Characterization of carbon nanofibers by SEM, TEM, ESCA and Raman spectroscopy

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By Preeti Kaushik

Aim of the work

Investigate the structure, morphology and composition of carbon nanofibers (CNFs) using different characterization techniques:

-Scanning electron microscopy (SEM)

-Transmission electron microscopy (TEM)

-High resolution electron microscopy(HRTEM)

-Electron spectroscopy for chemical analysis(ESCA)

-Raman spectroscopy

Introduction

- Carbon nanofibers (CNFs) : cylindrical or conical structures, have diameters varying from a few to hundreds of nanometers and lengths ranging from less than a micron to millimeters.

- Carbon nanotubes (CNTs) have graphene layers parallel to tube axis but in CNFs the orientation of graphene layers is not parallel to fiber axis.

- CNTs are CNFs with graphene layers wrapped into perfect cylinders.

- Like CNTs, CNFs also have good electrical, thermal and mechanical properties which make them suitable for many applications.

Characterization methods

- SEM: Examination of length, diameter and morphology of CNFs.
- TEM and HRTEM: Observe the crystal structure and graphite layer arrangement.
- ESCA: Finding the chemical composition and carbon bonding in the material.
- Raman scattering: To study the quality of the material and the microscopic structure of the CNFs.

SEM and TEM

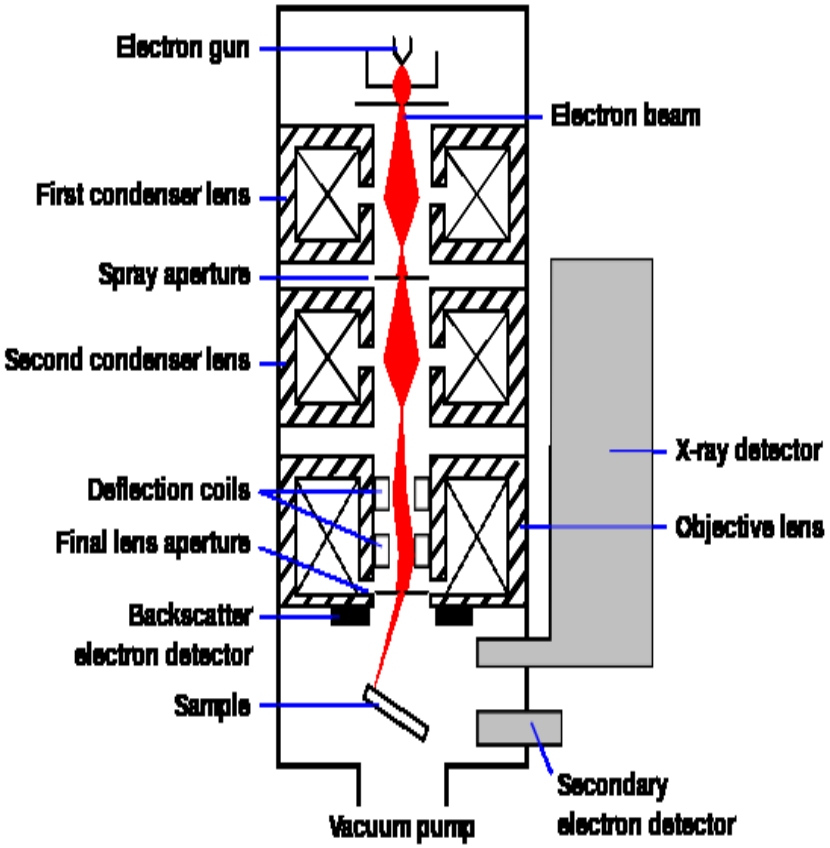
SEM-

- Image: Scanning with a focused beam of electrons
- Source of electrons: thermionic emission, field emission
- Electron gun operating voltage: 0 to 60 keV
- Detected signals: Secondary electrons (SE), Backscattered electrons (BSE), X-rays, cathode - luminescence light
- Resolution: Tens of nm
- Penetration depth: upto 1 nm

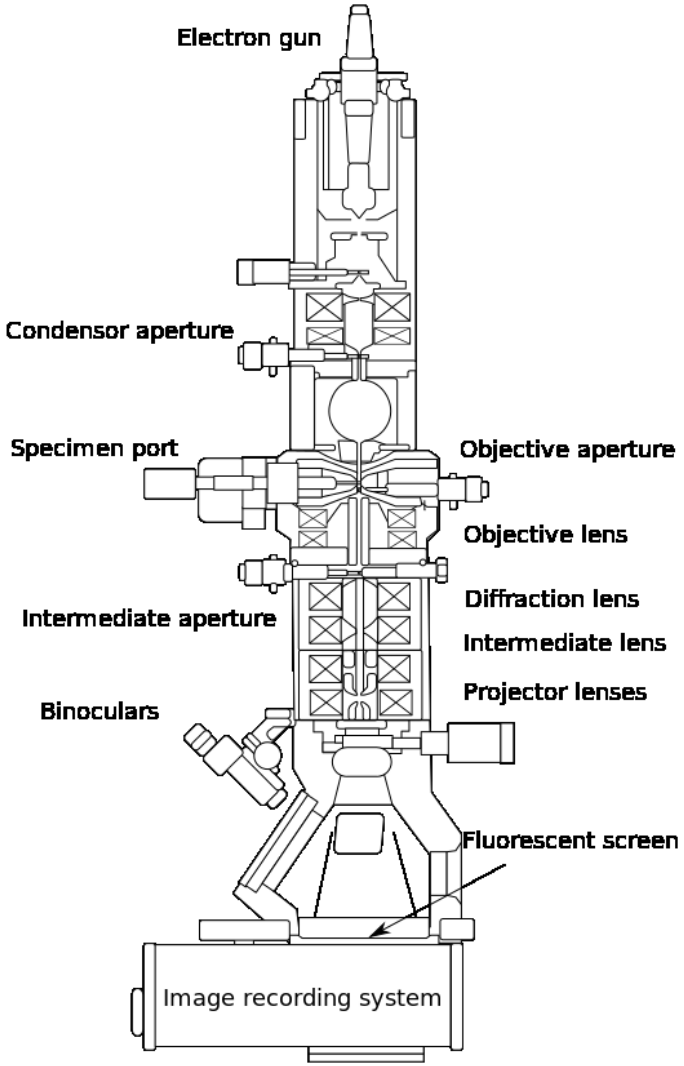
TEM-

- Image: By electrons transmitted through the ultra-thin sample
- Electron beam: up to 300 keV (limited to 100 keV)
- Penetration depth: upto 1 A^{o}

SEM


Electron gun
Electron beam
First condenser lens
Spray aperture
Second condenser lens
X-ray detector
Deflection coils
Objective lens
Final lens aperture
Backscatter
electron detector
Sample
Secondary
electron detector
Vacuum pump

TEM


Electron gun
Condensor aperture
Specimen port
Objective aperture
Objective lens
Diffraction lens
Intermediate aperture
Intermediate lens
Projector lenses
Binoculars
Fluorescent screen
Image recording system

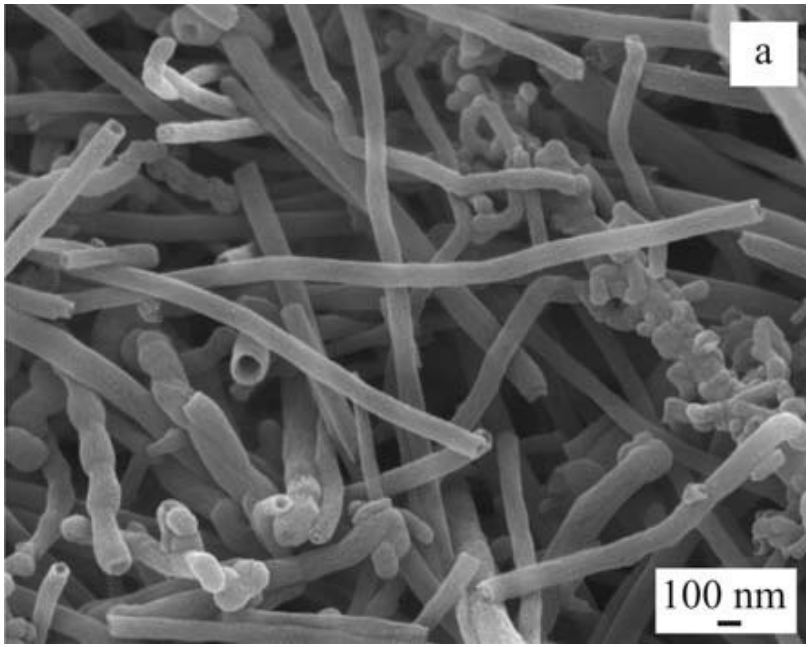
Raman Spectroscopy

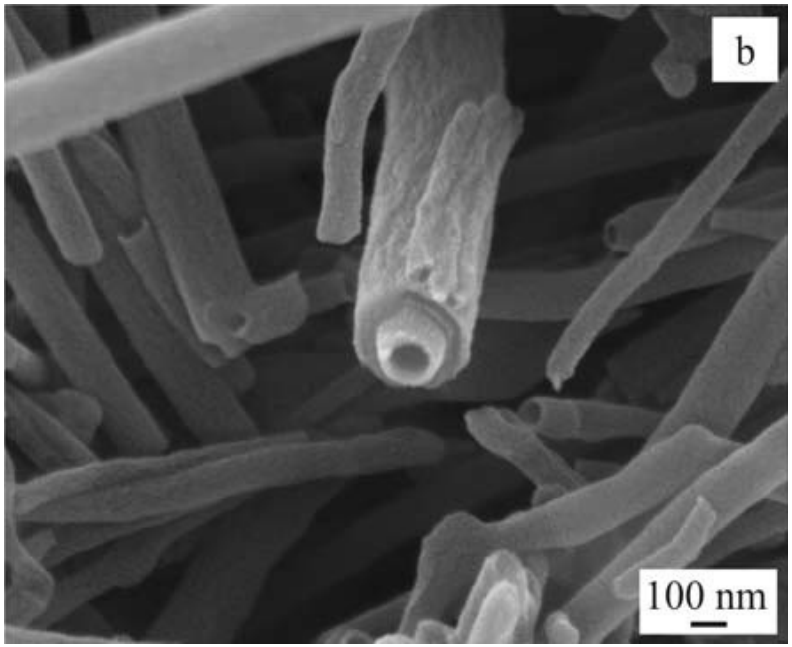
- Principle: Inelastic scattering of monochromatic radiation.
- Energy is switched between the photon and the energy levels of molecule.
- Raman spectra: G-band (1570 cm^{-1})

  D-band(1350cm^{-1})

  RBM (Radial Breathing mode < 200 cm^{-1})
- I_D:I_G: Defect density of the sidewall.

Results and discussion

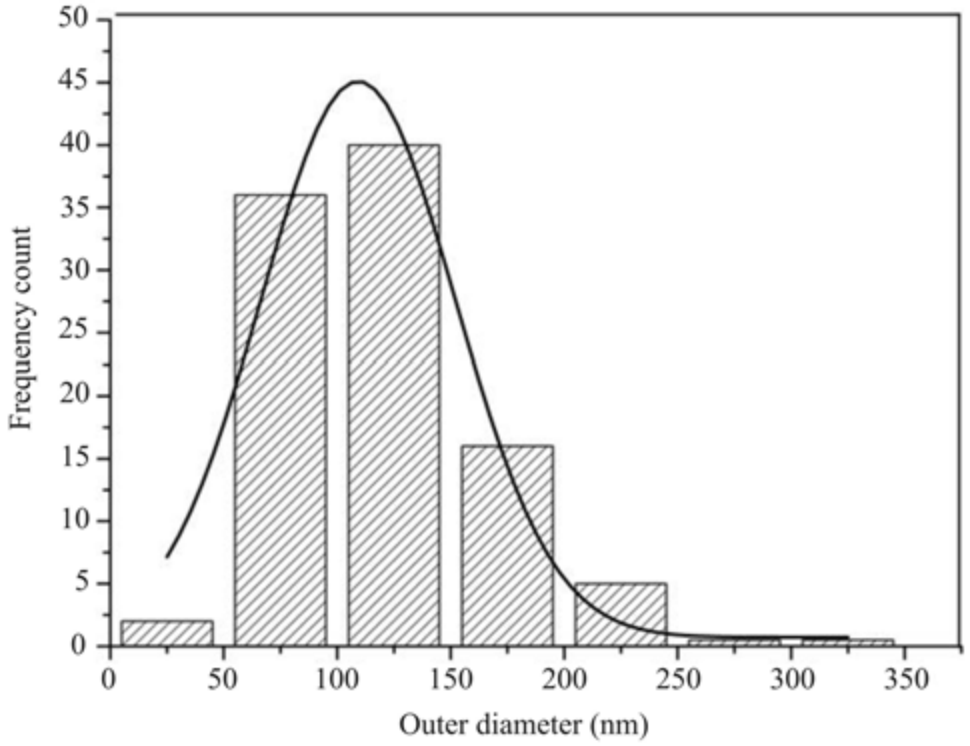




SEM images -(a) Morphology of the carbon nanofibers, characteristic morphology with mix of cylindrical and bamboo-shaped nanofibers, (b) an example for smooth CNF of small diameter and rough CNF of large diameter

SEM Observations

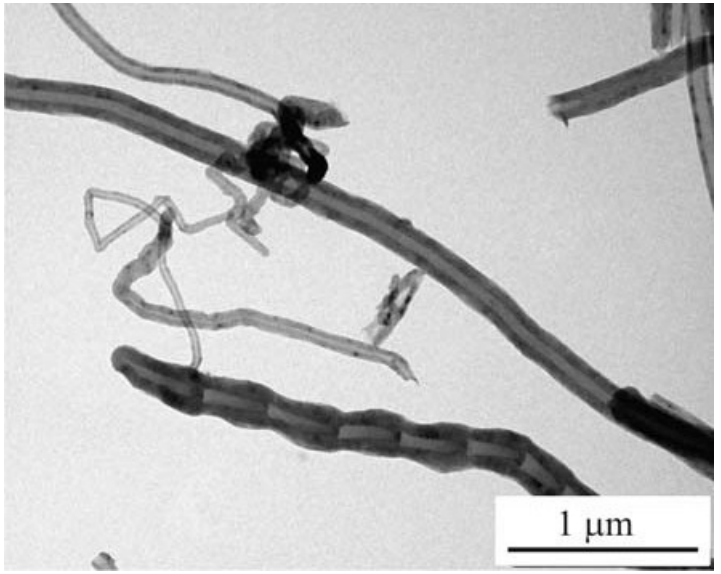
- Cylindrical hollow tubes, usually with free ends and smooth surface
- Bamboo-shaped nanofibers with a waved surface.
- Nanofibers with a straight-line shape and rough surface.
- The outer diameter is 50–250 nm and inner diameter from 20 nm to 230 nm.
- The length of the CNFs is up to several micrometers.



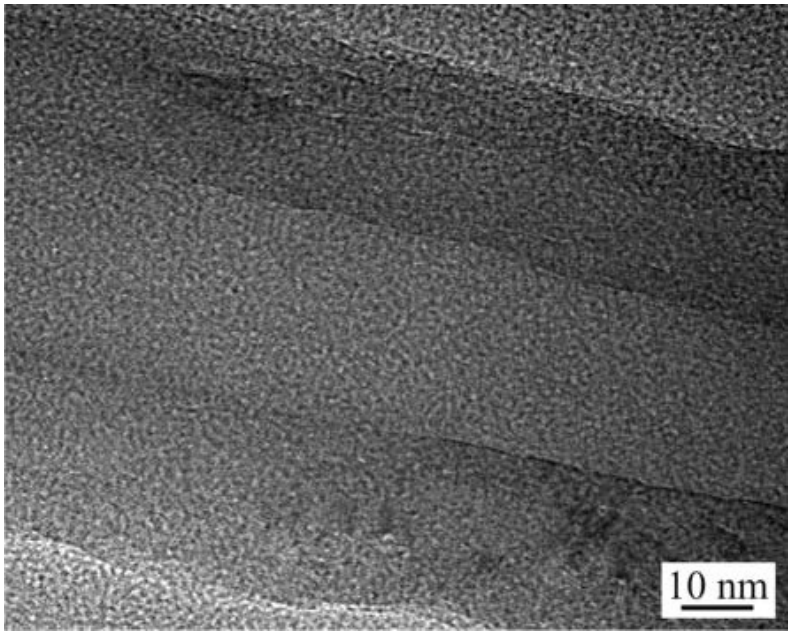
Histogram illustrating the distribution of the diameters of the fibers

TEM Observations

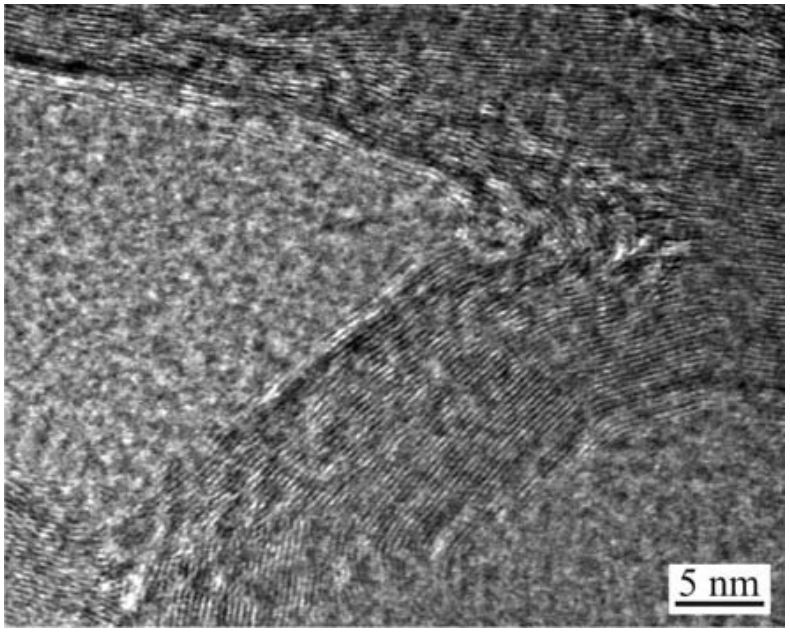
- In cylindrical hollow fibers the wall is smooth and uniform, graphite layers are parallel to the axes of the fibers.
- The bamboo-shaped fibers are composed of multi-walled graphite structure. As the carbon diffusion was not continous during growth, there was a periodic variation of fiber diameter.



Characteristic morphology of CNFs by TEM, cylindrical and bamboo-like CNFs.

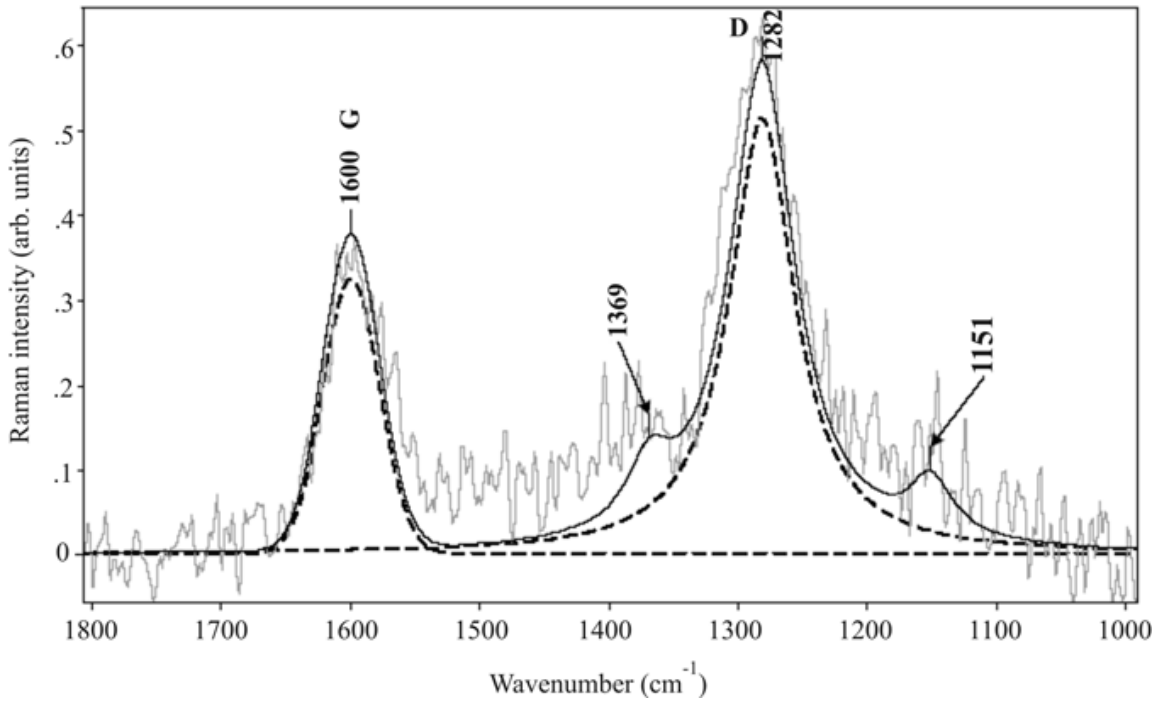


HRTEM of a cylindrical nanofiber with the wall thickness of approximately 28 nm and hole diameter of approximately 30 nm. The interlayer spacing of the graphite layers is approximately 0.35 nm.



HRTEM of a bamboo-shaped nanofiber with the wall thickness of approximately 18 nm. The interlayer spacing of the graphite layers in this wall is approximately 0.33 nm.

- G-band at 1600 cm^{-1} related to graphitic layer and the D-band at 1282 cm^{-1} related to disordered structures in carbon materials.



Raman spectra of carbon nanofibers at 1064 nm excitation wavelength

- The additional two weak noisy bands observed at around 1150 and 1370 cm^{-1} can be assigned to the mixed bonds between sp^2 and sp^3 carbon for amorphous carbon structures

- The ratio of intensities of D-band to G-band ($I_D/I_{G)}$ was 1.69.

- An increase in relative intensity of the D-band near-infrared excitation (1064 nm) is related to a larger electron-phonon interaction for D-band with respect to G-band.

Conclusion

- Cylindrical and bamboo shaped fibers identified.
- Cylindrical fibers: defect-free, distinct graphite layers parallel to the fiber axis.
- Bamboo-shaped fibers: contain defects at the nano-level.
- Outer diameter of the fibers: 50 nm to 600 nm
- Length of the fibers: several micrometers to several tens of micrometers.
- The fibers contain 99.05 at.% carbon and 0.95 at.% oxygen with a binding energy of O(1s) electrons of 532.7 eV.
- G-band at 1600 cm^{-1} and D-band at 1282 cm^{-1} are very similar to the positions of the same bands for carbon fibers and different carbon nanotubes

Thank you