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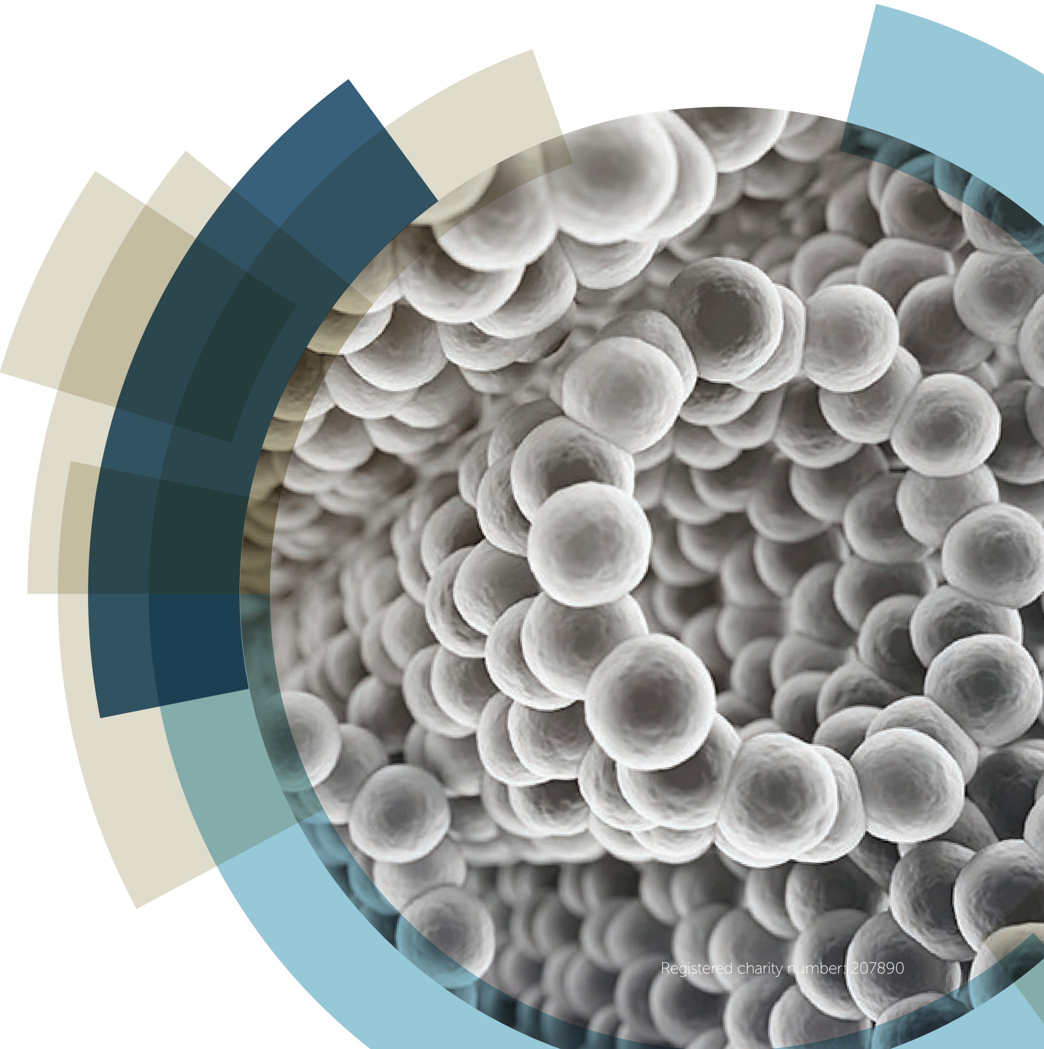
13 June 2016, London, UK

7th UK-Japan Symposium on Fundamental Research Advances in Carbon Nanomaterials

Book of Abstracts



Foreword

Dear Colleagues

It is my pleasure to welcome you to the 7th UK-Japan Symposium, one of a series of joint events held by the Royal Society of Chemistry and our long-standing partner the Chemical Society of Japan.

We have worked closely with the Chemical Society of Japan for a number of years to support scientific collaboration and exchange between our two countries. In 2010 we formalised our relationship by signing an international cooperation agreement, which we renewed in 2015.

The theme for this year’s symposium is fundamental research advances in carbon nanomaterials. We are proud to bring together leading Japanese and UK scientists to discuss this important topic. Understanding the chemical properties of these materials is vital if we are to develop their many potential applications, from energy storage and conversion to drug delivery.

We are grateful to the Chemical Society of Japan for their help in organising this symposium, in particular Executive Director Nobuyuki Kawashima, and we look forward to continuing to working even more closely together in the future.

In addition, I would like to thank the Japanese Society for the Promotion of Science for their generous support and contribution.

I hope that today offers an opportunity to build relationships and find new opportunities for researchers from the UK and Japan to collaborate on this important topic.

I wish you all an informative, productive and enjoyable day.

Dr Robert Parker
Chief Executive Officer
Royal Society of Chemistry

Welcome address

Dear Colleagues

The Chemical Society of Japan (CSJ) is delighted to be co-organizing with the Royal Society of Chemistry (RSC) this 7th RSC-CSJ Joint Symposium on Fundamental Research Advances in Carbon Nanomaterials.

CSJ and RSC entered into an International Cooperation Agreement in July, 2010 and it was renewed in March, 2015 during the 95th CSJ annual meeting. Many cooperation programs are realized based on this agreement. Individual interchanges in Chemistry have continued since more than 150 years ago when the five young nobles from the Choshu clan secretly came to the UK in 1863 and studied at UCL, followed by 19 students from the Satsuma clan in 1865. Both groups were well taken care of by Prof. Alexander William Williamson, UCL, who was President of the London Chemical Society, which developed into the Royal Society of Chemistry.

The theme of the 7th joint symposium is a key area to open a wide range of applications of carbon nanomaterials in the fields of energy, electronics, optics and biomedical applications. We strongly believe that further interdisciplinary research by materials scientists, chemists and physicists will find new fields both in fundamental studies and the development of applications.

I would like to thank Dr. Robert Parker, Chief Executive Officer, Dr. Kathleen Too, International Development Manager- Asia, and Dr. Hiromitsu Urakami, Representative of Japan office of RSC, and Prof. Shigeo Maruyama, representing CSJ as Chair, for their great effort to make this symposium possible.

It is our hope that the symposium will provide a springboard for tomorrow's activities in this field and contribute to strengthen our friendship. We look forward to continuing our close partnership between CSJ and RSC reflecting our deep and long history.

Nobuyuki Kawashima
Executive Director and
Secretary General
The Chemical Society of Japan

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Nanoscale
Horizons

PCCP

Programme

Monday 13 June 2016

Time	Event	
09:15	**Registration, tea and coffee**	
09:45	**Welcome addresses** Robert Parker, CEO, *Royal Society of Chemistry* Shigeo Maruyama, *Chemical Society of Japan* Nobuo Ueno, Director, *Japan Society for the Promotion of Science in London*	
Session 1: **Session chair:** Nicole Grobert, *University of Oxford, UK*		
10:15	**Carbon nanotube film and graphene as electron-blocking-layer and transparent electrode for various solar cells** Shigeo Maruyama *University of Tokyo, Japan*	INV01
10:50	**Studying chemical reactions inside the world's tiniest test tube through a lens of electron microscope** Andrei N. Khlobystov *University of Nottingham, UK*	INV02
11:25	**Bottom-up fabrication and optical properties of high-quality two-dimensional atomic layers** Ryo Kitaura *Nagoya University, Japan*	INV03
12:00	**Poster session and lunch**	
Session 2: **Session chair:** Shigeo Maruyama, *University of Tokyo, Japan*		
14:00	**Scaling-up carbon nanomaterials production: From blue sky research to end-user applications** Nicole Grobert *University of Oxford, UK*	INV04
14:35	**Polymer-wrapped carbon nanotube for highly durable electrocatalyst support** Tsuyohiko Fujigaya *Kyushu University, Japan*	INV05
15:10	**Tea and coffee**	
Session 3: **Session chair:** Alexei A. Kornyshev, *Imperial College London, UK*		
15:40	**Ionic liquids at interfaces and nanoconfinement, and the physics of supercapacitors at the nanoscale** Alexei A. Kornyshev *Imperial College London, UK*	INV06
16:15	**Tip-enhanced Raman spectroscopy applied to nano-carbons** Yuika Saito *Gakushuin University, Japan*	INV07
16:50	**Playing with fire** Zoe Schnepp *University of Birmingham, UK*	INV08
17:25	**Concluding remarks and Prize giving**	
18:15	**Reception at the Embassy of Japan in London**	

Please note that this is a draft programme and timings may change.

Speaker biographies

Tsuyohiko Fujigaya
Kyushu University, Japan

Tsuyohiko Fujigaya was received his B. S. and M S. degrees in Polymer Chemistry from Tokyo Institute of Technology University, Japan, in 1998 and 2000, respectively, and his Ph. D. degree in chemistry and biotechnology from Tokyo University, Japan, in 2005. He then spent a year as a postdoctoral fellow in Prof. Chad Mirkin's lab at Northwestern University, United States. And now he is an Associate Professor of Applied Chemistry of Kyushu University, Japan. His research focuses on the developments of the functional materials based on carbon nanotube/polymer composites such as the carbon nanotube-based electrocatalyst for polymer electrolyte fuel cell, controlled release of molecules for drug delivery system. He has been awarded several prizes, including the The Best Paper Award from The Photopolymer Science and Technology (2003), Award for Encouragement of Research in Polymer Science from The Society of Polymer Science (2009) and Iijima Award from The Fullerenes, Nanotubes and Graphene Research Society (2012).

Nicole Grobert
University of Oxford, United Kingdom

Nicole Grobert is a Professor of Nanomaterials at the Department of Materials at the University of Oxford, a Fellow of Materials at Corpus Christi College Oxford, and a Visiting Professor at the BioNano Electronics Research Centre at Toyo University in Japan.

She has held two successive distinguished Royal Society Fellowships and her research focuses on "Establishing growth systematics for the controlled generation of 0D, 1D, and 2D nanostructured carbon and non-carbon-based materials: from blue sky research to end-user applications." Her work has been published in over 160 research articles and six patents.

Nicole is also involved in Science Policy and she serves on a number of high-level advisory committees including the World Econonic Forum Future Technology Pioneers Programme Committeee, No 10 Round Table on Advanced Materials, Ministerial Nanotechnology Committee, and DEFRA meetings on Nanotechnology. She spoke twice at The House of Lords Science and Technology Select Committee and she has been Vice-President of the British Carbon Group. Moreover, she has been a member of the Royal Society and Royal Academy of Engineering working group on Nanotechnology commissed by the UK government in July 2003 and in 2015, Nicole has been elected Chair of the Young Academy of Europe - an international, non-governmental association of individual scientists and scholars who are experts and leaders in their respective fields.

Andrei Khlobystov
University of Nottingham, UK

Andrei Khlobystov is Professor of Nanomaterials and Director of Nanoscale & Microscale Research Centre, University of Nottingham. He previously held a Royal Society University Research Fellowship, awarded RSC Corday-Morgan Medal, European Young Investigator Award and elected a Fellow of the Royal Society of Chemistry.

Trained as a chemist (MSc Moscow State University 1997; PhD University of Nottingham 2002), Prof. Khlobystov started his post-doctoral career at the Department of Materials, Oxford University (2002-2004) where he began exploring carbon nanotubes as nanoscale containers for molecules. In 2004 he established the Nottingham Nanocarbon Group. He performed a chemical reaction inside carbon nanotubes (Guinness world record for the World's Tiniest Test Tube, 2005) and demonstrated that nanoscale confinement can lead to new products inaccessible by other synthetic methods. His team discovered important mechanisms of interactions between carbon nanostructures and molecules or nanoparticles which enabled the design of nanoreactor systems with tuneable size and functionality applied for a range of reactions, including catalytic and electrochemical processes. TEM remains key in Prof. Khlobystov's research, not only for the structural characterisation of individual molecules, but also as a new tool for the study and discovery of chemical reactions at nanoscale.

Ryo Kitaura
Nagoya University, Japan

Ryo Kitaura was born in Hyogo Prefecture, Japan in 1974. He obtained B.E. (1998) degree from Osaka Prefecture University, M.E. (2000) and Ph. D. (2003) degrees from Kyoto University. After working as a researcher at Toyota Central R&D Laboratory, he worked as an assistant professor from 2005 and as an associate professor from 2008 at Faculty of Science, Nagoya University. He has worked on growth, structural characterization and electronic and optical properties of low-dimensional materials including one- and two-dimensional materials including carbon nanotubes, nanopeapods, nanowires, graphene and transition metal dichalcogenides. His current research focuses on electronic and optical properties of two-dimensional materials.

Alexei Kornyshev
Imperial College London, UK

Alexei Kornyshev graduated in 1970 from the Moscow Institute of Engineering Physics with a degree in theoretical nuclear physics. He matured as a scientist at the Frumkin Institute of Electrochemistry (Acad.Sci.) in Moscow, where he did there his PhD (1974) with Prof. R.R.Dogonadze in Theoretical and Mathematical Physics and DSc in Chemistry (1986), having worked there till 1991. In 1992 he was invited to Research Centre Jülich, Germany, where he then worked for 10 years leading a Theory Division in the Institute for Materials and Processes in Energy Systems of Research Centre “Juelich”, Germany, a position combined later with a Professorship of Theoretical Physics at the University of Düsseldorf. In 2002 he joined Imperial College London where he holds a chair of Chemical Physics since then.

His interests span widely in theoretical condensed matter chemical physics and its application to electrochemistry, nanoscience, biological physics and energy research, using methods of theoretical physics and computer simulations, and working in close collaboration with experimentalists. An author of >250 original, refereed papers published in physics and chemistry journals, and ≈30 monographic/feature articles and book-chapters, he is known by his works in the theory of solvation; solid-liquid and liquid-liquid electrochemical interfaces (including functionalised and electrovariable interfaces); electron and proton transfer in complex environment (including membranes and complex electrodes) and single molecules; physical theory of fuel cells; interaction, recognition and assembly of biomolecules, DNA biophysics. In the area of the latter he has performed a series of works published together with S.Leikin (NIH) known as Kornyshev and Leikin theory, developed further later with his co-workers, D.J.Lee and A.Wynveen. Room temperature ionic liquids at electrified interfaces and in nanoconfinement and their applications to supercapacitors and electroactuators is an important direction of his current research, where since 2007 he has published a series of seminal papers, with M.V.Fedorov, S. Kondrat, R.Qiao and others. In 2010 together with Prof. M. Urbakh (TAU) and Prof. M.Flatte (Univ. Iowa) he has launched “electrovariable nanoplasmonics”, and continues working on the theory of self-assembled electrochemically controlled nanoplasmonic systems since then, cooperating on experimental front with the laboratory of Dr. J. Edel and Prof. A. Kucernak.

Through his research career he has led many international projects with groups in USA, Germany, Denmark, Israel, France, Canada, Russia, and Estonia. He was a recipient of 1991 Humboldt Prize in Physical Chemistry/Electrochemistry, 2003 Royal Society Wolfson Award, 2003 Schönbein Silver Medal (“for outstanding contributions to understanding the fundamentals of fuel cells”), 2007 Barker Electrochemistry Medal (“for his pioneering works and outstanding achievements in the application of modern theory of condensed matter to electrochemical systems”), and 2010 Interdisciplinary Prize, Medal and Lectureship of the RSC (“for his many outstanding contributions at the interfaces of chemistry with both physics and with biology”). He is an elected/appointed Fellow of 5 learned societies: IUPAC, Institute of Physics, Royal Society of Chemistry, Royal Society of Biology, International Society of Electrochemistry, and a Foreign Member of the Royal Danish Academy of Science. He is a senior Editorial Panellist of Scientific Reports (Nature Publishing Group), and is a Member of Editorial Boards of Journal of Physics Condensed Matter (IOP) and ChemElectroChem (Wiley).

Shigeo Maruyama
University of Tokyo, Japan

Shigeo Maruyama received his Ph.D. in School of Engineering from the University of Tokyo in 1988. He worked as a research associate until 1991, as a lecturer for a year, as an associate professor from 1993, as a full professor from 2004, and as a distinguished professor from 2014 at the University of Tokyo. From April 2015, he also work as a cross-appointment fellow for Advanced Industrial science and technology (AIST). He joined Professor Richard Smalley group at Rice University as visiting fellow for about 2 years during 1989 through 1991. During this period, he started to study chemical physics of clusters, fullerenes, and carbon nanotubes. Later, he invented the new CVD technique of SWNTs from low pressure alcohol in 2002, so-called Alcohol Catalytic CVD (ACCVD). Current research topics are growth, optical characterization, thermal characterization and solar cell application of carbon nanotubes and graphene. He has served as program officer of Japan Society for the Promotion of Science (JSPS) during 2009-2012, and as the president of "*The Fullerenes, Nanotubes and Graphene Research Society,*" since 2011. He also served as Director of *The Japan Society of Applied Physics* since 2014 and as Executive Director in 2015. He is an Editor of "*Nanoscale and Microscale Thermophysical Engineering*," and an associate editor of "*Int. J. Heat Mass Transfer*." He has published more than 200 ISI-listed papers which have been cited more than 7,800 times, resulting the h-index of 47 (Google Scholar shows 12,900 citations and h-index 58).

Yuika Saito
Gakushuin University, Japan

Yuika Saito received a Ph.D. in physical chemistry in 2001 from the University of Tokyo.

From 2001-2003 she was a Research Fellow at the University of Leeds UK. From 2003-2006 she was a Postdoctoral researcher at the Institute of Physical and Chemical Research (RIKEN) Japan, 2006-2011 a Tenure-track lecturer in Osaka University, 2011-2016 an Associate professor in the Department of Applied Physics at Osaka University and in 2016 became Professor in the Department of Chemistry at Gakushuin University. Her research interests are: Near-field Raman microscope, Polarization measurements, Optical properties of nanomaterials and nano-carbons.

Zoe Schnepp
University of Birmingham, UK

Zoe Schnepp is passionate about green chemistry, both in her research and the potential for changing negative public perceptions of chemistry. With diverse interests in nanotechnology, catalysis and materials from biomass, Zoe leads a growing group in the School of Chemistry at the University of Birmingham, UK. Prior to her Birmingham Fellowship, she held Postdoctoral Fellowships in the International Center for Young Scientists at the National Institute for Materials Science in Japan and the Max Planck Institute for Colloids and Interfaces in Germany. She received her PhD from the University of Bristol. Zoe has been involved in numerous public engagement events, including Soapbox Science and TEDx and has written articles for The Conversation, Nanowerk.com and The Independent.

Invited speaker presentations

INV01 Carbon nanotube film and graphene as electron-blocking-layer and transparent electrode for various solar cells
Shigeo Maruyama
University of Tokyo, Japan

INV02 Studying chemical reactions inside the world's tiniest test tube through a lens of electron microscope
Andrei N. Khlobystov
University of Nottingham, UK

INV03 Bottom-up fabrication and optical properties of high-quality two-dimensional atomic layers
Ryo Kitaura
Nagoya University, Japan

INV04 Scaling-up carbon nanomaterials production: From blue sky research to end-user applications
Nicole Grobert
University of Oxford, UK

INV05 Polymer-wrapped carbon nanotube for highly durable electrocatalyst support
Tsuyohiko Fujigaya
Kyushu University, Japan

INV06 Ionic liquids at interfaces and nanoconfinement, and the physics of supercapacitors at the nanoscale
Alexei A. Kornyshev
Imperial College London, UK

INV07 Tip-enhanced Raman spectroscopy applied to nano-carbons
Yuika Saito
Gakushuin University, Japan

INV08 Playing with fire
Zoe Schnepp
University of Birmingham, UK

Carbon nanotube film and graphene as electron-blocking-layer and transparent electrode for various solar cells

Shigeo Maruyama[1*,2]

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It was found that a film of single-walled carbon nanotubes (SWNTs) can be a dual-functional layer as electron-blocking-layer and transparent electrode through studies of nanotube-silicon heterojunction solar cells[1-3]. We have demonstrated efficient SWNT/Si solar cells using dry-deposited high-quality SWNTs[1] and honeycomb-structured SWNTs[2]. The SWNT/Si solar cells using the dry deposited SWNT film demonstrated the air-stable power conversion efficiency (PCE) of 11.6 % before any intentional doping process. With the stable copper oxide based doping, the PCE can be more than 13.5 %. Another long-term air stable doping using Lewis acid is also introduced. Adequately doped mm scale single crystal graphene[3] also exhibited the similar performance[4]. The dual functionality is also demonstrated for organic and perovskite solar cells. For organic solar cells, the SWNT/MoO_x/PEDOT:PSS layer was demonstrated as a dual functional layer replacing ITO and organic electron-blocking-layer. Using PTB7/PC_{71}BM mixture as active materials, the PCE of 6 % was obtained for glass substrate and 3.9 % on flexible PET substrate[5]. The dual-functional feature was also demonstrated in double-sided illumination perovskite solar cells using SWNT film instead of electron-blocking-layer and gold electrode with over 9 % PCE[6]. Another perovskite solar cell structure using SWNTs instead of ITO is also proposed[7].

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Studying chemical reactions inside the world's tiniest test tube through a lens of electron microscope

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Transmission electron microscopy (TEM) is one of the most direct methods for imaging individual molecules with atomic resolution, in direct space and real time. The latest achievements in high-resolution TEM not only provide exquisite structural information, but also help to answer some of the most fundamental and challenging questions of chemical science.

Fast electrons employed for TEM imaging transfer some of their kinetic energy to the specimen, which is traditionally viewed as detrimental to the analysis. However, if atomistic mechanisms of interactions between fast electrons and molecules are understood, we can embrace the changes in materials triggered by the act of observation to reveal valuable chemical information. The concept of the electron beam simultaneously acting as an *imaging tool and a source of energy* to drive chemical transformations offers an entirely new tool for studying chemical reactions of individual molecules with atomic resolution.

Atomically thin and structurally robust carbon nanotubes serve as ultimate nanoscale test tubes, providing an imaging platform for encapsulated molecules. The electron beam of TEM penetrates the walls of carbon nanotubes and enables time-resolved imaging of the reactions between the molecules, which can be followed by TEM with sub-Ångstrom resolution. Activated by the electron beam, the energy and dose rate of which can be set precisely, molecules undergo different chemical transformations determined by the imaging conditions. Some types of the reactions revealed under the e-beam are familiar to chemists (i.e. polymerisation) and their mechanisms can be studied and interpreted with the atomic precision, while others are newly discovered by TEM thus changing the way chemists make and study molecules.

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Bottom-up fabrication and optical properties of high-quality two-dimensional atomic layers

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The progress on graphene research has resulted in the discovery of its fascinating properties including the extremely high carrier mobility (~ 500,000 cm^2/Vs), the room temperature quantum hall effect and the fractional quantum hall effect, etc. The fascination with graphene research has led to searching for other two-dimensional systems, and hexagonal boron nitrides (hBN) and transition metal dichalcogenides (TMDs) have been isolated in its monolayer form. The family of two-dimensional systems, including metals, semiconductors and an insulator, now provides an excellent and widespread platform to explore novel chemistry and physics in two-dimensions.

To further explore the fundamental properties and possibility in future device applications of two-dimensional systems, the important point is preparation of high-quality samples to ensure their intrinsic properties. We have been focusing on growth of high-quality two-dimensional material by bottom-up methods including chemical vapor deposition (CVD) and molecular beam epitaxy (MBE).[1,2,3] Our strategy to fabricate high-quality samples is development of growth setup specific for two-dimensional systems and usage of hBN as a substrate. In this presentation, I am going to show recent results on preparation of high-quality TMDs and its heterostructures and their optical properties. In addition, I am also going to briefly talk about latest results on nanocarbon materials.

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Scaling-up carbon nanomaterials production: From blue sky research to end-user applications

Nicole Grobert

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Whilst nanomaterials are well established in the research arena they are yet to be exploited at the industrial scale due to their limited availability. A series of bottlenecks must still be overcome before their outstanding properties can be fully unlocked.

This fact applies to nanomaterials across the board including tailored 0D, 1D, 2D structures and combinations thereof. This talk addresses the challenges that need to be overcome related to up-scaling the production of novel nanomaterials, possible solutions and the necessity for the development of dedicated nanomaterials for end-user applications will also be discussed.

Polymer-wrapped carbon nanotube for highly durable electrocatalyst support

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Fuel cell is key technology to convert hydrogen energy into electric power quite efficiently. Especially, polymer electrolyte fuel cell (PEFC) is promising candidate for the energy source of car, portable electronic device, and house. Carbon nanotubes (CNTs) have been emerged as a better conductive supporting material for catalyst nanoparticle than conventional material such as carbon black due to their excellent electron conductivity, better electrochemical durability and fibrous structure. The key issue to utilize the CNTs as a supporting material is to develop a proper method to immobilize the metal nanoparticle or catalyst materials onto CNT surface. We have reported polybenzimidazole (PBI) adsorbed onto the surface of CNTs and acts as the good dispersant of CNTs[1-4]. By taking the advantage of uniform wrapping of PBI on CNTs surface, we utilized this composite (CNT/PBI) as a novel carbon supporting materials for the loading of metal nanoparticle such as Pt, Au, Pd to fabricate an electrocatalyst for PEFC (Figure 1). In the case of Pt composite (CNT/PBI/Pt), we revealed that the electrocatalyst shows excellent activity and durability in the single-cell PEFC measurements due to the unique graphitic structure of CNTs[2-5]. Our PBI-wrapping approach was also applicable to the anion-conductive fuel cell by functionalize the cationic polymer as an electrolyte as well as the metal-free oxygen reduction catalyst by calcinating CNT/PBI6 (Figure 1).

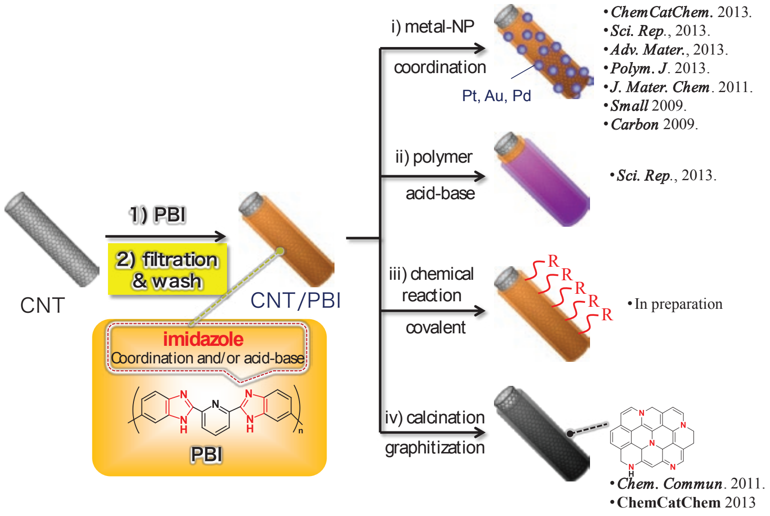

Figure 1 PBI-wrapping of carbon nanotube for electrocatalysts

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Ionic liquids at interfaces and nanoconfinement, and the physics of supercapacitors at the nanoscale

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World-wide rapid development of ultrananoporous and nanostructured carbon materials for electrodes demanded understanding of their performance at the nanoscale. In this talk, I will overview our current understanding of the mechanisms of charge storage and charging dynamics in supercapacitors with ionic liquids as electrolytes, focussing on the following points:

1. Charge storage equilibria: from flat interfaces to nanoscale pores

a) Double layer and electrical capacitance at flat interfaces
b) Renormalized interionic interactions in nanoconfinement: the superionic state in a nanopore
c) Approximate and exactly solvable models of charge storage: the capacitance of single cylindrical and slit pores as a function of voltage and the size of the pore; calculating the stored energy
d) The effect of pore size distribution and complexity of the pore space

2. Charging dynamics and the laws of ion transport in nanoconfinement

a) Charging of quasi single file pores
b) Charging of slit pores

3. Energy-to-power trade-off

a) new optimization scenarios for nano-engineering of supercapacitors;
b) ionophobic electrodes and pressing a spring concept

4. Leading-to-degradation: the unwanted 'electroactuation'

5. Latest developments

a) Sorbed water in the double layer: where is it?
b) New hints from the cyclic voltammetry
c) From energy storage to energy harvesting

6. Main challenge and to do list: how to improve both stored energy and power?

a) Electrochemists: what to measure (to check the theory) and to learn
b) Material scientists: in which direction to modify the materials of the electrodes

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Tip-enhanced Raman spectroscopy applied to nano-carbons

Yuika Saito
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Tip-enhanced Raman spectroscopy (TERS) is a powerful tool for high-resolution Raman spectroscopy. In this method, a metal coated nano-tip acts as a plasmonic antenna to enhance the originally weak Raman scattering from a nanometric volume of a sample. The technique enables to detect Raman scattering light from nano-scale area and also enhance the light intensity with combination of near-filed light and localized surface plasmon generated at a metallized tip apex. As the TERS developed, there is high demand to investigate the properties of near-field light e.g. polarization properties. We have analyzed the polarization properties of near-field light in TERS and successfully realized the quantitative nano-imaging by visible light. Nowadays TERS is widely used to investigate various nano-scale samples, for examples, carbon nanotubes (CNTs) and graphenes.

Methods

As illustrated in Figure 1, the system is inverted microscope based setup with oil emersion high NA objective lens (1.4NA). A metallic nano-tip irradiate by 488 nm CW incident laser is approached from the top of the sample plane by means of an atomic force microscopy (AFM) control. If a sample is brought near the tip apex within the confined light, TERS signal can be observed. Further, by scanning the sample, one can obtain Raman image at high spatial resolution equivalent of the apex of the nano-tip which is typically 10-30 nm.

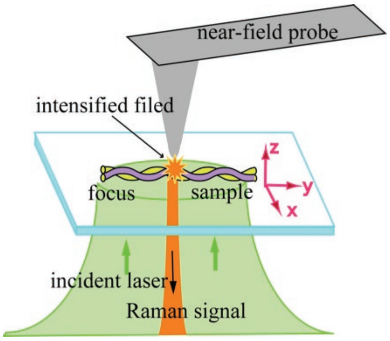

Figure 1. The concept of TERS

Localized metal- semiconductor transition in CNTs

The electronic properties of CNTs can change with a slight deformation, such as the one caused by the pressure of one single-walled CNT crossing over the other in an ‘‘X’’shape. The effect, however, is extremely localized. We present TERS investigation of the extremely localized semiconductor-to-metal transition of CNTs in such a situation, where we can see how the Fano interaction, which is a Raman signature of metallic behavior, grows towards the junction and is localized within a few nanometers of its vicinity. After exploring the deconvoluted components of the G-band Raman mode, we were able to reveal the change in electronic properties of CNTs at extremely high spatial resolution along its length.

Polarization nano-imaging of CNTs

Besides the photon confinement, the nano-tip carries several important functions for nanoscale imaging. The polarization properties in near-field spectroscopy also rely on the shape of the probe. It has been considered that the polarization condition at the nano-tip is mostly parallel to the probe axis. In actual near-field experiment, however, the perpendicular polarization also exists in the excitation volume due to the depolarization properties of the tip. We have evaluated the polarization properties of the near-field tip by defocused imaging technique. The tip apex was well approximated as a single dipole oscillated by the incident laser polarization. Using the tips whose dipole orientations were determined, we measured polarization TERS images of single-walled CNTs which exhibits a strong polarization anisotropy. The intensity of the graphite band (G-band) in TERS images clearly showed that the polarizations parallel to the dipole orientation are dominantly excited. The result indicate that the quantitative optical nano-imaging of CNTs was realized through this polarization evaluation.

Keywords

Tip-enhanced Raman Spectroscopy, Near-field, Polarization, Plasmonics, carbon nanotubes

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Playing with fire

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Carbon is one of the most influential materials of our age. On a bulk scale, porous carbons continue to be a key resource for soil improvement, water purification and air filters.[1] There is also huge international investment in specialized carbons such as nanotubes and graphene. More recently, nanostructured graphitic carbons with less defined structures have been found to show remarkable activity as electrocatalysts, battery electrodes and supercapacitors.[2] For both specialized and bulk applications, the structure of the carbon is crucial. However, the preparation of nanostructured and porous carbons often involves costly, hazardous or high energy processes. This leads to specialized carbon materials being too expensive for many applications.[3] Furthermore, if carbon nanostructures are to find large-scale use in new energy technologies, the synthesis must be sustainable.[4]

Recently, we demonstrated that iron could be used to catalyze the transformation of cellulose fibres and raw biomass into carbon nanotubes. Using combinations of iron and magnesium, we have also developed routes to porous carbons with hierarchical structure from simple biopolymers such as gelatin. This talk will overview these simple synthetic methods as well as the techniques used to characterize the bulk structure, such as synchrotron SAXS.

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Queen Mary, University of London, United Kingdom

Hierarchical Assemblies of carbon nanotubes for ultra-flexible li-ion batteries

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One of the most fascinating paradigm shifts in modern electronics is the fabrication of soft and flexible electronic devices. This development is fuelled by a continuous search for more compact and intuitive consumer electronics, medical implants, and the emergence of the 'Internet of Things'. While considerable progress has been made in the fabrication of flexible and stretchable logics and displays, the flexible batteries needed to power these devices remain challenging. Existing flexible batteries are often too heavy, bulky, and rigid, and require a radical redesign of the battery architecture to address these issues. Recent, progress towards flexible batteries includes the use of polymer substrates, composite membranes, paper based electrodes etc. However, many of these designs suffer from fast-capacity decay, limited flexibility, poor thermal management, and high weight.[1-4] Therefore design of highly flexible batteries requires judicious engineering of the electrodes to mitigate stress concentration and crack formation.

We propose a design where stress in the electrode is localised in the current collector and decoupled from the electro-active region, which remains unstressed during bending. To achieve this, we populate a flexible current collector with 3D CNT microstructures[5,6] which contain the electrochemical active material (Fe_2O_3 anodes and $LiNiCoO_2$ cathodes in this work). In order to remain unstressed as the electrode bends, the base of each active microstructure must be small, similar to trees. Figure 1 further illustrates our rationale behind the design of the electrode architecture. We found that this battery architecture not only imparts excellent flexibility (bending radii ~ 300 μm), but also high rate (20A/g), cycling stability (over 500 cycles at 1C with capacity retention over 70%).[7]

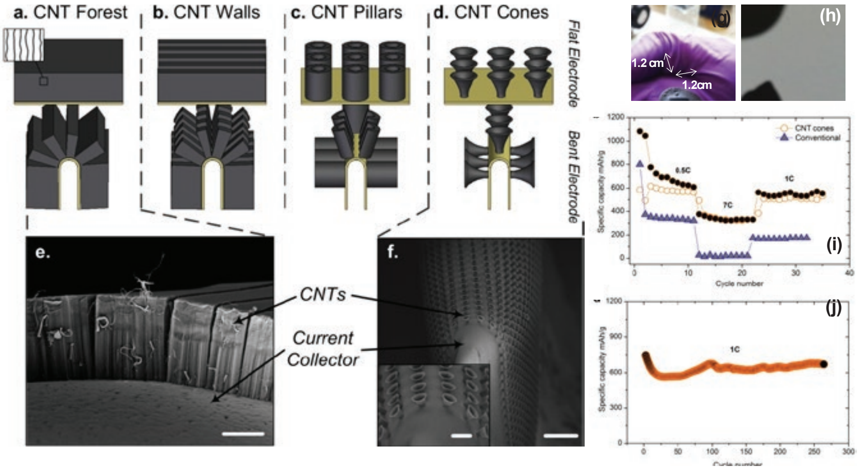

Fig 1: (a-d) Schematics of CNT forest and cones electrode architectures and their deformation when bent. (e) Scanning electronic microscopic (SEM) image showing cracks in a CNT forest bent to a radius of 3 mm. Scale bar, 40 μm. (f) SEM image of a bent CNT cone electrode. Scale bar, 400 μm. Inset shows the magnified view SEM image. Scale bar, 100 μm. (g-h) Camera image of electrode in flat and bent state. (i) Cycling performance of both microcone and conventional electrodes. (d) Extended life-time testing of the CNT cone electrodes.

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Nanocomposite films as a gas sensor for organic compounds

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This research concerns the physical and structural properties of carbon nanotube /conductive polymer composites and their use in gas sensors. A good sensor should be sensitive, reliable and low cost, with fast response and a short recovery time. Carbon nanotubes (CNTs) are well-suited because of their unique properties; their small size, hollow centre, large surface area and good electric conductivity [1]. However, it has been shown that pristine carbon nanotubes have a low response for volatile organic compounds – our target analyse - therefore we attempted to improve this property of CNTs by templating pyrrole on CNTs[2]. Polypyrrole is simple to prepare by oxidation of the monomer and its resistance is very sensitive to organic vapours, although much larger than that of CNTs. TEM and AFM of polypyrrole/CNT composites prepared from single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) show polypyrrole coated the CNTs successfully. There are significant changes in the range of diameters of nano tubes for SWCNTs from (7-10) nm to (8-35) nm and from (2-10) to (21-50) nm for MWCNTs. The composites were tested for the variation in their resistance upon exposure to a range of organic vapours (acetone, chloroform) and to water. The sensing devices comprised simple two-terminal devices over which a layer of the composite was applied by drop-coating. We investigated the effect of the CNT: polypyrrole ratio on the sensor response, S= $(R-R_0)/R_0$) where R0 is the resistance in an air atmosphere and R is the resistance at steady-state after exposure to an air/analyte mixture. In general, pure CNTs show a rapid response time, but very low response (typically S < 0.1) at room temperature. As the amount of polypyrrole in the composite is increased, S increases, the response time deteriorates. Interestingly, the response of the composites may even change sign as a function of target analyse concentration; this suggests that a simple mechanism based on swelling and its effect on the percolation behaviour of CNTs in the polypyrrole matrix is insufficient to explain the data.

Keywords
Gas sensors, conductive polymers, CNTs/Ppy, nanocomposite sensors

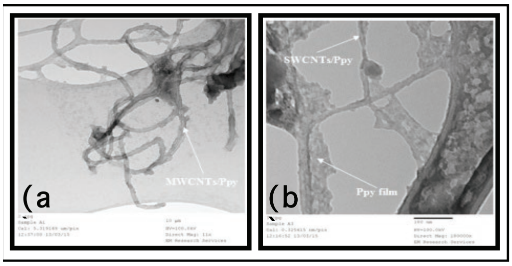

Figure1: TEM images of (a) hybrid MWCNTs (Mag11x), (b) SWCNTs after tamplated by Ppy.

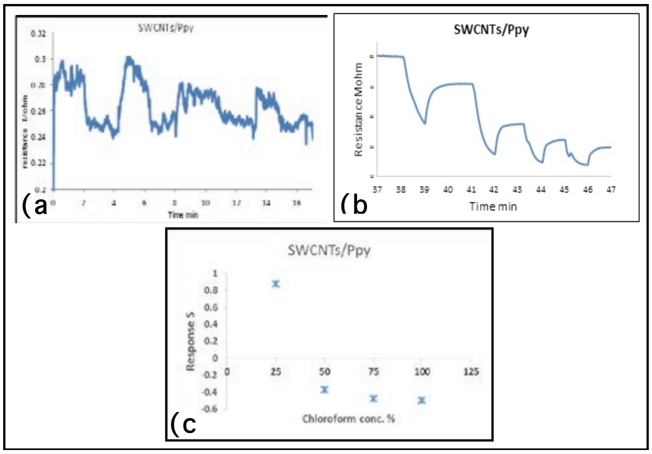

Figure2: (a&b) The sensitivity of the electrical resistance R of SWCNTs/Ppy films to chloroform (0-100) % exposure at 17oC;(c) The device sensitivity S=(R-R0)/R0 as a function of chloroform concentration.

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Fullerenes as containers for small molecules: Synthesis and properties of $H_2O@C_{60}$ and $HF@C_{60}$

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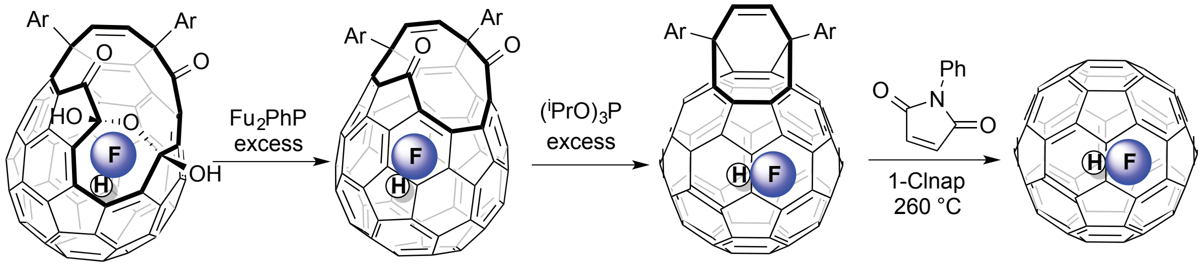
The high symmetry and a non-interacting inner surface of fullerenes provide a unique environment for encapsulating small molecules giving endofullerenes ($A@C_{60}$). The effective isolation of the guest from the environment allows many remarkable properties to be observed for molecular endofullerenes, for example due to the interaction of nuclear spins and molecular rotations.[1] The remarkable route to these systems is termed 'molecular surgery' where synthetic operations are used to open a hole in the fullerene allowing encapsulation of the guest, followed by a suturing technique to reform the pristine shell. The final closure to give $H_2@C_{60}$ and $H_2O@C_{60}$ was reported by Komatsu and Murata.[2]

We have developed an improved route to $H_2O@C_{60}$,[3] and the poster will report on physical studies it has enabled.

Hydrogen fluoride (HF) is one of the most studied small molecules, both theoretically and experimentally but its high chemical reactivity and tendency to form aggregates are limitations. We recently described the trapping of HF in an open fullerene,[4] and now report completion of the synthesis to form $HF@C_{60}$. Detailed theoretical studies on the closure reactions suggest a novel mechanism, and allowed selection of a successful reagent. Initial studies on $HF@C_{60}$ using cryogenic NMR, IR, and Inelastic Neutron Scattering will be reported.



$HF@C_{60}$

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Heads or tails: How do substituted fullerenes melt?

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We address the question as to whether the melting of chemically substituted fullerenes is driven by the dynamics of the fullerene moiety (the head) or the substituted sub-unit (the tail). To this end, we have performed quasielastic neutron-scattering experiments and classical molecular-dynamics simulations as a function of temperature on the prototypical fullerene derivative phenyl-C61-butyric acid methyl ester. To enable a direct and quantitative comparison between experimental and simulation data, dynamic structure factors for the latter have been calculated from atomic trajectories and further convolved with the known instrument response. A detailed analysis of the energy- and momentum-transfer dependence of this observable in the quasielastic regime shows that melting is entirely driven by temperature-activated tail motions. We also provide quantitative estimates of the activation energy for this process as the material first enters a plastic-crystalline phase, followed by the emergence of a genuine liquid at higher temperatures.

Carbon nanotube-quantum dot nanohybrids: Assembly with single particle control in aqueous solution

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We present a controlled assembly strategy for the formation of carbon nanotube - quantum dot nanohybrids, where the terminal ends of individual single-walled carbon nanotubes (SWCNT) are selectively functionalised with single quantum dots (QDs), via the formation of covalent bonds. The assembly, in environmentally friendly and biocompatible aqueous solution, was controlled towards the formation of monofunctionalized SWCNT-QD structures.

We use DNA wrapped carbon nanotubes, where the DNA acts as a surfactant for the dispersion of the nanotubes in water. Moreover, the DNA’s helical wrapping on the sidewalls of the tubes leaves only the terminal ends of the SWCNTs available for direct functionalization.

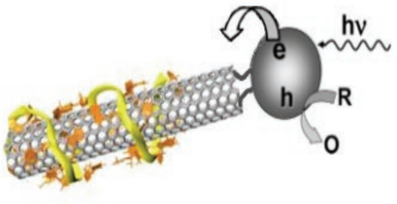
Atomic force microscopy has been used to image the nanostructures and allowed us to identify the nanodots exclusively at the terminal ends of the tubes.

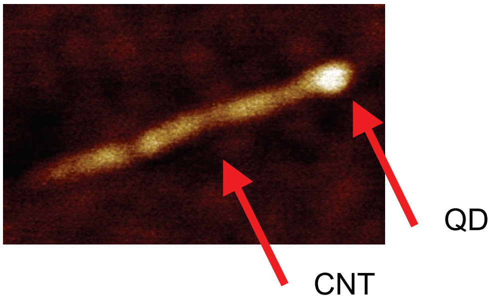
Photoluminescence studies in solution and on surfaces at the single nanohybrid level showed evidence of electronic coupling between the two nanostructures.

Quenching of photoluminescence of the CNT-QD nanohybrids in solution has been observed which indicates an electronic coupling between the two nanostructures as previously observed in QD-SWCNT composites [1].

The photoluminescence blinking dynamics of conjugated and un-conjugated individual quantum dots was investigated showing larger off-state probability densities for QDs attached to the tubes, suggesting an increased photoinduced charging of the nanocrystals.

The ability to covalently couple heterostructures with single particle control is crucial for the design of novel QD-based optoelectronic and light-energy conversion devices[2].





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An optimised graphene oxide print protocol; quarter density printing at high temperature

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Graphene, with its low cost and potential high electrical performance, suggests that widely-available, functionalised and printable graphene inks are on the horizon. This poster presents our efforts to develop graphene-based inks as well as an improved printing process to efficiently produce electrical components for use in bio-sensors, super-capacitors or photo-optical devices.

Graphene oxide ink has been widely researched but problems still exist with regards to its printability and conductivity. Here we present studies into the formulation of a highly optimised graphene oxide-glycol ink that can be reliably printed using a Dimatix inkjet system. The utilisation of a quarter density printing method at higher substrate temperatures yields superior print quality. The printed films were characterised by robust AFM and Raman studies along with optical and helium ion microscopy. The conducting properties of reduced films are also reported through probe station measurements and indicate that these materials can have applications in bio-MEMS sensor systems after further functionalisation.

Advanced characterisation of graphene deposited carbon paper electrodes for the all-vanadium redox flow battery

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Electrophoretic deposition (EPD) was employed for impregnating carbon paper (CP) electrodes with reduced graphene oxide (rGO). N,N'-dimethylformamide was the solvent used at a constant voltage of 300 V.EPD was carried out for 30 min and the inter-electrode distance (between the CP substrate and the graphite disk counter electrode) was 15 mm[1]. rGO enhanced CP showed a remarkable 60% reduction in charge transfer resistance for the V(IV)/(V) redox couple from cyclic voltammetry and impedance analyses. In a flow cell, the peak power density was 4% higher for rGO impregnated electrodes; the result is similar to that obtained from carbon felt electrodes impregnated with rGO[2]. Advanced characterization by means of X-ray tomography displayed how the rGO had penetrated into the CP substrates and were intertwined with the fibres and nodes.Raman analysis confirmed deposition of rGO on the CP electrodes.

Keywords

Reduced graphene oxide, electrophoretic deposition, carbon paper electrodes, cyclic voltammetry.

Acknowledgements

The authors are grateful for the funding provided by the EPSRC project EP/L014289/1.

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Inorganic synthesis in carbon nanoreactors: Stepwise formation of low-dimensional nanomaterials

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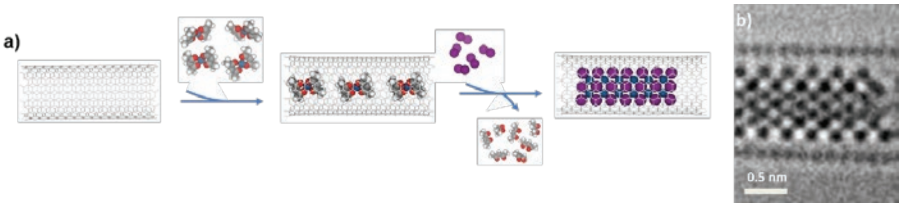
Preparation of inorganic nanomaterials with a desired structure and properties requires strict control of their size, shape and composition. We report a new universal approach for the formation of quasi one dimensional inorganic materials inside CNTs via the sequential encapsulation of molecular precursors which contain the appropriate elemental building blocks and subsequent reaction (figure 1a). The chemically inert nature of such nanosized containers makes CNTs ideal candidates for use as both reaction vessels, in which the precursors can be combined, and 1D templates which can direct the formation of products which are unfavoured or impossible to synthesise in the bulk phase.[1,2]

The stepwise synthesis inside nanotubes has enabled monitoring the formation of Pt compounds at each step of the reaction by aberration corrected high resolution transmission electron microscopy (AC-HRTEM) imaging verifying atomic structures of the products (figure 1b), and by an innovative combination of x-ray absorption fluorescence (XAF) spectroscopy and Raman spectroscopy monitoring oxidation states of platinum guest-compounds within the nanotube and vibrational properties of the host-SWNT respectively.



Our study reveals that electron transfer between guestcompound and host-SWNT can occur in either direction depending on the composition and structure of the latter. The new strategy for inorganic synthesis at the nanoscale was shown to be versatile, universal and enabled the formation of previously inaccessible quasionedimensional Pt-containing nanomaterials suitable for a variety of technological applications. These range from electronic devices where electronic doping of the nanotube is precisely modulated by electron transfer between the SWNT and encapsulated compound, to new catalytic platforms exploiting the unique chemical properties of platinum compounds where the shape of the crystal and oxidation state of the metal are controlled by steric and electron interactions with the host-nanotube.

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Fullerene-capped copolymers based on P3HT for organic solar cells

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Finding an inexpensive, clean and completely renewable energy source is the most pressing challenge of current times. Solar energy has long term potential because the earth receives enough energy from the sun in just one hour to meet all human energy requirements for an entire year. Current silicon-based solar technologies lead the market in terms of device efficiency and lifetime but they are expensive to implement on a global scale.[1] This is the major motivation for the development of organic solar cells (OSCs), which recently attracted much attention due to their low-cost, flexibility, lightweight and their use in large-area devices (Figure 1).[2-4]

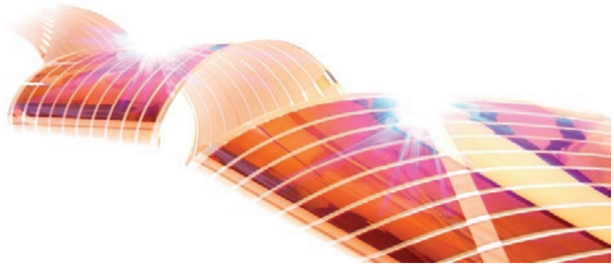

Figure 1. Flexible, lightweight, thin film OPV device.

OSCs are not without their problems, most notably lifetimes, which can be as low as 3 years. The individual layers play a vital role contributing towards the performance and lifetime of the final solar-powered device. Block copolymers (BCPs) have long-term structural stability and also their solid-state morphology being of the appropriate dimensions to efficiently perform charge separation and transfer to electrodes.[5] Our aim is to improve further the efficiency and lifetime of OSCs by creating highly original and industrially viable novel block copolymers. Hence, we focused on the synthesis and photovoltaic application of BCPs based on poly(3-hexylthiophene) (P3HT) due to its high hole mobility, good processibility and ease of synthesis.[6] Herein, the novel synthesis of the latest donor-acceptor (D-A) fullerene-capped BCPs based on P3HT will be presented and explored their detailed study of self-assembly and device performances.[7]

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CNT reinforced ceramic composite materials

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Carbon nanomaterials such as carbon nanotubes (CNTs) are often considered to be the ultimate reinforcement material for ultra-strong and ultra-light organic and inorganic composite materials. However, research on CNT composites has been hindered by the fact that commercially available CNTs are often tightly agglomerated and hence require sophisticated dispersion techniques to detangle them before they can be employed as fillers or reinforcements. Recent developments in the production and up scaling of nanotubes in the nanomaterials by design group at Oxford have paved the way towards the successful exploitation of CNT properties for the generation of multifunctional composite materials. Combining this with biomimetic ceramic microstructure architectures which are manufactured using new developments in freeze-casting, this promises to deliver a novel material that improves current ceramic materials significantly.

Vanadium electron transfer on modified carbon electrodes

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The Vanadium Redox Flow Battery (VRB), invented and developed by Maria Skyllas-Kazakos and her co-workers at the University of New South Wales, represents one of the possible options for efficient electrochemical energy storage [1]. One of the contemporary challenges of VRBs is their low power density and therefore catalysis of the redox reactions is desirable [2].

However, currently in the literature there is not even consensus which of the two half-cell reactions, the V^{2+}/V^{3+} or the VO^{2+}/VO_2^+ redox reaction, is faster. Similarly, reports contradict each other regarding the influence of carbon surface functional groups. Some paper assign catalytic activity for one or both half-cell reactions to carbon surface functional groups, others do not.

We will show that this uncertainty in the literature is due to two factors:

An apparent catalytic effect appears when porous electrode materials are investigated with linear or cyclic voltammetry. The porosity reduces the separation between anodic and cathodic peak suggesting enhanced kinetics when indeed only an interplay of enlarged electrochemical surface area and impeded diffusion within the porous electrode is present [3];

The faradaic current is proportional to both the electrochemical active surface area A^{ECSA} and the electron transfer constant k_0: I □ $A^{ECSA}\ k_0$. As both parameters vary with change in electrode composition, it is often difficult to distinguish catalytic from surface-area effects.

We have recently presented a method that allows to monitor changes in A^{ECSA} and k_0 while varying the concentration of surface functional groups on carbon electrodes [4]. The experimental procedure relies on electrochemical impedance spectroscopy, which yields an observable for A^{ECSA}, the double layer capacitance C_{DL}, and an observable for both A^{ECSA} and k_0, the charge transfer resistance R_{CT}. Combining C_{DL} and R_{CT}, the contribution from A^{ECSA} can be eliminated and only the effect of k_0 remains.

This method was employed to investigate the kinetics of the V^{2+}/V^{3+}, Fe^{2+}/Fe^{3+} and VO^{2+}/VO_2^+ redox reactions on multi-walled carbon nanotubes [4] and commercial graphite felt electrodes [5]. The surface chemistry of the carbon electrodes was modified by chemical and thermal treatments and monitored by SEM, XPS, FTIR, TGA-MS and Raman spectroscopy.

We will show unambiguously that surface functional groups on carbon enhance the kinetics of the V^{2+}/V^{3+} and Fe^{2+}/Fe^{3+} redox reactions, but impede the VO^{2+}/VO_2^+ redox reaction.

We will present possible reaction mechanisms that explain this diametrical behavior and discuss consequences for the VRB.

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Reversible hydrogen storage in novel carbon nanostructures

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Finding new hydrogen storage materials for mobile and stationary applications is a challenge for the future development of a hydrogen economy. In addition to complex hydrides, MOFs, or chemical hydrides, carbon-based nanostructure materials are a promising option. Their interaction with hydrogen is typically confined to relatively weak van-der-Waals forces underpinning physisorption, or to extremely stable covalent bonds in the case of chemisorption, thereby excluding these materials from use in real-world applications. Alkali-cluster intercalated fullerides (ACIFs) represent an exception to the above, wherein metastable C_{60}-H covalent bonds can be reversibly exploited to store high amounts of hydrogen with modest dehydrogenation enthalpy. This work is concerned with the structural investigation and hydrogen-storage mechanisms in mixed phases of Li_yC_{60}, Na_yC_{60} and $Na_xLi_{y-x}C_{60}$.

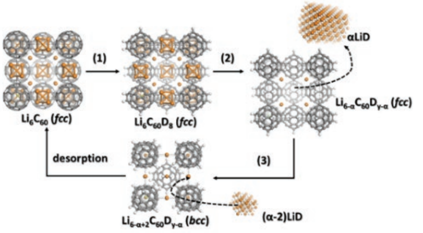

Figure 1: Hydrogen sorption process in Li6C601

ACIF compounds were synthesized by solid-state reactions between C60 and metal azides at 350-450 °C. Hydrogen uptake studies were carried out with a manometric apparatus up to 100 bar H_2 and 350 °C. Thermodynamic features were investigated by DSC analysis during hydrogen discharge under 1 bar H_2. The structure and absorption behaviour were investigated by means of *in situ* neutron diffraction up to 60 bar D_2.[1] These materials show reversible absorption up to 5 wt% H_2 at moderate temperature and pressure via a catalytic effect mediated by the intercalated clusters.[2–5] We have also identified a number of strategies to further improve absorption performance. On the one hand, the addition of catalysts (i.e. Pt or Pd) improves the catalytic activity towards hydrogen dissociation and allows for an increase in hydrogen absorption of Li6C60 up to 6 wt% H_2.[6] Furthermore, the destabilizing effect of Na in the co-intercalated $Na_xLi_{y-x}C_{60}$ compounds (y = 6, 12; x = 1-y) leads to an improvement of the hydrogen-sorption kinetics by about 70%, accompanied by a decrease in desorption enthalpy from 66 to 49 kJ/mol H_2. Overall, our results suggest that these materials are of potential interest for mobile applications.

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Thermal reduction of graphene oxide and the effect of reduction temperature on the performance of supercapacitors

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Graphene and graphene-based materials have attracted significant recent attention because of their unique properties and have emerged as a new class of promising electrode material in supercapacitors. Among the various approaches, chemical exfoliation of graphite has provided an affordable route to the large scale processing of graphene-based materials. The most common chemical means of graphite exfoliation is the use of strong oxidizing agents to yield graphene oxide (GO). While this yield isolated graphene oxide (GO) monolayers in suspension, polar surface oxides make GO electrically insulating[1,2] and thus GO is not a preferred electrode material for supercapacitors. Therefore in a subsequent preparation step, GO is typically reduced to what is commonly termed reduced graphene oxide (r-GO). Reduction strategies include mainly, thermal, chemical and electrochemical reduction procedures[3]. This study focuses on thermal reduction of GO and to understand the effect of reduction temperature during the thermal reduction of GO on the structure, morphology and electrochemical performance of r-GO as electrode materials in supercapacitors. Free standing, flexible GO paper was synthesised using graphite oxide derived from vein graphite following Hummer's method[4]. As synthesized GO was thermally reduced at 200 °C, 400 °C, 950 °C in inert atmosphere to obtain reduced GO. The morphology and chemical structure of GO and r-GO were characterized by means of scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Thermal properties were investigated using thermo gravimetric analysis. For electrochemical characterisation, two-electrode symmetrical supercapacitor cells were constructed and characterized by cyclic voltammetry and electrochemical impedance spectroscopy. Tetraethylammonium tetrafluoroborate ($TEABF_4$) dissolved in Propylene Carbonate (PC) was used as the electrolyte. It was observed that experimentally, even at a reduction temperature of 950 °C, full exfoliation to single layered graphenes could not be achieved. However, drastic changes in the chemical structure and pore structure take place in GO with reduction temperature as observed with SEM, XRD, FTIR and Raman spectroscopy. Even by reducing at 950 °C, all the functional groups on GO plates could not be removed and some stable oxide functional groups were observed remaining on r-GO plates as well. However, such surface functionalities on graphene introduce good wetting properties and acceptable electrical conductivity to these graphene-based materials. On the other hand, this represents a fundamental limitation that must be overcome if r-GO is to achieve properties that resemble those of mechanically exfoliated graphene. Crucially, current knowledge of the bonding configuration or location of the residual oxygen is lacking. The insight into why oxygen remains despite robust reduction treatments is necessary.

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Analysis of the chemical reaction between CO_2 and amine supported on porous carbons using ZLC desorption curves

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Amine impregnated materials as adsorbents for a carbon capture process have been the focus of numerous studies. In general, such materials exhibit promising selective adsorption of CO_2 from dilute gas streams. Porous carbons are a suitable support for amine which subsequently reacts with the CO_2. The majority of the studies have concentrated on designing materials with higher CO_2 capacities and an increased interaction efficiency between the CO_2 and amine sites. In this work an adsorption model is proposed to investigate the reaction kinetics between the CO_2 and amine in the adsorbed phase. The zero-length column (ZLC) technique was used to investigate the interaction between the amine and CO_2 in the gas phase at low partial pressures. An unusual double curvature behaviour in the ZLC desorption response has been observed and it was assigned to the complex reaction kinetics between CO_2 and amine. It was found that the reaction between CO_2 and amine is a non-linear process which cannot be modelled by a simple first order rate equation. A new model that accounts for the reaction in the adsorbed phase is proposed which accurately represents the experimental data.

The effect of sonication pre-treatment on single wall carbon nanotubes

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Owing to impressive mechanical, structural and electronic properties, single wall carbon nanotubes (SWCNTs) are being widely researched towards nanodevices. Sonication is the treatment used to disperse the tubes allowing them to become untangled.

The agitation present in sonication processes separates SWCNTs and can also have an adverse effect on the structural integrity of the graphitic lattices. The aim of this project is to study sonicated samples of SWCNTs to evaluate the damage caused by Atomic Force Microscopy (AFM) and Raman Spectroscopy. By assessing damaging, strategies can be devised towards its minimisation; resulting in dispersed good quality SWCNTs.

Results show that SWCNTs dispersion improves with sonication time. In this scheme, SWCNTs sonicated for one hour show improved dispersion in comparison to the unsonicated sample, and SWCNTs sonicated for two hours show further improved dispersion, supporting the notion of sonication as an effective technique to ‘debundle’ SWCNTs. Raman analysis show that SWCNTs sonicated for two hours suffered considerable structural damage (Fig. 1). These results suggest that a trade-off may be needed in determining adequate sonication times, balancing dispersion and graphitic damage.

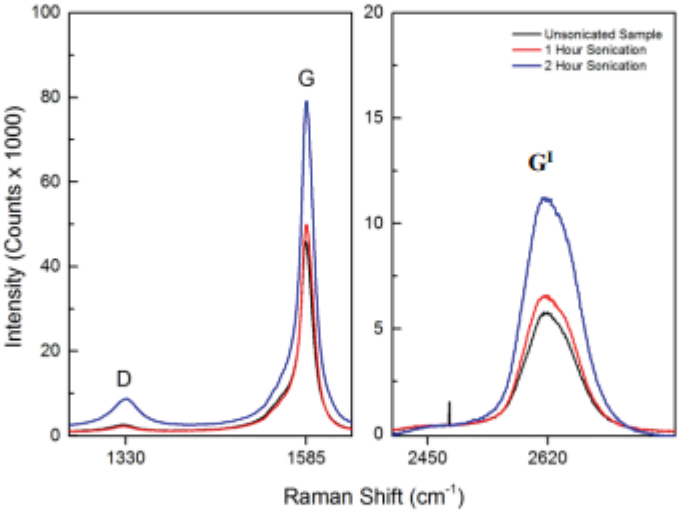

Fig. 1 Raman bands which have been focused on and magnified to allow further analysis

Revealing the chirality of electrons in twisted graphene tunnel transistors using Landau level spectroscopy

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Multilayer transistors based on graphene[1-5] and other van der Waals crystals exhibit many interesting physical properties: high on-off current switching ratios, mechanical flexibility, photoresponsivity, light emission, and resonant tunnelling with gate voltage-tuneable negative differential conductance at room temperature. In these devices, we have recently demonstrated the strong sensitivity of in-plane momentum conserving tunnel transitions to any small misalignment or twist angle between the crystalline lattices of the two graphene electrodes[4-5].

Here, we investigate the effect of a magnetic field applied perpendicular to the graphene layers on the current-voltage characteristics of devices in which the graphene lattices are carefully aligned to within 1 degree. The magnetic field quantises the electronic states in the conical, gapless conduction and valence bands into a ladder of unequally-spaced Landau levels. Tunnelling of electrons between the Landau levels of the two graphene electrodes gives rise to a complex pattern of sharp resonant peaks in the differential conductance $G=|dI/dV|$, see Fig. 1. To analyse the dependence of G on an applied magnetic field, bias voltage and gate voltage, we use a Bardeen transfer Hamiltonian approach which incorporates the two-component spinor-spatial character of the Dirac-Weyl fermions. We demonstrate how the intensity of the energy- and momentum- conserving tunnel transitions reveal the effects of chirality[6], which is a unique feature of electron dynamics in graphene and related materials.

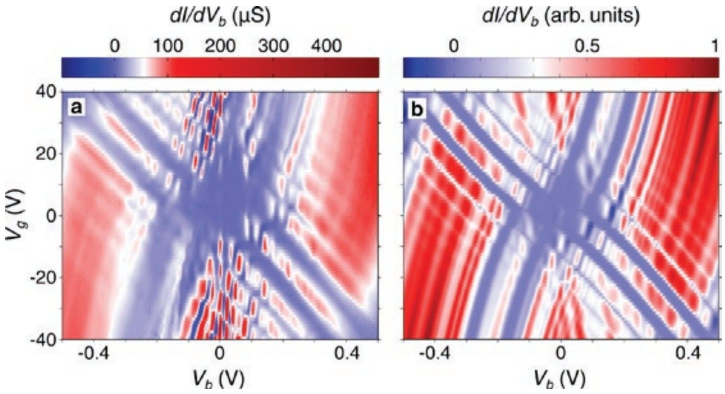

Fig. 1. (a) Colour maps displaying the inter-LL resonant tunnelling peaks in the differential conductance over a wide range of bias and gate voltages, V_b *and* V_g*, at T = 4 K with a magnetic field B = 4 T applied perpendicular to the graphene layers. (b) Colour map showing the corresponding results of Bardeen transfer Hamiltonian calculations.*

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A rapid and accurate minimal model for targeted nanographene design

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Advances in the experimental production of nanographene – using top-down fabrication, such as e-beam lithography, or by bottom-up, surface-assisted chemical synthesis[1] – have provided much impetus to directly link theory and experiment. The benefits are two-fold. On the theoretical side, there exists an important opportunity to develop more accurate theoretical models of nanographene by direct comparison of simulation results with experimental measurement. Such comparisons are vital for understanding the 'missing' physics in the theoretical description of nanographene, which has thus far been a bottleneck for accurate simulation. On the experimental side, the creation of accurate, theoretical design tools can greatly assist in removing experimental trial and error, thus opening up the potential for quantum engineering. The benefit of theoretically informed experiments would be to circumvent time-consuming and often expensive procedures for determining specific features of the nanographene (size, functionalisation, patterning, etc.) that would lead to targeted applications and new intellectual property.

In order to meet these aims, we have developed a computationally and physically transparent minimal model for nanographene[2] that is coupled to a 'graphene user interface' or GRUI. The minimal model has substantially greater computational efficiency compared to density functional theory calculations enabling it to reach large unit cell sizes for realistic modelling without compromise to accuracy. The GRUI can be directly interfaced with experiment and can also be employed for rapid predictive simulation in nanographene device design. We will demonstrate the accuracy of the method and portray example results (e.g., spin transport) pertaining to my group's collective work on patterned and defected graphene nanoribbons devices (top-down), and for chemically-synthesised nanographene (bottom-up) determined via directed, kinetic self-assembly simulation.

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Sustainable carbon fibres for energy storage

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Due to the increasing utilization of renewable energy sources, the development of energy storage devices is essential. Furthermore the recent advances in portable electronic devices fabrication also requires higher power and energy densities combined with mechanical flexibility.

Carbon fibres have attracted a great deal of attention due to their exceptional mechanical properties since late 50s[1]. However their fabrication price still limits their utilization at a larger scale. We focus our attention focuses on cheaper and more environmental friendly precursors such as cellulose and lignins. Lignin is the most abundant aromatic polymer in nature since it constitutes about 15-30 wt% of the global biomass after cellulose (40-60%) and hemicellulose (10-30%). Today with the increasing development of biorefineries involving the production of cellulosic biofuels, new utilization for lignin into high value added products are necessary. Lignins stand as a promising replacement for the fabrication of much cheaper carbon fibres offering at the same time acceptable mechanical properties.

In this study we compare the energy storage efficiency of sustainable copolymer carbon fibres against oil-based polymer ones, respectively produced by electrospinning of cellulose, lignin and polyacrylonitrile. The carbon fibre mats are used as free-standing electrode papers for their use in flexible supercapacitors.

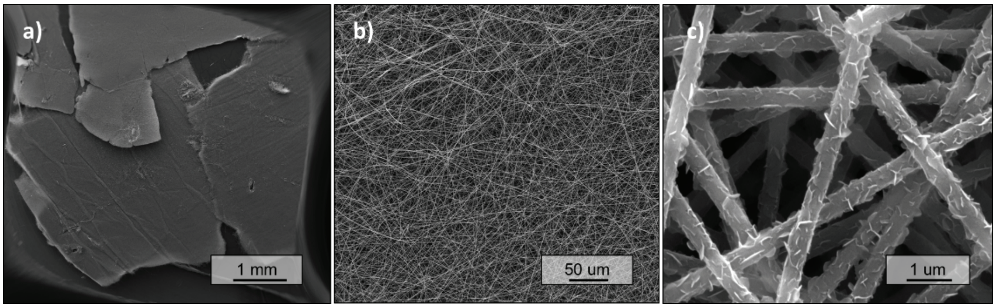

Figure 1: Polyacrylonitrile carbon fibres containing a) and b) ferrocene and c) manganese dioxide nanoflakes on the surface

We also compare the efficiency of the modified fibre networks by addition of ferrocene and manganese oxide. We are currently investigating the electrochemical properties of the carbon fibre mats synthetized.

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1D and 2D nano-material extraction and in a fluctuating g-field

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Recent years have seen great interest in the application of 1D carbon nanomaterials (carbon nanotubes) and 2D nanomaterials such as graphene because of their unusual and valuable physical and electronic properties for applications in electronics, photonics and as structural materials [1]. More recently analogues of these materials such as 2D transition metal dichalcogenides (MoS2, WS2 etc) have attracted interest as direct band-gap semi-conductors which could significantly extend the properties available for electronic and photonic applications [2].

If the promise of these materials is to be successfully realised significant advances in production processes are necessary. For many applications bulk production of >>kg/day will be required for which currently the simplest route is liquid phase exfoliation of natural crystalline forms. Efficiency and rate of production need to be increased, quality needs to be enhanced, and separation and fabrication technologies require development to meet the requirements of an efficient large-scale production process [3].

Particle based separations are inherently low resolution; centrifugation can only separate broad classes of materials in a single stage or throughput becomes very low using density gradient methods. Membrane and column chromatography alternatives are similarly hampered by lack of resolution and throughput [4]. Interfacial partitioning, the differential partitioning of particulate materials between the bulk phases and the interface of a biphasic system (e.g. oil and water) offers a highly selective way to separate particles based on their surface energy and size resulting in high resolution separations, with the potential for continuous operation in a scalable process [5]. Several striking examples of the application liquid-liquid partitioning to the sorting of carbon nanotubes have recently been published [6].

Our poster will highlight the capabilities existing at Brunel University London for the development of liquid extraction processes in a fluctuating g-field for the isolation of nano and micro particulate materials and the development of liquid-liquid and solid-liquid fractionation methodologies operating in batch, continuous or counter-current modes for their subsequent purification and fabrication. The technology is inherently cross-cutting having broad application to for example minerals processing and in particulate bioprocessing.

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Rapid synthesis of graphene quantum dots with tuneable properties

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Graphene, a 2-dimensional (2D) sheet of hexagonally arrayed carbon atoms, is one of the thinnest materials ever made.[1] It is exceptionally strong, transparent to light, yet, electronically fascinating and offers endless technological possibilities.

Graphene is expected not to show any luminescence, but most interestingly by "cutting" graphene sheet into a smaller size (<20 nm) results in making graphene quantum dots (GQD).[2] However, producing GQD in an economically and environmentally friendly way is still challenging.

Reaction chemistry in supercritical fluids (SCF) offers a rapid, greener and efficient alternative to traditional synthetic routes. The synthetic process has many advantages including independent control over reaction parameters (e.g. temperature, pressure) and hence particle properties. Furthermore, it offers significantly fewer steps and faster reaction times (few seconds).[3]

Herein, we present a rapid, green and innovative approach for synthesis of green and blue luminescent GQD with tuneable optical properties and low cytotoxicity using supercritical fluid as a route to efficient cutting of graphene (GO) to give GQD.

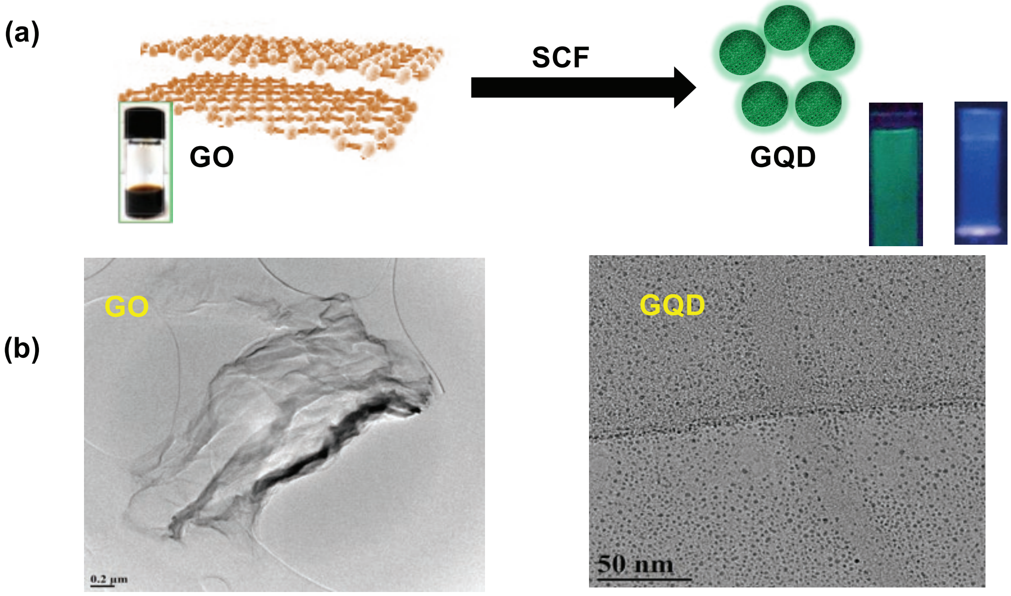

Fig. 1 (a) Schematic for the synthesis of GQD from graphene oxide (GO). (b) Transmission Electron Microscopy images for GO and GQD sample.

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Refinement of steam purification process for carbon nanotubes

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The steam purification process typically used to clean carbon nanotubes of amorphous carbonaceous species, has been further probed and advanced to enhance cleansing ability. By applying this refined technique to our prefabricated arrays of highly aligned areas of electrospun carbon nanotube composite nanofibres, it has led us to areas of highly aligned, highly crystalline, pure nanotubes. ‘Raman spectroscopy suggested a reduction in number of defects after steam treatment, indicating significant improvement on the original material. Further analysis revealed that the radial breathing mode peak intensity, used for nanotube diameter calculation, is also altered. Therefore, suggesting that some carbon nanotubes are more resistant to steam assisted oxidation, meaning that specific carbon nanotube diameters are preferentially oxidised. Thermogravimetric analysis of the refined steam purified nanotubes demonstrated a significant improvement in both quality, with respect to defect density, and in crystallinity, resulting in an overall increased resistance to oxidation. The treated carbon nanotubes are shown to withstand oxidation in temperatures of above 900 °C under ambient conditions. Applying this purification method to electrospun nanofibres realises the potential for next generation of lightweight composite materials which can be used in high temperature extreme environments.

Stabilising the lowest energy charge-separated state in a {metal chromophore - fullerene} assembly: A tuneable panchromatic absorbing donor-acceptor triad

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The conversion of solar light into electrical energy remains one of the major challenges facing modern society due to the constantly increasing demand for energy and the depletion of the world's resources. Nature efficiently utilises photosynthetic systems - cascades of energy and electron transfer reactions triggered either directly by photoexcitation or indirectly by energy transfer from light-harvesting antenna systems. In terms of charge separation, the characteristics of the individual electron acceptors and electron donors directly determine the overall efficiency of the system, whilst the environment of the photosynthetic reaction centres plays a crucial role in slowing down undesirable charge recombination processes. Thus, for the efficiency of artificial light harvesting devices to approach the levels of photosynthetic systems, the design, synthesis, and characterisation of efficient, artificial energy capacitors as well as the incorporation of chromophores which feature panchromatic absorptive, redox, and electrical properties are of critical importance.

This study reports the synthesis of a new C_{60} fullerene-bipyridine-Pt-catecholate donor-acceptor triad with exciting photophysical properties. The triad possesses tuneable panchromatic light absorption and is demonstrated to form a very low-lying charge-separated state with an energy of 0.77 eV and a lifetime of 890 ps. A combination of transient absorption and time-resolved IR spectroscopies is applied to investigate the photophysical properties of the triad, and the results are corroborated by extensive spectroscopic studies of the triad in the ground state. Furthermore, we monitor the photogeneration of the C_{60} monoanion using time-resolved infrared (TRIR) spectroscopy revealing the characteristic IR signature of C_{60} monoanion in solution at 1530 cm^{-1} which is completely unprecedented.

The bespoke design of the triad enables us to avoid the formation of the undesirable fullerene triplet excited state which is a common problem amongst previously reported C_{60}-donor assemblies, and the lifetime of the final charge separated excited state is one of the highest reported for structurally similar systems which makes it an ideal potential building block for artificial photosynthetic devices.

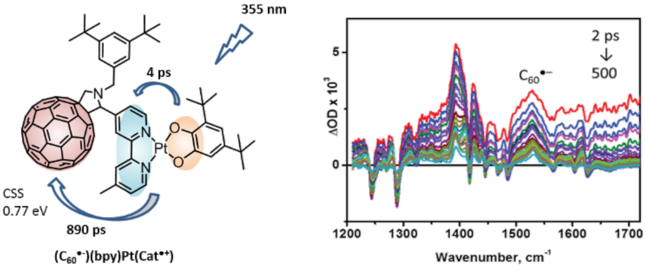

Figure 1. Schematic representation of the photophysical processes in the fullerene-bipyridine-Pt-catecholate triad (left) and the TRIR spectra of the triad at different time delays indicating formation of the C60 monoanion formation upon photoexcitation.

Heteroatom-doped carbons for electrochemical energy conversion

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We produce **carbon foam** at gram scale and surface area >2500 m^2/g by decomposition of sodium ethoxide. In its undoped form, it has potential applications in **hydrogen storage**: a H_2 uptake of 2.6 wt% via physisorption at 77K is measured. The material is also an ideal Pt **catalyst support**, with high electrochemical surface area and impressive fuel cell performance. Heteroatom doping can be performed by changing the precursors. By decomposing "amino-ethoxides", **nitrogen-doped carbon** foam is produced. This is an effective **Pt-free electrocatalyst** in acid media, giving insight into the oxygen reduction reaction in metal-free catalyst systems. In alkaline media, the activity is comparable to Pt, and negligible degradation occurs over 60,000 potential cycles, far out-performing Pt. By decomposing "fluoroethoxides", superhydrophobic **fluorinated carbon** nanospheres are produced, which can be printed or sprayed onto arbitrary substrates. These are applied in electrolysis and fuel cell gas diffusion layers in order to improve water management. **Graphene oxide** can be formed into extremely strong membranes with extremely **low hydrogen permeability**, and promising **proton conducting properties**. Therefore we explore this material as a fuel cell membrane. Finally, **sulfonated graphene** has increased proton conductivity compared with graphene oxide, improving the **fuel cell** performance.

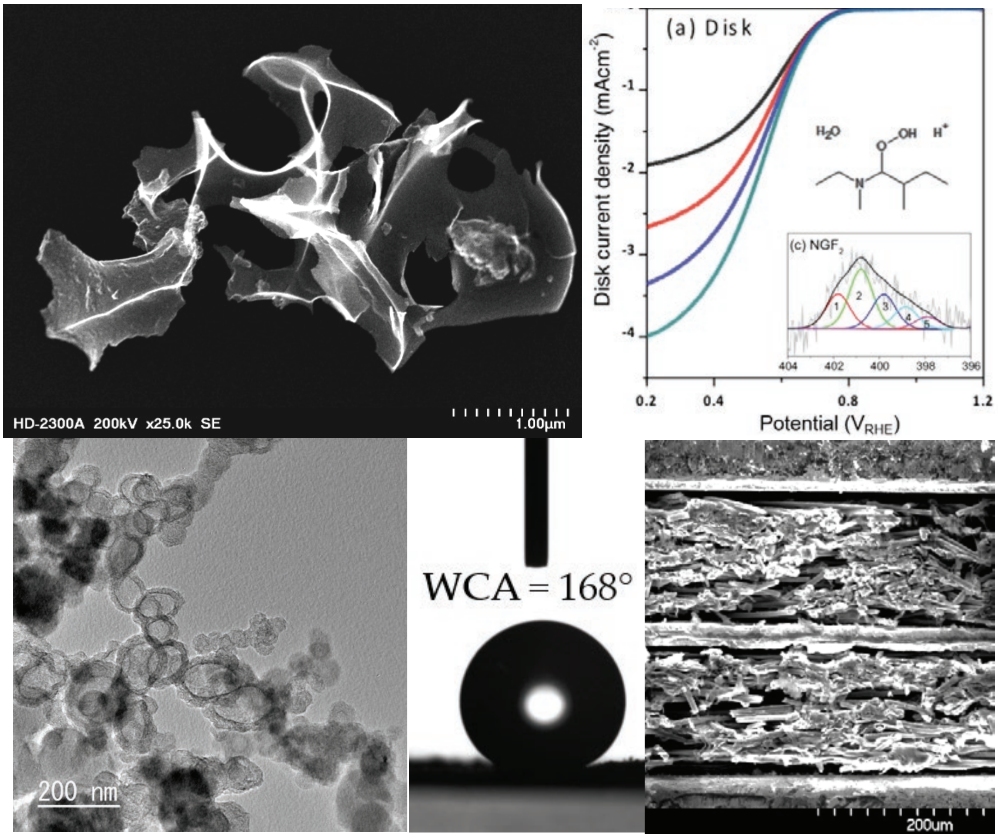

Figure: TEM image of our carbom foam; oxygen reduction reaction on nitrogen-doped carbon foam; superhydrophobic fluorinated carbon spheres; graphene oxide membrane fuel cell.

Nanomaterial *fillers* for thermal management applications

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The development of more efficient thermal management and low weight-to-strength ratio materials are of great interest for a very wide range of applications as current technologies are likely to reach their performance limits. Key areas that require a step change in materials technologies include aeronautics, vehicles, health-care, energy storage, conversion, and generation systems.

The use of carbon and non-carbon-based nanomaterials as fillers in tailored matrix materials is a possible way forward to tackle this challenge. Here, we report three case studies, namely Epoxy and silicon resin matrices, Cooling fluid matrices, and Composite laminate matrices in which filler materials at micro- and nano-scales are utilised to improve the thermal and mechanical properties of epoxy, silicon resins, cooling fluids, and composite laminates.

Epoxy and silicon resin matrices

This study aims to improve the thermal conductivity of polymer composites for thermal management applications. Various fillers such as hexagonal boron nitride platelets, copper powder, graphite flakes, graphite powder and carbon fibres were used in different polymer matrices including epoxy and silicone resins, to prepare thermally conductive composites. While the incorporation of 5 wt.% fillers was not sufficient to improve the thermal conductivity, the thermal conductivity of epoxy filled with 33 wt.% hexagonal boron nitride platelets (10 µm) reached 0.9 W/m.K, corresponding to an improvement of 350 % compared to the pure epoxy. Similarly, for epoxy filled with the same amount, but larger (40 µm) hexagonal boron nitride platelets, a thermal conductivity of 1.2 W/m.K was achieved, which corresponds to an improvement of 500 % compared to the pure epoxy. We observed similar trends with other fillers which are described in the poster, together with the processing recipe and microscopy results.

Cooling fluid matrices

This study aims to improve the thermal properties of coolants using the fillers. Different classes of fillers such as graphitic materials (graphite, graphene and carbon nanotubes) and exfoliated hexagonal boron nitride were used to tune the dielectric properties of the cooling fluids. Thermal conductivity and specific heat capacity of the stable dispersions (cooling fluid plus the filler) were measured as a function of sonication parameters. It was shown that for a water solution with surfactant and 0.1 wt. % of carbon (graphite/graphene), the thermal conductivity improved by 10 %.

In future work, different (filler) concentrations are going to be studied, as well as different fillers.

Composite laminate matrices

We report a novel processing recipe for the manufacturing of carbon-nanotube-reinforced composite laminates for improved through-thickness mechanical and thermal management properties. Early analyses of a prototype composite indicated a uniform distribution of carbon nanotubes within the matrix, which is necessary for the reinforcement to positively contribute towards the through-thickness properties. The tailored synthesis and characterisation of carbon nanotubes as well as the post-curing mechanical and thermal analyses are also reported.

An SThM technique to assess the thermal conductivity of individual multi-walled carbon nanotubes

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The demand for advanced thermal materials with ultra-high thermal conductivities (K > 400 W m^{-1} K^{-1}) has increased exponentially in recent years. This stems from the necessity to remove excessive heat produced by advanced electronic components in order to enhance their performance[1]. Multi-walled carbon nanotubes (MWCNTs) possess outstanding thermal conductivities (~3000 W m^{-1} K^{-1}, (see Fig. 1a))[2], which has created significant interest in their use in the heat management industry. However, commercially available MWCNTs often have high levels of impurities and defects resulting in the nanotubes displaying thermal conductivity values close to that of amorphous carbon (a-C) (0.3-10 W m^{-1} K^{-1})[3]. Currently there are no standard procedures to acquire the thermal conductivity of nanomaterials due to the complex nature of this class of materials. Therefore, in this study the potential use of a scanning thermal microscopy (SThM) technique combined with finite element (FEM) modelling (Fig. 1b) & c)) has been investigated, in order to determine the thermal conductivity of individual nanotubes. The values acquired were subsequently assessed by comparing the quality of the nanotubes using transmission electron microscopy (TEM), Raman and X-ray (XRD) spectroscopy methods and scanning thermal analysis (STA).

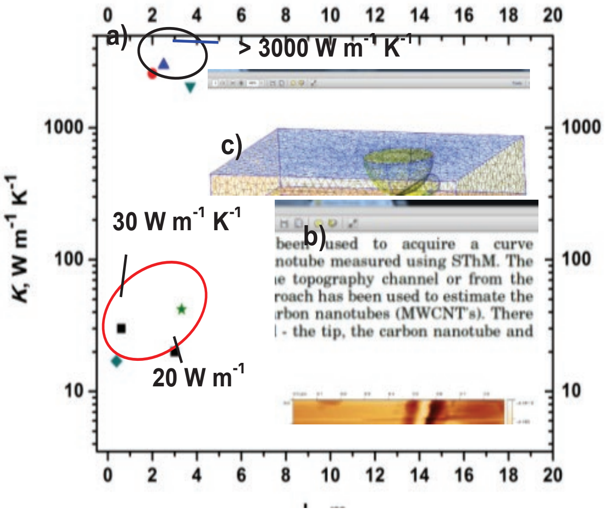

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Fig. 1 a) shows the acquired thermal conductivity of two nanotubes using the SThM + FEM method: nanotube 1 (N1) has a value of 30 W m^{-1} K^{-1}, for a 0.6 μm length and 10 nm diameter; nanotube 2 (N2) has a value of 20 W m^{-1} K^{-1}, for a 3 μm length and 40 nm diameter. These values are very low compared to those reported in literature[3,4], however, they are not the lowest (17 W m^{-1} K^{-1})[4]. The low thermal conductivity is corroborated by the TEM results that revealed a high content of point and lattice defects, despite a high degree of crystallinity and the presence of a layer of a-C on top of the nanotubes. The Raman ratio $(ID/IG)_{N1}$ = 0.7) and $(ID/IG)_{N2}$ = 0.7) also confirmed a high number of defects and carbonaceous impurities; whilst the STA showed the presence of a catalyst (1.9 wt.% for N1 and 3.7 wt.% for N2) that XRD confirmed to be composed of Fe and Fe-C based compounds.

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Quaternary heteroatom-doped carbon nanospheres as anodes in lithium and sodium ion batteries

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In this work we report the fabrication of microporous carbon nanospheres (MCNs) doped with nitrogen (N), phosphorous (P), sulphur (S) and oxygen (O), and we evaluate their electrochemical performance as anodes in lithium ion and sodium ion batteries (LIBs, SIBs). The MCNs obtained from a carbonisation process of highly-crosslinked organophosphazene nanospheres (OPZs), synthesized by a facile and robust chemical reaction between hexachlorocyclotriphosphazene (HCCP) and 4,4'-sulphonyldiphenol (BPS). The OPZs were carbonized at 700, 850 and 1000 °C and a high heteroatom-doping content was observed by X-ray Photoelectron Spectroscopy (XPS) analysis. The graphitization degree of the CNSs was calculated from the I_D/I_G ratio of the Raman spectra and the textural properties (specific surface area, pore size distribution) were characterized by N_2 sorption isotherms. The chemical and textural characteristic of the CNSs were correlated to the carbonisation temperature. The electrochemical performance of the CNSs as anode material was evaluated by testing lithium half-cells. The CNSs showed high initial discharge capacity which was significantly decreased after few cycles due to the electrolyte decomposition and the solid-electrolyte interface (SEI) formation. Long charge-discharge cycling showed an impressive stability and Coloumbic efficiency as high as 99.9% after 1000 cycles. The CNSs were also tested as anodes in SIBs in order to investigate their storage ability of a different alkali ion such as Na^+ and a comparison with LIBs' results is presented.

Graphene materials for biomedical applications: From proteins to tissue

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In this abstract, two applications of graphene materials will be introduced: (i) the prevention of biofouling in droplet-based microfluidic devices and (ii) a new 3D cell culture model.

In electrowetting-on-dielectric (EWOD) based microfluidics, the biofouling induced by proteins is a major limitation due to its impact on wettability of the surfaces, which jeopardize its function. Furthermore the proposed solutions to limit it (bi-phasic systems and surfactants addition) modify the liquid/surface interaction and the surface cannot be used for specific interactions. By using graphene oxide nanosheets (GOns), the main idea was to take advantage of the GOns/proteins interactions and to avoid the protein migration at the liquid/surface interface. Firstly, the wetting properties of GOns and GOns/BSA (Bovine serum albumin) aqueous solutions were characterize. They showed that GOns helped to keep the surface tension close to the water surface tension and allowed the depinning of the triple contact line during the evaporation[1] and contact angle hysteresis measurements.[2] The EWOD static and dynamic characterizations showed a significant improvement of the wetting/dewetting cycle[2] and of the droplet displacement with GOns/BSA droplets[1] compared to BSA ones. Furthermore, Horse Radish Peroxidase retained its enzymatic activity after its EWOD displacement with GOns[1] suggesting that they do not affect the protein conformation.

For liver tissue engineering, reproducing the high hepatocytes density seen in-vivo and ensuring their oxygenation are the main obstacles to 3D cell culture. The engineered polymer scaffolds typically used in 3D culture models possess limited porosity and specific surface area and as a result, the oxygen diffusion and cell density are limited. We will present the recently developed 3D graphene presents, which solves these issues with its higher porosity and specific surface area (10 times) than polymer scaffold. The potential of this scaffold for 3D liver cell culture was investigated through a collaboration with CiNTRA a laboratory at the Nanyang Technological University working on 3D graphene (3D-C). HepG2 cells (liver cell line) were cultured on the collagen-coated 3D-C and grew over two weeks. The cell viability assessed by H&E staining showed the presence of cell nucleus. The high cellular oxygenation ability was proved by the low lactate production (aerobe status) and by the non-expression of hypoxia induced factors (HIF-1α) as well.[3]

These two applications show two kinds of interactions between graphene and biomaterials. At the protein level, GOns have strong interactions with proteins and inhibit their diffusion at the liquid/solid interface. They present interesting properties for microfluidic devices and sensors. At the cellular level, the structure of 3D-C will enable promising applications in tissue engineering due to the significant oxygen diffusion in the structure.

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Fullerene derivatives based spin on carbon hardmasks

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One of the primary challenges experienced in lithography is pattern collapse during wet developing processes when trying to achieve high aspect ratio features. In order to avoid pattern collapse, very thin photoresist films have been adopted in order to provide good lithographic resolution. However this approach limits the depth that resist features can be etched into the substrate. To address this problem, a multilayer etch stack is frequently used. Spin-on-Carbon (SoC) hardmasks are increasingly employed in this process. Using this method the aspect ratio of the lithographic features increases significantly. As carbon offers high etch resistance in silicon plasma etch processes it will be the predominant material in the organic hard mask base layer. A thin silicon topcoat deposited on the carbon rich material can be patterned with a thin photoresist film and the pattern can be transferred to the underlying carbon layer by oxygen plasma etch. The resulting structures are high aspect ratio carbon features suitable for substrate etching. Regarding manufacturability, it is preferable to spin coat the carbon layer rather than the chemical vapour deposition. However, soluble carbon compounds tend to contain a high level of carbon–hydrogen bonds. Hydrogen is a problem, being typically displaced by fluorine during silicon plasma etching, which leads to pattern distortion due to buckling of the lines as fluorine content increases – so called line wiggling.

We have previously introduced a fullerene based SoC with low Ohnishi number which provides high etch durability and its low hydrogen level allows for high resolution etching without wiggling.

The use of the materials in such etch stacks is illustrated and demonstrated in figures 1-3. A 20nm thin silicon film was sputtered on top of the carbon layers. Resist patterns were defined by e-beam and EUV lithography (figure 2) and transferred to the silicon thin film using SF_6/CHF_3 etch chemistry. The carbon layer was then etched with an O_2 plasma using the silicon mask and finally the pattern was transferred into the silicon substrate using the same process used to etch the topcoat.

Some results from external evaluations of the original 100 series will be presented, together with recent developments with the newer 200 and 300 series formulations (offering improved thermal stability and etch durability.

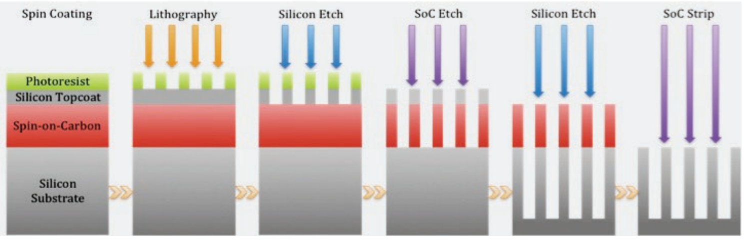
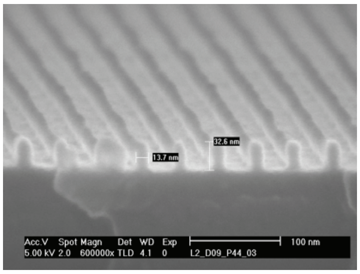


Figure 1. Process schematics for multilayer etch stack

Figure 2. EUV defined features in HSQ resist on 22nm pitch. The 22 nm half-pitch is underdosed resulting 13.7nm linewidth. Stack is ~30nm HSQ on top of 20nm sputtered silicon layer and 50nm of IM-HM-110



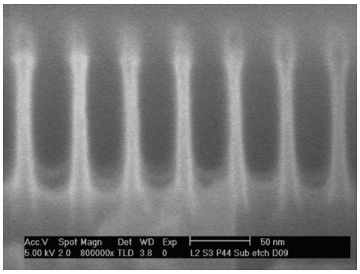


Figure 3. 12nm lines etched into Si using SoC hard mask. Only 1.7nm linewidth loss

Sustainable carbons for the oxygen reduction reaction in fuel cells

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The most recent global agreement in Paris on limiting the climate change by a maximum of 2 °C in order to prevent making global warming catastrophic and irreversible, is a milestone in trying to save our planet. It is clear that major changes need to be carried out in order to reduce and on the long run completely avoid carbon dioxide emission. One solution could be the shift to a hydrogen based energy economy, where hydrogen could be won from renewable energy resources and used in fuel cells, to produce electricity and heat. With a high electrical efficiency, polymer electrolyte membrane (PEM) fuel cells are a promising opportunity for future automotive, stationary and portable power applications, already becoming more popular by the commercialisation of fuel cell cars.

Currently, electro-catalysts for the oxygen reduction reaction (ORR) at cathodes of PEM fuel cells involve platinum and Pt-alloys. Pt catalysts show a number of shortcomings, such as slow ORR kinetics, but most crucial low availability and high cost, which is why alternative catalytic materials are highly desirable.[1]

We use a new approach for an environmentally friendly and low cost production of heteroatom doped materials called hydrothermal carbonisation (HTC). Here, in a matter of hours any biowaste can be converted into useful carbon materials under moderate temperatures and self-generated pressure.[2] By using this process we are able to convert biowaste into different multifunctional nanoporous carbon materials containing nitrogen, sulphur and boron heteroatoms as well as inorganic nanoparticles, such as iron, with a high specific surface area, large pore volume and tuneable pore sizes. Our aim is to understand how these parameters can influence the catalytic activity towards the ORR in order to synthesise true novel materials that can compete with commercially used platinum catalysts to make fuel cells more affordable and especially more sustainable. We will present the physical, chemical and electrochemical characterisation of the synthesised carbon materials and compare their ORR performance with the commercial platinum catalyst.

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Probing the adsorption of carbon nanotubes at liquid/liquid Interfaces: Electrochemistry as a tool for investigation & modification

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The processing of carbon nanotubes (CNTs) into stable assemblies is of major importance in nanoscience and technology. Recently, several efforts have been made to assemble CNTs at the liquid/liquid interface[1]. In the presence of electrolyte in both phases, modified liquid/liquid interfaces can be polarized and charge transfer processes followed by electrochemical methods[2].

Here, we investigated the properties of CNTs assembly at the water/1,2-dichloroethane (DCE) interface. The interfacial layer was formed by adsorption of nanotubes from the DCE phase to the interface. Ion transfer voltammetry was used to probe the electrical nature of the layer of single walled CNTs (SWCNTs). A decrease in effective interfacial area and ion transfer rate constant was observed. The result was interpreted in terms of adsorption of background electrolyte ions ($BTPPA^+$ and $TPBCl^-$) on the SWCNTs surface as measured by X-ray photoelectron spectroscopy (XPS). Furthermore, we demonstrate the potential-controlled polymerization of pyrrole at the interface-assembled CNTs to form SWCNT/polypyrrole composite films.

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One-pot, tether-free regioselective synthesis of fullerene *tris-*, *tetrakis-* and *pentakis-*adducts

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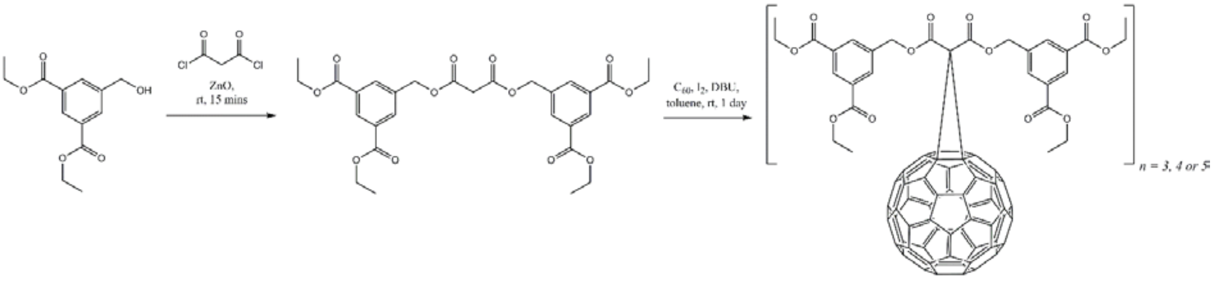
Achieving regioselective exohedral addition patterns to fullerene cages in good yields is a prerequisite to the use of these fascinating molecules in various biomedical applications. Fullerene multi-adducts can lead to increased water-solubility and regioisomerically pure samples have the well-defined molecular structure required by the pharmaceutical industry.[1] Regioisomerically pure *bis*-, *tris*- and *tetrakis*-adducts of C_{60} are usually synthesised via various multi-step tether-directed approaches.[2] Tether-free synthesis routes have also been developed for *tris*- through to *hexakis*- fullerene adducts, relying on extensive high performance liquid chromatography (HPLC)[3] and increased regioselectivity as the number of addends on the fullerene precursor increases.[4] Hexakis-adducts with high T_h symmetry have been synthesised via the Bingel-Hirsch cyclopropanation reaction, using the templating effect of 1,9-dimethylanthracene (DMA).[5] Furthermore, *hexakis*-adducts can be preferentially synthesised in a modified Bingel reaction where DMA has no templating effect – a large excess of a halogen is used instead.[6]



We report the regioselective synthesis of multiple adducts of C_{60} fullerene and a novel malonate bearing isophthalate groups. We synthesised the diisophthalate-malonate using a fast and high-yielding solvent-free method.[7] Aiming for the highest degree of functionalisation, we attempted to maximise the number of the specific malonate addends on C_{60} via a modified Bingel reaction in the presence of excess iodine. Complete conversion of C_{60} was achieved, resulting in tetrakis-adduct as the majority product, with smaller amounts of *tris*- and *pentakis*-adducts. The resulting derivatives were isolated via recycling HPLC and thoroughly characterised by MALDI mass spectrometry, UV-vis, ^{1}H-NMR and ^{13}C-NMR spectroscopies, and cyclic voltammetry. We hypothesise that, due to their size and structure, the diisophthalate-malonate addends act as templating groups directing addition of following addends to specific positions on the fullerene cage, therefore resulting in a higher degree of regioselectivity.

Thus, we offer a simple synthetic route to the *tris-, tetrakis*- and *pentakis*-adducts of C_{60} with increased regioselectivity. These compounds bear multiple isophthalate groups which give functional properties to these systems for use in nanomedicine, including potential cation binding and building blocks for water-soluble materials.

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In-situ x-ray photoelectron spectroelectrochemistry using a graphene window

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In-situ combination of electrochemistry with X-ray photoelectron spectroscopy (XPS) measurements would provide a powerful technique for studying a variety of electrochemical processes. By probing chemical compositions and states at the electrode|solution interface, significant insights can be gained in areas including catalytic mechanisms, ion intercalation and differentiation between redox mediator mechanisms.

Advances in near-ambient pressure (NAP)-XPS systems, which operate at pressures of tens of mbar, have allowed significant volumes of liquid to be stable within a NAP-XPS chamber. Previously, the presence of liquid was precluded by the requirement for ultra-high vacuum conditions in traditional XPS systems. The primary problem in probing the electrode|solution interface using XPS is the very low penetration depth of XPS measurements (ca. 10 nm at best). This has been circumvented using a thin liquid meniscus on a bulk electrode,[1] but a more elegant method utilised a bi-layer graphene electrode supported on a micro-porous Si_3N_4 grid array.[2] Such a configuration produces both an atomically thin XPS window and an electrode|solution interface across the Si_3N_4 pores, which provides an ideal platform for *in-situ* electrochemical XPS experiments. However, due to the relatively small size of the pore array, the latter method required the use of a highly focused synchrotron X-ray source.

Here, we present fabrication of an electrochemical cell, in which a chemical vapour deposition grown monolayer graphene electrode is suspended over a single mm-sized aperture. Using a standard lab-based NAP-XPS system, electrochemically controlled gold deposition on the graphene was then studied as a test system, with gold deposition confirmed upon observation of an Au 4f signal in the XPS spectrum.

Smart magnetic buckypapers for electronics applications

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Buckypapers (BPs), first produced by Liu et al.,[1] are macroscopic membranes composed of entangled carbon nanotubes (CNTs). These materials have the potential to be implemented in a vast range of applications, ranging from sensors to supports for catalysts. The next generation of these BP materials should be smart materials, with added functionality such that they can be controlled indirectly via external stimuli. With this concept in mind, we report buckypapers that can be controllably manipulated with an external magnetic field.

We have developed a post-synthesis method to create BPs in which the magnetic regions are can be designed by selectively depositing different kinds of multi-wall carbon nanotubes (MWNTs)[2-4] in specific geometries. This allows for tailoring of the movement the BP undergoes in response to external magnetic field stimulation. These magnetic BPs have been employed as a magnetically controlled switch in an electrical relay and their conductivity was measured to establish their suitability for applications in electrical systems.[5]

Acknowledgements

The authors thank the Royal Society, the European Research Council (ERC-2009-StG-240500), the Engineering and Physical Sciences Research Council (DTA, IAA Awards) and the Japanese Society for the Promotion of Sciences Summer Program for their generous financial support.

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Hybrid graphene-quantum dot transistor: Controlling carrier concentration, mobility and photoresponsivity

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Advances in high-performance graphene-based devices[1] exploit not only the unique electronic properties of graphene, but also additional functionalities achieved by combining the graphene with other materials or nanostructures.[2] Here we investigate photosensitive planar transistors consisting of a monolayer of CVD graphene decorated with a layer of near-infrared PbS colloidal quantum dots (QDs)[3]. We demonstrate that the polarity of the conductivity, carrier concentration, mobility, and photoresponsivity of SLG can be controlled by the choice of ligands surrounding the QDs.[4] By varying the length of capping ligands from 0.5nm to 10nm (PbS core diameter is 4.5nm), and by preserving their integrity, we are able to significantly increase the carrier mobility and device photoresponsivity up to 10^9 AW^{-1}. We explain the increase of mobility in terms of the spatial correlation between positive (ionized impurities in SLG) and negative (ionized QDs) scattering centers, and efficient charge transfer from the QDs to SLG. These phototransistors have high sensitivity over an extended wavelength range and are of technological interest for electronics and optoelectronics. The functionalization of SLG by the QDs provides a strategy for the nanoscale control of mobility and carrier concentration required by emerging 2D electronics.

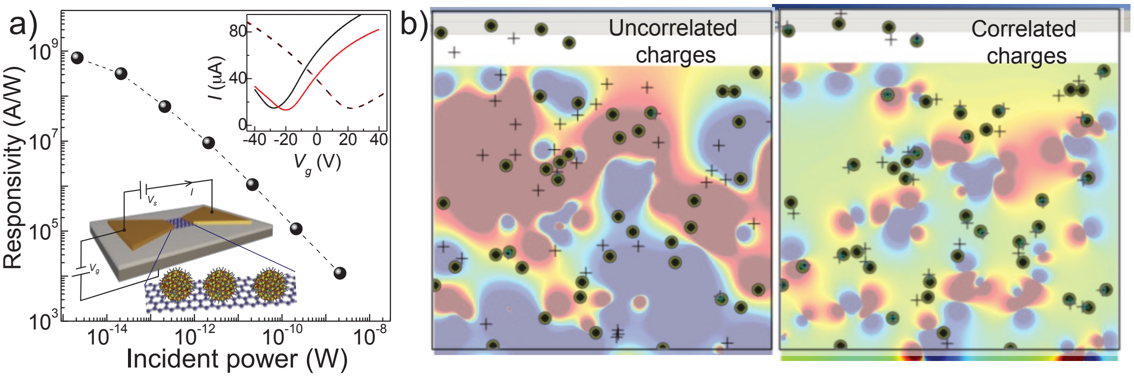

Figure 1. (a) Dependence of room temperature photoresponsivity on illumination power (l = 514nm) incident on a 60 μm² graphene layer. (Lower inset) Schematic diagram of the QD-SLG device and (Top inset) I(V_g) characteristics of pristine SLG device (dashed lines) and the same device decorated with QDs in the dark (black lines) and under illumination with l = 514 nm at P = 10 W/m² (red lines). (b) Numerically simulated electrostatic potential maps of a small area (size 50 nm x 50 nm) of the device for uncorrelated and correlated distributions of charges, acceptor-like impurities in SLG (black circles) and donor-like QDs (red crosses), at concentration $n_{QD} = n_i = 1.7 \times 10^{12}$ cm^{-2}.

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Core-shell structured carbon nanoparticles derived from light pyrolysis of waste tires

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The ever growing transportation industry has driven the fast development of modern society, but meanwhile caused serious pollution issues to the environment. Waste tire disposal management is one of the major concerns, as about 1.4 billion unit of tires are produced globally every year, and around 800 million tires are discarded. Pyrolysis is an economical and environmental-friendly way to deal with waste tire rubbers. Carbon black nanoparticles (CB_{lp}) were derived from waste tire rubbers via a melt-extrusion pyrolysis process at 300 ^{o}C. A polymeric shell was observed on the surface of CB_{lp}, which was formed by bound rubber. The chemical structure and content of the bound rubber shell were characterized and quantified, and compared with the commercial carbon black N330 and pyrolytic carbon black (CB_p). The average particle size of CB_{lp} is about 22 nm, with a rubber shell thickness of 7-12 nm. Functional carboxylic group and ZnO were detected on the surface of CB_{lp} by FTIR and XRD, respectively, which are absent from N330 and CB_p. The core-shell structure of CB_{lp} facilitate the dispersion and interfacial interaction in natural rubber, and lead to a higher reinforcement effect as compared those of N330 and CB_p. The light pyrolysis process provides a facile and clean approach to generate useful carbon nanoparticles out of waste tire rubbers.

Keywords

Waste tire rubber; light pyrolysis; carbon black; core-shell structure

Graphene/bismuth composite as electrode for supercapacitors

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Supercapacitors have been considered as the next generation of energy storage devices. Compared with batteries, supercapacitors have the potential of achieving greater energy density while maintaining high power density. In previous studies, carbon and metal oxide have been synthesized and their electrochemical properties were analyzed. However, only a few studies have been reported on metal and metal composite materials. Recently, bismuth has been reviewed as one of the extensively studied elements in solid state physics due to its electronic properties, such as a long Fermi wavelength and the high Hall coefficient [1]. Bismuth has a Fermi wavelength around 30 nm [1, 2]. With the thickness of bismuth film reduced, it develops a high density of states crossing the Fermi level, which leads to the failure of band gap opening [1]. In addition, in spite of its heavy metal status, bismuth is considered as a safe and non-toxic material. A large amount of bismuth is produced as a by-product of the copper and tin refinery industry. All these make bismuth a promising candidate as electrode in supercapacitor.

Reduced graphene oxide (rGO)/ Bismuth was synthesized for the first time using a polyol process at a relatively low reaction temperature of 60°C, using a short reaction time of 3 hours. The prepared sample is structured with 50-100 nm diameter bismuth particles distributed on the rGO sheet. Bismuth, as a pentavalent post-transition metal, exhibits good electrochemical properties. The prepared rGO/Bi reached a specific capacitance value of 773 F g^{-1} at a current density of 0.2 A g^{-1}. This material not only has good power density but also shows good stability in cycling tests with a high current density of 5 A g^{-1}. The specific capacitance calculated from charge/discharge curves are higher than previous reported studies of any other rGO/metal, such as rGO/Ru and rGO/Au. The relatively high abundance and low price of bismuth make this rGO/Bi material a promising candidate for use in electrode materials in future electronic devices.

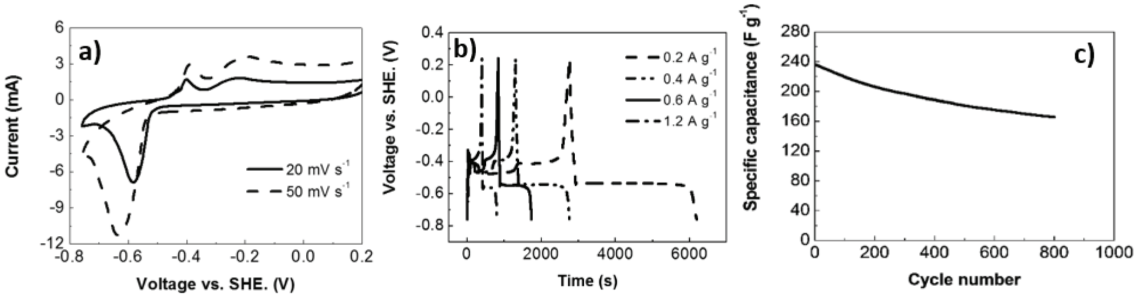

Figure Electrochemical properties of rGO/Bi a) cyclic voltammetry b) charge/discharge behaviours c) cycling test at the current density of 5 A g^{-1}.

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Carbon dots enhanced C_3N_4 for photocatalytic CO_2 conversion

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Photoreduction of carbon dioxide to valuable hydrocarbon fuel using solar energy and a photocatalyst may provide a sustainable and green energy supply for the future. Up to now, many different inorganic and organic semiconductor materials have been designed as photocatalyst systems for carbon dioxide photoconversion driven by visible light. But photoconversion efficiency and stability of these artificial photocatalyst systems are still very moderate. Here we report a metal-free polymer hybrid photocatalyst is formed by coupling graphitic-carbon nitride couple with nitrogen-doped carbon quantum dots, which shows an unexpected carbon dioxide photoreduction reaction activity without sacrificial donors. We measured an apparent initial quantum yield of approximately 0.3 % for wavelength λ= 420 nanometers. Furthermore, the photocatalyst made of Earth-abundant, environmentally friendly, lightweight elements exhibits excellent stability during the conversion process.

NEXAFS Spectroscopy to predict interface dynamics in strained polymer nanocomposites following excessive nanoparticle sonication

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For both structural and functional applications, achieving nanoparticle dispersion and alignment are crucial challenges in the fabrication of nanocomposites: the former ensures homogeneous bulk properties, and the latter allows for constructive translation/generation of properties from the nano- to the macro-scale. Sonication is a commonly used procedure to achieve nanoparticle dispersion. Ultrasonic energy delivered during sonication, however, can alter nanoparticle structure therefore compromising their unique properties. Nanoparticle alignment is often achieved by applying uniaxial strain to composite melts, the efficiency of which depends on adequate polymer-filler interaction for effective load-transfer. In this context, thorough elucidation of interface phenomena derived from processing will enable property prediction and, ultimately, device fabrication by design.

Here, we present our findings to monitor the effects of excessive sonication of multiwall carbon nanotubes (MWCNTs) in strained ethylene-vinyl acetate/MWCNT composites, which, under optimal processing conditions, exhibit photo- and thermo-active behaviour. Sonication induced visible damage to sp^2 graphitic lattice in MWCNTs, as was evidenced in aberration-corrected transmission electron microscopy, as well as in NEXAFS and Raman spectroscopy. Increased levels of strain applied during composite fabrication did not align MWCNTs, as intended. Further, load-transfer monitoring of MWCNT D* bands in Raman spectroscopy revealed a stick-slip scenario, where strain overcomes non-covalent interactions. This lack of connectivity was followed by an abrupt change in chemical environments around nanotubes, and a correlative trend was observed in the surrounding polymeric system. As a consequence, the dynamic conformation of polymeric C=O groups could be modelled from angular- and strain-resolved C=O π^* NEXAFS resonances.

The impact of extensive processing on the structure-property paradigm was high. Indeed, we had previously reported that moderately sonicated systems produced nanocomposites capable of a mechanical response upon thermal stimulus, with potential applications in artificial muscles or tactile displays. However, aggressively sonicated systems yielded a non-actuating composite.

This work highlights the importance of correlating interface effects and fabrication procedures to predict successful interfacial molecular architectures in both structural and functional polymer nanocomposites, which can be conveniently monitored by NEXAFS spectroscopy.

Magnetic properties study of carbon nanotube - single molecule magnet hybrids

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Single-molecule magnets which retain magnetization for long periods of time in the absence of an external magnetic field at liquid-helium temperatures are being investigated vigorously these days by multiple research groups for potential applications in the fields of molecular spintronics, data storage devices and quantum computing. But, any real application of SMM requires their communication with the outside macroscopic world, to allow read-and-write processes1. Carbon nanotube (CNT) offers a unique solution to linking SMM to the outside world. Given the vast potentials of this field, we are working on synthesizing CNT-SMM hybrids in which SMM is encapsulated into CNT.

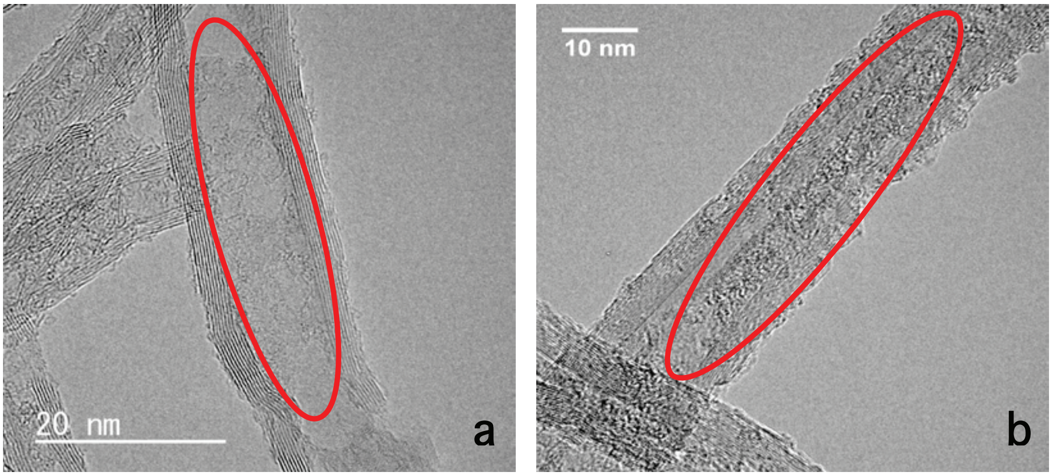

Figure 1. Comparison of TEM image of empty MWNTs (a) and TEM image of Dy(acac)$_3$@MWNT (b)

We have synthesized CNT-SMM hybrid comprising Dy(acac)3 (acac = acetylacetone) and MWNT (inner diameter; 4.5 nm ± 0.5 nm; Aldrich). We clearly observed the stark contrast inside the nanotubes and further presence of Dysprosium was confirmed by energy dispersive X-ray (EDX) spectroscopy. These kinds of hybrids are expected to show remarkable physical and magnetic properties.

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Highly stable and conductive microcapsules for enhancement of heating generating performance

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Planar heat generating devices, including electro-heat, photo-heat, magno-heat and chemo-heat conversion systems, are suffered from low efficiency due to unexpectedly excessive heat dissipation. Base on the convective heat transfer equation: $Q = h A (T_1\text{-}T_2)$, where Q is the heat transferred per unit time, h is the heat transfer coefficient, A presents the effective heat transfer area of the solid surface, T_1 is the heater's surface temperature and T_2 is the environmental temperature. At a giving power input, one promising way could be to increase T_1 to improve the heating efficiency.[1]

In our work, we tried to dope highly stable and conductive microcapsules inside the heat generating systems. The capsules contain paraffin with high heat capacity and low vapour pressure. The capsule shell is comprised of graphene oxide (GO) and carbon nanotubes (CNT). Capsules fill the space and voids between heat generating sheets without altering the degree of sheet orientation and alignment, and thus conserve the conductance of the system. The heat generated by capsules can effectively prevent convective heat dissipation, and thus increase the maximum temperature of the heat generators.

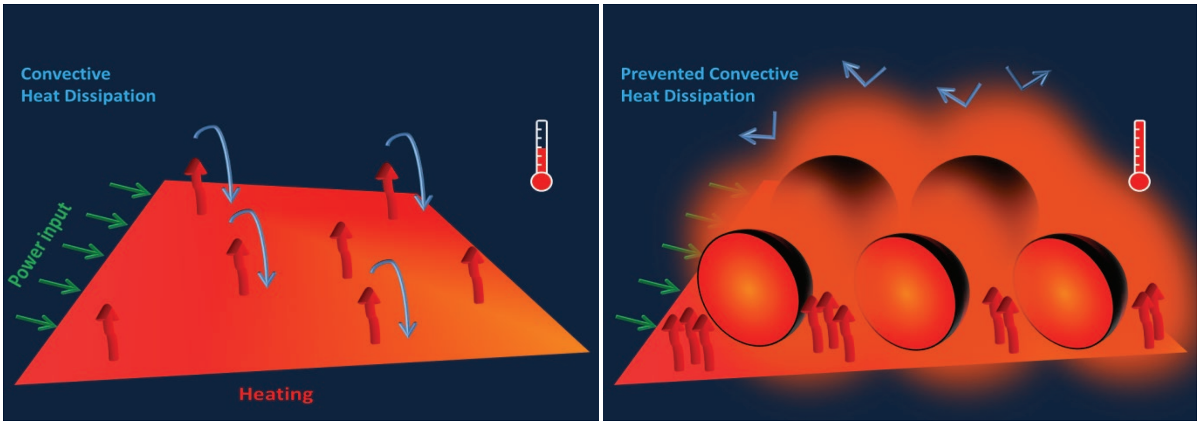

Figure 1 (a) The maximum temperature of heating generator is always limited by the inevitably convective heat transfer between heating system and surrounding environment. (b) Microcapsules with nanocarbon shell fill the space and voids between heating sheets without altering the degree of sheet orientation and alignment, and thus conserve the conductance of the system. The heat released by capsules can effectively prevent convective heat dissipation, and thus increase the maximum temperature.

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Probing the dipolar coupling in N@C_{60}–CuPc

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Due to the long decoherence time of the electron spin, N@C_{60} are promising carbon based nanomaterials for quantum information processing[1]. However, challenging was met in realization of a two-qubit gate, due to the lack of controllability of dipolar coupling strength.

Towards the tunable dipolar coupling in endohedral fullerene, we synthesized a series of hetero-spin systems of endohedral fullerene–phthalocyanine dyads (Figure 1 a). With the spectrum feature of dipolar coupling resolved by electron spin resonance measurement (Figure 1 b), we further discovered two chemical methods to control the dipolar coupling in these dyads: a) by changing the length of the spacer units between the fullerene and the phthalocyanine and b) by changing the concentration of the solution containing the dyad [2].

Our experiment demonstrated that by increasing the spin-to-spin distance by 25% with a longer bridge group the dipolar coupling strength was decreased by 50%, which is consistent with the distance dependency. We also showed experimentally that the dipolar coupling strength in such dyads is dependent on the solution concentration. Detailed study further revealed that the concentration dependence is caused by the aggregation of the macrocycle moiety and the resulting antiferromagnetism.

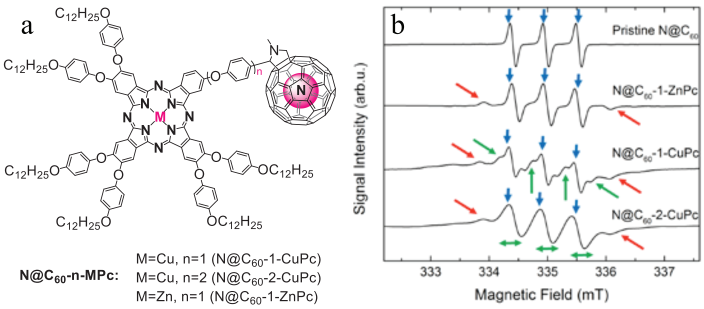

Figure.1 Molecular structure of N@C_{60}–phthalocyanine dyads (a) and electron spin resonance signal of the dyads (b). The peaks of hyperfine coupling and zero-field splitting are labelled with blue and red arrows, respectively. The dipolar coupling features, such as fine shoulder peaks and line-broadening, are marked with green arrows.

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Solution processable carbon nanoelectrodes for single-molecule investigations

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Since the 1970s, researchers have tried to use molecules as building blocks in electronic circuits for the prospect of size reduction offered by molecular-level control. Until recently, different strategies including scanning probe techniques, lithographic approaches, and mechanical/electromigration break junctions have made it possible to investigate molecules in a practical way. Nevertheless, despite the substantial progress in single-molecule electronics from both fundamental and technological standpoints, challenges remain. Principal among these are the time and cost involved in nano-gap fabrication, the reliable control of the nano-gap size, and the need for a facile (and scalable) technology for the establishment of electrical contact between individual molecules and metal electrodes.

The use of carbon-based nano-electrodes, in particular, has emerged as a promising approach because of the intrinsic nanoscale size of CNTs and graphene, and the reduced electronic mismatch granted by having molecules and electrodes of the same material (Carbon atoms).

Herein we present a facile solution based assembly method for producing molecular transport junctions (MTJs) by covalently linking metallic single-wall carbon nanotubes (SWCNTs) with electrically functional molecules. As a proof of principle, the single-molecule junction conductance of a series of oligophenyles was measured and found to be in line with literature values.

For our studies we employed DNA wrapped SWCNTs separated by length via size exclusion chromatography, and sorted by chirality and electronic structure via ion exchange chromatography[1] (DNA-wrapping further leaves only the terminal ends of the SWCNTs available for direct functionalization). Building on our recent bottom-up assembly strategy for the formation of end-to-end CNT junctions,[2] we linked metallic single-chirality (7, 4) SWCNTs in amidation reactions with three different diamine conjugated molecular linkers. To confirm junction formation we cast low-coverage films on doped silicon wafer substrates coated with a hydrophobic layer shown to induce partial alignment of DNA-wrapped CNTs. The electrical properties of the MTJs fabricated in this study were investigated by measuring their current-voltage (I-V) characteristics as a function of the distance between a metallic AFM tip used as a mobile electrode, and a fixed macroscopic Au electrode Our findings are of general interest for the controlled assembly of CNT junctions as a platform for molecular conductance investigations, towards the fabrication of solution-processable single-molecule devices.

References

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2. Palma, M., et al., *Controlled formation of carbon nanotube junctions via linker-induced assembly in aqueous solutio*n. Journal of the American Chemical Society, 2013. 135(23): p. 8440-3.

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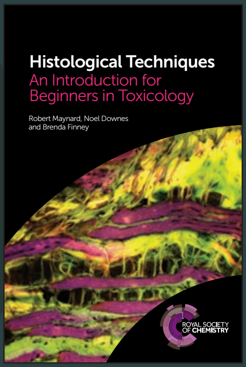

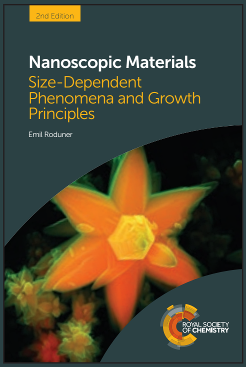

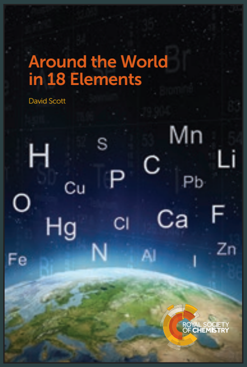

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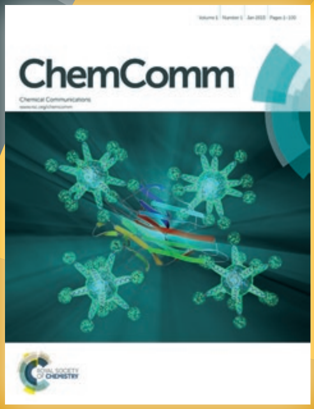

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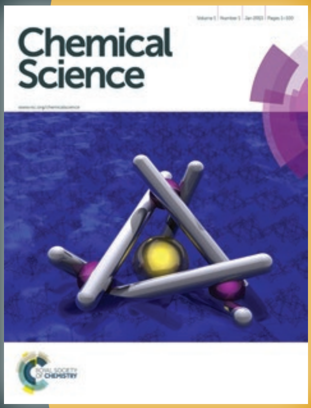

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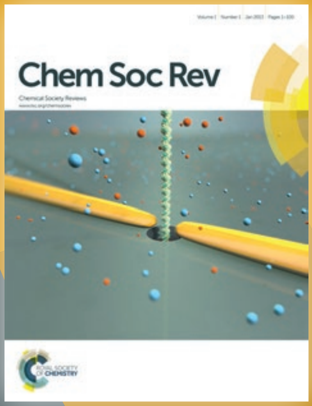

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