

Separation of Semiconducting and Metallic Single-Walled Carbon Nanotubes

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ABSTRACT

Obtaining a monodisperse population of single-walled carbon nanotubes based on length, diameter and chirality is one of the foremost technological challenges before incorporating them in electronic and optoelectronic devices and other applications. Several separation techniques involving covalent chemistry, non-covalent encapsulation and physical methods have been developed over the years in order to achieve a high degree of selectivity of certain nanotube species based on size, chirality and electronic type. This paper discusses about the various post-synthetic separation techniques developed primarily to isolate semiconducting and metallic variants of single-walled carbon nanotubes and draws in a comparison between them.

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1. INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) are quasi one-dimensional hollow cylinders with walls of one atomic thick layer of carbon with exceptional structural, mechanical, optical and electronic properties. SWCNTs can be semiconducting or metallic conductors without requiring additional doping and at the same time possess extremely high tensile strength and elasticity along with chemical and thermal stability. The typical lengths of SWCNTs range from tens of nanometres to centimetres with diameters ranging from 0.5 nm to 2 nm. The properties of SWCNTs are strongly dependent on their size and atomic

structure. SWCNTs are considered to be the frontrunners to replace the semiconductor components required in integrated circuits for being nano-materials with such interesting electronic properties. The vast potential of SWCNTs due to their diverse properties has inspired their application in field effect transistors (FETs), logic gates, conductive films, field emission sources, infrared emitters, sensors, scanning probes, nano-mechanical devices, interconnects, mechanical reinforcements, hydrogen storage elements and catalytic supports¹⁻⁶. However, in order to optimize the performance of these devices, the SWCNTs should be sorted according to their size, diameter and chirality to obtain specific populations which are electronically pure – uniformly metallic or uniformly semiconducting with a specific band gap. This becomes important as well as challenging considering that all known growth methods produce a mixture of SWCNTs with a distribution of chiral indices centred on a mean diameter, though enrichment in some types has been achieved⁷. Over the last decade, development of sorting techniques to obtain monodisperse SWCNTs has been a top priority among the researchers with greater emphasis being put on development of techniques for separating semiconducting and metallic SWCNTs.

2. ELECTRONIC STRUCTURE OF SWCNTs

The electronic structure of SWCNTs is usually described in terms of the electronic structure of a folded graphene sheet (a single layer of sp^2 - hybridized carbon atoms in a honeycomb lattice)⁸⁻¹⁰. SWCNTs can thus be made by rolling up graphene sheets to form cylinders and the electronic properties of the SWCNT are primarily determined by the direction in which the graphene sheet was rolled up to form the nanotube. This direction is given by the chirality vector \mathbf{C}_h , which is defined as:

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \quad (1)$$

where \mathbf{a}_1 and \mathbf{a}_2 are the unit vectors of the hexagonal honeycomb lattice (fig. 1). The integers (n, m) define the chiral vector and therefore describe the structure of any SWCNT. The diameter d of the nanotube is determined by the magnitude of the chirality vector:

$$d = |\mathbf{C}_h|/\pi \quad (2)$$

The unique electronic structure of graphene manifests itself in the interesting electrical properties of SWCNTs. An additional quantization arises from electron confinement around the SWCNT circumference when the graphene sheet is rolled up into the nanotube. The circumferential component of the wave vector (\mathbf{k}_C) becomes quantized and can only take up values fulfilling the condition:

$$\mathbf{k}_C \cdot \mathbf{C}_h = 2n \quad (3)$$

where n is an integer⁸⁻¹⁰. This causes the graphene band to split into one dimensional subbands labeled by n . The electronic property of the SWCNT is determined by the position of these subbands. If the subbands pass through the Fermi (K) point of the Brillouin zone of graphene, then the SWCNT is metallic, else it is semiconducting.

The chiral indices (n,m) of a SWCNT can indicate whether it is metallic or semiconducting. If $n = m$, the SWCNT is metallic (armchair nanotubes); there is a very small band gap (metallic at room temperature) when $n - m = 3i$, where i is an integer; and truly semiconducting if $n - m \neq 3i$ ⁸⁻¹⁰. Nanotubes with $m = 0$ are called zigzag nanotubes (fig. 1).

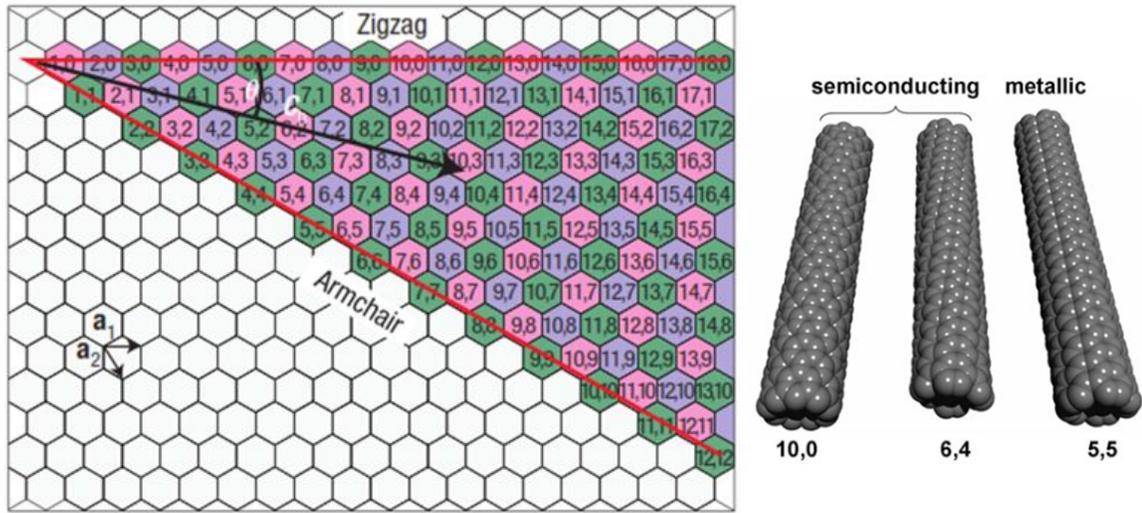


Fig. 1: The chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ and the chiral angle θ are depicted on the graphene sheet where \mathbf{a}_1 and \mathbf{a}_2 are the unit vectors of the graphene lattice and (n,m) are the chiral indices. Chiral indices of metallic nanotubes (at room temperature) are depicted as green while those of semiconducting nanotubes are depicted in pink ($n - m = 3i + 1$) and purple ($n - m = 3i + 2$). On the right, three SWCNTs are shown with different chiral vectors (different rolling directions of the graphene sheet). *Fig. reproduced from ref. 11 and 18.*

The bandgap of semiconducting SWCNTs is inversely proportional to their diameters. The dominant optical transitions also vary with the diameter and chiral vector in semiconducting as well as metallic SWCNTs. It is therefore essential to obtain a population of SWCNTs which is monodisperse in diameter as well as electronic type (chirality) for application in devices with uniform electronic and optical properties.

3. DISPERSION METHODS

Sorting of SWCNTs according to their length, diameter, electronic type and chiral handedness is essential to achieve optimal performance in all applications. In this paper we will mainly look into dispersion processes to separate semiconducting and metallic SWCNTs. The sorting techniques developed so far can be roughly categorized into three classes: (1) physical techniques, such as dielectrophoresis¹² and ultracentrifugation¹³; (2) selective destruction of one type of SWCNT, such as by electromagnetic irradiation^{14, 15} or hydrogen peroxide¹⁶; (3) selective chemistry: covalent or non-covalent functionalization. Some of these techniques can also be combined for a higher efficiency of dispersion of SWCNTs with greater purity.

Selective chemical functionalization of the SWCNTs followed by electrophoretic separation, ultracentrifugation and/or chromatographic methods offers tremendous flexibility in obtaining a monodisperse population of SWCNTs with respect to length, diameter and electronic type.

3.1. Selective Chemical Functionalization of SWCNTs

Molecular and supramolecular strategies of selective chemical functionalization of SWCNTs have been developed over the years. Chemistry on SWCNTs includes covalent sidewall functionalization, covalent chemistry at open ends or defect sites, non-covalent encapsulation by surfactants, non-covalent exohedral functionalization with polymers (polymer wrapping) and endohedral functionalization (molecular insertion into the interior of the SWCNT).

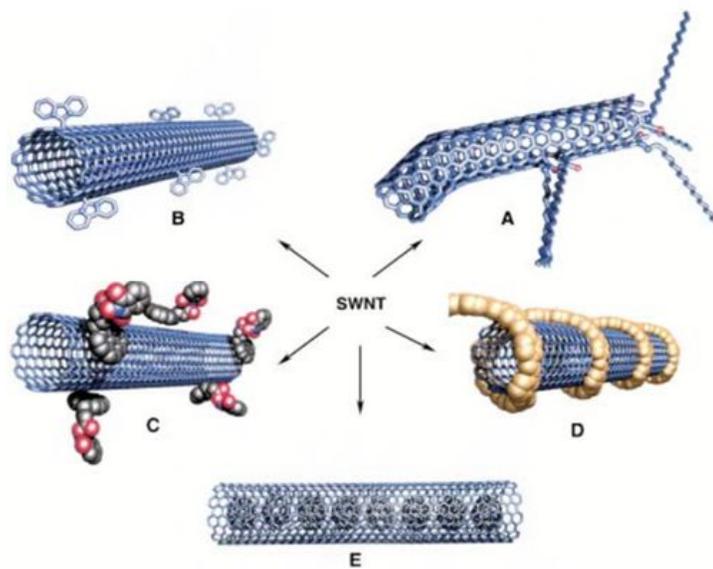


Fig. 2: Different possibilities of chemical functionalization of SWCNTs: **A**, Covalent functionalization at defect sites or open ends. **B**, Covalent sidewall functionalization. **C**, Non-covalent surfactant encapsulation. **D**, Non-covalent polymer wrapping. **E**, Endohedral functionalization. *Fig. adopted from ref. 17.*

In the following sections, dispersion of semiconducting and metallic SWCNTs by covalent sidewall chemistry and non-covalent techniques are discussed.

3.1.1. Dispersion of SWCNTs by Covalent Sidewall Chemistry

Covalent sidewall chemistry on SWCNTs has been developed which can disperse the population based on electronic type and diameter. The chemical reactions are selective and discriminate between metallic and semiconducting nanotubes. It has been demonstrated that metallic nanotubes react faster with diazonium salts in aqueous solutions than semiconducting nanotubes under controlled conditions ¹⁹. The primary reason for this difference in reactivity is attributed to the availability of electrons due to higher density of states (DOS) near the Fermi level in metallic SWCNTs which assists the reaction with diazonium cations by forming a stable charge-transfer state before bond-formation. The reaction of metallic nanotubes with the diazonium salts suppresses their radial breathing modes (RBM) and can be detected from their Raman spectra (fig. 3).

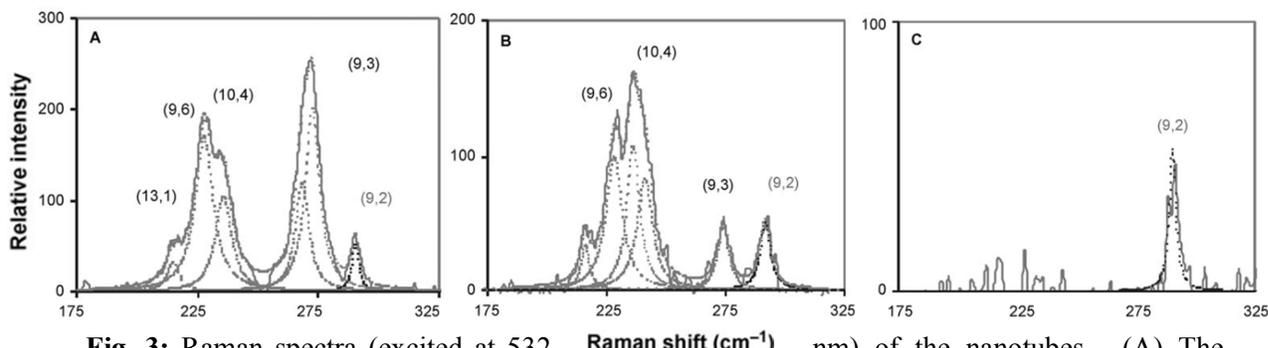


Fig. 3: Raman spectra (excited at 532 nm) of the nanotubes. (A) The spectra before addition of diazonium salt. (B) and (C) show an intermediate and heavy level of functionalization, respectively. The RBM bands related to the metallic nanotubes disappear progressively while that of the semiconducting species (9,2) remains almost unaffected. *Fig. reproduced from ref. 19.*

Another way to characterize and detect metallic and semiconducting SWCNTs is UV/Vis–NIR spectrophotometry²⁰. The transitions between the van Hove singularities of the DOS, characteristic of one dimensional systems, can be detected from the absorption spectra. The transition energies are characteristic of the chiral angle and diameters of the nanotubes. An empirical formula²¹ that describes the first transition energy (E_{11}) of a nanotube species related to its chiral angle (θ) and diameter (d) is given below:

$$E_{11} = \frac{1241}{A_1 + A_2 d} + A_3 \frac{\cos 3\theta}{d^2} \quad (4)$$

where A_1 , A_2 and A_3 are constants adjusted to account for the spectroscopic data. The transitions related to metallic nanotubes are depleted upon careful addition of 4-chlorobenzenediazonium tetrafluoroborate to a suspension of nanotubes due to the selective functionalization of the metallic species, as shown in fig. 4.

The disappearance of the E_{11} transitions of the metallic nanotubes on addition reaction on the sidewalls is due to the disruption of the conjugated π -system of the nanotube because the addition reaction changes the hybridization of carbon from sp^2 to sp^3 at the reaction site and thus changes the electronic properties of the metallic nanotubes.

The complexes formed by the metallic SWCNTs after addition reaction on the sidewalls can be dissolved in organic solvents and enriched thereafter by gel chromatography²². Diazonium compounds with a long alkyl tail cause metallic SWCNTs to be selectively soluble in tetrahydrofuran (THF)²³.

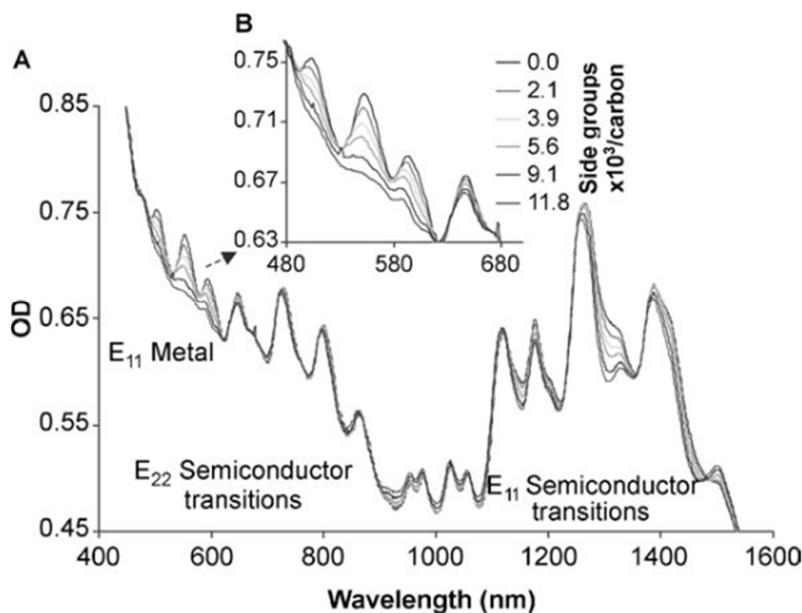


Fig. 4: UV/Vis–NIR absorption spectra of SWCNTs after addition of various amounts of aryl diazonium salts. The disappearance of the E_{11} metallic transition (magnified in inset (B)), suggests selective reaction of the metallic nanotubes with diazonium salts.

Fig. adopted from ref. 19.

Covalent sidewall chemistry has also been used to selectively destroy small diameter metallic nanotubes on reaction with nitronium ions (NO_2^+) due to their preferential and high reactivity with metallic nanotubes²⁴⁻²⁶. The metallic nanotubes are reduced to amorphous carbon and fragments are removed by filtration thereafter.

An interesting feature was noticed on covalent attachment of dichlorocarbene to nanotube sidewalls which converted the metallic SWCNTs to semiconductors²⁷. An energy gap is opened up at the Fermi level on the formation of carbon-carbon bonds on the sidewall of metallic SWCNTs. There is no separation method involved in this process and it can be particularly useful for application in FETs where the presence of any metallic fraction can adversely affect the device performance.

Although the dispersion methods involving covalent chemistry on SWCNTs provided an initial thrust to realize the potential of SWCNTs in different applications by obtaining monodisperse populations with respect to electronic types and diameters, they often cause substantial and in some cases irreversible changes to the properties of the SWCNTs. As a result, non-covalent functionalization for dispersion of SWCNTs is preferred in many

cases to minimize the perturbation to the properties of the nanotubes upon functionalization.

3.1.2. Dispersion of SWCNTs by Non-Covalent Methods

Surfactant encapsulation and polymer wrapping of SWCNTs are the two most prominent non-covalent approaches to functionalize and selectively disperse SWCNTs.

3.1.2.1. Dispersion by Surfactant Encapsulation of SWCNTs

Selective adsorption of SWCNTs based on electronic type by amines has been reported²⁸. The adsorption of methylamine on metallic and semiconducting SWCNTs was studied by using the local density functional theory and ultrasoft pseudopotential plane-wave methods²⁹. It was found out from the calculated adsorption energies that metallic SWCNTs are more strongly adsorbed by methylamine than semiconducting SWCNTs regardless of adsorption modes (interactions through different spatial orientations of methylamine). This enabled selective functionalization of metallic SWCNTs with propylamine and isopropylamine in THF and their subsequent enrichment by centrifugation. An advantage of this relatively simple process is that the weakly adsorbed amines are easily removable after the separation and the adsorption process does not affect the electronic structure of the SWCNTs.

Selective non-covalent functionalization and solubilization of semiconducting SWCNTs by a porphyrin derivative with long alkyl chains, 5,10,15,20-tetrakis (hexadecyloxyphenyl)-21H,23H-porphine (THPP) was achieved³⁰. A purified sample of SWCNTs was added to a solution of THPP in chloroform. The chloroform was removed by a rotary evaporator and the solid mixture was extracted repeatedly with hexanes and subjected to vigorous centrifugation to remove free THPP. Thereafter, tetrahydrofuran (THF) was added to the solid sample to dissolve the THPP coated SWCNTs. The entire process was repeated for the undissolved residue. Finally, the SWCNTs free of porphyrin, were obtained a solid residue (“free-SWCNT” sample). The organic residues were removed from both the samples and they were purified. The recovered SWCNT sample was found to be enriched in semiconducting SWCNTs as seen from the presence

of significant absorption bands (fig. 5b) at $\sim 5390\text{ cm}^{-1}$ and $\sim 9710\text{ cm}^{-1}$ corresponding to E_{11} and E_{22} transitions respectively, whereas the absorption of the metallic free-SWCNT sample is negligible over the near-IR region. Thus this process makes it possible to separate semiconducting SWCNTs from metallic SWCNTs and can be demonstrated from the near-IR absorption spectra of the solubilized sample and the free-sample.

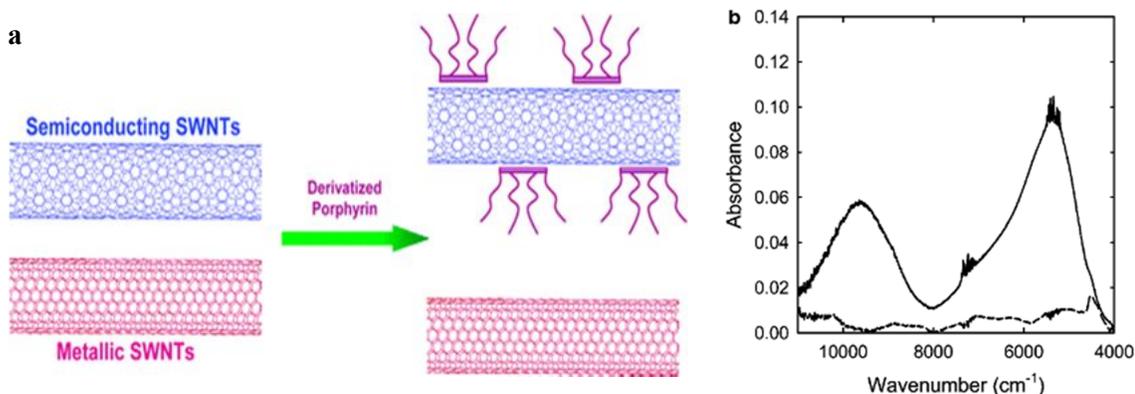


Fig. 5: (a) Selective non-covalent interaction of porphyrins with long alkyl chains with semiconducting SWCNTs. (b) Near-IR absorption spectra of the semiconducting recovered-SWNT (—) and metallic free-SWNT (----) samples after the same thermal treatment. *Fig. adopted from ref. 30.*

The selectivity of semiconducting SWCNTs by porphyrins is generally attributed to the speculation that semiconducting SWCNT is more like a conjugated macromolecule with similar surface properties as radical ion pairs and thus more favourable to interactions with free-base porphyrin molecules³¹.

Surfactants like sodium dodecylbenzene sulphonate (SDBS)³² has been effectively used as dispersing agent for breaking up bundles (aggregates) of nanotubes. The surfactant efficiently coats the nanotube surface since the carbon surface of the nanotube is extremely hydrophobic and so the interaction with the aliphatic chain of the surfactant in aqueous solution is energetically favourable. Surfactant encapsulation provides steric repulsion and colloidal stability to the dispersion and when combined with physical processes like sonication and ultracentrifugation, it causes very efficient debundling of aggregates into individual SWCNTs.

3.1.2.2. Dispersion by Polymer Wrapping of SWCNTs

Dispersion of SWCNTs by DNA, which wraps its helix around the cylindrical structure of the nanotube, was reported³³. Selectivity of SWCNTs with respect to diameter was achieved. DNA wrapping of SWCNTs combined with ion-exchange chromatography (IEX) allowed sorting of SWCNTs by electronic type. Small diameter (< 1.2 nm) SWCNTs were individually wrapped by single-stranded DNA (ssDNA) in aqueous solution. According to molecular modeling, the helical wrapping of the SWCNT surface by ssDNA is achieved through π -stacking. The binding free energy favours the ssDNA-SWCNT binding as compared to SWCNT-SWCNT. The effective charge density of the DNA-SWCNT hybrid varies with the electronic type of the SWCNT and is governed by the DNA helical pitch³⁴. This variation allows electronic type sorting of DNA wrapped SWCNTs by IEX and is confirmed through fluorescence and Raman spectroscopy. One important drawback of this process was that the electronic type and diameter sorting are convoluted by length variations of the SWCNTs. The results can thus be improved if the SWCNT sample is initially sorted by length through techniques like size-exclusion chromatography (SEC).

Another direction that has been developed to disperse SWCNTs in the recent years is by using aromatic organic polymers with special emphasis on fluorene based polymers³⁵. Molecular mechanics simulations suggest that aromatic polymers can wrap SWCNTs by aligning their backbone along the nanotube surface in order to maximize the π - π interaction between the aromatic polymer and the SWCNT. A small change in the structure of these polymers causes different selectivities with respect to diameter and electronic type of the SWCNTs.

Nish *et al.*³⁵ demonstrated that a polyfluorene derivative poly [9,9-dioctylfluorenyl-2,7-diyl] (PFO) can efficiently solubilize individual SWCNT species and changing the polymer backbone and/or the length of alkyl side chain can drastically alter the selectivity based on diameter and chiral angle. The highly resolved photoluminescence (PL) excitation maps and Raman spectra (fig. 6 a & b) confirms the high degree of selectivity

by PFO on CoMoCAT SWCNTs (synthesized by chemical vapour deposition with silica-supported Co-Mo catalyst).

This was for the first time that such an efficient helicity and diameter discrimination was achieved by non-covalent wrapping by aromatic fluorene based polymers. This also opened up a research direction in synthetic chemistry of conjugated polymers to design the molecules to disperse and solubilize individual species of SWCNTs based on chiral indices and diameter.

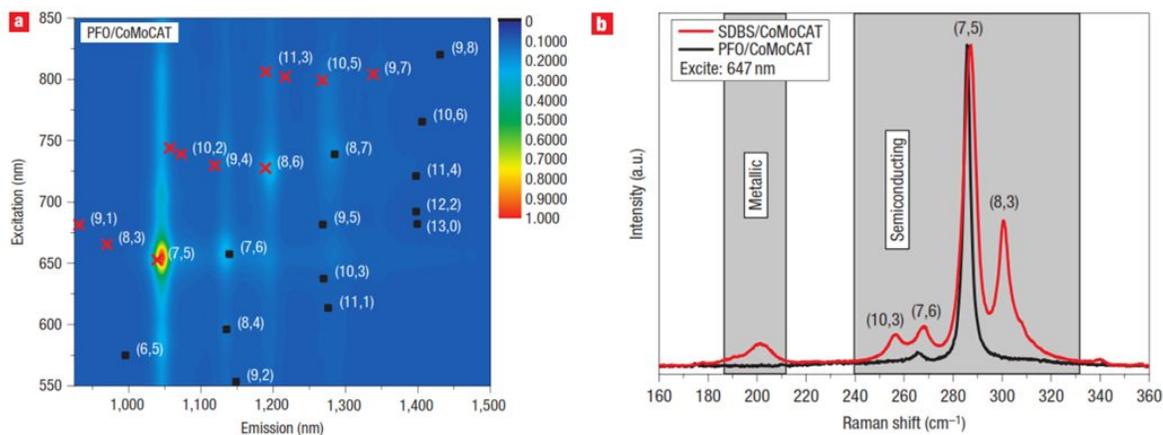


Fig. 6: Photoluminescence excitation (PLE) map and Raman spectra obtained using PFO to solubilize SWCNTs from the CoMoCAT process. **(a)** The strength of PL emission is shown as a false colour plot in the PLE map, with different SWCNT species labeled by their (n,m) indices. A prominent (7,5) peak dominates the emission. **(b)** A comparison between the Raman spectra (taken using a 647 nm light source) of surfactant (SDBS)-wrapped SWNTs (red line) and PFO wrapped SWNTs (black line), normalized with respect to the semiconducting (7,5) nanotube. The removal of both the metallic and other semiconducting species by the PFO/toluene solution is emphasized. *Fig. adopted from ref. 35.*

The sorting of SWCNTs by these polymers were limited to the small diameter tubes (0.8-1.2 nm) until recently the selection was also extended to larger diameter SWCNTs (0.8-1.6 nm) using polyfluorene derivatives with varying lengths of the alkyl side chains. In the work by Gomulya *et al.*³⁶, four different derivatives of polyfluorene with varying lengths of alkyl side chains were synthesized: poly(9,9-di-n-hexylfluorene-2,7-diyl) (PF6), poly(9,9-di-n-dodecylfluorene-2,7-diyl) (PF12), poly(9,9-di-n-pentadecylfluorene-2,7-diyl) (PF15) and poly(9,9-di-n-octadecylfluorene-2,7-diyl) (PF18) and also compared with commercially available poly(9,9-di-n-octylfluorene-2,7-diyl) (PF8) (previously

referred to as PFO in this paper). All the five polymers have the same backbone and were used to disperse SWCNTs synthesized by: (1) high-pressure carbon monoxide (HiPco) having diameters between 0.8-1.2 nm; and (2) arc plasma jet (SO) with mean diameter of about 1.4 nm.

The dispersion of semiconducting SWCNTs was demonstrated by optical spectroscopy (fig. 7). High performance network FETs were also fabricated using the dispersed semiconducting SWCNTs and mobilities of upto $14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons were reported with on/off ratio of 10^5 . Such a high performance of the FETs would not have been possible without very efficient removal of the metallic SWCNTs.

In fig. 7 (a), the optical density (OD) of the dispersion increases with the increase in the lengths of the alkyl side chains of the polymers as we go from PF8 to PF18. PF6, with the shortest alkyl side chain, is unable to wrap the SWCNTs. PF12, PF15 and PF18 show a higher density of semiconducting SWCNTs with larger diameter (those with absorption peaks around 1400 nm); (the relation between the energy of the electronic transitions and the diameter of the SWCNTs is described by equation 4).

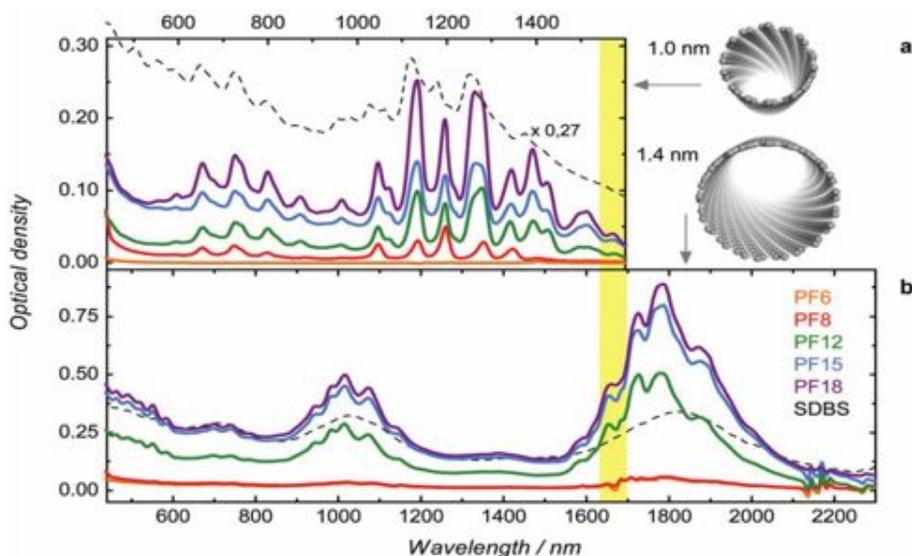


Fig. 7: (a) Absorption spectra of HiPco SWCNTs with average diameter of 1 nm dispersed with different polyfluorene derivatives in toluene (solid lines with colour-codes given in (b)) and dispersed with SDBS in water (dashed line). **(b)** Absorption spectra of SO SWCNTs with average diameter of 1.4 nm dispersed with different polyfluorene derivatives in toluene (solid lines), and dispersed with SDBS in water (dashed line). *Fig. adopted from ref. 36.*

Large diameter SO SWCNTs were efficiently sorted by PF12, PF15 and PF18 (as shown in the absorption spectra of the dispersions in fig. 7 (b)). PF6 and PF8 could not select any nanotube species in this case. The dispersion of the large diameter SWCNTs by PF12, PF15 and PF18 is a huge improvement over the dispersion by SDBS, which was previously considered to be the only option to disperse large diameter nanotubes. It is thus confirmed that the polyfluorene derivatives with longer side chains selects more and larger SWCNTs and makes it possible to select an extremely broad distribution of semiconducting SWCNTs with bandgaps from 0.6 eV to 1.3 eV.

The sorting of different species of SWCNTs using the polyfluorene derivatives is schematically shown in the graphene sheet (chirality) map in fig. 8.

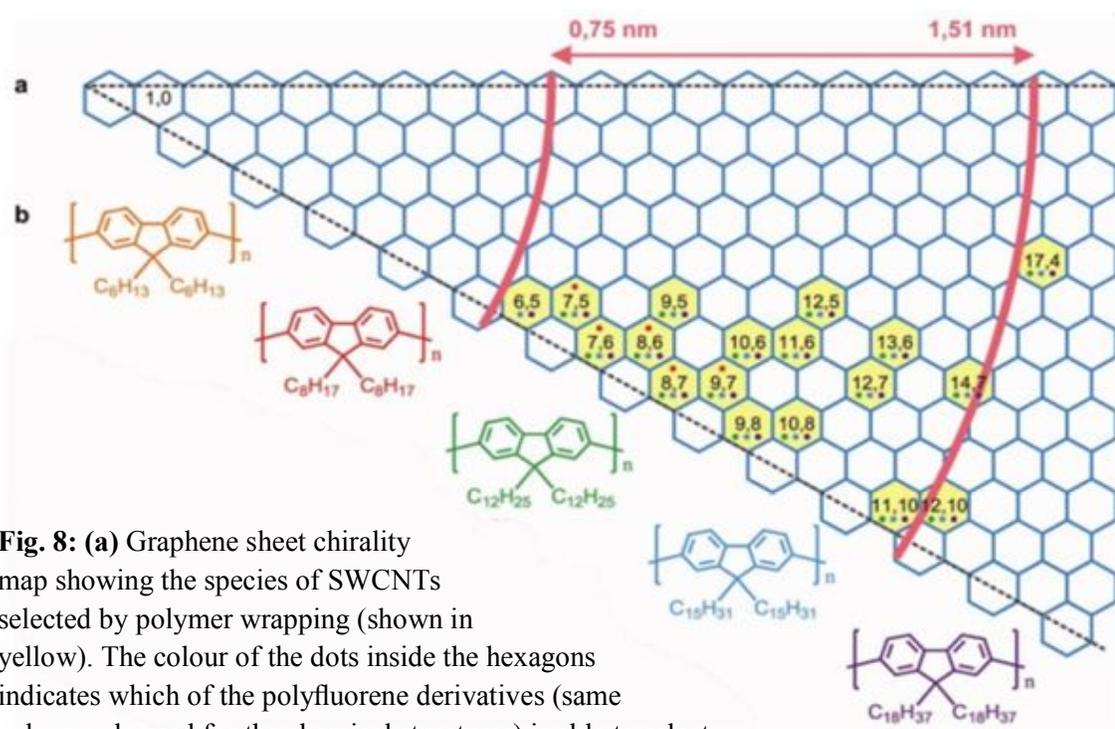


Fig. 8: (a) Graphene sheet chirality map showing the species of SWCNTs selected by polymer wrapping (shown in yellow). The colour of the dots inside the hexagons indicates which of the polyfluorene derivatives (same colour code used for the chemical structures) is able to select the nanotubes. (b) Chemical structures of the polyfluorene derivatives used (top to bottom): PF6, PF8, PF12, PF15, and PF18. *Fig. reproduced from ref. 36.*

3.2. Dispersion of SWCNTs by Physical Methods

Post-synthetic sorting of SWCNTs based on electronic type by physical methods includes: dielectrophoretic separation, ion-exchange and gel permeation chromatography (IEX and GPC, respectively) and ultracentrifugation.

3.2.1. Dielectrophoretic Separation

Metallic and semiconducting SWCNTs possess different dielectric constants. Alternating current (a.c.) dielectrophoretic separation³⁷ of metallic and semiconducting SWCNTs is based on this fact. The SWCNTs are sorted according to their dielectric constants in a.c. electric field applied across a microelectrode array (fig. 9 a). When a drop of SWCNTs suspended in solution placed over the microelectrode array and an a.c. electric field applied, the metallic SWCNTs, which are more polarizable, are selectively deposited on the substrate between the electrodes. The electric field also causes the deposited metallic SWCNTs to align in its direction (fig. 9 b). This method can also be useful in aligning a sample of semiconducting SWCNTs

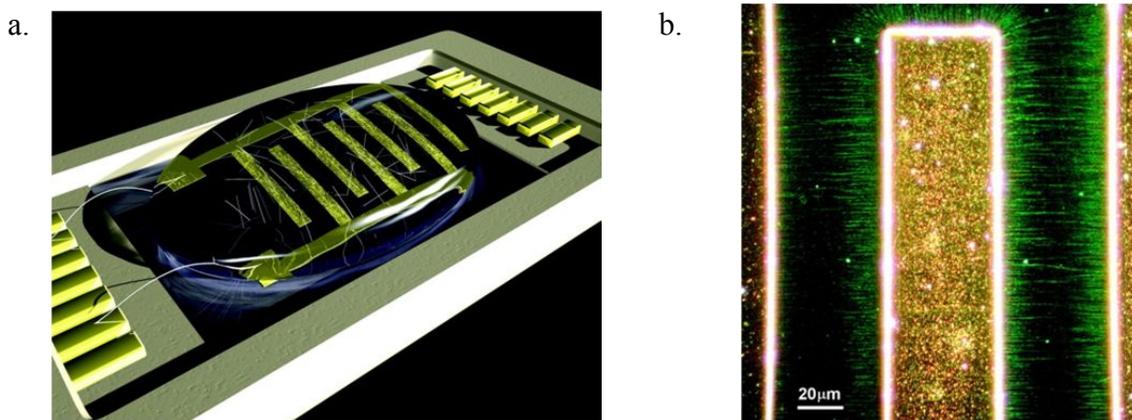


Fig. 9: (a) Schematic of the experimental setup for the dielectrophoresis of a SWCNT solution. The gold microelectrodes are 30 nm thick and 50 μm wide, with a 50-μm pitch on a p-type silicon substrate with 600 nm of SiO₂. (b) Incident-light dark-field microscope image shows the Rayleigh scattered light from the dielectrophoretically deposited aligned metallic SWCNTs and the electrodes (the SWCNTs appear green to the eyes). *Fig. adopted from ref. 37.*

It has been demonstrated that the sorting of metallic SWCNTs by this process becomes more efficient on increasing the frequency of the applied alternating current³⁸.

3.2.2. Chromatographic Separation

Recently, chirality separation of SWCNTs was achieved on a large scale by single-surfactant multicolumn gel chromatography³⁹. In this separation method, SWCNTs produced by high-pressure catalytic CO (HiPco) decomposition were used as the starting material and dispersed in purified water with sodium dodecyl sulfate (SDS), a surfactant. Several medical plastic syringes, filled with an allyl dextran-based size-exclusion gel (Sephacryl S-200, GE Healthcare), were used as the gel columns and were connected vertically in series. The gel medium interacts selectively with different SWCNT structures and exhibits the least interaction with metallic SWCNTs. The SWCNT dispersion was applied onto the top column along with the subsequent addition of SDS aqueous solution in order to elute the unbound SWCNTs. The unbound SWCNTs flowed from one column to another due to gravity and were finally collected from the bottom column, whereas the semiconducting SWCNTs got trapped in the columns. The adsorbed SWCNTs in different columns were desorbed by disconnecting the series of columns and adding SDS aqueous solution to each of them. The process was repeated with the unbound SWCNTs until there was no further adsorption of semiconducting SWCNTs in the columns.

The semiconducting SWCNTs obtained from each column were separated by diameter and chirality and this was confirmed through optical absorption spectroscopy, photoluminescence and Raman spectroscopy. It was also confirmed that the unbound-SWCNTs were metallic. Thirteen individual species of semiconducting SWCNTs were obtained by this method (fig. 10). This simple separation method is thus successful in achieving separation of SWCNTs based on chirality and diameter and with high electronic purity.

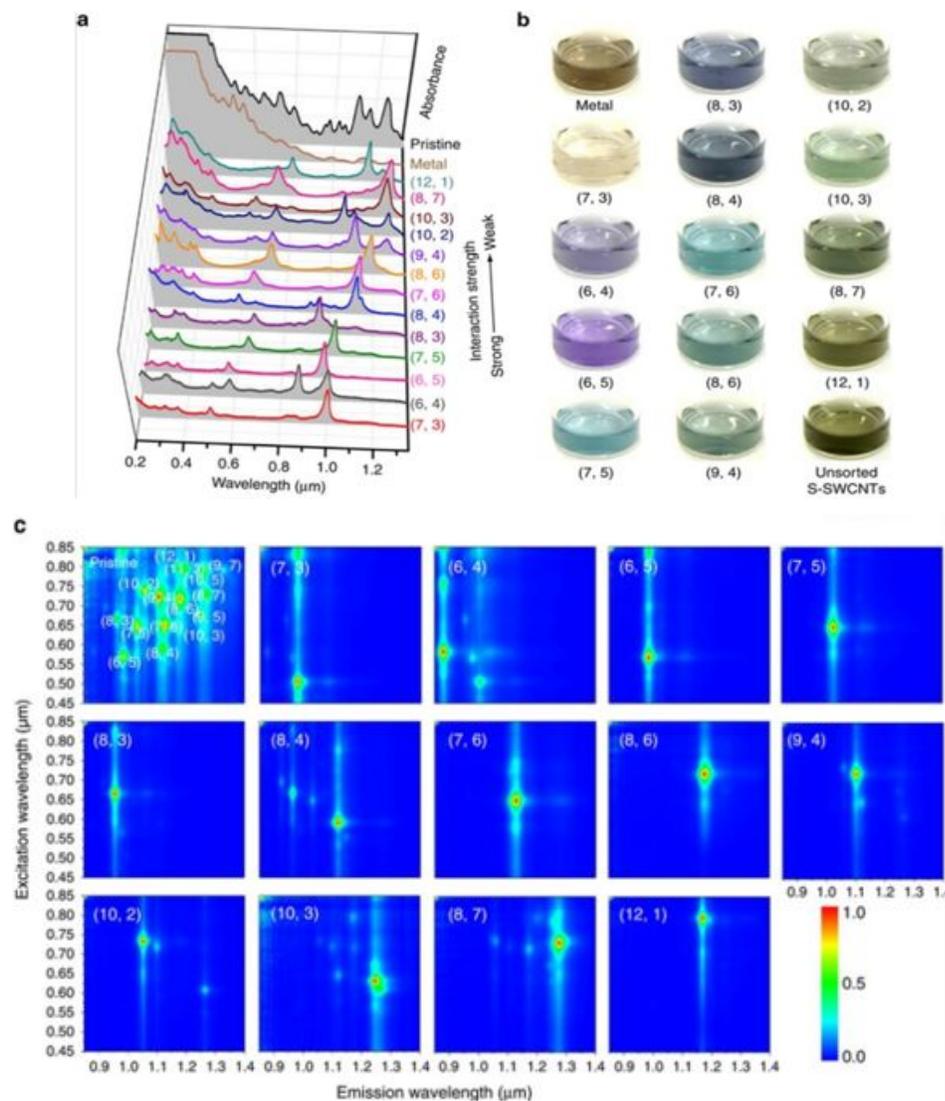


Fig. 10: Optical absorption spectra (a), photographs showing distinct colours (b) and photoluminescence contour maps (c) of the 13 isolated semiconducting SWCNT species, the metallic species (in a and b) and the pristine HiPco mixture. *Fig. adopted from ref. 39.*

3.2.3. Density Gradient Ultracentrifugation

Density gradient ultracentrifugation (DGU) incorporates a density gradient inside the centrifuge tube in which SWCNTs are loaded. This causes sedimentation of the SWCNTs through the gradient until the SWCNTs reach their respective isopycnic points (when the density of the SWCNTs becomes equal to that of the gradient). Finally, the SWCNTs form layers in the centrifuge tube according to their buoyant densities. Co-surfactant

mixtures⁴⁰ of sodium cholate and sodium dodecyl sulphate were used to selectively encapsulate large-diameter (1.1–1.6 nm) SWCNTs based on electronic types due to difference in polarizabilities of metallic and semiconducting SWCNTs. The SWCNT-surfactant hybrids had different buoyant densities due to the use of two different surfactants and thus sorted through DGU. Purities of about 99% were reported and confirmed through optical absorbance spectroscopy (fig. 11 b) and thin-film FET charge transport measurements.

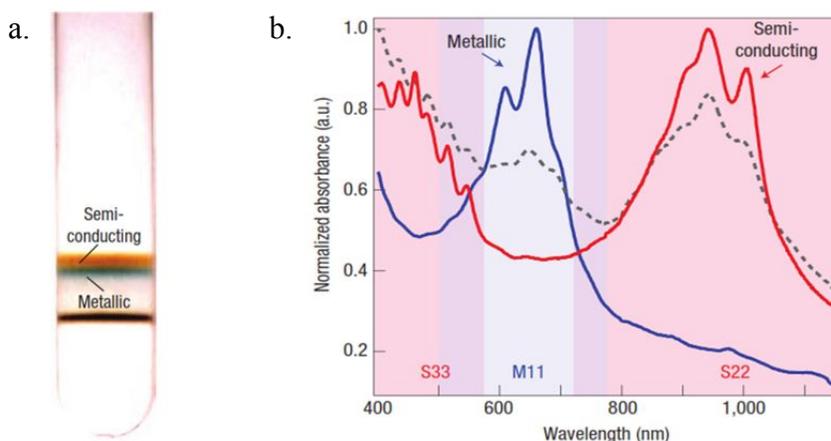


Fig. 11: (a) SWCNTs coated with co-surfactant mixture are sorted according to electronic type through DGU. (b) Optical absorption spectra confirms electronic type sorting as distinct peaks for metallic (blue) M11 transitions (first-order optical transitions for metallic SWCNTs) and semiconducting (red) S22 and S33 transitions (second and third-order optical transitions for semiconducting SWCNTs respectively) are seen. The dashed line (black) shows the spectra of the unseparated SWCNT sample. *Fig. adopted from ref. 40.*

4. DISCUSSION

Several sorting methods to separate metallic and semiconducting SWCNTs have been discussed in this paper. There are certain advantages and disadvantages involved with all these methods and researchers are still striving hard to develop more efficient strategies towards obtaining monodisperse SWCNTs.

Covalent functionalization of SWCNT sidewall or defect sites and open ends, on one hand, seems to be promising due to scalability and cost-effectiveness, but on the other hand, it adversely alters the electronic properties of the SWCNTs. During any covalent addition reaction with the SWCNT, the hybridization of carbon is changed from sp^2 to sp^3 and this saturation leads to the disruption of the conjugated π -electron system. This changes the pristine electronic property of the SWCNT. Although, some authors¹⁹ have claimed that this can be reversed by thermal treatment after the separation, in some cases the process is irreversible and may also introduce defects in the structure of the SWCNT. Most of the times this alteration in the electronic structure is undesirable except when selective destruction of a particular SWCNT species is required. Also, covalent functionalization can be advantageously used to convert metallic SWCNTs into semiconductors which no other technique has achieved to do so far.

Non-covalent separation techniques do not alter the electronic properties of the SWCNTs and hence more sought after than covalent functionalization. Surfactant encapsulation offers an efficient way of individualization and solubilization of SWCNTs. Together with physical methods like density gradient ultracentrifugation (DGU) and chromatography, surfactant encapsulation of SWCNTs can sort them according to electronic type and diameter. Unlike polymer (or DNA) wrapping of SWCNTs, surfactant encapsulation can be disadvantageous because surfactants are thought to wrap the entire material, including impurities, in a given raw nanotube sample.

Although DNA-wrapping of SWCNTs combined with ion-exchange chromatography (IEX) allows sorting of SWCNTs by electronic type and diameter, disadvantages of using DNA include irreversible wrapping, inability to disperse large diameter SWCNTs (> 1.2 nm), high cost and lack of scalability.

Dielectrophoretic separation of metallic and semiconducting SWCNTs not only allows efficient sorting by electronic type but also causes specific alignment of the separated metallic SWCNTs on the substrate. However, the major drawback of this separation method is the low quantity of material that can be separated. A possible way to scale-up can be the use of an array of larger electrodes.

The spectacular dependence of chirality separation of SWCNTs on the polymer backbone and side-chains in separation by polymer wrapping is one of its biggest advantages. A significant progress has been made in individualization of semiconducting SWCNTs with wide diameter range based on chirality by altering the length of alkyl side-chains of polyfluorene based polymers. But the selective interaction of these polymers with different chirality SWCNTs governing the binding mechanism is not well understood. Attempts to unravel the interaction mechanism has been made through molecular dynamics simulation with some initial results suggesting van der Waals interaction between long alkyl chains of the polymers with the nanotube walls ³⁶. It has been reported that longer alkyl chains results in better binding with nanotube walls and polyfluorene derivatives with longer alkyl chains have been shown to efficiently disperse even larger diameter SWCNTs. In the paper by Gomulya *et al.* ³⁶, PF18, PF15 and PF12 were synthesized which succeeded in dispersing higher densities (higher OD in the absorption spectra) of semiconducting SWCNTs which was directly related to the length of the alkyl side-chains. It will be interesting to find out till what length limit of the side-chains, the dispersion process gets better (higher densities of specific semiconducting SWCNTs achieved). Molecular dynamics simulation suggests that the selectivity decreases with the increase in the length of the alkyl chain due to more possible configurations of polymer wrapping. Therefore, there is an obvious trade-off at some limit. Nish *et al.* ³⁵ reports that there can be more than one type of interaction involved between the polymers and the SWCNTs and that the systems are more complicated than what can be currently modeled. A better understanding of the polymer-SWCNT interaction by development in computational modeling can lead to the designing of polymers with specific backbone and side-chains to obtain SWCNTs with desired chiral indices. This would be ultimate goal in the separation of SWCNTs with respect to chiral indices on demand.

The multicolumn gel chromatographic separation (section 3.2.2.) of semiconducting SWCNTs is one of the most promising separation methods for industrial scale-up owing to its simple procedure and extremely efficient sorting of semiconducting species of

SWCNTs according to their chiral indices in large quantities. Although, this sorting procedure was carried out for small diameter HiPco SWCNTs, it will be interesting if this sorting method can also be extended to larger diameter SWCNTs.

5. CONCLUSIONS & FUTURE OUTLOOK

In the recent years substantial progress has been made towards development of sorting techniques to select SWCNTs according to their chirality, electronic type and size. An effective strategy for sorting SWCNTs should not only be efficient in attaining highest purity levels of the dispersed populations, but also be scalable in order to meet commercial demands, cost-effective, preserve the electronic properties of the SWCNTs and be applicable to a wide distribution SWCNT length and diameter. So far, separation by polymer wrapping and multicolumn gel chromatography fulfill most of these conditions and seem to be highly promising for commercialization.

Another direction of research that has emerged is to develop selective growth methods which results in the synthesis of specific types of SWCNTs. Attempts have been made to control the reaction conditions (such as, pressure, temperature, catalyst, carbon feedstock) with some success in achieving narrow diameter distribution of SWCNTs by using bimetallic catalysts (CoMo⁴¹ and FeRu⁴²). However, synthesis of specific (*n,m*) SWCNTs has still remained elusive.

Most of the researchers have highlighted their separation methods by analytical techniques like optical absorption spectroscopy, photoluminescence and Raman spectroscopy. Fabrication of devices like FETs with the separated SWCNTs and their performance parameters like carrier mobilities and on/off ratios were also reported. But there is lack of any uniform standards to assess the purity levels of the separated SWCNT population.

For practical applications, especially in nanoelectronics, precise assembling of the separated and purified SWCNTs can be very important for optimal device performance.

Recently, a very dense surface coverage (> 500 nanotubes / μm) of aligned semiconducting SWCNTs was achieved by Langmuir-Schaefer technique⁴³. In the coming years, it is expected that more emphasis will be put on developing precise assembling techniques for optimal performance of SWCNT based devices.

SWCNTs currently face stiff competition from graphene, which is easier to process and has seen huge progress in a short span of time. However, graphene (which is metallic in its pristine form) lacks some of the fascinating electronic properties of SWCNTs. It is expected that since some promising separation techniques of SWCNTs have already come to light, a greater emphasis will be now on the applications.

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