Allotropes of carbon as nanomaterials summary report

Historically carbon is classified into three principal forms (allotropes):

- diamond
- graphite
- amorphous carbon

The properties of these materials vary depending on the arrangement of the carbon atoms.

Principle allotropes of carbon

Allotrope	Structure	Properties
Diamond	3D network of C atoms, each bonded to 4 others	Hard, clear
Graphite (pencil "lead")	Stacked layers of C in honeycomb lattices	Soft, black
Amorphous carbon	No crystal structure	Black powder

There has been great progress in the understanding of carbon structures since a single sheet of graphite, known as graphene, was first described in 1962. The era of carbon nanotechnology began in 1985 with the discovery of buckminsterfullerene by Kroto *et al*, followed by the production of carbon nanotubes by Iijima *et al* in 1991. Figure 1 shows an overview of the structures of the carbon allotropes.

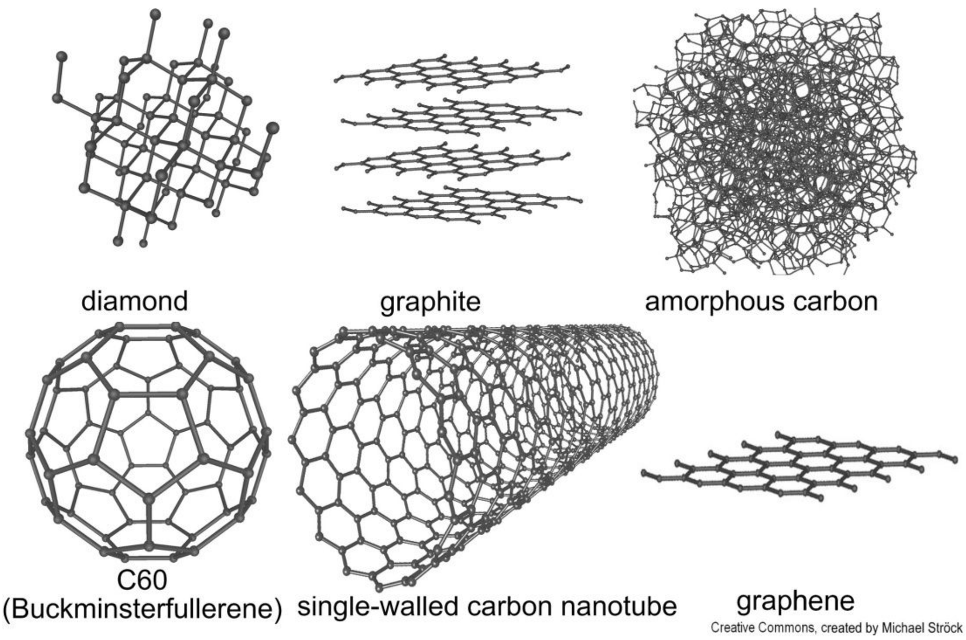


Figure 1: Carbon allotropes

Summary of carbon allotrope nanomaterials

Graphene

- Flat single layer of carbon atoms in a honeycomb lattice
- Stacks to form graphite
- Rolled to form carbon nanotubes
- Wrapped up to form buckyballs

Properties:

- good thermal and electric conductor
- incredibly strong

Applications:

- semiconductor circuits and computer parts (transistors, electrodes, ultra-capacitors)
- single-molecule gas detection
- nanoribbons
- solar cells
- biodevices
- anti-bacterial materials

Carbon nanotubes (CNTs)

- Single or multiple graphite sheets rolled up into nanoscale tube
- Single-wall carbon nanotubes – SWNTs
- Multi-wall carbon nanotube, MWNTs
- Semiconducting or metallic behaviour depending on:
    - arrangement of the graphite rings
    - diameter of the tube
    - degree of twists of the graphene sheet
- Unique electronic, magnetic, mechanical, and optical properties

Applications:

- novel single-molecular transistors
- molecular computing elements
- electron field emitting flat panel displays
- gas and electrochemical storage
- molecular-filtration membranes
- artificial muscles

Buckminsterfullerene (C_{60}) – Bucky balls

- Discovered in 1985 by Kroto *et al* (Nobel Prize 1996)
- Carbon molecule with a soccer-ball-like structure
- 12 pentagons and 20 hexagons facing symmetrically
- Can modify surface or hollow centre

Applications:

- superconductors
- hydrogen storage
- high-efficiency solar cells
- chemical sensors

Buckypaper

- Thin sheet of aggregated carbon nanotubes
- Inadvertently developed in Richard Smalley's lab
- Nanotubes in liquid suspension are filtered through a fine mesh
- The nanotubes stick together forming a thin film disk

Properties:

- "harder than diamonds"
- "stronger than steel at a fraction of the weight"

Potential applications:

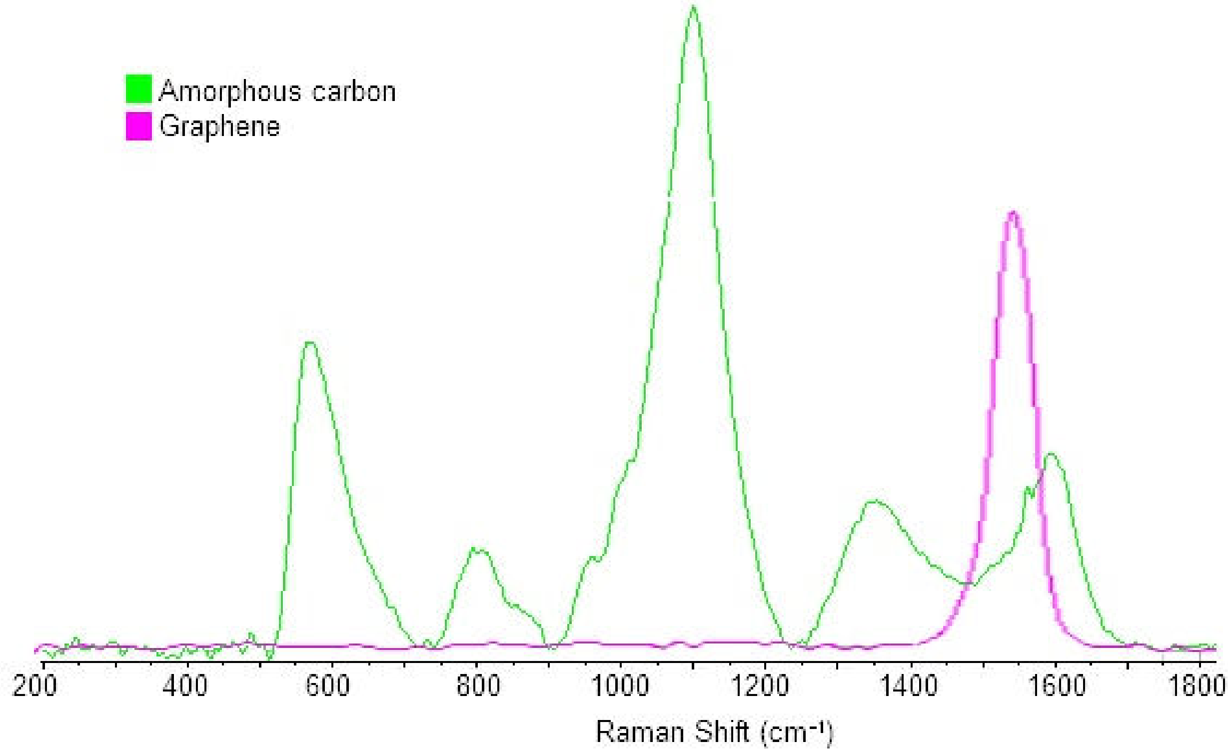
- Heat sinks
- Armour
- Illuminating devices
- Electromagnetic protective skins

Results summary

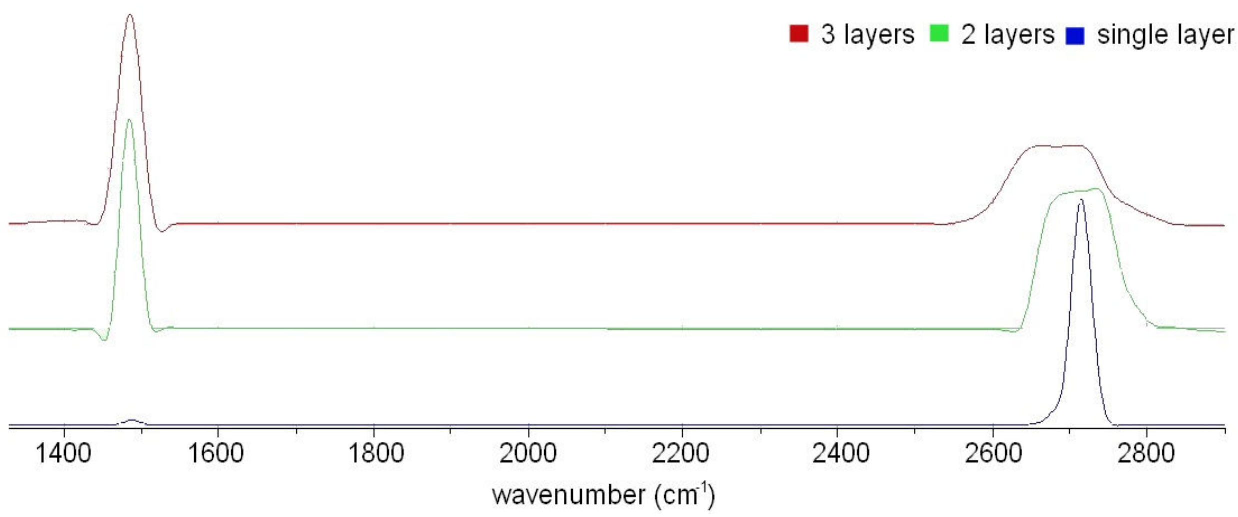
Characteristics of graphene:

- Raman spectroscopy

Graphene can be distinguished from amorphous carbon by its sharp G-band peak which arises from the highly ordered structure. Formation of multiple layers of graphene can be detected by changes in the spectrum, as the peak close to 1500 cm^{-1} grows and the higher peak at 2700 cm^{-1} broadens and decreases.



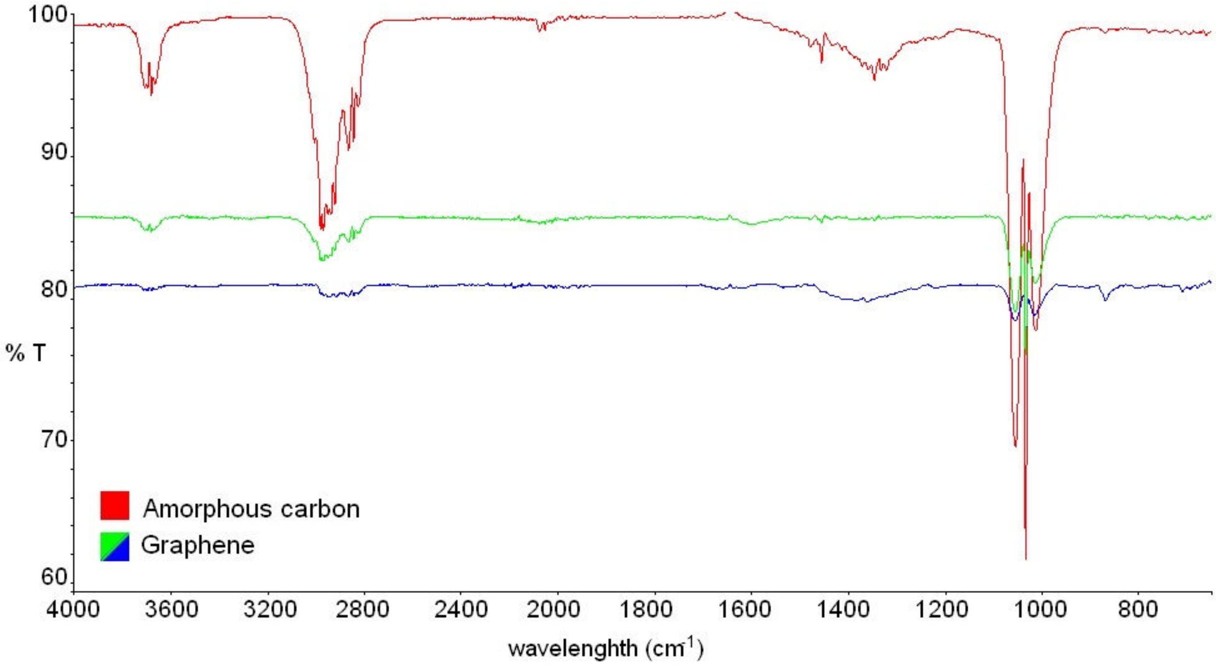
Raman spectrum of amorphous carbon and graphene



Raman spectrum showing layering of graphene

- FTIR spectroscopy

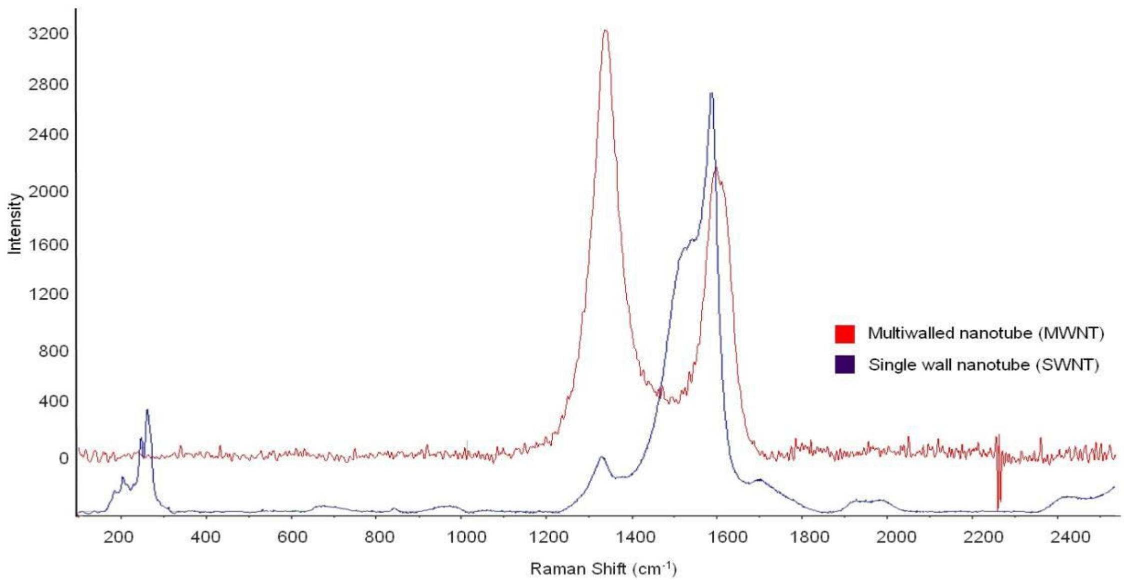
As a pure carbonaceous material, the graphene spectrum does not show the characteristic absorption peaks of impurities in amorphous carbon such as O-H (~3440 cm^{-1}), C-H (~2900 cm^{-1}), and C-O (~1059 cm^{-1}) stretches.



FTIR spectrum of amorphous carbon and graphene

Characteristics of carbon nanotubes (CNTs)

- Raman spectroscopy

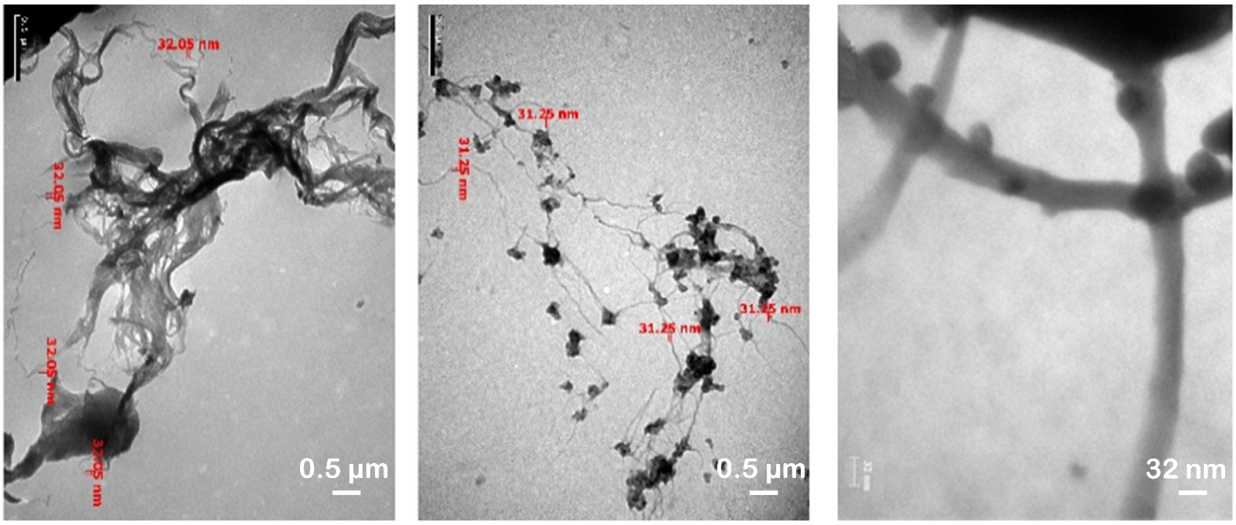


Overlaid Raman spectrum of single and multiwall carbon nanotubes

Single-walled carbon nanotubes (SWNTs) can be prepared by various methods, including pyrolysis of precursor organic molecules, and electrochemical synthesis, while MWNTs are predominantly produced via arc vaporisation of graphite. As shown above, Raman can be used to distinguish between SWNTs and MWNTs at the carbon defect (~ 1300 cm^{-1}) and radial breathing mode (~ 300 cm^{-1}) peaks. The carbon defect peak indicates the presence of amorphous carbon in sample, which will be more abundant in MWNTs due to the increased layers. The radial breathing peak can be correlated with tube diameter. The sharper this peak, the narrower the range of tube diameters present in the sample.

- SEM

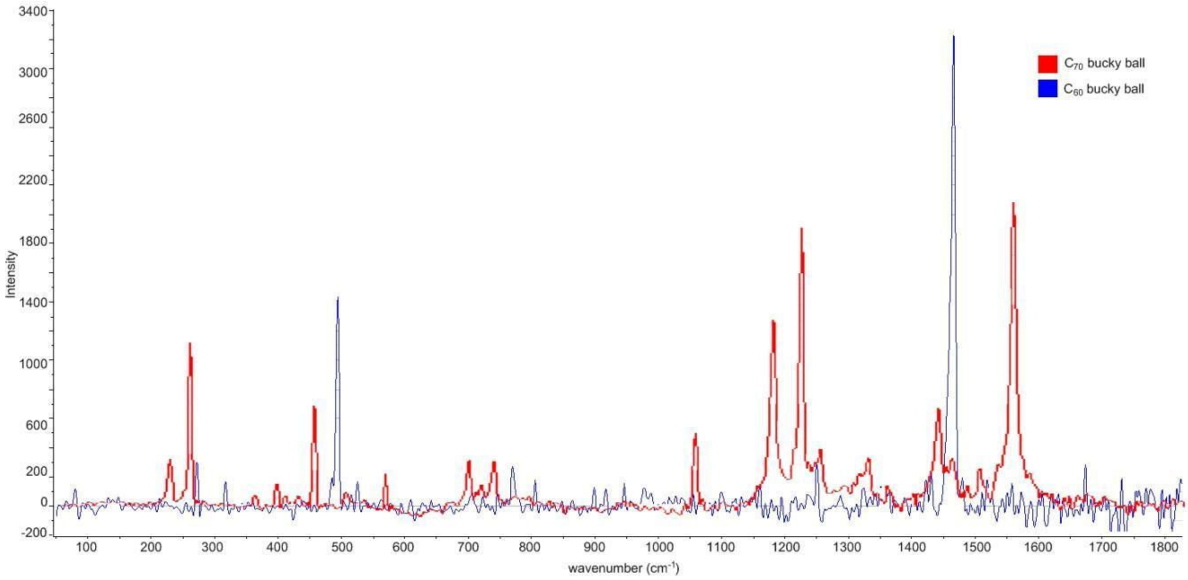
As can be seen by SEM, a variety of different sizes of CNTs may be produced in the same batch. Further treatment is necessary to isolate a narrow range of tube sizes.



Scanning electron microscopy (SEM) image of carbon nanotubes

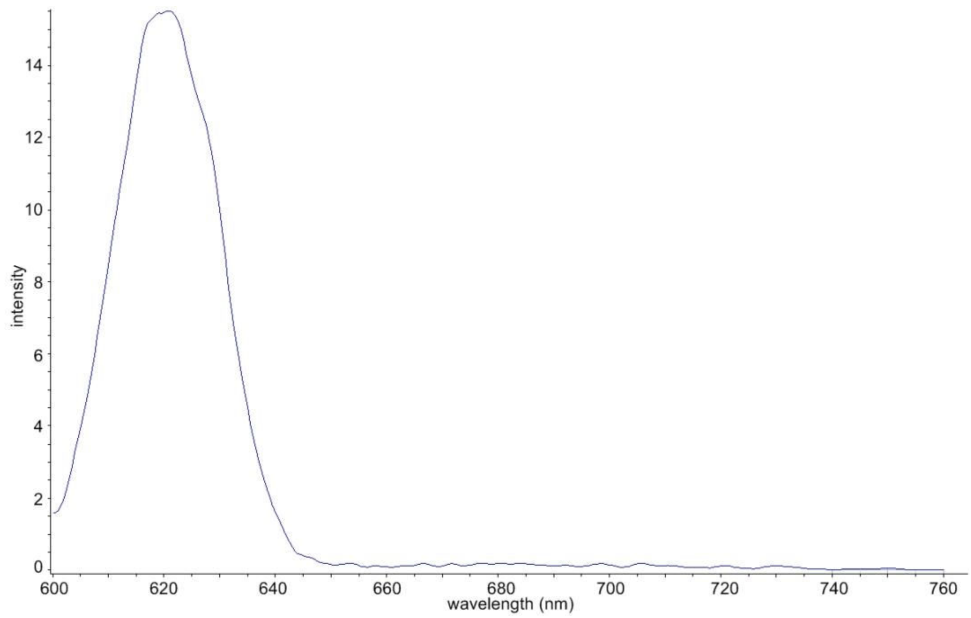
Characteristics of buckminster fullerene balls

- Raman and fluorescence spectroscopy



Raman spectrum of C_{60} and C_{70} molecules

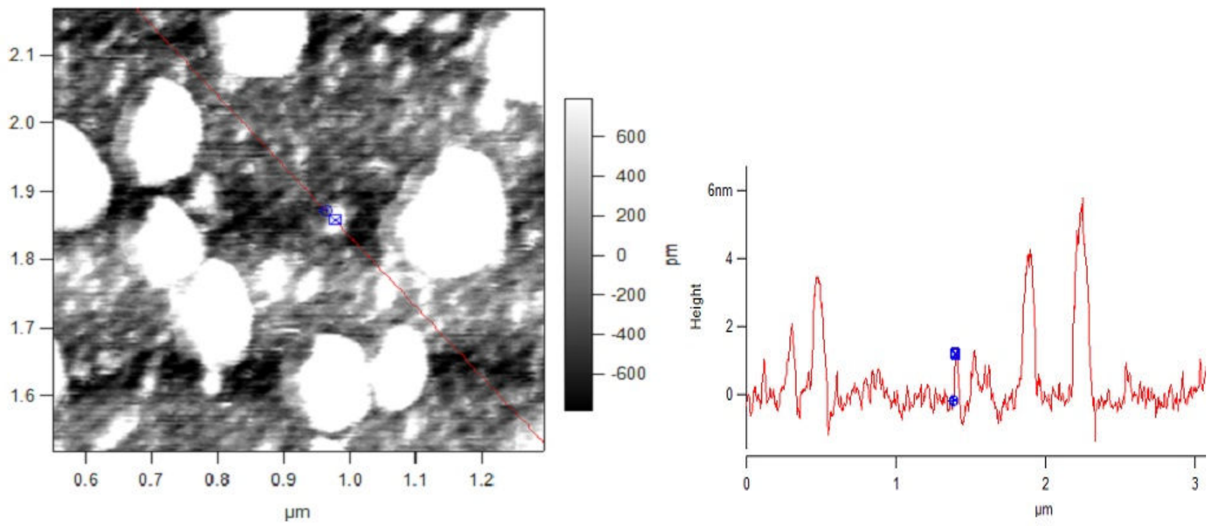
C_{60} buckminster fullerene can be characterised by Raman spectroscopy. The spectrum is much simpler than that of C_{70} due to the symmetry of molecule and can be used to distinguish it from CNTs or graphene. Bucky balls can also be distinguished from other allotropes as it is the only one which fluoresces.



Fluorescence spectrum of Buckminster fullerene

- Atomic Force Microscopy (AFM)

Individual bucky balls have a diameter of 0.7 nm as can be seen by AFM. The figure below shows the measuring of height using AFM. The point highlighted in blue in the image and the corresponding size distribution graph shows a single ball with diameter of 0.7 nm and 1.4 nm as expected. The balls may agglomerate during preparation or storage resulting in formation of larger particles.

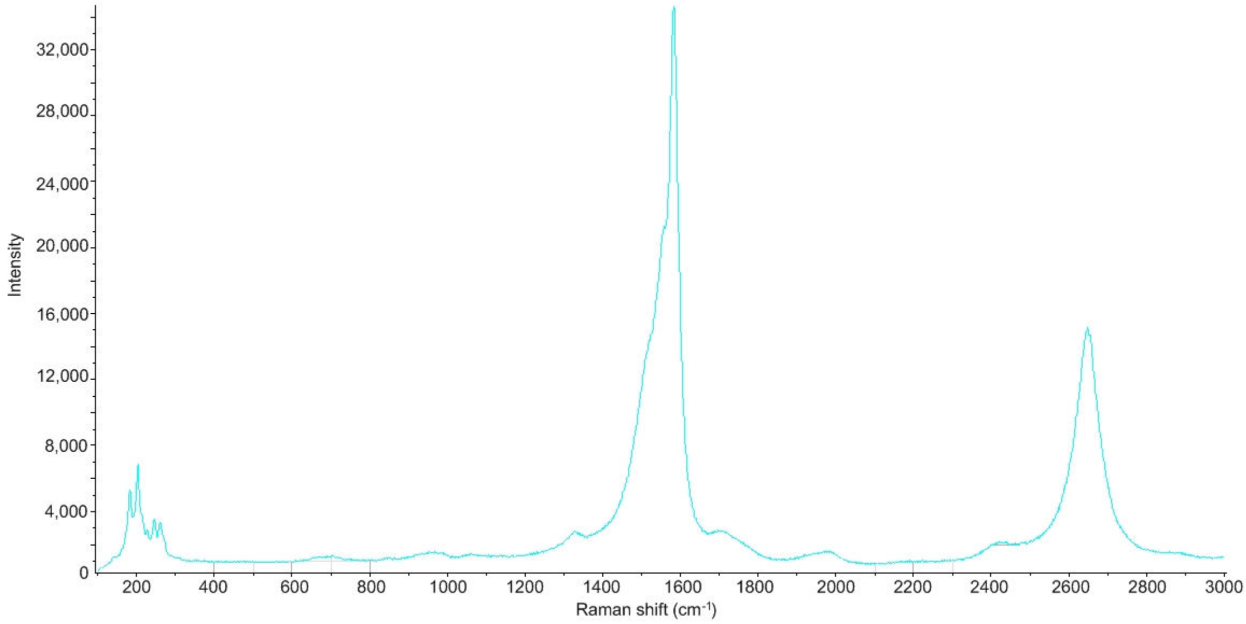


Atomic force microscopy image and associated height measurement for Buckminster fullerene

Characteristics of bucky paper

- Raman spectroscopy

As can be seen in Figure 10, the Raman spectrum of bucky paper is very similar to CNT as it is formed by deposition of tubes on a film. The radial breathing mode (~ 300 cm^{-1}) may be narrowed as the repeated filtering reduces the range of CNTs deposited. The defect carbon peak (~ 1300 cm^{-1}) is also reduced by the filtration process as amorphous carbon is removed.



Raman spectrum of bucky paper sample

- Atomic Force Microscopy (AFM)

As the Raman spectrum for bucky balls is so similar to that of CNTs the best method to distinguish from other allotropes is via visual examination (e.g. AFM). The images below show the textured surface of bucky paper which allows clear distinction from CNTs.