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REVIEW PAPER

Carbon Nanotube–Purification and Sorting Protocols

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ABSTRACT

Carbon nanotubes (CNTs) have shown extraordinary mechanical, thermal, electrical, and electronic properties. Electronic properties of CNT are very sensitive to its diameter and chirality, making it metallic or semiconducting, depending upon its chiral vector. The extraordinary properties of CNTs have led to demonstration of several applications but commercial realisation of these devices require consistent quality of CNTs, and these should be free of any impurity. For development of electronic devices, CNTs should not just be pure but also of similar length, diameter, and electronic behaviour. Such demanding requirements need development of elaborate purification and sorting protocols. In this paper, a brief review of the existing technologies and the research done is presented .

Keywords: Arc-discharge, carbon nanotubes, single-walled carbon nanotubes, multi-walled carbon nanotubes, SWCNTs, MWCNTs purification, sorting

1. INTRODUCTION

Graphitic nanotubules of carbon, better known as carbon nanotubes (CNTs), after their discovery[1] in 1991, have become strong candidate for many future device applications. Most promising among these is the tube with single graphitic shell, which is called single-walled carbon nanotube (SWNT)[2]. Tubes with multiple walls is called multi-walled carbon nanotube (MWNT). Several promising results on electrical, electronic, mechanical, and thermal properties of SWNTs have been demonstrated[3], but there are many technical challenges still to be overcome to enable commercialisation of CNT-based devices. Commercialisation requires acceptable device repeatability, within a batch and from batch-to-batch. Arc-discharge[4], laser ablation, and chemical vapour deposition (CVD) including its several variants, are few techniques employed for growth of the CNTs.

Current growth processes produce CNTs mixed with different amorphous and crystalline impurities such as catalyst particles, graphitic nanoparticles, and amorphous carbon. Nature and degree of impurities vary with growth technique, arc-discharge having the highest amount of catalyst particles, and CVD, the least. The presence of impurities can lead from erroneous device behaviour to total failure, depending upon nature and quantum of impurities. Removal of such impurities from the as-grown product is called purification[5]. Purification usually involves chemical treatment[6], i.e. dry oxidation[7-9], and wet oxidation followed by filtration and annealing. Several variants of this process sequence have been demonstrated. As both these processes are chemically aggressive and cause damage to CNT structure, milder techniques such as magnetic separation, etc., have been developed. Even the CNTs that are produced vary in diameter and chirality and these physical variations result in changes in their electronic and optical behaviours. About one-third of all possible SWNTs exhibit metallic properties and the remaining two-third act as semiconductors.

Moreover, the bandgap of semiconducting SWNTs scales inversely with tube diameter. Such inconsistencies in nature of CNTs lead to unpredictable results and degradation in device performance thus preventing their widespread applications as high-performance field-effect transistors, optoelectronic near-infrared emitters/detectors, chemical sensors, materials for interconnects in integrated circuits, and conductive additives in composites[10]. So, the CNTs need to be separated into different grades based on their nature, length, diameter, and chirality. This process of separation of CNT mixture into different grades is called sorting. This is a relatively complex and a slow process. Yield is also very low with current techniques such as chromatography[11], field flow fractionalisation[12], electrophoresis[13], polymer wrapping[14], etc.

Different applications require CNTs with different levels of purity and sorting. Applications in which CNTs are consumed in bulk can tolerate higher levels of impurities and do not require sorting. In contrast, electronic applications such as fabrication of CNT field-effect transistor (CNTFET) are very sensitive to impurities and require efficient sorting after purification. Several purification protocols[15-20] have been developed and a lot of success has been achieved in separating CNTs from other impurities, but sorting of CNTs based on their nature, length, and diameter is still an unfinished task and needs to be completed for success

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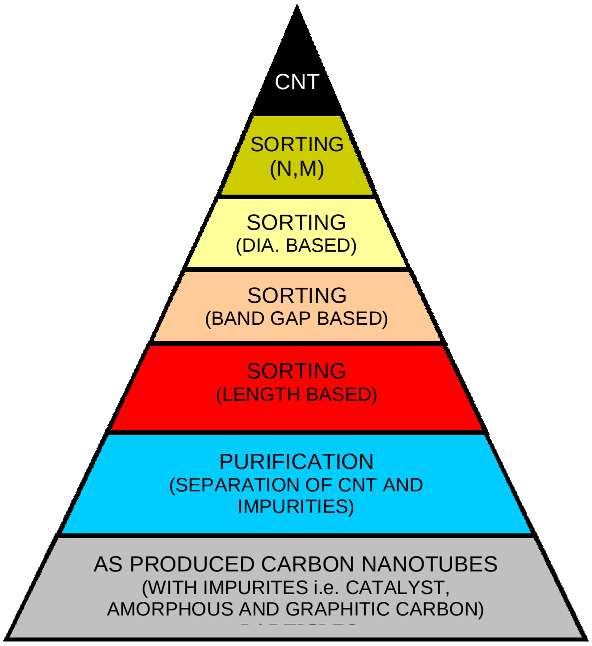

Figure 1. Carbon nanotube purification and sorting pyramid.

of CNT-based electronics and its integration with *Si* technology. The ultimate aim in sorting is to develop the ability to separate CNT-based on its chiral vector. Figure 1 illustrates the purification and sorting pyramid of CNTs.

2. PURIFICATION OF CARBON NANOTUBE

The CNT purification necessitates removal of carbonaceous (amorphous and graphitic) and catalyst particles. Purification methods consist of one or more of the following steps: Dispersion, dry oxidation (thermal/microwave), wet oxidation/ chemical treatment, filtration (including chromatographic methods) and annealing. Most researchers have proposed a combination of these methods[15-22], with slightly different parameters, which might be due to variation in CNT sources. The CNTs on their own are insoluble in most of the solvents, and tend to agglomerate, disabling any further chemical processing on these. Impurities are also trapped inside these agglomerates, making these unavailable for acid digestion. So separation and dissolution of impurities can be carried out only after CNTs are dispersed in suitable media.

Technique such as ultrasonication is mainly used for dispersion. Even after dispersion, direct acid treatment is less effective for removal of catalyst particles due to carbonaceous coating over them. Thus, wet oxidation is coupled with dry oxidation to break carbon shell and expose catalyst surface for acid attack. This step needs strict control on oxidation temperature, as in presence of oxygen, the metal particle catalyse indiscriminate oxidation of carbon and ultimately destroy the CNTs. To circumvent this problem, Chiang[8,9], *et al.* proposed a scheme that begins with long, low-temperature oxidative cracking of the carbonaceous shells encapsulating the metal particles. This was done with wet oxygen by bubbling 20 per cent O_2 in argon through water. This process effectively removes carbon coating over metal particles, which are then easily dissolved by acid treatment. Microwave heating[21,22] has also been employed to break carbon coating over metal particles enabling efficient removal of catalyst in acid treatment step.

Acid treatment step poses two challenges: (a) to remove reaction products coated on the CNT surface, and (b) to restore CNT structure damaged by rigorous acid treatment. For removal of reaction products, when starting material is small (e.g., milligrams), the CNTs can be vacuum filtered, followed by washing with a dilute base to remove the nanoparticles (rendered soluble in the base by functionalisation with carboxylic groups). For larger (gram) quantities, vacuum filtration becomes untenable because of the complex filtration path formed by the overlapping nanotubes, making the permeate flow rate extremely slow. In this case, bulk of acid is decanted, followed by repeated cycles of centrifugation, decanting of the supernatant solution, and re-suspension in deionised water to further neutralise the reaction products. The buffer solution along with surfactant is added to keep the naturally hydrophobic nanotubes from agglomerating. The surfactants used are easy to remove by washing with either water or methanol. Amorphous carbon impurities and metal catalysts in the raw CNTs can then be removed by centrifugation and filtration.

Recently, Shim[23], *et al.* devised an integrated scheme to purify MWNTs using electrophoresis induced by the application of an AC electric field to a set of microelectrodes in a microliquid channel. This purifying method is different from conventional methods based on chemical processes and has potential applicability in the development of microdevices that can simultaneously perform the purification and fabrication of MWNTs. For restoration of the CNT structure, annealing of purified sample under vacuum or inert atmosphere is carried out[24,25].

In this study, an effective purification protocol combining dry-oxidation and wet-oxidation techniques has been developed. Parameters were optimised for simultaneous reduction of non-CNT carbon and catalyst particles while inducing minimal damage to SWNT structure. Effect of acid on SWNT structure was studied by carrying out refluxing with 0.1 M HNO_3 to 5 M HNO_3. Defects increase with increasing acid concentration as evident from growing strength of *D*-band (Fig. 2). By 0.1 M HNO_3 refluxing, structure remains intact but majority of metallic impurities were also not removed. On the other hand, 5 M HNO_3 refluxing reduces metal content from 32 per cent to 8 per cent but does severe damage to SWNT structure and hence cannot be used. Thus a step of dry-oxidation was introduced prior to wet-oxidation to remove amorphous carbon coating over nanoparticles. Dry-oxidation at 693 K very effectively reduces amorphous carbon without introducing defects in SWNT structure, as evident from negligible D-band. Oxidised sample was then refluxed with an optimum acid concentration for removal of metallic impurities. By optimising dry-oxidation temperature and duration was eliminated The need of highly concentrated acids,long refluxing was eliminated enabling effective SWNT purification with low defects.

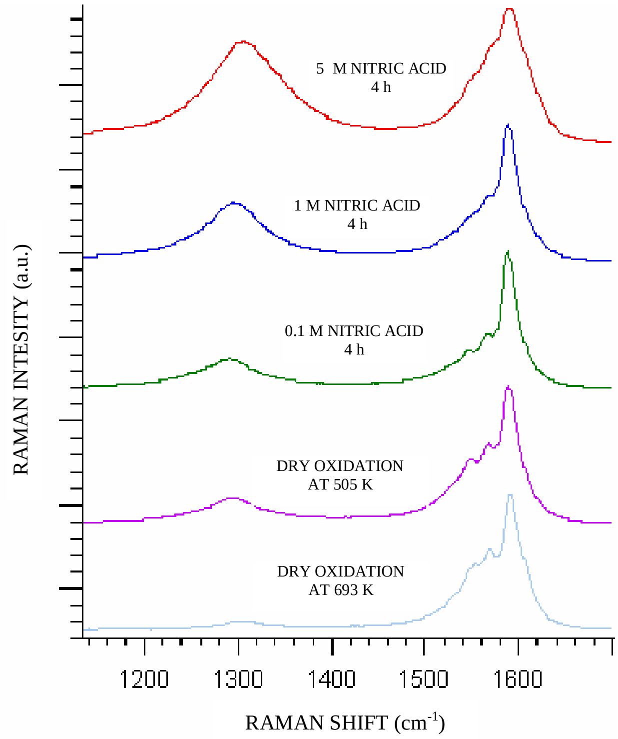

Figure 2. Raman characterisation of CNT purified by dry and wet-oxidation. Raman spectra were taken on vacuum-filtered samples over 0.2 μm PTFE membrane using 785 nm laser. Dry-oxidation step at 693 k effectively removes amorphous carbon without introducing defects in SWNT structure, as evident from absence of *D*-band.

3. CARBON NANOTUBE SORTING

Resultant of purificaton process is mixture of CNTs free of impurities such as amorphous carbon, catalyst, and graphitic paricles. But this mixture contains CNTs of different lengths, diameter, and bandgap. The next challenge is to sort this mixture into different grades of CNTs with narrow distribution of length, diameter and bandgap. The separation of SWNTs into different grades is expected to simplify and allow an array of applications such as nanoelectronic devices (transistors and logic circuits)[27], field emission displays[28], nanosensors[29], actuators[30], and composites[31].

3.1 Separation of CNT from Bundles

The SWNT being highly polarizable, they readily form parallel bundles or ropes. Girifalco[32], *et al*. computed potential energies of interaction, cohesive energy per unit length, compressibility, and equilibrium separation distance between two parallel and infinitely long CNTs of same diameter. They calculated a van der waals binding energy of ~500 eV per micrometer of tube to tube contact. This bundling perturbs the electronic structure of the tubes and confounds all attempts to separate the tubes by size or type or to use them as individual macromolecular species. Fei[33], *et al*. used phosphotungstic acid (HPW) for separation of CNT from bundles and further purification. As the HPW can spontaneously attach to graphite walls as polyanions and provide static repulsion, the CNT aggregates were divided into individual and small bundles and turned into a stable solution by sonication in the presence of HPW. O'Connell[34,35], *et al.* devised a scheme for separating nanotubes from bundles by vigorous ultrasonic treatment followed by centrifugation to obtain individual nanotubes in aqueous micellar suspensions. Unbundling the SWNTs into single nanotubes or very small bundles was an essential step. The high surface area of individual or lightly bundled nanotubes enables surface interaction of various reagents and attachment of functional groups on surface of the SWNT.

3.2 Sorting of CNTs based on Length

Sorting of SWNTs according to their length becomes particularly important in light of their potential applications. For example, nanotubes of shorter length (20–300 nm) are ideal for nano- and microelectronics whereas nanotubes whose length is in microns, are preferred for structural and composite applications. Various techniques have been employed for obtaining SWNTs sorted by length. This is typically achieved by chromatographic techniques[11,36-38], for SWNTs with sizes of less than 300 nm while field-flow fractionation[12] and capillary electrophoresis[13] is more suited for longer SWNTs. For chromatography, SWNTs need to be thoroughly dissolved or dispersed in small bundles each containing only a few nanotubes. This makes the choice of dispersion media very critical and a variety of surfactants have been used to obtain highly dispersed SWNT solutions.

Initial experiments were carried out by size exclusion chromatography of surfactant stabilised dispersions with water as the mobile phase[11,36]. Later on several other media and surfactant combinations have been used[39-41]. Huang[38],*et al.* carried out length separation by size-exclusion chromatography (SEC) over DNA-wrapped CNTs. In elutant of chromatography column, average length decreases monotonically from > 500 nm in the early fractions to <100 nm in the late fractions with length variation < 10 per cent in each of the measured fractions.

3.3 Sorting of CNTs based on Electronic Properties

The SWCNTs have unique distinction of existing in different structures with different electronic properties. The SWNT exhibits either semiconducting or metallic behaviour depending upon its chiral vector[3]. The stochastic nature of the SWNT growth, generates mixtures of metallic and semiconducting SWNTs in a 1:2 ratio. For separation of metallic and semiconducting nanotubes, several approaches like interaction of CNTs with zwitterions[42], surfactant amines[43], and diazonium salts[44] have been utilised. Semiconducting SWNTs have enhanced chemical affinity towards octadecylamine (ODA). This reduces the tendency of semiconducting SWNTs to aggregate as concentration is increased by means of partial solvent evaporation. The supernatant is primarily composed of semiconducting SWNTs while precipitate is enriched with metallic SWNTs. Chen, *et al.*[45] utilised suspended SWNTs in Triton X-100 surfactant and then exposed the suspension to bromine solution followed by centrifugation. This led to enrichment of the supernatant in semiconducting nanotubes and the sediment in metallic nanotubes. In contrast, when diazonium salts are used in aqueous solution, metallic SWNTs undergo preferential electron transfer.

Other approaches, such as, AC dielectrophoretic separation[46-48], and DNA assisted separation[49-50], have also yielded fair results for separating metallic and semiconducting nanotubes. The phosphate groups on a DNA-CNT hybrid provide a negative charge density on the surface of the CNT, the distribution of which is a function of the DNA sequence and electronic property of the tube. Everything else being equal, the DNA-metallic CNT has less surface charge than DNA-semiconducting CNT due to the opposite image charge created in the metallic tube. Zheng[51], *et al.* separated semiconducting and metallic nanotubes by ion-exchange liquid chromatography using custom single-stranded DNA (ssDNA). Metallic tubes eluted first from the ion exchange column because of their reduced effective charges. However, there are critical drawbacks in using DNA for CNT functionalisation. First, DNA-wrapped SWNTs have limited stability in aqueous density gradients and thus are not amenable to repeated centrifugation. Furthermore complete removal of the DNA wrapping after enrichment has not been demonstrated. Finally, the availability and cost of specific, custom oligomers of ssDNA are prohibitive.

Recently, Arnold[52], *et al.* were successful in sorting CNTs by diameter, bandgap, and electronic type using structure-discriminating surfactants, eliminating the requirement of DNA. These surfactants were used to engineer subtle differences in buoyant densities of nanotubes. Using the scalable technique of density-gradient ultracentrifugation, employing competing mixtures of surfactants, SWNTs of predominantly a single-electronic type were obtained. Maeda[53], *et al.* employed a separation method involving a dispersion-centrifugation process in a tetrahydrofuran solution of amine, which made metallic SWNTs highly concentrated to 87 per cent in a simple way.

3.4 Sorting of CNTs based on Diameter and Chirality

The CNT based electronic applications are most prone to variations in diameter and chirality. A study involving large number of carbon nanotube transistors confirmed that the nanotube diameter and the metal contact material play key roles in determining the on- and off-state currents of these devices[54]. In the absence of diameter sorting techniques, initially emphasis was given on controlling dia during growth itself. Diameter selective growth has been reported by all growth techniques, i.e, arc-discharge[55-56], laser ablation[57-58], and CVD[59-76]. The CVD relies on use of templates created by anodic oxidation of aluminium or zeolites. Anodised aluminium templates with custom pore diameter can be easily obtained as the diameter of pore is proportional to the applied voltage of electrochemical cell. Catalyst particles are then seeded inside these templates. Such templates can then be used to grow individual CNTs[72]. These techniques have been used for diameter control of SWNTs[55-69], double-walled carbon nanotubes (DWNTs)[70], and MWNTs[71-76]. Tang[59], *et al.* have grown 0.4 nm SWNTs, within a single-crystal $AlPO_4$-5 zeolite. These SWNTs preferentially have zigzag (5,0) form as opposed to the other two possible chiralities of similar diameter i.e. (3,3) armchair and (4,2) chiral.

Bachilo[77], *et al.*, carried out structure selective growth of SWNTs using CVD over silica supported *Co* nanoclusters formed by mixed salts of *Co* and *Mo*. Two structures (6,5) and (7,5) together comprised more than half of population. Techniques for post-growth dia modification by heat treatment[78], and boron doping[79] have also been suggested, but these have limited range, introduce defects and diameter control is partial. Few techniques for diameter selective sorting[80-83] have been reported with partial success. But still sorting CNT based on their chirality is a distant dream and to develop the ability to selectively grow the CNT with multiple chiralities on a single wafer for development of large scale CNT- based electronics is the most challenging task.

3.5 Purity Evaluation

Any purification methodology is meaningful only if accurate methods for qualitative and quantitative estimation of CNT purity are available. Initially, estimation of CNT purity was carried out using only microscopy. The scanning electron microscope (SEM), transmission electron microscope (TEM) and scanning tunnelling microscope (STM) were extensively used for purity evaluation. These tools were very intuitive as they gave visual indication of sample state. But these techniques give only qualitative estimates about nature and structure of CNT and impurities. Obtaining meaningful quantitative estimate is very cumbersome as it involves measuring structural parameter of hundreds of CNTs one by one. Even after this, the estimates that are obtained are from a localised area and multiple images needs to be taken for accurate estimates, making microscopy techniques prohibitive for quantitative estimation.

Other techniques such as thermal gravimetric analysis (TGA), near-infrared (NIR) spectroscopy[84], Raman spectroscopy[85-90], were introduced for quantitative analysis. The TGA of CNT sample is carried out in air/O_2 to study oxidative response. Carbonaceous content of sample is converted to CO/CO_2, which is evolved and final residue contains only metal oxides. Thus an estimate of metal content in sample can be easily computed by TGA. Estimating composition of carbonaceous content is relatively difficult by microscopy or thermal analysis. Spectroscopic techniques such as Raman and NIR spectroscopy provide rapid, convenient, and unambiguous method to measure bulk purity and composition of carbonaceous content of SWNT samples.

Characteristic absorption spectra for bulk SWNT samples show three interband transitions: S_{11} (4,000–8,000 cm^{-1}), S_{22} (7,750–11,750 cm^{-1}) and M_{11} (12,500–17,500 cm^{-1}). The intensity of S_{11} is subject to doping-induced modulation[84]. Because SWNTs are susceptible to doping by many species and doping affects both absorption and Raman spectroscopy, the spectroscopic analysis should be carried out only after de-doping of samples by heating them to 600 °C in an inert atmosphere. Raman can be used to obtain information about CNT structure, i.e. MWNT/SWNT, degree of defects, estimation of SWNT diameter etc. Diameter-selective Raman spectroscopy scattering at about 180 cm^{-1}, is associated with the radial breathing mode (RBM) of CNT. The frequency of RBM is inversely proportional to the tube dia and can be used for accurate determination of SWNT diameter.

As a means of assay, absorption spectroscopy has the advantage of providing a global measurement of the relative metallic/semiconducting SWNT content. The small spot size of the excitation used in a Raman spectroscopic assay requires statistical averaging over numerous measurements in order to be considered accurate. However in samples having wide distribution of nanotube dia, the absorption bands S_{22} and M_{11} may overlap making the Raman-based assay more useful. But one needs to be very careful while taking spectra as both spectroscopic techniques are dependent on environmental conditions. Anglaret [87],*et al.*, observed monotonic Raman frequency upshift and intensity reduction when a laser spot was moved along the same SWNT. Thus instead of single characterisation technique a combination of microscopic and spectroscopic techniques are used to verify the results such as TEM-Raman[90] or TEM-NIR.[91]

Analysis of nanotube chirality was earlier done only by STM, which was very cumbersome and expensive. Now other techniques such as spectroflourimetry[92], photoluminescence mapping[93], near-field Raman spectroscopy[94], etc. have also been developed for rapid analysis of nanotube chirality.

4. CONCLUSIONS

Most of the research on purification has been carried out with samples in small quantity and hence scalability of these methods needs to be tested. While substantial progress has been made in purification and separation of SWNTs, emphasis is required on quality control and quality assurance across the laboratories. Much work remains before pure SWNTs of specific lengths, diameter, and chirality can be made available for applications. Apart from purification and sorting of CNTs, adequate standards for purity evaluation also need to be evolved. Spectroscopic results are highly dependent on CNT doping and environmental conditions, making comparison of results and their reproduction very difficult. Recently, standard for measurement of electrical properties of CNTs has been defined[95]. It provides methods for the electrical characterisation of carbon nanotubes and the means of reporting performance and other data. These methods enable creation of a suggested reporting standard that can be used by anyone as and when technologies are being developed. Similar standards for purity evaluation techniques such as microscopy and spectroscopy would go a long way in establishing uniformity and would aid meaningful comparison of yield and efficiency of different purification techniques.

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