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Selective Separation of Single-Walled Carbon Nanotubes in Solution

Hongbo Li and Qingwen Li

Suzhou Institute of Nano-Tech and Nano-Bionics, CAS
P. R. China

1. Introduction

SWCNT can be conceptualized by wrapping a one-atomic-layer thick graphene into a hollow cylinder. As shown in Figure 1, the wrapping way is represented by the chiral vector (n, m) , which denote the number of unit vectors along two directions in the crystal lattice of graphene sheet.¹ Because of the symmetry and unique electronic structure of graphene, the structures of SWCNTs strongly affect their electrical properties. In particular, their band gaps can vary from zero to about 2 eV and electrical conductivity can be in a range of a metal or semiconductor. For a given (n,m) nanotube, when $n = m$, the nanotube is metallic; when $n - m$ is a multiple of 3, the SWCNTs are semiconducting with geometry-dependent band gaps.

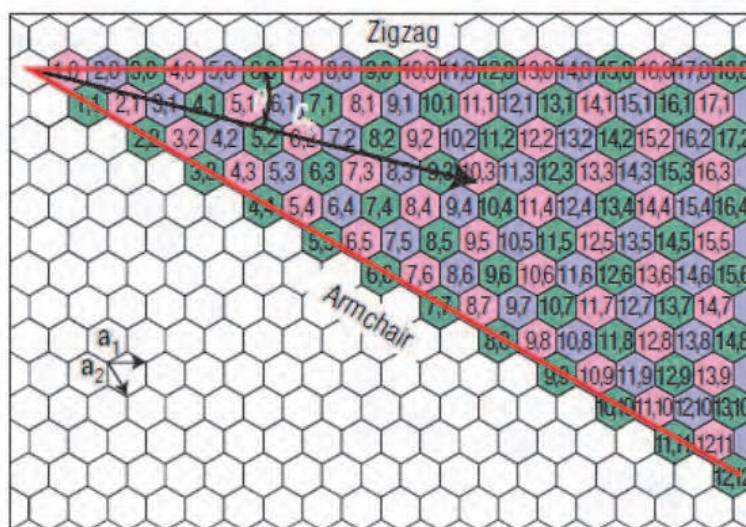


Fig. 1. A SWCNT is formed by rolling up a graphene along a chiral vector. The circumference of the SWCNT is determined by a chiral vector $Ch = na_1 + ma_2$, where (n,m) are integers known as the chiral indices and a_1 and a_2 are the unit vectors of the graphene lattice. Reproduced from ref.1.

Metallic SWCNTs (m-SWCNTs) may show ballistic behaviors and are ideal conducting connectors and electrodes for electronic devices due to their excellent electron transport

behavior, optical transparency and flexibility.²⁻⁵ Semiconducting SWCNTs (s-SWCNTs), with mobilities as high as $79\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$,⁶ are considered to be among the most promising candidates for next-generation high-performance field-effect transistors (FETs). The unique electronic properties of SWCNTs make them the ideal building blocks for nanoelectronics and thin film devices.^{7, 8} Unfortunately, the established CNT synthetic methods often lead to the growth of the mixture of nanotubes, typically with 1/3 m-tubes and 2/3 s-tubes, hard to selectively harvest the CNTs with a specific electronic type (m- / s-) or with a desired chirality, which has greatly hindered their widespread applications. Therefore, the mass m/s separation of SWCNTs is of great significance for their advanced applications in high-performance nanoelectronic devices. Chiral separation is also required for the uniform property of electronic devices. Since none of current synthetic techniques produce identical populations of SWCNTs, over the past two decades, many post-synthetic approaches have therefore been developed in an attempt to separate monodisperse SWCNTs into different fractions by their electronic types, diameters and chiralities. This chapter provides a brief introduction of the recent progress in the separation of SWCNT, in particular with an emphasis on the chromatographic approach.

2. Several important post-synthetic separation approaches

One of the earliest developed enrichment techniques of SWCNTs is based on the selective removal strategy with bulk SWCNT powders and films. The enrichment of m- or s- type SWCNTs can be obtained by removing the other type (usually m-SWCNTs) through electrical breakdown⁹, plasma^{10, 11}, irradiation^{12, 13} effects or chemical reagents^{11, 14-17}. These “dry” physical or chemical removal techniques are scalable and compatible with existing semiconductor processing for SWCNT-based nano-devices. However, as the selective removal is an irreversible process, the removed fraction cannot be used any more. Hence in recent years, separation of monodisperse SWCNTs, such as selective dispersion, dielectrophoresis, centrifugation, and chromatography has been greatly developed. SWCNTs can be thus sorted by electronic types and chiralities to some extent. Great efforts are still required to further understand the separation mechanism and therefore able to optimize the SWCNT sorting at lower cost and higher purity.

2.1 Selective functionalization

Both theoretical calculations and experimental studies have shown that the electronic properties, diameters and chiralities of SWCNTs may affect their interaction with some compounds, containing small organic molecules, surfactants, DNA and conjugated polymers. Such an interaction in return leads to the differentiation and sorting of SWCNTs of different types.

Metallic SWCNTs are usually believed to have a higher reactivity than semiconducting SWCNTs due to the higher electron density of states (DOS) at their Fermi levels¹⁴ and smaller ionization potential¹⁸. By covalent reaction on the sidewalls of SWCNTs, one type of SWCNTs (generally m-SWCNTs) tends to be functionalized first, leading to its selective dispersion in a solution and leaving the other one insoluble in the pristine form. As illustrated in Figure 2, Strano et al. first reported that diazonium reagents preferred to react with m-fractions rather than s-fraction, making s-SWCNTs well suspended in aqueous solution, and achieving SWCNT manipulation under controlled conditions.¹⁴ Selectivity is

dictated by the availability of electrons near the Fermi level to stabilize a charge-transfer transition state preceding bond formation. Later Doyle et al. found that several 4-substituted benzenediazonium salts, Ar-R ($\text{Ar} = \text{N}_2^+-\text{C}_6\text{H}_4$ and $\text{R} = \text{Cl}, \text{NO}_2, \text{OMe}$) at pH 10 showed the highest reactivities for s-SWCNTs with the largest band gaps.¹⁹ Additionally, nitronium ions^{20, 21} and osmium tetroxide (OsO_4)²¹ were also found to react preferentially with m-SWCNTs due to their larger electron density near the Fermi level. However, azomethine ylides derived from trialkylamine-N-oxides exhibited selective reactions with s-SWCNTs by cycloaddition, which was achieved by preorganizing the starting N-oxides on the nanotube surface prior to generating the reactive ylide.²² Separation of m-SWCNTs from functionalized s-SWCNTs was also successfully accomplished by inducing solubilization of s-SWCNTs in the presence of lignoceric acid. Although covalent functionalization seems an easy approach for the separation of m- or s-SWCNTs, it remains a challenge as a result of uncontrollable reaction selectivity and possible structural damages on CNTs themselves.

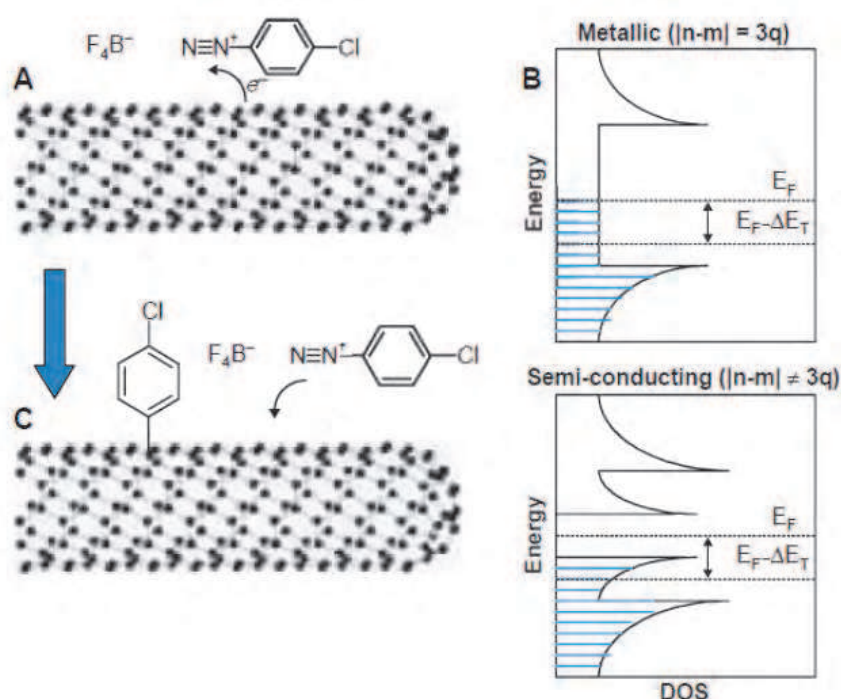


Fig. 2. (A) Diazonium reagents extract electrons, forming N_2 gas and leaving a stable C-C covalent bond at the nanotube surface. (B) The extent of electron transfer is dependent on the density of states in that electron density near E_F leads to higher initial activity for metallic and semimetallic nanotubes. (C) A functionalized nanotube may exist as a delocalized radical cation, which tends to receive electrons from neighboring nanotubes or react with fluoride or diazonium salts. Reproduced from ref.14.

In comparison with covalent functionality, non-covalent functionality is a more popular separation method, as it is a non-destructive process. By interacting with the hydrophobic surface of SWCNTs or matching their chiral structures, some organic molecules may selectively adsorb onto or wrap along SWCNT species. In 2003, Chattopadhyay and coworkers reported that octadecylamine (ODA) had a higher affinity to carboxyl functionalized s-SWCNTs than m-fractions. S-SWCNTs were thus retained in the supernatant due to the increased solubility by stronger ODA adsorption, whereas m-SWCNTs were

selectively precipitated.²³ As such, through the selective interaction of amine with s-SWCNTs, a self-sorted s-SWCNT network could be fabricated by spin-coating SWCNT solution on amine-functionalized surfaces,²⁴ where the chirality separation of nanotubes and simultaneous control of density and alignment may be achieved in one step. The field-effect transistors fabricated based on this method showed an on/off ratio as high as 900,000.

Interestingly, in the case of neutral SWCNTs without carboxyl group, both theoretical calculations and experiments have shown that the amine groups prefer to selectively interact with m-SWCNTs. Maeda et al. showed that m-SWCNTs could be highly concentrated to 87% by applying a dispersion-centrifugation process in a tetrahydrofuran solution of propylamine.²⁵ Similar results were also obtained in the m/s separation of SWCNTs by using bromine²⁶ and porphyrins²⁷. The porphyrin and its derivatives tend to attach onto the sidewalls of s-SWCNTs, making them enriched in the supernatant. While due to the formation of charge-transfer complex between bromine and m-SWCNTs, m-SWCNTs can be thus effectively sorted out by centrifugation.

In addition to m/s recognition, control on the structures of dispersants may also lead to the selective separation of SWCNTs by diameter and chirality. Ortiz-Acevedo et al. proposed a novel approach to coat SWCNTs with reversible cyclic peptides (RCPs) that covalently wrap around CNTs through the oxidation of thiols incorporated into the peptide backbone.²⁸ By controlling the length of the RCPs, they demonstrated limited diameter-selective solubilizations of SWCNTs. Some aromatic polymers were also found to selectively solubilize certain nanotube species. As illustrated in Figure 3, Nish et al. reported that the polymer poly(9,9-dioctylfluorenyl-2,7-diyl) was very selective to nanotubes.²⁹ They suggested that the SWCNT-polymer bonding was strongly influenced by both the relative orientation of the polymer chain to the nanotube structure, and the possible charge transfer that occur from metallic tubes and lead to changes in the conformation of the polymer.

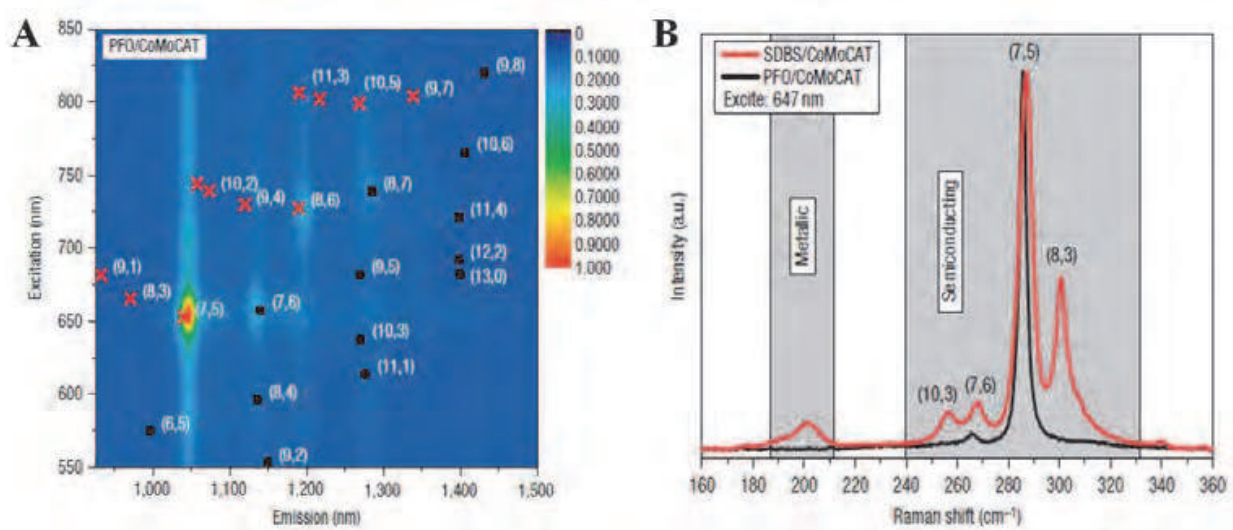


Fig. 3. (A) The PLE map shows the strength of the PL emission as a false color plot, with the different species labeled by their (n,m) indices. The emission is dominated by a very prominent (7,5) peak. (B) A comparison between the Raman spectra, taken using a 647 nm light source, of surfactant-wrapped SWCNTs (red line) and PFO wrapped SWCNTs (black line), normalized with respect to the semiconducting (7,5) nanotube. Reproduced from ref.29.

Small organic molecules are also designed for the diameter-selective and chiral separation. Tromp et al. used oligo-acene adducts as a diameter-selective molecular anchor for separation and functionalization of SWCNTs.³⁰ SWCNT field effect transistors fabricated from diameter-sorted SWCNTs showed remarkably improved electrical properties compared to non-sorted SWCNTs. More recently, Wang et al. reported that the enantiomers of SWCNTs can be separated based on molecular recognition with chiral diporphyrin nanotweezers.³¹ The chiral nanotweezers consisting of phenanthrene spacer and two chiral porphyrins may discriminate the diameter and handedness of CNTs simultaneously by taking into account the relationship between the (n, m) selectivity and the structures of previously reported chiral nanotweezers. Owing to the relatively narrow cleft made by two porphyrins, the nanotweezers showed high selectivity toward (6,5)-SWCNTs possessing the smallest diameter among the major components of SWCNTs grown from CoMoCAT.. In addition, the single enantiomer of (6,5)-SWCNTs could be enriched through the molecular recognition with 1. These results imply that it is crucial for the selective functionalization of SWCNTs to generate a broad variety of molecular anchors and functional backbones with excellent diameter selectivity.

2.2 Dielectrophoresis

Due to different dielectric constants of m- and s-SWCNTs under an alternating current (a.c.) electric field, SWCNTs can be sorted by their electronic types via dielectrophoresis. Early in 2003, Krupke et al. developed an alternating current dielectrophoretic method to separate m-SWCNTs from s-SWCNTs in suspension.³² As shown in Figure 4A, when SWCNT suspension was placed on an array of microelectrodes and applied with an alternating current, an opposite movement of m- and s-tubes occurred along the electric field gradient. M-SWCNTs were attracted toward the microelectrode array, leaving s-SWCNTs in the solvent. Principally, a complete separation between metallic and semiconducting SWCNTs may be possible if all tubes in the suspension are dispersed as individual tubes (no bundles). However, this method was only available for the sorting of m- and s-SWCNTs on a small scale.

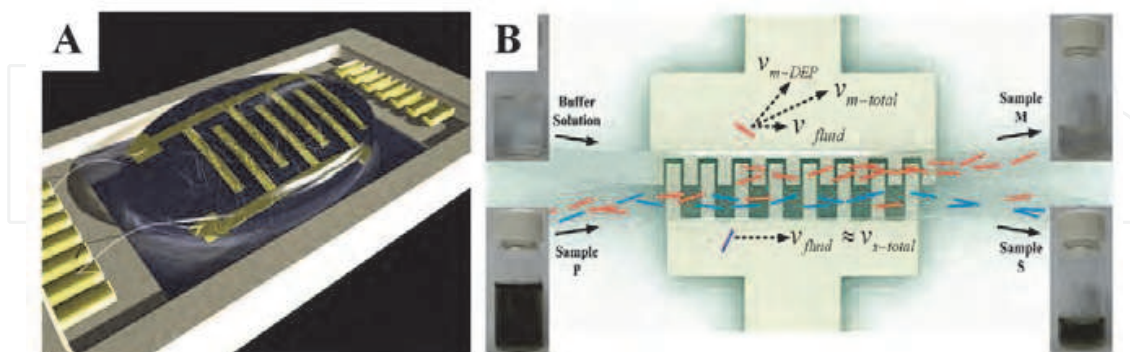


Fig. 4. (A) Schematic of dielectrophoresis of SWCNT suspension by using a microelectrode array. Reproduced from ref.32. (B) The continuous separation mechanism based on dielectrophoresis by using an H-shaped microfluidic channel. Reproduced from ref.33.

Later, Shin et al. developed this technique and established a nondestructive, scalable method for SWCNT separation by using an H-shaped microfluidic channel, where highly pure m-SWCNTs were continuously extracted from a suspension, as shown in Figure 4B.³³

Two laminar streams were generated in an H-shaped microfluidic channel with two inlets and two outlets. The flow conditions were carefully controlled to minimize diffusive and convective transport across the boundary between the two flows. Dielectrophoretic force from the embedded electrode at the junction extracted m-SWCNTs from a stream of nanotube suspension toward the other stream of buffer solution without nanotubes. Thus, the highly pure m-SWCNTs were obtained simultaneously at separate outlets. However, the separation efficiency and purity of s-SWCNTs is still difficult to be enhanced. Moreover, this method is only compatible with the m/s separation, ineffective for the chiral separation.

2.3 Centrifugation

Centrifugation is a process widely used in industry and in laboratory settings for the separation of mixtures driven by the centrifugal force. More-dense components in the mixture migrate away from the axis of the centrifuge, while less-dense components in the mixture migrate towards the axis. Increasing the effective gravitational force on a test tube, more dense components will be precipitated on the bottom of the tube. The less dense components are collected in the supernatant solution. SWCNTs are usually synthesized in a highly mixed status with a broad distribution of lengths, diameters and chiralities, leading to the sorting a tough issue. However, centrifugation is found effective for the separation of SWCNTs. To date with this simple technique, the SWCNTs can be sorted by the m/s, diameter and chirality.

2.3.1 Density gradient ultracentrifugation

Density gradient ultracentrifugation (DGU) is a technique commonly utilized to separate and isolate different sub-cellular components, DNA from RNA, and even different sequences of DNA by their compositions. Arnold et al. firstly described the sorting of DNA-wrapped SWCNTs by DGU,³⁴ this technique has been well developed for SWCNT sorting with multiple purposes, such as separation by m/s, diameter and chirality, even the separation of the mirror-image isomers of seven (n,m) species.³⁵⁻⁴¹ In this process, SWCNT suspension is added to centrifuge tubes containing liquid mixtures arranged to form a spatially varying density profile. Under strong centrifugation, SWCNT species are separated by migrating to regions matching their individual densities. Hence, the sorting efficiency is greatly dependent on the dispersants and DGU processing.

Salts like sodium cholate (SC) or cosurfactants are often added to optimize the fine sorting of monodispersed SWCNTs. Arnold et al reported in 2006 that the sorting of SWCNTs by diameter, bandgap and electronic type using structure-discriminating surfactants to engineer subtle differences in their buoyant densities.³⁵ Density gradients were formed from aqueous solutions of a non-ionic density gradient medium, iodixanol. Gradients were created directly in centrifuge tubes by one of two methods: by layering of discrete steps and subsequent diffusion into linear gradients or by using a linear gradient maker. As shown in Figure 5, they have isolated the SWCNTs of narrow diameter distributions, more than 97% of which are within a 0.02-nm-diameter range. Furthermore, by using cosurfactants, they obtained bulk quantities of SWCNTs of predominantly a single electronic type. By a hydrodynamic model, Nair et al. described the motion of surfactant-suspended single-walled carbon nanotubes in a density gradient.⁴² The theoretical results predicted that the number of surfactant molecules adsorbed on each nanotube determined its effective density and, hence, its position in the gradient after centrifugation has been completed.

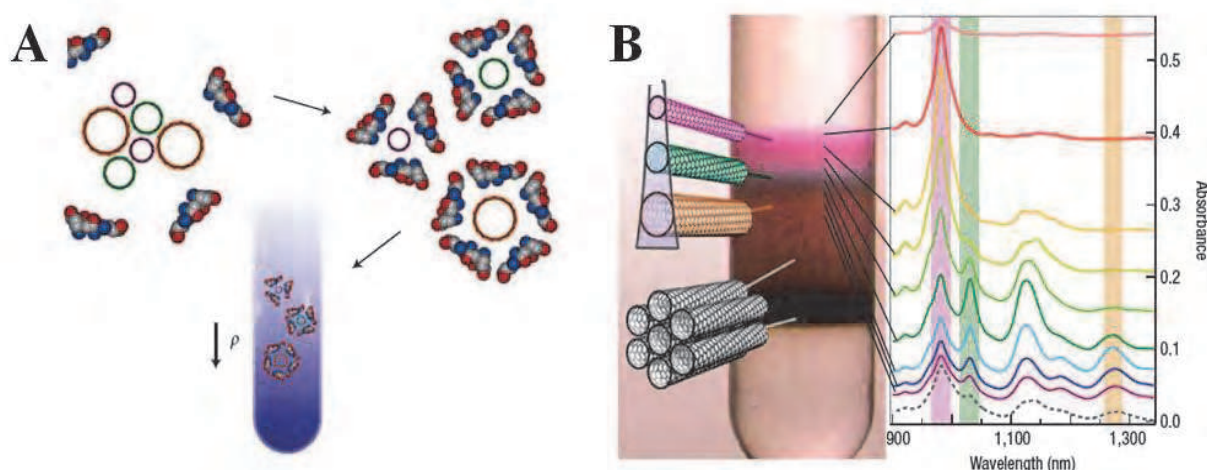


Fig. 5. Sorting of SWCNTs by electronic type, diameter and bandgap using DGU. (A) Schematic of surfactant encapsulation and sorting; (B) Photographs and optical absorbance (1 cm path length) spectra after separation using DGU. Visually, the separation is made evident by the formation of coloured bands of SC encapsulated, CoMoCAT-grown SWCNTs (7–11 Å) sorted by diameter and bandgap. Bundles, aggregates and insoluble material sediment to lower in the gradient. The spectra indicate SWCNTs of increasing diameter are more concentrated at larger densities. Three diameter ranges of semiconducting SWCNTs are maximized in the third, sixth and seventh fractions (highlighted by the pink, green and light brown bands). These have chiralities of (6,5), (7,5) and (9,5)/(8,7), and diameters of 7.6, 8.3 and 9.8/10.3 Å respectively. Reproduced from ref.35.

In 2008, Yanagi et al. achieved the separation of m- and s-SWCNTs using sucrose as a gradient medium in sucrose-DGU.³⁶ By lowering the temperature during sucrose-DGU and tuning the concentrations of the surfactants, m- and s-SWCNT samples were obtained with high purity, estimated to be 69% and 95%, respectively, from their optical absorption spectra. They pointed out that the temperature during centrifugation was also an important parameter that improved the m/s separation capability. Recently Antaris et al. found that nonionic, biocompatible block copolymers were useful to isolate m- and s-SWCNTs using DGU.⁴⁰ Separations conducted with different Pluronic block copolymers revealed that Pluronics with shorter hydrophobic chain lengths led to the purity levels for s-fraction sorting higher than 99% when Pluronic F68 was used. In contrast, X-shaped Tetronic block copolymers showed a specific affinity to m-SWCNTs, yielding metallic purity levels of 74% for Tetronic 1107.

In addition to m/s separation, by further tuning the surfactant component, enhanced diameter-dependent and chiral sorting of SWCNTs can be achieved by DGU. Zhao et al. used sodium deoxycholate (DOC) and sodium dodecyl sulfate (SDS) as cosurfactant encapsulating agents to form a DOC-restricted SDS wrapping morphology around the SWCNTs and thus 97% pure isolation of (6,5) SWCNTs was achieved.³⁷ Interestingly, via optimizing surfactant structure or DGU processing, enantiomer separation of SWCNTs is obtained. Green et al. reported that by using chiral surfactant, such as sodium cholate, left- and right-handed SWCNTs can be discriminated.³⁸ This sorting strategy can be employed for simultaneous enrichment of SWCNTs by handedness and roll-up vector having diameters ranging from 0.7 to 1.5 nm.

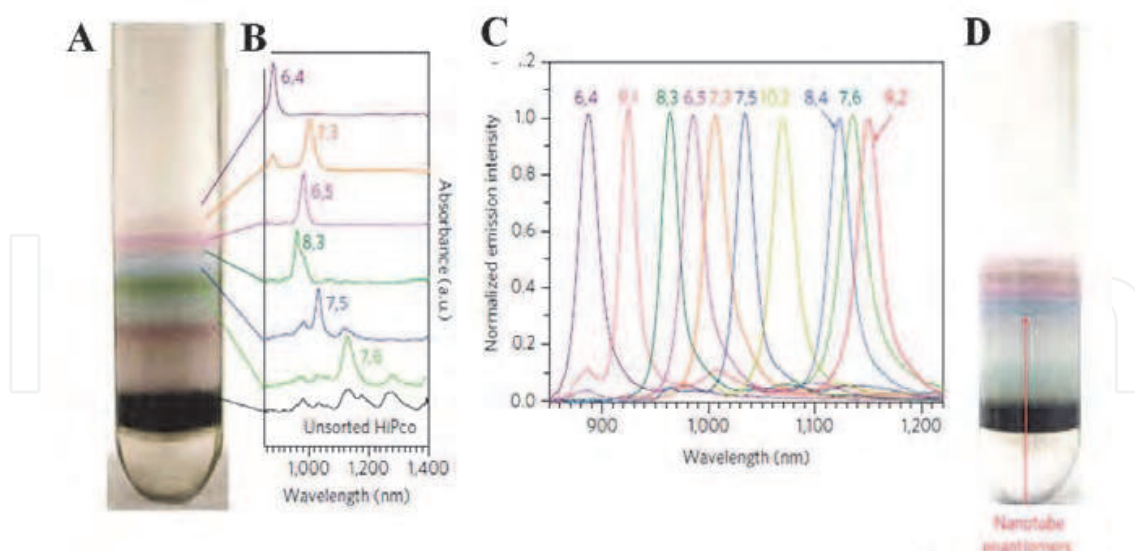


Fig. 6. Sorting of HiPco SWCNTs by (n,m) structure using single-step nonlinear DGU. (A) Image of a centrifuge tube containing HiPco SWCNTs sorted by one 18-h nonlinear DGU run at 268,000g (max). (B) Near-infrared absorption spectra of the marked colored layers. (C) Photoluminescence spectra of 10 separated fractions excited at the E_{22} peak of each main (n,m) component. (D) Image of a centrifuge tube showing resolved pairs of enantiomer bands sorted from HiPco SWCNTs by nonlinear DGU with sodium cholate. Reproduced from ref.41.

However, simultaneously sorting many SWCNTs species in a single step still is a bottleneck. Recently, Ghosh et al. made a breakthrough for SWCNT sorting.⁴¹ They showed that highly polydisperse HiPco SWCNTs were readily sorted in a single step to enable fractions enriched in any of ten different (n,m) species by introducing nonlinear density gradients. Furthermore, minor variants of the method allowed separation of the mirror-image isomers of seven (n,m) species. They prepared centrifuge tubes with nonlinear, S-shaped gradients designed to have very small variations of density with depth at densities typical of suspended nanotubes. A photograph of such a tube after centrifugation shows extensive color banding (Figure 6A). Absorption spectra of the separated fractions (Figure 6B) clearly indicate that different (n,m) species have been sorted into distinct layers. From top to bottom, the bands are identified as (6,4), (7,3), (6,5), (8,3), (7,5) and (7,6). The (6,5) band is purple in color; (8,3) and (7,6) are green; and (7,5) is blue. Further evidence of effective sorting is displayed in Figure 6C, which shows normalized emission spectra of ten fractions separated from DGU-processed samples containing single or co-surfactants, each excited at the E_{22} peak of its dominant species. The enriched species are (6,4), (7,3), (6,5), (9,1), (8,3), (9,2), (7,5), (8,4), (10,2) and (7,6). By adding a co-surfactant to sodium cholate in their nonlinear DGU method, they achieved effective and highly reproducible single-step enantiomeric sorting of several (n,m) species in HiPco samples. Further they found optimal enantiomer separation with a surfactant mixture of 0.7% sodium cholate plus 0.175% sodiumdodecyl sulphate in a slight variant of the nonlinear DGU gradient described earlier. The enantiomers of (6,5), (8,3), (8,4), (6,3) and (6,4) SWCNTs were able to be separated by this technique. This novel approach promised a scalable, relatively simple, and refined separation method of SWCNTs.

2.3.2 Normal speed centrifugation

In comparison with DGU usually set the speed at about 2×10^5 g, normal centrifugation is found also available for the sorting of SWCNTs at low speed of about 2×10^4 g. More recently, Tanaka et al. reported a rapid and scalable method for the separation of metallic and semiconducting SWCNTs by normal speed centrifugation.⁴³ When SDS dispersed SWCNT suspension was mixed with liquid agarose gel and then centrifuged, it was found that m-fraction was favorably enriched in supernatant, and s-fractions were retained in the precipitated gel. Such separation effect resulted from the selective interaction of s-SWCNTs with agarose gel. Upon centrifugation, s-SWCNTs were selectively trapped in the gel, whereas metallic nanotubes remained in the free state with SDS micelles in the solution as illustrated in Figure 7A. The effective separation is greatly dependent on the dispersant and gel. It is also found that the purity of the m- and s-SWCNTs obtained by centrifugation can be improved by optimizing the gel concentration and composition of agarose.

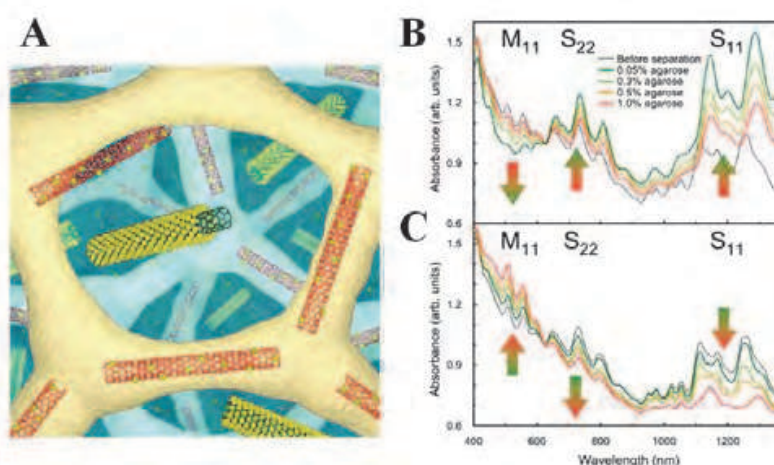


Fig. 7. (A) Model of MS separation using agarose gel. Red, s-SWCNTs; beige, agarose gel matrix; green, m-SWCNTs; yellow, SDS. Spectral results of (B) Gel fraction and (C) Solution fraction separated by centrifugation method at various concentrations of agarose (0.05-1.0%). Reproduced from ref.43.

The purity of s-SWCNTs in the compressed gel could be increased by decreasing agarose concentration in the starting gel (Figure 7B), while the purity of the metallic tubes collected in the supernatant tended to increase with agarose concentration up to approximately 1.0% (Figure 7C), beyond which the metallic nanotube purity increased only slightly. When the separation was repeated for the solution fraction concentrated m-SWCNTs, m-SWCNTs could be further enriched. Due to the selective entrapment of s-SWCNTs in agarose gel, the effective m/s separation could be also realized by simple frozen, thawed, and squeezed procedures. Although this method was reported to be readily scalable and not restricted by equipment limitations, the melting and mixing of excessive agarose with SWCNT dispersion made the sorted SWCNTs containing agarose impurities, which were hard to be removed.

2.4 Chromatography

Chromatography is a popular method used for purification of individual chemical or biological compounds from their mixtures. Different compounds exhibit different

physicochemical properties, leading them to behave diversely between mobile and stationary phases. Based on the similar properties of SWCNTs to biological macromolecules in sizes and surface properties, earlier from 1998, researchers have made efforts to separated SWCNTs by the chromatography. Due to the diversity of the stationary and mobile phases, SWCNTs dispersed in solution can be sorted following different separation mechanisms, such as size-exclusion chromatography (SEC)⁴⁴⁻⁵⁰, anion exchange chromatography (IEC)^{8, 51-54} and electrokinetic chromatography^{46, 50, 55-57}. By tuning the stationary phase and eluents, the dispersed SWCNTs have been successively sorted by length, m/s, diameter and chirality.

2.4.1 Size-exclusion chromatography

Among numerous chromatographic methods, gel filtration chromatography, or gel permeation chromatography is widely applied in the efficient and low-cost separation of biological macromolecules.⁵⁸ Its separation is based on differences in the sizes or weights of the analytes, which govern their access to the pore beads packed in a column. In general, the smaller analytes can enter the pores more easily and therefore spend more time in these pores, increasing their retention time. Conversely, larger analytes spend little if any time in the pores and are eluted quickly. It can be thus inferred that the pore sizes of gel beads for the column packing play a critical role in the separation of an analyte with a desired range of molecular weights. Since the lengths of SWCNTs in suspensions prepared by ultrasonication are in a wide range from 50 nm to 1000 nm, SWCNTs are separated according to their lengths by the size-exclusion chromatography. Many porous packing media as the stationary phases have been used.

In 1998, Duesberg et al. reported that carbon nanospheres, metal particles, and amorphous carbon could be efficiently removed by size exclusion chromatography when applied to surfactant stabilized dispersions of SWCNT raw material.⁴⁴ In addition, length separation of the tubes was achieved. 1wt% sodium dodecylsulfate (SDS) solution was used to disperse and stabilize SWCNTs. Controlled-pore glass (CPG) with an average pore size of 300 nm (CPG 3000Å, Fluka) was packed in the column. Different fractions of SWCNTs were eluted out sequentially with 0.25wt% SDS aqueous solution. Later, Farkas et al. accordingly undertook to length sort of cut SWCNTs by size exclusion chromatography (SEC) using a HPLC system,⁴⁵ promising that efficient length separation with good resolution is feasible on a preparative scale. Further by using three silica-based column resins in series with pore sizes of 2000, 1000, and 300 Å, Huang et al. demonstrated that DNA dispersed SWCNTs with very narrow length distribution could be sorted out.⁴⁷ The atomic force microscopy revealed that the average length decreased monotonically from >500 nm in the early fractions to <100 nm in the late fractions, with length variation $\leq 10\%$ in each of the measured fractions.

Polysaccharide-based porous beads were also applied for the separation of SWCNTs. Heller and Arnold et al. reported that by the gels of sephacryl S-500, the concomitant length and diameter separation of SWCNTs were achieved.⁴⁶ As shown in Figure 8, separation by diameter was concomitant with length fractionation, and nanotubes that were cut shortest also possessed the greatest relative enrichments of large-diameter species. They demonstrated that the longer sonication time led to an increase in the electrophoretic mobility of CNTs in the gels and thus determined the degree of both length and diameter separation of the nanotubes.

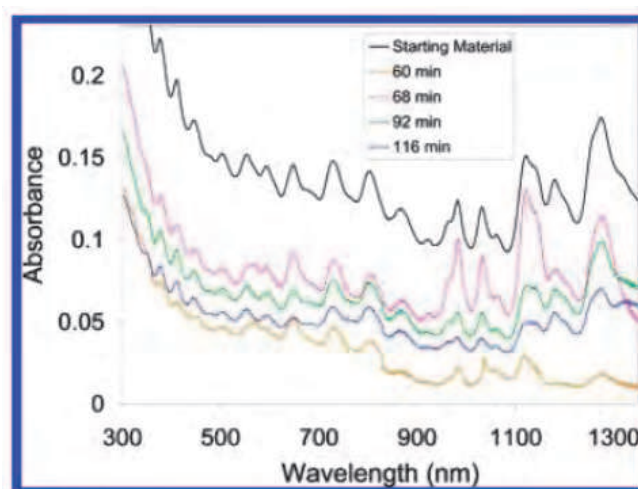


Fig. 8. Absorption spectra of selected fractions of nanotubes probe-tip sonicated for 3 h and separated by a size exclusion column. The spectra show changes in the concentrations of the nanotube species with respect to elution time. Reproduced from ref.46.

The stationary phase played an important role in the chromatographic separation of carbon nanotubes, Moshhammer et al first demonstrated that by size exclusion chromatography of Sephacryl S-200 gel, SDS-dispersed SWCNTs could be fractionated according to electronic structure type.⁵⁰ More recently, Liu et al achieved the m/s separation of SWCNTs by using agarose derived filling gel.⁵⁹ Sepharose 2B gel (a bead-formed cross-linked agarose gel matrix, GE Healthcare, bead size range 60-200 μ m) was used. When SWCNTs dispersed in SDS solution were applied to the top of the gel column, from Figure 9A, m- and s-SWCNTs could be sorted with a two-step elution using SDS and sodium deoxycholate (DOC) solution, respectively. Importantly, by the successive addition of DOC solutions with concentrations ranging from 0.05 to 2 wt % and fractional collection at each concentration,

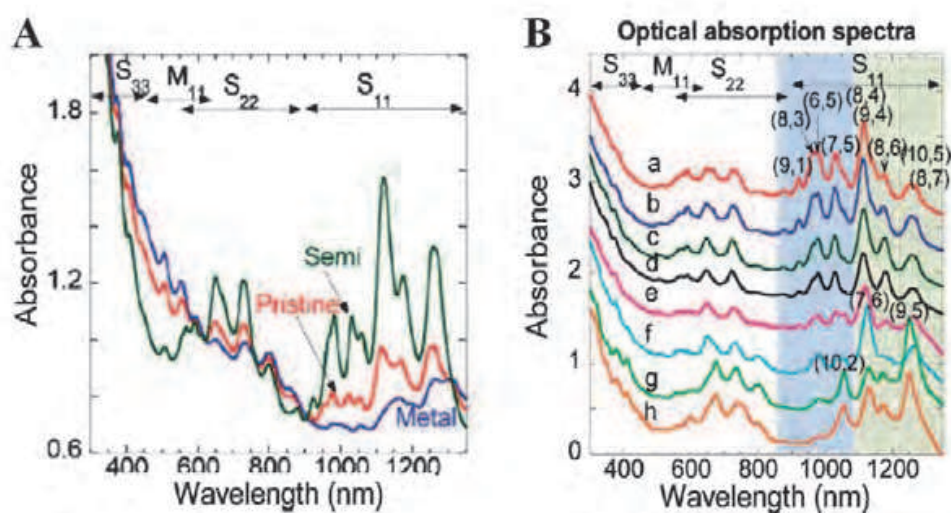


Fig. 9. (A) Optical absorption spectra (normalized at 620 nm). (B) Optical absorption spectra of the selectively enriched s-SWCNTs fractions by fractional collection with DOC eluants of different concentrations: (a) DOC 0.05 wt %, fraction 1, (b) DOC 0.05 wt %, fraction 3, (c) DOC 0.05 wt %, fraction 6, (d) DOC 0.05 wt %, fraction 9, (e) DOC 0.1 wt %, (f) DOC 0.25 wt %, (g) DOC 0.5 wt %, and (h) DOC 2 wt %. Reproduced from ref.59.

they found that smaller-diameter enriched s-SWCNTs were eluted first with the DOC solution at lower concentration and the larger-diameter enriched s-SWCNTs preferred to be eluted at higher DOC concentrations, as displayed in Figure 9B. Thus, diameter-selective enrichment of semiconducting fraction was achieved. These results indicate that agarose gel is effective for simultaneous sorting of CNTs by their electronic types and diameters, which predicts the SWCNT separation in a simple, low-cost and scalable way.

2.4.2 Ion-exchange chromatography

Ion exchange chromatography is a process that allows the separation of ions and polar molecules based on their charge. It can be used for almost any kind of charged molecule including large proteins, small nucleotides and amino acids. The surface of stationary phase displays ionic functional groups that interact with analyte ions of opposite charge. In comparison with size-exclusion chromatography, by anion exchange chromatography, more refined separation of SWCNTs can be achieved, not only by m/s, and diameter, but also by chirality. Earlier in 2003, Ming Zheng's group reported that bundled SWCNTs were effectively dispersed in water by their sonication in the presence of single-stranded DNA (ssDNA) and demonstrated that DNA-coated carbon nanotubes could be fractionized with different electronic structures by ion-exchange chromatography, as shown in Figure 10A and B.⁵¹ A strong anion-exchange column HQ20 (Applied Biosystems) functionalized by quarterized polyethyleneimine was chosen, which is expected to bind to the negatively charged phosphate groups of DNA. A linear salt gradient (0 to 0.9 M NaSCN in 20 mM MES buffer at pH 7) at a flow rate of 2 ml/min was used to fractionalize SWCNTs. Further by a systematic search of the ssDNA sequence with d(GT)*n*, *n* = 10 to 45, they found that wrapping of carbon nanotubes (CNTs) by ssDNA was sequence-dependent.⁵² The electrostatics of the DNA-CNT hybrid depends on tube diameter and electronic properties, enabling nanotube separation by anion exchange chromatography. Optical absorption and Raman spectroscopy showed that the early fractions were enriched in the smaller diameter and metallic tubes, whereas the fractions collected later were enriched in the larger diameter and semiconducting tubes.

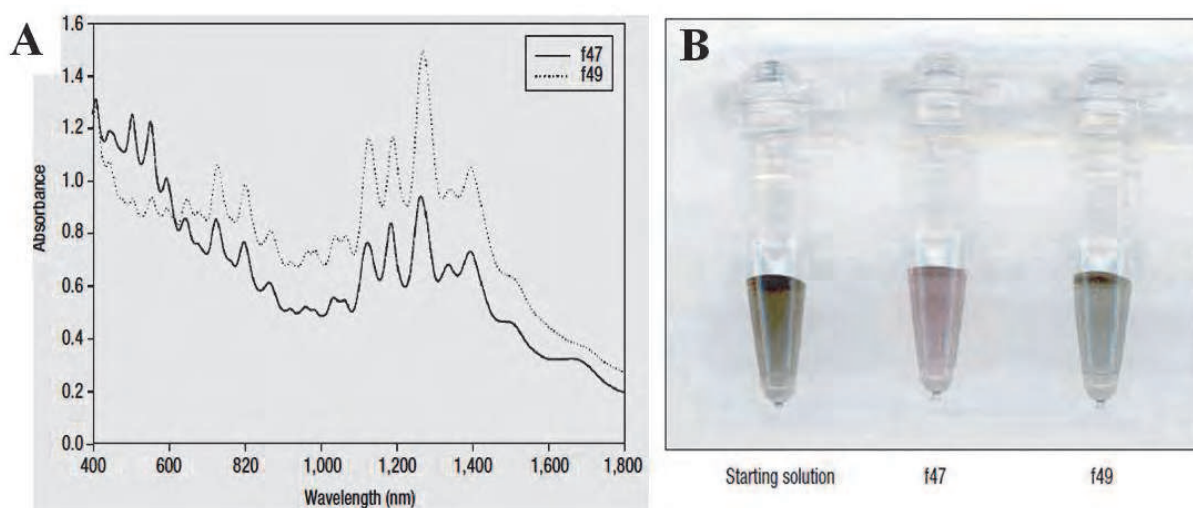


Fig. 10. Separation of DNA-CNT by anion exchange chromatography. (A) Electronic absorption spectra of two fractions f47 and f49. (B) Visual comparison of DNA-CNT solutions of the starting material, f47 and f49. Reproduced from ref.51.

However the separation resolution by this approach was not perfect. They proposed that a major issue was probably related to the broad distribution of tube length, since the dispersed CNTs were randomly cut during the long-term ultrasonic process, resulting in the tubes ranging from 50 to 1000 nm in length. Hence, in 2007, they combined the SEC with IEC to improve the separation resolution of small diameter SWCNTs.⁵³ They first narrowed the length distribution of SWCNTs by conducting SEC separation and then performed a chiral separation by the IEC. (9,1) tubes were separated from the same diameter but different chirality and much more abundant (6,5) species. Such exquisite separation was suggested as a result of chirality dependent interactions between DNA-wrapped SWCNTs and the IEX resin. These interactions could be electrostatic in nature, arising from chirality-dependent DNA-wrapping, and/or electrodynamic in nature, originating from chirality-dependent van der Waals forces.

Similar separation results were also reported by the group of Hongjie Dai.⁸ With separated SWCNT fraction, they fabricated FET devices with s-tubes of small diameters, achieving the high on-/off-current ($I_{\text{on}}/I_{\text{off}}$) ratios up to 105 owing to s-SWCNTs with only a few (n,m) chiralities in the fraction. This was the first time that chemically separated SWCNTs were used for short channel, all-semiconducting SWCNT electronics dominant by just a few (n,m)s.

After single-chiral tube specie was separated by SEC-IEC technique, by designing an effective search of a DNA library of 10^{60} in size, as shown in Figure 11A, all 12 major single-chirality semiconducting species were separated from a synthetic mixture by Ming Zheng group.⁵⁴ They identified more than 20 short DNA sequences, each of which recognizes and enables chromatographic purification of a particular nanotube species from the mixture. Recognition sequences exhibit a periodic purine-pyrimidines pattern, which can undergo hydrogen-bonding to form a two-dimensional sheet, and fold selectively on nanotubes into a well-ordered three-dimensional barrel, as illustrated in Figure 11B-D. They proposed that the ordered two-dimensional sheet and three dimensional barrel provided the structural basis for the observed DNA recognition of SWCNTs.

It is clearly indicated that for the surface properties of dispersed SWCNTs, which may be tailored by dispersants, and the interaction of dispersed CNTs with stationary phase are both critical issues to determine the selectivity and efficiency of chromatographic methods for SWCNT sorting. Ss-DNA appears more selective than SDS for the recognition of SWCNTs of different structures; however, it's very costly and currently difficult to be applied for a large-scale separation.

2.4.3 Electrokinetic chromatography

Electrokinetic chromatography is a well-established chromatography technique performed under electric field, taking the advantages of electrically driven force and the tunable selectivity of stationary phase. Earlier in 2003, Doorn et al. found that capillary electrophoresis (CE) could be performed on polymer-stabilized bundles and SDS suspensions of HiPco SWCNTs.⁵⁵ They showed, for poly(vinylpyrrolidone) (PVP)-stabilized tube bundles, that separations resulted in the fractions containing bundles of different electronic properties, which were dependent on bundle sizes.. CE on SDS dispersed CNT suspensions separated their large aggregates from smaller bundles and produced a relatively pure fraction of individual isolated nanotubes. Isolation of the aggregates from individual nanotubes more likely is attributed to the differences in molecular weight or diameter, leading to different migration behaviors under electric field.

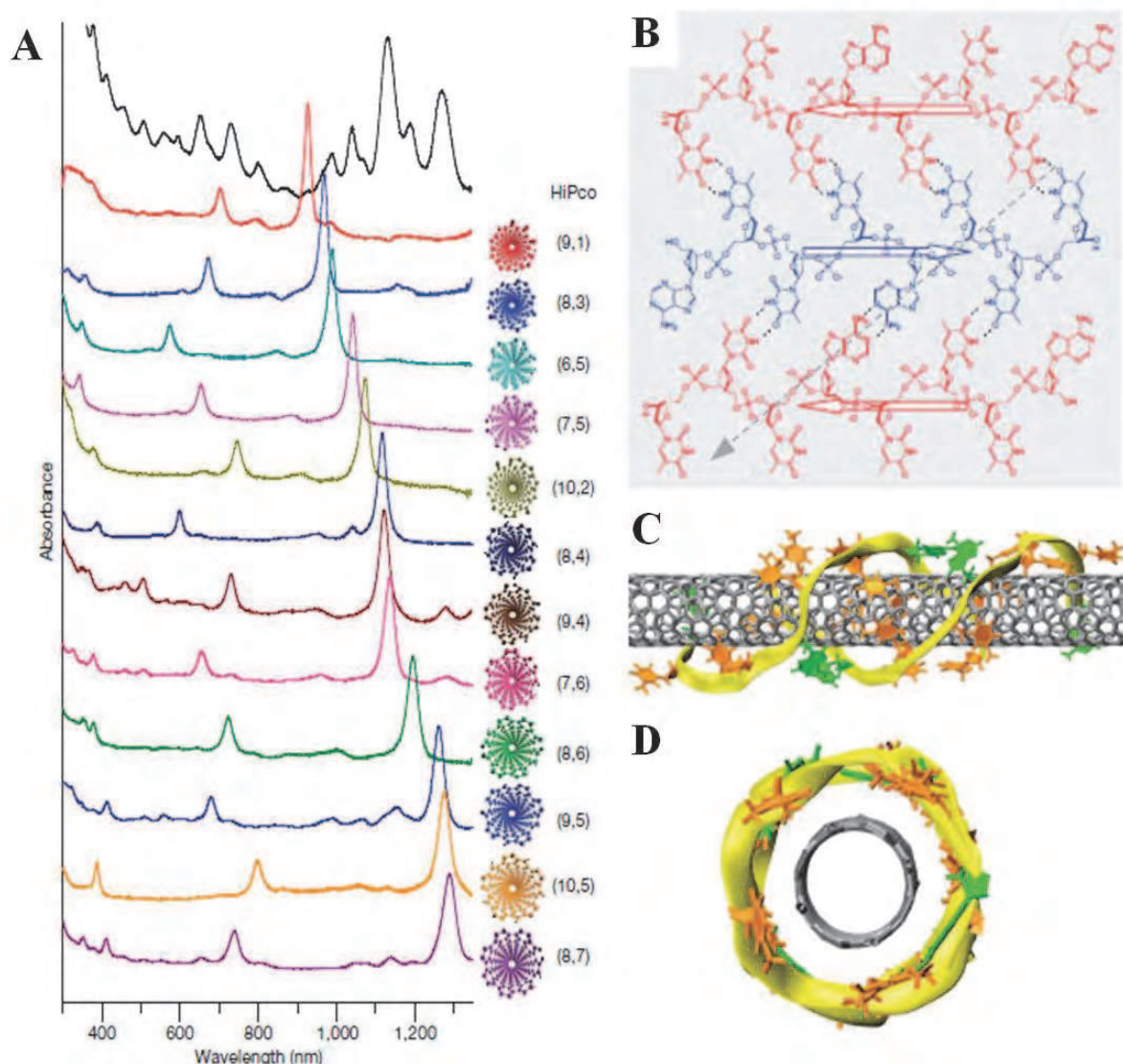


Fig. 11. (A) Optical absorption spectra and atomic structures. Ultraviolet-visible-near-infrared absorption spectra of 12 purified semiconducting SWCNTs (ranked according to the measured E_{11} absorption wavelength) and the starting HiPco mixture. The structure of each purified SWCNT species (viewed along the tube axis) and its (n,m) notation are given at the right side of the corresponding spectrum. (B) A 2D DNA sheet structure formed by three anti-parallel ATTTATTT strands. The dotted lines between bases indicate hydrogen bonds. The open arrow in each strand denotes 5' to 3' direction. The dashed grey arrow (top right to bottom left) represents the roll-up vector along which the DNA barrel in c is formed. (D) A DNA barrel on a (8,4) nanotube formed by rolling up a 2D DNA sheet composed of two hydrogen-bonded anti-parallel ATTTATTTATTT strands. (D) The structure in c viewed along the tube axis. Color coding: orange, thymine; green, adenine; yellow ribbons, backbones. Reproduced from ref.54.

Agarose gel electrophoresis, where agarose gel is the stationary phase, was successfully applied to sort SWCNTs by length, diameter and electronic type. In 2004, Heller et al. performed the concomitant length and diameter separation of SWCNTs by the gel electrophoresis.⁴⁶ HiPco SWCNTs were suspended in sodium cholate hydrate.

Electrophoresis was performed in a 7 × 10 cm, 1% agarose gel in TAE buffer (trisacetate-EDTA) with 50 mM sodium cholate at 100 V. Nanotube fractions were removed from the gel via electroelution by creating a second set of eight wells in the gel 4.5 cm from the original 40 μ L sample wells. Material was pipetted out of the second set of wells after 30 min of electrophoresis and repeatedly after an additional 5 min of applied potential to obtain six fractions. Highly resolved fractions of nanotubes with average lengths between 92 and 435 nm were sorted out. They demonstrated that nanotubes that have been cut shortest also possess the greatest relative enrichments of large-diameter species.

In 2008, by modulating the dispersant and electrophoresis condition, Tanaka et al. performed a better m/s separation of SWCNTs with agarose gel electrophoresis.⁵⁶ As illustrated in Figure 12, when the SWCNTs were isolated with SDS and embedded in agarose gel, only the m-SWCNTs were separated from the starting gel under an electric field. Such method is available for the sorting of other kinds of SWCNTs produced by arc and laser ablation methods. It affords a solution containing 70% pure m-SWCNTs and leaves a gel containing 95% pure s-SWCNTs. SDS and agarose played a synergic role for such separation effect.

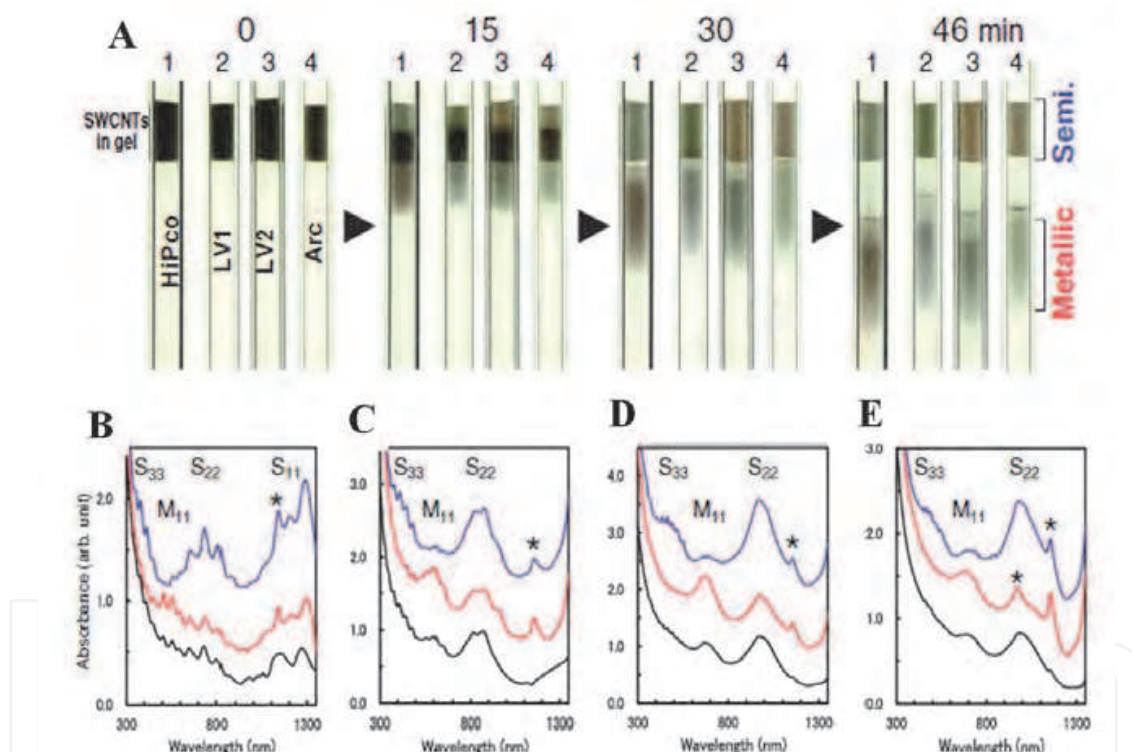


Fig. 12. M/s separation of various kinds of SWCNTs by AGE. (A) Sequential photographs showing the progress of separation. Tube 1, HiPco SWCNTs (1.0 ± 0.3 nm); tube 2, LV1 SWCNTs (1.2 ± 0.1 nm); tube 3, LV2 SWCNTs (1.4 ± 0.1 nm); and tube 4, Arc SWCNTs (1.4 ± 0.1 nm). Agarose gel concentrations of gel samples are 0.2% (HiPco, LV1, and LV2 SWCNTs) and 0.5% (Arc SWCNTs). (b-e) Absorption spectra of separated SWCNTs: (B) HiPco-, (C) LV1-, (D) LV2-, and (E) Arc-nanotubes. Blue and red spectra indicate semiconducting and metallic fractions, respectively. Results for the SWCNT dispersion before separation (black line). The peaks (970 and 1160 nm) derived from water are indicated by asterisks. Reproduced from ref.46.

Similar m/s separation results were also reported by Moshhammer et al.⁵⁰ They proposed that in the SDS-dispersed “starting” suspensions, s-SWCNTs were primarily in the form of small bundles whereas m-SWCNTs were predominantly suspended as individual tubes. They thought that the selective dispersion ability of SDS led to the different mobilities of m- and s-SWCNTs during the gel electrophoresis and finally sorted SWCNTs into two fractions. However such an explanation seems kind of intuitive and the detailed mechanism is still not clear. Considering that SDS dispersed SWCNTs are charged and dominant in micelles, by employing thionine (TN) as a probing molecule and monitoring color changes and absorption bands of TN molecules, we roughly estimate the migration and adsorption properties of SDS micelles in the gel as well as on SWCNT surfaces during the electrophoresis.⁵⁷ Figure 13A illustrated the electrophoresis results of SDS gel and SDS-SWCNT gels with and without the TN probe, respectively. It was observed that although TN is a positively charged dye, when dissolved in 1% SDS solution, TNs interact with SDS micelles to form negatively charged SDS-TN micelles and migrate toward the anode under the electric field. The electrophoresis of SDS-SWCNT gel with TNs also resulted in the separation of SWCNTs into two fractions. The staying fraction in the initial gel showed a Spanish green color, pretty similar to that observed in the staying fraction of SDS-SWCNT gel without TNs. The moving fraction, however, showed two color regions, a light blue region (arrow direction), which migrated faster and

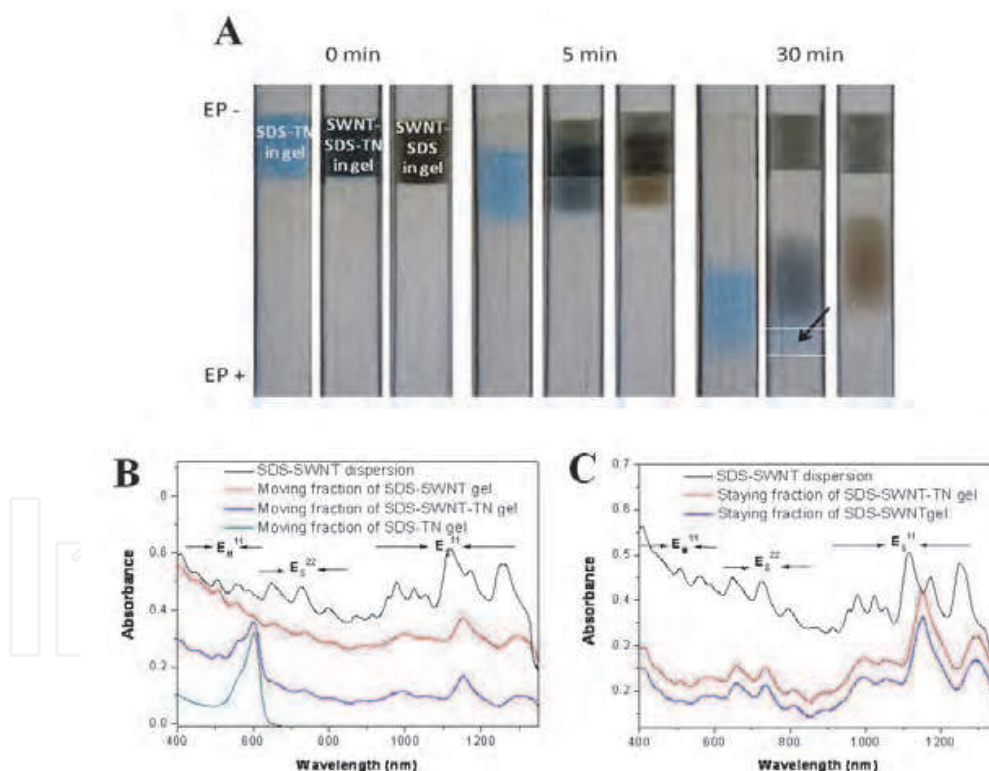


Fig. 13. (A) Sequential photographs of SDS-TN gel, SWCNT-SDS gel, and SWCNT-SDS-TN gel performed by agarose gel electrophoresis at 0, 5, and 30 min, respectively. (B) Optical absorption spectra of initial SDS-SWCNT dispersion and the moving fractions collected from the three kinds of gels after agarose gel electrophoresis shown a; (C) Optical absorption spectra of initial SDS-SWCNT dispersion as well as the staying fractions collected from SDS-SWCNT gels with and without TNs after agarose gel electrophoresis. Reproduced from ref.⁵⁷

displayed color similar to the case of SDS-TN, and a gray-blue region (the region above arrow), different from the color obtained with SDS-SWCNTs without TN probe. By analyzing their corresponding absorption spectra (Figure 13B and C), we proposed that the unique interaction of s-SWCNTs with agarose and the exfoliation of some SDS molecules from SDS-s-SWCNT entities lead to the m/s separation of SWCNTs. Understanding the role of SDS in the separation may help us to further optimize the purification of each fraction and develop a more effective and low-cost separation strategy.

3. Applications of separated SWCNTs

Separated m- and s-SWCNTs offer many unique opportunities for a variety of technological applications.⁶⁰ Regarding metallic nanotubes, in principle, they may carry an electrical current density of 4×10^9 A/cm², which is more than 1000 times greater than the copper. Since in 1997 first electrical devices based on metallic SWCNTs were fabricated,^{2, 5} their potential applications in nanocircuitry, conductive nanocomposites and transparent conductive films have been widely investigated. The electrical conductive performance in the films from the separated m-SWCNTs was consistently much better than that in the films from as-purified SWCNTs.⁶¹⁻⁶³ For examples, employing the DGU method, Hersam and co-workers enriched m-SWCNTs of different diameter ranges for transparent conductive films.⁶¹ For enriched metallic HiPco SWCNTs, the resulting film exhibited a sheet resistance of ~ 231 Ω /square for 75% optical transmittance at 550 nm, in comparison with ~ 1340 Ω /square in the reference film of the same optical transmittance from nonseparated HiPco SWCNTs. The films of enriched m-SWCNTs from laser-ablation- and arc-discharge-produced nanotube samples generally exhibited better performance, with less than 140 Ω /square sheet resistance at optical transmittances of over 70% in the visible and near-IR spectral regions.

The separated m-SWCNTs can also enhance the transparent conductive performance in composite films with conductive polymers.^{63, 64} Wang et al. prepared the composite films of enriched m-SWCNTs with poly(3,4-ethylenedioxythiophene)/poly-(styrenesulfonate) (PEDOT/PSS) in various compositions, by the spraying method.⁶³ The sheet resistance indicated that the composite films prepared from enriched m-SWCNTs were consistently and substantially better in device performance than those with nonseparated SWCNTs, which could be applied in electronic devices such as organic light-emitting diodes (OLEDs). In comparison to m-SWCNTs at a similar energy level, s-SWCNTs have a large density of electronic states and present diameter-dependent transition bands. S-SWCNTs are capable of carrying a high current with an electron/hole mobility. Hence, s-SWCNTs are widely investigated due to the pursued applications in field-emission transistors (FETs).^{9, 11, 15} To maximize the performance of FETs, it is desirable to obtain SWCNTs with similar diameter, chirality and thus band-gaps, and connect them in parallel to build each FET device for sufficient on-currents and reproducible device characteristics. The lengths of SWCNTs should also be controllable to meet the requirement of desired channel length. The well-refined separation of s-SWCNTs according to their length, diameter, and chirality are very significant for the application of SWCNTs in nanoelectronics.

S-SWCNTs separated from post-synthetic methods have already been used in FETs. For example, with a small-diameter s-SWCNT fraction separated by the SEC-IEC chromatography, Zheng et al. fabricated FET devices composed of separated s-SWCNTs in parallel, with high on-/off-current ($I_{\text{on}}/I_{\text{off}}$) ratios up to 10^5 owing to s-SWCNTs with only a few (n,m) chiralities in the fraction.⁸ In addition, nanoelectronic devices composed of single

chirality-enriched (10,5) tubes were fabricated with $I_{\text{on}}/I_{\text{off}}$ ratios as high as 10^6 .⁶⁵ The performance of the FETs made with the slightly bigger (10,5) tubes was better than the previously reported results using (7,6) and (8,4) tubes, even larger single-chirality s-SWCNTs were preferred in order to further improve the device performance. Similarly, the s-SWCNTs from agarose gel-based separation were also used in thin-film FETs, with performance better than that in devices fabricated with non-separated SWCNTs.⁴³ Recently Lee et al. demonstrated that the CoMoCat SWCNTs treated with diazonium salts and purified by DGU could be used to fabricate solution-processable FET devices with a full semiconductor device yield.⁶⁶ By increasing the network thickness, the effective mobility of the devices could be raised to $\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while keeping the on-off ratio higher than 5 000. The removal of impurities was found to be essential for achieving high-on-off-ratio devices. It was easier to achieve a full semiconductor device yield using the CoMoCat SWCNTs, which were very small in diameter and where the difference between chiralities were significantly large in terms of the reactivity with diazonium salts.

4. Conclusions and outlook

The separated SWCNTs with uniform structure, eg single electronic (m- or s-) type and chirality, have presented better performance than non-separated SWCNTs in nanoelectronics and thin-film devices. For real industry applications of SWCNTs, a simple, low-cost, high-purity and scale-up separation technique is highly demanded. So far by post-synthetic techniques, especially by density gradient ultracentrifugation and chromatography technique, SWCNTs have been separated according to their lengths, electronic types, diameters and chirality in a certain scale. For the density gradient ultracentrifugation method, the relative expensive equipment and the careful process make it less competitive than a well-established chromatography method. Considering the effective roles of stationary phase and mobile phase, we propose that the chromatography will offer more opportunities for the refined separation in a simple, lower-cost and scalable way for the industrial applications of SWCNTs.

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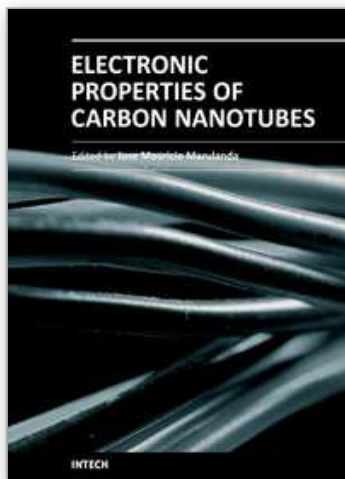
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Electronic Properties of Carbon Nanotubes

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Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. These one-dimensional (1D) graphene sheets rolled into a tubular form have been the target of many researchers around the world. This book concentrates on the semiconductor physics of carbon nanotubes, it brings unique insight into the phenomena encountered in the electronic structure when operating with carbon nanotubes. This book also presents to reader useful information on the fabrication and applications of these outstanding materials. The main objective of this book is to give in-depth understanding of the physics and electronic structure of carbon nanotubes. Readers of this book should have a strong background on physical electronics and semiconductor device physics. This book first discusses fabrication techniques followed by an analysis on the physical properties of carbon nanotubes, including density of states and electronic structures. Ultimately, the book pursues a significant amount of work in the industry applications of carbon nanotubes.

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51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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Phone: +86-21-62489820
Fax: +86-21-62489821

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