

Defence Science Journal, Vol. 58, No. 4, July 2008, pp. 437-450  
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REVIEW PAPER

## Carbon Nanotubes and Related Structures

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### ABSTRACT

Carbon nanotubes have attracted the fancy of many scientists worldwide. The small dimensions, strength, and the remarkable physical properties of these structures make them a unique material with a whole range of promising applications. In this review, the structural aspects, the advantages and disadvantages of different for their procedures synthesis, the qualitative and quantitative estimation of carbon nanotubes by different analytical techniques, the present status on their applications as well as the current challenges faced in the application field, national, in particular DRDO–DMSRDE status, and interest in this field, have been discussed.

**Keywords:** Carbon nanotubes, nanomaterials, nanotechnology, nanostructures, CNTs, chirality

### 1. INTRODUCTION

The discovery of fullerenes<sup>1</sup> provided exciting insights into carbon nanostructures and how architectures built from  $sp^2$  carbon units based on simple geometrical principles can result in new symmetries and structures that have fascinating and useful properties. Carbon nanotubes (CNTs) represent the most striking example. About a decade after their discovery<sup>2</sup>, the knowledge available in this field indicates that nanotubes may be used in a number of applications. There have been great improvements in synthesis techniques, which can now produce reasonably pure nanotubes in gram quantities. Studies of structure-topology-property relations in nanotubes have been strongly supported, and in some cases, preceded by theoretical modelling that has provided insights for experimentalists into new directions and has assisted the rapid expansion of this field<sup>3-5</sup>.

The uniqueness of the nanotube arises from its structure and the inherent subtlety in the structure,

which is the helicity in the arrangement of the carbon atoms in hexagonal arrays on their surface honeycomb lattices. The helicity (local symmetry), along with the diameter (which determines the size of the repeating structural unit) introduces significant changes in the electronic density of states, and hence, provides a unique electronic character for the nanotubes. These novel electronic properties create a range of fascinating electronic device applications. The other factor of importance in what determines the uniqueness in physical properties is topology, or the closed nature of individual nanotube shells; when individual layers are closed onto themselves, certain aspects of the anisotropic properties of graphite disappear, making the structure remarkably different from graphite.

The combination of size, structure, and topology endows nanotubes with important mechanical properties (e.g., high stability, strength and stiffness, combined with low density and elastic deformability) and with special surface properties (selectivity, surface

Received 17 June 2007, revised 01 October 2007

chemistry), and the applications based on these properties have been highlighted. In addition to the helical lattice structure and closed topology, topological defects in nanotubes (five member Stone-Wales defects near the tube ends, aiding in their closure)<sup>6,7</sup>, akin to those found in the fullerenes structures, result in local perturbations to their electronic structure<sup>8</sup>; e.g., the ends or caps of the nanotubes are more metallic than the cylinders, due to the concentration of pentagonal defects<sup>9</sup>. These defects also enhance the reactivity of tube ends, giving the possibility of opening the tubes<sup>10</sup>, functionalising the tube ends<sup>11</sup>, and filling the tubes with foreign substances<sup>12,13</sup>.

### 1.1 Speciality of Carbon Nanotubes

Carbon nanotubes are one of the most commonly mentioned building blocks of nano technology. With one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, these seem to be a wonder material. However, when one hears of some companies planning to produce hundreds of tons per year, while others seem to have extreme difficulty in producing grams, there is clearly more to this material than meets the eye.

In fact, nanotubes come in a variety of forms: long, short, single-walled, multi-walled, open, closed, with different types of spiral structure, etc. Each type has specific production costs and applications. Some have been produced in large quantities for years while others are only recently being produced commercially with decent purity and in quantities greater than a few grams<sup>14,16</sup>.

### 1.2 Carbon Nanotubes and Related Structures

The term nanotube is normally used to refer to the carbon nanotube, which has received enormous attention from researchers over the last few years and promises, along with close relatives such as the nanohorn, a host of interesting applications. There are many other types of nanotube, from various inorganic kinds, such as those made from boron nitride, to organic ones, such as those made from self-assembling cyclic peptides (protein

components) or from naturally-occurring heat-shock proteins (extracted from bacteria that thrive in extreme environments). However, carbon nanotubes excite the most interest, promise the greatest variety of applications, and currently appear to have by far the highest commercial potential. Carbon nanotubes are often referred to in the press, including the scientific press, as if these were one consistent item. These are in fact a hugely varied range of structures, with similar huge variations in properties and ease of production.

The structure of nanotubes remains distinctly different from traditional carbon fibres that have been industrially used for several decades (e.g., as reinforcements in tennis rackets, airplane frame parts, and batteries, to name a few)<sup>4</sup>. Most importantly, nanotubes, for the first time, represent the ideal, most perfect and ordered, carbon fibre, the structure of which is entirely known at the atomic level. It is this predictability that distinguishes nanotubes from other carbon fibres and puts these along with molecular fullerene species in a special category of prototype materials.

Among the nanotubes, two varieties, which differ in the arrangement of their grapheme cylinders, share the limelight. Multi-walled nanotubes (MWNT), are collections of several concentric graphene cylinders and are larger structures compared to single-walled nanotubes (SWNTs) which are individual cylinders of 1-2 nm dia (Fig. 1). The former can be considered as a mesoscale graphite system, whereas the latter is truly a single large molecule. However, SWNTs also show a strong tendency to bundle up into ropes, consisting of aggregates of several tens of individual tubes organised into a one-dimensional triangular lattice<sup>3-14</sup>.

## 2. CARBON NANOTUBES STRUCTURE

Carbon nanotubes were discovered in 1991 by Sumio Iijima of NEC and are effectively long, thin cylinders of graphite, which one will be familiar with as the material in a pencil or as the basis of some lubricants. Graphite is made up of layers of carbon atoms arranged in a hexagonal lattice, like chicken wire (Fig. 1).

**Table 1. Summary of techniques: (a) arc discharge, (b) chemical vapour, and (c) laser ablation<sup>14-18</sup>**

Method	Arc discharge	Chemical vapour deposition	Laser ablation
Who	Ebbesen and Ajayan, NEC, Japan, 1992	J.B. Nagy, Univ. of Namur, Belgium and Endo, Shinshu University, Nagano, Japan	Smalley, Rice, 1995
How	Connect two graphite rods to a power supply, place them a few mm apart, and throw the switch. At 100 amp, carbon vapourises and forms a hot plasma.	Place substrate in oven, heat to 600 – 800 °C, and slowly add a carbon-bearing gas such as methane/ethylene/acetylene. As gas decomposes, it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90 per cent		Up to 70 per cent
SWNT	Short tubes with dia of 0.6 – 1.4 nm	20 to 100 per cent Long tubes with diameters ranging from 0.6–4 nm	Long bundles of tubes (5–20 $\mu$ m), with individual diameter from 1–2 nm.
MWNT	Short tubes with inner dia of 1–3 nm and outer dia of approx. 10 nm	Long tubes with dia ranging from 10–240 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.
Process	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure possible	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Conclusion	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

**Table 2. Analytical method for quantitative/qualitative analysis of CNT samples<sup>26</sup>**

Parameter	Technique	Analysis
Purity	TGA	Quantitative—residual mass after TGA in air at 5 °C/min to 800 °C
	SEM/TEM	Qualitative—amorphous carbon impurities
	EDS	Qualitative—metal content
	Raman	Qualitative—relative amount of carbon impurities and damage/disorder
Thermal stability	TGA	Quantitative—burning temperature in TGA in air at 5 °C/min to 800 °C, $dM=dT$ peak maximum
Homogeneity	TGA	Quantitative—standard deviation of burning temperature and residual mass taken on 3–5 samples
	SEM/TEM	Qualitative—image comparison
Dispersability	Ultra-sonication	Qualitative—time required to fully disperse (to the eye) low conc. CNT in DMF using standard settings
	UV/VIS/NIR	Quantitative—relative change in absorption spectra of sonicated low concentration CNT/DMF solution
Electronic property	AFM/UVSTM	Quantitative—band gap, conductivity of a single CNT could be measured through DOS plot

**Table 3. Research results (All values are for single-walled carbon nanotubes unless otherwise stated<sup>3,18,28</sup>)**

<b>General properties</b>	
Average dia of SWNT's	: 1.2–1.4 nm
Interlayer spacing	:
(n, n) Armchair	: 3.38 Å
(n, 0) Zig-zag	: 3.41 Å
(2n, n) Chiral	: 3.39 Å
<b>Optical properties</b>	
Fundamental gap	
For (n, m); n-m is divisible by 3 [metallic]	: 0 eV
For (n, m); n-m is not divisible by 3 [semiconducting]	: ~ 0.5 eV
<b>Electrical transport</b>	
Resistivity	: $10^{-4}$ Ω/cm
Maximum current density	: $10^{13}$ A/m <sup>2</sup>
<b>Thermal transport</b>	
Thermal conductivity	: ~ 2000 W/m/K
Phonon mean free path	: ~ 100 nm
Relaxation time	: ~ $10^{-11}$ s
<b>Elastic behaviour</b>	
Young's modulus (SWNT)	: ~ 1 TPa
Young's modulus (MWNT)	: 1.28 TPa
Maximum tensile strength	: ~30 GPa

of diameters and lengths. These were essentially the distant relatives of the highly defective carbon nanotubes grown via CVD deposition. The latter types of fibres (e.g., the lower quality carbon nanotubes made commercially by the Hyperion Corporation and more perfect nanotubes structures revealed by Ando<sup>28</sup>, *et al.* The real molecular nanotubes arrived when they were found accidentally while a catalyst (*Fe*, *Co*) material was inserted in the anode during electric-arc discharge synthesis. For the first time, there was hope that molecular fibres based purely on carbon could be synthesised and the excitement was tremendous, since many physical properties of such a fibre had already been predicted by theory. It was really the theoretical work proposed on SWNTs and the availability of nanoscale technology (in characterisation and measurements) that made the field take off in 1991<sup>28, 31</sup>.

The greatness of a single-walled nanotube is that it is a macro-molecule and a crystal at the

same time. The dimensions correspond to extensions of fullerene molecules and the structure can be reduced to a unit-cell picture, as in the case of perfect crystals. A new predictable (in terms of atomic structure-property relations) carbon fibre was born. The last decade of research has shown that indeed the physical properties of nanotubes are remarkable. A carbon nanotube is an extremely versatile material: it is one of the strongest materials, yet highly elastic, highly conducting, small in size, but stable, and quite robust in most chemically harsh environments. It is hard to think of another material that can compete with nanotubes in versatility.

As a novel material, fullerenes failed to make much of an impact in applications. It seems, from the progress made in recent research, that the story of nanotubes is going to be very different. There are already real products based on nanotubes in the market, for example, the nanotube-attached AFM tips used in metrology.

The US, Europe, and Japan have all invested heavily in developing nanotube applications. Nanotube-based electronics tops this list and it is comforting that the concepts of devices (such as room temperature field-effect transistors based on individual nanotubes) have already been successfully demonstrated. As in the case of most products, especially in high technology areas such as nano electronics, the time lag between concept demonstration and real products could be several years to several decades and one will have to wait and see how long it is going to take nanotube electronics to pervade high technology. Other more obvious and direct applications are some of the bulk uses, such as nanotube-based polymer composites and electro-chemical devices. Table 4 shows the main properties and potential applications of CNTs<sup>3,18,28</sup>.

What is also interesting is that new and novel applications are emerging, as for example, nanotubes affecting the transport of carriers and hence luminescence in polymer-based organic light-emitting diodes, and nanotubes used as actuators in artificial muscles. It can very well be said that some of these newly found uses will have a positive impact on the early stages of nanotube product development. There are also general challenges that face the

**Table 4. Main properties and potential applications of carbon nanotubes**

Properties	Potential applications
<b>Mechanical</b>	
100 time stronger than steel (stress) and 6 time lighter	Reinforcement for composite materials, space elevators
High flexibility of CNTs, unlike carbon fibres	Actuators
Expansion by charge injection	Atomic force microscope (AFM) tips
<b>Electrical</b>	
Metallic or semiconductor behaviour, according to chirality (way a grapheme sheet is rolled on itself)	Conductive plastics (electromagnetic shielding, protection against antistatic discharges)
As conductive as copper	Electronical nanocomponents (diodes, transistors...)
Easy turnable field emission	Electron gun, field emission display, AFM tip
<b>Physico-chemical</b>	
High specific area (several hundreds of m <sup>2</sup> /g)	Hydrogen storage for fuel cell cars
Cavities enabling molecules storage inside the carbon nanotube	Batteries with improved lifetime - Nanometric test tubes
Chemical treatment on CNTs, enabling to fix other molecules to CNTs	Electronical nanocomponents, material protection....
High thermal resistance (up to 1500 °C under vacuum)	Biosensors for harmful gases, chemical analysis...

development of nanotubes into functional devices and structures. First of all, the growth mechanism of nanotubes, similar to that of fullerenes, has remained a mystery<sup>29, 31</sup>. With this handicap, it is not really possible yet to grow these structures in a controlled way. There have been some successes in growing nanotubes of certain diameter (and to a lesser extent, of predetermined helicity) by tuning the growth conditions by trial and error. Especially for electronic applications, which rely on the electronic structure of nanotubes, this inability to select the size and helicity of nanotubes during growth remains a drawback.

More so, many predictions of device applicability are based on joining nanotubes via the incorporation of topological defects in their lattices. There is no controllable way, as of yet, of making connections between nanotubes. Some recent reports, however, suggest the possibility of constructing these interconnected structures by electron irradiation and by template-mediated growth and manipulation.

For bulk applications, such as fillers in composites, where the atomic structure (helicity) has a much smaller impact on the resulting properties, the quantities of nanotubes that can be manufactured still falls far short of what industry would need. There are no available techniques that can produce nanotubes

of reasonable purity and quality in kilogram quantities. The industry would need quantities in tonnes of nanotubes for such applications.

The market price of nanotubes is also too high presently (~\$ 200/g) for any realistic commercial application. But it should be noted that the starting prices for carbon fibres and fullerenes were also prohibitively high during their initial stages of development, but have come down significantly. In the last two to three years, there have been several companies that were set up in the US to produce and market nanotubes. It is hoped that in the next few years, nanotubes will be available to consumers for less than US \$100/g. Another challenge is in the manipulation of nanotubes. Nano technology is in its infancy and the revolution that is unfolding in this field relies strongly on the ability to manipulate structures at the atomic scale. This will remain a major challenge in this field, among several others<sup>27</sup>.

#### 4. NATIONAL SCENARIO

In India, several labs are involved in the research of CNTs and related structure. Laboratories like Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, (under Prof Rao),

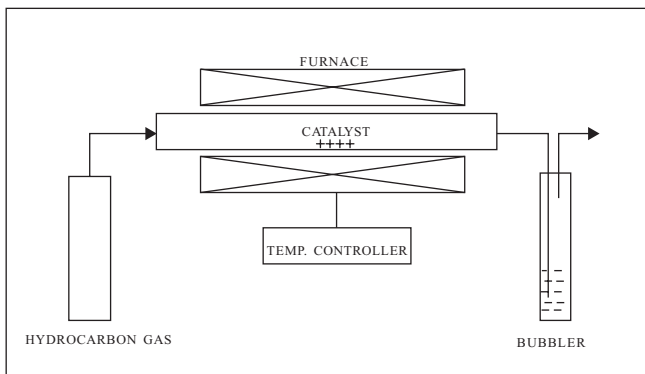


Figure 3(a). Schematic diagram of experimental setup.



Figure 3(b). Existing CCVD Unit No. 1 at DMSRDE, Kanpur.



Figure 3(c). Existing CCVD Unit No. 2 at DMSRDE, Kanpur.

Banaras Hindu University, Varanasi, (under Prof Srivastava), IITs (like Madras, Bombay), NCL, Pune, have already done excellent work in the field of CNTs. But except Prof Srivastava at BHU, other works mainly involve the synthesis and characterisation of CNTs<sup>28</sup>. Prof Srivastava has used CNTs in some application field, eg, CNT-based hydrogen-storage system, CNT-based filter, etc.<sup>30</sup>

Among DRDO labs, DMSRDE, Kanpur, has taken the lead in the synthesis, characterisation, and applications of CNTs and related structures. Other labs, like Defence Bioengineering and Electromedical Lab (DEBEL), Bangalore, Defence Research Development Establishment (DRDE), Gwalior, have their programmes to use CNTs in sensor applications along with DMSRDE in collaboration with University of Arkansas, USA. Solid State Physics Laboratory (SSPL), Delhi, has also started working in the field of sensor and CNT-based field-emission device. Advanced



Figure 3(d). High temperature catalytic CCVD furnace (1600 °C).

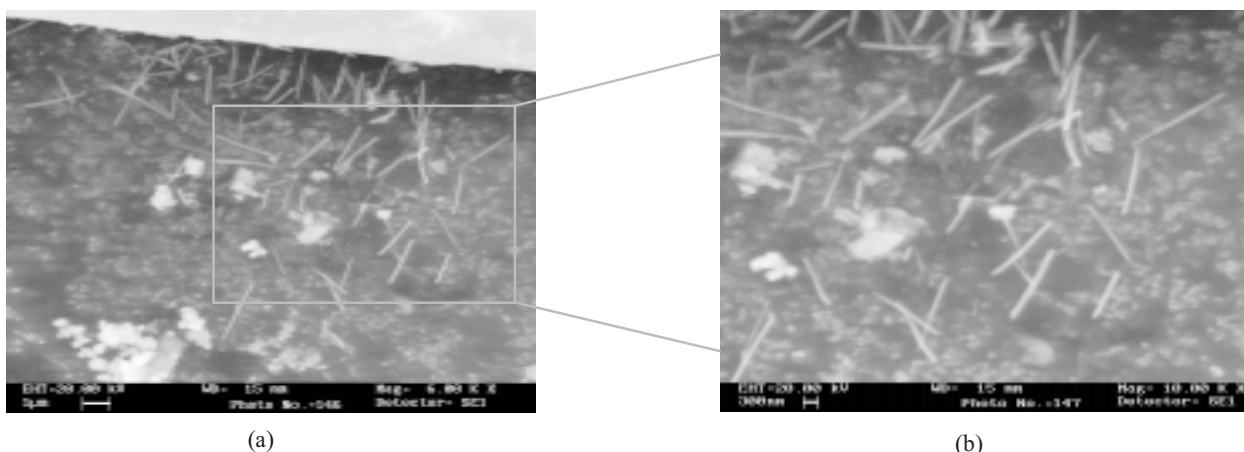


Figure 7. Synthesis of *Mo-W*-sulphide nanotubes/nanorods by CCVD method.

The catalyst (about 30 g) was sprayed over the quartz boat and was placed in the central position of the quartz tube placed inside the furnace. The quartz tube used to carry out the deposition has a length of 1.5 m with outer dia 8 cm and inner dia 7 cm. The catalyst was then activated by passing nitrogen gas (99.9 % pure) for 30 min at a 140 ml/min flow rate. The temperature of

the reaction was fixed at 600 °C/700 °C depending on the catalyst used. Acetylene gas (99.999 % pure) was then passed at 25 ml/min for 15 min through the reaction chamber while nitrogen gas flow rate was maintained at 200 ml/min. Prior to sampling of the tubes, the furnace was cooled down to room temperature by flowing nitrogen gas (140 ml/min).

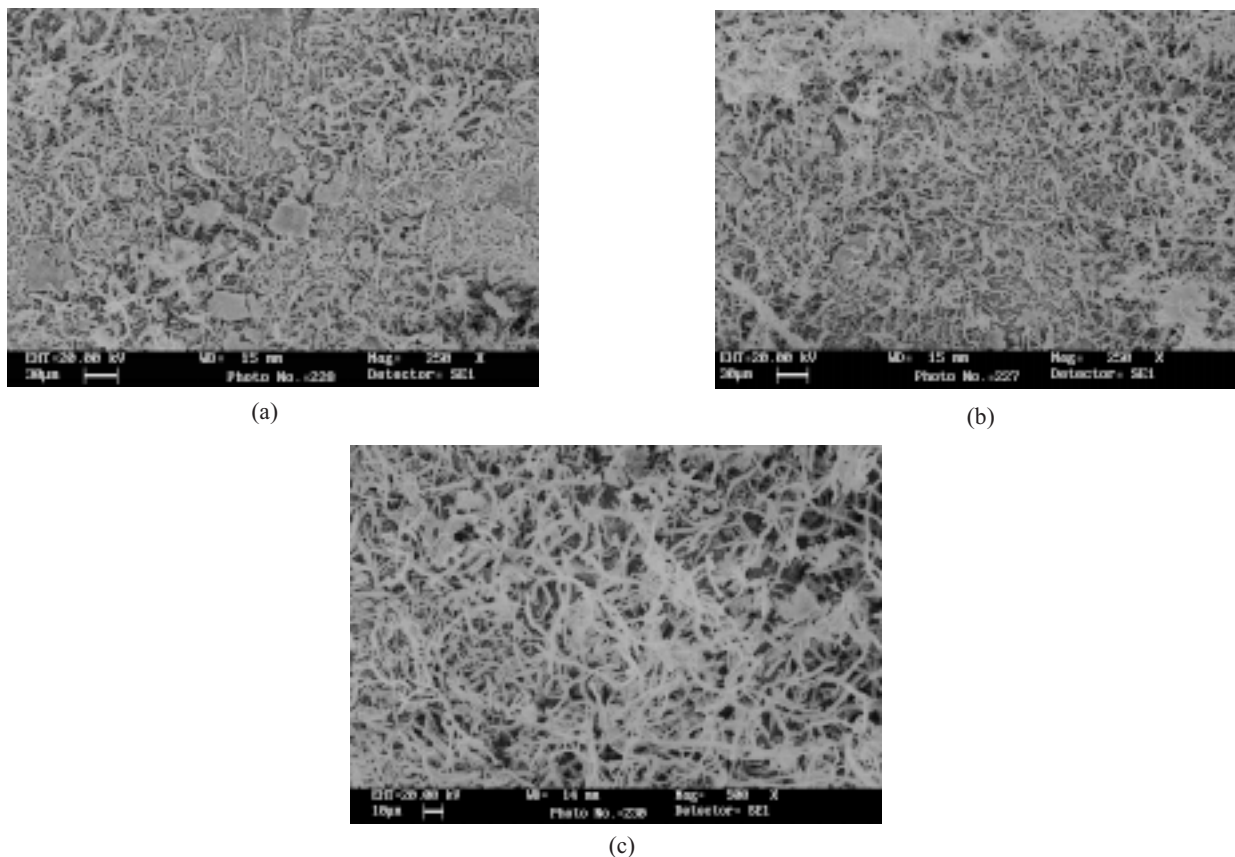
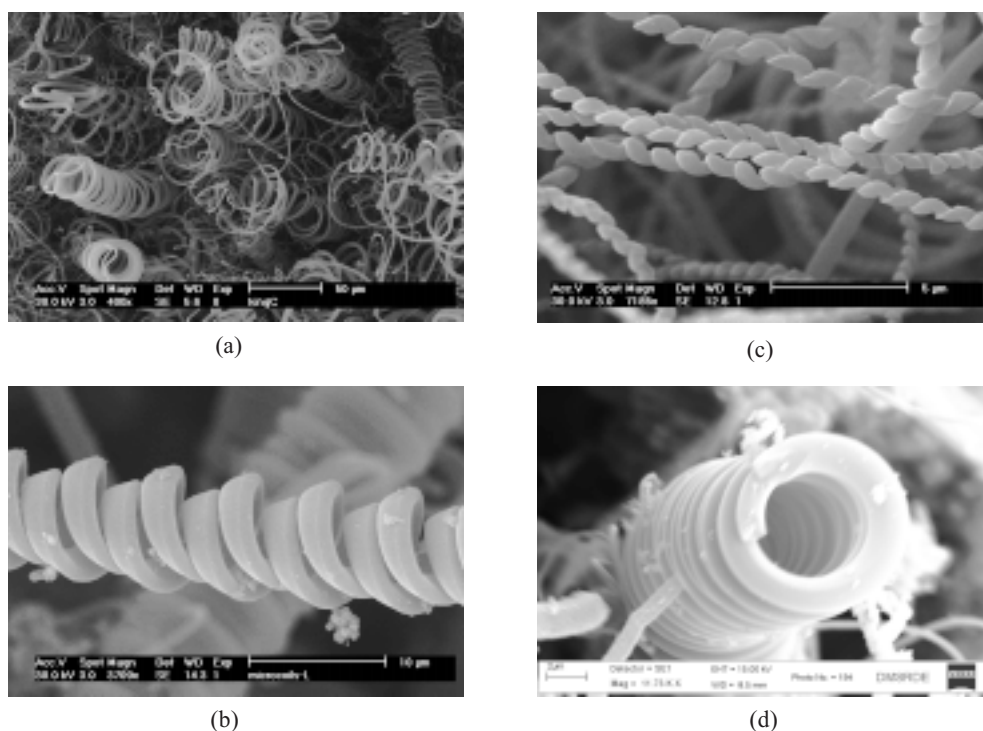


Figure 8. Boron nitride nanotubes synthesised by CCVD method using CNTs as templates.



**Figure 9. SEM images of coiled carbon networks: (a) quasi-aligned carbon microcoiled thin film; (b and d) double-helical carbon microcoiled; and (c) carbon nanofiber coiled.**

The sample was collected as black powder from the quartz boat. In this way, nanotubes were obtained in gram quantity<sup>32-35</sup>.

Under optimised conditions, the synthesised MWNTs were  $\sim 90$  per cent aligned (2-D alignment) and  $\sim 95$  per cent pure using existing CCVD furnaces. For SWNTs, purity is 25–30 per cent.

The batch size  $\sim 30$  g time required to run per batch  $\sim 30$  min. The number of graphene walls can be controlled in between 12–30, having dia ranging from 10–50 nm. The samples have been characterised by SEM/TEM (both low and high resolution), thermal/Raman<sup>32-33</sup>. Three-dimensional aligned CNTs formation over support (eg, quartz, alumina, Si wafer, etc.) has been achieved<sup>34</sup>.

#### 4.2.1 Inorganic Nanotubes

Boron nitride nanotubes have been successfully synthesised using CNTs as templates and characterised by SEM/HREM, XRD, XPS analysis. The template technique has been extended for synthesising other

inorganic nanotubes (e.g., SiC nanotubes/nanofibres). Batch size 500 mg, reaction time 4 h, dia range 40–50 nm. Mixed sulphide nanotubes (e.g., Mo-W-sulphide nanotubes) have been synthesised and the process has been optimised to get control over percentage of Mo and W in the nanotubes (e.g., Mo: W = 1:1, 3:1, 5:1, 10:1, 15:1, 20:1, etc.)<sup>36,37</sup>

#### 4.2.2 Coiled Carbon (Micro/Nano) Networks

The nano/microcoils have been synthesised without using external magnetic field and with/without sulphur/phosphorous promoters by simple CCVD technique and characterised by SEM with EDAX/TEM/Raman/Thermal<sup>38-41</sup>. Simply by controlling the catalyst particle diameter, either micro-or nano-coiled carbon fibres have been synthesised. Batch size  $\sim 15$  g, batch reaction time  $\sim 1$  h, purity of product  $\sim 85-90$  per cent;

Diameter distribution:

- Coiled nanofibre 100–400 nm
- Coiled microfibre 1.5–3  $\mu\text{m}$
- Coiled nanotube 20–45 nm



## 5. APPLICATIONS

DMSRDE is using CNTs/coil structures in the following fields of application:

- As electromagnetic absorber coating in collaboration with University of Arkansas, USA.
- Gas/chemical/hat sensor (CNT-based) in collaboration with DEBEL/DRDE.
- Hydrogen storage (CNT-based).
- Lightweight composite materials (CNT-based) in collaboration with ASL, Hyderabad.

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