 (2.80)	9.32
Ni	2.22	8.01
Pd	1.80	6.43
Cu	1.17	5.17
Pt	0.92	7.20
Au	0.65 (0.99)	3.39 (0.99)

*Binding energies of a single metal atom to pristine graphene and the carbon monovacancy. In cases of non-zero magnetic moment, the value of the magnetic moment per unit cell is shown between brackets in units of  $\mu\text{B}$ .*



*Top and side views of our fully optimised structures for individual metal atoms on a pristine graphene layer, and on a pristine monovacancy (i.e. ‘substitutional’ metal atoms).*

The results of the calculated binding energies of the different metal atoms to the graphene surface are given in the table above. A clear pattern is visible, from the strong carbide forming metals (Ti and Ni) which show correspondingly strong binding energies, through the intermediate bonding species (Pt and Pd), and finally the metal from Group 11, Au, which do not form carbides and equally shows here only weak bonding to the graphene surface. The binding energy trend is Ti>Ni>Pt>Pd>Au. The same trend is reflected in choice of bonding site (see the figure above). The Ti atom sits above the centre of a graphene hexagon, maximizing the number of metal-carbon bonds, whereas for decreasing binding energy there will be a change in the nature of the interaction and the metal atoms will instead sit above individual carbon atoms. This allows for charge transfer interaction while minimizing disruption of the  $\pi$ -bonded network of the graphene.

A similar site has been found for the ground state on the semiconductor (8,0) and metallic (6,6) tube for the case of Ti47 in previous studies. Other metals such as Ni and Pt were reported to be more stable above bond centred sites<sup>47</sup>, and this is also reflected in our

calculations where Ni and Pt atoms were most stable above a C-C bond. However for the other metals studied, the difference in energy between the metal atom sitting above the bond centre site or above a carbon atom was less than 0.1 eV, *i.e.* within the error bounds of our calculations.

In general bond lengths are longer for the more weakly interacting metals (see Figure above). It may seem that the metal with the strongest interaction, Ti, breaks this trend slightly through its adoption of a hexagon-centre, however the perpendicular distance to the graphene layer is the shortest, 1.66 Å. The trend certainly holds if we take the perpendicular distance from the metal atom to the graphene layer.

Consequently, for all studied metals the calculations predict that isolated metal atoms will bind on arrival at graphene surfaces. We consider next the diffusion pathways for the metal atoms over the graphene surface for the case of Ti, Pd and Au. In the case of Ti, the migration occurs over carbon-carbon bond centres. The migration barrier for Ti is 0.7 eV. This relatively high value suggests that Ti will not surface diffuse until higher temperatures. If we assume a simple first order Arrhenius type diffusion with the Debye attempt frequency of  $10^{13}$  Hz, this implies the Ti atom will only start becoming mobile at around 0°C. This is discussed further below.

In the case of Pd and Au, the migration activation barrier can be estimated by the energy difference between different sites. The migration barrier in those cases is significantly lower, <0.1 eV, suggesting that these metal atoms will be highly mobile on the surface even below liquid nitrogen temperature.

### **Metal atom-pristine vacancy interaction**

There are a number of potential trap sites for surface diffusing metal species, including other metal atoms, and surface point defects. We consider here the binding of metal atoms to the carbon monovacancy (V). Although the structure can be considered also as ‘substitutional’ metal atoms in the graphene lattice, we find that the metal atom remains significantly displaced out of the graphene plane, and hence we prefer to retain the term metal-monovacancy (M-V) complex.

While there is in principle the potential for metal atoms to spontaneously kick-out carbon atoms from the graphene sheet, our calculations show no thermodynamic driving force for such a process. Carbon atom kick-out requires 13.8 eV<sup>54</sup> (from the combined formation energies of a monovacancy, 8.3 eV and a carbon interstitial 5.5 eV), and for all of the metals considered the calculated metal atom-monovacancy binding energy was sufficient to overcome this energy barrier.

The calculations show that all the metal atoms considered bind extremely strongly to pre-existing monovacancies, and the calculated binding energies (all over 3 eV) are sufficiently high to render the atoms immobile until high temperatures (>1000°C). Thus pristine undecorated monovacancies will act as strong traps to metal atom migration over the surface of graphene and nanotubes.

The data presented here for metal atom binding to monovacancies will apply in conditions of ultra-high vacuum (UHV), for example metal atom evaporation under UHV conditions, or in electron microscopy columns where vacancies are produced spontaneously by sample

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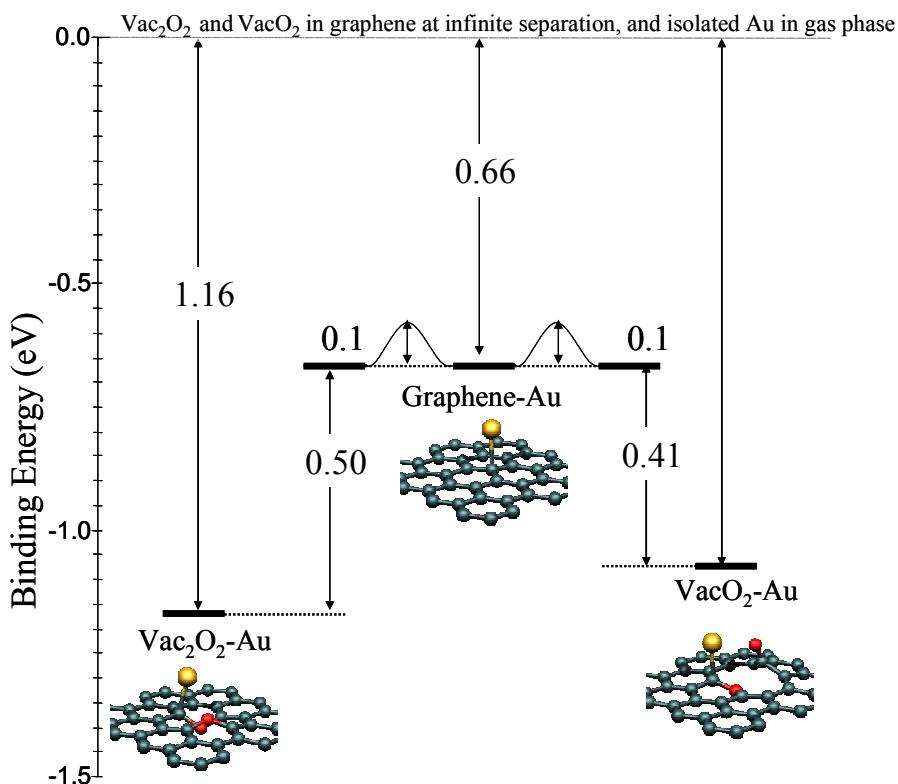
<sup>54</sup> M. I. Heggie, I. Suarez-Martinez, G. Haffenden, G. Savini, A. El-Barbary, C. Ewels and C. Cousins. *Irradiation Damage in Graphite from First Principles*, In: *Management of Ageing Processes in Graphite Reactor Cores* (Edited by GB Neighbour), Royal Society of Chemistry (London), 81-89 (2007).

interaction with the electron beam. However when graphene or nanotubes containing monovacancies are exposed to air, such defects will spontaneously oxidise<sup>55</sup>. This will significantly modify the binding behaviour of metal atoms, however this is beyond the scope of the current study. We nonetheless expect the general trends in monovacancy binding energies with metal type shown here to continue for oxidised vacancies.

### **Metal atom-oxygenated vacancy interaction**

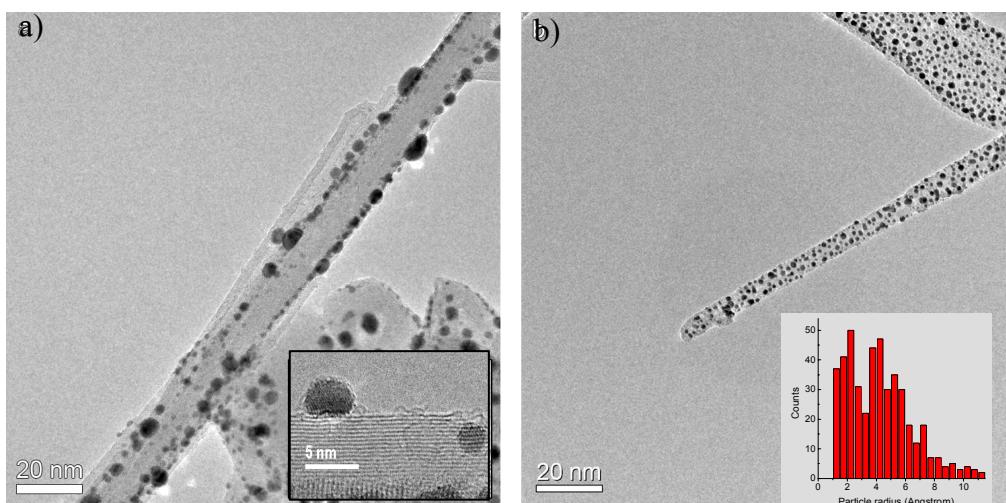
We take gold as our key example, although we observe similar behaviour for Rh, Pd, Pt and Ni, scaled roughly with their single atom binding energies to graphene. Although the binding of a single atom with the perfect graphitic layer is weak – 0.66 eV compared with the binding energy of Ti to graphene, which is 1.81 eV – it increases to 1.07 eV when the Au atom is next to an oxygenated vacancy ( $\text{VacO}_2$ ) and to 1.16 eV when next to an oxygenated divacancy ( $\text{Vac}_2\text{O}_2$ ). These centres have no net spin, unlike the isolated atom on graphene.

Our calculated barrier for Au diffusion on the graphitic surface is 0.1 eV. A simple first order Arrhenius type equation with the Debye attempt frequency ( $10^{13}$  Hz) suggests that isolated Au atoms on the graphitic surface at room temperature will be moving at more than  $2 \times 10^{11}$  hops/second. However, when attached to a  $\text{VacO}_2$  the lower limit barrier to leave the defect site is 0.51 eV (see Figure below) which corresponds to  $2 \times 10^4$  hops/second at room temperature. Thus the dwell time for Au at oxygenated defects will be significantly higher than on sections of pristine tube, and hence oxygenated defects will trap Au atoms for long enough to reduce their mobility and act as nucleation sites.



*Our DFT calculated binding energies (in eV) and barriers for Au to graphene, oxygenated divacancy ( $\text{Vac}_2\text{O}_2$ ) and oxygenated vacancy ( $\text{VacO}_2$ ). This shows that oxygenated vacancies act energetically as trap sites for surface migrating gold atoms*

<sup>55</sup> S.M. Lee, Y. H. Lee, Y. G. Hwang, J. R. Hahn, H. Kang, *Phys. Rev. Lett.* (1999) 82 p217



*Gold clusters formed at the CNT surface after a nominal gold evaporation of 5 Å a) pristine MWCNTs. The inset shows a higher magnification image with a typical cluster. b) oxygen plasma treated CNT. The inset shows the particle radius distribution. Scalebars are identical.*  
*(Taken from Reference 56)*

This is confirmed in experiments where nanotubes are pre-treated with an oxygen plasma before depositing metals (see Figure above). This pre-treatment creates a high density of oxygenated vacancies on the nanotube surface, each acting as a pinning and nucleation point for gold clusters. The resultant material has a higher density of small and more homogenous metal nanoparticles, and tests for gas sensing show significantly higher sensitivity<sup>57</sup>.

### ***Interfacial oxygen : The case of Titanium***

Titanium is a more complex case than the other metals examined here. Theoretical studies of pure metals on graphite suggest Ti as the best metal for contacts followed by Pd and possibly Rh, yet while low resistance Ohmic contacts have been experimentally reported in the case of Ti<sup>1-3</sup>, experimental results give Pd as the best choice due to better reliability and reproducibility<sup>2,6</sup>. One of the reasons invoked for this discrepancy is the high chemical reactivity of Ti compared to the other metals<sup>2,6,58</sup>. Ti wets nanotube surfaces experimentally, typically forming an amorphous oxidised or partially oxidised layer<sup>59</sup>.

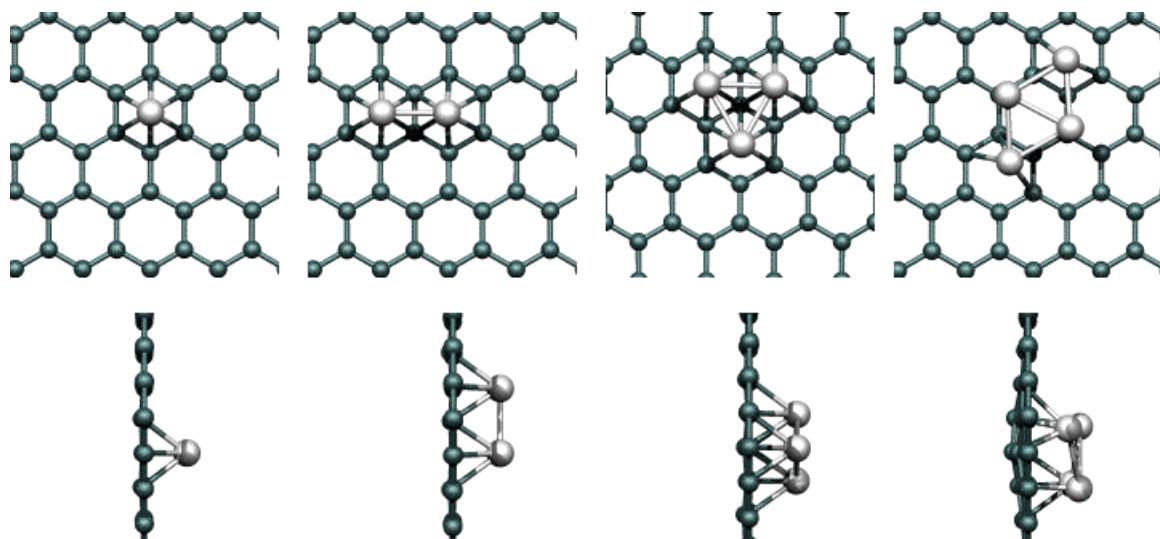
Calculations for small Ti clusters confirm the tendency of Ti to wet the carbon surface. A single Ti atom strongly binds to graphene (2.64 eV), with Ti above a hexagon centre with short Ti-C bonds (2.24 Å), in good agreement with previous studies. We have examined a range of 2D and 3D structures for Ti<sub>n</sub> on graphene (*n*=1-4). For each cluster size the most stable structure is planar parallel to the graphene (see Figure below). This is in contrast to Ti<sub>4</sub> in the gas phase where we find the most stable form is tetrahedral, in agreement with previous Ti cluster calculations.

<sup>56</sup> I. Suarez-Martinez, C. Bittencourt, X. Ke, A. Felten, J. –J. Pireaux, J. Ghijssen, W. Drube, G. Van Tendeloo, C. P. Ewels, *Carbon* **47** 1549 (2009).

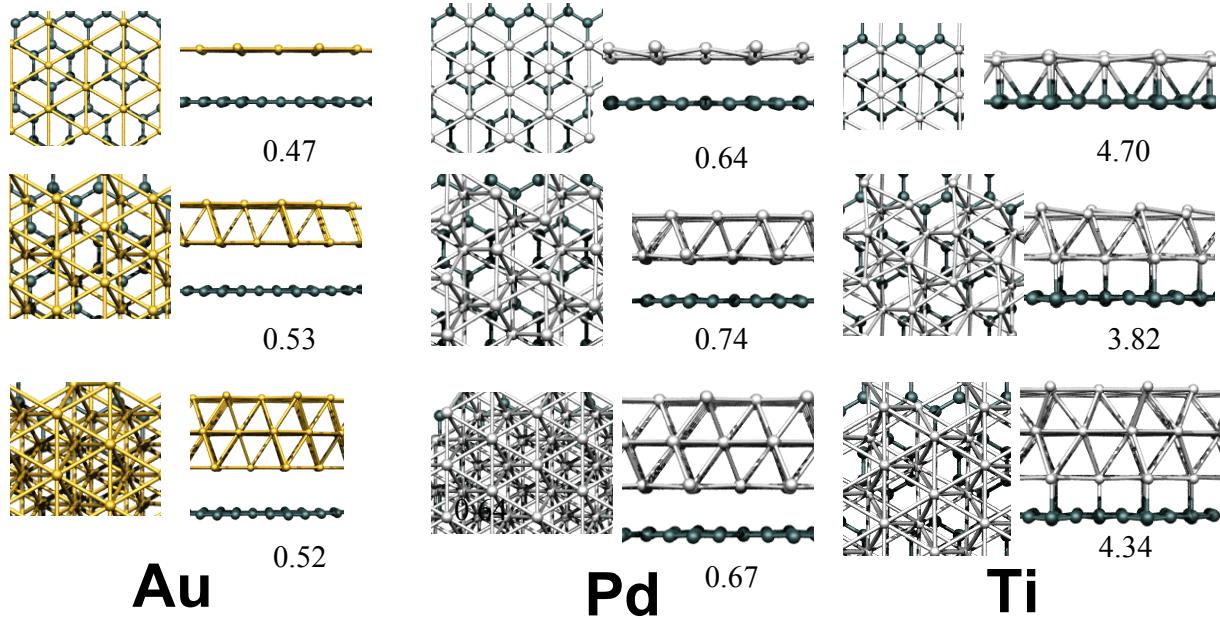
<sup>57</sup> J. –C. Charlier *et al*, *Nanotechnology*, *in press* (2009).

<sup>58</sup> A. Kanda, Y. Ootuka, K. Tsukagoshi, Y. Aoyagi, *Appl. Phys. Lett.* **79** (9), 1354, (2001).

<sup>59</sup> A. Felten, I. Suarez-Martinez, X. Ke, G. Van Tendeloo, J. Ghijssen, J. –J. Pireaux, W. Drue, C. Bittencourt, C. P. Ewels, *Chem. Phys. Chem.*, *in press* (2009).



*Top and side view of our DFT optimized structures of one to four Ti atoms on graphene.*

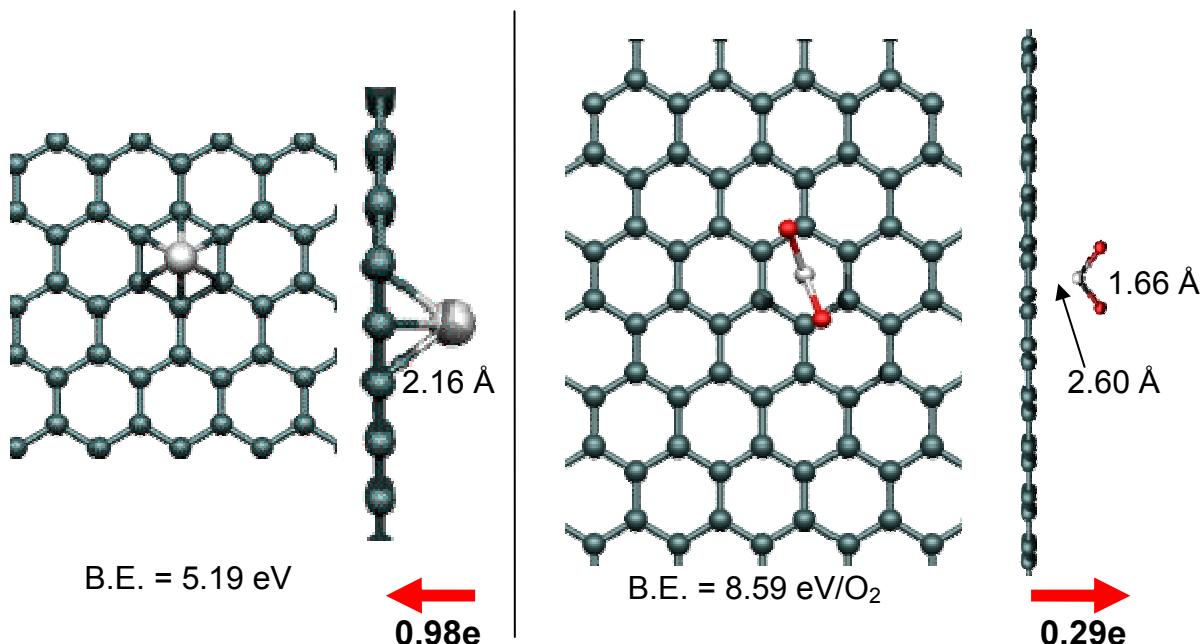


*Monolayer, bilayer and trilayer coverage of graphene sheets with different metal species, with binding energy / metal atom quoted in eV, using a reduced basis set for the Ti (which overestimates Ti bulk cohesive energy at 8.05eV/atom). This shows the rapid energetic convergence with layer thickness. Note these are not necessarily energetic ground state structures (for example clustering has not been examined), but are more likely metastable.*

A continuous monolayer of epitaxial Ti forms a buckled layer on average 2.0 Å above the graphitic layer, with Ti-C distances of 2.13 Å or 2.39 Å depending on whether the Ti atom lies above C atoms or hexagon centres respectively. In this case our binding energy is 5.43 eV/Ti atom. Our calculated barrier for Ti diffusion on the graphitic surface is 0.75 eV, as compared to ~0.1eV for Au and Pd. Thus while a simple first order Arrhenius type equation with the Debye attempt frequency ( $10^{13}$  Hz) suggests that isolated Au or Pd atoms on the graphitic surface at room temperature will be moving at more than  $2 \times 10^{11}$  hops/second, Ti atoms will only be moving at 2 hops/second, i.e. Ti atoms are almost immobile. This is consistent with the Ti coating being amorphous whereas Pd and Au particles are crystalline after deposition. Cohesive energy arguments can also be used to support preferential surface wetting of Ti. While our calculated LDA cohesive energy for bulk Ti is 6.44eV/atom, higher

than our Ti binding energy to graphene in the monolayer (5.43 eV/atom), for smaller clusters the cohesive energy drops. For example, for  $Ti_4$  in gas phase our calculated cohesive energy is 3.13 eV/atom, less than the 4.32 eV/atom binding energy for  $Ti_4$  on graphene, and we also find planar  $Ti_4$  on graphene to be more stable than tetrahedral  $Ti_4$  on graphene. Thus while bulk amounts of Ti metal might in principle prefer to cluster, nanoscopic amounts will thermodynamically favour wetting, and the slow kinetics and presence of oxygen will then preclude rearrangement.

Introducing  $O_2$  strongly modifies the interaction of Ti with the graphitic layer. The two O atoms bind strongly to the single Ti atom (8.59 eV/ $O_2$ , Ti-O bonds of 1.66 Å), which significantly weakens the Ti-C interaction (bonds dilated to 2.60 Å). Essentially the  $TiO_2$  unit becomes molecular and sits above the graphene  $\pi$ -cloud, again in agreement with previous calculations<sup>60</sup>. Oxygen significantly weakens the Ti-C interaction, as seen here:



*Single Ti atom on a graphene sheet, with charge transfer of 0.98e from Ti to the sheet. On introduction of an  $O_2$  molecule, it spontaneously bonds with the Ti atom, removing it from the surface, and changing the direction of charge transfer.*

The calculations also show strong qualitative variations in charge transfer behaviour. An isolated Ti atom on graphene has a net spin of  $2.41\mu_B$ , and Mulliken distribution analysis shows a strong net charge transfer from the Ti to the graphene layer resulting in a Ti charge of +0.98e. On addition of oxygen the Ti charge increases to +1.36e, however due to the charge on the oxygen atoms (-0.83e/O) the result is a much weaker net charge transfer in the opposite direction from the graphene to the  $TiO_2$  unit of 0.29e.

Thus we clearly see that the presence of oxygen at the interface between Ti and nanotube critically controls the extent of the Ti-C interaction. Blackstock *et al.*<sup>61</sup> recently investigated a similar problem at Ti/organic monolayer interfaces. They observed a formation of 1-2 nm

<sup>60</sup> M. I. Rojas, E. P. M. Leiva, *Phys. Rev. B* **76**, 155415 (2007).

<sup>61</sup> J. J. Blackstock, C. L. Donley, W. F. Stickle, D. A. A. Ohlberg, J. J. Yang, D. R. Stewart, R. S. Williams, *J. Am. Chem. Soc.* **130**, 4041 (2008).

thick  $\text{TiO}_2$  layer at the interface and attributed it to the vacuum conditions, surface water and oxygen diffusion from the metal oxide substrate.

For Rhodium in contrast, on the graphene surface a single Rh atom sits above a hexagon centre with binding energy of 3.22eV compared to the isolated atom<sup>62</sup>. The system has net magnetic moment of 0.998  $\mu\text{B}$  with average C-Rh distance of 2.238 Å, Rh sitting 1.709 Å above the graphitic layer. Maintaining the same spin, neither sitting above a carbon atom or over a C-C bond centre are stable sites, these sites being 0.42eV and 0.35eV less stable than the ground state respectively. This provides a minimum migration barrier of 0.35eV for Rh diffusion on the graphitic surface over bond centred sites. This means Rh will be surface mobile at room temperature, unlike Ti, although slower moving than Pd, Pt or Au. As for Au and Ti, we find strong binding for Rh to oxygenated vacancies, consistent with nanocluster formation nucleated at vacancy sites. However unlike Ti, when we introduce  $\text{O}_2$  to a single Rh atom on a pristine surface, although they form strong Rh—O bonds, the Rh maintains strong bonds with the underlying carbon. This is consistent with evidence that Rh forms more consistent Ohmic contacts with graphitic carbons than Ti does.

The quantity of oxygen present in the initial surface layer crucially controls the Ti-nanotube interaction. Later surface oxygenation of the Ti particle is less important for the contact behaviour. This is because initial Ti deposition preferentially forms Ti-O bonds, strongly reducing the interaction between the Ti and the nanotube. Once there is no oxygen available the remaining Ti forms Ti-C bonds with strong interaction as seen in the large charge transfer<sup>56</sup>.

The theoretical calculations predict mobility for Ti at temperatures not far above room temperature, so gentle surface heating during deposition (up to 100°C) may be sufficient to crystallize the Ti layer under vacuum (however Ti surface mobility is reliant on the absence of oxygen). A crystallized Ti layer should lead to significantly improved contact behaviour, and this is consistent with experimental studies of post-deposition heating which appear to promote TiC formation<sup>63,64</sup>.

## Scientific and European context

Although the results in this Section are possibly less fundamental than those in most of the others, this work has more immediate direct applied science application than many of the other chapters, and was performed in direct response to experimental and industry needs, within the framework of a European research project. A combination of the theory presented here with the associated experimental development has since formed the basis of a number of European initiatives, including the formation of Europe's largest nanotechnology research network (NanoTP, of which I am the vice-chairman), and the launch of a new European Commission research call instigated by Intel Europe.

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<sup>62</sup> C. Bittencourt, I. Suarez, A. Felten, X. Ke, W. Drube, G. Van Tendeloo, C. Ewels, in preparation (2009).

<sup>63</sup> J.-O. Lee, C. Park, J.-J. Kim, J. Kim, J. W. Park and K.-H. Yoo, *J. Phys. D: Appl. Phys.* **33** (2000) 1953.

<sup>64</sup> R. Martel, V. Derycke, C. Lavoie, *et al*, *Phys. Rev. Lett.* **87**, 256805 (2001).

## Section 5: Nitrogen and Phosphorus doped Fullerenes

Thus far we have concentrated on the behaviour of defects in graphene, graphite, and carbon nanotubes. Although the curvature and inter-layer interaction varies in these cases, resulting in varying defects behaviour, their pristine forms all demonstrate perfect hexagonal lattices. We now turn to the behaviour of heteroatom impurities in fullerenes, since this allows exploration of the introduction of pentagons to the host lattice. The result is a molecule with more localised non-aromatic bonding, showing strong single- and double- bond character.

As before I have been involved in many studies of fluorination and oxidation of pristine fullerenes, but for reasons of space this work is not covered here, and I focus instead on the behaviour of nitrogen and phosphorus dopants (azafullerenes and phosphofullerenes respectively), and oxidation behaviour of the resultant heterofullerenes. This follows from previous studies of azofullerenes such as C<sub>58</sub>N<sub>2</sub>.<sup>65</sup>

As well as interest in heteroatom doped fullerenes for their novel chemistry, there are a number of areas of application where they may be promising, notably in radical chemistry. There is also great interest in biological applications of fullerenes. Notably water soluble fullerenes have been studied for their role as anti-cancer,<sup>66</sup> anti-HIV,<sup>67</sup> and protective agents against free-radical induced liver damage.<sup>68</sup> Of key interest is their behaviour as free radical scavengers and antioxidants.<sup>68</sup> With its triply degenerate lowest unoccupied molecular orbital (LUMO) and high electron affinity, C<sub>60</sub> is a strong acceptor capable in principle of trapping up to six electrons in solution. The fullerene oxides show a rich chemistry in reactions both with fullerenes, and with themselves.<sup>69,70,71</sup> They are thermally labile and liberate oxygen on heating. Understanding heterofullerene oxidation allows comparison with homo- and functionalised fullerenes, and is of interest for medical applications. If heterofullerenes are to see eventual application in light harvesting devices, understanding their oxidation behaviour will be essential for lifecycle analysis and eventual device degradation.

All calculations in this chapter were carried out using supercells, fitting the charge density to plane waves within an energy cut-off of 225 Ry. Atom-centered Gaussian basis functions are used to construct the many-electron wave function. These functions are labelled by multiple orbital symbols, where for each symbol the Gaussians are multiplied by spherical harmonics including all angular momenta up to maxima *p* (*l*=0,1) and *d* (*l*=0,1,2), respectively. Following this nomenclature, the basis sets used for each atom type were *pdddp* (P), *ddd* (N), *ddpp* (O), and *ppp* (H). Carbon atoms used a contracted sum basis set equivalent of C44G\*. Calculation were performed on a large hexagonal unit cell (*a*=14.28Å, *c*=12.29Å), with Brillouin zone sampling 1x1x1 *k*-points within the Monkhorst-Pack scheme. Radical calculations were performed spin polarised. In the analysis, standard states for carbon, nitrogen and phosphorus were taken as C<sub>60</sub>, N<sub>2</sub> and P<sub>4</sub> respectively.

<sup>65</sup> C.P. Ewels, *Nano Letters* **6**, 890 (2006).

<sup>66</sup> N. Miyata, Y. Yamakoshi, in "Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials", Eds: K. M. Kadish, R. S. Ruoff, vol. 2. Electrochemical Society, Pennington, NJ, p. 345 (1997).

<sup>67</sup> S. H. Friedman, D. L. DeCamp, R. P. Sijbesma, G. Srđanov, F. Wudl, G.L. Kenyon, *J. Am. Chem. Soc.* **115**, 6506 (1993).

<sup>68</sup> N. Gharbi, M. Pressac, M. Hadchouel, H. Szwarc, S.R. Wilson, F. Moussa, *Nano Lett.* **5**, 2578 (2005).

<sup>69</sup> M. P. Barrow, N. J. Tower, R. Taylor, T. Drewello, *Chem. Phys. Lett.* **293**, 302 (1998).

<sup>70</sup> S. Lebedkin, S. Ballenweg, J. Gross, R. Taylor, W. Krätschmer, *Tetrahedron Lett.*, **36**, 4971 (1995).

<sup>71</sup> A. L. Balch, C. A. Costa, B. C. Noll, M. M. J. Olmstead, *J. Am. Chem. Soc.*, **117**, 8926 (1995).

## Nitrogen doped fullerenes and hydroazafullerenes

One of the most striking achievements of fullerene chemistry is the possibility of substituting one or more cage carbon atoms with heteroatoms. A particularly prominent example is the azafullerenyl radical  $C_{59}N^{\bullet}$ .<sup>72</sup> However,  $C_{59}N^{\bullet}$  is highly reactive, and in crystals it dimerizes forming bisazafulerene ( $C_{59}N_2$ ).<sup>73,74</sup> The two  $C_{59}N$  units in the dimer are only bound by  $\sim 0.78\text{ eV}$ .<sup>75</sup> UV or visible light illumination<sup>76,77</sup> as well as high temperature treatment<sup>78</sup> can separate the dimer and form  $C_{59}N^{\bullet}$  radicals, which are seen in electron paramagnetic resonance (EPR) as three equidistant sharp lines indicative of  $^{14}\text{N}$  hyperfine interaction ( $a=3.6\text{ G}$ ) with the unpaired electron.<sup>76,77,78</sup> In order to stabilize the monomeric  $C_{59}N^{\bullet}$  radicals, samples with diluted  $C_{59}N^{\bullet}$  in a  $C_{60}$  matrix or even  $C_{59}N^{\bullet}$  encapsulated within carbon nanotubes have been prepared<sup>79,80,81</sup> with the hope of developing novel spintronic devices.<sup>82</sup>

Azafullerenyl radicals can alternatively be produced via the parent hydroazafullerene  $C_{59}\text{HN}$ .<sup>83</sup> Vibrational infra-red and Raman spectroscopy studies of  $C_{59}\text{HN}$  powder show full transformation from  $C_{59}\text{HN}$  to  $(C_{59}\text{N})_2$  at 700K, while an unknown intermediate metastable phase was identified above 540 K<sup>84</sup>. However the transformation pathway from  $C_{59}\text{HN}$  to bisazafulerene at high temperatures was not clear. The work presented in this section provides strong evidence for a unique rather stable intermediate phase grown by the bonding of a  $C_{59}N^{\bullet}$  radical to a  $C_{59}\text{HN}$  neighbor. The stability and possibility of controlled structural and electronic manipulation using the various high-temperature phases of  $C_{59}\text{HN}$  qualify this material as another candidate for future spintronic devices.

The question is thus: what happens to  $C_{59}\text{HN}$  when it is heated to high temperatures? It seems reasonable that on heating, a  $C_{59}\text{HN}$  fullerene will eventually lose its hydrogen atom, which will diffuse away, forming  $H_2$  and leaving the system. This results in a  $C_{59}N^{\bullet}$  radical next to  $C_{59}\text{HN}$ , or at very high temperatures and after prolonged thermal treatment, next to another  $C_{59}N^{\bullet}$  radical. We can examine this process via our AIMPRO calculations of isolated  $C_{59}N^{\bullet}$ ,  $C_{59}\text{HN}$ , and combinations of the two. Our calculated energy to form isolated  $C_{59}N^{\bullet}$  and  $H^{\bullet}$  radicals from  $C_{59}\text{HN}$  is 2.95 eV, although it is more likely that hydrogen will diffuse over azafullerene surfaces and thus this is an upper limit only on the hydrogen binding energy.

Mulliken population analysis of the unpaired electron of isolated  $C_{59}N^{\bullet}$  gives as expected the highest concentration (10.9%) on the  $\alpha$ -carbon next to nitrogen (the atom sharing a hexagon-

<sup>72</sup> W. Andreoni, F. Gygi, and M. Parrinello, *Chem. Phys. Lett.* **190**, 159 (1992).

<sup>73</sup> J.C. Hummelen, B. Knight, J. Pavlovich, R. Gonzales, F. Wudl, *Science* **269**, 1554 (1995).

<sup>74</sup> C.M. Brown, L. Christofolini, K. Kordatos, K. Prassides, *et al*, *Chem. Mater.* **8**, 2548 (1996).

<sup>75</sup> W. Andreoni, A. Curioni, K. Holczer, K. Prassides, *et al*, *J. Am. Chem. Soc.* **118**, 11335 (1996).

<sup>76</sup> K. Hasharoni, C. Bellavia-Lund, M.K. Keshavarz, G. Srdanov, and W. Wudl, *J. Am. Chem. Soc.* **119**, 11128 (1997).

<sup>77</sup> A. Gruss, K.-P. Dinse, A. Hirsch, B. Nuber, and U. Reuther, *J. Am. Chem. Soc.* **119**, 8728 (1997).

<sup>78</sup> F. Simon, D. Arčon, N. Tagmatarchis, S. Garaj, L. Forro, and K. Prassides, *J. Phys. Chem. A* **103**, 6969 (1999).

<sup>79</sup> F. Fülöp, A. Rockenbauer, F. Simon, S. Pekker, L. Korecz, S. Garaj, and A. Janossy, *Chem. Phys. Lett.* **334**, 233 (2001).

<sup>80</sup> A. Rockenbauer, G. Csanyi, F. Fülöp, S. Garaj, *et al*, *Phys. Rev. Lett.* **94**, 066603 (2005).

<sup>81</sup> F. Simon, H. Kuzmany, B. Nafradi, T. Feher, L. Forro, *et al*, *Phys. Rev. Lett.* **97**, 136801 (2006).

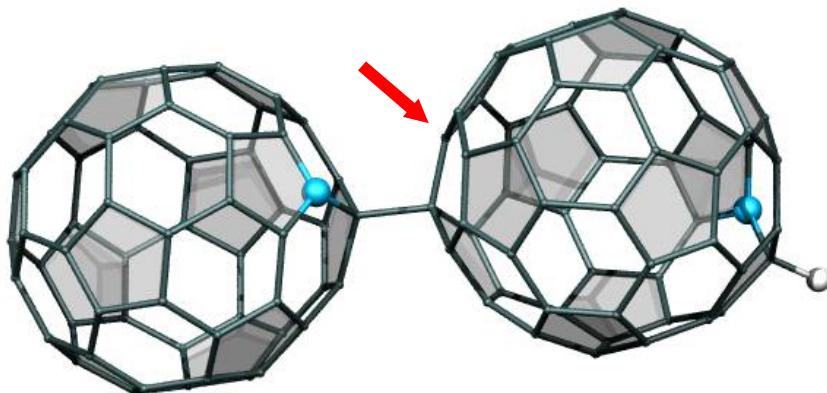
<sup>82</sup> J. Morton, A. Tyryshkin, A. Ardavan, S. Benjamin, K. Porfyrakis, S. A. Lyon, G. Briggs, *Nature Physics* **2**, 40 (2006).

<sup>83</sup> M. Keshavarz, M. Gonzales, R. Hicks, *et al*, *Nature* **383**, 147 (1996).

<sup>84</sup> N. Tagmatarchis, T. Pichler, M. Krause, H. Kuzmany, H. Shinohara, *Carbon* **44**, 1420 (2006).

hexagon bond with nitrogen), 5.4% on the nitrogen itself, and the rest distributed at very low concentrations over the azafullerene. This agrees with other calculations<sup>8,9</sup> and explains the magnitude of the hyperfine coupling constant  $a$  measured by EPR.

$C_{59}N^\bullet$  is a chemically active radical and may thus bond to neighbouring neutral  $C_{59}HN$ . Our calculations found many thermodynamically stable structures in which the  $\alpha$ -carbon in  $C_{59}N^\bullet$  forms a weak covalent bond (1.66Å) to a carbon atom in the neighboring  $C_{59}HN$  cage, with the binding energy dependant on which carbon atom of the  $C_{59}HN$  cage forms the cross-link. Bonding via non- $\alpha$  carbons on the  $C_{59}N^\bullet$  led to less stable structures and so are not considered further here.



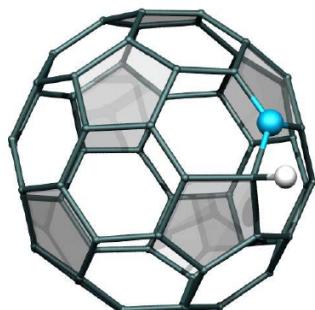
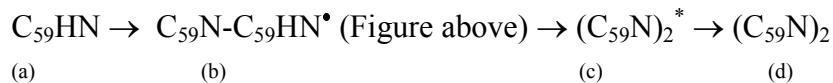
$C_{59}N\text{-}C_{59}HN$  (nitrogen: blue, hydrogen: white, pentagons: shaded). The unpaired spin is primarily localised on the carbon atom indicated by a red arrow – see text for details.

For these structures, Mulliken population analysis shows the unpaired electron primarily resides on the  $C_{59}HN$  rather than the  $C_{59}N$  cage. For example in the above structure, by far the highest concentration (15.4%) of the electron resides on the carbon atom of  $C_{59}HN$  marked with a red arrow, neighbouring the atom forming a covalent link with  $C_{59}N$ . Notably, only 1.3% (0.1%) of the electron resides on the nitrogen atom of the  $C_{59}N$  ( $C_{59}HN$ ) cage. Thus, the unpaired electron is transferred from the  $C_{59}N$  onto the  $C_{59}HN$  cage, far from both nitrogen atoms.

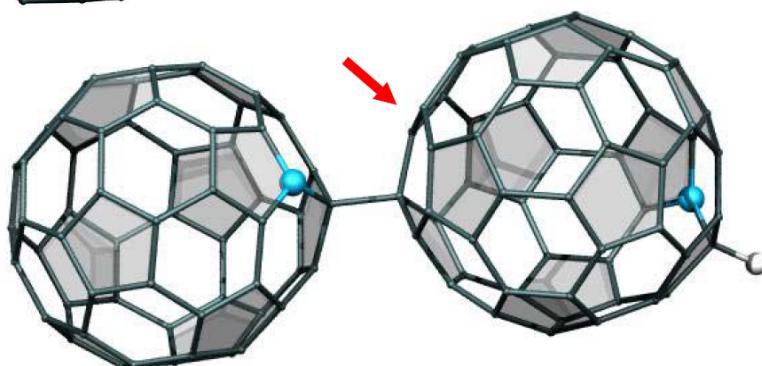
We next consider what happens when  $C_{59}N\text{-}C_{59}HN^\bullet$  loses its second hydrogen atom upon further heating. The lowest energy structure for bisazafullerene  $(C_{59}N)_2$  is well-known, with cross bonding between the two  $\alpha$ -carbon atoms sharing hexagon-hexagon bonds with a nitrogen atom. We obtain a binding energy of 0.737eV, in good agreement with a previous calculated value of ~0.781eV,<sup>75</sup> however higher than experimental binding energies in the range 0.3-0.52eV found in this and previous<sup>78</sup> studies. We therefore suggest that, instead of immediately forming this  $(C_{59}N)_2$  isomer, there is an intermediate step in which the  $C_{59}N\text{-}C_{59}HN^\bullet$  structure discussed above loses its hydrogen atom, *without any reorganization of the inter-fullerene bonding*. We thus have an isomer with one  $C_{59}N$  cage (referred to hereafter as the ‘bonding fullerene’) bonded into the rear of the second (the ‘leading fullerene’). In other words, after releasing the second H, the resultant structure (referred to hereafter as  $(C_{59}N)_2^*$ ) needs extra energy to rearrange into a standard dimeric bisazafullerene  $(C_{59}N)_2$  structure.

The binding energies for such intermediate structures fall in the range 0.23-0.45eV with the majority between 0.3-0.43eV, depending which carbon of the leading fullerene forms the cross-linking bond (compared to two isolated  $C_{59}N$  cages). The most stable binding site (besides the standard dimeric bisazafullerene) is the non-hydrogenated form of the figure above. The barrier for this  $(C_{59}N)_2^*$  to reconfigure to the standard  $(C_{59}N)_2$  will also be around 0.45eV since rearrangement will require breaking and reforming the cross-linking bond.

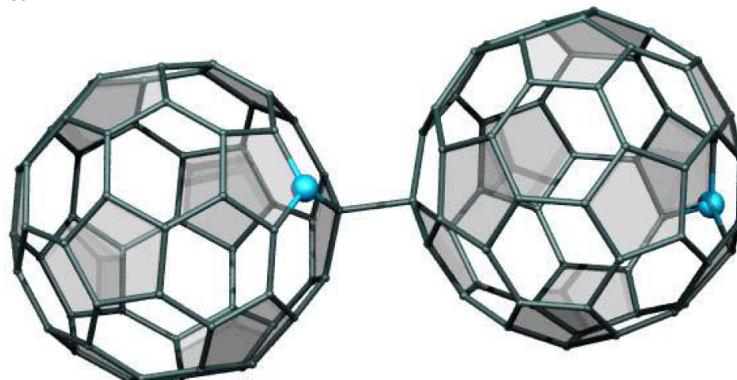
To summarise the transformation sequence of C<sub>59</sub>HN structures from the calculations:



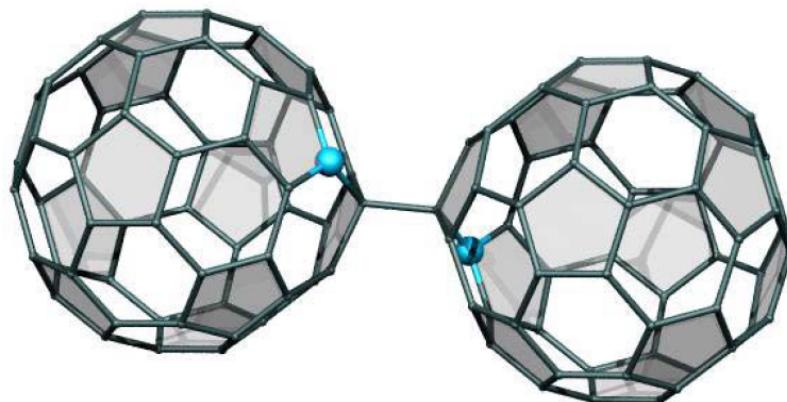
(a)  $C_{59}HN$ . The nitrogen atom is shown in blue, hydrogen atom in white, pentagons are shaded. The associated radical  $C_{59}N$ , has the same structure without the hydrogen atom, with the resultant unpaired spin primarily located on the carbon atom currently bonded to the hydrogen.



(b)  $C_{59}N-C_{59}HN$ . When (a)  $C_{59}HN$  loses its H atom, the resultant  $C_{59}N$  radical bonds to a neighbouring  $C_{59}HN$  fullerene. Unpaired spin mainly on the atom indicated by an arrow.

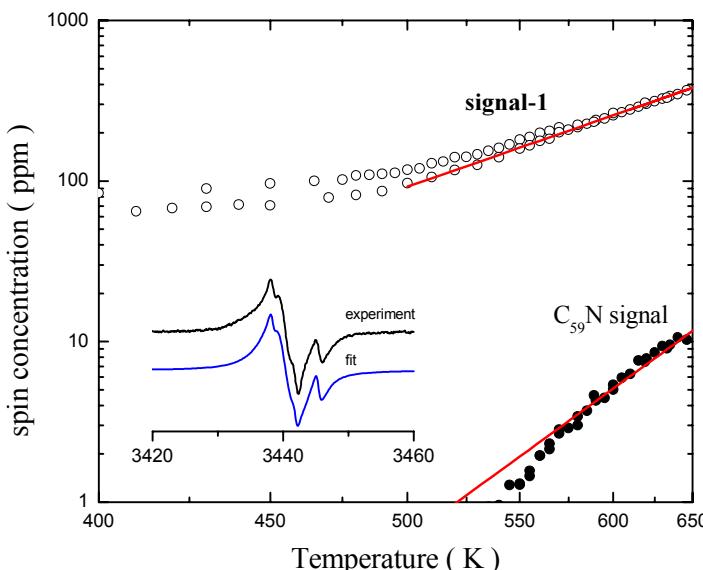


(c) Metastable form of  $C_{59}N-C_{59}N$ , when (b) loses its remaining hydrogen atom.



(d) Stable form of the bisazafullerene  $C_{59}N-C_{59}N$  dimer, 0.29eV more stable than (c).

$C_{59}N-C_{59}HN^{\bullet}$  ((b) above) is a radical and should be observable in EPR. Additionally the last standard bisazafullerene structure ( $C_{59}N_2$ ) is known to dissociate at high temperatures into monomeric  $C_{59}N^{\bullet}$  radicals characterized with a typical N hyperfine splitting EPR signal.<sup>78</sup>  $(C_{59}N)_2^*$  should behave similarly, also generating  $C_{59}N^{\bullet}$  radicals with the same EPR signal.



The temperature dependence of the concentration of paramagnetic centers responsible for **signal-1** (open circles) and  $C_{59}N^{\bullet}$  radical EPR signal (solid circles) at high temperatures.

Inset: Experimental EPR spectrum taken at  $T=580$  K and corresponding fit with the **signal-1** and  $C_{59}N$  components – see text for details.

Radical formation in  $C_{59}HN$  powder was followed with high temperature EPR performed at JSI Slovenia. As prepared  $C_{59}HN$  powder already shows a structureless EPR signal at room temperature (referred to hereafter as **signal-1**, inset in the figure above). This signal has at room temperature a  $g$ -factor 2.0022(3), linewidth 3.2(1) and its intensity corresponds to a concentration of about 800 ppm. The high purity of starting material and the fact that it has been exposed to air for a prolonged time before being sealed in a quartz tube rules out the possibility that this is an impurity signal. On the other hand, a very similar signal with nearly identical  $g$ -factor was found in  $C_{59}N$  doped  $C_{60}$ .<sup>80</sup> There, it was attributed to delocalised electrons, first over a cluster of  $C_{59}N$  and its first  $C_{60}$  neighbors and at higher temperatures over larger distances. Given the resemblance in calculated electronic structure of  $C_{59}N-C_{59}HN^{\bullet}$  (first structural figure above) and  $C_{59}N-C_{60}$  we attribute **signal-1** to  $C_{59}N-C_{59}HN^{\bullet}$ . The unpaired electron has transferred from the  $C_{59}N$  onto the  $C_{59}HN$  far from both nitrogen atoms, explaining the absence of a nitrogen hyperfine coupling in the EPR spectrum.

On heating **signal-1** remains almost unchanged up to ~500 K apart from a small decrease in its intensity due to increased temperature. This suggests that  $C_{59}N-C_{59}HN^{\bullet}$  centers are largely thermodynamically stable from 300-500 K. Above 500-530 K **signal-1** decreases rapidly and at 530 K a very weak set of three equidistant lines appears on top of **signal-1**. Fitting of the high-temperature EPR spectra (inset to Figure above) thus involves two main components, a line corresponding to **signal-1**, and a set of three equidistant lines typical of  $C_{59}N^{\bullet}$ . Finally, careful examination of the high temperature spectra also shows a weak signal at  $g=1.9985(7)$  attributed to a very small concentration of  $C_{60}^-$  centers.

These temperatures correlate well with both the DFT results presented here and previous high temperature IR studies<sup>84</sup>. Around  $T=540$  K the  $C_{59}N\text{-}C_{59}HN^\bullet$  radical loses its second hydrogen, forming diamagnetic  $(C_{59}N)_2^*$ . On cooling this structure cannot regain hydrogen, and the  $C_{59}N\text{-}C_{59}HN^\bullet$  EPR signal is irrevocably lost. Since the stable  $(C_{59}N)_2$  dimer separates into  $C_{59}N^\bullet$  radicals upon heating<sup>78</sup>, it seems reasonable that  $(C_{59}N)_2^*$  will behave similarly, explaining the observed  $C_{59}N^\bullet$  radical signal above 540K.

As mentioned above, the room temperature intensity of **signal-1** does not change much after the first high-temperature treatment. In the EPR figure above we show the variation of spin concentration responsible for **signal-1** and  $C_{59}N^\bullet$  during the second thermal cycle (in all subsequent cycles we found analogous behavior). The intensity of both signals increases with temperature suggesting the creation of novel centers with increasing temperature. Interestingly, both centers appear at around 500-540 K with activated high-temperature behavior. For the creation of  $C_{59}N^\bullet$  centers we estimate the binding energy to be  $E_{bind}=0.52\text{eV}$ , comparable (but larger) to the binding energy found in the previous bisazafullerene study.<sup>78</sup> This might suggest that the  $C_{59}N^\bullet$  centers found in this study formed from  $(C_{59}N)_2$  thermolysis. However, this binding energy does not match our calculated DFT value and is instead closer to that calculated for  $(C_{59}N)_2^*$ . We thus propose that the binding energy  $E_{bind}=0.52\text{eV}$  in fact represents an average binding energy for  $(C_{59}N)_2^*$ .

The binding energy for the creation of **signal-1** centers is smaller, i.e. 0.230eV. This matches extremely well the calculated binding energy for  $C_{59}N\text{-}C_{59}HN^\bullet$ , giving us extra confidence in the assignment of **signal-1**. The EPR results thus provide strong evidence for the first direct observation of hydrogen removal from  $C_{59}HN$ , creating intermediate  $C_{59}N\text{-}C_{59}HN^\bullet$  units and high temperature  $C_{59}N^\bullet$  radicals simply by its thermal homolysis. In addition, the fact that both signals first appear at approximately the same temperature suggests that the thermal activation for hydrogen removal from  $C_{59}HN$  and  $C_{59}N\text{-}C_{59}HN^\bullet$  should be very close.

## Oxidation of phosphorus and nitrogen doped fullerenes

Oxidation is one of the key fullerene reactions and has received widespread attention amongst the fullerene community. Single oxygen addition results in either a 6,6-closed epoxide isomer,<sup>85</sup> or a 5,6-open oxidoannulene (an ether structure, oxa-homo[60]fullerene).<sup>86</sup> The fullerene epoxide 6,6-closed  $C_{60}O$  is the simplest fullerene derivative and the key fullerene oxidation product that plays an important role in the synthesis of various organic, organometallic and polymeric fullerene derivatives.<sup>87,88,89</sup> The epoxide is one of the most versatile functionalities and provides easy access to further modifications.<sup>87</sup>  $C_{60}O$  readily oxidises further;  $C_{60}O_n$ ,  $n=2\text{-}7$  has been observed in the mass spectra of fullerene oxides.<sup>87,90,91</sup> There have been various theoretical studies of fullerene oxidation,<sup>92,93,94</sup> notably

<sup>85</sup> K. M. Creegan, J. L. Robbins, W. K. Robbins, J. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, *J. Am. Chem. Soc.*, **114**, 1103 (1992).

<sup>86</sup> R. B. Weisman, D. Heymann, S. M. Bachilo, *J. Am. Chem. Soc.* **123**, 9720 (2001).

<sup>87</sup> M. P. Barrow, N. J. Tower, R. Taylor, T. Drewello, *Chem. Phys. Lett.* **293**, 302 (1998).

<sup>88</sup> S. Lebedkin, S. Ballenweg, J. Gross, R. Taylor, W. Krätschmer, *Tetrahedron Lett.*, **36**, 4971 (1995).

<sup>89</sup> A. L. Balch, C. A. Costa, B. C. Noll, M. M. J. Olmstead, *J. Am. Chem. Soc.*, **117**, 8926 (1995).

<sup>90</sup> J. M. Wood, B. Kahr, S. H. Hoke, L. DeJarme, R. G. Cooks, D. Ben-Amotz, *J. Am. Chem. Soc.* **113**, 5908 (1991).

<sup>91</sup> C. Taliani, G. Ruani, R. Zamboni, R. Danieli, S. Rossini, V. N. Denisov, V. M. Burlakov, F. Negri, G. Orlandi, F. Zerbetto, *J. Chem. Soc. Chem. Commun.* 220 (1993).

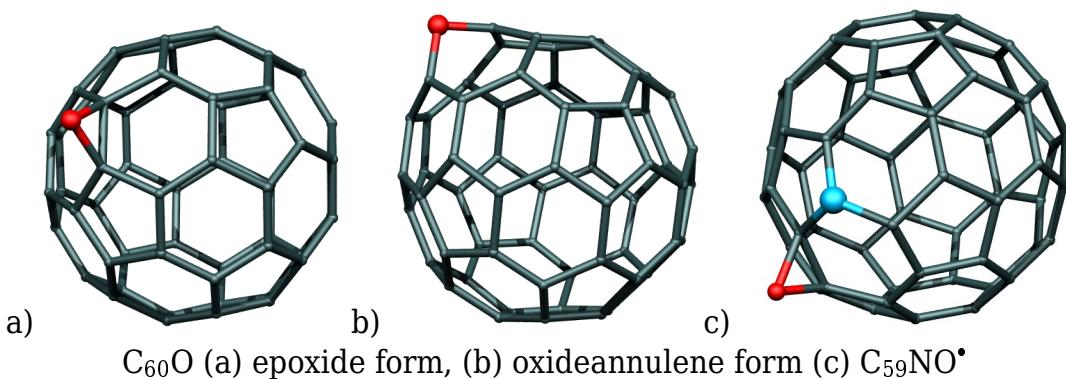
<sup>92</sup> N. P. Curry, B. Doust, D. A. Jelski, *J. Cluster. Sci.* **12**, 385 (2000).

showing that the reactivity of buckminsterfullerene with oxygen is local, and 6,6-double bonds adjacent to an existing epoxide functionality are more easily oxidized than the others.<sup>92</sup>

However much less is known about the oxidation behaviour of heterofullerenes, and this is the motivation behind the results presented in the following sections.

### Fullerene and azafullerene Oxidation

For C<sub>60</sub> we find the epoxide and oxideannulene forms have identical formation energies within the error of our calculations (with slight preference for the oxideannulene), in agreement with previous theoretical studies.<sup>92,93,94,95</sup> Oxidation is exothermic, 1.13eV using C<sub>60</sub> and O<sub>2</sub> as reference states.



Due to its lower symmetry, C<sub>59</sub>N<sup>•</sup> has many more potential oxidation sites. Unlike C<sub>60</sub>, we find the most stable structures are the epoxides. The most stable form for C<sub>59</sub>NO<sup>•</sup> is with epoxide oxygen over a hex-hex backbond of one of the pentagonal carbon neighbours of the nitrogen (Figure c above). The epoxide forms over the closest double bond to the nitrogen, and the exothermicity, at 1.16eV, is almost identical that of C<sub>60</sub>O. However there is almost no variation in exothermicity with choice of double bond site (less than 0.22eV). Sites next to the nitrogen atom are less stable (1.13eV in the hex-pent bonds, endothermic by +0.08eV in the N- $\alpha$ C hex-hex bond), and bonding the oxygen directly to the nitrogen is strongly endothermic (+1.41eV).

Thus oxidation behaviour for C<sub>59</sub>N<sup>•</sup> appears similar to that of C<sub>60</sub>, with similar exothermicities and preferential oxidation of carbon double bonds on the fullerene cage avoiding the immediate proximity of the nitrogen atom.

### Phosphorus doped fullerenes

There is only one experimental demonstration of the analogous phosphofullerenyl radical C59P<sup>•</sup>,<sup>96</sup> with no information in the literature concerning any equivalent dimerisation processes. Phosphofullerenes, primarily C<sub>59</sub>P, have been grown by simultaneous evaporation of phosphorus and carbon in a radiofrequency furnace, observed by mass spectrometry.<sup>96</sup> Mass spectrometry of as-grown phosphofullerenes high temperature synthesised from graphite and phosphorus found a range of species, the most common being C<sub>59</sub>P, C<sub>59</sub>PO, with weaker signals from C<sub>58</sub>P<sub>2</sub>. C<sub>59</sub>P<sup>+</sup> has been studied theoretically by a number of groups,

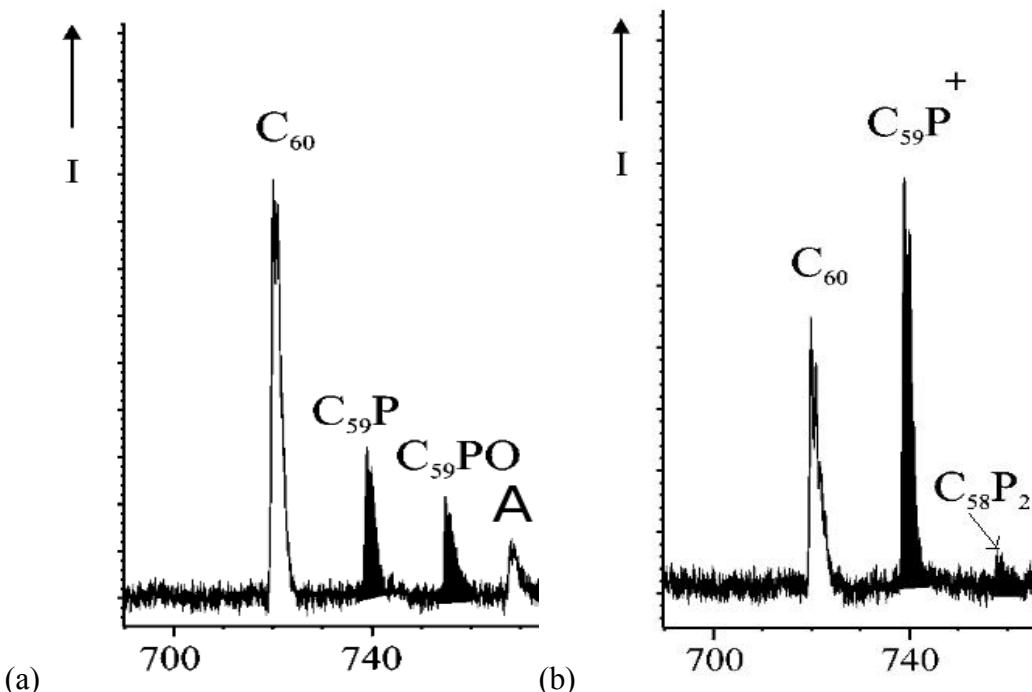
<sup>93</sup> M. Manoharan, J. Org. Chem. 65, 1093 (2000).

<sup>94</sup> D. L. Kepert, B. W. Clare, Inorg. Chim. Acta 327, 41 (2002).

<sup>95</sup> B. Wang, L. Chen, J. Mol. Struct. (theochem) 469, 127 (1999).

<sup>96</sup> C. Möschel, M. Jansen, Z. anorg. Allg. Chem. 625, 175 (1999).

showing a total energy per atom relative to  $C_{60}$  of 0.37eV, significantly lower than that for  $C_{59}N$  (1.82eV) but nonetheless the second most stable  $C_{59}X$  species considered, with the lowest dipole moment.<sup>97</sup>



*Mass spectra for phosphorus doped fullerene synthesis, (a) negative ions, (b) positive ions (in both cases all peaks correspond to  $|z|=1$ , x-axis is  $m/z$ ). The  $C_{59}PO$  peak is only present as a negative ion. Its presence, despite no deliberate introduction of oxygen to the system, shows the strong affinity of oxygen for  $C_{59}P$ . Peak 'A' is due to  $C_{64}$ . Taken from Reference<sup>96</sup>.*

Given the large atomic radius of P (0.98Å, compared to 0.67Å for carbon and 0.56Å for nitrogen) it is no surprise the  $C_{59}P^\bullet$  radical shows distortion from the perfect sphere ( $C_s$  symmetric structure with P-C bonds of 1.76 and 1.80Å). Substitution is endothermic (+0.65eV) with respect to  $C_{60}$  and  $P_4$ .<sup>26</sup>  $C_{59}P^\bullet$  forms a stable dimer,  $(C_{59}P)_2$  bisphosphofullerene with 2.02eV binding energy and 1.878Å bond between the two  $\alpha$ -carbons.

Unlike the azafullerenes, initial oxidation of  $C_{59}P^\bullet$  is dominated by the phosphorus atom, which traps and strongly binds an oxygen atom to form a phosphine oxide fullerene radical  $C_{59}PO^\bullet$ . This is highly exothermic (2.90eV) and suggests once oxygen is bound at this site it will be difficult to remove by simple heating. This is in agreement with the experimental observation of a strong  $C_{59}PO$  signal in mass spectrometry of synthesis products, despite using an oxygen-free synthesis environment, in contrast to azafullerene behaviour.<sup>98</sup> Phosphine oxide formation is commonly observed for organic phosphides, and is consistent with a study of high temperature mixing of  $C_{60}$  and P, which resulted in a highly oxidised phosphorus-carbon material with XPS data showing evidence of P-O bonds.<sup>99</sup>

<sup>97</sup> T. M. Simeon, I. Yanov, J. Leszczynski, Int. J. Quantum Chem. 105, 429 (2005) and references therein.

<sup>98</sup> S. Glenis, S. Cooke, X. Chen, M. M. Labes, *Chem. Mater.* **6**, 1850 (1994).

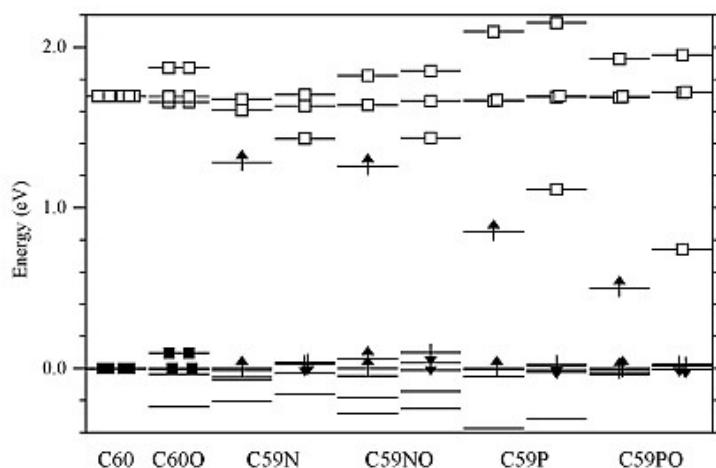
<sup>99</sup> N. Feldtner, W. Brockner, P. Scharff, M. M. Dadras, *J. Non Cryst. Solids* **333**, 301 (2004).

Further oxidation of  $C_{59}PO^\bullet$  to  $C_{59}PO_2^\bullet$  occurs as for  $C_{60}$  and  $C_{59}N^\bullet$ , reinforcing the idea that the phosphorus chemistry is largely decoupled from that of the fullerene cage. Regardless of synthesis route, the stable phosphofullerene radical will not be  $C_{59}P^\bullet$ , but  $C_{59}PO^\bullet$ .

Molecule	Oxidation Exothermicity (eV)	Oxygen bonding arrangement
$C_{60}$	-1.13	epoxide and oxideannulene
$C_{59}N$	-1.16	Epoxide
$C_{59}P$	-2.90	Directly to P
$C_{59}PO$	-1.21	Epoxide

*Summary of calculated exothermicities for oxygen addition to various fullerene derivatives*

The figure below shows calculated eigenvalues for many of the fullerene derivatives discussed here. Note the singly occupied molecular orbital (SOMO) of  $C_{59}PO^\bullet$  lies in the lower half of the gap. This suggests that while  $C_{59}N^\bullet$  and  $C_{59}NO^\bullet$  (whose SOMOs lie very close to the LUMO) will behave as donors,  $C_{59}P^\bullet$  has a deep lying SOMO and so could in principle act as either donor or acceptor, and  $C_{59}PO^\bullet$  will act as an acceptor. This is consistent with the mass spectra data where peaks for  $C_{59}P^\bullet$  are seen for both positive and negatively charged species, while the  $C_{59}PO^\bullet$  peak is only seen amongst the negative charged species.<sup>96</sup>



Calculated eigenvalues (eV) for (a)  $C_{60}$  (b)  $C_{60}O$  (c)  $C_{59}N^\bullet$  (d)  $C_{59}NO^\bullet$  (e)  $C_{59}P^\bullet$  (f)  $C_{59}PO^\bullet$ . HOMOs have been aligned at 0.0eV for clarity. Filled (empty) squares indicate filled (empty) levels. Arrows indicate filled states for spin polarised calculations.

It is tempting to propose that the oxygenated phosphor group may have implications for phosphofullerene dynamics due to potential steric hindrance within the crystal. For example we initially wondered whether it might encourage breakage of the  $\alpha$ -C bond in the dimer, resulting in a crystal of heterofullerene radicals, each with net dipole moment. However the dimer bond remains strong, and even calculations of heterofullerene dimers with bulkier side groups ( $C_{59}PS-C_{59}PS$ ) show the  $\alpha$ -C bond remains unbroken.

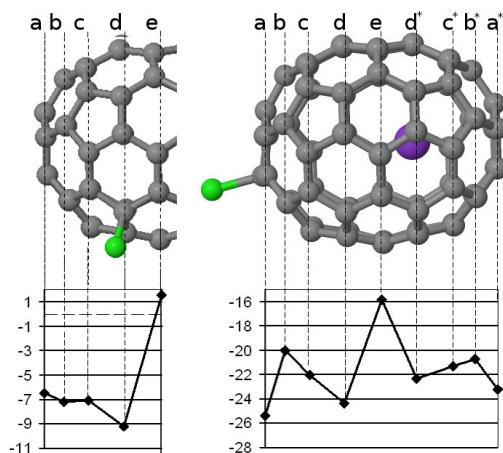
## Summary and Conclusions on Fullerene doping

To conclude this section, we have examined the reaction chemistry of both aza- and phosphor-fullerenes, exploring their interaction and hydrogenation with temperature, as well as their oxidation behaviour.

We have investigated the high-temperature transformations of hydroazafullerene  $C_{59}HN$  by DFT calculations, EPR spectroscopy and TEM microscopy. Evidence for a unique intermediate phase characterized by  $C_{59}N-C_{59}HN^\bullet$  bonding was found. The unpaired spin density shifts away from the  $C_{59}N^\bullet$  radical to a bonded  $C_{59}HN$  fullerene cage, as seen in both Mulliken population analysis and EPR spectra. This structure appears to be remarkably stable even at temperatures as high as 500 K and even after losing its second hydrogen atom. Further high temperature treatment is needed to gradually transform to a known bisazafullerene  $(C_{59}N)_2$  dimer.

In general azafullerene oxidation is similar to that of pristine  $C_{60}$  but with increased preference for epoxide bonding. Notably for the azafullerene  $C_{59}NH$  and its radical  $C_{59}N^\bullet$  there is poor interaction between oxygen and the heteroatom. However the phosphofullerene  $C_{59}PH$  and its radical  $C_{59}P^\bullet$  form phosphine oxides, with non-labile oxygen addition to the phosphorus atom. This drops the SOMO of the radical sufficiently that the molecule becomes an acceptor rather than a donor. We suggest that the stable phosphofullerenes are likely instead to be phosphine oxide forms.

I mention in passing our latest results where we have examined chlorination of  $C_{70}$  and  $K@C_{70}$ , a metallic endofullerene ( $C_{70}$  containing a single K atom). The calculations successfully reproduced experimental ‘magic number’ isomers such as  $C_{70}Cl_{10}$ , and show that  $K@C_{70}$  shows very different chlorination behaviour to its parent fullerene (different reaction pathways and magic isomer numbers). This suggests all bets are off for the chemistry of metallic endofullerenes as compared to conventional fullerene chemistry, and it would be interesting to now investigate metallic endo-heterofullerenes such as  $K@C_{59}NH$ .



*The energy landscape (kcal/mol) of the different positions for initial chlorine atom addition reaction for  $C_{70}$  and  $K@C_{70}$ .*

## Section 6: Generalising to other nanoforms

In his book, “The Periodic Table”, Primo Levi says: “every element says something to someone (something different to each) [...] one must perhaps make an exception for carbon, because it says everything to everyone”<sup>100</sup>. Carbon is, indeed, an extraordinary element. The electronic configuration of  $1s^2\ 2s^2\ 2p^2$  allows carbon atoms to form three different types of bonding, i.e. single, double and triple bonds. This versatility of carbon to bond with other atoms is based on the fact that carbon can hybridise its 2s and 2p atomic orbitals in three different manners:  $sp^3$  (for single bonding, tetrahedral),  $sp^2$  (for double bonding, trigonal planar) and  $sp$  (for triple bonding, linear).

Thus far we have considered defect and functionalisation behaviour in graphite, graphene, nanotubes and fullerenes on an individual case-by-case basis. However these species represent only a small fraction of the vast array of  $sp^2$ -hybridised carbon forms, particularly once  $sp^2$ -based amorphous carbons are also considered. Even though all these forms are primarily based on  $sp^2$  hybridised carbon atoms, their chemistry can vary dramatically<sup>101</sup>.

I developed the following figure with Irene Suarez and Nicole Grobert which demonstrates some of the  $sp^2$ -based carbon nanoforms and links them based on their underlying topology:

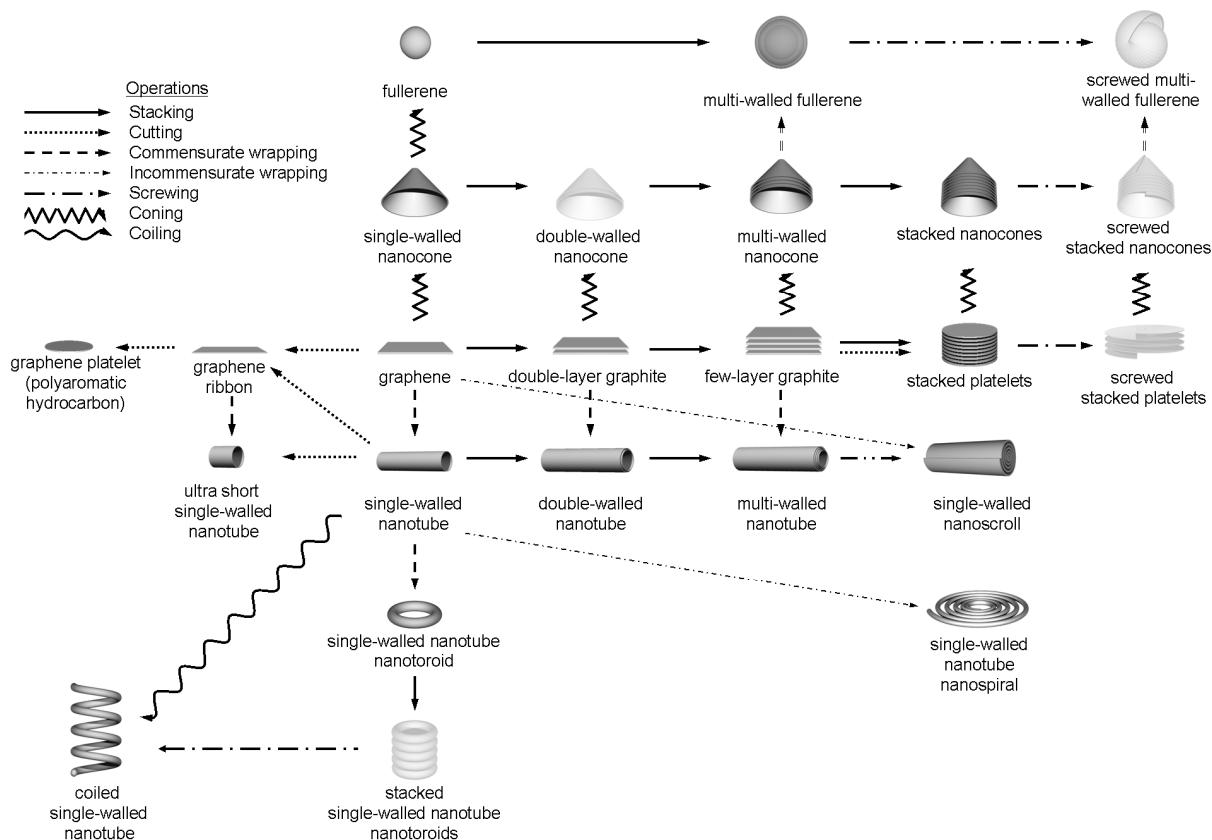


Figure 1 : Family of carbon nanoforms, grouped by underlying topology and linked by structural operations such as stacking or cutting<sup>102</sup>.

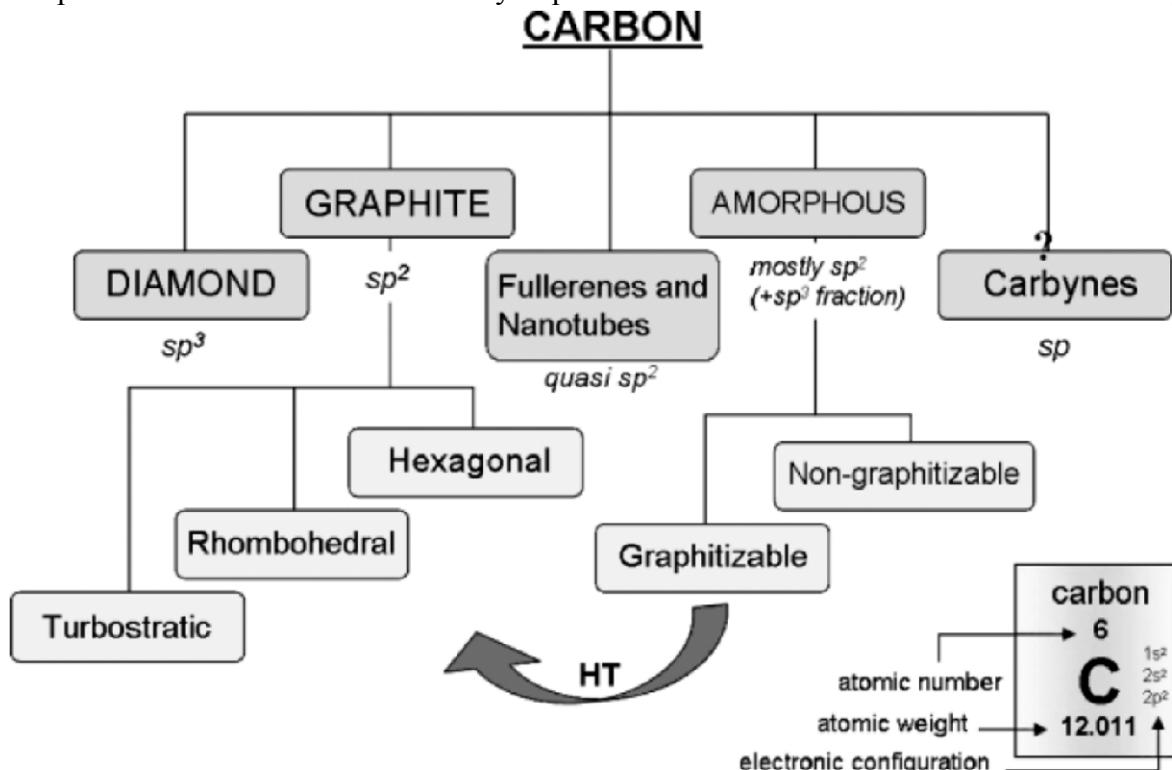
However even this figure only covers a small subsection of carbon nanoforms. Partitioned nanotubes, such as the ‘bamboo’ structured nitrogen-doped multi-walled carbon nanotubes, are extremely common, as well as variants on the stacked-cone fibrous structure such as

<sup>100</sup> P. Levi. The Periodic Table. Schocken Ed. (1995)

<sup>101</sup> Delgado, J. L., Herranz, M. A., Martin, N. The nano-forms of carbon. *J. Mater. Chem.* **18**, 1417 (2008).

<sup>102</sup> I. Suarez-Martinez, N. Grobert, C. P. Ewels, Carbon submitted (2010-2011)

stacked ‘bells’. Finally, as shown in the carbon ‘family tree’ of Falcao *et al.*<sup>103</sup> nanoforms only form one small subset of the  $sp^2$ -based carbon materials, which as well as including graphite and graphite-like carbons also contains the vast family of  $sp^2$ -based amorphous carbons. These remain relatively unexplored theoretically due to their structural complexity, yet represent one of the most industrially important sectors of this vast and rich carbon family.

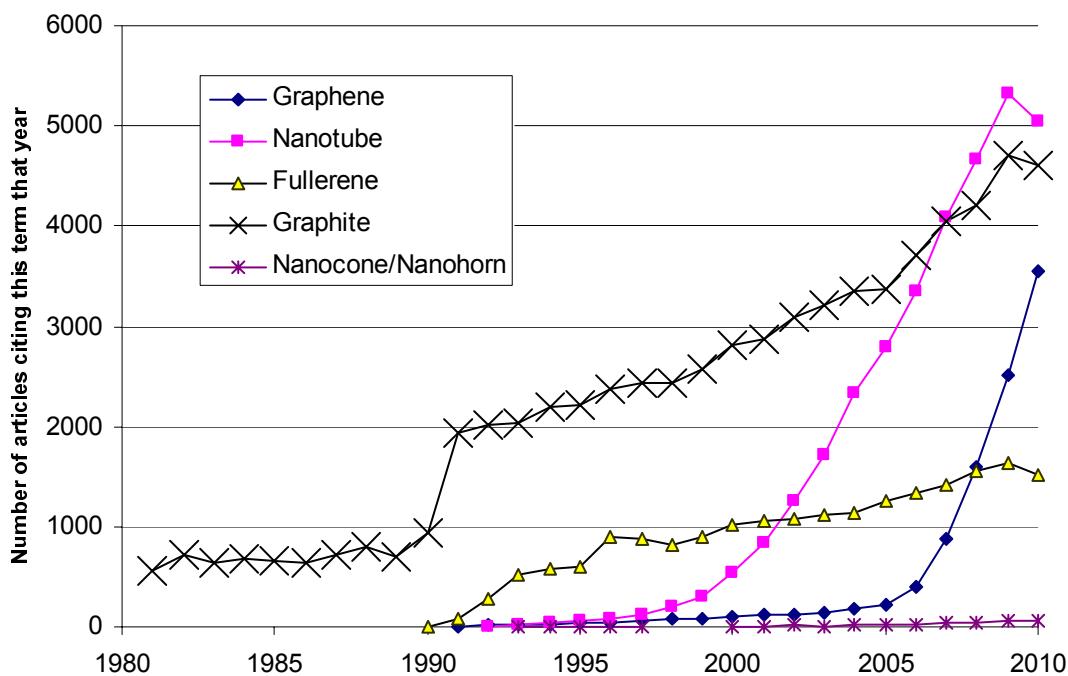


Summary of different carbon forms, taken from Reference <sup>103</sup>.

It is clear from this brief overview that the current status of theoretical modelling of structural behaviour and reactivity for nanoscale carbons is extremely restricted in its scope, remaining largely confined to fullerenes, simple cylindrical nanotubes, and individual graphene layers. In addition, most studies confine themselves to the properties of a single given nanoform.

Having worked on different carbon materials, starting with graphite, but moving through the arrival of fullerenes at the end of the 1980s, followed by nanotubes and more recently graphene, it is possible to observe certain trends in the output of the research community. There is often a tendency to “rediscover the wheel” on arrival of a new carbon form. After the “gold rush” of initial studies of physical and electronic behaviour of the pristine form, there is typically a second wave of studies which start to examine chemical functionalisation and changes in behaviour on introduction of defects. Another surge follows once the carbon form is no longer of such intrinsic novelty value, and instead has properties which start to become routinely exploited in hybrid/composite applications, i.e. the carbon object becomes just another ingredient in a more complex system. Fullerenes and nanotubes both then spawned a secondary research community exploring structural analogues developed from other layered (typically inorganic) materials, and the same is now beginning for graphene. Surprisingly there is often much less overlap and “cross-talk” between these research communities than one might expect. Much of what has been discovered concerning behaviour under irradiation of carbon nanotubes is very similar to that known for irradiated graphite. Are there lessons we can learn from this, anticipating the arrival of future carbon nanoforms?

<sup>103</sup> E. H. L. Falcao, F. Wudl, J. Chem. Tech. And Biotech. 82:524-531 (2007)



Articles from “Web of Science” citing the terms listed, published per year. Key dates are visible such as the boost in graphite articles associated with the arrival of nanocarbons, the jump in fullerene publications in 1996 with the Nobel prize, the incredible rise of graphene articles (possibly, in 2010, at the expense of the other carbon materials?) The graphite ‘tail’ is long, to 1 article in 1900. Note duplication is not as high as might be expected, for example in 2010 only 270 articles cited both ‘graphite’ and ‘nanotube’.

While it is important to investigate these materials individually, the field is limited by a lack of predictive models applicable to multiple forms. An underlying framework capable of quantitatively extracting chemical behaviour such as oxidation response directly from atomic structure would be useful. Previous studies have examined C-C bond reactivity in carbon nanotubes, considering local structural parameters such as nanotube diameter<sup>104</sup>, pyramidalisation angle ( $\theta_p$ )<sup>105</sup>  $\pi$ -orbital misalignment angle ( $\phi$ ) and local bond curvature<sup>106,107</sup>. However most are limited in the information they provide and none have successfully provided a generic transferable measure of bond reactivity for different nanoforms.

In this section I describe a generic geometric model for early stage nanoform oxidation based on local curvature, which successfully predicts oxidation enthalpies and epoxide or annulene bonding in graphene, fullerenes and nanotubes. The model is used to examine a new nanoform, carbon nanocones, showing that nanocone oxidation is exothermic around sharp tips but endothermic on the sidewalls. The model provides a rapid, useful tool for predicting chemistry in carbon nanomaterials.

### Single oxygen atom addition

Single oxygen atom addition was the first functionalisation observed in fullerene chemistry<sup>108</sup>. As discussed in more detail in Section 5, two isomers of  $C_{60}O$  are possible: the closed epoxide form on the bond between two hexagons ([hex:hex] bond), where the underlying C-C bond beneath the oxygen is slightly dilated, and the annulene form (the ether oxa-homo[60]fullerene) on a pentagon-hexagon ([pent:hex]) bond, where the underlying C-C

<sup>104</sup> Lu, L. et al. *J. Mol. Struct. (THEOCHEM)* **725**, 255 (2005).

<sup>105</sup> Niyogi, S. et al., Chemistry of Single-Walled carbon nanotubes. *Acc. Chem. Res.* **35**, 1105 (2002).

<sup>106</sup> Li, J., Jia, G., Zhang, Y., Chen Y., *Chem. Mater.* **18**, 3579 (2006).

<sup>107</sup> Miyata, Y., Kawai, T., Miyamoto, Y., Maniwa, Y., Kataura, H., *Phys. Stat. Sol. B* **244**, 4035 (2007)

<sup>108</sup> Diederich, F., et al. *Science* **252**, 548 (1991)

bond is clearly broken. The annulene form is much harder to obtain since its kinetic reaction barrier for oxygen addition is 60% higher than for the epoxide<sup>109</sup>, due to the rupture of a  $\sigma$ -like bond. The epoxide form can easily be obtained by photo-oxidation of C<sub>60</sub><sup>110</sup> or the reaction of C<sub>60</sub> with dimethyldioxirane<sup>111</sup>, however the annulene form requires photolysis of C<sub>60</sub>O<sub>3</sub> prepared by ozonating C<sub>60</sub><sup>112</sup>.

Oxidation of graphene requires more aggressive methods such as plasma treatments<sup>113</sup>. Indeed, pristine (defect-free) graphene is inert to O<sub>2</sub> up to 875°C<sup>114</sup>. Instead graphene oxidation most probably occurs through defects such as vacancies<sup>113,115</sup>.

Carbon nanotube oxidation also requires aggressive methods and normally involves tube damage and mass loss<sup>116</sup>. Those methods, such as plasma or acid treatments, can however improve the reactivity of the carbon nanotube<sup>117</sup>. Little is known of the oxidation behaviour of, for example, carbon nanohorns (nanocones)<sup>118,119</sup>, and their low structural symmetry means they have been difficult to study theoretically.

Here we compare the first stage of oxygen addition to pristine graphene, fullerenes, and nanotubes, using oxygen as a simple test case for bond functionalisation. We derive a general predictive rule for bond chemistry based only on local geometry, confirming the model via oxidation of carbon nanocones. In a fraction of second this geometric model accurately predicts the results of density functional calculation taking typically several days.

## Computational Approach

As in previous chapters, we use the density functional code AIMPRO<sup>120,121</sup> within the Local Density Approximation (LDA). The LDA gives O<sub>2</sub> binding energy to graphene as well as O<sub>2</sub> singlet/triplet energy differences closer to experiment than the generalized gradient approximation<sup>122</sup>. Nanotubes are described via a supercell of 5 primitive unit cells, while graphene is simulated using an 8x8 supercell. Nanocones considered were <sup>1</sup>C<sub>310</sub>H<sub>40</sub>, <sup>2a</sup>C<sub>274</sub>H<sub>34</sub>, <sup>2b</sup>C<sub>272</sub>H<sub>34</sub>, <sup>3</sup>C<sub>234</sub>H<sub>28</sub>, <sup>4</sup>C<sub>189</sub>H<sub>21</sub>, <sup>5</sup>C<sub>153</sub>H<sub>15</sub> and <sup>6</sup>C<sub>128</sub>H<sub>10</sub>, where the superscript indicates the number of pentagons in the structure. For molecules such as oxygen, fullerenes and nanocones, supercells were large enough to avoid interaction between molecules in neighboring cells. Structures were geometrically optimized, with a single  $k$ -point for the molecules, a 1x1x2 grid for the nanotubes and a 2x2x2 for graphene. Hartwigsen, Goedecker and Hutter relativistic pseudopotentials were used for all atoms<sup>123</sup>. Atom-centered Gaussian basis functions are used to construct the many-electron wave function with angular momenta up to  $l=2$  (22 independent functions per C atom, 40 per O, 12 per H). Electronic level occupation was obtained using a Fermi occupation function with  $kT = 0.04$  eV.

<sup>109</sup> Shang, Z., Pan, Y., Can, Z., Zhao, X., Tang, A. *J. Phys. Chem. A* **104**, 1915 (2000).

<sup>110</sup> Creegan, K.M. et al., *J. Am. Chem. Soc.* **114**, 1103 (1992).

<sup>111</sup> Elemes, Y. et al., *Angew. Chem. Int. Ed. Engl.* **31**, 351 (1992).

<sup>112</sup> Weisman, R. B., Heymann, D.M, Bachilo, S. *J. Am. Chem. Soc.* **123**, 9720 (2001).

<sup>113</sup> Hahn, J.R., Kang, H., Lee ,S.M, Lee, Y.H. *J. Phys. Chem. B* **103** (45), 9944 (1999)

<sup>114</sup> Hahn, J. R. Kinetic study of graphite oxidation along two lattice directions. *Carbon* **43**, 1506 (2005).

<sup>115</sup> Carlsson, J. M., Hanke, F., Linic, S., Scheffler, M. *Phys. Rev. Lett.* **102**, 166104 (2009).

<sup>116</sup> Dujardin, E., Ebbesen, T.W., Krishnan A., Treacy, M.M.J. *Adv. Mater.* **10** (8), 611 (1998)

<sup>117</sup> Suarez-Martinez, I. et al., *Carbon* **47**, 1549 (2009).

<sup>118</sup> Yoshida, S. & Sano, M. *Chem. Phys. Let.* **433**, 97 (2006)

<sup>119</sup> Pagona, G., Tagmatarchis, N., Fan, J., Yudasaka, M., Iijima, S. *Chem. Mater.* **18** (17), 3918 (2006).

<sup>120</sup> Briddon P. R., Jones, R. *Phys. Stat. Sol. B* **217**, 131 (2000).

<sup>121</sup> Rayson, M. H. , Briddon, P. R. *Comput. Phys. Commun.* **178**, 128 (2007).

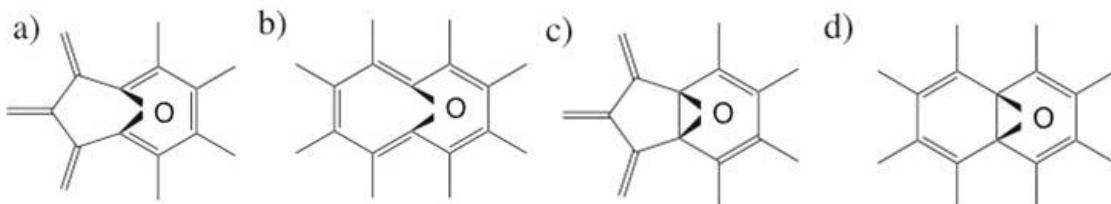
<sup>122</sup> Giannozzi,P., Car R., Scoles, G. *J. Chem. Phys.* **118** (3), 1003 (2003).

<sup>123</sup> Hartwigsen, C., Goedecker, S., Hutter, J. *Phys. Rev. B* **58**, 3641 (1998).

In the energetic analysis that follows, reaction enthalpies are calculated as the energy difference between the oxidized carbon nanoform and the sum of energy of the non-oxidized form and the O<sub>2</sub> molecule in the stable triplet state, *i.e.* E<sub>R</sub> = E(Form-O) - E(Form) - ½ E(O<sub>2</sub>). Thus E<sub>R</sub> provides a measure for the exothermicity of oxidation. Calculations are carried out on the addition of a single oxygen atom on all probable different bonds for each structure.

### **Oxidation of conventional carbon nanoforms**

In agreement with previous literature, two isomers are found for the C<sub>60</sub> oxide (C<sub>60</sub>O)<sup>124,125</sup>. Oxidation of the [pent:hex] bond results in the 1,5-oxido[9]annulene structure (Figure a below) where the C-C distance is 2.13 Å. Oxidation of the [hex:hex] bond results in the epoxide isomer (Figure c below) with C-C bond of 1.53 Å. The enthalpy of reaction E<sub>R</sub> of these two forms is roughly the same (-1.16 and -1.17 eV respectively).



*Isomers of an oxidised polycyclic aromatic bond: a) 1,5-oxido[9]annulene b) 1,6-oxido[10]annulene, c) epoxide on a [pent:hex] bond and d) epoxide on a [hex:hex] bond. These represent “extreme” cases with pure single- and double-bonds. In reality the bond order is a function of local curvature and aromaticity (see text).*

In graphene all the bonds are equivalent and only one isomer is possible. Single oxygen atom addition results in the epoxide form and is endothermic with formation energy of +0.50 eV, consistent with the observed thermal stability of pristine (defect-free) graphene in air.

For armchair and zigzag nanotubes, C-C bonds can be classified as circumferential or axial depending on which of these orthogonal directions is closest to the bond orientation. While the length difference between those two types of bonds is insignificant, the difference in bond orientation results in different functionalisation behaviour. Oxidation of axial bonds always results in epoxide structures. On the other hand, for small diameter tubes (<~18 Å), oxidation of circumferential bonds breaks the underlying C-C bond giving the annulene form. This is always energetically favoured over axial epoxide bonding since the annulene releases some of the strain energy of these smaller diameter tubes. For tubes of diameter larger than 18 Å, all bonds oxidize to the epoxide form (close to a previous literature value<sup>104</sup>). As diameter increases the formation energies converge on the value for graphene.

### **Predicting oxidation behaviour from local curvature**

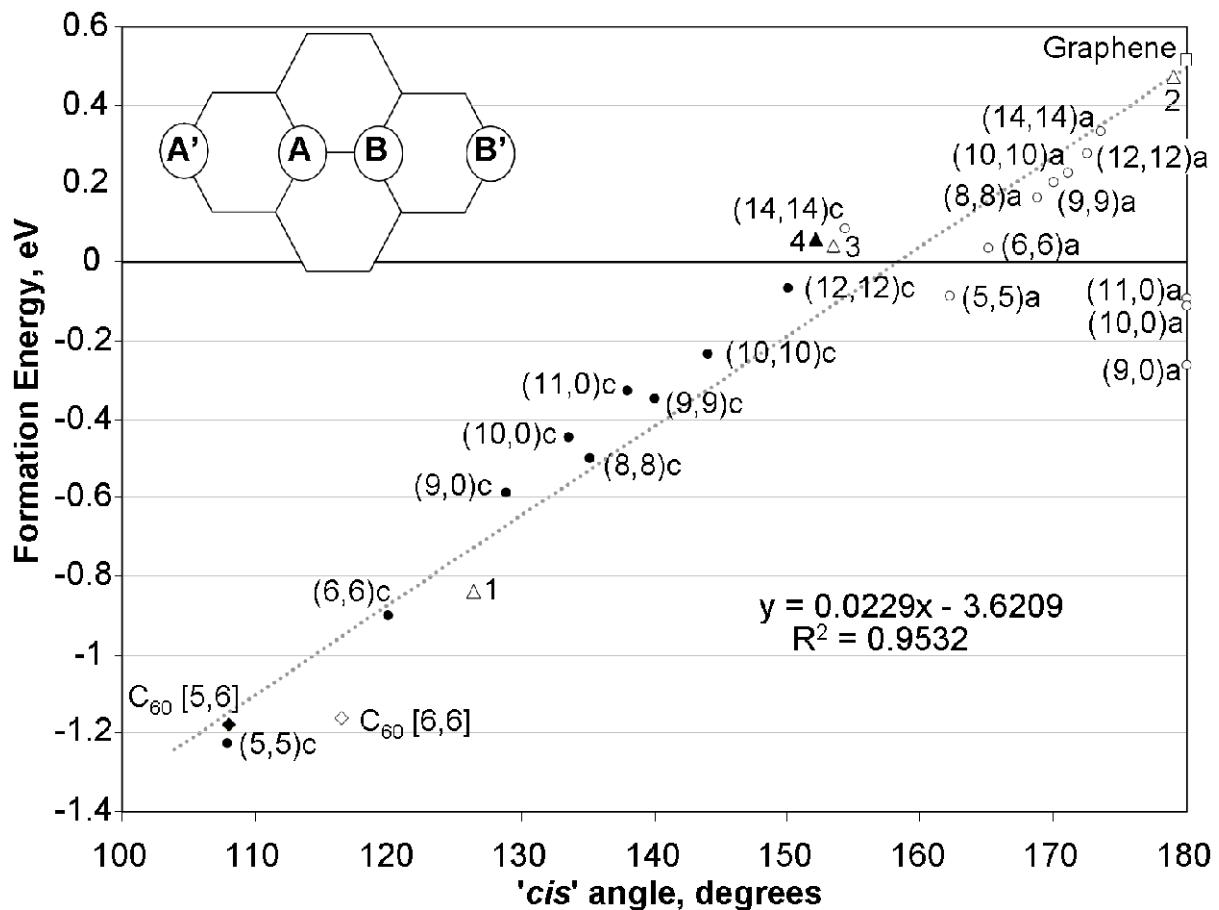
In order to predict oxidation behaviour of a bond from its local environment we considered a range of possible local geometric parameters. Local variations in bond length are insignificant in most nanotube and nanocone walls, and thus bond length is not sufficient to predict the bond oxidation chemistry. Pyramidalisation angle is atom specific and gives no information on, for example, bonds at different orientations to a nanotube axis. Nanotube diameter and local bond curvature are not transferable to other nanoforms, and our DFT

<sup>124</sup> Steckel, J., Jordan, K., Avouris, P. Oxygen Atom Reactions with Circumtrindene and Related Molecules: Analogues for the Oxidation of Nanotube Caps. *J. Phys. Chem. A* **106** (11), 2572 (2002).

<sup>125</sup> Raghavachari, K. & Sosa, C. Fullerenes derivatives – Comparative theoretical study of C<sub>60</sub>O and C<sub>60</sub>CH<sub>2</sub>. *Chem. Phys. Lett.* **209** (3), 223 (1993)

calculations show that bonds in the nanocone walls do not necessarily exhibit the same oxidation behaviour as bonds in a nanotube of an equivalent local curvature.

Instead we have been able to quantify local curvature and reactivity via a new geometric parameter we term the ‘cis’-angle of a bond. We define this for the bond AB in the inset of the following figure as the angle between the vectors A’A and B’B projected onto an averaged plane, *i.e.* the angle between two vectors, each formed from the position of one atom in a given C-C bond and its associated cis- position atom in the polygon behind it (not containing the second atom of the C-C bond). When for example the left polygon is a pentagon, the point A’ is taken as the midpoint of the opposing bond within the polygon. Unlike  $\pi$ -orbital misalignment angle ( $\phi$ ), the ‘cis’- angle is primarily linked to misorientation of  $p_z$ -orbitals along the bond rather than perpendicular to it. Additionally it incorporates information concerning the curvature of the surrounding lattice. It varies from  $\sim 93^\circ$  for small fullerenes such as  $C_{28}$  to a maximum of  $180^\circ$  for graphene.

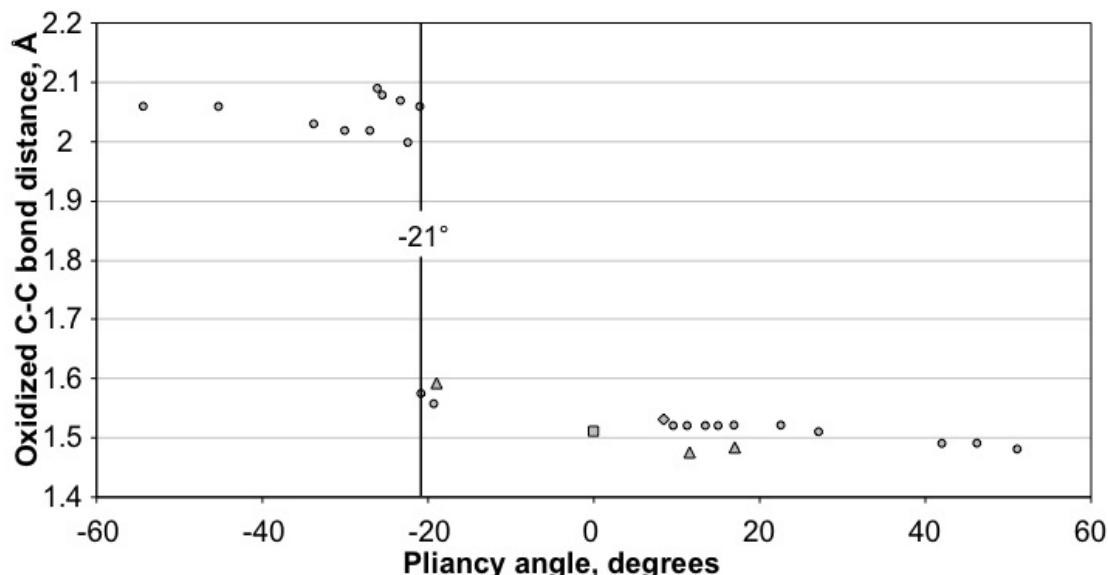


Enthalpy for C-C bond oxidation (eV) versus the associated ‘cis’-angle ( $^\circ$ ) for bonds in graphene (square), fullerenes (diamonds), nanotubes (circles) and a 2-pentagon nanocone (triangles). Filled points indicate that oxidation results in an annulene form, empty points indicate that the form is an epoxide. For definition of cis-angle, see text.

The above figure shows the variation of oxidation enthalpy with ‘cis’-angle for C-C bonds in all studied nanotubes (circles),  $C_{60}$  (diamonds) and graphene (square). Oxidation enthalpy is directly proportional to the ‘cis’-angle, giving a linear fit within the calculation error. Oxidation only becomes exothermic for ‘cis’-angles of less than  $\sim 165^\circ$ , corresponding to nanotubes of diameters  $<\sim 16$  Å (armchair tubes smaller than (13,13)). The only special case for which ‘cis’-angle is not proportional to oxidation enthalpy is for C-C bonds along the axis of zigzag nanotubes, which necessarily all give the same ( $180^\circ$ ) ‘cis’-angle.

While the ‘*cis*’-angle gives information on the thermodynamics of oxidation, it does not distinguish the bond oxidation chemistry (epoxide or annulene). This is of key importance since the different kinetics of these two functionalisations can determine whether oxidation occurs or not.

For this reason we next consider a second geometric parameter we refer to as the ‘*pliancy angle*’, defined as the difference between the ‘*cis*’-angle of a bond and the average of the *cis*-angles of its four adjacent bonds. The pliancy angle reflects the relative reactivity of a bond compared to its neighbours, since epoxide and annulene formation require significantly different distortion of the neighbouring lattice. It clearly separates [hex:hex] bonds into two families: those with a pliancy angle of less than  $-21^\circ$  oxidize to the annulene form, the rest to epoxides (see Figure below). Full DFT geometry optimization of oxidized C<sub>60</sub>, C<sub>70</sub> and nanocones with 1, 2 and 6 pentagons confirm that [hex-pent] bonds always oxidize into the annulene form.



*Variation of C-C bond length ( $\text{\AA}$ ) between two hexagons after oxygen addition to the bond, with respect to the pliancy angle of the same bond prior to oxidation, for bonds in graphene (square), fullerenes (diamonds), nanotubes (circles) and a 2-pentagons nanocone (triangles).*

*The pliancy angle is defined in the text. For bonds with pliancy angle  $< -21^\circ$  the oxidized bonds form annulenes,  $> -21^\circ$  they are shorter epoxide bonds.*

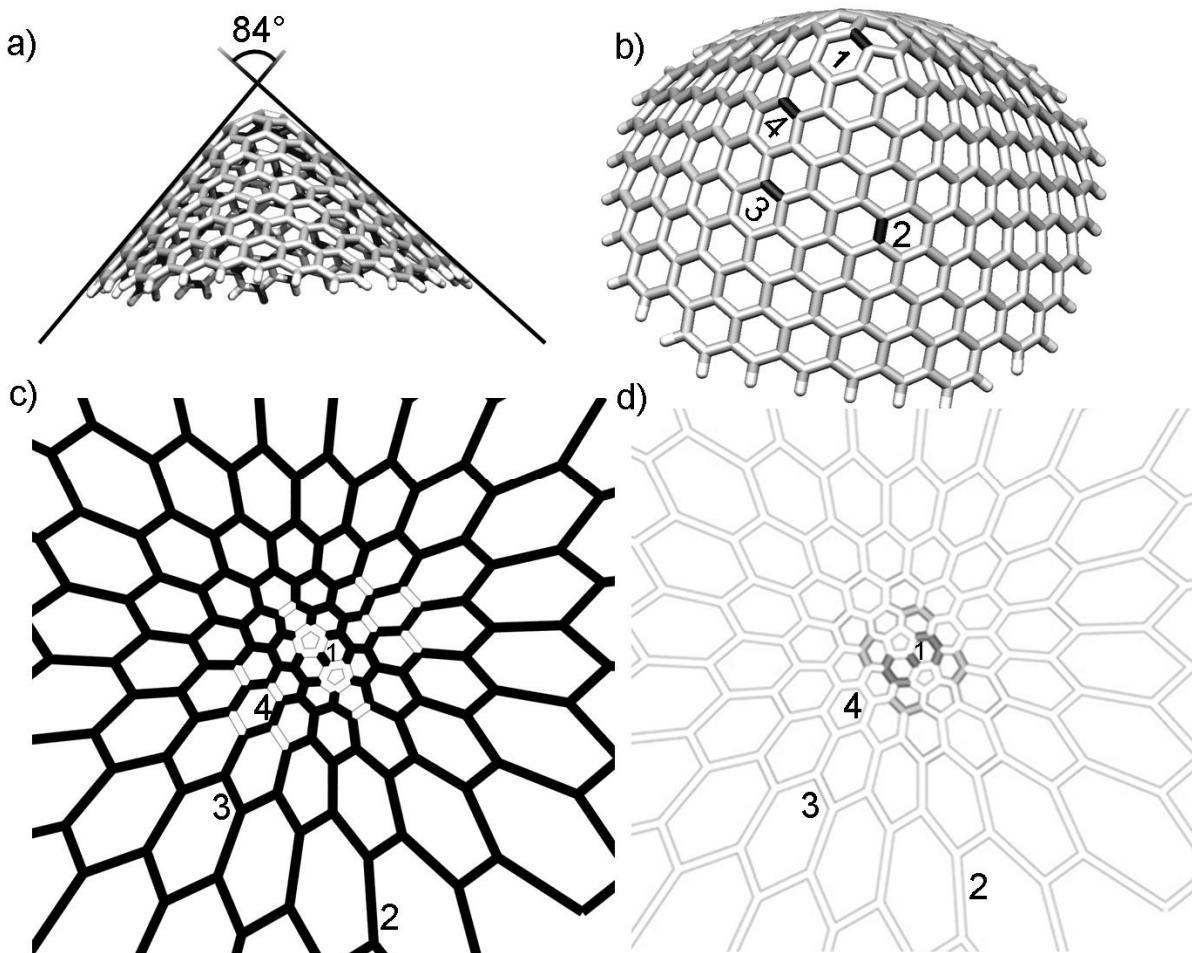
## Carbon nanocones

To determine whether the *cis*- and pliancy angles are genuinely predictive, we next examine carbon nanocones. Carbon nanocones (also referred to as carbon nanohorns) are commonly synthesized via laser ablation<sup>126</sup>. They are  $n \times 60^\circ$  positive wedge disclinations in a graphene layer, and can be visualized as removing  $n$   $60^\circ$  sections from graphene and connecting the exposed edges, forming  $n$  pentagons at the apex.  $n$  is related to the disclination angle ( $\alpha$ ) via  $\alpha = 2\sin^{-1}(1-n/6)$ , and since the number of pentagons must be an integer, nanocones only have tip angles of  $113^\circ$ ,  $84^\circ$ ,  $60^\circ$ ,  $39^\circ$  and  $19^\circ$ , for  $n=1,5$  respectively. The precise location of the pentagons can be varied.

*Ab initio* calculations on nanocones are computationally expensive as they have low symmetry and many atoms. We choose here an  $84^\circ$  cone with two pentagons at the tip

<sup>126</sup> Iijima, S. et al., *Chem. Phys. Lett.* **309**, 165 (1999).

separated by a C-C bond in a model of 274 C atoms and 34 H to saturate the edge ( $^{2a}\text{C}_{274}\text{H}_{34}$ ) (see Figure a below). Preferentially oxidized bonds will be those resulting in epoxide bonds with highest binding energies for oxygen. The cis- and pliancy angles allow predictive mapping of the chemistry of the nanocone, bond by bond.



(a) Side view of a 84° nanocone with two pentagons at the tip separated by a C-C bond. In (b) bonds which have been oxidised and geometrically optimised by DFT are marked in black. (c) Schlegel projection of the nanocone. Using the pliancy angle of each bond, bonds predicted to oxidise to an annulene (epoxide) form are marked in white (black). (d) cis- angle prediction of the enthalpy of oxidation of the bonds predicted to form epoxides: the darker the bond, the more reactive it is to oxidation (for key see following Figure)

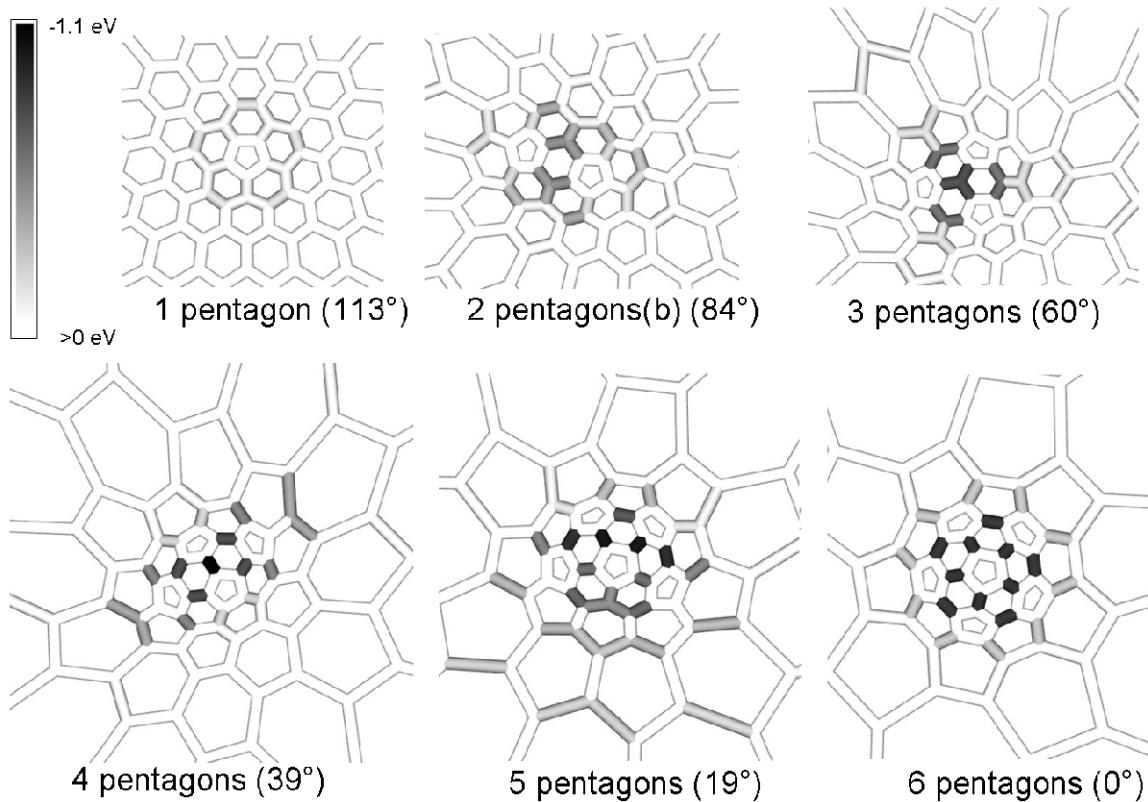
The predicted bond chemistry (epoxide or annulene) for each bond based on the pliancy angle is shown in Figure c above, where bonds marked in white will oxidize into annulene forms and bonds marked in black will result in epoxide forms.

Annulene bonded forms can be excluded due to kinetic limitations in their formation, and the cis- angle next allows us to map the predicted reactivity of the remaining epoxide bonds in the nanocone. Figure d above shows the predicted oxidation enthalpies for epoxide bonds determined from the bond cis-angles, with darker bonds indicating higher predicted reactivity. According to this prediction, the C-C bond at the nanocone tip between pentagons should oxidize to an epoxide structure with binding energy -0.73 eV (bond 1 in Figure b), while oxygen bonding to the nanocone sidewall far from the tip should be endothermic. A few sidewall bonds are predicted to oxidize to annulene forms (white bonds in Figure c).

We tested the prediction by geometrically optimizing multiple oxidized structures using DFT (testing bonds labeled 1-4 in Figure b above), and found excellent qualitative and

quantitative agreement. The [hex:hex] bond at the tip (bond 1 in Figure b above) forms an epoxide with a formation energy of -0.84 eV. On the nanocone sidewalls, [hex:hex] bonds 2 and 4 give endothermic epoxides, while [hex:hex] bond 3 gives an exothermic annulene form. These results are included in the earlier enthalpy and pliancy-angle plots. Thus the cis- and pliancy angles for a bond appear excellent tools for predicting its  $sp^2$ -carbon chemistry.

Other parameters do not provide this quantitative information on functionalisation behaviour of carbon nanoforms. Local variations in bond length are insignificant in most nanotube and nanocone walls, and thus bond length is not sufficient to predict the bond oxidation chemistry. Nanotube diameter and local bond curvature are not transferable to other nanoforms, and our DFT calculations confirm ‘cis’-angle predictions that bonds in the nanocone walls do not necessarily exhibit the same oxidation behaviour as bonds in a nanotube of an equivalent local curvature. Pyramidalisation angle is atom specific and gives no information on, for example, bonds at different orientations to a nanotube axis. The key difference with  $\pi$ -orbital misalignment angle ( $\phi$ ) is that the ‘cis’- and pliancy angles are primarily linked to misorientation of  $p_z$  orbitals *along* the bond rather than perpendicular to it.



*Schlegel projections showing oxidation enthalpy of epoxide forming C-C bonds in different carbon nanocones based on their cis-angle. Bonds oxidising to annulene forms are marked white irrespective of their oxidation thermodynamics due to their kinetically restricted reactivity. Darker bonds will form exothermically stable epoxides and therefore could lead to bridging with other forms such as fullerenes.*

We have calculated the ‘cis’- and pliancy angles for a range of carbon nanocones with different tip angles of 1 to 6 pentagons. The above figure shows which of these bonds will react exothermically to give epoxides: The clustering of reactive bonds observed suggests the presence of oxygen at “fullerene-like” nanocone tips, but not on the pristine sidewalls. Furthermore the figure suggests that oxidation will only be likely at sharper nanocone tips with multiple pentagons in reasonably close proximity.

We have used this technique to study various carbon nanostructures. There are some interesting observations that can be made, for example, the symmetry breaking for the 5-pentagon nanocone as compared to a nanotube cap (6 pentagons) results in a series of quite reactive bonds running down the cone side away from the tip not seen in the 6-pentagon structure. Thus this cone may be more chemically reactive to strongly oxidising species, despite its lower number of pentagons. In C<sub>70</sub> it is possible to see the bonds associated with circumferential functionalisation differentiating themselves from the fullerene caps. These bonds are predicted to be less reactive, in agreement with experimental observation (the only isomers of C<sub>70</sub>O isolated to date all feature O attached to the fullerene caps).

### **Summary of universal oxidation model**

We have compared the early stage oxidation behaviour of C-C bonds in a variety of pristine carbon nanoforms: graphene, fullerenes, nanotubes and nanocones. It is somewhat surprising that although oxidation behaviour depends on both aromaticity and curvature, both in principle long ranged effects, it appears possible to quantitatively predict oxygen binding energy and structure for a non-oxidized bond based on its ‘cis’- and pliancy angles, both relatively localized parameters. Proximity to point defects and edge sites will significantly modify the oxidation behaviour of a C-C bond, but these effects lie outside the scope of the current study. Our DFT calculations show that for graphene, nanotubes and nanocone sidewalls, epoxide oxidation is endothermic, and therefore oxidation behaviour will be controlled by the presence of defects (such as vacancies and divacancies). For tubes of diameter larger than 18 Å all oxidation is epoxide-type, and thus this could be considered a minimum diameter above which nanotube surface chemistry is “graphene-like”.

Epoxide oxidation of fullerenes and sharp-angle nanocone tips is exothermic, with reactive [hex:hex] epoxide bonds present across the whole nanocone tip, and not just adhering to a simple “localised double bond” model (*i.e* [hex:hex] bonds connecting two pentagons). All pentagon bonds tested in a variety of nanoforms were found to give annulene oxidized forms.

The predictive model presented here provides a rapid way to immediately identify the most chemically reactive bonds in a structure, avoiding the need for computationally expensive calculations of oxidized structures. It should be applicable to any kind of curved graphene-based structures (including sp<sup>2</sup>-based amorphous carbons), allowing within seconds a detailed analysis of reaction chemistry for new nanoforms and topologically defective nanostructures (such as dislocations in graphene), studies which with conventional DFT approaches would typically take weeks or months. Importantly, while we used single oxygen atom addition as our test case, the model should also apply to other key chemical “first step” functionalisations of carbon nanomaterials that involve the dilation of an underlying C-C bond, such as the [1+2] cyclo-addition of 1,1-dichlorocarbene<sup>127,128,129</sup>, addition of (COOEt)<sub>2</sub>C and its derivatives<sup>130</sup>, and (R)-oxycarbonylaziridino<sup>131</sup>.

<sup>127</sup> Kamaras, K., Itkis M. E., Hu, H., Zhao, B., Haddon, R. C., *Science* **301**, 1501 (2003).

<sup>128</sup> Hu H., et al., *J. Am. Chem. Soc.* **125**, 14893 (2003).

<sup>129</sup> Chen J., et al., *Science* **282**, 95 (1998).

<sup>130</sup> Coleman, K. S., Bailey, S. R., Fogden, S., Green, M. L. H., *J. Am. Chem. Soc.* **125**, 8722 (2003).

<sup>131</sup> M. Holzinger, et al., *J. Am. Chem. Soc.* **125**, 8566 (2003).

## Section 7 : Future Research

This section of the thesis details my future research plans and strategy in the coming years. It is broken down into sub-sections:

### I. Research Strategy

The practical details of where I intend to work, what political and scientific landscape my work forms part of, and I intend to create.

### II. Research Problems

New materials science problems and directions I intend to tackle.

### III. Research Techniques

New techniques I intend to develop or exploit

### IV. Detailed Example : Graphene

Describing one example research area in more detail.

### V. Science Communication

Future directions for my science communication work

### I. Research Strategy

Before discussing the science projects I intend to pursue, I first briefly discuss general research strategy. I intend to continue my work based at the Institute of Materials in Nantes, for a number of reasons.

The IMN is one of the three largest materials research institutes in France, and contains a wide range of scientific disciplines and techniques. In recent years it has put emphasis on materials modelling, and as a result the laboratory now has four full time *ab initio* theoretical modellers, two numerical modellers, one ‘pencil and paper’ theorist, and several others who spend some of their research time with modelling (plus associated postdocs and PhDs). Critical for me is the *embedding* strategy of the IMN: instead of creating a separate, and potentially isolated, theory group, the researchers working in modelling are distributed throughout the research groups. This facilitates collaboration and cooperation with experimentalists, makes it easier to identify and address pressing experimental problems, and avoids “ghettoisation” of the theoretical research. It particularly suits my research style since I enjoy working closely with experimental groups (often performing experiments myself) and see myself as a Materials Scientist who uses computational tools.



Nonetheless our strength of numbers in applied materials modelling at the IMN means we now have sufficient critical mass to establish a national reputation as a centre of excellence in this area. Towards this aim in 2010 we initiated at the IMN a successful international workshop and materials modelling conference ICAMM, to be repeated biannually. We have been able to pool financial resources for purchase of shared laboratory supercomputer facilities, and are in contact with theoretical modelling groups at Rennes in order to strengthen the Rennes-Nantes materials modelling presence in the north west of France. Within the Institute we are establishing regular internal meetings and presentations for the materials modellers. While there are other laboratories in France with strong reputations for theoretical development, my aim is to help establish the IMN as a world renowned centre for applied atomic scale materials modelling.

The IMN is strengthening its position in the research environment of west france, with “Laboratory of Excellence” and “Equipment of Excellence” applications in place, and key roles in the northwest C’Nano network and theoretical chemistry networks. It is well placed to allow me to develop my future research themes, as one of the three largest materials labs in France and an emerging key player in the restructuring and regrouping of materials-related laboratories in the west of France. The laboratory is very open for internal collaborations, and I now have joint publications with most of the research groups in the lab.

The Physics of nanomaterials group of which I am part includes many specialists in nanocarbon characterisation, notably Prof. Bernard Humbert on optics of nanoscale carbons who is replacing Serge Lefrant on his retirement, and with whom I work well and currently have one joint ANR project and a joint PhD student. Nanocarbon composites are also well represented, notably by Jean-Luc Duvail for mechanically confined polymer-nanotube composites who intends to diversify to other nanoscale carbons in the near future. Also within the IMN Luc Brohan’s group represent acknowledged world-leaders in nanoscale oxide synthesis and characterisation (notably for photoabsorption and storage) which again will form an important axis of my future research (see below).

Where there are gaps in local expertise I have formed contacts with other groups across France. I collaborate with Marc Monthoux at CEMES Toulouse on novel nanoscale carbons and am building links with CRPP Bordeaux (Alain Penicaud and Cecile Zakri) on their nanocarbon synthesis work. For electron microscopy collaboration I still work closely with the LPS Group in Orsay where I spent my Marie Curie fellowship (notably with Alberto Zobelli), and I hope this collaboration will continue and expand in future. I also have good links with Florian Banhart at Strasbourg (via the NanoTP network and with an ANR planned). I am working with MinateC on graphene science (via an ANR) and I have an ANR with groups in Nancy (including Ted McRae) on individual nanotube chemistry and nanotube separation. I am in regular contact with Martine Mayne and Brigitte Bouche-Fabre at CEA Saclay with their expertise in bulk nanotube growth, doping and carbon thin films. In the future I would like to strengthen ties with the theory group of Laurent Pizzigali at Poitiers whose work modelling defects in bulk semiconductors is very complimentary to mine.

Beyond this a key strength of my research activity lies in my European-wide network of collaborations. I collaborate regularly with groups in the UK, Belgium, the Netherlands, Ireland, Spain, Slovenia and Greece amongst others, and we have submitted several European grant applications together in different configurations, including the successful FP6 STREP “Nano<sup>2</sup>hybrids”. These groups represent acknowledged world leaders in different fields – single nano-object transport, gas sensing, plasma treatments, carbon chemistry, TXM, ESR, etc. With Carla Bittencourt I have now established a COST network to provide support to these informal research networks. Many of our joint European projects are either initiated or developed by me, and I organise many European and international meetings (including the annual NanoteC conferences) which act as meeting points for these and other groups to share and develop ideas. I form a key member of an expanding network of theoretical modellers using and developing the AIMPRO code, whose annual meetings are now financially supported through the COST programme. I have been an invited speaker at expert advisory meetings at the EU and given confidential advice on future project calls, and am a member of the Phantoms Nano-ICT committee developing a European Graphene research and applications roadmap. I will continue to develop my leadership role at the European level, with further EU applications planned and I anticipate increasing involvement in policy and call design.

## II. Research Project

Carbon is a material that continually reinvents itself. We have seen this with fullerenes, nanotubes and now graphene, and it would be naïve to imagine the process will stop there.

I see my research very much as a carbon scientist who utilises computational tools, rather than as a theoretical modeller who happens to work with carbon. Such an approach requires extensive collaboration, both with experimental groups in the field of interest, and with groups who are developing new theoretical tools. For this reason the following section detailing directions for my future work focuses primarily on the materials problems I intend to tackle, and my vision of how the discipline will develop. I am assuming that concurrently with this there will continue to be new developments in theoretical modelling techniques that I will have access to, and I have described some of these briefly at the end.

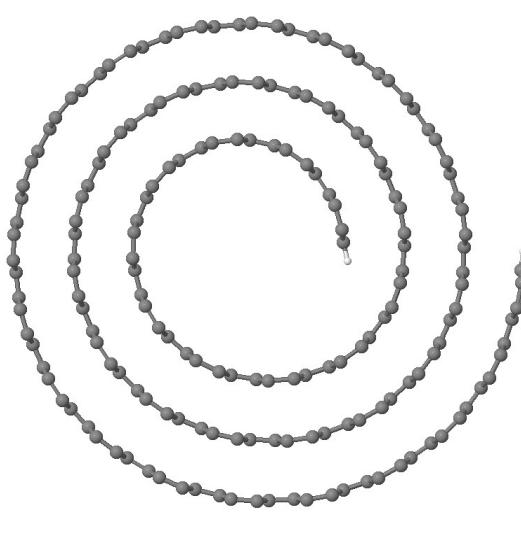
Funding in France is now primarily project based through FP7 and the ANR with a 15-20% success rate, so it is difficult to plan and develop a detailed long-term research programme. Instead I present a range of avenues to be explored, with common general themes, which can then be developed depending on availability of project funds.

### 1. New Carbon Structures

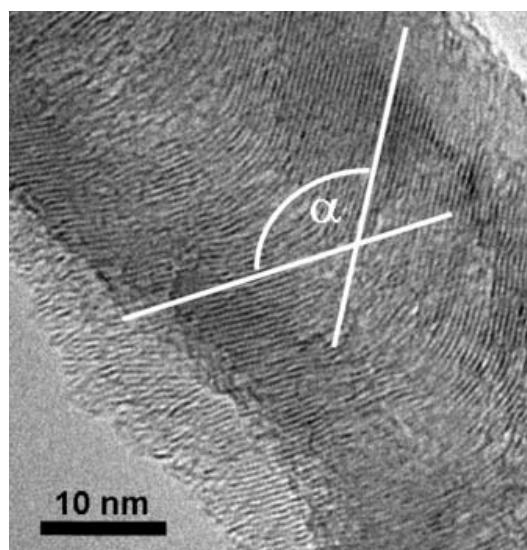
The primary carbon nanomaterials: fullerenes, graphene and nanotubes, represent only a small fraction of the existing carbon nanostructures. Most others remain largely unstudied, and many have unique properties that have yet to be properly exploited. For example:

#### 1.1. Carbon nanoscrolls

The simplest nanoscrolls are single graphene sheets rolled up, although similar scrolling operations can be applied to multiple graphite layers, as well as wrapping graphene layers around alternative cores (for example scrolls around nanotube cores). There are circumstances in which nanoscrolls may make superior replacements for either nanotubes or graphene, and may also ultimately be cheaper to produce. Two reasons I think nanoscrolls are of particular interest:



Carbon nanoscroll, DFT optimised with pinned ends by Julien Morin during his M1 Stage in 2009.



Herringbone nanofibre showing layers oriented at an angle to the fibre axis<sup>132</sup>

<sup>132</sup> M. Monthioux, L. Noé, L. Dussault, J. -C. Dupin, N. Latorre, T. Ubieto, E. Romeo, C. Royo, A. Monzon, C. Guimon, J. Mat. Chem. 17, 4611-4618 (2007)

**Mechanical reinforcement:** Recent experimental Raman studies of DWNT-epoxide resin composites under tensile loading showed a lack of mechanical load transfer from the external to internal walls in the nanotubes.<sup>133</sup> Thus the internal walls simply add additional weight to the system and are not useful for mechanical reinforcement. Carbon nanoscrolls would overcome this restriction, since the continuous carbon surface means that tensile stress applied to the external surface will be transferred to the interior surfaces. It will be interesting to model this and try to stimulate experimental studies, and I am in discussions with Prof. Andreas Schaper in Marburg and Irene Suarez in Perth on this subject.

**Spin wires:** There has been interest in the spin states along the metallic zig-zag edges of graphene nanoribbons under the action of an applied electric field, which separates spin-up and spin-down conductors to the two opposing ribbon edges<sup>134</sup>. However practical application of such a system will be limited, not least because the ribbon edges are exposed to the environment and hence susceptible to gas absorption, chemical attack, and external fields. Rolling the graphene into a nanoscroll means that one edge is surrounded by the rolled tubular structure, protecting it from its environment and in principle creating an isolated spin wire. I had a Masters MR1 student in 2009, Julien Morin, who performed preliminary calculations of this system suggesting that indeed the two edges have decoupled spin states.

## 1.2. Herringbone nanofibres

Another system of interest are herringbone nanofibres, a series of stacked nanocones resulting in a long fibre which normally contain a screw dislocation down its core (without this dislocation the cones are only contacted via weak inter-layer forces and the fibres are extremely mechanically weak). These are actually one of the most common form of carbon nanotube, typically produced at slightly lower growth temperatures than conventional multi-walled tubes and often in the presence of growth impurities such as nitrogen or alloyed catalyst particles. However they are often not reported, more commonly regarded as an unwanted by-product of conventional nanotube growth, for which growth conditions are then modified.

However such fibres should be of great interest in themselves, firstly for intercalation (e.g. Li storage). In principle inter-layer expansion due to intercalates may be incorporated by adjustment of the pitch of the screw dislocation core, which should render them mechanically robust to repeated intercalation and de-intercalation. Their morphology means that while conventional carbon nanotubes are primarily sidewalls, with associated emphasis on sidewall behaviour (mechanical strength, high mobility, ...), herringbone nanofibres are primarily *edge site* structures, with graphene edges exposed along their entire length. This makes them interesting candidates for controlled edge-site chemistry, for example for functionalisation for biological detection.

This brings me to the next related subject:

## 2. Design of Carbon Nanostructures using Wet Chemistry

Carbon chemistry is the most advanced of any element in the periodic table, and I suspect we are on the brink of another true materials science revolution in the field of carbon. To date materials science remains at its core a ‘bulk art’. Defects and impurities are considered stochastically. Even in silicon, one of the most highly engineered materials in existence, our

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<sup>133</sup> S. Cui, I. Kinloch, R. Young, L. Noe, M. Monthioux, Adv. Mat. 21, 3591 (2009)

<sup>134</sup> Y. -W. Son, M. L. Cohen, S. G. Louie, Nature 444, 347-349 (2006)

most precise methods for materials content control are techniques such as implantation and annealing to give delta-doped layers. We are far from true atomic-control of content.

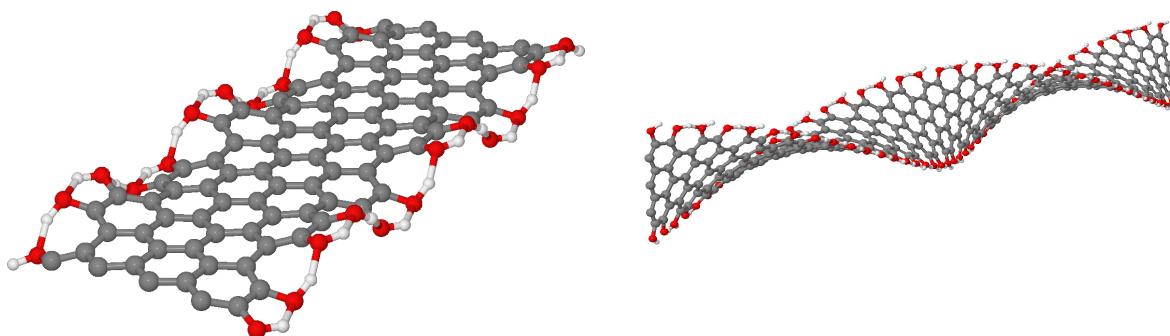
Carbon bridges the disciplines of materials science and molecular chemistry, being both a bulk material and yet subject to atomic-level control via organic chemistry. This atomic-scale design and control has yet to be applied successfully to bulk carbon materials, and is in its infancy for carbon nanomaterials, the most advanced of which is fullerene chemistry. There are two areas I expect rapid and dramatic advances in the coming years, which I intend to try and drive through predictive theoretical models and formation and direction of interdisciplinary collaborations:

## 2.1. Edge design in graphene

The edges of graphene nanoribbons are the subject of increasing study. Our recent calculations show that by changing the functional groups along the ribbon edge it is possible to control the band gap of the material.<sup>135</sup> I am in discussion with Peter Nemes at Incze<sup>136</sup>, Hungary who can produce largely defect-free edges (either zig-zag or armchair type) with controlled functional groups along their edge,<sup>137</sup> and we intend to start joint experimental-theory work on this. With control over exactly what functional groups appear along the edges of graphene nanoribbons, or the edges of herringbone nanotubes for example, we open up interesting possibilities such as:

**Band gap control:** By switching edge groups from -H to -OH or =O we have recently shown that the band gap of graphene ribbons can be strongly varied. This opens the possibility also for band gap design through edge-site functionalisation, for example, for periodic variation of edge-site chemistry to create quantum dots along a graphene nanoribbon.

**Mechanical Distortion:** Other recent calculations we have performed show that certain functional groups such as -OH can introduce tension or compression along graphene ribbon edges, resulting in mechanical distortion such as edge rippling or even ribbon twisting,<sup>138</sup> resulting in changes in carrier mobility. Edge design could allow modification of inter-layer spacing in herringbone fibres. Edge-induced ripples in graphene nanoribbons lying on a substrate may induce periodicity in the substrate-graphene interaction, for example resulting in a series of quantum dots along the ribbon length.



-OH groups along an armchair edge graphene nanoribbon cause spontaneous buckling to accommodate strain (article in preparation)

Similar edge-site distortion can cause twisting in nanoribbons seen experimentally by colleagues at Bordeaux (in preparation).

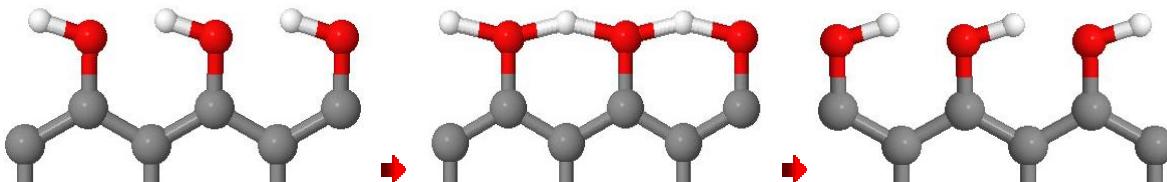
<sup>135</sup> Ph. Wagner, C. Ewels, A. Lopez, S. Roche, P. Briddon, in preparation (2011)

<sup>136</sup> Group of Lazlo Biro, Research Institute for Technical Physics and Materials Science, Budapest, Hungary

<sup>137</sup> B. Krauss, P. Nemes-Incze, V. Skakalova, L.P. Biro, K.V. Klitzing, J.H. Smet, Raman Scattering at Pure Graphene Zigzag Edges., Nano Lett. 10 (2010) 4544-4548.

<sup>138</sup> Ph. Wagner, C. Ewels, P. Briddon, A. Penicaud, in preparation (2011)

**Superprotic Conduction:** An example of unique edge effects we are currently examining is superprotic conduction. Placing –OH groups along zig-zag edges of a graphene nanoribbon creates a line of closely spaced and mechanically confined OH groups, which exhibit strong hydrogen bonding between them. The calculated barriers for conversion between a covalent –OH group with hydrogen bond, and a H atom hydrogen bonded between two neighbouring oxygen atoms is zero within the error bounds of our calculations. Equally we might expect rotation of an OH group to be almost barrierless. Thus we might imagine a fully –OH bonded zig-zag edge capable of high speed hydrogen transfer. Introducing a single missing hydrogen and then applying a field gradient could allow H atoms to rotate around their host oxygen atoms and then hop to their neighbouring oxygen atoms in a collective motion, transferring a hydrogen atom the length of the ribbon.



Possible proton transfer mechanism along –OH terminated zig-zag edges via H-bonded state.

**Organic and Polymer Chemistry:** The above examples have considered the role of edge chemistry on the behaviour of the graphene, or the edge itself. Another fascinating area for study is the study of organic and polymer chemistry in the controlled environment of a graphene edge, subject to the mechanical and spatial confinement associated with the graphene host, i.e. treating the graphene edge as a confined polymer chain in itself. We recently showed that Br<sub>2</sub> on a graphene surface is stabilised in a unique Br<sup>+</sup>-Br<sup>-</sup> configuration, which although well known in organic chemistry (for centuries), is only normally a transition state during saturation of carbon bonds. However due to the mechanical resistance of the graphene lattice, when Br<sub>2</sub> bonds to a C-C bond in graphene it is unable to transform to a fully sp<sup>3</sup>- configuration and complete the full bromination reaction, and instead the Br<sup>+</sup>-Br<sup>-</sup> intermediate is stabilised.<sup>139</sup> Thus graphene may allow us to study this reactive chemistry intermediate in more detail, and there may be other examples of stabilisation of reactive chemical intermediates. Equally graphene edges can be considered a special case of a polymer backbone, held largely rigid and linear. Thus controlled edge functionalisation of graphene ribbons, for example with styrene units, might allow us to better analyse and understand the behaviour of polymer chains.

## 2.2. Carbon Design

Various synthetic chemistry groups are working on wet chemistry routes to the production of fullerenes, graphene and carbon nanotubes. This is a field that has been slow to develop (understandably!), but recent reports at conferences I have attended in 2010 suggest it is an area approaching maturity. The idea is to produce carbon nanomaterials through controlled ‘click-’ chemistry, for example through Diels-Alder reactions. Thus starting from a molecular feedstock, we build up piece-by-piece to a full ‘bulk’ carbon nanomaterial.

If achieved, this will represent a paradigm shift for materials science. No bulk material has ever been built in this way (no metals, oxides, or semiconductors – the only materials to come close are molecular crystals and crystallised polymers). It will require a new way to think about many aspects of materials science. The first of these is defects and doping. Instead of our current approach to consider random or semi-random defect distributions, controlled

<sup>139</sup> A. Yaya, C. P. Ewels, I. Suarez-Martinez, Ph. Wagner, S. Lefrant, A. Okotroba, L. Bulusheva, P. R. Briddon, Phys. Rev. B, in press (2011)

chemical growth from doped feedstocks could result in materials such as graphene nanoribbons with regular periodic arrays of dopant atoms. We will truly be able to design our carbon materials properties, and it is clear that in this case the role of theory to predict and design will be critical. I am in discussions with Hermann Wegner in Basel who says that within the next three years they hope to be able to grow systematically short nanotube segments through wet chemistry routes (early results are promising), and it is my intention to provide theoretical modelling support and guidance for this (this collaboration is mentioned in a national grant application he has written).

For me, this last point represents a real ‘next frontier’ for the discipline of materials science, and in particular carbon science, and one in which I suspect much of my future research will be based.

### **3. Nanoscale Interfaces and Modelling of “Realistic” Systems**

Much of the important physics and chemistry of nanomaterials occurs at their interfaces. This can be seen in nanoelectronics of carbon nanotubes, where Schottky barriers at the nanotube-contact interface can dominate the electrical response of the device.<sup>140</sup> While typical experimental nanotube resistances are  $\sim 13\text{k}\Omega/\mu\text{m}$ , nanotube-nanotube junctions show resistances around  $200\text{k}\Omega$ ,<sup>141</sup> dominating the resistance of percolating networks. Interfaces control charge transfer and exciton separation, alternatively providing recombination sites, and are thus critical for OLED and light harvesting applications. Equally surface chemistry of nanomaterials dominates their efficiency as catalysts and detectors.<sup>142</sup>

It is in recognition of the importance of atomic-scale control of nanomaterial interfaces that Carla Bittencourt and I created the EU COST Network NanoTP,<sup>143</sup> bringing together around 150 research scientists from across Europe with common interest in this theme.

#### **3.1. Realistic nanoscale interfaces**

Nanoscale interfaces represent a challenge for the computational modelling community, since the systems are typically low symmetry, complex, and large. Their behaviour can be controlled by external factors such as absorbed gases or the behaviour of an underlying substrate. It is critical to model *realistic systems* incorporating these effects, which is currently often not the case. Modelling needs to take into account:

1. *Effect of environment.* Vacancies and interstitials behave differently depending on whether they are in isolated nano-objects (graphene, SWNT) or in bundles, composites, etc.<sup>144</sup> Equally important is any substrate interaction, resulting in charge transfer,<sup>145</sup> interaction with substrate defect sites, etc.
2. *The importance of absorbed surface oxygen.* For example our modelling shows that metal interaction with defects in carbon nanotube surfaces changes completely in the presence of oxygen,<sup>146</sup> also substitutional phosphorus dopants change from donor to

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<sup>140</sup> S. Heinze, J. Tersoff, L. Martel, V. Derycke, J. Appenzeller, Ph. Avouris, Phys. Rev. Lett. 89, 106801 (2002).

<sup>141</sup> M. Topinka, M. Rowell, D. Goldhaber, M. McGehee, D. Hecht, G. Gruner, Nano Letters 9(5), 1866 (2009)

<sup>142</sup> J. -C. Charlier, L. Arnaud, I. V. Avilov, M. Delgado, F. Demoisson, E. Espinosa, C. Ewels *et al*, Nanotechnology 20, 375501-375510 (2009)

<sup>143</sup> www.nanotp.org (COST Network MP0901)

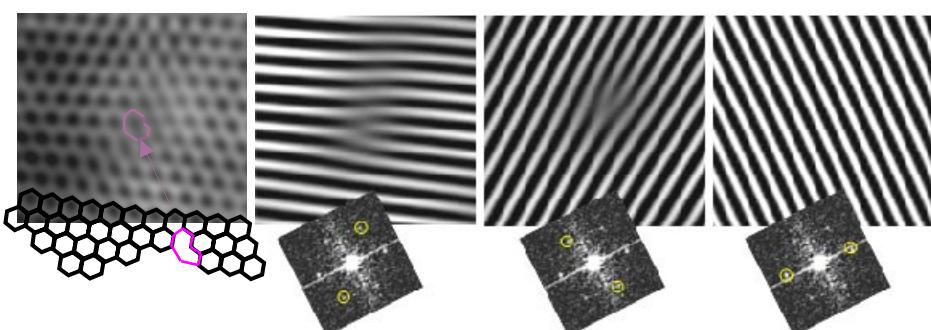
<sup>144</sup> R. H. Telling, C. P. Ewels, A. A. El-Barbary, M. I. Heggie, Nature Materials 2, 333–337 (2003).

<sup>145</sup> S. Sque, C. P. Ewels, R. Jones, P. R. Briddon, Phys. Status Solidi A, 204 (9), 2898-2902 (2007).

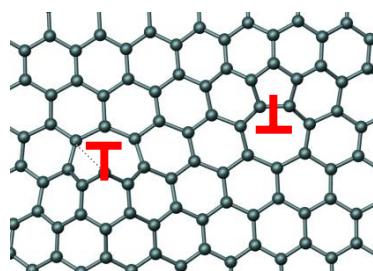
<sup>146</sup> A. Felten, I. Suarez-Martinez, X. Ke, G. Van Tendeloo, J. Ghijssen, J. -J. Pireaux, W. Drube, C. Bittencourt, C. P. Ewels, Chem. Phys. Chem. 10 (11), 1799-1804 (2009).

acceptor character on exposure to oxygen.<sup>147</sup> Few theoretical studies take this into account. We have shown that oxygen also removes any localised spin associated with metal impurities on nanotube surfaces, and will affect transport behaviour.

3. *Metastability.* While computational modelling typically searches for ground state structures, these may not always be the most relevant. A key example is vacancy pairs in graphite, where we have identified a metastable intermediate with two vacancies at 3<sup>rd</sup> neighbour spacing.<sup>148</sup> Although less stable than a 1<sup>st</sup> neighbour divacancy pair, this may be the most common vacancy-species over a significant temperature range, as vacancies diffuse towards each other and become temporarily stuck in this configuration. We are currently examining vacancy mediated plastic deformation in graphene, where vacancies induced by the electron beam in a TEM can then act as nucleation sites for dislocations when the graphene is strained.<sup>149</sup> Study of metastable structures requires consideration of the formation and treatment processes of the material, its lifecycle and characterisation conditions.



*Shuffle dislocation core in graphene viewed using HAADF, and with image filtering applied (image construction using only specific points from the electron diffraction).<sup>149</sup>*



*Possible separation of a mono-vacancy into a pair of dislocations (one glide, one shuffle) via motion of the shuffle dislocation core.*

Beyond characterisation of interfaces and their behaviour, the next stage is to move to *controlled interface design*. The first step towards this is interface treatments such as plasma, chemical functionalisation, electron or ion-beam irradiation, ultimately with spatial control, which selectively modify the surfaces of nanomaterials and hence their interface behaviour. Another route is via templating (such as composite deposition in nanoporous membranes), leading to self-organisation between nanomaterials.

My work on nanoscale interface design and control has thus far been driven by collaboration with experimental groups and providing theoretical support to experimental studies, and I expect this to continue. In particular key areas to explore include:

<sup>147</sup> V. Krstic, C. P. Ewels, T. Wågberg, M. S. Ferreira, A. M. Janssens, O. Stéphan, M. Glerup, ACS Nano 4 (9), 5081 (2010)

<sup>148</sup> C. P. Ewels, A. Zobelli, A. El-Barbary, P. Briddon, M. I. Heggie, in preparation (2011).

<sup>149</sup> C. P. Ewels, C. D. Latham, M. I. Heggie, U. Bangert, in preparation (2011).

### **3.2. Polymer-Nanocarbon interfaces**

My PhD student, Abu Yaya, is examining the interaction between the conjugated polymer poly (paraphenylen vinylene) and carbon nanotubes, in close collaboration with Dr. Jean-Luc Duvail, Prof. Eric Faulques, and others within the PMN group at the IMN. Auto-organisation between the polymer and nanotubes when mechanically confined leads to strong nanotube-polymer coupling, confirmed through our theoretical modelling. Future avenues include incorporation of pre-cursor in the calculations and more complex polymer species, as well as new carbon nanomaterials, notably graphene flakes and nanoribbons.

### **3.3. Oxide-Nanocarbon interfaces**

A longer term goal is to increase my involvement in the modelling of nanoscale oxide materials. Oxide-nanocarbon interfaces are of great interest, and such hybrid materials are under investigation for battery and fuel cell design (IMN ST2E group), light harvesting and associated electron transport (IMN CESES group), and for catalyst and detection applications (various NanoTP colleagues). Previous studies of metal nanoparticle-nanotube interaction are overly simplistic since the majority of the metal nanoparticles are actually oxidised. The structure of such interfaces remains a key question, the nature of any interfacial bonding (particularly with defects in the carbon surface), and associated electronic and chemical coupling. I am co-supervising a PhD student Nicolas Rousseau and one of his roles will be to examine the surface structure of titanate based oxides, coupling theoretical modelling to experimental IR and Raman spectroscopy.

## ***III. New Tools for Computational Materials Modelling***

These are interesting times for computational modelling in the field of nanoscale materials. Computing and theoretical advances are pushing upwards the scale of manageable simulation towards routine calculations with many thousands of atoms. At the same time we are seeing advances in experimental apparatus such as new aberration corrected transmission electron microscopes allowing sub-angstrom imaging and spectroscopy, nanometric Fresnel lenses allowing NEXAFS and polarisation dependent spectroscopy of individual nanoobjects using TXM and STXM, and tip-enhanced Raman spectroscopy tools allowing spatially localised mapping of vibrational spectroscopy.

The result is a new convergence between theory and experiment, opening up rich fields for investigation and collaboration between the two. It also means that new theoretical tools need developing, some of which I intend to pursue at the IMN:

### **III.1. Input structures from microscopy**

Faster computing and algorithms mean the time-limiting step for many studies is now the creation of initial input structures for the calculations. With the advent of atomic resolution electron microscopy, in particular HAADF dark field imaging, there is the possibility to automate the creation of input structures based on microscopy images, which can then be optimised using density functional codes. This could in principle allow rapid structure identification (and exclusion of poor models) based on the microscopy.

### **III.2. ‘Statistical spectroscopy’**

Current theoretical models of EELS or EXAFS spectra typically consider single electron transfer events,<sup>150</sup> however experimental signals are normally an average of excitations from

<sup>150</sup> W. Zhang, V. Carraetta, Z. Li, Y. Luo, J. Yang, J. Chem. Phys. 131, 244505-6 (2009)

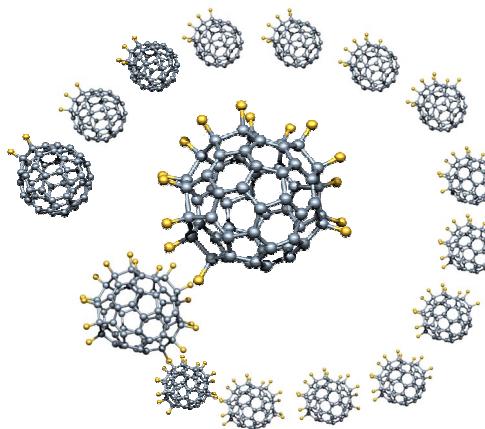
multiple sites. Our recent study of oxygen-based defects in nanotubes has shown that charge distribution around defects varies significantly depending on the defect species,<sup>151</sup> and hence it would be of interest in future to use the increased computing power available to consider many different excitations and produce sums of the results.

### III.3. Automated system evolution

In order to study systematic addition of functional groups to fullerenes, with Dr. Van Lier I have developed a meta-code, “SACHA” able to generate functionalised structures, perform DFT calculations and analyse the results, allowing automatic following of chemical addition pathways.<sup>152</sup> Such an approach can be expanded and developed significantly.

For example it would be exciting to develop the code to follow multiple addition pathways and surface migration routes, allowing automatic determination of complete addition routes and thus quantitative prediction of isomeric compositions resulting from a given addition reaction.

Dr. Zobelli (LPS) is currently exploring this concept to look at evolution of electron induced radiation damage in carbon nanomaterials over time, and other directions we could develop this include defect migration and self-organisation, graphene edge structure optimisation, and growth processes. In some ways this represents a move towards a highly driven Monte Carlo type approach with steps being calculated “on the fly”.



There are also code developments for which I do not intend to directly participate myself but will continue to collaborate with developers in Newcastle and Luleå and apply to the subjects discussed above. These include the incorporation of screened exchange in our DFT code AIMPRO allowing accurate calculation of band gaps and defect-associated gap states, new methods for k-point grid optimisation and possible incorporation of Van der Waals corrections (with Dr E. Bichoutskaia in Nottingham).

Accurate modelling of interfaces can require incorporation of solvent molecules which we currently treat only cursorily. Equally the interaction of gas molecule species such as NO<sub>2</sub> with oxidised point defects in graphene is extremely difficult to model using conventional geometrical optimisation routines, since the system contains many local minima which must be approximately located by the user, hence leaving elements of doubt as to whether all such minima have indeed been located. Once such interactions are complicated through the introduction of secondary species such as water molecules (for example in the complexation of metal ions), the problem rapidly becomes intractable. In future as code speed increases, the use of molecular dynamics in such systems will allow us to sample a wide number of configurations and develop realistic statistical solutions to the results of gas absorption.

Finally in this section I have only addressed electronic ground state calculations. Calculation of electronic excited states is still largely in its infancy and is currently restricted to small, high symmetry systems. Techniques are in development by groups such as that of Lucia Reining at the Ecole Polytechnique. It is not my intention to become strongly involved in

<sup>151</sup> C. Bittencourt, C. Navio, A. Nicolay, B. Ruelle, T. Godfroid, J. Dauchot, R. Snyders, M. Hecq, J. Colomer, X. Ke, G. Van Tendeloo, I. Suarez, C. P. Ewels, Carbon, submitted (2011).

<sup>152</sup> C. P. Ewels, G. Van Lier, P. Geerlings, J. -C. Charlier, J. Chem. Inf. Model., 47 (6), 2208-2215 (2007).

such calculations at present since I prefer to focus on the areas discussed above. However when such techniques become more routine it is clear that there would be great benefit from leaving the ground state and examining excited state behaviour in many of my proposed areas of research.

An example of this is one of the core ideas I proposed in our ANR ‘SPRINT’ with Nancy. If we can produce solutions of separated nanotubes, these can then be exposed to laser light via the use of Raman scattering apparatus. Only the tubes in resonance with the Raman laser excitation energy will be excited. Since tube excitation energy is a function of their chirality and diameter, by choosing our Raman excitation energy we can selectively choose which tubes in the solution are excited. The innovative suggestion is to then perform in-situ functionalisation chemistry during this laser excitation, with the hope/expectation that the chemistry behaves differently on excited and ground-state tubes. This would be a powerful analytic tool, for example for separating tubes, since selectively functionalised tubes could then be easily separated from the others using conventional chemical techniques. While we plan to investigate this experimentally over the next three years it will be difficult to explore the excited state surface chemistry with current theoretical modelling tools.

## **IV. Detailed Project Example : Graphene**

In the previous sections I have addressed general lines of research, here I address in slightly more detail a single specific example: modelling of graphene. This describes some of the areas I will be exploring with my postdoc Dr Viktoria Ivanovskaya and PhD student Philipp Wagner over the coming three years.

Precise modelling of the structural and electronics characteristics of complex structures such as graphene-based nanomaterials and nanodevices is clearly strategic for providing a visual description of what really happens inside a nanodevice, optimizing its performances, and improving the understanding of nanoscale properties. The engineering and integration of such new *carbon-based* low-dimensional materials, along with the mastering of quantum phenomena emerging at the nanoscale, additionally increases demand for more realistic simulation of atomic-scale features of device components (material interfaces, chemical heterogeneity, conductance properties) as well as for a more sophisticated treatment of quantum physics (inelastic interactions, out-of-equilibrium phenomena, many-body effects), which will ultimately dominate underlying device characteristics, the design of novel functionalities, and circuitry performance.

### **IV.1 Self-organisation and patterning on the graphene surface**

It would be desirable to introduce ‘electronic patterning’ into the surface of the graphene through interaction with its surrounding environment, for example to facilitate band gap engineering. While most defect distributions in 3D solids are random and statistical, with graphene it is possible to take advantage of the unique 2D surface structure to encourage an organisation of external influencing factors and hence periodic patterning of the graphene. Patterning may have many positive influences on graphene behaviour, with the possibility of enhancing available conduction channels, introducing spin-dependent conduction pathways and spin-filtering. Anisotropy of the conduction in graphene can also be induced<sup>153</sup>.

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<sup>153</sup> C.-H. Park, L. Yang, Y.-W. Son, M.L. Cohen, S. G. Louie, “Anisotropic behaviours of massless Dirac fermions in graphene under periodic potentials”, Nature Physics **4**, 213 (2008).

Patterned networks on graphene surfaces can be achieved using one of three approaches, and we intend to investigate all of these theoretically. This will be via DFT structural calculations to determine ground state structures and patterns, as well as activation barriers for diffusion and self-organisation. The resultant materials will then be examined for the change in electronic structure of the graphene and resultant effects on conductance.

#### ***IV.2 Covalent bond patterning (chemisorption)***

This involves active modification of the graphene layer through addition of covalently bonded surface species. We will initially focus on fluorine (introduced through fluorine plasma treatment). My previous work<sup>154</sup> shows auto-organisation of fluorine atoms on the surface of carbon nanotubes into different networks depending on treatment temperature and plasma conditions. This prior study will be extended to examine graphene fluorination, as well as other addends, for example other single-bond addends such as -H, -OH and -CN, or divalent addends such as oxygen. Thermodynamically preferred surface arrangements of addends will be determined as well as surface migration barriers and associated modifications of the graphene electronic structure.

Random oxygen addition through wet chemistry leads to a range of bonding arrangements in graphene oxide<sup>155</sup>, however controlled low plasma oxygen plasma treatment appears able to create thermodynamically stable functionalised arrays on graphitic surfaces<sup>156</sup>, and in this way it may be possible to create a regular arrays of epoxide-bonded oxygen across the graphene surface. This material would have radically different electronic properties to that of conventional graphene oxide. This work will be performed in direct collaboration with experimental colleagues in Belgium, through comparison of calculated stable auto-organised surface structures with experimental HRTEM, XPS and STM.

#### ***IV.3 Molecular self-assembling (physisorption)***

Weakly bonded molecules on the graphene surface are more able to rapidly auto-arrange. Within this subtask the lowest energy surface arrangement of selected molecular species will be investigated, notably those including aromatic benzenoid rings to allow strong interaction with the graphene network. With some charge transfer these are expected to induce local band bending in the underlying graphene layer, and the resultant periodic potential may induce weak localisation in the graphene. The use of non-zero spin species such as ferrocene may also induce spin dependent effects in the underlying graphene with the possibility of ferro- and anti-ferromagnetic ordering of arrays and resultant unusual temperature dependent spin behaviour. Ferrocene-aromatic carbon interaction has already been observed where ferrocene is used as a spacer molecule in C<sub>60</sub> networks to increase the lattice vector and hence the superconductivity transition temperature<sup>157</sup>.

#### ***IV.4 Graphene Ripples, Torsion and Stepped Substrates***

The third way to induce periodic fluctuations in potential across the surface of graphene is through periodic mechanical deformation of the graphene sheet. This can either be achieved

<sup>154</sup> C. P. Ewels, G. Van Lier, J. -C. Charlier, M. I. Heggie, P. R. Briddon, “*Pattern formation on carbon nanotubes*”, Phys. Rev. Lett. **96** 216103 (2006).

<sup>155</sup> K.A. Mkhoyan, A.W. Contryman, J. Silcox, D.A. Stewart, G. Eda, C. Mattevi, S. Miller, M. Chhowalla, “*Atomic and Electronic Structure of Graphene-Oxide*”, Nanoletters, Article ASAP (2009).

<sup>156</sup> C. Bittencourt, G. van Lier, X. Ke, I. Suarez-Martinez, A. Felten, J. Ghijssen, G. van Tendeloo, C.P. Ewels, “*Spectroscopy and defect identification for Fluorinated Carbon Nanotubes*”, Chem. Phys. Chem., (2009).

<sup>157</sup> P. Espeau, M. Barrio, D. O. Lopez, J. L. Tamarit, R. Ceolin, H. Allouchi, V. Agafonov, F. Masin, H. Szwarc, “*Phase equilibria in the C-60 plus ferrocene system and solid-state studies of the C-60 center dot 2 ferrocene solvate*”, Chem. Mater. **14** (1) 321 (2002).

through the formation of ripples or twists in the sheet, or by placing the graphene on a non-atomically flat substrate.

Free-standing graphene has been shown to exhibit rippling with characteristic wavelengths of around 10-25 nm<sup>158</sup>, and this intrinsic rippling has recently been reproduced on rough SiO<sub>2</sub> surfaces<sup>159</sup>. Calculations by Bettinger et al suggest unterminated edge sites will cause spontaneous buckling of graphene ribbons<sup>160</sup>. Ripples will introduce periodic modulations in the graphene electronic structure, and there is evidence that rippling leads to weak localisation<sup>161</sup>. This effect will become increasingly important as the ribbon width shrinks. We will examine the effect of ripple periodicity and direction on the electronic structure and transport behaviour of graphene ribbons.

Recent theoretical modelling of graphene on SiO<sub>2</sub><sup>162</sup> and GaAs<sup>163</sup> demonstrates strong charge transfer. Our calculations of carbon nanotubes on diamond show charge transfer effects that can be modulated as a function of surface chemistry of the nanotube<sup>164</sup>. Similar behaviour for graphene is expected. Stepped surfaces should also introduce periodic potential variation in graphene. At each step site there will be disruption of the graphene-substrate contact distance and hence local band distortion and the formation of weak quantum wells. Although such an effect is currently accidental, deliberate off-angle surface cleavage could be imagined, with cleavage angle used to control step spacing and hence periodicity in the *electronic patterning* of the potential in the graphene. Surface mismatch cleavage along two crystallographic directions would also lead to steps in more than one direction, creating viscinal surfaces and allowing electronic patterning of the graphene in two dimensions. Using the previous results from graphene ripples and buckled graphene we will choose appropriate step spacing in a model substrate (e.g. diamond or GaAs) and investigate how this distorts the graphene ribbon above it, both physically and electronically.

#### **IV.5 Multilayer graphene and inter-layer defects**

Transport studies of graphene to date have concentrated on intra-layer transport properties, focusing mainly on the analysis of the effect of disorder<sup>165</sup>. Nonetheless the *inter-layer* conductance behaviour of graphene-based systems is of great importance. Many experimental graphene systems are few- or multi-layer. The complex architectures that will be required for future graphene-based device design will likely require overlap between graphene layers, and integration of graphene into real devices will require interaction between graphene and metal contacts. We propose a novel theoretical architecture allowing study of

<sup>158</sup> C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, S. Roth, “The structure of suspended graphene sheets”, *Nature* **446**, 60 (2007).

<sup>159</sup> V. Geringer, M. Liebmann, T. Echtermeyer, S. Runte, M. Schmidt, R. Ruckamp, M.C. Lemme, M. Morgenstern, “Intrinsic and extrinsic corrugation of monolayer graphene deposited on SiO<sub>2</sub>”, *Phys. Rev. Lett.* **102**, 076102 (2009).

<sup>160</sup> V. B. Shenoy, C. D. Reddy, A. Ramasubramaniam, Y. W. Zhang, “Edge-stress-induced warping of graphene sheets and nanoribbons”, *Phys. Rev. Lett.* **101** (24) 245501 (2008).

<sup>161</sup> F.V. Tikhonenko, D. W. Horsell, R. V. Gorbachev, A. K. Savchenko, *Weak Localization in Graphene Flakes*, *Phys. Rev. Lett.* **100**, 056802 (2008).

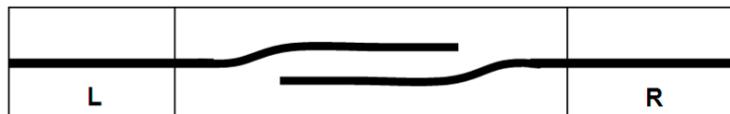
<sup>162</sup> P. Shemella, S. K. Nayak, “Electronic structure and band-gap modulation of graphene via substrate surface chemistry”, *Appl. Phys. Lett.* **94**, 032101 (2009).

<sup>163</sup> T. A. G. Eberlein, R. Jones, P. R. Briddon, “On the doping of graphene”, *Phys. Rev. B* **78** (4), 045403 (2008).

<sup>164</sup> S. Sque, C. P. Ewels, R. Jones, P. R. Briddon, “Modelling the effect of doping metallic carbon nanotubes on their ability to transfer-dope diamond”, *Phys. Status Solidi A* **204** (9), 2898-2902 (2007).

<sup>165</sup> A. Lherbier, X. Blase, Y.-M. Niquet, F. Triozon, S. Roche, “Charge transport in chemically doped 2D graphene”, *Phys. Rev. Lett.* **101**, 036808 (2008).

the inter-layer structure and transport properties associated with individual defects, molecules and other bridging systems. This consists of two single-layer graphene electrodes, which overlap as shown here:



*Schematic of inter-layer transport model system. Cross-section of two pieces of graphene nano-ribbon, (L) and (R) leads, and central unit cell region allowing ‘test cell’ construction for inter-layer structural and transport effects. Sheet curvature has been exaggerated for clarity and will be minimised in real calculations.*

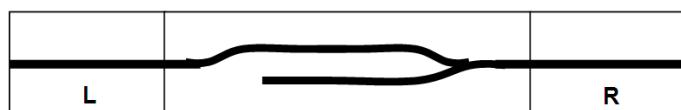
Such an arrangement will serve as a ‘single-molecule’ testing stage, and allow structural, electronic and transport investigation of a number of different effects. The models and related quantities obtained here within the frame of DFT (electronic density, electrostatic potential, and wave functions) can be fully exploited by quantum transport calculations by colleagues at CEA Grenoble (Stephan Roche) and Oakridge National Laboratories (Alejandro Lopez).

### Pristine Graphene

Inter-layer coupling for pristine graphene will be determined as a function of orientation and overlap (nothing inserted between the layers), as well as width of nanoribbon. This configuration will allow determination of appropriate cell-sizes to minimise effects of nanoribbon curvature on energetics and transport properties. Beyond this, we know that layer-to-layer (mis)orientation is responsible for large changes in the electronic properties<sup>166,167</sup>, so that an accurate analysis of the transmission with different angles between ribbons will be performed.

### Edge sites

Inter-layer coupling at edge sites, where one layer has no edge-site terminating groups such as –H or –OH, allows investigation of cross-linking between layers:



Different unterminated edge orientations (‘zig-zag’ or ‘armchair’) can be either metallic or semi-conducting, and preliminary calculations suggest that their interaction with neighbouring layers is also different, with cross-linking only occurring for certain edge types<sup>168</sup>. Cross-linking will induce  $sp^3$ -bonding across the graphene ribbon and undoubtedly lead to strong modifications in transport behaviour. The more detailed study proposed here can also be correlated with experimental microscopy studies of bi-layer graphene edge states recently reported in the literature<sup>169</sup>.

<sup>166</sup> S. Latil, V. Meunier, L. Henrard, « *Massless fermions in multilayer graphitic systems with misoriented layers: Ab initio calculations and experimental fingerprints* », Phys Rev B **76** (20) 201402 (2007).

<sup>167</sup> J.Hass, F.Varchon, J.E.Millan-Ottoya, M.Sprinkle, N.Sharma, W.A.de Heer, C.Berger, P.N.First, L.Magaud, E.H.Conrad , "Why multilayer graphene on 4H-SiC(000-1) behaves like a single sheet of graphene", Phys. Rev. Lett. **100**, 125504 (2008).

<sup>168</sup> I. Suarez-Martinez, G. Haffenden, C. Latham, P. R. Briddon, M. I. Heggie, in preparation (2011).

<sup>169</sup> Z. Liu, K. Suenaga, P. J. F. Harris, S. Iijima, “Open and Closed Edges of Graphene Layers”, Phys. Rev. Lett. **102** (1) 015501 (2009).

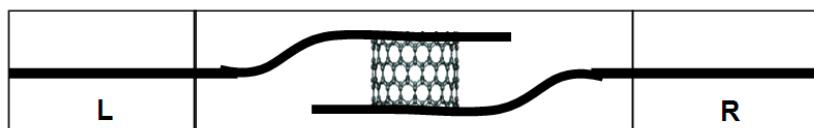
### ***Inter-layer point defects and molecules***

This cell arrangement will allow us to explore inter-layer coupling via single cross-linking point defects, such as intimate Frenkel pairs (interstitial-vacancy, I-V, species)<sup>170</sup>, cross-linking vacancy pairs in neighbouring sheets ( $V_2$ )<sup>171</sup>, interstitial bridges (I and  $I_2$ )<sup>172</sup>, as well as cross-linking impurity species such as S and N. Structures optimised here will form the basis of transport models at the CEA.

This configuration also permits insertion of molecular species between the graphene layers. We will be able to investigate whether tunnelling is feasible via selected organic species, and potentially even complex spin-dependent architectures; for example, if a molecule with associated spin such as ferrocene is inserted between the two graphene layers, does this result in a spin-dependent conduction channel?

### ***Nanotube vias for graphene circuits***

Future graphene-based device design will require 3D architecture design to allow device density competitive with other current and emerging technologies. In order to achieve such architectures it is necessary to envisage vias or inter-connects between different layers in the device<sup>173</sup>. There has been a strong research drive recently to achieve this in next generation chip design by using carbon nanotubes as interconnects<sup>174</sup>, and such an approach may also hold promise for graphene-based devices. Indeed there is recent industrial interest in such a process<sup>173</sup>. In this case it will be necessary to fuse the nanotube tip into the graphene, and indeed nanotube-graphene junctions ('hammerheads') have recently been theoretically proposed in the literature<sup>175</sup>. Suenaga *et al* have demonstrated inter-nanotube tube fusion, both tip-to-tip and tip-to-sidewall using nickel nanoparticles as catalysts with a HRTEM<sup>176</sup>. A similar approach could allow growth or deposition of nanotubes whose tips are fused seamlessly into the graphene network. This novel architecture has the potential to not only serve as interconnect, but if the nanotube segment is semi-conducting, opening the way for intriguing new device designs.



*Schematic of dual graphene lead calculation, with an inter-layer carbon nanotube 'via'.*

<sup>170</sup> C. P. Ewels, R. H. Telling, A. A. El-Barbary, M. I. Heggie, P. R. Briddon, "Metastable Frenkel Pair Defect in Graphite: Source of Wigner Energy?" Phys. Rev. Lett. **91** (2) 025505 (2003).

<sup>171</sup> R. H. Telling, C. P. Ewels, A. A. El-Barbary, M. I. Heggie, "Wigner defects bridge the graphite gap", Nature Materials **2**, 333 (2003)

<sup>172</sup> C. D. Latham *et al*, Phys. Rev. B (2010)

<sup>173</sup> "New Nano-scale Carbon Composite", Research Report, Fujitsu Laboratories, July 2008.

<sup>174</sup> G.F. Close, S. Yasuda, B.C. Paul, S. Fujita, H.S.P. Wong, "Measurement of Subnanosecond Delay Through Multiwall Carbon-Nanotube Local Interconnects in a CMOS Integrated Circuit", IEEE Trans. Electron Devices **56** (1), 43 (2009).

<sup>175</sup> J. Gonzalez, F. Guinea, J. Herrero, "Propagating, evanescent, and localised states in carbon nanotube-graphene junctions", arXiv:0901.1557v1 [cond-mat.mes-hall] (2009).

<sup>176</sup> C. Jin, K. Suenaga, S. Iijima, "Plumbing Carbon Nanotubes", Nature Nano. **3**, 17 (2008)

## V. Science Communication

Finally, a description of my intended future projects would not be complete without a brief discussion of future science communication projects. Science communication is a critical part of our role as scientists, and is something I both enjoy and believe in passionately. It is also becoming a critical tool in the current political climate to raise public visibility for the CNRS and its researchers. Science communication projects need careful design, consideration of target audiences and how to reach them. Good communication operates at a number of different levels and in different directions.

I will continue in my role as Trustee for the Vega Science Trust in order to keep this important science video platform alive, active, and available to the scientific community. Vega has a history of innovation, much of which I have played an active role in (such as being the first European science video platform online), and I am convinced it still has a role to play in future as an innovator in science communication techniques.

As well as local events such as ‘Fête de la science’ and the schools links I have established, I mention here briefly two other potential projects:

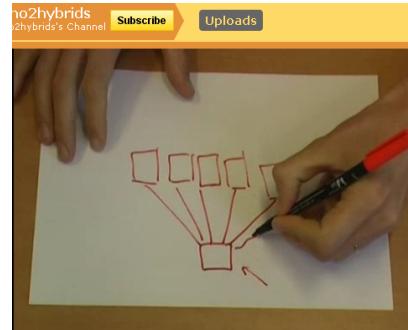
### V.1. Live Events

Last year with Pascale Launois and Sophie Lanone I began developing a project for the Palais de la Découverte at Paris concerning nanoscience and nanotechnology. The project did not reach completion due to restrictions in budget and timing but I think there is potential to develop the idea in future (I had planned the basic format, identified necessary commercial and academic links, established a format and associated schools outreach activities, etc.) Probably easiest is to first attempt a smaller event at the local level, and I am in preliminary discussions with the Natural History museum in Nantes on this subject.

### V.2. Internet Video: “Science Doodles”

Science video communication via the internet faces a number of challenges: how to produce films that are of high scientific quality, that are easy, cheap and quick to do (and so do not act as a significant draw on the time of researchers), but that remain of interest to the general public. One solution I have is ‘science doodles’.

Science doodles will be a series of short (~1.5 minute) videos for YouTube, in which we see only a piece of paper, a pen, and the hand of a scientist. Scientists will explain a concept they find interesting, simply by talking through it and drawing ('doodling') at the same time. The concept is designed to overcome most scientists fear of appearing in front of cameras, and to simplify production as much as possible to reduce overheads in editing, lighting, etc. allowing scientists to produce similar videos in their own labs with little experience or equipment. At the same time it is unusual and should appeal to audiences.



In 2011 I am on the editorial advisory panel of Materials Today and I hope to develop the idea with them, since they have access to a large audience of scientists. It will allow Materials Today to develop an online video presence, and could possibly be organised in collaboration with the Vega Science Trust and/or NanoTP to give it increased credibility. I will also discuss with Jean-Michel Courty and team at the CNRS INP communication section, with whom I am in regular contact but have yet to launch any communication projects.

## **APPENDICES**

## Appendix A : Scientific Output

I have an average of 9 articles / year since 2008. Currently also 6 articles submitted or with editors. Articles are available by clicking their titles (in pdf version) or via [www.ewels.info](http://www.ewels.info)

**Total citations : 1201**

**Facteur-h : 19**

*By journal:*

Nature Materials (1), Adv. Materials (1), Nano Letters (2), Phys. Rev. Lett. (5), ACS Nano (2), Phys. Rev. B (11), Carbon (2), Chem. Comm. (1), Chem. Mater. (2), EPJB (2), J. Phys. Chem (2), Inorg. Chem. (1), PCCP (1), J.Org.Chem (1), Chem. Phys. Lett. (1), Nanotechnology (1), J. Nanosci. Nanotech. (5) ...

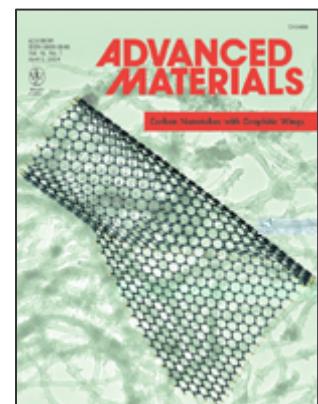
### 1. Revues à comité de lecture (68)

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**NB: PDF copies of my publications are available from the Web:**  
<http://www.ewels.info/science/publications/>

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1. [\*'Bromination of Graphene and Graphite'\*](#)  
A. Yaya, C. P. Ewels, I. Suarez-Martinez, Ph. Wagner, S. Lefrant, A. Okotrub, L. Bulusheva, P. R. Briddon  
Physical Review B, accepted (2011)
2. [\*'Behaviour of hydrogen ions, atoms, and molecules in alpha-boron studied using density functional calculations'\*](#)  
Ph. Wagner, C. P. Ewels, I. Suarez-Martinez, V. Guiot, S. F. J. Cox, J. S. Lord, P. R. Briddon  
Physical Review B, accepted (2011)
3. [\*'Purification of single-walled carbon nanotubes'\*](#)  
A. Yaya, C. Ewels, Ph. Wagner, I. Suarez-Martinez, A. G. Tekley, L. R. Jensen  
European Physical Journal : Applied Physics, accepted (2011)
4. [\*'Fingerprint of electron-mediated magnetic coupling in phosphorus-doped single-walled carbon nanotubes'\*](#)  
V. Krstic, C. P. Ewels, T. Wågberg, M. S. Ferreira, A. M. Janssens, O. Stéphan, M. Glerup  
ACS Nano **4** (9), 5081 (2010)
5. [\*'Comment on "Increase in specific heat and possible hindered rotation of interstitial C2 molecules in neutron-irradiated graphite"'\*](#)  
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67. '*Theoretical and Isotopic Infrared Absorption Investigations of Nitrogen-Oxygen Defects in Silicon'*  
R. Jones, **C. EWELS**, J. Goss, J. Miro, P. Deák, S. Öberg, F. Berg Rasmussen,  
Semiconductor Science and Technology **9**, 2145-48, (1994). ([abstract](#), [full text](#))
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R. Jones, J. Goss, **C. EWELS**, S. Öberg  
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### 3. Actes de colloques à comité de lecture (13)

1. ['NO<sub>2</sub> and CO interaction with plasma treated Au-decorated MWCNTs: Detection pathways'](#)  
R. Leghrif, E. Llobet, A. Felten, J. -J. Pireaux, Z. Zanolli, J. -C. Charlier, I. Suarez, C. Ewels  
Proc. Eurosensors XXIII Conf. (Procedia Chemistry) **1** (1), 931-934 (2009)
2. ['NO<sub>2</sub> gas adsorption on titania-based nanotubes.'](#)  
D. Arcon, P. Umek, P. Cevc, A. Jesih, C. P. Ewels, A. Gloter,  
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3. ['Structure and Energy of the 90 degree Partial Dislocations in Wurtzite-GaN'](#)  
G. Savini, M. I. Heggie, C. P. Ewels, N. Martsinovich, R. Jones, A. T. Blumenau  
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4. ['Nanotube alignment and dispersion in epoxy resin'](#)  
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R. Bouanani-Rabi, B. Pajot, **C. P. EWELS**, S. Öberg, J. Goss, R. Jones, Y. Nissim, B. Theys, C. Blaauw, Shallow Level Centers in Semiconductors, ed. C. A. J. Ammerlaan, B. Pajot, World Scientific, Singapore, p. (1997).
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8. ['A First Principles investigation of vacancy oxygen defects in Si'](#)  
**C. EWELS**, R. Jones, S. Öberg Mat. Sci. Forum Vol. **196-201**, 1297-1301 (1995).
9. ['The NNO defect in Silicon'](#)  
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10. ['Vacancy- and acceptor- H complexes in InP'](#)  
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12. ['H passivated defects in InP'](#)  
**C. P. EWELS**, S. Öberg, P. Briddon, J. Goss, R. Jones, S. Breuer, R. Darwich, B. Pajot, Solid State Communications **93** 5, 459-460 (1995)
13. ['The Hydrogen complexes in GaAs and InP doped with Magnesium'](#)  
R. Rahbi, B. Pajot, **C. EWELS**, S. Öberg, J. Goss, R. Jones, Y. Nissim, B. Theys, C. Blaauw, Solid State Communications **93** 5, 462 (1995).

## 4. Publications dans des revues sans comité (10)

1. ['Seeing the Future'](#)  
C. P. Ewels, Infocus, Royal Microscopical Society, 6, 4-21 (2007).
2. ['Women in Carbon Science'](#)  
C. P. Ewels, N. Grobert, British Carbon Group Newsletter, **34** June (2007).
3. ['From pencils to nanotechnology - the art and design of new molecules'](#)  
An article for the "[Art of Prison Survival](#)", a magazine for prisoner artists in the US.
4. ['Overcoming Defects'](#) review of "Extended Defects in Semiconductors"  
C. P. Ewels, Chemistry World, **4** (9) 73-74 (2007).
5. ['Tilting at Windmills'](#)  
Chris Ewels, New Humanist Magazine, September 2003
6. ['A spoonful of Graphite : Carbon nanoscience and public health'](#)  
British Carbon Group Newsletter, December 2005
7. ['Profile : Harry Kroto'](#), C. Ewels, [Viewfinder](#), January 2004
8. ['Surfing past terrestrial television'](#)  
by Chris Ewels. Times Higher Education Supplement, September 17th, 1999.
9. ['Dial P for Pizza'](#)  
S. Jenkins, **C. EWELS**, 'Lateral Thoughts', Physics World, **11** (5), 76 (1998).
10. 'Vielkopfige Hydra - Neue Medien verandern die wissenschaftliche Kommunikation' - 'Many-headed Hydra - The new media and scientific communication'  
by Dr. Bernd Eggen and Chris Ewels. (Circulation 6000) Zeitschrift fur Kulturaustausch, p.550, ISSN 0044-2976, E7225F Teil II. (Dec 1995), Germany.



## 5. Communications à des congrès, symposium

**NB: PDF copies of many of my conference posters are available from the Web:**  
<http://www.ewels.info/science/posters/>

### 2010:

Materials Today “The New Carbon Era” virtual conference

**Invited Oral :** “Shaping the defective nanoworld”

FSAS2010, Crete, Greece

Oral : “Heteroatom doping, oxidation and cross-linking in fullerenes”

EDS2010, Sussex (proceedings editor)

Oral : “Progress in nanotube-related extended defects”

NanoteC’2010, Oxford, UK (co-organisateur + 3 Poster)

ICAMM 2010 Nantes (co-organisateur + 1 Poster)

Christian Colliex EELS retirement meeting (1 Poster)

ChemOnTubes, 11-15 April 2010, Arcachon, France

Oral : Comparative study of oxidation and oxygen bridging in carbon nanoforms +Poster

AIMPRO’2010 – 19-22nd April, Nottingham University

**Invited Oral :** « Oxidation of carbon nanoforms »

NanoTP Scientific Kick-Off Meeting, Bessy, Berlin, March 18-20 2010 (Poster; organisateur)

JSI’2010, January 2010, IMN (national meeting – Journées surfaces interfaces)

**Invited Oral :** “Défauts dans les nanotubes de carbone” + Poster

### 2009:

January 21<sup>st</sup> 2009 : Brussels, EU “Research Marketing Workshop”,

**Invited expert, invited oral** presentation. “Communicating advanced materials Research”

14 June 2009 : Carbon 2009, Biarritz

2 Posters, Postdoc Oral “A jungle of carbon nanoforms: Is the nanotube the king?”

May 2009 : DNC09, Lausanne, CECAM, Switzerland

**Invited Oral:** “Phosphorus doped CNTs and Metal interaction with CNTs”

August 2009 : NanoteC (co-organiser, 7 posters)

2008

ChemOnTubes (international), Zaragoza, Spain

Oral : “Metal decorated Carbon Nanotubes: towards gas sensing applications”, + Poster

CMM2008 : Condensed Matter and Materials Physics, Londres UK

**Invited :** “Modelling Carbon Nanotubes : Towards reality in carbon nanoscale materials”

GDR-I Nano-I “Science and Applications of Nanotubes” (international), Autrans, France

Oral : “Interaction of carbon nanotubes with their environment” + 4 Posters

JNB2 (national), Nantes (**local organising committee** + 1 Poster, +oral postdoc),

2nd Int. Symp. Structure-Property Relationships in Solid State Materials, Nantes

**Invited:** “Manipulating carbon nanomaterials through deliberate defect design : A marriage of experiment and modelling”

NanoteC’08 (international) **co-organiser**, 2 Posters

TRNM’08 : Towards Reality in Nanoscale Materials ’08 (international), Levi, **Finland**

**Invited:** “Tuning the properties of carbon nanomaterials”

AIMPRO’08 (international) **organiser**

Oral : “Modelling realistic nanotubes: Surface deposition, tube filling and cones”

2007

NanoteC’07 (international), Brighton UK (**co-organiser**, session chair, 3 Posters)

RFCT pole Ouest (national), Rennes

Orale: “Modélisation de nanomatériaux”

CECAM, Lyon (international) (2 posters)

Capital Carbon (international), Londres UK

**Invited :** “The Future of Fullerenes”

2006 :

AIMPRO’06 (international), Exeter, UK

Oral : « SACHA : A first attempt at pre-processing AIMPRO calculations »

Carbon 2006 (international), Aberdeen, UK **(co-organiser)**

Oral: “Nitrogen doping in carbon nanosystems”

France-Isreal Symp. on Diamond and Carbon Nanostructures, Ein Bokek, **Israel**

**Invited:** “Structure and properties of defects and doping in carbon nanosystems”

GDR-E Nanotubes (international), Houffalize, Belgique 3 posters

JNB1 (national), Rennes, France 1 poster

European Forum Nanosciences, Brussels (1 Poster)

AIMPROII (international), Exeter UK

Oral : « Nitrogen in Carbon Nanomaterials »

SLONANO’06, Ljubljana

**Invited Keynote :** « Structure and properties of defects and doping in carbon nanomaterials »

Jul 2000	EDS2000, Brighton	(Oral Presentation)
Jul 2000	Eurocarbon, Berlin	(Oral Presentation)
Jul 2000	Transdiam2, Amiens	(Oral Presentation)
Sep 2000	BA Science Festival, London	(organised “Scinematheque”)
Jan 2001	AIMPRO2001, Exeter	(Oral Presentation)
Jan 2001	Databases and the Web, Oxford	(netskills training course)
Mar 2001	WideGap2001, Exeter	(Poster Presentation)
Mar 2001	Copyright Clearance in the Media	(BUFVC training course)
Jul 2001	Transdiam3, Amiens	(Poster Presentation)
Jul 2001	IWFAC2001, St Petersburg	(Poster Presentation)
Jul 2001	NanoteC’01, Brighton	(Oral Presentation, <b>co-organiser</b> )

Sep 2001	BA Science Festival, Glasgow (organised “Scinematheque”, 2001 Vega Awards)
Dec 2001	Aimpro2001, Exeter (Oral Presentation)
Feb 2002	Carbon Polymorphs Workshop, Rutherford Appleton Lab.
Jul 2002	Gordon Conference (Defects) (Poster Presentation)
Aug 2002	NanoteC'02 (Co-Organiser, poster, chaired session)
Oct 2002	GDR Nanotubes Montpellier (Poster Presentation)
Dec 2002	UCL Leuven, Belgium (Invited Lecture)
Mar 2003	Kirchberg, Austria (Poster Presentation)
Apr 2003	Aussois, France (Nanotube Training Workshop)
Aug 2003	NanoteC'03 (Co-Organiser, session chair)
Oct 2003	GDR Nanotubes Lyon (Oral Presentation in French)
Dec 2003	AIMPRO'03, Exeter (Oral Presentation)
Mar 2004	UCL Leuven, Belgium (Invited Lecture in French)
Mar 2004	Gif sur Yvette, DFT Workshop (participant)
Jul 2004	Carbon 2004, Rhode Island USA (2 Oral, 2 Poster presentations)
Oct 2004	NanoteC'04 and GDR-E (1 Oral, 2 Poster presentations)
Oct 2004	SLONANO (1 Invited Oral, 3 posters, session chair)
Dec 2004	AIMPRO'04, Newcastle (1 Oral)
Jan 2005	IMN Nantes (Invited Lecture in French)
Feb 2005	Cambridge University (Invited Lecture)
Apr 2005	Dresden, Computational Techniques (participant)
Apr 2005	1st EU Nano-Policy Open Meeting (Invited Speaker)
	Workshop on Research Training in Nanosciences : Current status and future needs
May 2005	EDGE, Austria (1 Poster)
June 2005	NT'05, Gothenburg, Sweden (5 Posters)
Aug 2005	NanoteC'05 (Co-organiser, Session Chair, 2 Posters)
Oct 2005	GDR-E, Houffalize, Belgium (3 Posters, session chair)

## 6. Séminaires, workshops (13)

**Invited lecture tour**, IOP Ireland Lecture Tour, 7-14<sup>th</sup> February 2010.

“Shaping the Defective Nanoworld”, C. Ewels

University of Cork, University of Ulster (Belfast), and Trinity College Dublin.

July 1<sup>st</sup> 2009 : Workshop on polymer/nanotube interaction with Taiwan, IMN Nantes  
Oral : “Interaction of PPV with carbon nanotubes”

**Invited Novosibirsk**, May 2009

Orals: “BN Nanotubes”, “Structure, properties of defects and doping in C nanosystems”

Journée Européen, Ecole Polytechnique, Nantes (national) (2008)

**Invited** : « European Research Mobility : A personal example »

Public Lecture Series, JSI Slovenia (2007)

**Invited** : “Topology, structure and defects in carbon nanosystems”, C. P. Ewels

Video on the web at: [http://videolectures.net/kolokviji\\_ewels\\_tsd/](http://videolectures.net/kolokviji_ewels_tsd/)

ENCRE2007 Reunion CNRS pour nouveaux rentrants, La Rochelle

**Invited** : « Communication »

Franco-Taiwan Workshop 2007, Hsinchu University, **Taiwan**

**Invited** : “Defects in Carbon based nanomaterials”

2006

IV Quincena Francesa, Ambassade de France / Alliance Française, **Panama**

**Invited** : « Introduction to Nanotechnology and Nanomaterials »

L'INRA en Europe (national), Paris, France

**Invited** : “Researcher mobility in Europe : Personal experience of the Marie Curie scheme”

Seminar, Department of Chemistry, Newcastle University, UK

**Invited** : “Defects in graphite, carbon nanotubes and BN nanotubes”

## 7. Livres et ouvrages

PhD Thesis, ["Density Functional Modelling of point defects in semiconductors"](#)  
(Exeter University, 1997). (version electronique sur www.ewels.info)

## 8. Chapitres d'ouvrages (6)

### 1. 'Nomenclature of Carbon Nanoforms'

I. Suarez-Martinez, N. Grobert, C. P. Ewels,  
Opening chapter in "Handbook of Carbon Nanomaterials", Ed. N. Tagmatarchis,  
Pan Stanford Publishing, ISBN-10: 9814267872, EAN: 9789814267878 (2010)

### 2. '[Nitrogen and boron doping in carbon nanotubes](#)'

C. P. Ewels, M. Glerup, V. Krstic,  
Book chapter in "Chemistry of Carbon Nanotubes", edited by V. A. Basiuk and E. V. Basiuk, ISBN 1-58883-129-9, American Scientific Publishers (2008).

### 3. '[Doping of Carbon Nanotubes](#)'

M. Glerup, V. Krstic, C. P. Ewels, M. Holzinger, G. Van Lier  
Book chapter in "Doped Nanomaterials and Nanodevices", edited by Wei Chen, American Scientific Publishers (2009).

### 4. '[Irradiation damage in graphite from first principles](#)'

M. Heggie, I. Suarez-Martinez, G. Savini, A. El-Barbary, C. Ewels, R. Telling  
in "Management of Ageing Processes in Graphite Reactor Cores", ISBN:978-0-85404-345-3, Ed. G. B. Neighbour (Royal Society of Chemistry) 83 (8) (2007).

### 5. 'Oxygen point defects in silicon'

**C. P. EWELS**, R. Jones, in "Properties of Crystalline Silicon", Ed. Robert Hull, EMIS Datareview, INSPEC (1999).

### 6. 'Oxygen-Carbon, Oxygen-nitrogen and oxygen-dimer defects in Si'

**C. P. EWELS**, R. Jones, S. Öberg, in "Early Stages of Oxygen Precipitation in Silicon", ed. R. Jones, Kluwers Academic Press, Series 3, Vol. 17, p.141-163 (1996).

## 9. Logiciels

“SACHA”, meta-code for predicting isomer structures and addition patterns (Fortran 90).

G. Van Lier, C. P. Ewels, P. Geerlings, Comp. Phys. Commun., **179** 165-170 (2008).

C. P. Ewels, G. Van Lier, P. Geerlings, J. -C. Charlier, J. Chem. Inf. Model., **47** (6), 2208-2215 (2007).

This code was written by me in Fortran 90 following earlier manual work to identify functional group addition patterns with Dr van Lier. Code now developed to ‘grow’ isomeric metal nanoclusters, and perform carbon nanostructural transformations.

## 10. Autres

### Scientific Artwork

My nanotechnology related artwork can be viewed at [www.ewels.info](http://www.ewels.info).

The images have been used for many book, journal and magazine covers, in brochures and film and TV programmes, and have been exhibited at the Florida Art Museum.



### Scientific Videos

As part of the nano<sup>2</sup>hybrids project my postdoc and I produced many videos which are now available on YouTube, and the award winning nano<sup>2</sup>hybrids project site ([www.nano2hybrids.net](http://www.nano2hybrids.net) or [www.youtube.com/nano2hybrids](http://www.youtube.com/nano2hybrids)).

Of particular interest are a series on carbon nanotubes, their synthesis, observation and applications, for a general audience, in English, French and Spanish (see for example <http://www.youtube.com/watch?v=MCi4GRV05Bo>

### Websites

1. [www.ewels.info](http://www.ewels.info) (~200 visitors per day)

Includes a nanotechnology image gallery and introductory information on nanotechnology.

2. Scientific conference websites :

I run websites for a range of conferences (the NanoteC series, Carbon2006, Oxygen '96, ...)

As well as for the British Carbon group ([www.britishcarbon.org](http://www.britishcarbon.org)).

3. Developed a new website for Gem Nantes, the gemmology DUG in Nantes

<http://www.gemnantes.fr/>

### Television Programmes

I am credited in the production of 13 TV programmes that have been broadcast on the BBC. TV/video production work includes:

1. '*The Next Big Thing*' : Series of 10 programmes shown on BBC2 Science Night, a Vega / Open University collaboration. Background research and planning, sat on editorial advisory board, chose some topics covered.
2. '*Revolutionaries of Science*' : Archive series of eminent scientists. Sound recordist for Max Perutz, Fred Sanger recordings in Cambridge, John Cornforth recordings in Sussex. Basic editing and graphics. Organised, filmed and sound recording for Millie Dresselhaus recordings.
3. '*Royal Society Lectures*' : Broadcast quality recordings of Paul Hoffman and Paul Davies public lectures.
4. '*Introduction to nano2hybrids*' : Broadcast quality short documentary detailing the set-up of a European science project (role of director, some script editing)