

# A New Industrially Relevant Route to High Quality Graphene

*Leaders in Performance and  
Speciality Chemicals*

**Paul Ladislaus  
Advanced Materials Division**

HVM Graphene+ 2014 Conference  
*Oxford, United Kingdom*  
15 May 2014

[www.hvm-uk.com](http://www.hvm-uk.com)



Committed to Responsible Care

# Thomas Swan & Co. Ltd.

- Independently owned
- Medium sized enterprise (SME)
  - **168 employees**
  - **ca. £27M revenue (2012/13)**
- UK manufacturing base
  - **Consett, Co. Durham, UK.**
- Export performance
  - **UK/EU/Outside EU**
- Commitment to highest standards





# Our Business

## Performance Chemicals

- **Proven reliability** in tyre & rubber, coating additives & household care.

## Custom Manufacture

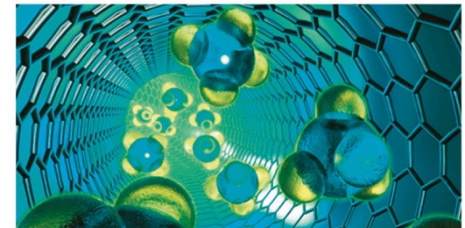
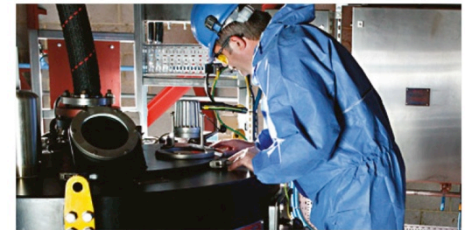
- **Flexible and responsive** with over 100 custom manufacturing products.

## Advanced Materials

- **Excited by new opportunities** for high performance materials in emerging markets.

## Thomas Swan Group

- **Appetite for venturing** and early investors in new technologies.



# Our Capabilities

- Established manufacturing infrastructure

- Capital Engineering
- Quality Control
- Environmental Control
- Scheduling/Logistics

- Regulatory Affairs

- Process Engineering

- Process design and piloting
- Flexible chemistries
- Proven scale-up experience

- Underpinned by recognised accreditations

- ISO 9001
- ISO 14001
- OHSAS 18001
- Responsible Care

.....and Customer Care excellence.

# Advanced Materials Division

*Reliability & Quality in carbon nanomaterials.*

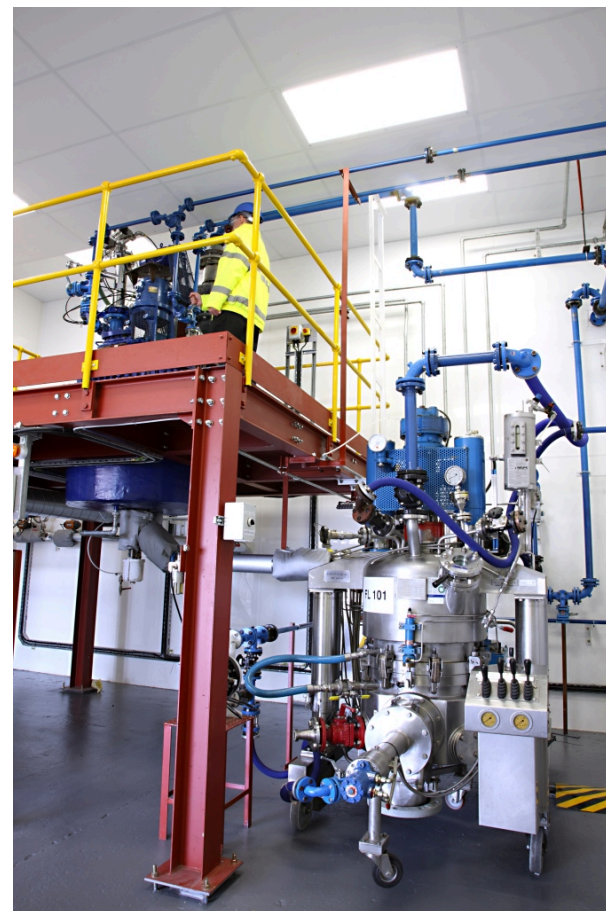


## Elicarb<sup>®</sup> Carbon Nanotubes:

### Single wall (SW) and multi-wall (MW) products:

From initial investments with the University of Cambridge in 2004 to .....

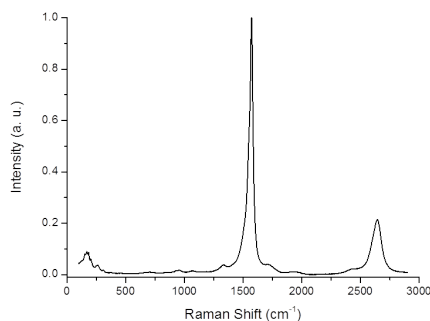
- World leading SW manufacturing capability.
- Scaled to support both existing and emerging opportunities.
- Proven ability to supply multi-kg quantities at competitive pricing to global customers.
  - high quality nanotubes
  - low catalyst residues
  - high surface area



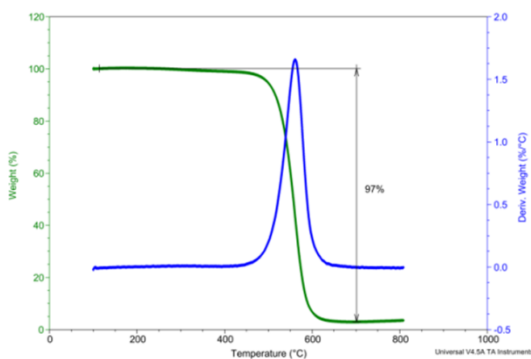
500kg/yr washing facility for Elicarb<sup>®</sup> SW Low Residue products at Thomas Swan's Consett site.

# Elicarb<sup>®</sup> SW products

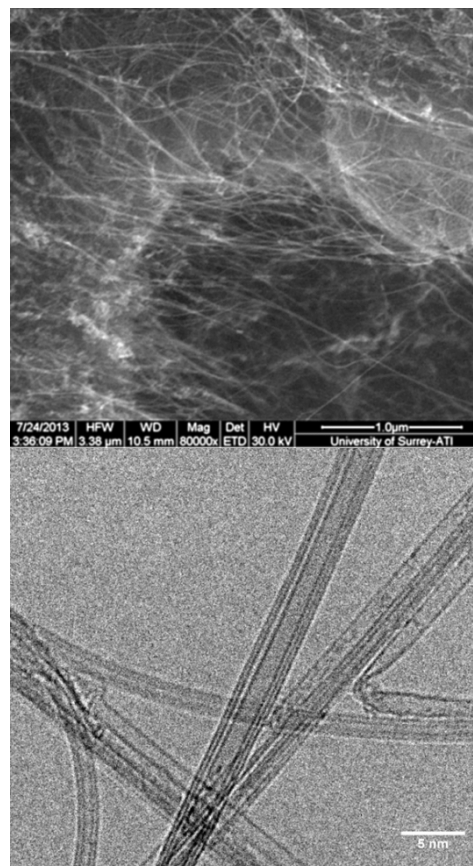
- **Elicarb<sup>®</sup> SW** and **Elicarb<sup>®</sup> SW Low Residue** are market leading SWNT products for advanced electronics.



Raman shows high graphitic carbon content



TGA shows high carbon content

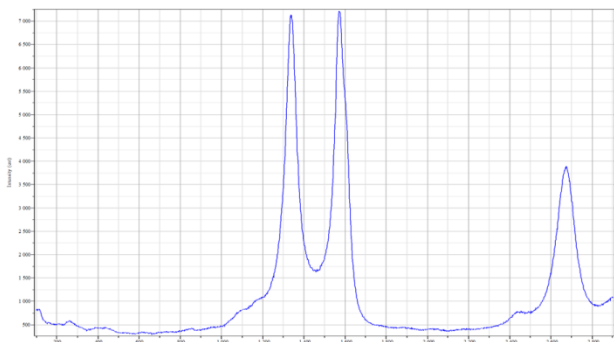


SEM shows high SW carbon nanotube content.

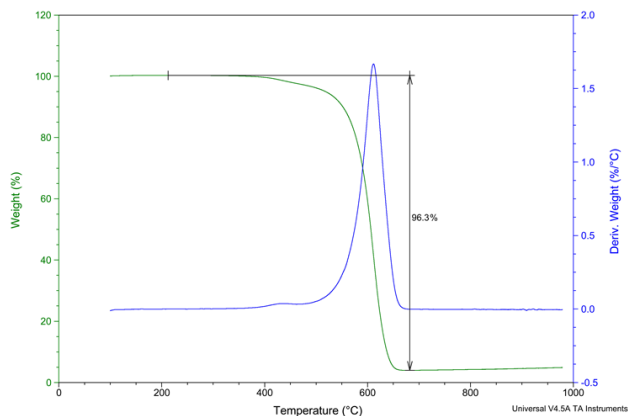
TEM shows high SWNT & DWNT content.

# Elicarb<sup>®</sup> MW products

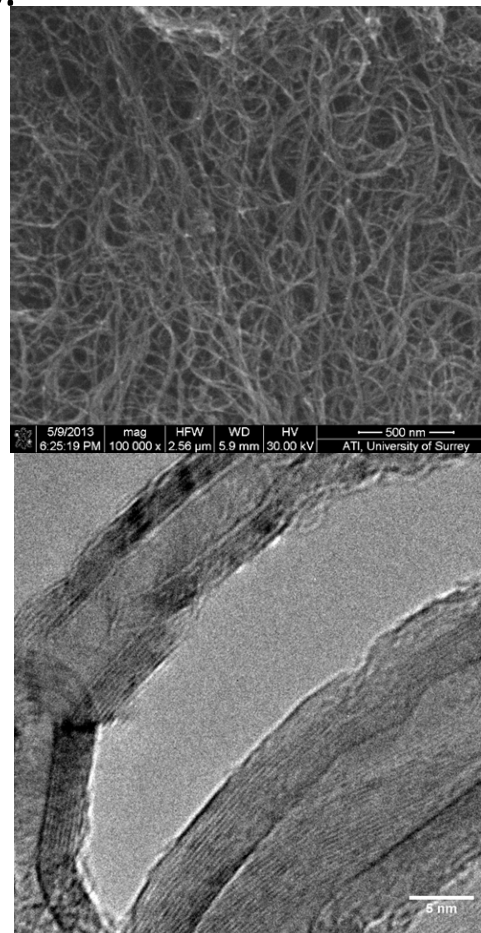
- **Elicarb<sup>®</sup> MW** is a specialist MWNT product which Thomas Swan provides in development & prototyping quantities.



Raman shows typical MW graphitic carbon content



TGA shows high carbon content



SEM shows high MW carbon nanotube content.

TEM shows multi-wall structure.



# Advanced Materials – Graphene

- Thomas Swan selected liquid phase exfoliation of graphite as a route to graphene.
- Aiming for Graphene Nanoplatelets which are substantially non-oxidised with no catalyst residues.
- Process developed in collaboration with Prof. J. Coleman at CRANN, Trinity College Dublin (TCD).
- Exclusively licensed to Thomas Swan & Co. Ltd.
- Target applications include:
  - Conductive inks
  - Super-capacitors & batteries
  - Barrier & separations
  - Thermal management

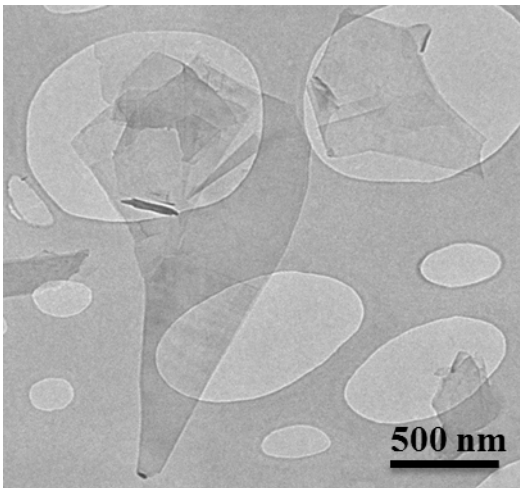
## Elicarb<sup>®</sup> Graphene:

“Industrially relevant route to high quality graphene”.

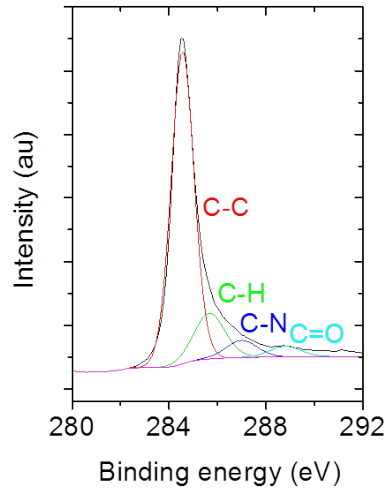


# Graphene - TCD Lab Exfoliated

Graphene platelets produced by liquid phase exfoliation at TCD are non-oxidised, with typical X-Y size of 1000nm and 5-7 carbon layers in depth.

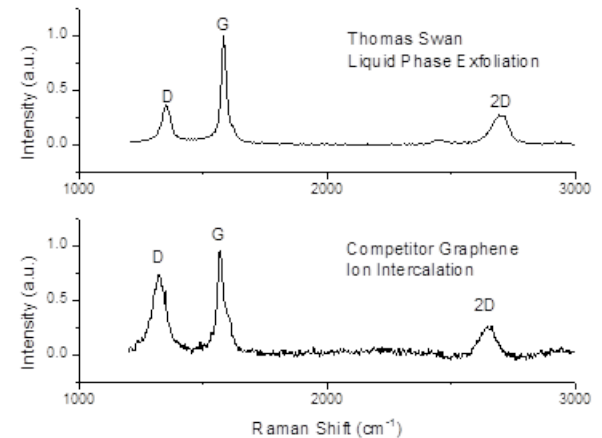


Transmission electron micrograph showing typical graphene platelets. The average platelet diameter is 1000nm.

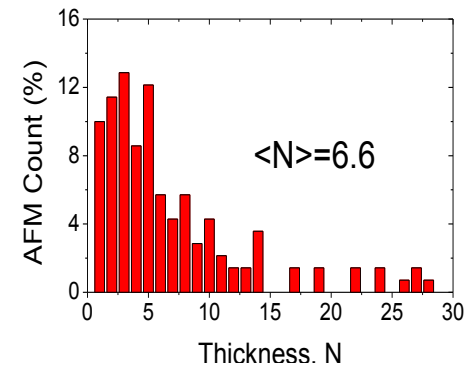


XPS analysis of solvent exfoliated graphene. The N, O, and H signals are consistent with the presence of solvent residues.

AFM analysis of mean thickness in NMP exfoliated GNPs shows an average plate thickness between 5 and 7 carbon layers.



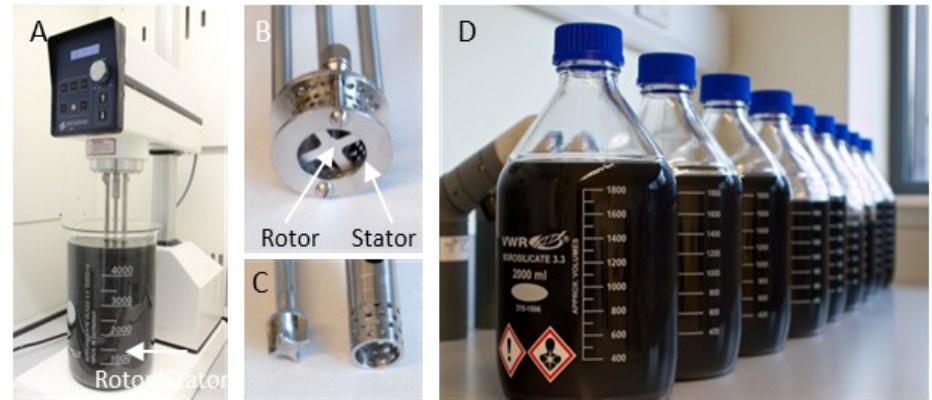
Raman spectrum shows a strong graphite band (D/G ratio = 0.36) when compared with the competitor material prepared by ion intercalation (D/G ratio = 0.75).



# TCD - High Shear Liquid Exfoliation

- Liquid phase exfoliation by high shear mixing.
  - No ultrasonics
  - No aggressive chemistry
  - Ambient conditions.
  - Range of solvents – including water.
  - Stabilised graphene dispersions.
- Patented process.
- Full scientific details published in April 2014:

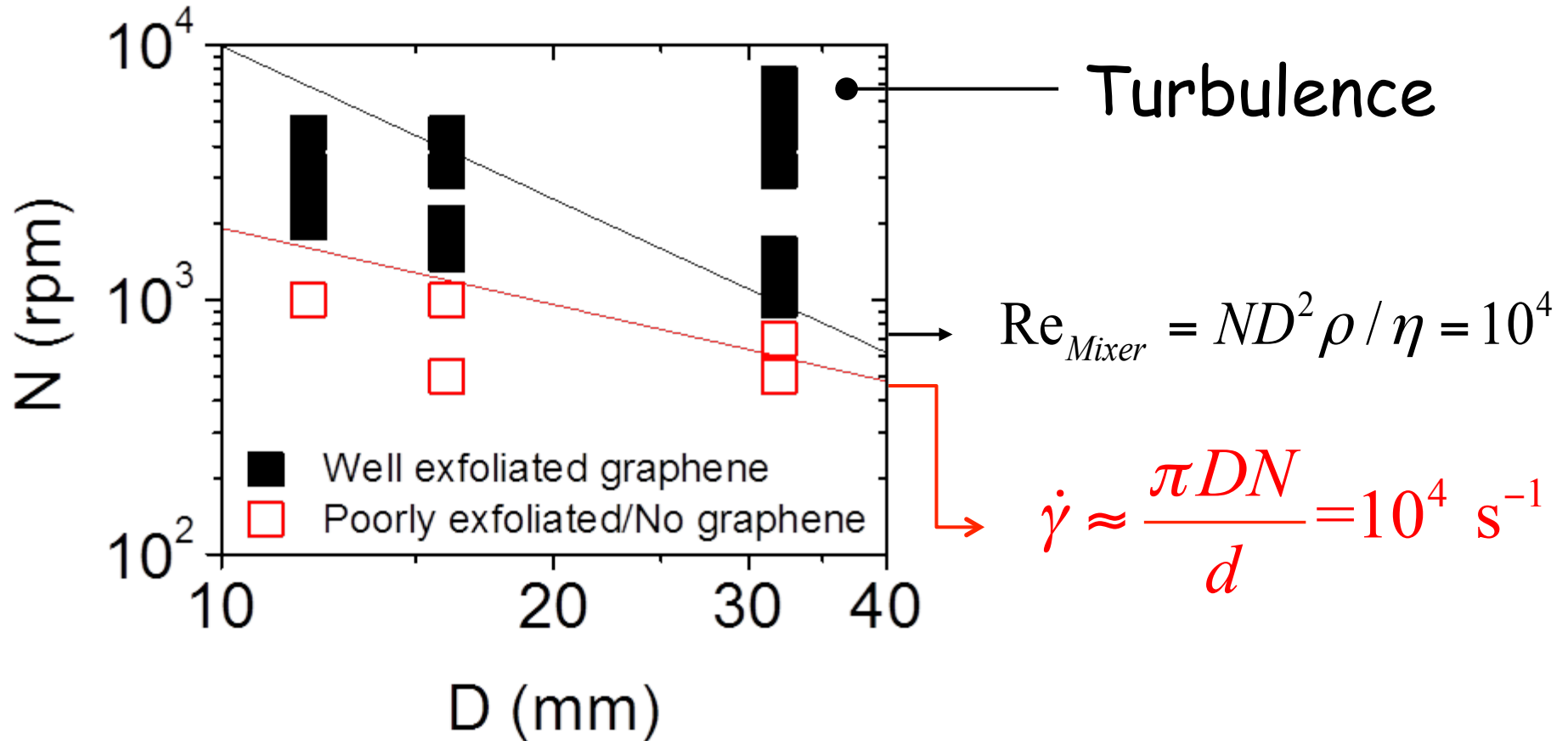
Paton *et al.*, Scalable production of large quantities of defect-free, few-layer graphene by shear-exfoliation in liquids, *Nature Materials* (2014)



Typical Rotor/Stator equipment used for preparing graphene dispersions.

- Liquid phase exfoliation process is being scaled at Thomas Swan, Consett.
- Current status is g/day pilot which will reach kg/day by end 2014.

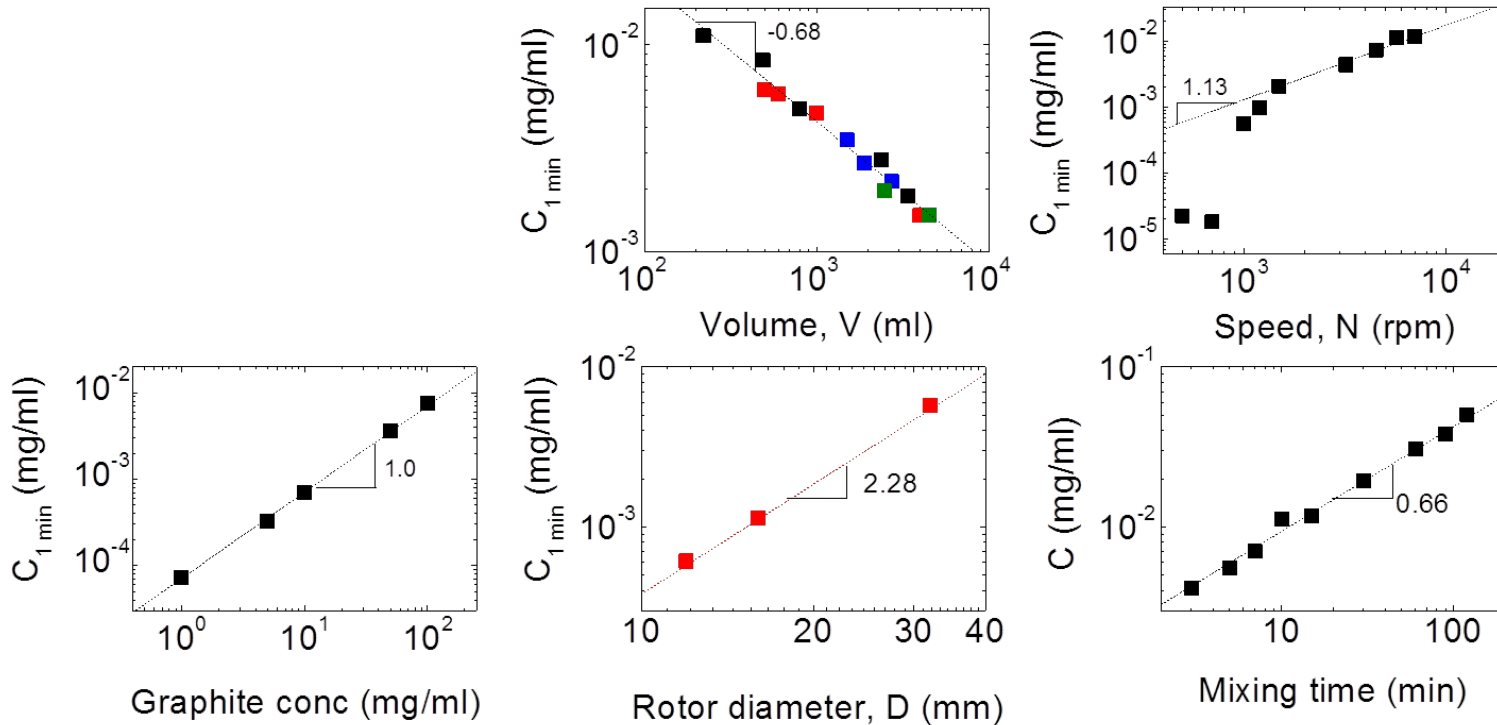
# What is the Exfoliation Mechanism?



Minimum shear rate more important than turbulence

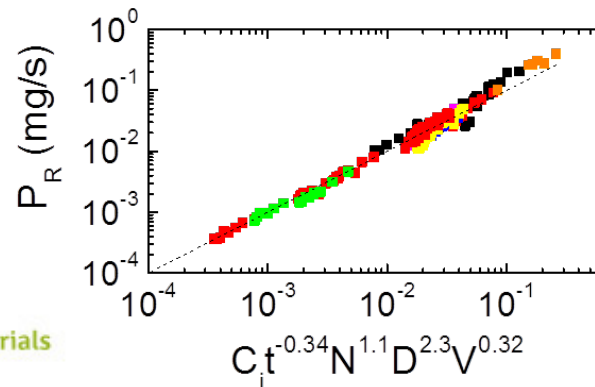


# Scale Up Parameters are Available



$$P_R = CV / t$$

$$P_R \propto C_i t^{-0.34} N^{1.1} D^{2.3} V^{0.32}$$





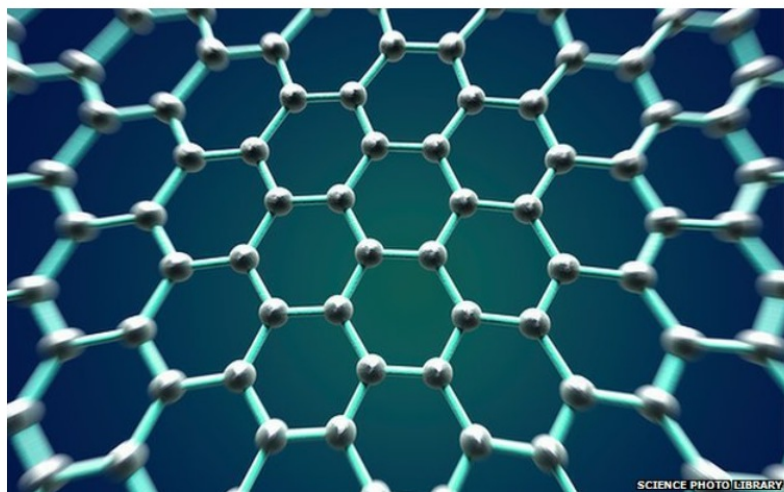
# Generation of Significant Public Interest



22 April 2014 Last updated at 14:03



## Graphene 'wonder material' made with kitchen blender



In graphene, carbon atoms are arranged in a honeycomb structure, one atom thick

Scientists have outlined how they managed to make the "wonder material" graphene using a kitchen blender.

Science of  
Materials



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NATURE MATERIALS | ARTICLE



## Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids

Keith R. Paton, Eswaraiah Varrla, Claudia Backes, Ronan J. Smith, Umar Khan, Arlene O'Neill, Conor Boland, Mustafa Lotya, Oana M. Istrate, Paul King, Tom Higgins, Sebastian Barwich, Peter May, Pawel Puczkarski, Iftikhar Ahmed, Matthias Moebius, Henrik Pettersson, Edmund Long, João Coelho, Sean E. O'Brien, Eva K. McGuire, Beatriz Mendoza Sanchez, Georg S. Duesberg, Niall McEvoy, Timothy J. Pennycook *et al.*

[Affiliations](#) | [Contributions](#) | [Corresponding author](#)

*Nature Materials* (2014) | doi:10.1038/nmat3944

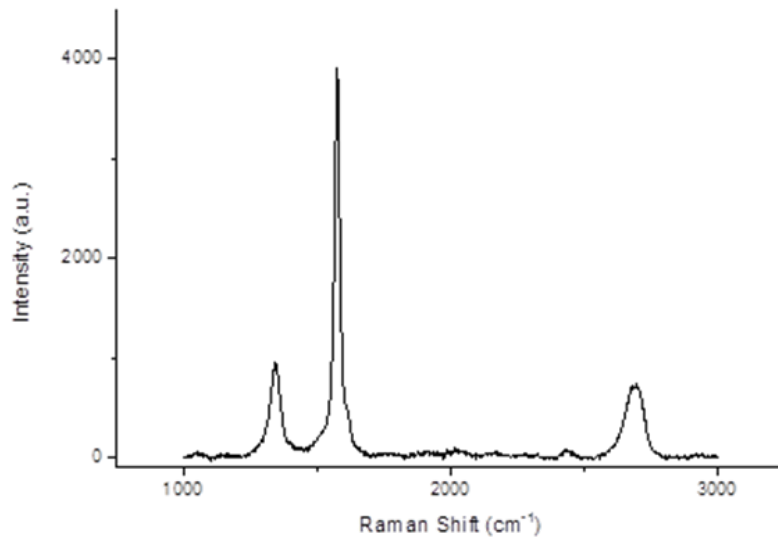
Received 27 September 2013 | Accepted 11 March 2014 | Published online 20 April 2014



Abstract

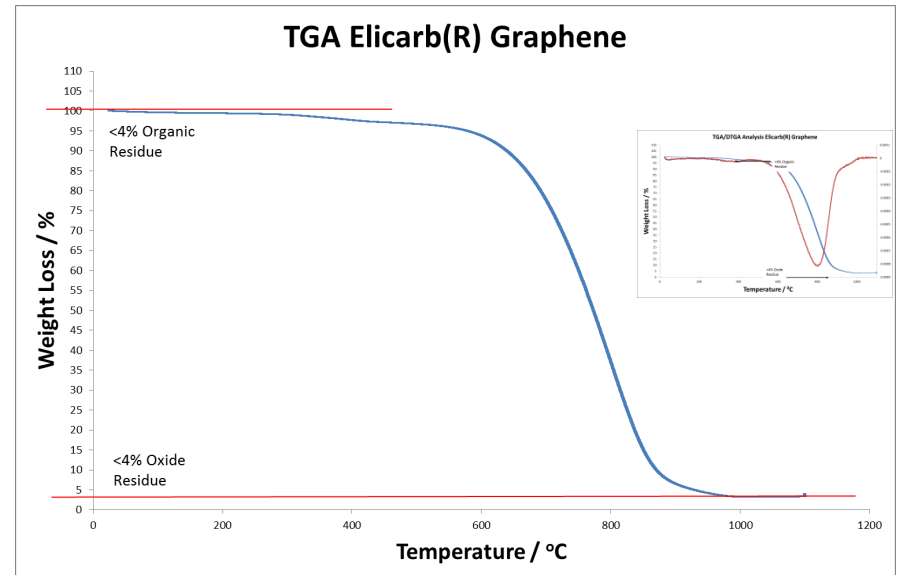


# Thomas Swan Elicarb<sup>®</sup> Graphene



Raman spectra of Elicarb<sup>®</sup> Graphene Powder (514 nm excitation laser wavelength).

The Raman spectrum shows high quality sp<sup>2</sup> network with D/G ratio of 0.23 and D/D' of 4.8

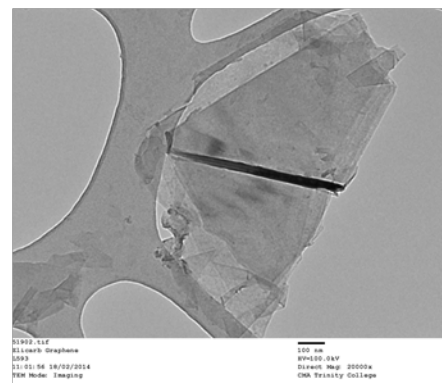
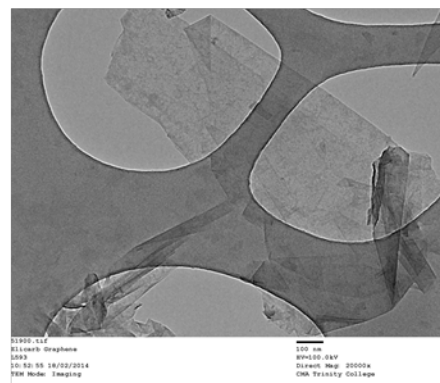
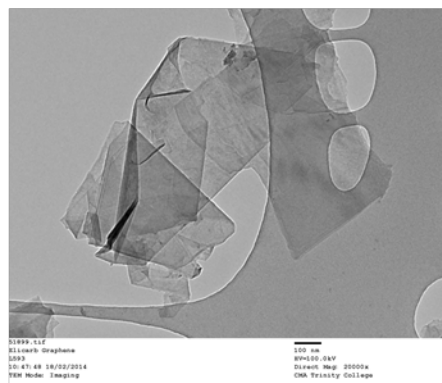
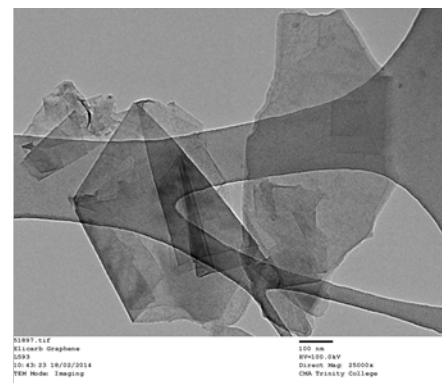
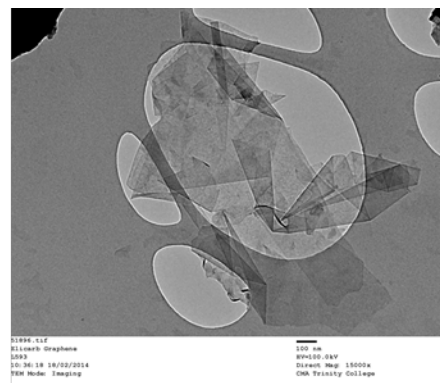
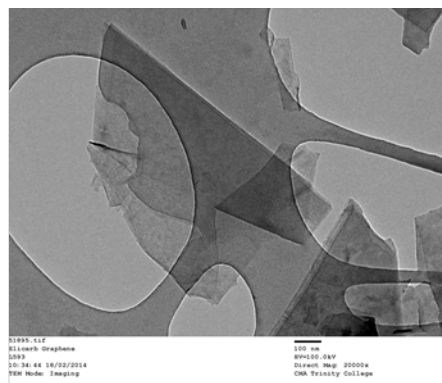
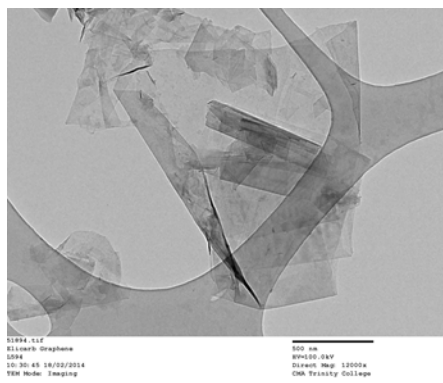


TGA to 1100°C in air of Elicarb<sup>®</sup> Graphene Powder exfoliated in water/surfactant shows a small surfactant residue (loss at ca. 300°C).

Primary decomposition of graphene at 800°C.



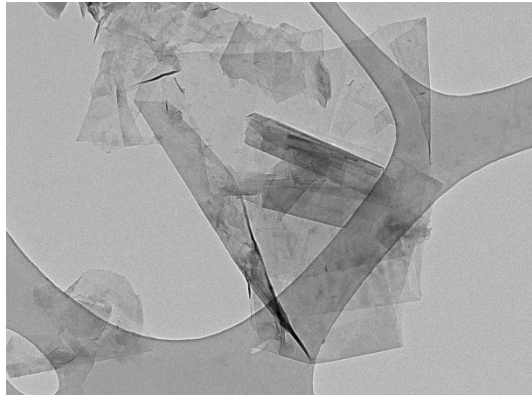
# Thomas Swan Elicarb<sup>®</sup> Graphene



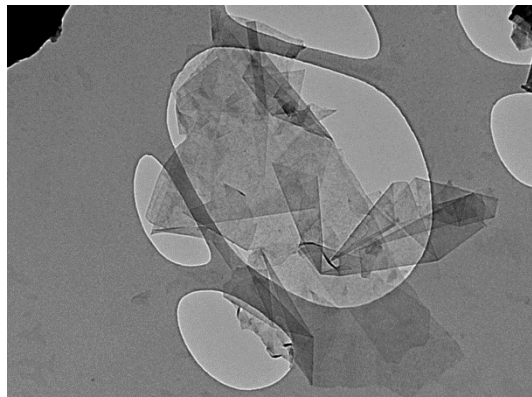
**TEM analysis of typical Elicarb<sup>®</sup> Graphene Powders.**



# Thomas Swan Elicarb<sup>®</sup> Graphene

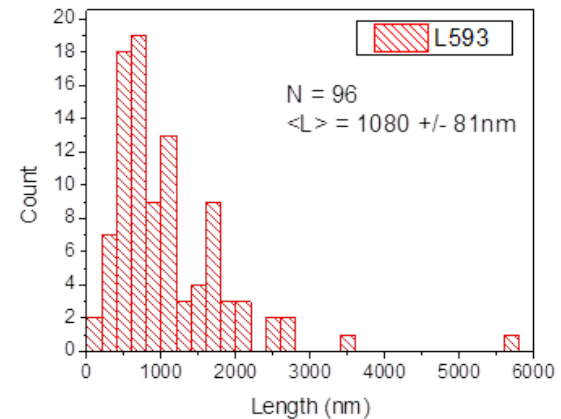
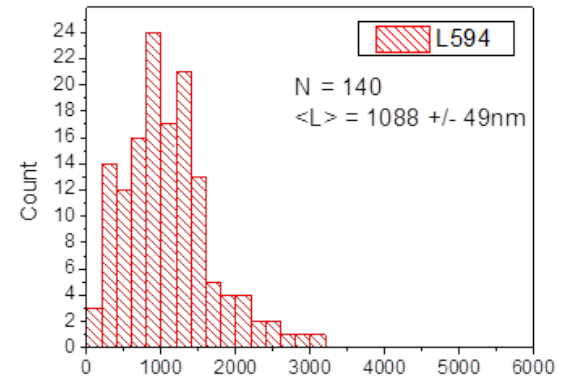


51894.tif  
Elicarb Graphene  
1294  
10:30:45 18/02/2014  
TEM Mode: Imaging  
500 nm  
HV:100.0kV  
Direct Mag: 12000x  
CMA Trinity College



51896.tif  
Elicarb Graphene  
1293  
10:36:18 18/02/2014  
TEM Mode: Imaging  
100 nm  
HV:100.0kV  
Direct Mag: 15000x  
CMA Trinity College

**TEM analysis of Elicarb<sup>®</sup> Graphene Powder shows very consistent flake size between batches.**



**TEM Image particle size analysis of Elicarb<sup>®</sup> Graphene Powder. Average X-Y dimension is ca. 1 micron.**





# Thomas Swan Elicarb<sup>®</sup> Graphene

## Sheet Resistance:

- 4 point probe
- Filtered solids

**10  $\Omega/\square$  for 25 $\mu\text{m}$  film.**

## Graphene platelet thickness:

- 5-7 carbon layers.

## Elicarb<sup>®</sup> Graphene Products:

Products are available commercially



Elicarb<sup>®</sup>Graphene  
Powder



Elicarb<sup>®</sup>Graphene  
Dispersion (AQ)



## Summary: Elicarb<sup>®</sup> Graphene Products

- We have developed a scalable route to pristine graphene nanoplatelets.
- Typical particle size is 1000nm in X-Y dimension and 5-7 carbon layers in Z dimension.
- The products have low defect levels and high conductivity / low sheet resistance.
- Development products are now available for evaluation.

## Follow up Questions

Many thanks for your attention.

I am happy to answer questions.

[pladislaus@thomas-swan.co.uk](mailto:pladislaus@thomas-swan.co.uk)

We would be delighted to discuss the needs of your application.

# Advanced Materials Division

*Reliability & Quality in carbon nanomaterials.*

# Appendix



## Nanomaterial Safety & Regulatory

Continuing safe commercialisation of new nanomaterials remains a priority for the materials industry. This is an evolving framework and Thomas Swan takes a pro-active role.....

- **Compliance**  
.....with existing legislation.....plus external verification.
- **Awareness**  
.....of new scientific publication and changing regulatory requirements.
- **Support**  
.....increased understanding through in-house studies and collaborations (eg. NanoReg).
- **Engagement**  
.....with Industry associations such as CIA Nanomaterials Issue Team.
- **Communication**  
.....of new information as we enhance our understanding.