Unique Nanocarbons from Critically Opalescent Solutions (UNCOS)

22\textsuperscript{nd} July 2014

Carbon nanomaterial production using CO\textsubscript{2}
Raymond L.D. Whitby

Brighton Nanoscience & Nanotechnology Group

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

Introduction to graphene

\textbf{Graphene} is a one-atom-thick planar sheet of sp\textsuperscript{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
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 cm²/(V·s)), ex. Si at RT ~ 1400 cm²/(V·s),
  carbon nanotube: ~ 100,000 cm²/(V·s), organic semiconductors (polymer, oligomer): <10 cm²/(V·s)

\[ \mu_d = \mu E \]

Where \( \mu_d \) is the drift velocity in m/s (SI units)
\( E \) is the applied electric field in V/m (SI)
\( \mu \) is the mobility in m²/(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 \( \sigma \) (sigma), of the material, or
\[ \rho = \frac{1}{\sigma} \]

Thermal properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal conductivity W/(m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon carbide (SiC)</td>
<td>0.004 - 0.04</td>
</tr>
<tr>
<td>Air</td>
<td>0.025</td>
</tr>
<tr>
<td>Wood</td>
<td>0.04 - 0.4</td>
</tr>
<tr>
<td>Hollow FEP film transistor</td>
<td>0.012</td>
</tr>
<tr>
<td>Alcohol-based resins</td>
<td>0.1 - 0.21</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>0.25</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>0.128</td>
</tr>
<tr>
<td>Rubber</td>
<td>0.18</td>
</tr>
<tr>
<td>LPG</td>
<td>0.21 - 0.26</td>
</tr>
<tr>
<td>Cement, Portland</td>
<td>0.20</td>
</tr>
<tr>
<td>epoxy (alko-siloxane)</td>
<td>0.30</td>
</tr>
<tr>
<td>epoxy (silicon-dioxide)</td>
<td>0.59</td>
</tr>
<tr>
<td>Water (liquid)</td>
<td>0.6</td>
</tr>
<tr>
<td>Thermal grease</td>
<td>0.7 - 3</td>
</tr>
<tr>
<td>Thermal silica</td>
<td>1 - 7</td>
</tr>
<tr>
<td>Glass</td>
<td>1.1</td>
</tr>
<tr>
<td>Soil</td>
<td>1.5</td>
</tr>
<tr>
<td>Concrete, stone</td>
<td>1.7</td>
</tr>
<tr>
<td>Ice</td>
<td>2</td>
</tr>
<tr>
<td>Sandstone</td>
<td>2.4</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>12.11 - 45.0</td>
</tr>
<tr>
<td>Lead</td>
<td>35.3</td>
</tr>
<tr>
<td>Aluminium</td>
<td>237 (pure)</td>
</tr>
<tr>
<td>(120 - 180) (alloys)</td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td>318</td>
</tr>
<tr>
<td>Copper</td>
<td>401</td>
</tr>
<tr>
<td>Silver</td>
<td>429</td>
</tr>
<tr>
<td>Diamond</td>
<td>600 - 3320</td>
</tr>
<tr>
<td>Graphene</td>
<td>(4800-440) - (5300-480)</td>
</tr>
</tbody>
</table>
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

Optical properties

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

Preparation methods of graphene

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

Bottom up approach
(from carbon precursors)
- By chemical vapour deposition (CVD) of hydrocarbon
- By epitaxial growth on electrically insulating surfaces such as SiC
- Total Organic Synthesis

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical exfoliation</td>
<td>Low-cost and easy, No special equipment needed, SiO$_2$ thickness is tuned for better contrast</td>
<td>Serendipitous, Uneven films, Labor intensive (not suitable for large-scale production)</td>
</tr>
<tr>
<td>Epitaxial growth</td>
<td>Most even films (of any method), Large scale area</td>
<td>Difficult control of morphology and adsorption energy, High-temperature process</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>Straightforward up-scaling, Versatile handling of the suspension, Rapid process</td>
<td>Fragile stability of the colloidal dispersion, Reduction to graphene is only partial</td>
</tr>
</tbody>
</table>
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

Wei Gao, et al., Nature Chem., 2009, DOI: 10.1038/NCHEM.281

Graphene architecture

Graphene dried from isopropyl alcohol

Low temperature folding of graphene

Young-Kwan Kim, et al., Carbon, 48, 4283–4288 (2010)
How clean is your graphene?

NaOH → 3 hrs

Compare this to
Z. Wang, et al., Carbon, 47, 73 (2009)

Consider a titration analysis...

Same for fulvic acids, dissolved CO₂, etc

The answer...

Very careful!

Always check!

4M HCl       4M NaOH


2 µm

pH=neutral

University of Brighton
From graphite intercalation compound

\[ d = 3.365 \, \text{Å} \]

\[ \text{Li-THF-Naphthalene} \rightarrow \text{RT, 2 days} \]

\[ \text{NG} \rightarrow \text{NGPs} \]

\[ d_1 = 12.8 \, \text{Å} \]

\[ d_2 = 21.27 \, \text{Å} \]

\[ \text{Microwave} \rightarrow \text{Acetone or DMF} \rightarrow \text{Ultrasonication} \rightarrow \text{Ion-exchanged tetraalkylammoniumbromide} \]

\[ \text{GICs} \]

\[ \text{Worm-like structure} \]

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

\[ \begin{align*}
1 & \xrightarrow{\text{Heat, 200-300 °C}} \\
2 & \xrightarrow{+ \triangle H} \\
3 &
\end{align*} \]

• 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 N₂ atmosphere up to a temperature of 850°C.

• Grinding of the carbonized copolymers up to 4 hours.

• Process the powder of carbonized copolymers in sc-CO₂ medium.

• Ultrasonication of the powder in the NMP solvent.

Single layer graphene – new production route
Heating a copolymer

XRD Analysis

200 (a), 300 (b), 500 (c), 600 (d), 700 (e) and 850 (f) °C.
Single layer graphene – new production route


Single layer graphene – new production route

Single layer graphene – new production route


Acrylonitrile – Methyl methacrylate

carbonised PAN co MMA 9:1 sample processed in sc-CO₂ and NMP sonication
Acrylonitrile – Butylacrylate

PAN co BA 9:1 sample after carbonised, processed in sc-CO₂ and in NMP sonication

Acrylonitrile – Styrene

PAN co styrene
Acrylonitrile - 2,4 diamino, -6 diallyl amino, 1,3,5-triazine (DDAT)

Acrylonitrile – Ethyl methacrylate

PAN co DDAT 9:1

PAN co EMA 9:1
Acrylonitrile – Ethyl methacrylate – Methyl methacrylate

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 only sc-CO$_2$

PAN co EMA co MMA processed in both sc-CO$_2$ and NMP

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

Effect of heating rate

PAN co EMA co MMA  
9:1:1 at 10 °C min⁻¹  
PAN co EMA co MMA  
9:1:1 at 20 °C min⁻¹  
PAN co EMA co MMA  
9:1:1 at 40 °C min⁻¹
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 °C min\(^{-1}\)) are better for obtaining single layer graphene than high heating rates.

UNCOS project webinar, 21/7/14.

Novel Nanomaterials for Water Treatment and Land Remediation

Professor Andy Cundy

School of Environment and Technology

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 / functionalisation capability – can use to target specific contaminants

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

_ArsenX*, a nano-particle based selective resin designed to remove arsenic (arsenate and arsenite) from water._

(Source: USEPA 2007)

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

Limitations
Cost
Upscaling potential (e.g. engineering issues, back pressures etc)
Human and environmental health concerns
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.

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.
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.........

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........

permeability = $3 \times 10^{-3}$ ms$^{-1}$
Example 1: Iron : cryogel composites

α-Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles physically embedded into macroporous polymer walls, preventing significant agglomeration and “wash-out” while maintaining reactivity.

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

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

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

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

\[
\equiv\text{SiH} + \text{Ag}^+ + 2\text{H}_2\text{O} \rightarrow \equiv\text{SiOH} + \text{Ag}^0 + \text{H}_3\text{O}^+ + \frac{1}{2}\text{H}_2
\]

Katok et al. (2012), *Angew. Chem.*
**Example 2: Modified Si-based nanocomposites**

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

![Graph showing metal uptake over time](image)

**Example 3: Attrition-resistant, tailored nanoporous carbons**

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


![Image of tailored nanoporous carbon](image)
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.

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.
Acknowledgements:

Current and previous sources of funding:

CommercialISE POC fund (SEEDA, ESF), Marie Curie FP7 Intra-European and International Incoming Fellowships programme, Leverhulme Trust, FP7 IAPP programme (Carbosorb, proj no. 230676, WasClean, proj no. 612250).

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