Unique Nanocarbons from Critically Opalescent Solutions (UNCOS)

22nd July 2014

Carbon nanomaterial production using CO_2

Raymond L.D. Whitby

Brighton Nanoscience & Nanotechnology Group

Marie-Curie Industry-Academia Partnerships and Pathways Agreement (PIAP-GA-2009-251429 UNCOS)

PEOPLE

MARIE CURIE ACTIONS

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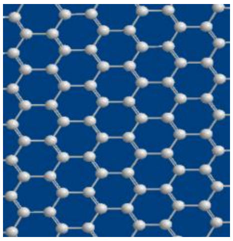
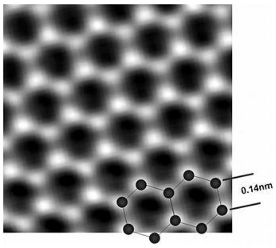
Introduction to graphene

***Graphene** is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice*



Molecular structure of graphene



High resolution transmission electron microscope images (TEM) of graphene

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Properties of graphene

- Electronic properties
- Thermal properties
- Mechanical properties
- Optical properties
- Relativistic charge carriers
- Anomalous quantum Hall effect

Electronic properties

- High electron mobility (at room temperature ~ 200.000 cm^2/(V·s),, ex. Si at RT~ 1400 cm^2/(V·s), carbon nanotube: ~ 100.000 cm^2/(V·s), organic semiconductors (polymer, oligomer): <10 cm^2/(V·s)

$$v_d = \mu E$$

Where **U_d** is the drift velocity in m/s (SI units)
E is the applied electric field in V/m (SI)
µ is the mobility in m^2/(V·s), in SI units.

- Resistivity of the graphene sheet ~10^{-6} Ω·cm, less than the resistivity of silver (Ag), the lowest resistivity
substance known at room temperature (electrical resistivity is also as the inverse of the conductivity *σ* (*sigma*), of the material, or

$$\rho = \frac{1}{\sigma}$$

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Thermal properties

Material	Thermal conductivity W/(m·K)
Silica Aerogel	0.004 - 0.04
Air	0.025
Wood	0.04 - 0.4
Hollow Fill Fibre Insulation Polartherm	0.042
Alcohols and oils	0.1 - 0.21
Polypropylene	0.25 [6]
Mineral oil	0.138
Rubber	0.16
LPG	0.23 - 0.26
Cement, Portland	0.29
Epoxy (silica-filled)	0.30
Epoxy (unfilled)	0.59
Water (liquid)	0.6
Thermal grease	0.7 - 3
Thermal epoxy	1 - 7
Glass	1.1
Soil	1.5
Concrete, stone	1.7
Ice	2
Sandstone	2.4
Stainless steel	12.11 ~ 45.0
Lead	35.3
Aluminium	237 (pure) 120—180 (alloys)
Gold	318
Copper	401
Silver	429
Diamond	900 - 2320
Graphene	(4840±440) - (5300±480)

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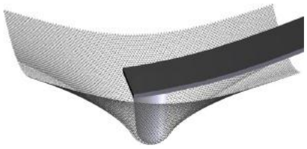
Mechanical properties

- High Young's modulus (~1,100 Gpa)
High fracture strength (125 Gpa)

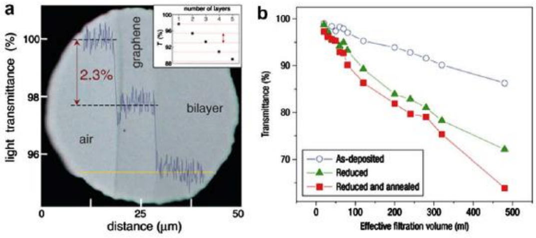
- Graphene is as the strongest material ever measured, some 200 times stronger than structural steel



A representation of a diamond tip with a two nanometer radius indenting into a single atomic sheet of graphene *(Science,* **321** (5887): 385)

Optical properties

- Monolayer graphene absorbs $\pi\alpha \approx 2.3\%$ of white light (97.7 % transmittance), where α is the fine-structure constant.



Preparation methods of graphene

Preparation methods

Top-down approach
(From graphite)

Bottom up approach
(from carbon precursors)

- Micromechanical exfoliation of graphite (Scotch tape or peel-off method)
- Creation of colloidal suspensions from graphite oxide or graphite intercalation compounds (GICs)

- By chemical vapour deposition (CVD) of hydrocarbon
- By epitaxial growth on electrically insulating surfaces such as SiC
- Total Organic Synthesis

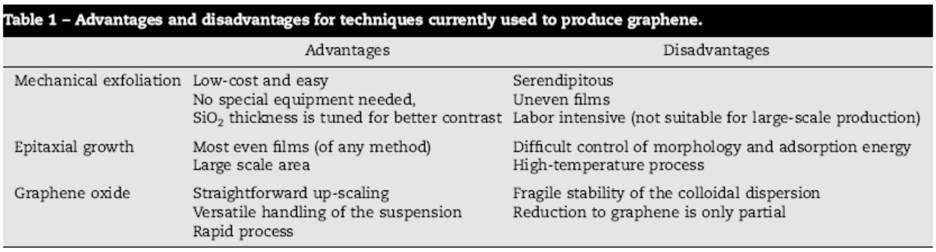
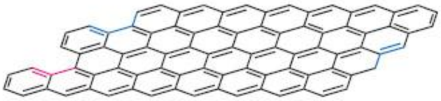
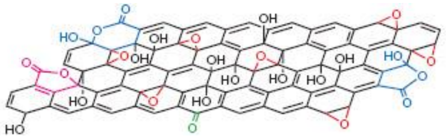


Table 1 – Advantages and disadvantages for techniques currently used to produce graphene.

	Advantages	Disadvantages
Mechanical exfoliation	Low-cost and easy No special equipment needed, SiO_2 thickness is tuned for better contrast	Serendipitous Uneven films Labor intensive (not suitable for large-scale production)
Epitaxial growth	Most even films (of any method) Large scale area	Difficult control of morphology and adsorption energy High-temperature process
Graphene oxide	Straightforward up-scaling Versatile handling of the suspension Rapid process	Fragile stability of the colloidal dispersion Reduction to graphene is only partial

Graphene and graphene oxide





Graphene and graphene-based materials have interesting properties

Exfoliation of graphite oxide (GO) to graphene oxide and then reduction to graphene is an affordable route to the large scale processing of graphene-based materials

Sasha Stankovich, et al. J. Mater. Chem., 16, 155–158 (2006)
Andrei Geim, et al., Nat. Mater., 6, 183–191 (2007)
Sasha Stankovich, et al. Carbon, 45, 1558–1565 (2007)
Wei Gao, et al., Nature Chem., 2009, DOI: 10.1038/NCHEM.281
Yanwu Zhu, et al., ACS Nano, 4, 1227–1233 (2010)

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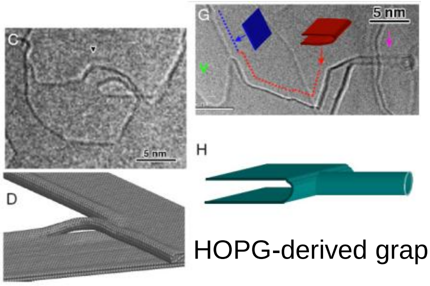
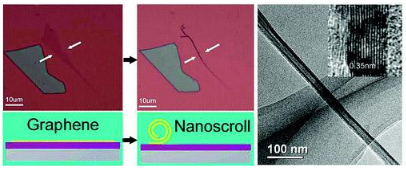
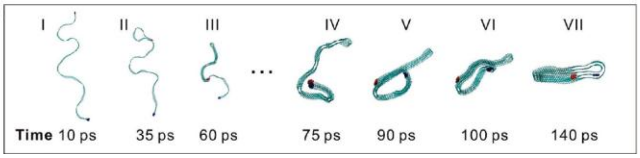
Graphene architecture



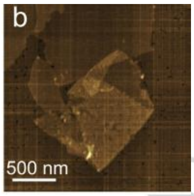
HOPG-derived graphene



Graphene dried from isopropyl alcohol



Low temperature folding of graphene



Cu^{2+} folding SLGO

Xu Xie, et al., Nano Letts., 9, 2565–2570 (2009)
Jian Yu Huang, et al., PNAS, 106, 10103-10108 (2009)
Sheng-Tao Yang, et al., J. Coll. Int. Sci., 351, 122–127 (2010)
Zhiping Xu, et al., ACS Nano, 4, 3869–3876 (2010)
Young-Kwan Kim, et al., Carbon, 48, 4283–4288 (2010)
Raymond L.D. Whitby, et al., ACS Nano, 6, 3967–3973 (2012)

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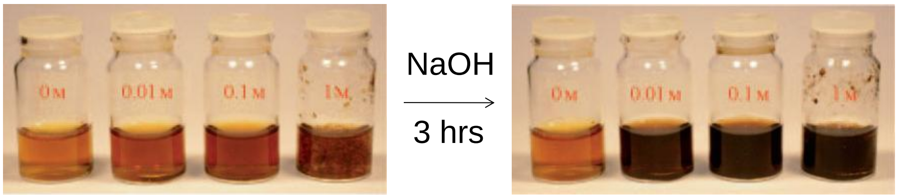
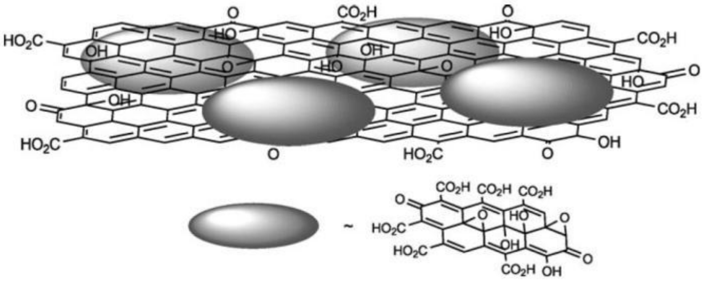
How clean is your graphene?





J.P. Rourke, et al., *Angew Chemie Int Ed*, **50**, 3173-3177 (2011)
Compare this to
Z. Wang, et al., *Carbon*, **47**, 73 (2009)

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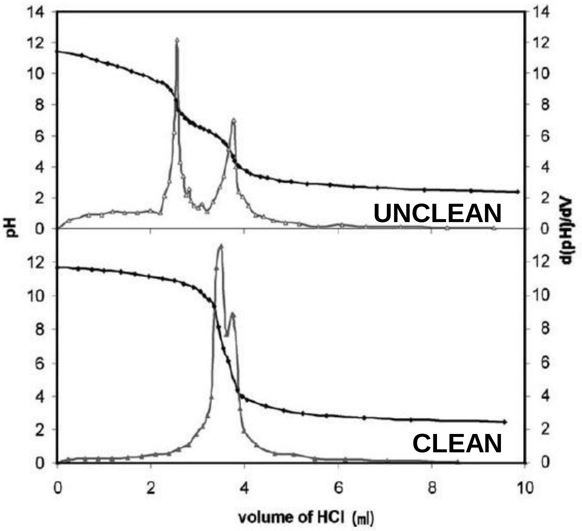
Consider a titration analysis...



Same for fulvic acids, dissolved CO_2, etc

Z. Wang, R.L.D. Whitby, et al., *Carbon*, **47**, 73 (2009)

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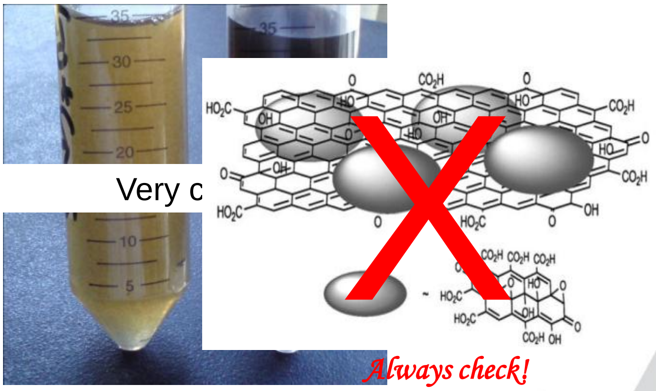
The answer...

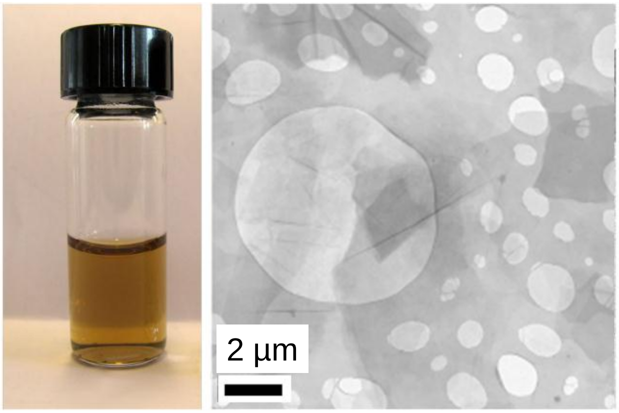


Very c

Always check!

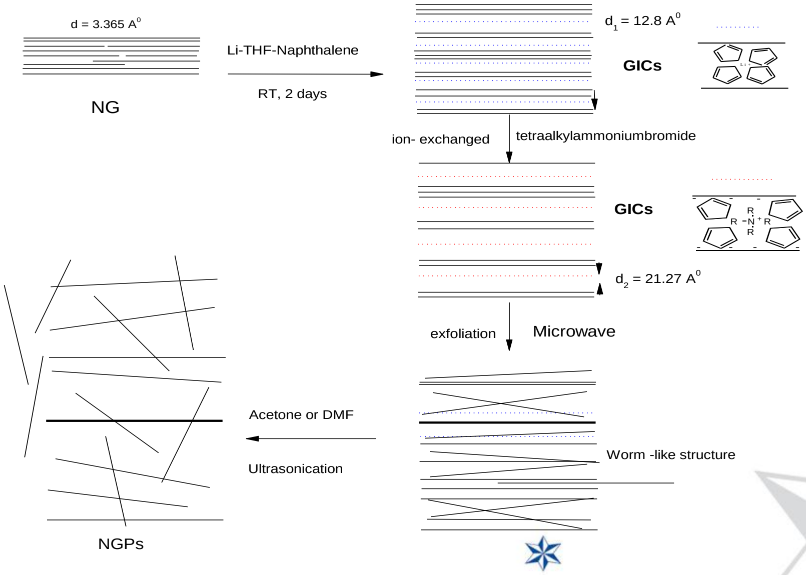
4M HCl 4M NaOH

R.L.D. Whitby, et al., *Carbon*, **49**, 722 (2011)



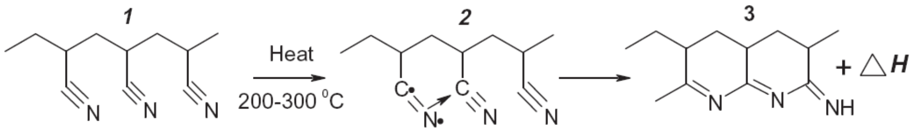
pH=neutral

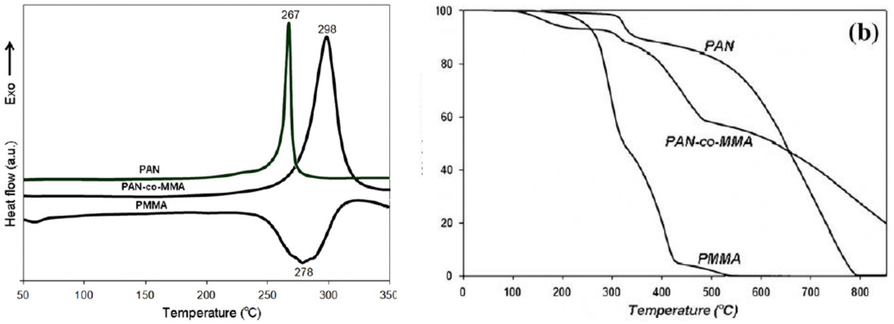
From graphite intercalation compound



Quang Trung Truong and Dai Soo Lee, IC-ME&D 2010, Sunchon, Korea (*Manuscript for Journal of nanosciences and nanotechnology*)

Single layer graphene – new production route

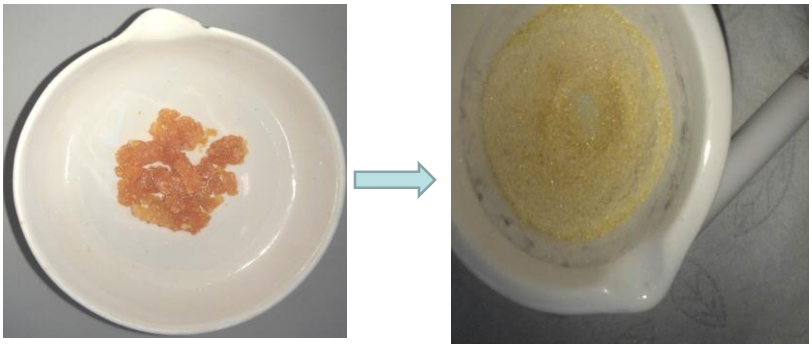


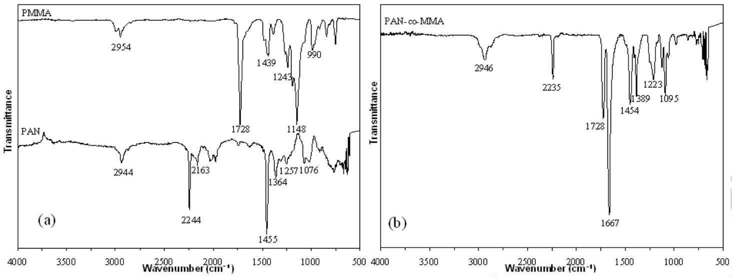


A.Korobeinyk, R.L.D. Whitby, S.V. Mikhalovsky, et al., European Polymer Journal, 48, 97 (2012)

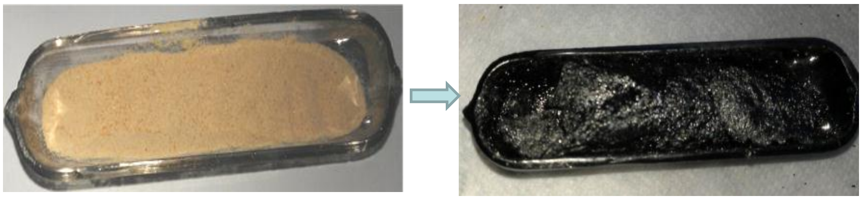
Single layer graphene – new production route

- Synthesis of PAN-Co-MMA by varying different ratio of monomers (5:5, 6:4, 7:3, 8:2, 9:1, 10:1, 12:1 etc.).
- Synthesis of PAN-Co-BA by varying different ratio of monomers (5:5, 6:4, 7:3, 8:2, 9:1, 10:1, 12:1 etc.).
- Thermal treatment of the copolymers in the N_2 atmosphere up to a temperature of 850ºC.
- Grinding of the carbonized copolymers up to 4 hours.
- Process the powder of carbonized copolymers in sc-CO_2 medium.
- Ultrasonication of the powder in the NMP solvent.

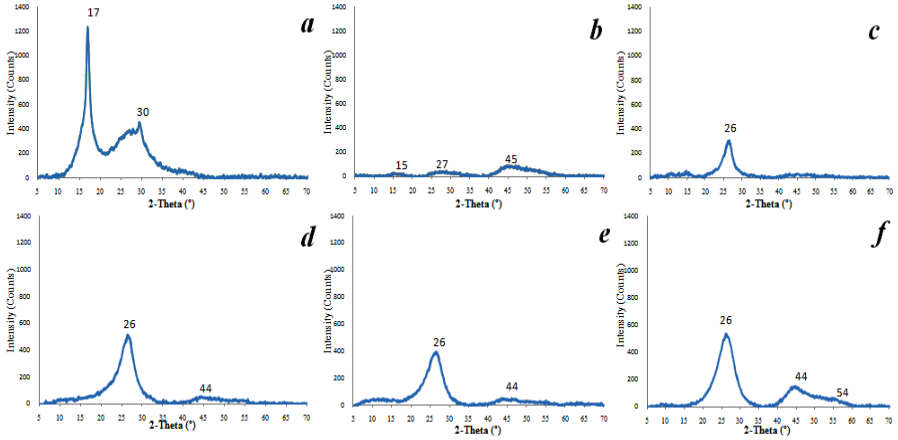




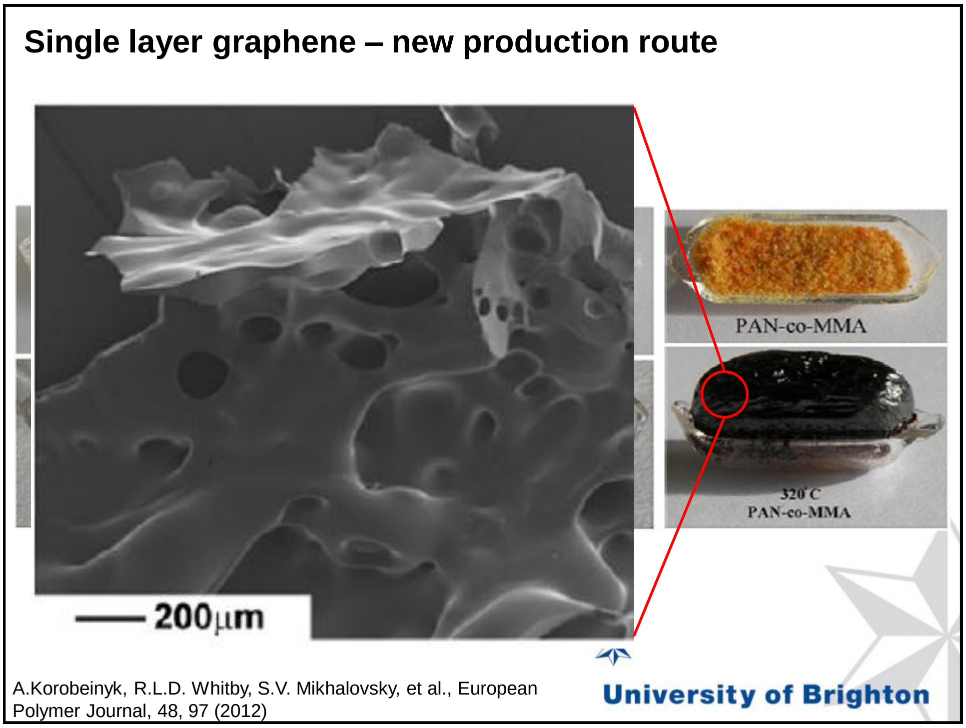
Heating a copolymer



XRD Analysis



200 (***a***), 300 (***b***), 500 (***c***), 600 (***d***), 700 (***e***) and 850 (***f***) ºC.



Single layer graphene – new production route

A.Korobeinyk, R.L.D. Whitby, S.V. Mikhalovsky, et al., European Polymer Journal, 48, 97 (2012)

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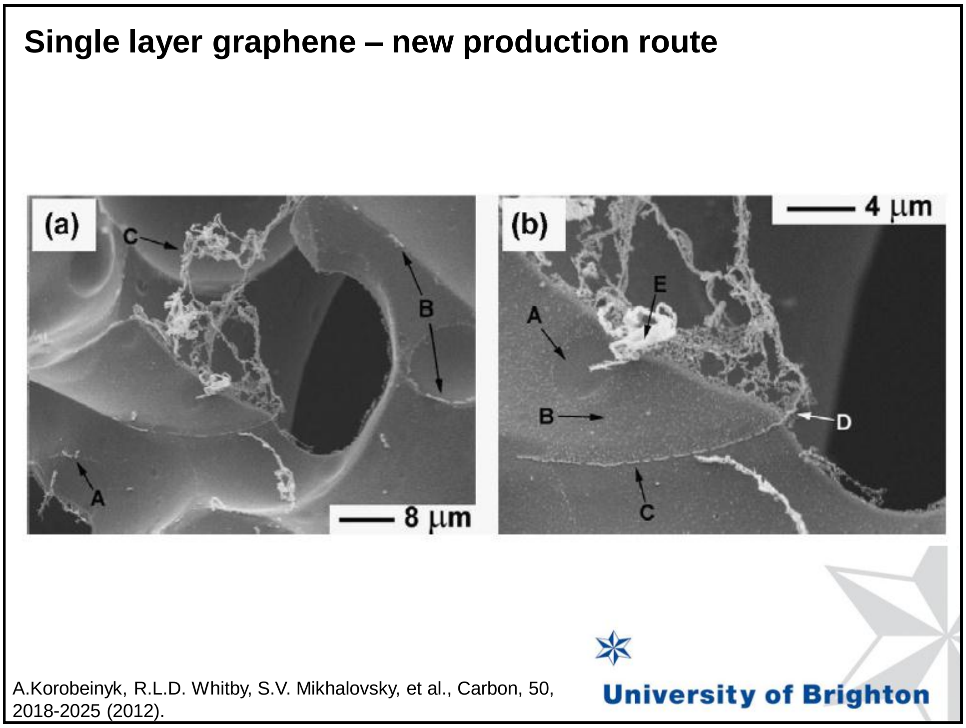

Single layer graphene – new production route

A.Korobeinyk, R.L.D. Whitby, S.V. Mikhalovsky, et al., Carbon, 50, 2018-2025 (2012).

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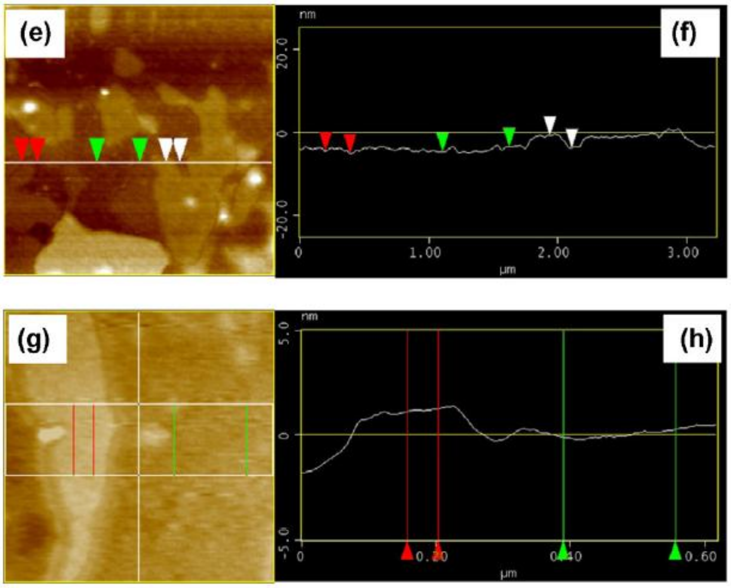

A.Korobeinyk, R.L.D. Whitby, et al., Carbon, 50, 2018-2025 (2012).

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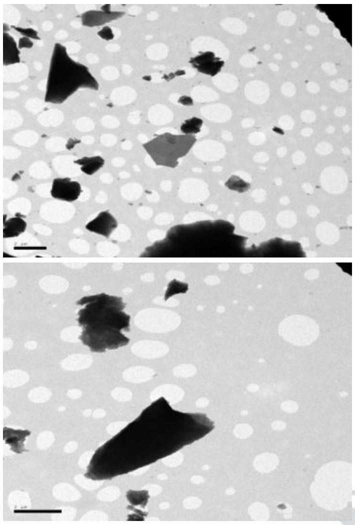
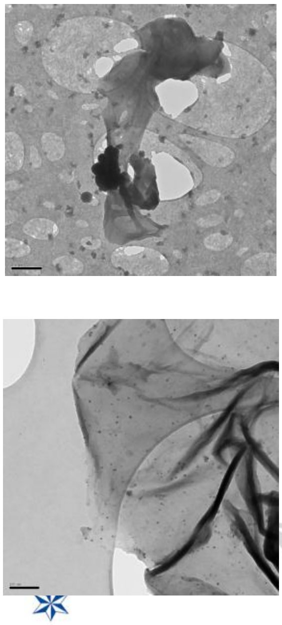
Acrylonitrile – Methyl methyacrylate



carbonised PAN co MMA 9:1 sample processed in sc-CO_2 and NMP sonication

Acrylonitrile – Butylacrylate



PAN co BA 9:1 sample after carbonised, processed in sc-CO_2 and in NMP sonication

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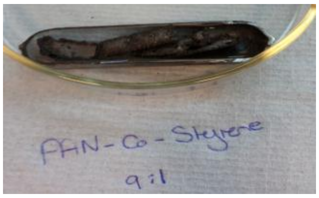
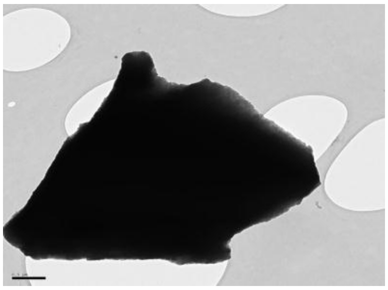
Acrylonitrile – Styrene





PAN co styrene

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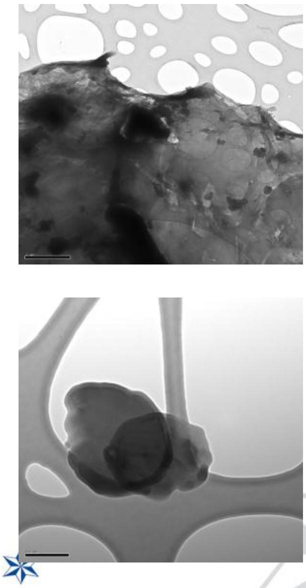
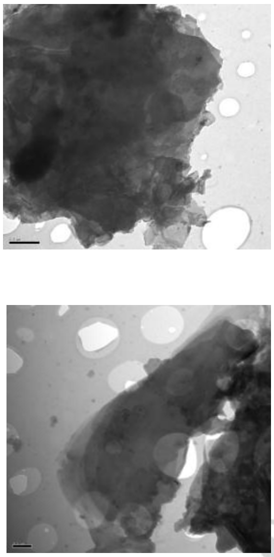
Acrylontrile - 2,4 diamino, -6 diallyl amino, 1,3,5-triazine (DDAT)

PAN co DDAT 9:1

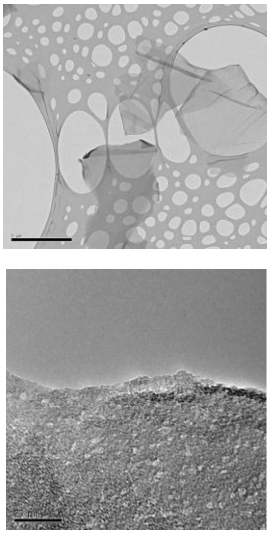


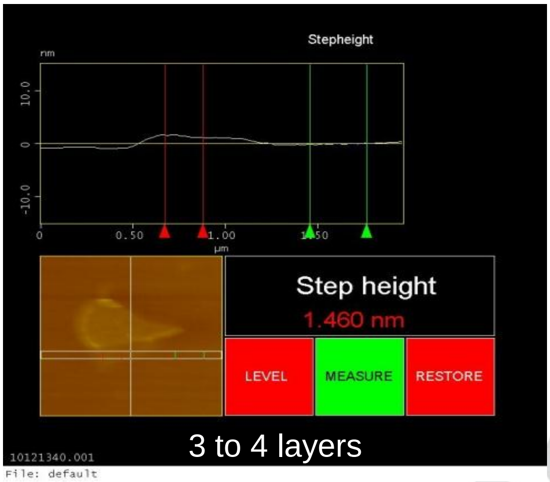
Acrylonitrile – Ethyl methacrylate

PAN co EMA 9:1



Acrylonitrile – Ethyl methacrylate – Methyl methacrylate





Step height
1.460 nm

3 to 4 layers

10121340.001
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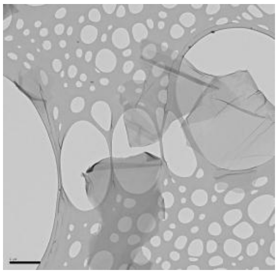
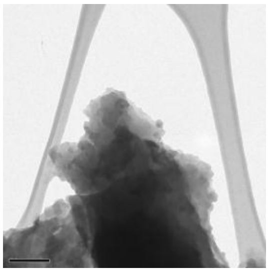
PAN co EMA co MMA 9:1:1 at 850 degree

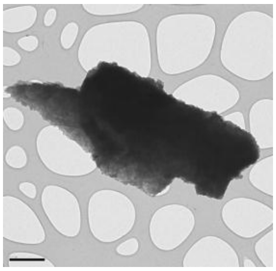
Effect of processing solvent (sc-CO_2 and NMP)



PAN co EMA co MMA processed in both sc-CO_2 and NMP

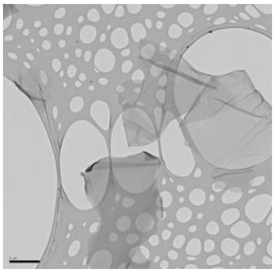
PAN co EMA co MMA processed in only sc-CO_2



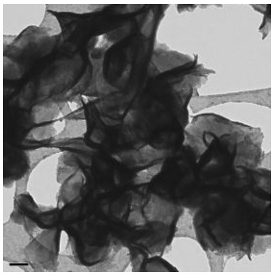


PAN co EMA co MMA processed in only NMP

Effect of monomer ratio



PAN co EMA co MMA 9:1:1



PAN co EMA co MMA 9:1:2

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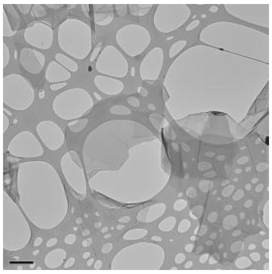
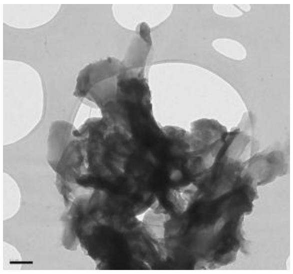
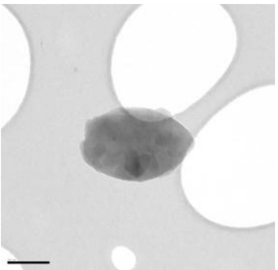
Effect of heating rate

PAN co EMA co MMA 9:1:1 at 20 ^{o}C min^{-1}







PAN co EMA co MMA 9:1:1 at 10 ^{o}C min^{-1}

PAN co EMA co MMA 9:1:1 at 40 ^{o}C min^{-1}

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Conclusions

- ❖ Out of all the copolymers synthesised, PAN co EMA co MMA in 9:1:1 ratio is the best copolymer for synthesising single layer graphene
- ❖ Processing in both supercritical carbon dioxide and sonication in NMP are necessary for obtaining high quality graphene
- ❖ Lower heating rates (10 ^{o}C min^{-1}) are better for obtaining single layer graphene than high heating rates

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UNCOS project webinar, 21/7/14.

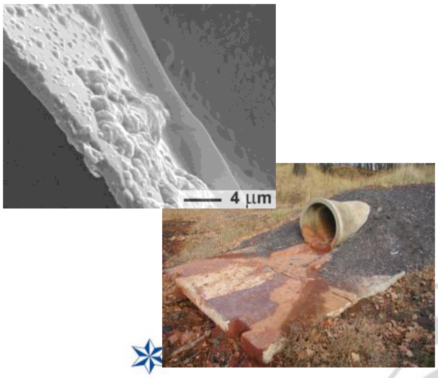
Novel Nanomaterials for Water Treatment and Land Remediation

Professor Andy Cundy

School of Environment

and Technology

R.L.D. Whitby, K. Katok, R. Busquets, I.N. Savina, C.J. English, M. Vaclavikova and S.V. Mikhalovsky



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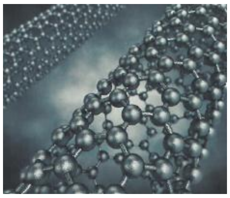
Nanomaterials / nanoparticles as water and soil clean-up tools

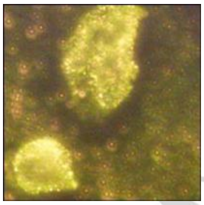
Key features of nanoparticles:

Very reactive (high surface area on which chemical reactions can take place)

Novel properties – increase in number of surface atoms (i.e. surface energy) e.g. gold (and other noble metals) at bulk scale is unreactive, at nano-scale is very reactive, plus quantum and shape effects.....

Surface modification / funtionalisation capability – can use to target specific contaminants





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Nanomaterials / nanoparticles as water and soil clean-up tools

Used to adsorb, stabilise or degrade range of contaminants, or used in catalysis applications

Field trials and prototype devices use nano-filters, bead-type devices or directly injected nanoparticles as clean-up tools

Nanoscale zero-valent iron encapsulated in an emulsion droplet (Source: USEPA 2007)

ArsenX^{np}*, a nano-particle based selective resin designed to remove arsenic (arsenate and arsenite) from water.*

http://www.solmetex.com/newpdfs/SolmetexArsenXDS.pdf

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Benefits and limitations of a nano-approach to water and land clean up:

Benefits:

High reactivity and capacity – effective contaminant removal even at low concentrations – important for emerging trace contaminants such as estrogens etc.

Less waste generation, as less quantity of nanomaterial required in relation to bulk form

Novel reactions

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Benefits and limitations of a nano-approach to water and land clean up:

Limitations

Cost

Upscaling potential (e.g. engineering issues, back pressures etc)

Human and environmental health concerns

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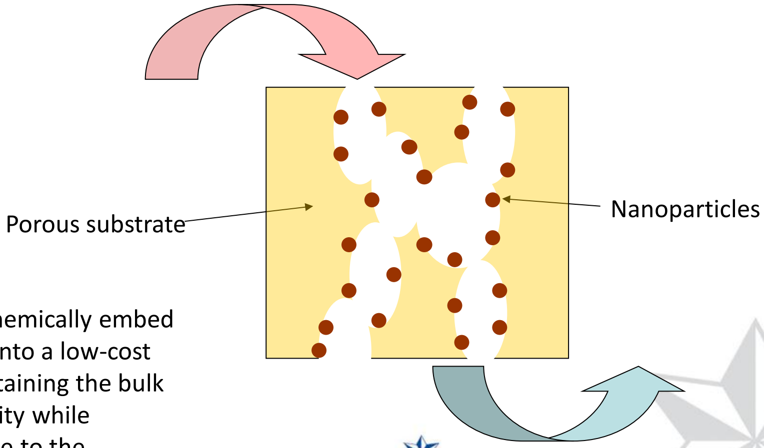
The nanocomposite approach

Use of nanoparticles in a static, or contained, system, or using nano-structured materials, may avoid the last two problems



Physically or chemically embed nanoparticles into a low-cost bulk carrier, retaining the bulk of their reactivity while avoiding release to the surrounding environment

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The nanocomposite approach

In addition, nano-structured materials (including nano-structured carbons) may offer the potential to target particular contaminant groups

Illustrate this using recent work carried out at the University of Brighton and with European academic and industrial partners: examines the use of nanocomposite and nanostructured devices as high through-flow or flow-over reactive devices for treatment of contaminated waters, soils and liquid wastes.

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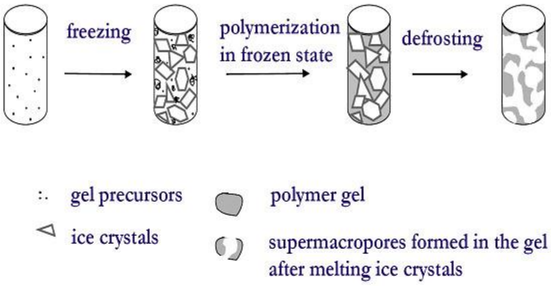
Example 1: Iron : cryogel composites

Uses **cryogels** (MPPS® technology developed by Protista Biotechnology AB (www.protista.se)) as substrate / scaffold

Easy to manufacture, high mechanical strength and shape recovery, capable of generation in variety of geometries, high through-flow……..



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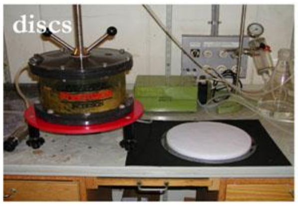

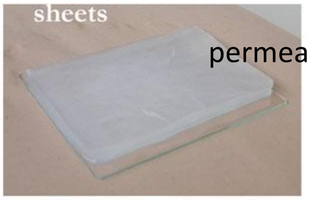

permeability = $3 * 10^{-3}$ ms^{-1}

Example 1: Iron : cryogel composites

α-Fe_2O_3 and Fe_3O_4 nanoparticles physically embedded into macroporous polymer walls, preventing significant agglomeration and ”wash-out” while maintaining reactivity

Contaminated Water

Nanoparticles are embedded inside the polymer scaffold

Clean Water

Despite physical embedding of the nanoparticles into the polymer, high reactivity is retained due to short diffusion pathways

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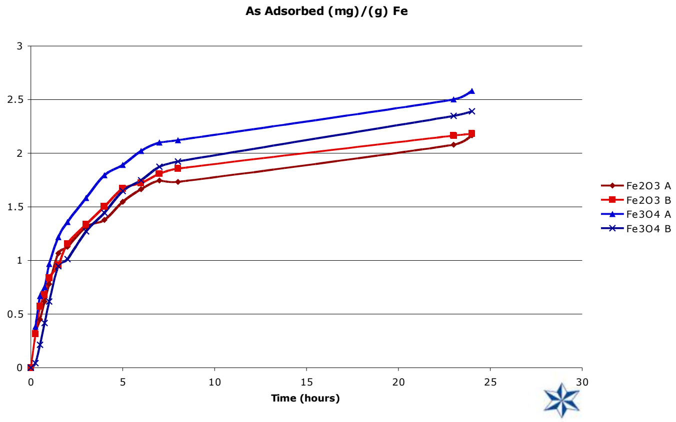
Performance data indicate rapid and effective adsorption of As(III) at range of pHs (3-9), comparing favourably with other nano-based devices.



See Savina et al (2011) Jnl Haz Mat

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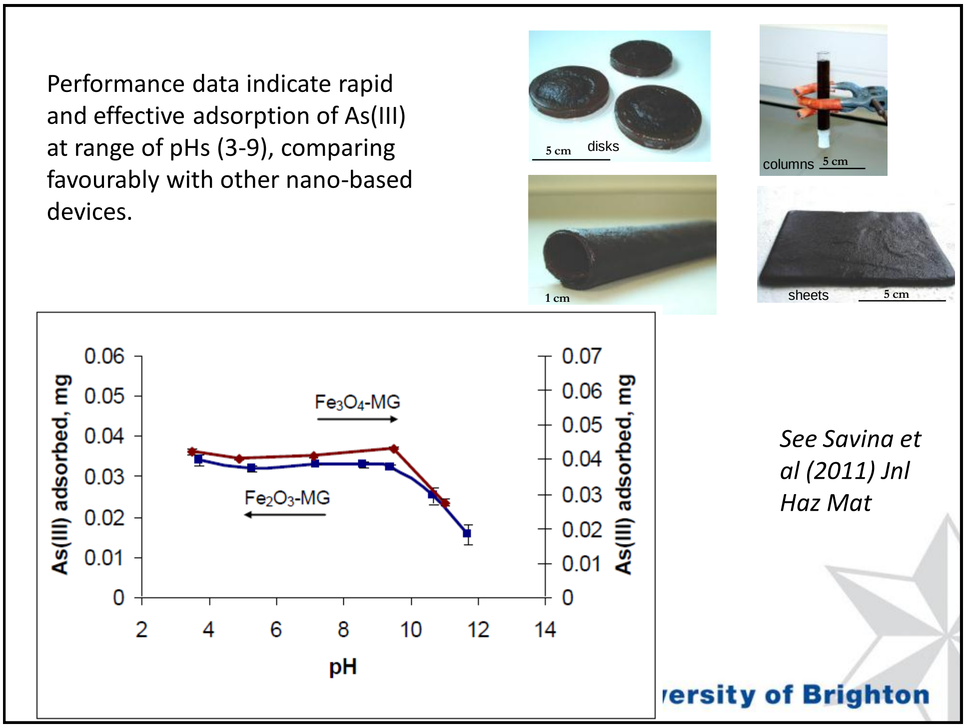

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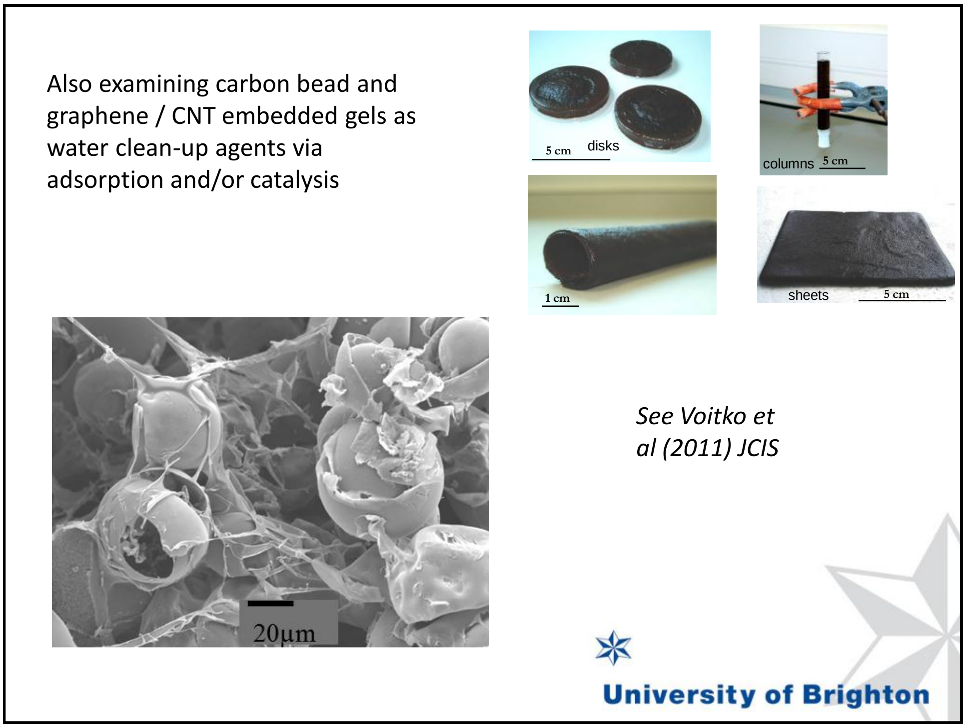
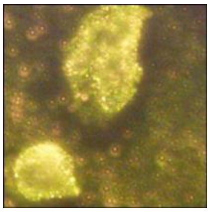


Also examining carbon bead and graphene / CNT embedded gels as water clean-up agents via adsorption and/or catalysis

See Voitko et al (2011) JCIS

Example 2: Modified Si-based nanocomposites

Generation of noble metal nanoparticles on modified silica surfaces



Nanosilver and nanogold are highly reactive removal agents for Hg, pesticides and other organic contaminants, while modified silica surfaces can be used to recycle metals from effluent discharges etc.

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Example 2: Modified Si-based nanocomposites

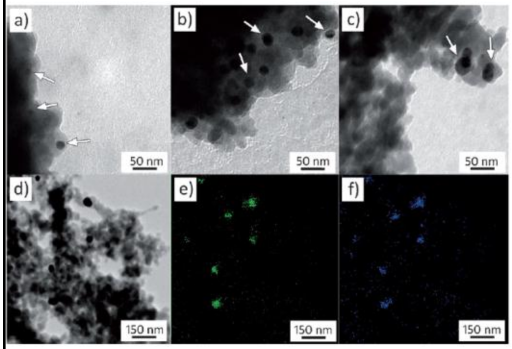

Figure 1. Modification of C-120 type silica (specific surface area 114 $m^2 g^{-1}$) using triethoxysilane generates silicon hydride groups. These are subsequently used to reduce a silver nitrate solution to AgNPs, which are affixed to the top of silica. TEM images reveal the distribution of near-spherical AgNPs, appearing as darker contrast particles (white arrows) against the fused silica substrate, with particle sizes averaging a) 11 nm, b) 31 nm, and c) 45 nm. d) EDX mapping analysis reveals the corresponding location of silver and mercury in the TEM image for the e) Ag (L_α peak) and f) Hg (M_α peak) after their reaction and shows that the distribution of Hg correlates only to the location of AgNPs.

Modified silica surfaces (grafted with weakly reducing $\equiv$ SiH groups) used to generate size controlled noble metal nanoparticles

$$\equiv \mathrm{SiH} + \mathrm{Ag}^+ + 2\,\mathrm{H_2O} \rightarrow$$
$$\equiv \mathrm{SiOH} + \mathrm{Ag}^0 + \mathrm{H_3O}^+ + {}^1\!/_2\,\mathrm{H_2}$$

Katok et al. (2012), *Angew. Chem.*

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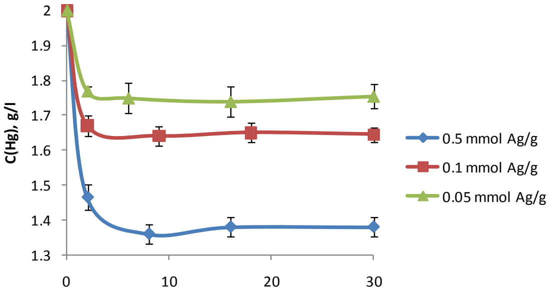
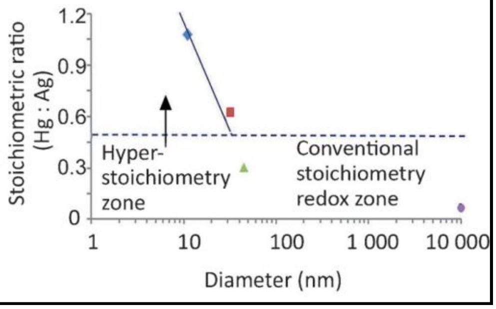
Example 2: Modified Si-based nanocomposites

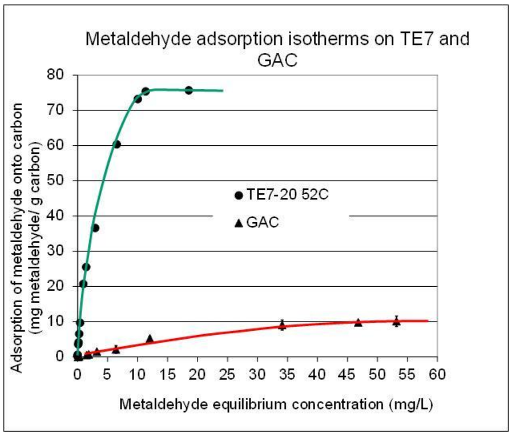




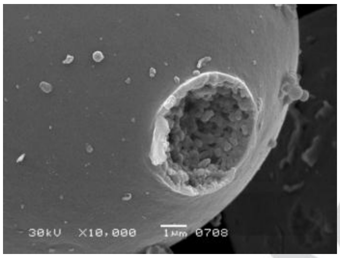
Katok et al. (2012), *Angew. Chem.*

Example 3: Attrition-resistant, tailored nanoporous carbons

"Tailored" phenolic resin-derived carbons: Independent Control of nano and Meso/Macro structure



Busquets et al. (2014), *Water Res.*



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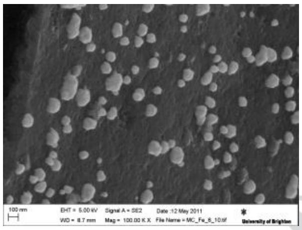
Example 3: Attrition-resistant, tailored nanoporous carbons

Beads are produced on industrial scale by partner MAST Carbon International Ltd. Currently collaborating in independent UK water industry tests to examine column and moving bed applications for water treatment, and low-temperature recycling of beads for re-use.

Combination of beads with Fe and Fe/Cu nanoparticles as absorbents for mixed contaminants in various configurations (water filter, PRB material) is being examined in 8 partner EU "WasClean" project.

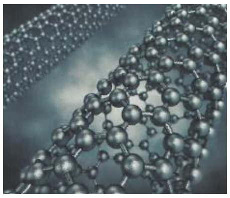
MAST Carbon
INTERNATIONAL
www.MASTcarbon.co.uk



Towards practical application

Indicates utility of combining novel materials with nanoparticle technologies to produce flexible nanocomposite devices for water treatment and other environmental applications

While many current embodiments of nanocomposite devices are in bead or fibrous format, use of flexible, low-cost "scaffolds" such as modified silica surfaces, polymers, activated carbons etc. allows a variety of device configurations to be developed, targeted at particular end-use applications and which can be "retrofitted" to existing treatment facilities



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See also: http://www.bbc.co.uk/podcasts/series/discovery

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