NPL National Physical Laboratory | NGMC National Graphene Metrology Centre

Graphene Characterization Methods and Issues

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Innovate UK
Technology Strategy Board

Department for Business, Energy & Industrial Strategy

GRAPHENE FLAGSHIP

FUNDED BY BEIS

Outline

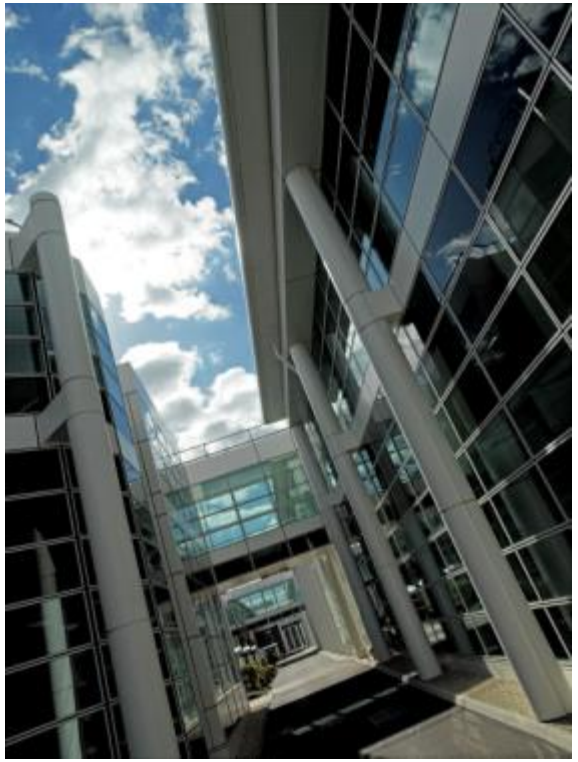
- National Physical Laboratory (NPL)
- Graphene and Related 2D Materials
- Industrial Case Study
- International Standardisation
- Measurement Techniques
- Quality Control

About NPL …

NPL
National Physical Laboratory

The UK's national standards laboratory

- Founded in **1900**
- World leading **National Measurement Institute**
- 600+ specialists in **Measurement Science**
- State-of-the-art laboratory facilities
- The heart of the UK's **National Measurement System** to support business and society
- Experts in **Knowledge Transfer**



Graphene at NPL

NPL National Physical Laboratory

- Two dimensional ‘wonder material’ with exciting properties and many application areas

- NPL has 20+ scientists and engineers working on 2D material related projects (and 10+ students)
- Improved access for Industry, Academia and Government to 2D material capability:
  - Characterisation
  - Metrology
  - Standardisation
  - Quality Control

NGMC National Graphene Metrology Centre

- Formalised strategic partnering with key organisations
  e.g. The National Graphene Institute (NGI), University of Cambridge

Characterisation of Graphene

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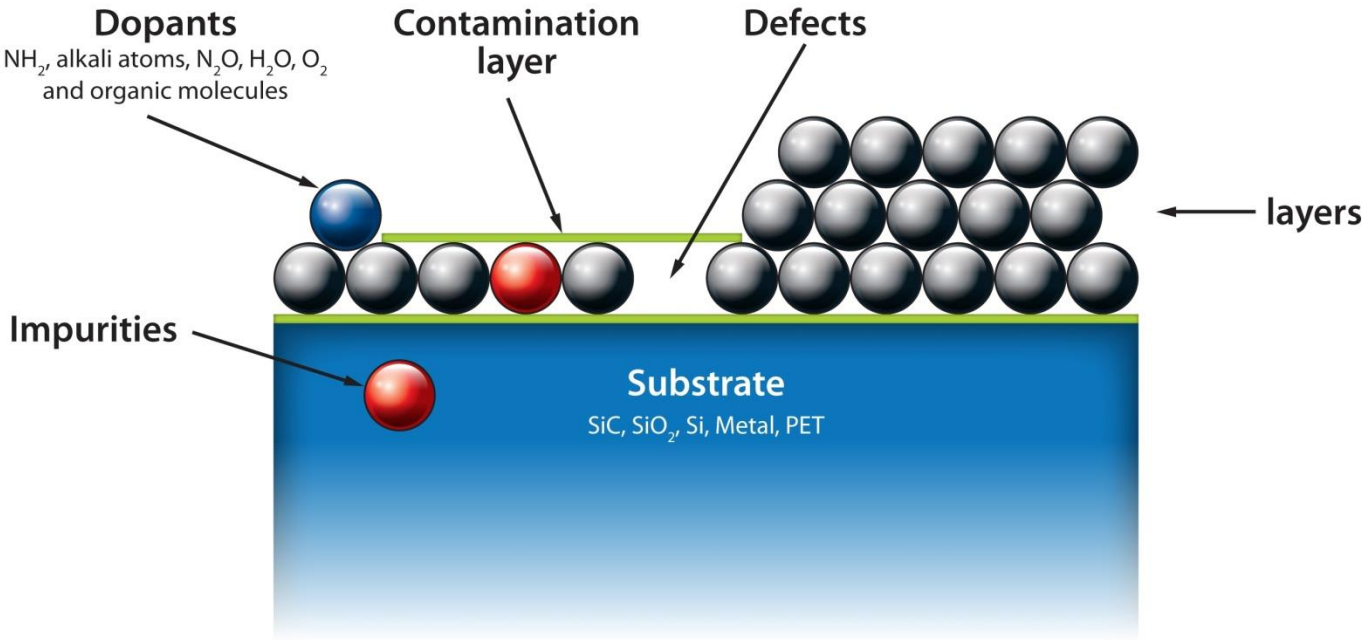
SIMS
Quantify dopant concentration and impurities
$>10^8$ atoms/cm^2, 10^{16} atoms/cm^3
Identification of contamination, depth profile

XPS and UPS
Quantify adventitious contamination,
layer thickness (< 1 layer precision)
Work function, chemical bonding

Raman and TERS
No of layers, chemical structure
Defects and edge type
Doping, contamination

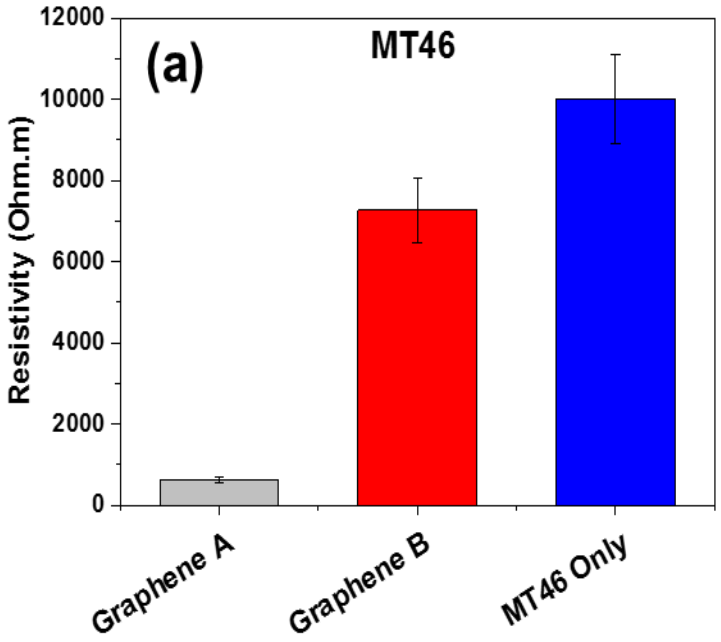


Characterisation of Printed Graphene Films

NPL National Physical Laboratory

DZP Technologies
Delivering printed electronics innovation

- Commercial company using graphene powders to make printed graphene electrodes
  - Different polymer binders/composites used



Brennan *et al.* App. Surf. Sci. **403** 403-412 (2017)

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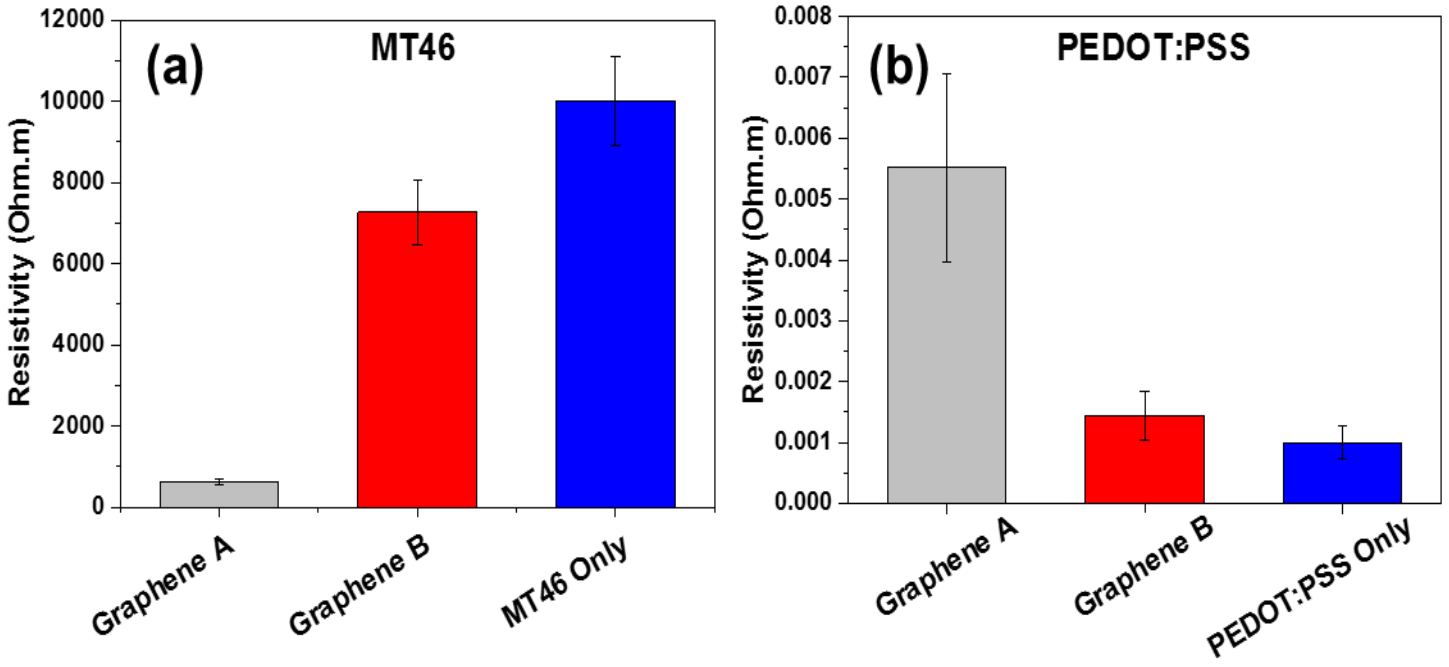

Brennan *et al.* App. Surf. Sci. **403** 403-412 (2017)

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ISO Standardisation

NPL National Physical Laboratory

ISO International Organization for Standardization

IEC International Electrotechnical Commission

Terminology Standard

Measurement Technical Report

Structural Characterisation of Graphene Flakes

Structural Characterisation of GO Flakes

Chemical Characterisation of Graphene/rGO/GO Flakes

Structural Characterisation of CVD Graphene

ISO TR 19733 Measurement Matrix

- ISO Technical Report on measurands and associated measurement techniques
- Illustrated Matrix
- Description of each
- Pros and Cons

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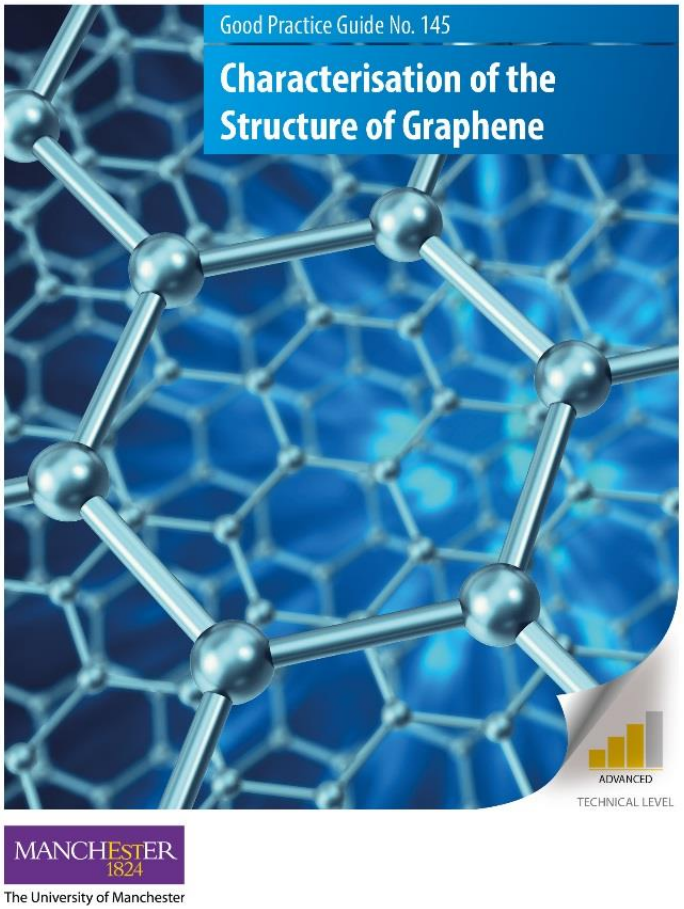
Good Practice Guide

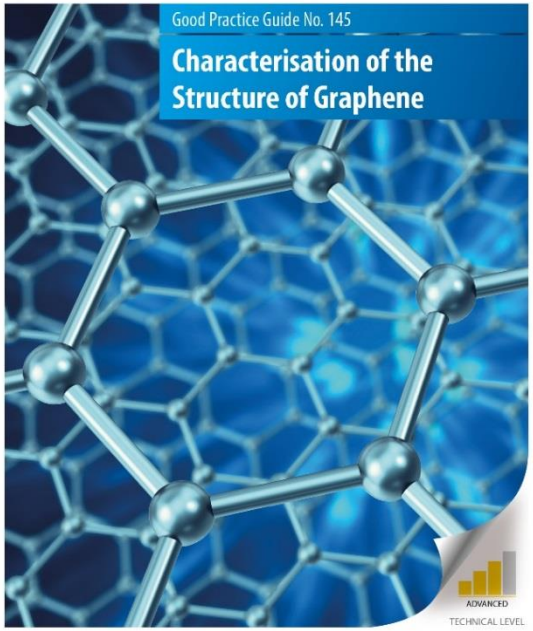
- Instigated by need of industry due to lack of comparability and consistency between materials sold by graphene producers.
- Good practice guide (GPG) series released by NPL

  Rapid dissemination to industry
- Joint NPL and NGI (Manchester) GPG
  - www.npl.co.uk/graphene-guide
- Technique, issues, protocol, data analysis
- GPG used as interim source as international standard developed

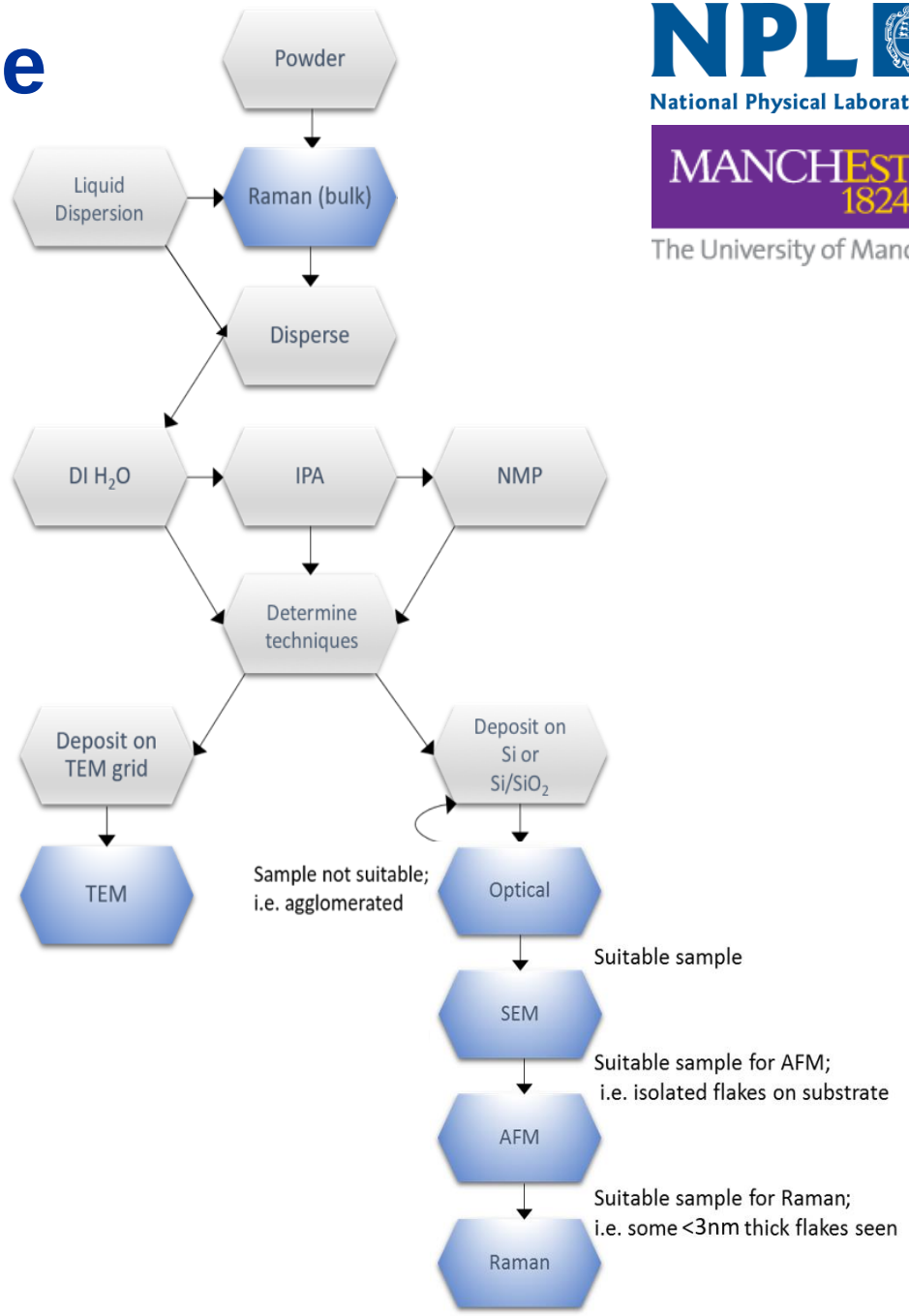


Good Practice Guide

NPL National Physical Laboratory



MANCHESTER 1824 The University of Manchester



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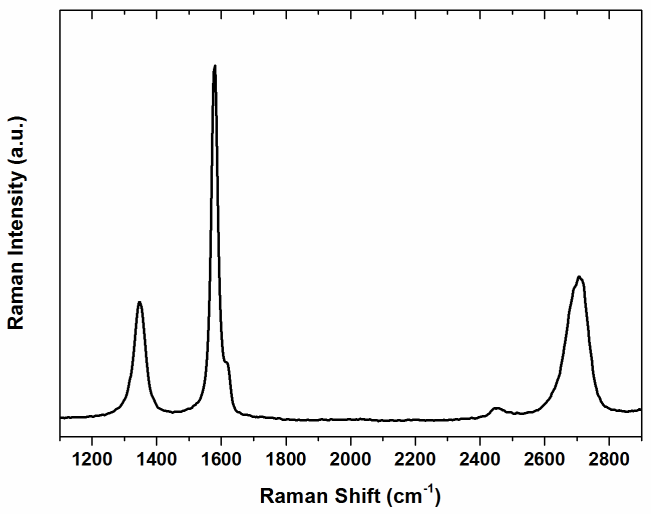
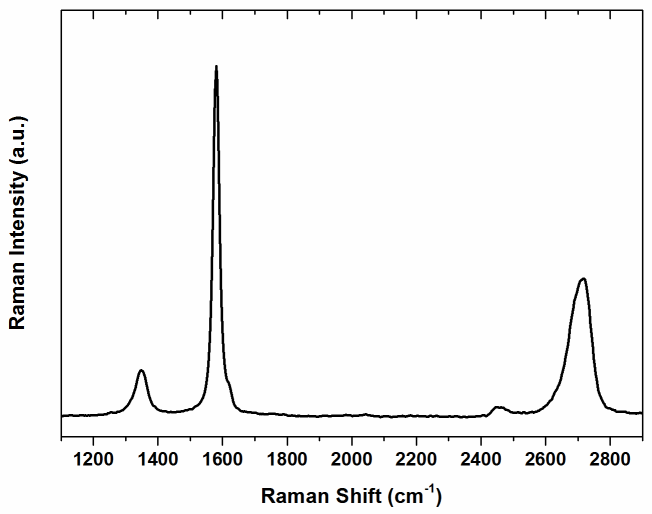
Raman Spectroscopy

- Determination of crystal structure through optical method
- Provides understanding of many measurands such as sp^2 versus sp^3 carbon structure, level of disorder and number of layers
- Raman spectra for bulk powder as first step to determining material provided
- Also on individual flakes





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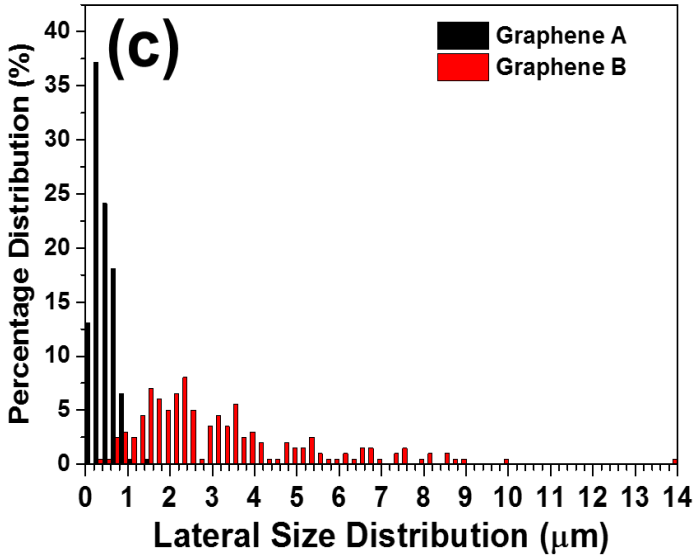
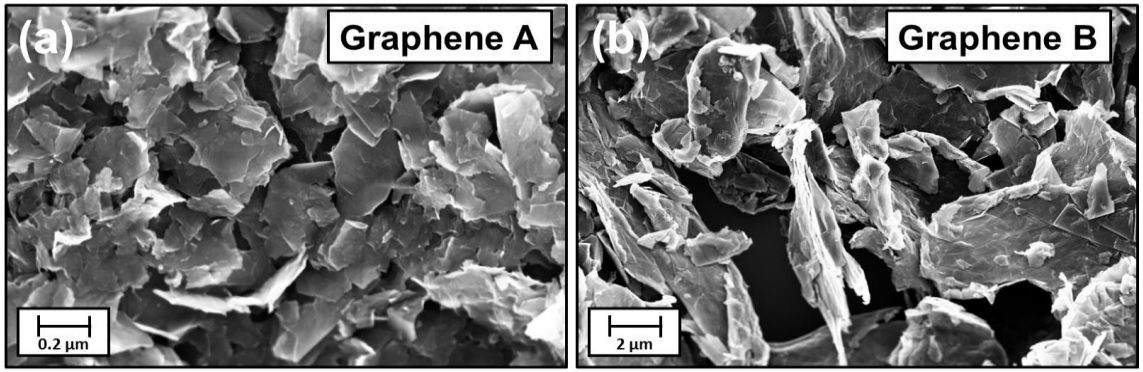
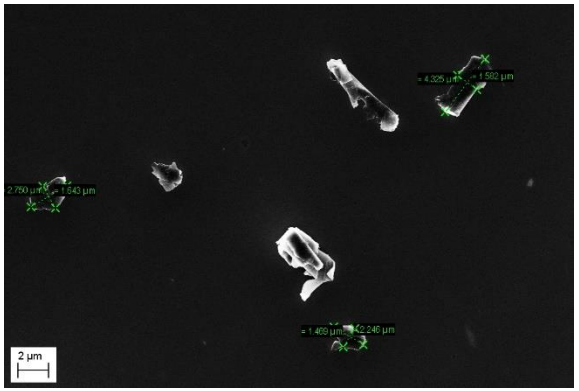
Scanning Electron Microscopy (SEM)

- Determination of lateral flake size using electron microscopy
- Primary particles are not the same size and so the distribution must be investigated



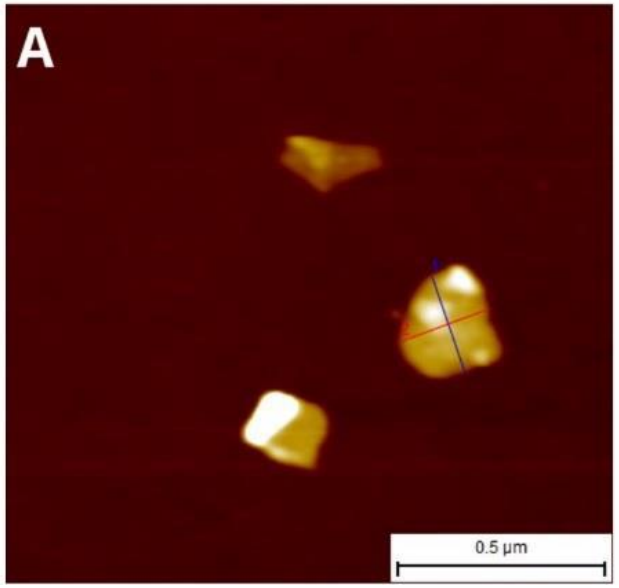


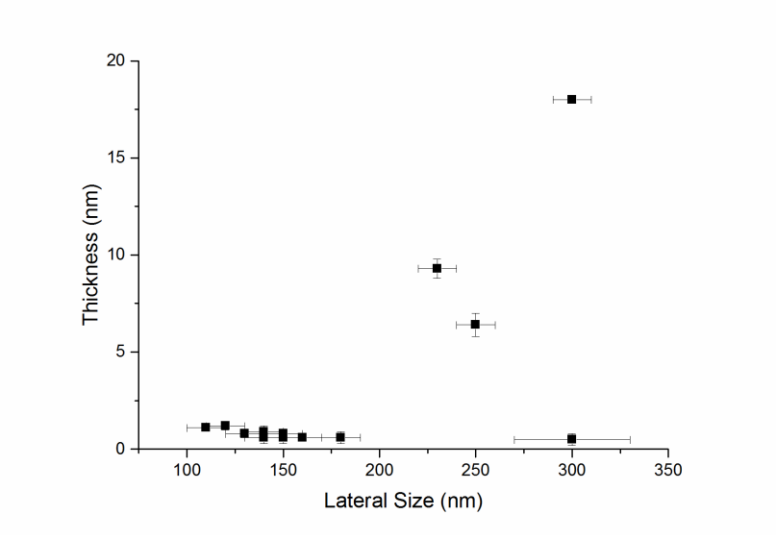


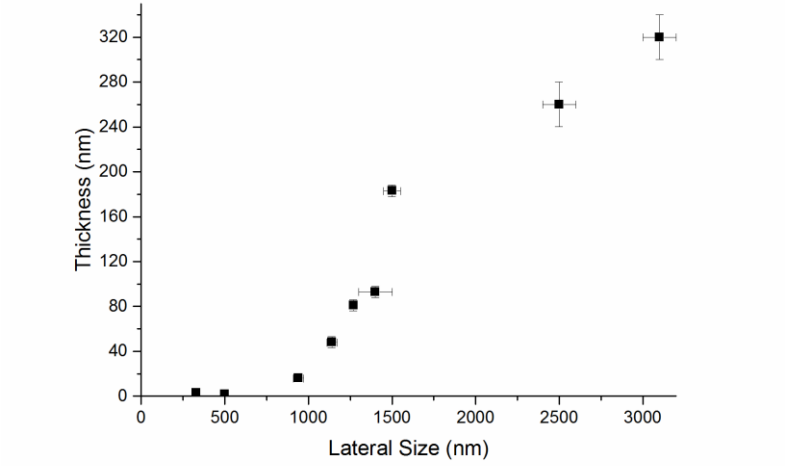
Brennan *et al.* App. Surf. Sci. **403** 403-412 (2017)

Atomic Force Microscopy (AFM)

- Thickness of the flakes determined using a scanning probe microscopy technique
- Thickness can be related to lateral size using AFM
- A relation may be found, particularly for top-down production processes
- Issues with the measurement time required







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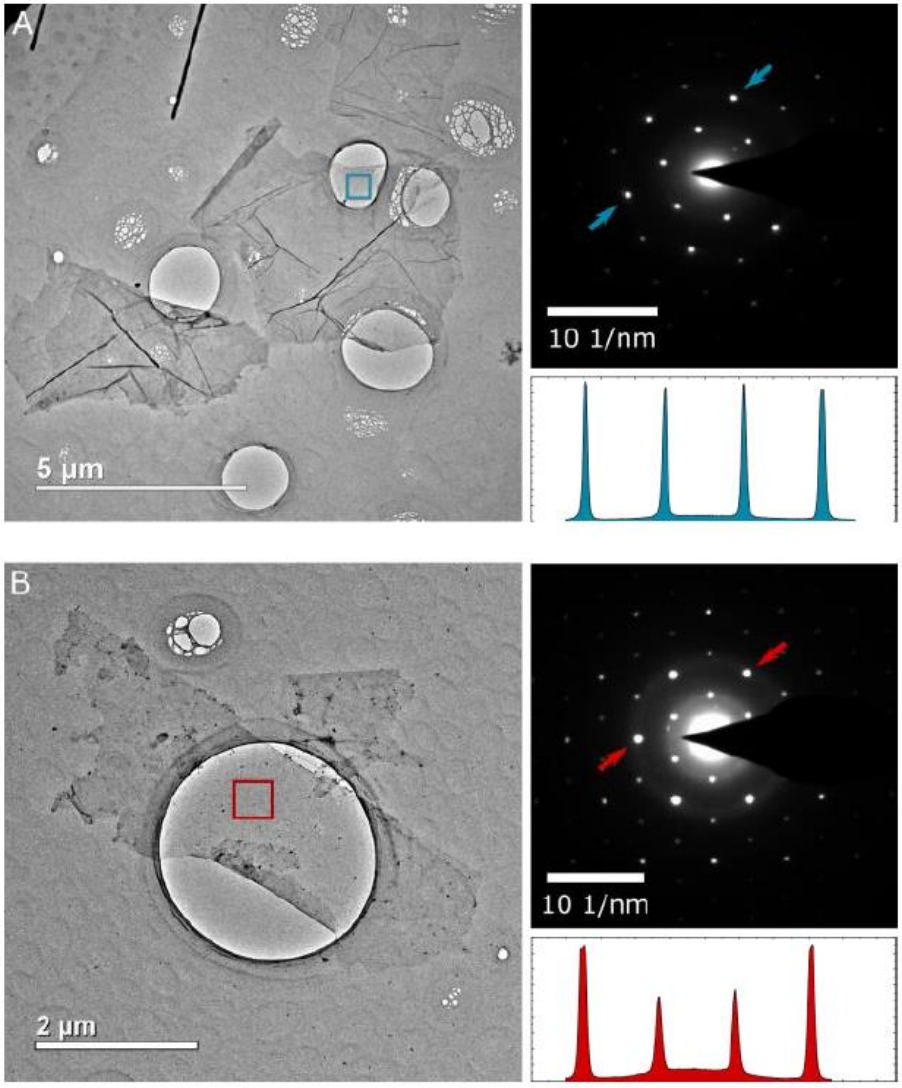
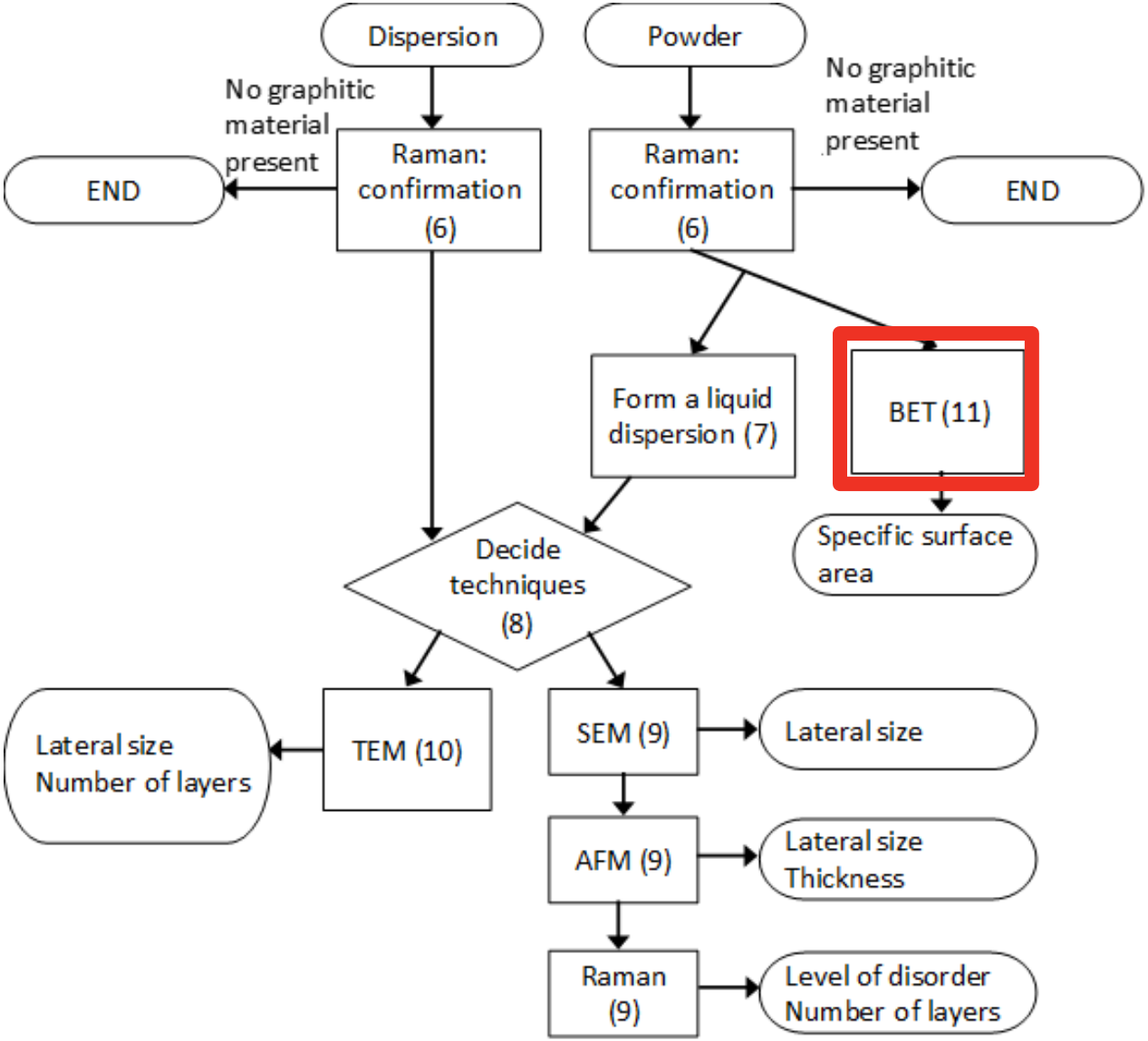
Transmission Electron Microscopy (TEM)



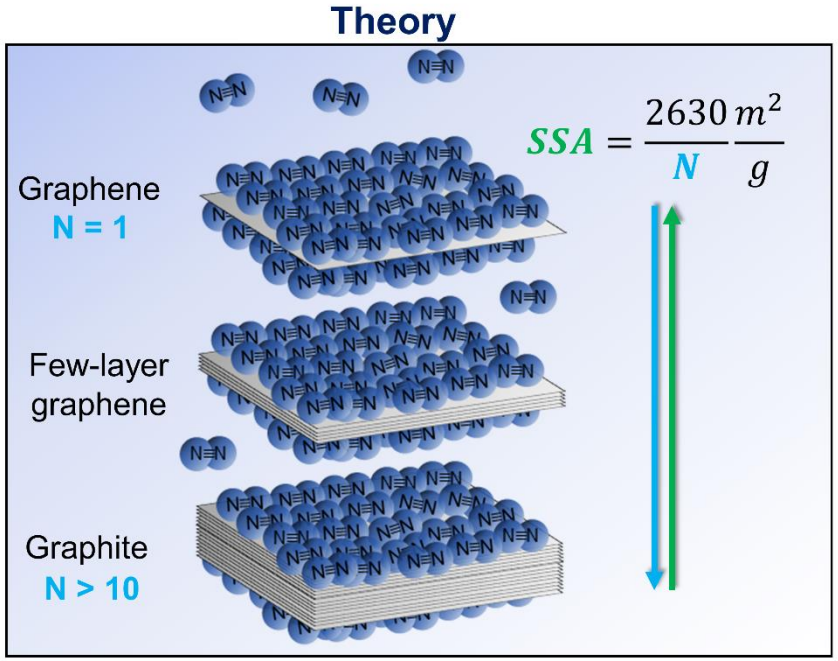
- High resolution electron microscopy technique
- Determination of flake size, number of layers and level of disorder
- Image showing single layer (top) and bilayer (bottom) flakes
- Selected area electron diffraction (SAED) used in combination

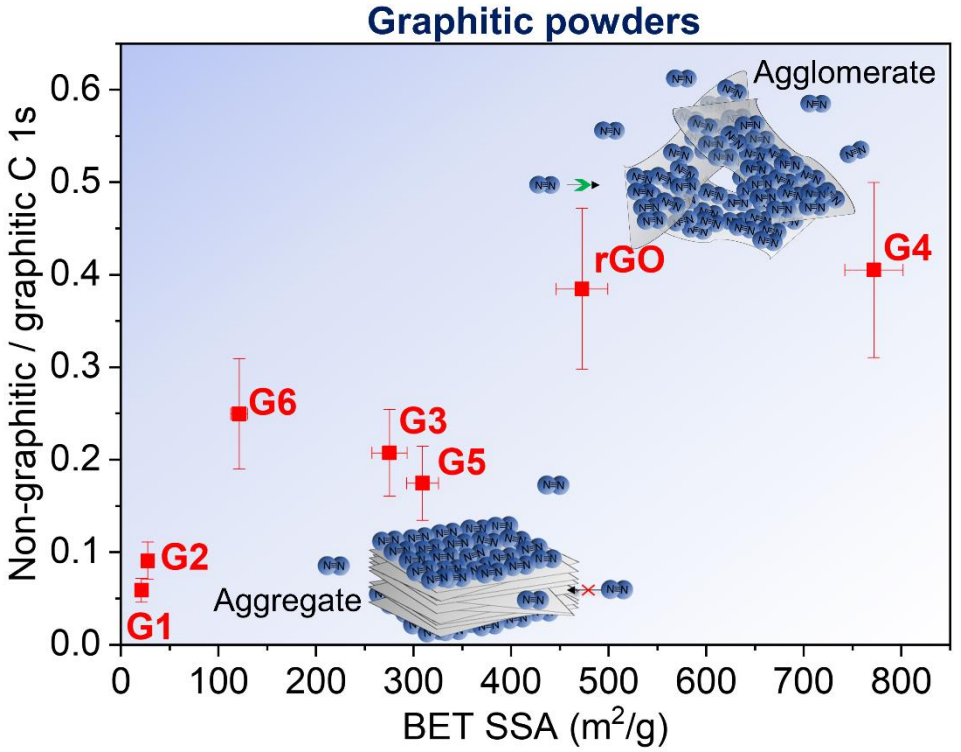
ISO TS 21356-1



BET Method

- Brunauer-Emmett-Teller (BET) method is used to determine the specific surface area (SSA) of a powder
- Calculated through the adsorption of gas molecules (typically nitrogen) on a solid surface.
- ‘Bulk’ technique that can provide comparisons between material





Marchesini *et al.* Under Review (2020)

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Chemical Techniques

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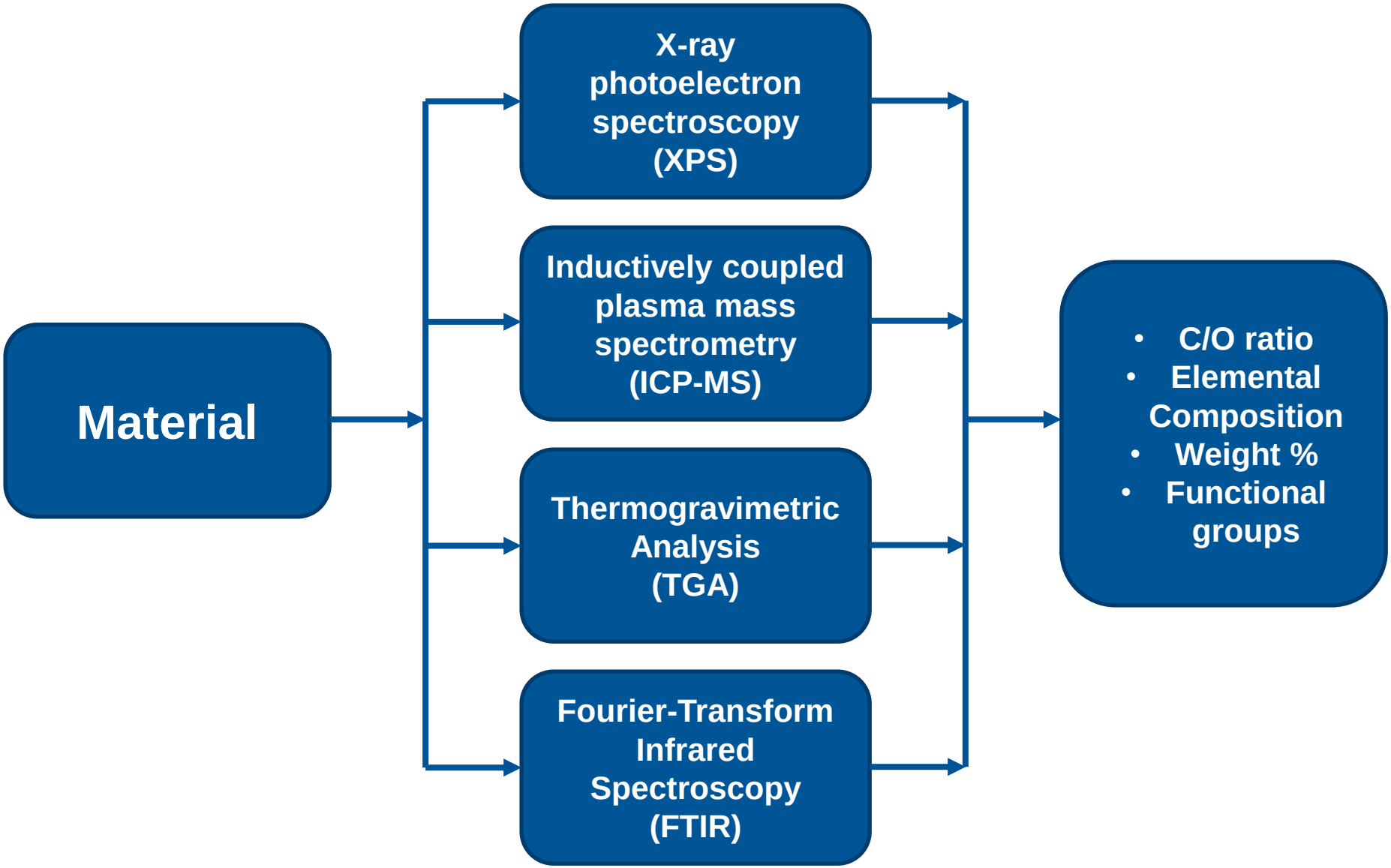
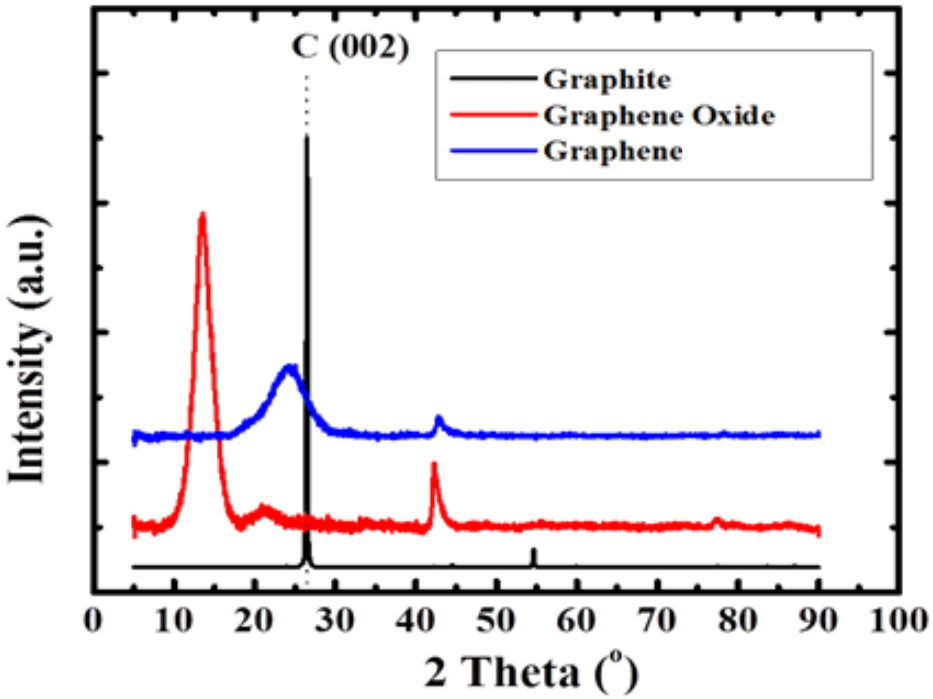


X-Ray Diffraction (XRD)

- Method to obtain crystallographic information by observing the diffraction pattern due to an X-ray beam hitting a sample.
- Used as a tool to determine crystallinity of powders
- Generally used to understand crystallite size, but peak width variations can be attributed to different changes in disorder
- Is a ‘bulk’ technique.
- Issues of not knowing what the material is just from an XRD spectra, but can compare known samples



Siburian *et al.* Orient. J. Chem. **34** 182-187 (2018)

Underpinned by Metrology

- Rigorous scientific investigation required to understand measurement
  - Use of academic research
  - Several years timeframe
- Develop to be applicable to Industry
- Using the VAMAS framework
  - International collaboration for measurement and material comparison
- New Area now initiated ‘TWA 41: Graphene and Related 2D Materials
  - Co-chaired by NPL and NIM, China
- 7 experimental projects now underway:
  - Raman spectroscopy, XPS, ICP-MS, AFM, FTIR, BET, TGA

Validation

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- Graphene Flagship has launched a new validation service
- Measurements of graphene-enhanced bulk composite materials
- Free of charge to full Flagship Consortium partners
- https://graphene-flagship.eu/VSFAQ
- **GF_ValidationService@npl.co.uk**

GRAPHENE FLAGSHIP

Graphene Council Service

NPL National Physical Laboratory

The Graphene Council

Verified Graphene Producer

The Verified Graphene Producer™ Program

The graphene market is crowded and becoming increasingly confusing, with new companies regularly appearing on the scene. There are at least 180 companies world-wide claiming to produce and supply graphene materials of various grades and morphology.

In a review of material specification sheets for 60 graphene products, The Graphene Council found that more than 45 different material characteristics were listed, but not one of them was common to all of the materials claiming to be graphene. In fact, less than 75% of the products reviewed shared a common listed specification.

This makes it impossible for a buyer to compare materials from different suppliers without actually testing each sample, and a full graphene sample characterization by a world-class lab costs approximately $12-15,000 - per sample!

As a result, The Graphene Council has created the **Verified Graphene Producer™** program to help reputable graphene companies to differentiate themselves from the competition.

The Graphene Council Verification Program™ is based on the most recent developments of globally recognized graphene standards, surveys of graphene producers, researchers and users, as well as analysis of commercially available graphene products, and is an important step in providing customers and end-users a degree of confidence that they are sourcing material from a reputable supplier.

This involves an in-person inspection of graphene production facilities, analysis of random samples of graphene products and independent testing and characterization of the material by internationally recognized and qualified labs.
If you are interested in our **Graphene Producer Verification Program™,** contact us today for a confidential discussion.

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Quality Control

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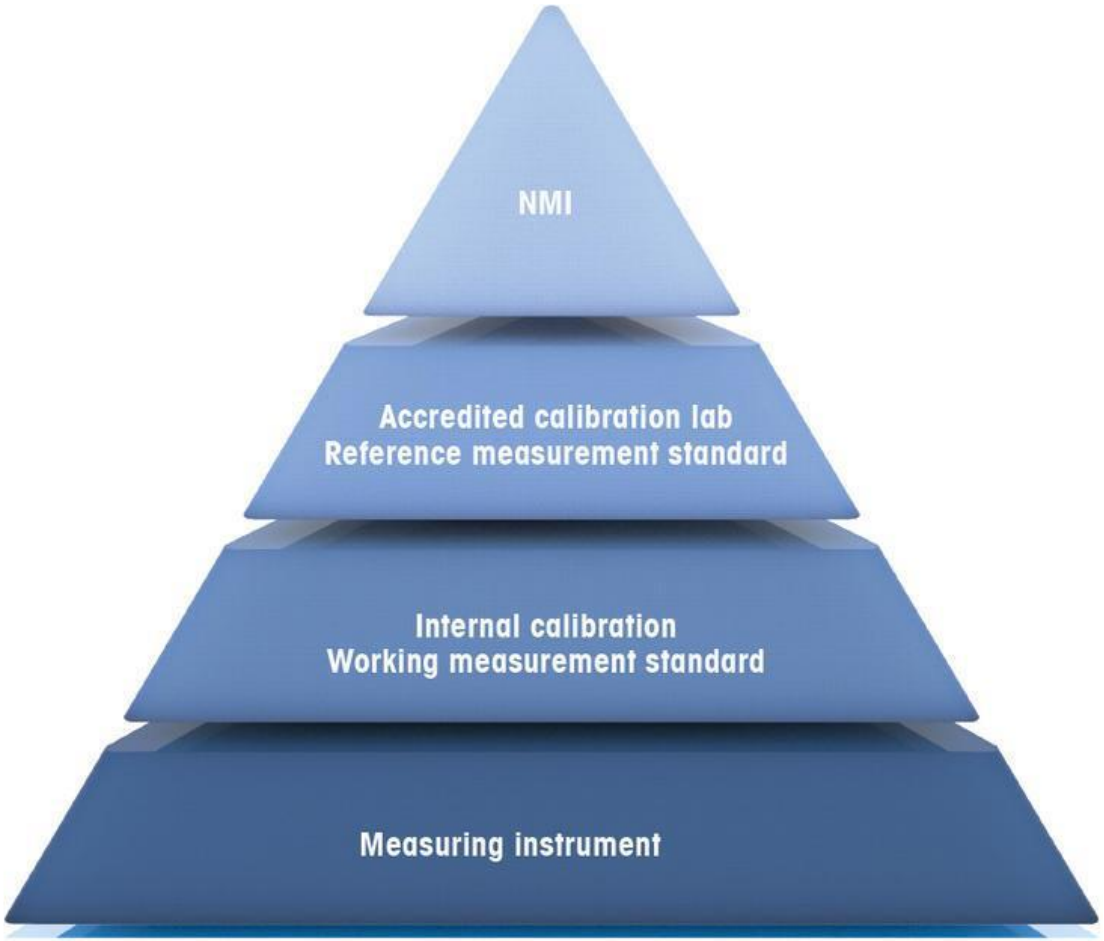
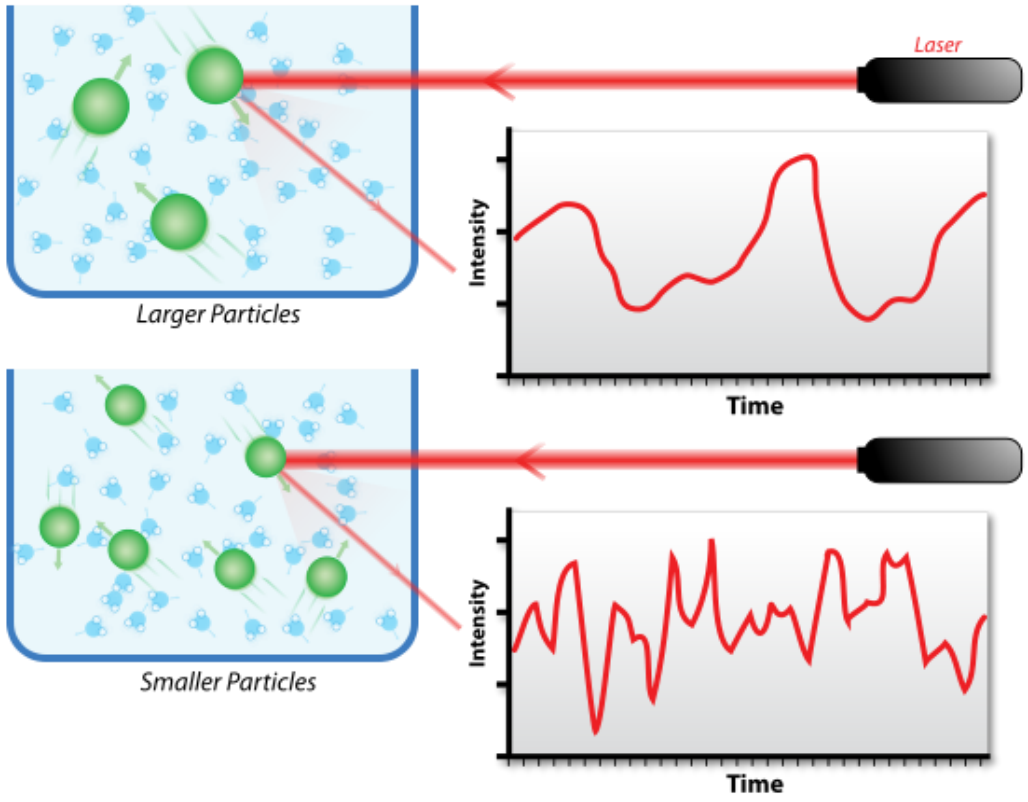
- Measurement standards crucial for industry
- Accurate and precise measurements typically slower and expensive
- Rapid measurement methods with known and validated uncertainty required
- Technician-level expertise



Nanoparticle Sizing

- Industry developing new techniques for in-house QC
- **Dynamic Light Scattering (DLS)** is one technique used
- Particle sizing technique typically used for spherical nanoparticles
- Larger particles given more weight



https://en.wikipedia.org/wiki/Dynamic_light_scattering
ISO 22412:2017 Particle size analysis – Dynamic light scattering (DLS)

Summary

- The structural and chemical properties of graphene are directly linked to the final product performance
- A series of measurement techniques required to really understand ‘what is my material?’
- ISO graphene terminology standard for consistent language
- A joint NPL-Manchester GPG used to develop ISO measurement standards for consistent comparisons worldwide
- Quality control methods required for graphene industry
- Metrology is required to instill trust between researchers, companies and the consumer

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