

# Towards monochiral carbon nanotubes: A review of progress in sorting of single-wall carbon nanotubes

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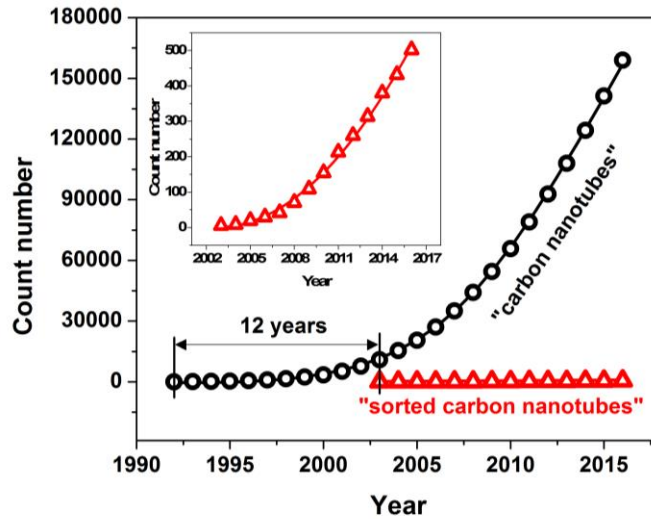
## **Abstract:**

The discovery of carbon nanotubes (CNTs) revealed that this new form of carbon can challenge traditional materials on many fronts. Remarkable electrical, thermal, mechanical and optical properties of individual CNTs have attracted significant attention, and so scientists have begun to consider their implementation in the everyday life. Unfortunately, CNT aggregates are composed of a wide range of CNT types, which has a strongly negative influence on the observed performance of macroscale devices made from them. Recently, however, it has become evident that different CNT types can be sorted according to length, diameter, electrical character, chiral angle and even handedness, which reignited interest in them. This review aims to demonstrate the state-of-the-art of all the mainstream methods of sorting CNTs (preferential synthesis, selective destruction, (di)electrophoresis, ultracentrifugation, chromatography, (co)polymer isolation and aqueous two-phase extraction). It is concluded with an overview of already tested applications using sorted CNTs and gives overlook of the field for the future.

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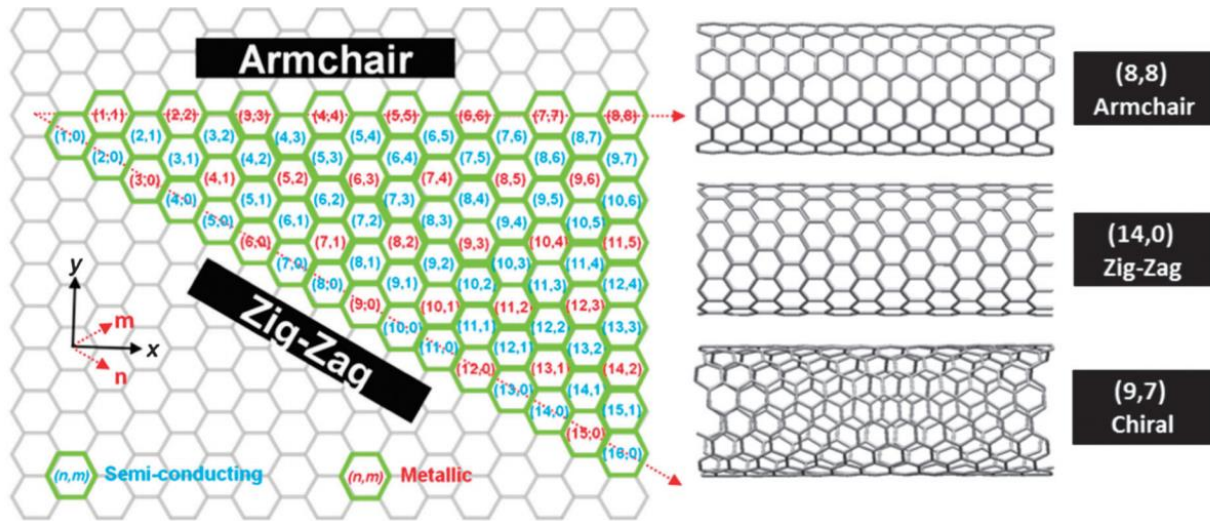
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## 1. Introduction



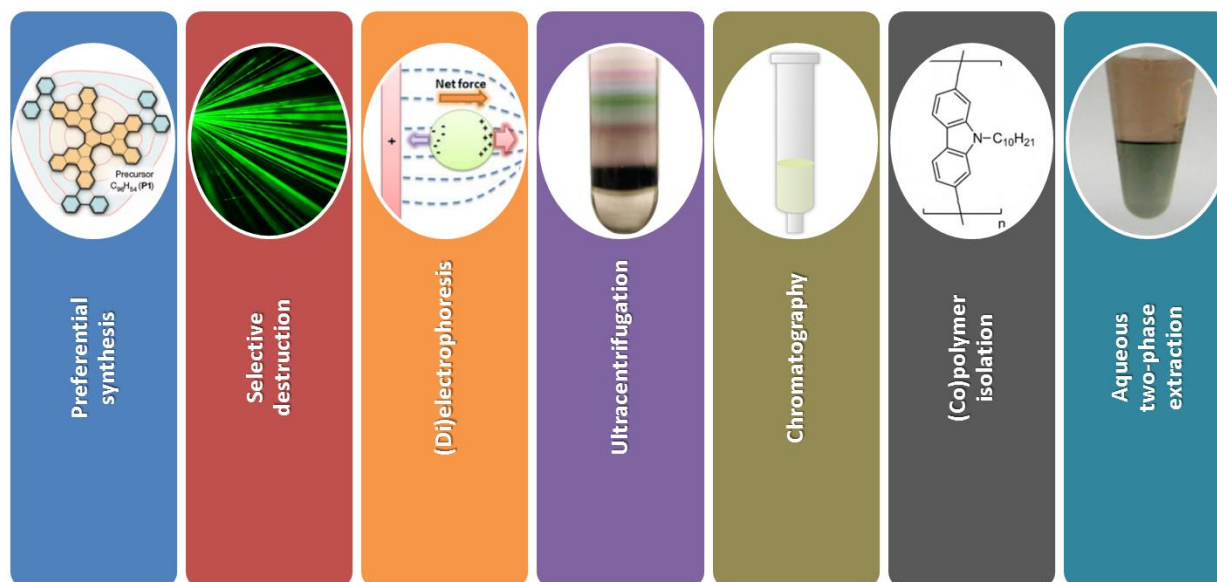
**Fig. 1.** Trends in research on carbon nanotubes and sorted carbon nanotubes represented as number of journal publications in the last 10 years as reported by the Web of Science database.

Single-wall carbon nanotubes (SWCNTs) are *quasi*-1D objects, which constitute one of the allotropic forms of carbon. They can be imagined as seamlessly rolled up hollow cylinders made of graphene (a sheet of carbon atoms) with diameters between 0.4 and 5 nm [1]. These nanostructures have revealed remarkable electrical [2-5], thermal [6-9], optical [10-12] and mechanical [13-15] properties, which have fuelled vigorous research all around the world (Fig. 1). CNTs come in a wide range of varieties depending how they are assembled from individual carbon atoms. The most common way to classify them is based on the way the conceptual graphene sheet is rolled up. So-called chirality or chiral vector, which is denoted by  $(n,m)$  indices, describes the number of unit vectors along two directions of hexagonal lattice to form a CNT. If  $n=m$ , a particular CNT is called *armchair*, and if  $m=0$  it is called *zig-zag* (apparent shapes of CNT “circumference” for these particular types). CNTs, which fall between these two extrema and do not satisfy any of the aforementioned rules are referred to as *chiral*.



**Fig. 2.** Helicity map of SWCNTs of different (n,m) chiral vectors. Reproduced with permission [1]. Copyright 2012, The Royal Society of Chemistry.

Most of the properties of CNTs are highly dependent on the chiral vector. A very good example is their electrical properties. If  $n - m$  is a multiple of 3, bands cross at the Fermi level, and thus CNTs are expected to show metallic or quasi-metallic character [16]. Otherwise they are moderately semiconducting. However, it has to be noted that there are exceptions to this rule due to the curvature effects in small diameter SWCNTs. In such case, certain CNTs which should be metallic are semiconducting and vice versa (e.g. (5,0) or (9,1)) [17]. Moreover, the chiral vector plays a fundamental role in a wide range of optical properties of CNTs. Electroluminescence [18], photoluminescence [19, 20] and other phenomena are directly influenced by the arrangement of atoms in a CNT. Possibly the most evident illustration of this phenomenon comes from the influential paper of Kataura *et al.*, who described how the inherent structure of a CNT affects the possible optical transitions [11]. It has been shown how Raman spectroscopy can give insight about the electrical character of a particular CNT. Lastly, chirality can also influence thermal conductivity [21] and mechanical properties [22, 23] to some extent.



**Fig. 3.** Helicity map of SWCNTs of different (n,m) chiral vectors. Reproduced and modified with permission [24-28]. Copyright, Macmillan Publishers (2010, 2014), Springer-Verlag (2009), American Chemical Society (2010, 2015).

A new avenue of research has been opened more than 10 years after their discovery when it has been found that sorting of individual CNTs is possible [29-33]. Since then, the scientific interest in this topic has been growing at an exponential rate as presented in Fig. 1 and indicated by other review articles [34-36]. The challenge of sorting CNTs resembles the problem of Cinderella, who had a hard time separating lentils from ash. Over the years, the CNT separation methods of limited scope have become much more advanced. Currently CNT sorting by diameter, length, electrical character, chirality and handedness is possible by an arsenal of techniques (Fig. 3).

In this review article, comprehensive description of the up to date progress in sorting of SWCNTs using all the main-stream separation methods is given (Fig. 3). Possible applications of chirality-sorted CNT material are highlighted with suggestions for the most immediate directions of research, which should be taken to make further advances of the field.

## **2. Sorting methods**

The methods developed to obtain CNTs of particular type can be divided into three categories: preferential synthesis, selective destruction and post-synthesis sorting. In the first approach, synthesis parameters are tuned to produce CNTs of predetermined chiral angle. The main difficulty is to engineer a catalyst or a CNT precursor to accomplish the target. In the second method, pre-synthesized CNT material is subjected to conditions, which are able to preferentially etch away unwanted CNT types. Some of the material is sacrificed, which has a negative effect on the yield of the process. Lastly, there is a wide range of techniques, which can resolve complex mixtures of CNTs in post-synthetic sorting. Many types of CNTs are differentiated into fractions. In some cases, to reach the highest level of enrichment post-processing is carried out using material already enriched with certain CNTs from preferential synthesis. In this section, we present the methods and stress their strong and weak points.

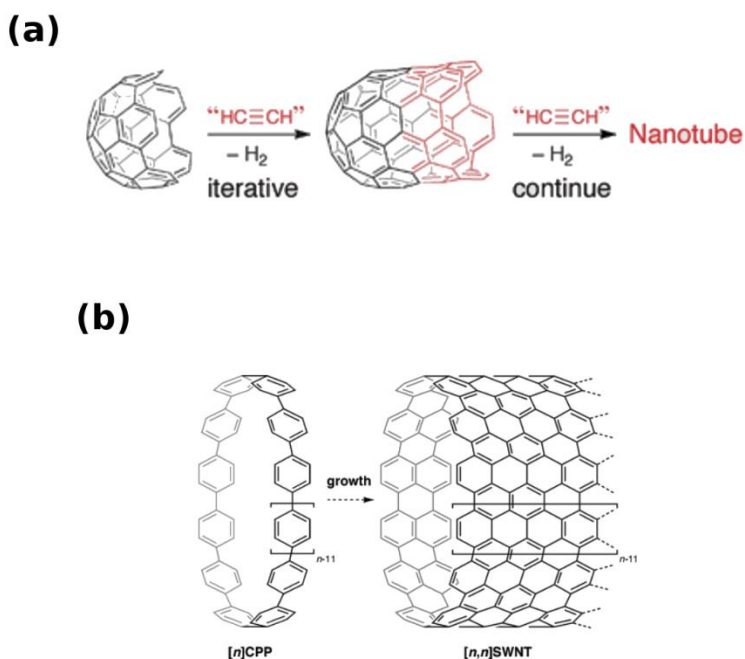
### **2.1 Preferential synthesis**

Direct synthesis of CNTs of particular chiral angle has been considered as the “Holy Grail” of the nanotube science ever since the material was discovered. However, designing the process with such level of precision at the nanoscale is a tremendous challenge, and so we have to accept half-measures for now. Nevertheless, the synthetic routes to be presented have already shown promising results by giving CNT material with significant enrichment with CNTs of certain chiral angles.

#### *2.1.1 Organic synthesis*

From the organic chemistry point of view, synthesis of CNTs of particular chiral angle may be theoretically possible by executing total synthesis. In such process, an appropriate CNT seed

would be formed, from which CNT would then be elongated by sequential addition of appropriate building blocks. Such a seed could take a form of half-a-buckyball cap or cycloparaphenylene (CPP) / aromatic belt (Fig. 4), to which addition of “monomers” would ultimately produce semi-open and fully-open CNTs, respectively.



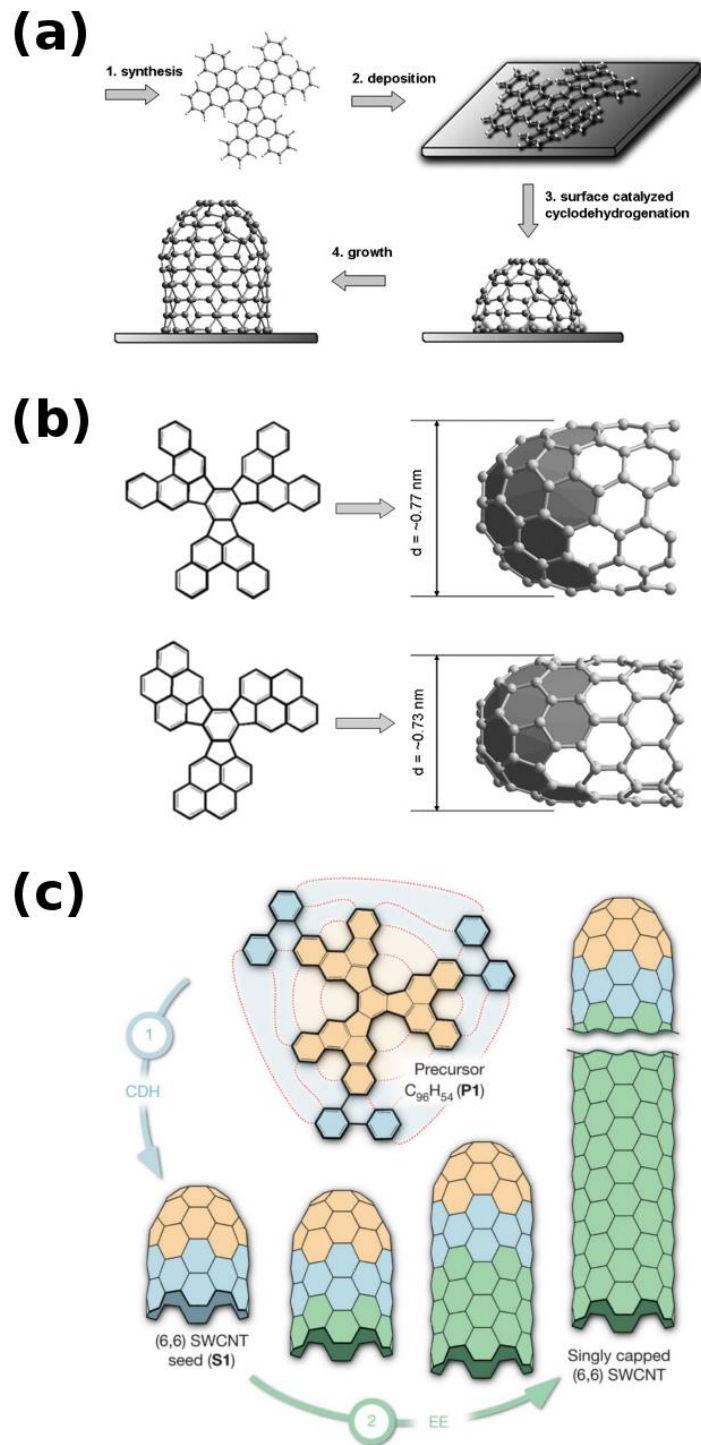
**Fig. 4.** Assembly of CNTs of particular chiral index from (a) half-a-buckyball cap and (b) cycloparaphenylene. Reproduced and modified with permission [37, 38]. Copyright, The Royal Society of Chemistry (2011), Wiley-VCH (2010).

It has been demonstrated theoretically [37] and experimentally on a model compounds [39] that the growth from half-a-buckyball seeds is indeed possible by *e.g.* Diels-Alders cycloaddition of benzene [39] or acetylene derivative [40]. Yu *et al.* presented how such cap can be formed and grew SWCNTs from it [41]. However, under these conditions, two populations of CNTs were formed: small-diameter (<0.7 nm) and large-diameter (>1.4 nm). Since the latter family was significantly bigger than the used CNT seed, the authors postulated that the caps could rearrange

to form bigger seeds by coalescence. The proportion of one fraction to the other was correlated with oxidation temperature, which opened up fullerenes to make the seeds. Moreover, the stronger the oxidation conditions, the thinner were the produced SWCNTs from these seeds.

Furthermore, interesting results came from attempts to synthesize the end-cap seed by total synthesis. The authors were able to produce complicated seed precursor molecules (Fig. 5a,b), but the CNT growth from them was met with limited success [42, 43]. However, when they designed a  $C_{96}H_{54}$  precursor, which transformed into an end-cap by cyclodehydrogenation, with the shortest possible “straight” segment (Fig. 5c), (6,6) CNTs have grown from the seed much more readily [24] (planar metal surface catalyst was also used instead of metal nanoparticles). The approach in fact could be classified as cloning, which will be described in the next section.

The corresponding attempts to carry out bottom-up synthesis from cycloparaphenylenes or aromatic belts, first of all, yielded a big family of these macrocycles as indicated in a review by Lewis [44]. A side product of these efforts has been the development of a diverse array of synthetic techniques to obtain them since they were first reported in 2008. Besides the potential use of these macromolecules as CNT seeds, they also revealed very interesting properties. For example, the larger the cycloparaphenylene ring, the bigger is the minimum energy to excite it. Coming back to the main topic, as shown by modeling of Li *et al.*, the growth rate of CNTs can be dominated by diameter or chiral angle of the seed [45]. The mode is dependent on the type of active species (Diels-Alder or ethynyl radical addition mechanism), which act as incoming building blocks. Formation of CNTs from cycloparaphenylene seeds (1.2 – 2.2 in diameter) was first confirmed experimentally by Omachi in 2013 [46]. The average diameter of the SWCNTs was close to the diameter of the employed seed this time..

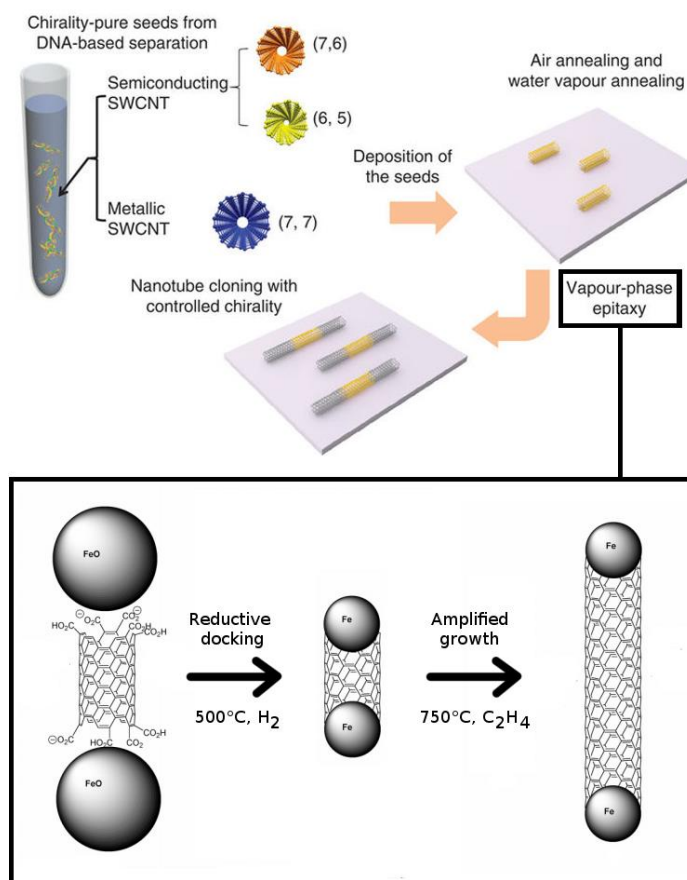


**Fig. 5.** (a) mechanism of cap formation from precursor molecule, (b) cyclodehydrogenation to form a cap for CNT growth, (c) assembly of extended cap for CNT growth. Reproduced and modified with permission [24, 42]. Copyright Elsevier (2010), Macmillan Publishers (2014).



### 2.1.2 Cloning

In 2006, Smalley *et al.* first proposed that CNTs of particular type could be used as seeds to amplify them while preserving their atomistic structure [47]. In the procedure (later called “*CNT cloning*”) parent CNTs are cut into shorter segments and then such templates are elongated by CVD with the assistance of a catalyst such as Fe (Fig. 6). In the initial study, SWCNTs were successfully amplified, while diameter and surface orientation was preserved. It has to be noted that the CNTs seeds had carboxylic groups at the ends (introduced during CNT cutting), which had to be first removed by the catalyst in the course of reductive activation under hydrogen.



**Fig. 6.** Cloning of CNTs and its mechanism. Reproduced and modified with permission [47, 48].

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At that point, there was no experimental evidence that the CNT extensions grown from the templates are in fact of the same chirality. Yao and co-workers have attempted catalyst-free synthesis from the seeds [49]. They have shown that the yield of the process was relatively low (9%), but could be improved (up to 40%) when quartz was used as a substrate and the temperature of the process was increased to 975°C. In their process however, the functional groups present at the end of the seeds were removed to activate the templates by high-temperature annealing under argon at 700°C. Based on the fact that the diameter and Raman spectra were consistent along the CNT axis, the authors concluded that the initial (n,m) chiral indices must have been preserved.

Next, Liu *et al.* used (7,6), (6,5), and (7,7) CNTs as templates, which were isolated by DNA-based chromatography [48]. During catalyst-free growth on quartz these CNTs were elongated by two orders of magnitude in length. Again Raman spectroscopy (measurements in RBM area) was used as a proof that the process was successful. It would be interesting to see confirmation of these results using electron diffraction patterns. The team later extended the study to CNTs of 7 different CNT helicities having a wide range of chiral angles, which gave insight about the cloning mechanism [50]. It was confirmed that the wider the chiral angle of the seed the larger the amplification growth rate. That however was found inversely proportional to the active lifetime of the growth. Armchair CNTs (6,6) and (7,7) revealed short active lifetimes of the growth and exceptionally small saturation lengths – 1/3 that of (6,5) CNTs. As pointed out by the authors, it would be vital to carry out theoretical simulations what is the underlying reason. Maybe the fully metallic character (in the absence of bandgap) affects the synthesis course in the way, which is still unknown to us.

### 2.1.3 Catalyst engineering

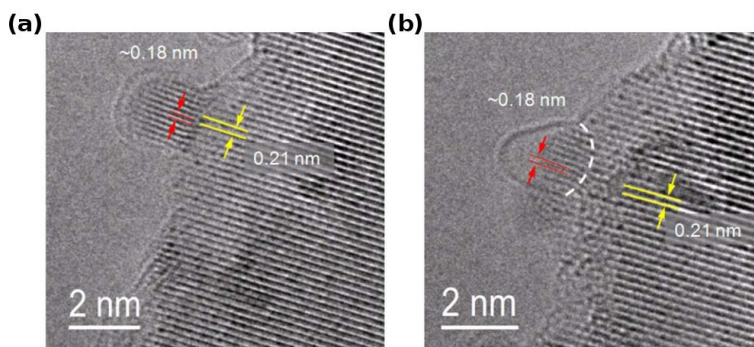
Because CNTs are most commonly produced by catalytic chemical vapor deposition (c-CVD), efforts are taken to design catalytic systems, which would offer high activity, selectivity and stability at low cost. Unfortunately, it is a challenging task to synthesize particular type of CNTs with high efficiency, and so often selectivity is achieved at the expense of yield [51]. Nevertheless, significant achievements on the front of chirality selective synthesis have been accomplished already (Table 1).

Table 1. Catalyst systems for selective synthesis of CNTs.

Catalyst system	Feedstock	Preferential selectivity	Ref.
CoMo/SiO <sub>2</sub>	CO	(6,5), (7,5)	[52]
CoFe/USY zeolite	C <sub>2</sub> H <sub>5</sub> OH	(6,5), (7,5)	[53]
Co <sub>x</sub> Mg <sub>1-x</sub> O	CO	(6,5) or (7,6), (9,4)	[54]
CoPt/SiO <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH	(6,5)	[55]
FeRu/SiO <sub>2</sub>	CH <sub>4</sub>	(6,5) or (8,4), (7,6), (7,5)	[56]
FeCu/MgO	CO	(6,5)	[57-59]
CoSO <sub>4</sub> /SiO <sub>2</sub>	CO	(9,8)	[60-62]
Co <sub>7</sub> W <sub>6</sub> /SiO <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH	(12,6) or (16,0) or (14,4)	[63, 64]
Ferrocene, CS <sub>2</sub>	CH <sub>4</sub>	(12,12), (9,9)	[65]
Ferrocene, NH <sub>3</sub>	CO, CO <sub>2</sub>	(13,12), (12,11), (13,11)	[66]

One of the first milestones has been reached by Bachilo *et al.*, who reported formation of predominantly (6,5) and (7,6) CNTs when CO was decomposed by a CoMo/SiO<sub>2</sub> catalyst [52]. The key was the bimetallic catalyst, wherein Co catalyst aggregation was suppressed by Mo oxides. The growth was also carried out at 750°C to prevent Co from sintering. As a consequence, material of narrow (n,m) distribution could be synthesized. Subsequent work indicated that lowering the temperature to 650°C and substituting Mo for Fe can improve the selectivity towards near-armchair CNTs [53]. The authors postulated that armchair and near-armchair CNT cap is more stable on the catalyst under these conditions, and so such CNTs are

preferentially extruded. Environmental TEM study confirmed that Co nanoparticles are ideal catalyst seeds to grow CNTs of narrow diameter distribution because of their high stability [54].



**Fig. 7.** Initial cap formation on Co catalyst. Reproduced and modified with permission [54]. Copyright 2012, Macmillan Publishers.

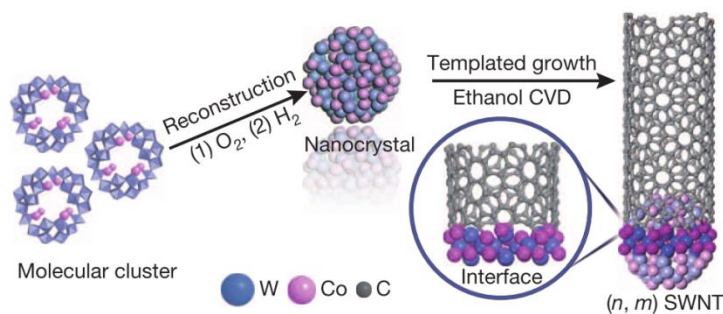
Their structure stays uniform with just slight fluctuations during CNT growth (Fig. 7). Interestingly, further decrease in temperature down to 400°C results in preferential growth of (7,6) and (9,4) CNTs. Lower temperature deactivates smaller catalyst particles, and thus CNTs of bigger diameter are formed.

Alloying of Co with Pt revealed that synthesis can be dominated with (6,5) CNTs also at high temperature [55]. A metal such as Pt was found to have a stronger anti-sintering action on Co than the metals mentioned before. These results are a strong proof of CoPt stability because we would normally expect formation of large diameter CNTs under these conditions.

Growth of (6,5) CNTs is also possible by using a Co-free catalyst. FeRu was found effective for synthesis of predominantly this type of CNTs at 600°C [56]. Similar to earlier results, increase in temperature (to 850°C in this case) resulted in driving the synthesis towards higher diameter CNTs: (8,4), (7,6) and (7,5). After the development of this catalytic system, a search was initiated to find a replacement for expensive Ru, which could impede commercialization of this

solution. Copper was proposed as suitable alternative [57-59]. FeCu was able to grow mainly (6,5) CNTs at 600°C even though monometallic catalysts made of Fe or Cu produced multi-wall CNTs or no CNTs under the same conditions, respectively. Cu (besides keeping Fe from sintering) is thought to facilitate reduction of iron oxides to metallic iron, from which CNTs can be readily assembled [58]. Moreover, the concentration of these two metals determines the purity of the resulting material, but have little effect on the chirality distribution [59].

Larger diameter chiralities can also be obtained. CoSO<sub>4</sub>/SiO<sub>2</sub> system showed high selectivity towards (9,8) CNTs [60]. Herein the role of sulfur-based functional groups is to prevent Co clusters from unwanted sintering – similarly to Fe, Me, Ru, or Pt in the previous studies. In the absence of sulfur groups the synthesis is not selective using Co/SiO<sub>2</sub>, but it can be recovered by S doping [62]. What is more, when the temperature of calcination is increased from 400°C to 800°C the selectivity shifts from (9,8) to smaller-diameter CNTs such as (6,5) [61]. Co<sub>147</sub> cluster (1.22 nm) probably rearranges to Co<sub>55</sub> (0.93 nm) as deduced from the stability window. These diameters are in good accordance with those of (9,8) and (6,5) CNTs, respectively.



**Fig. 8.** Templated growth from Co<sub>7</sub>W<sub>6</sub> catalyst. Reproduced with permission [63]. Copyright 2014, Macmillan Publishers.

An interesting approach was proposed by Yang *et al.*, who established a technique of preparation of Co-W alloys at low temperatures [63]. Decomposition of W and Co molecular cluster at about 1000°C can produce a bimetallic alloy as compared to circa 2400°C, which would be required if the material would be constructed from elements (Fig. 8). As formed Co<sub>7</sub>W<sub>6</sub> nanocrystals have a good structural match with (12,6) CNTs, which can be grown from them with high selectivity. It has been recently reported that such catalyst system can also be produced by simple magnetron sputtering [64]. Unfortunately, the results have shown that W compounds have very low stability under synthesis conditions and most of W atoms disappear within first minutes of reaction. It would be crucial to investigate whether it is possible to anchor/protect these nanoparticles to improve their stability while preserving the high selectivity.

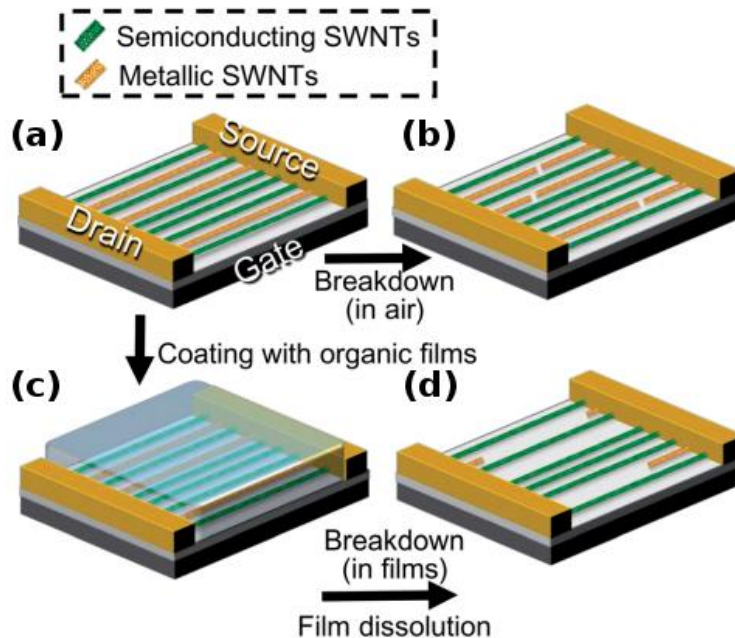
Selective synthesis of CNTs is not just about the catalyst, but there are other factors which have to be taken into consideration. For instance, it has been shown that a careful selection of reaction promoter can result in preferential synthesis of metallic CNTs [65]. Ferrocene catalyst when promoted with CS<sub>2</sub> gave mostly (12,12) and (9,9) armchair CNTs as compared with lack of selectivity when thiophene was employed for this purpose as usual [67]. In addition to other phenomena, sulfur counteracts sintering of iron clusters made from ferrocene. CS<sub>2</sub> with lower decomposition temperature than thiophene is able to produce smaller iron catalyst nanoparticles, which are then useful for templated growth of particular CNTs. Obtaining near-armchair CNTs is also possible when NH<sub>3</sub> is used as etchant during synthesis. [66] Catalyst pretreatment by NH<sub>3</sub> is suspected as the origin of this effect [68]. It has been determined that NH<sub>3</sub> causes catalyst restructuring [69] for epitaxial growth of CNTs [70]. In addition, NH<sub>3</sub> was found to affect the kinetics of CNT growth by making the process slower, but more controllable [71].

## 2.2 Selective destruction

In contrast to synthesis of particular CNTs or their isolation, one can also remove the unwanted ones by preferential destruction. There is a range of available techniques to accomplish this goal, which are simple in nature, but much less precise than other sorting methods. Most often, these strategies are directed at differentiation between metallic and semiconducting CNTs.

### 2.2.1 Electrical breakdown

It was observed that if semiconducting CNTs were protected by electrostatically coupled gate electrode metallic CNTs could be cut and etched by high current densities in the ambient [33]. The method was initially developed to study transport properties of multi-wall CNTs when they were stripped away from their constituting walls by sufficiently high current in a stepwise fashion [72]. Each single-wall CNT is better exposed to air than the inner walls of a multi-wall CNT. Because of that selective removal of more conducting metallic single-wall CNTs by current-induced oxidation can be used to enrich semiconducting character of the sample. It has to be noted however that in the process some of the semiconducting single-wall CNTs are sacrificed, but to a much smaller extent when gating field is applied [73]. Probably the best measure to show the magnitude of semiconducting enrichment is to create a field-effect transistor (FET) from CNTs and establish its on-off ratio. Although modest by today's standards, these initial studies showed switching ratios up to  $10^4$ , which were very encouraging at that time. Otsuka and co-workers took this problem a step further and coated CNTs with a 50-nm thick organic film to destroy metallic CNTs by Joule heating to a larger extent [74]. Greater length removal than in air was possible because a hot spot formed by high current could propagate and etch CNTs across a longer distance (Fig. 9). The absence of oxygen suppressed rapid local combustion of the material. Again up to  $10^4$  on-off ratios were obtained.



**Fig. 9.** (a,b) Electrical breakdown in air, (a,c,d) Electrical breakdown in organic films. Reproduced and modified with permission [74]. Copyright 2014, The Royal Society of Chemistry.

Enrichment of a sample with semiconducting CNTs is often carried out to produce CNT-based transistors of improved performance as compared with traditional materials. It has to be noted that the required purity to make a successful implementation of this technology is set at CNTs with less than 0.0001% contamination with metallic CNTs [75]. It may be challenging to accomplish this goal through electrical breakdown. In addition to the technical problem of constructing three-electrode devices to carry it out on a small amount of CNTs, most of the material would need to be sacrificed each time to reach this level of purity.

### 2.2.2 Light-assisted breakdown

High power long-arc xenon lamp is able to increase the content of semiconducting CNTs in a sample from 50% to 95% in 60 minutes [76]. Small diameter ( $d < 1$  nm) metallic CNTs are



destroyed much faster than the semiconducting ones, which leads to enrichment. FETs were produced to evaluate the performance of the predominantly semiconducting CNT material. On/off ratios on the order of  $10^4$  were obtained. It was found that majority of the metallic CNTs are removed at the beginning and prolonged treatment destroyed more and more semiconducting CNTs.

In a similar way, preferential removal of metallic CNTs can be accomplished by laser irradiation [77]. Interestingly, semiconducting CNTs with high chiral angles (*e.g.* (7,6)  $\theta = 27.5^\circ$ ) are more easily destroyed than those with low chiral angles (*e.g.* (11,1)  $\theta = 4.3^\circ$ ). Removal of 95% of metallic CNTs by irradiation can be accomplished much faster when the sample is pretreated with 4-brominebenzenediazonium salt, which binds selectively to metallic CNTs [78, 79]. In such case the process takes minutes instead of hours.

Yudasaka *et al.* showed very interesting results, wherein light irradiation can be used for selective breakdown of semiconducting CNTs when they are suspended in  $H_2O_2$  [80]. Moreover, by varying the wavelength or time of treatment it is possible to target removal of CNTs of certain diameter.

### 2.2.3 Plasma-assisted breakdown

Methane [81] and hydrogen [82] plasma can also etch away metallic CNTs, and so the material becomes enriched with semiconducting character. In addition to metallicity differentiation, smaller diameter CNTs are removed first due to higher strain in the C–C bonds. As a consequence, the treatment also improves the diameter distribution. What is more, during the treatment metallic nanoparticles (catalyst residue) are detached from CNT ends effectively cleaning the material. The process is scalable and can produce SWCNT material having  $10^4$  –  $10^5$  switching ratios.

#### 2.2.4 Microwave-assisted breakdown

Similar effects (diameter narrowing, purification from residual catalyst and removal of metallic CNTs) can be accomplished by subjecting CNTs to microwave radiation [83]. It was demonstrated that a household microwave oven is capable of carrying out the process. After certain amount of time, the removal of CNTs is indiscriminate and etches away also semiconducting ones, so the time of the treatment has to be carefully optimized [84, 85].

#### 2.2.5 Functionalization

To enhance the differences between metallic and semiconducting CNTs (for subsequent processing) selective side-wall chemistry can be employed. In such case, unwanted types are much easier to separate by a range of post-synthesis sorting methods (*e.g.* electrophoresis, chromatography). There are many chemical reactions available for this purpose (Table 2).

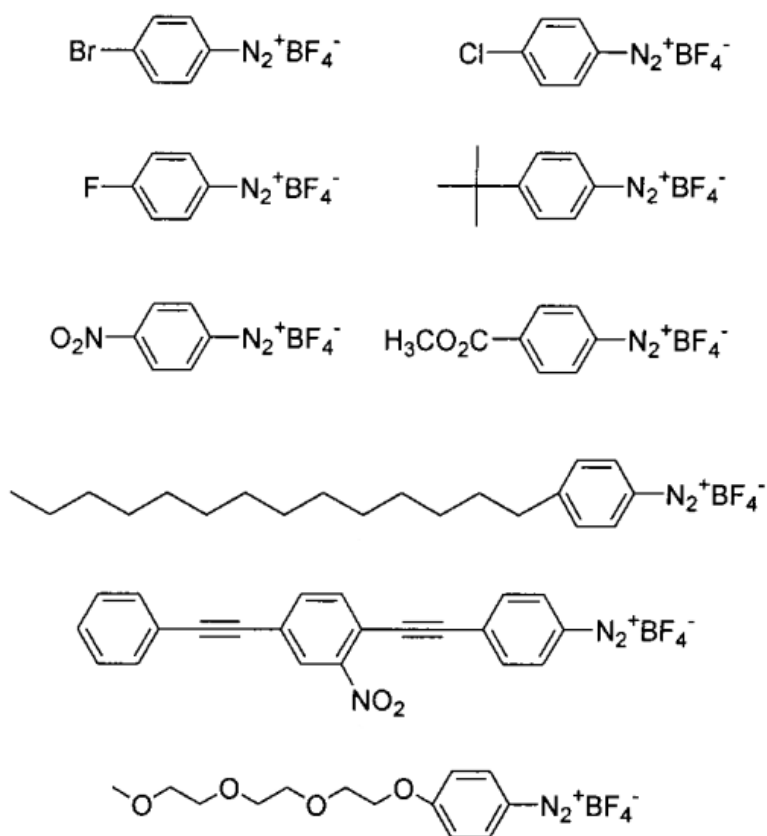
Table 2. Methods of selective functionalization of CNTs for enrichment of the parent material.

Separation type	Reactant	Preferentially attacks	Ref.
d	air	Small diameter CNTs	[86, 87]
d, (n,m)	air	Small diameter CNTs of a high chiral angle	[88]
d	O <sub>3</sub>	Small diameter CNTs	[89, 90]
d, M/S	H <sub>2</sub> O <sub>2</sub>	Semiconducting CNTs of small diameter	[91, 92]
d, M/S	H <sub>2</sub> O <sub>2</sub>	Semiconducting CNTs of selected diameter	[80]
M/S	SO <sub>3</sub>	Semiconducting CNTs	[93]
d, M/S	NO <sub>2</sub>	Metallic CNTs of small diameter*	[94]
d, M/S	H <sub>2</sub> SO <sub>4</sub> /HNO <sub>3</sub>	Metallic CNTs of small diameter	[95, 96]
d, M/S	F <sub>2</sub>	Metallic CNTs of small diameter	[97]
d, M/S	RLi	Metallic CNTs of small diameter	[98]
d, M/S	RMgX	Metallic CNTs of small diameter	[98]
M/S	HNO <sub>3</sub>	Metallic CNTs	[99]
M/S	OsO <sub>4</sub>	Metallic CNTs	[100]
M/S	NaClO <sub>x</sub>	Metallic CNTs	[101]
M/S	CCl <sub>2</sub>	Metallic CNTs	[102, 103]
M/S	RN <sub>2</sub> X	Metallic CNTs	[79, 104-107]

d (diameter), (n,m) (chiral angle), M/S (metallic/semiconducting character)

\* Modeling results

For instance, charged or charge-neutral functional groups can be introduced to alter mobility of particular CNT types [79]. It has been demonstrated how CNTs selectively functionalized by diazonium chemistry can be separated by electrophoresis into metallic and semiconducting fractions [104, 108]. As a matter of fact, diazotization of metallic CNTs is probably one of the most explored methods to accomplish differentiation of CNTs by electrical character. The presence of electrons near the Fermi level in metallic CNTs enables bond formation with diazonium salts much more easily than in the case of semiconducting CNTs [109]. The reaction is not limited to commonly employed p-hydroxybenzene marker, but much more sophisticated moieties can also be used [110] (Fig. 10).



**Fig. 10.** Examples of aryl diazonium salts used for functionalization of metallic CNTs. Reproduced and modified with permission [110]. Copyright 2001, American Chemical Society.

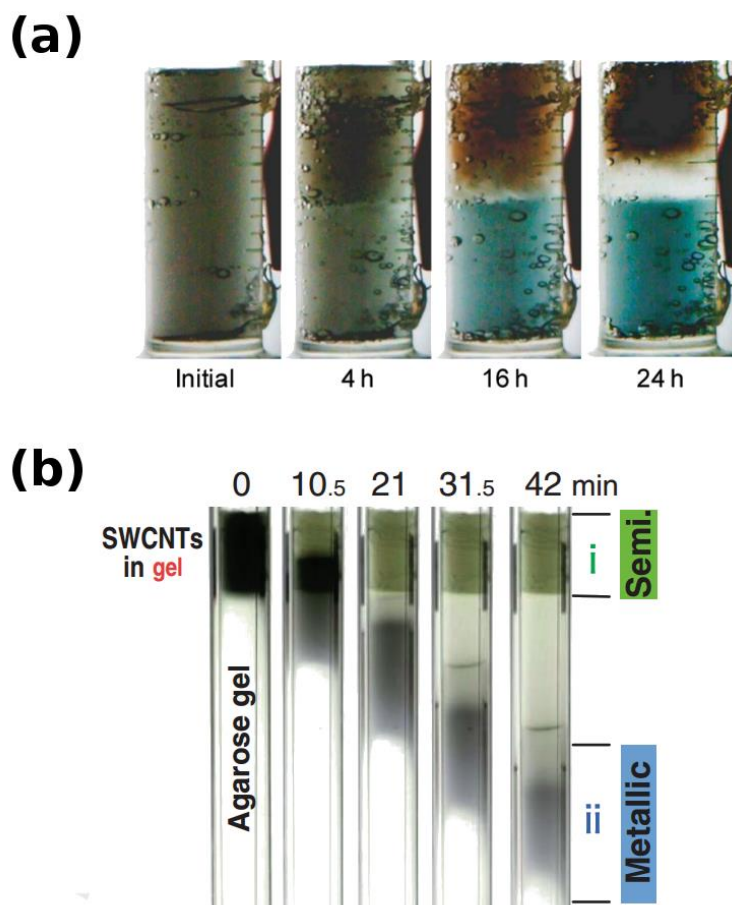
Such functionalization can also make the selected CNTs more soluble in a desired solvent or ready for extraction with a particular sensing molecule in a process similar to molecular recognition. Moreover, functional groups present in the diazonium salt can be selected such that they can be (de)protonated, which makes the subsequent separation by *e.g.* electrophoresis much more powerful. Finally, upon thermal annealing these functional groups grafted on the surface of metallic CNTs can be often removed, which regenerates the electrical character of parent CNTs [104]. Besides that, diazonium chemistry can also be helpful for isolation of complementary metallic CNTs from a given sample. The versatile nature of functionalization of CNTs with diazonium salts made this sorting route very popular.

It is worth to note that for some applications, removal of particular CNTs is not necessary, but it is sufficient to make them inactive. For example, aforementioned diazonium chemistry or functionalization with dichlorocarbenes [102, 103] opens bandgap in metallic CNTs at the Fermi level, which effectively converts them to semiconductors. Such undivided material may still show appropriate performance for its implementation in FETs

Furthermore, as the literature shows, the methods, which separate CNTs simply by diameter, are often underappreciated. It is true that CNT fractions with particular diameter distribution may have limited use by themselves, but such pre-sorted fractions are much easier to resolve into components of particular chirality by more complex techniques such as chromatography or aqueous two-phase extraction. Narrowing down the diameter distribution, which is often relatively easy to execute, limits the number of individual species in the mixture to be separated from each other.

### 2.3 (Di)electrophoresis

Application of electric field sorts individual CNT types according to their mobilities through a selected medium. We can distinguish three variations of this method, which are employed for CNTs: free electrophoresis, capillary electrophoresis and gel electrophoresis. In free electrolysis, separation is accomplished without a matrix, which could have a negative interaction with the analyte (Fig. 11a).



**Fig. 11.** (a) free-solution electrophoresis, (b) gel electrophoresis. Reproduced and modified with permission [111, 112]. Copyright, American Chemical Society (2011), The Japan Society of Applied Physics (2008).

Furthermore, capillary electrophoresis is carried out through capillaries with diameters smaller than 1 mm, which offers much higher resolution due to various effects (*e.g.* plug profile of the electroosmotic flow) when flow of the separated mixture takes place through microchannels. Lastly, gel electrophoresis employs a matrix, most commonly made of agarose, agar or polyacrylamide, which amplify the differences in mobilities of resolved species (Fig. 11b) based on size or particular interaction of the analyte with the stationary phase. A second dimension to this classification is created when a non-uniform electric field is engaged. In such case, the process is called dielectrophoresis and it is able to resolve not only charged, but also charge neutral molecules. All of these variations have been used for separation of CNTs (Table 3).

Table 3. Electrophoretic methods of separation of CNTs with targeted type of sorting and obtained performance.

Electrophoresis method	Separation type	CNT type	Enrichment and performance	Ref.
Free solution	M/S	As-made	95% pure semiconducting CNTs 10 <sup>5</sup> on/off ratio	[111]
	M/S	Diazotized	M/S=1.96 and M/S=0.76	[104]
Capillary	M/S	Diazotized	N/A	[113]
Agarose gel	M/S	As-made	95% pure semiconducting CNTs	[112]
	d, l	Oxidized Sonicated*	N/A	[114]
	d, l	Sonicated*	N/A	[115]
	d, l, curvature	As made	N/A	[116]
	M/S	As made	95% pure semiconducting CNTs 10 <sup>5</sup> on/off ratio	[117]
	M/S	Modified	98% pure semiconducting CNTs 10 <sup>6</sup> on/off ratio	[118]
AC dielectrophoresis	d, M/S, (n,m)	As made	N/A	[119]
	M/S	As made	N/A	[29]
	M/S	Sorted	Single chirality devices 10 <sup>5</sup> on/off ratio	[120]

d (diameter), (n,m) (chiral angle), M/S (metallic/semiconducting character)

\* Indicated where prolonged time or high power was employed than usual

Ihara *et al.* reported that separation of metallic from semiconducting CNTs can be carried out in a simple vertical free electrophoresis setup [111]. After several hours of the process, the top of the solution turned brown and the bottom became blue. What is interesting, change in density along the electrophoretic cell was not gradual as in conventional horizontal electrophoresis, but abrupt. Layers with different specific gravities were formed in the applied electric field. From the economic point of view, one may think that 16h of electrophoresis (maximum time of treatment reported in the study) makes this process not viable. However, it has to be noted that the process consumes only a few milliwatts of energy during this time as compared with energy intensive techniques such as ultracentrifugation also used for sorting. Although ultracentrifugation does consume more electric energy, its time span is often much shorter – particularly in the case when it enhances the aqueous two-phase extraction.

Furthermore, to improve the separation degree, a wanted or unwanted type of CNTs can be coupled with a marker, which would make it more mobile in the electric field. p-hydroxybenzene diazonium is a popular reactant, which not only has favorable interactions of nitrogen with metallic CNT side walls [31, 121], but it actually binds to them covalently [79]. Hydroxyl group can then be deprotonated in alkaline solution to make the grafted CNT much more mobile in the electric field due to its negative charge. One of the key advantages of such marker is the ability to be removed by thermal annealing at 300°C for 1h to recover the metallic CNTs. It has to be noted that excess of diazonium reactant would functionalize also semiconducting CNTs, so the reaction has to be carefully controlled. This way the ratio of metallic (M) to semiconducting (S) CNTs can be increased from 0.99 to 1.96 [104].

The approach to highlight metallic CNTs in the mixture was also successfully applied in the case of capillary electrophoresis [113]. The authors pointed out that for the separation to be effective,

surfactant used to disperse CNTs should ideally be removed by dialysis prior to separation. The reason is that the charge introduced by an ionic surfactant such as SDS dominates the charge introduced by grafted (de)protonated functional groups and migration becomes indiscriminant.

When agarose gel was used as medium, impressive separation results have been obtained. Report by Tanaka *et al.* showed that the parent mixture can be separated into two fractions: 95% semiconducting and 70% metallic [112]. Various surfactants (sodium dodecylsulfate, sodium dodecylbenzene sulfonate, sodium cholate, sodium deoxycholate) and gels (agarose, polyacrylamide, starch) were tested. It was found that the combination of SDS and agarose is most effective. In addition, semiconducting CNTs revealed affinity towards the agarose gel, which enhanced the mobility difference between separated CNT types. The adsorption is so strong that in fact M/S separation can be carried out without the presence of electric field by a freeze-thaw-squeeze approach [122].

Other CNT modification such as CNT cutting by oxidizing acids [114] or ball milling [123] enabled length differentiation by electrophoresis. Smaller diameter CNTs are more mobile and arrive at the collecting electrodes first. Interestingly, when CNT cutting is done by sonication two types of CNT populations are obtained: short of bigger diameter and long of smaller diameter. As the electrophoresis in this case is mostly influenced by the molecular size, the short but large diameter CNTs are preferentially deposited at the electrode before other [115]. Electromigration is also influenced by CNT curvature to some extent [116].

What is in accordance with the results presented from capillary electrophoresis, a non-ionic surfactant can improve the extent of separation. When coupled with agarose gel electrophoresis, high-purity semiconducting CNT can be obtained. When chondroitin sulfate was used as the surfactant, not only the purity of the fraction was at the level of 95%, but the yield of the



separation reached up to 25% (higher than in the case of density-gradient ultracentrifugation reported to be within the range of 1 – 2%) [117]. On/off ratio of transistors made from that material reached up to  $10^5$ . The authors carried out a follow up study, in which they employed azo naphthalene compound as a metallic CNT marker to increase its surface charge. Although the yield decreased down to 18%, semiconducting purity up to 98% was attained. That translated into FETs made from them with on-off ratios up to the level of  $10^6$ .

Dielectrophoretic separation is appealing to many research groups working with CNTs because of the fact that metallic and semiconducting CNTs have striking difference in their dielectric constants:  $\epsilon > 1000$  and  $\epsilon < 10$ , respectively [29]. Metallic CNTs, which are much easier to polarize and acquire the largest dipole moments, migrate faster towards the electrode than semiconducting CNTs [1]. Such separation by dielectrophoresis can also be accomplished by a continuous process in a so-called field flow fractionation [119]. When a material of predetermined structure (*e.g.* chiral angle) is obtained, instead of separation, dielectrophoresis can be utilized in the assembly mode, wherein it makes devices from individual CNTs [120]. Vijayaraghavan and co-workers showed how a 100 of FETs from nearly monochiral CNTs can be created in a  $100\ \mu\text{m} \times 100\ \mu\text{m}$  area. Their switching ratios were in the order of  $10^5$ .

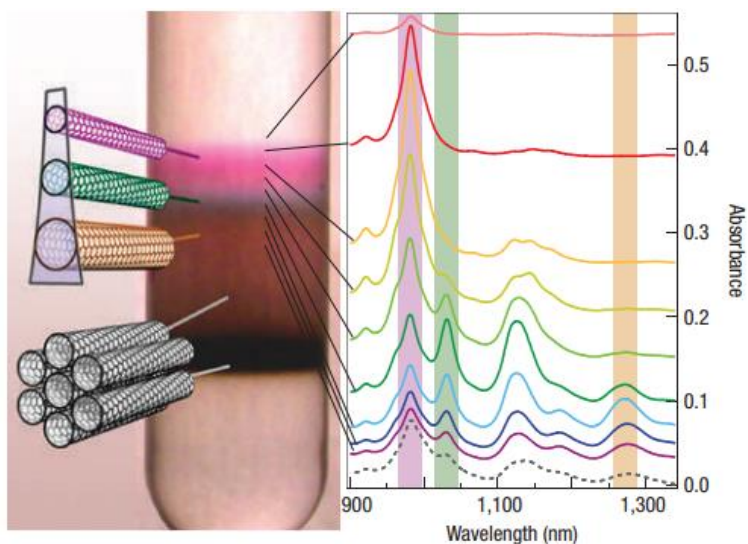
## 2.4 Ultracentrifugation

Separation by density-gradient centrifugation (DGU) is a relatively easy technique to execute, in which CNT mixtures can be separated into individual components based on their buoyant density difference. Depending on the process conditions, the material can be resolved by length, diameter, electrical character, chiral angle and even enantiomer form (Table 4). The most difficult part is to establish appropriate conditions of this multi-dimension parameter space (type of density-gradient medium, concentrations of components, temperature, centrifugation parameters, *etc.*) to make it successful for separation of a particular type of CNTs.

Table 4. Electrophoretic methods of separation of CNTs with targeted type of sorting and obtained performance.

Separation type	Medium	Surfactant	Enrichment	Ref.
d, M/S, (n,m)	Iodixanol	SC, DOC, STDOC	97% pure semiconducting CNTs of selected chirality (0.2 nm diameter distribution)	[124]
d	Iodixanol	SC	11 fractions of various CNT diameter distribution	[125]
l	Iodixanol	DOC	16 fractions of various CNT length (estimated standard deviation of 20%)	[126]
d	Iodixanol	SC, SDS	99% pure semiconducting CNTs with narrow diameter distributions	[127]
d, M/S, (n,m), e	Iodixanol	SC	Enantiomers of different CNT chiralities	[128]
d, M/S, (n,m), e	Iodixanol	SC, SDS	Enantiomers of different CNT chiralities	[26]
M/S	Iodixanol	SC, SDS	98% pure outer-wall metallic double-wall CNT 96% pure outer-wall semiconducting double-wall CNT	[129]
d, M/S, (n,m)	Iodixanol CsCl	SC	Single chiral extraction of (11,10)	[130]
M/S	Sucrose	SC	95% pure semiconducting CNTs 69% pure metallic CNTs	[131]

d (diameter), l (length), (n,m) chiral angle, M/S (metallic/semiconducting character), e (enantiomer form), SC (sodium cholate), DOC (sodium deoxycholate), STDOC (sodium taurodeoxycholate)



**Fig. 12.** DGU separation of SC-suspended CNTs in a density-gradient of iodixanol. Reproduced and modified with permission [124]. Copyright 2006, Macmillan Publishers.

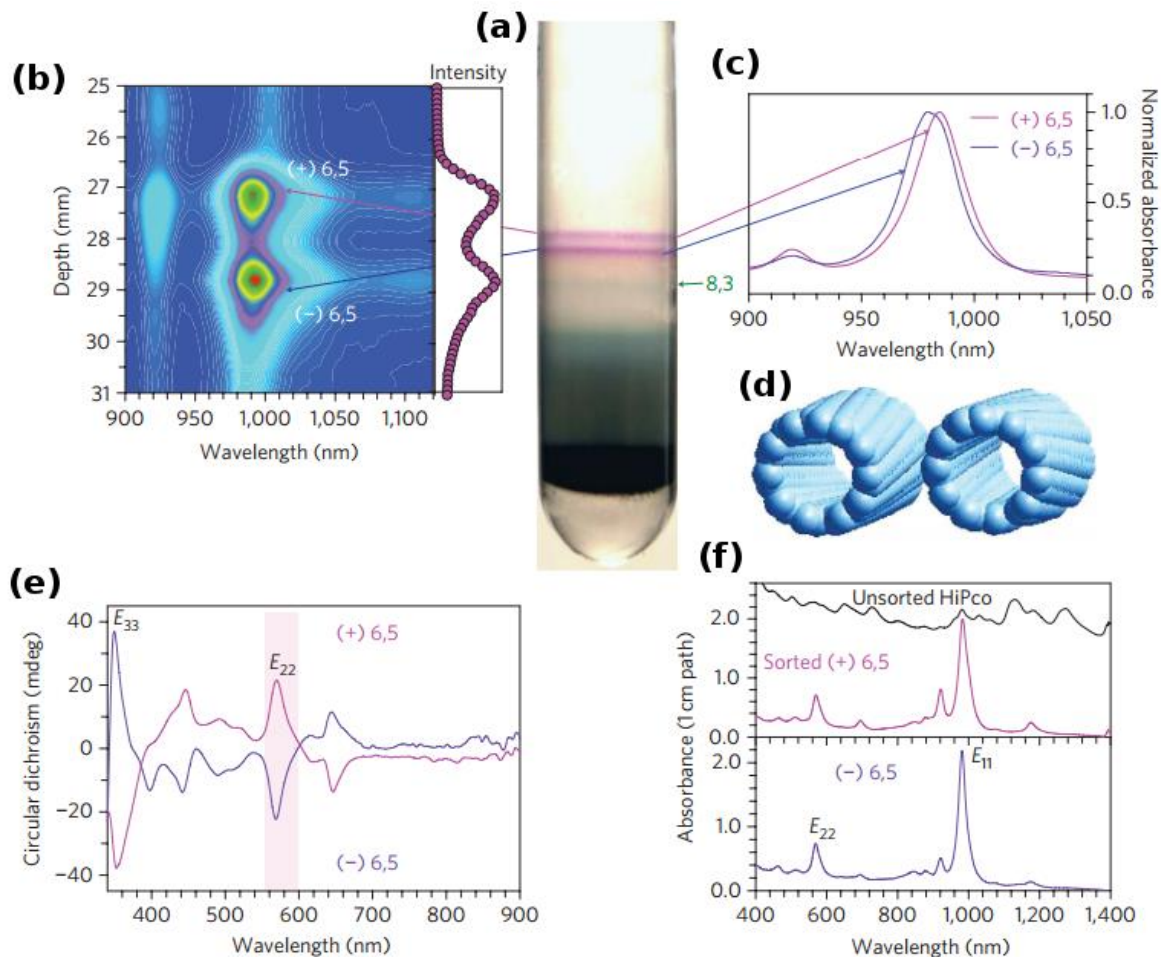
Pioneering work by Arnold *et al.* (Fig. 12) [124] revealed that complex CNT mixtures can be discriminated by employing ultracentrifugation. When the material is subjected to a high centripetal force in a density gradient medium, the components tend to separate into discrete bands based on their buoyant density. The reason is that subtle variation in CNT structure result in changes to their hydration layer when they are dispersed in water with the assistance of a surfactant. The surfactant was found to have a very important role because often its type and concentration predetermines the shape of the hydration layer, and thus the sorting type. For instance, sodium cholate was found to fractionate semiconducting SWCNTs according to their bandgap/diameter [125] and electrical character [124]. Sodium deoxycholate and sodium taurodeoxycholate were also effective as compared with sodium dodecylsulfate or sodium dodecylbenzenesulfonate, wherein CNTs were compressed into a narrow band, and so diameter based separation was unsuccessful. The strategy was very successful for the enrichment of CNTs of (6,5) and (7,5) chiralities. After three rounds of separation, the purity reached up to 97% with

just 0.2 nm diameter distribution. Variation in pH or addition of a co-surfactant gives additional degrees of freedom, which enable optimization and targeting a selected CNT type in a reduced number of iterations.

By using DGU, CNTs can also be sorted according to length. Simien and co-workers showed that CNTs dispersed by length using DOC as a surfactant and fractionated in iodixanol as density-gradient medium follow the electrical percolation theory [126]. Conductivity percolation threshold was found to be inversely proportional to the aspect ratio of CNTs, as expected.

Addition of NaCl to the CNT-surfactant mixture can alter the shape of the hydration layer, which in turn results in preferential isolation of different CNT type as proven by aqueous two-phase extraction [132]. Similar effect was observed in DGU, wherein addition of NaCl enabled isolation of high-purity semiconducting CNTs (99%) with diameter distribution centered at 1.4 nm. In the absence of NaCl, corresponding CNTs with diameter distribution centered at 1.6 nm were separated [127].

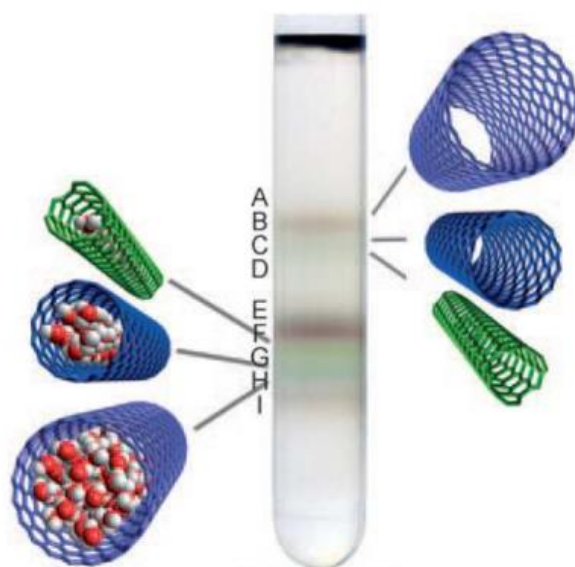
The work of Green [128] and then Ghosh [26] *et al.* showed that even the slightest differences in CNT structure can be used for differentiation (Fig. 13). The teams were able to separate left- and right-handed enantiomers of a selection of CNTs by taking advantage of the preferential affinity of chiral sodium cholate surfactants to one of the forms. After DGU of CNTs dispersed in SC or (combination of SC and SDS), two distinct purple bands were formed. Spectroscopic investigation revealed that although the intensity profiles are similar, they are offset by 2 nm. Circular dichroism corroborated the suspicion that these bands do come from (+) (6,5) and (–) (6,5) species. Comparable enantiomeric separation was also demonstrated for (9,1), (8,3) and four other CNT chiralities.



**Fig. 13.** Separation of CNT enantiomers by DGU. (a) Centrifuge tube with enantiomer bands, (b) Fluorescence spectral map, (c) Light absorbance spectra (900 – 1050 nm), (d) Models of two enantiomers, (e) Circular dichroism spectra, (f) Unscaled light absorbance spectra. Reproduced and modified with permission [26]. Copyright 2006, Macmillan Publishers.

Another important aspect from the nanoscale, which can have a significant influence on the result of sorting, is the presence of water inside individual CNTs. As it has been shown, empty end-capped CNTs and water-filled open CNTs appear as distinctive bands in the density gradient medium [133]. CNTs open up as a result of sonication-assisted dispersion in the presence of surfactant to individualize the material [134]. Just 15 minutes of sonication can open as much as

40% of CNT ends, which will then result in filling the cavities with water. These water filled CNTs have a different buoyant density from the empty ones, but what is striking, these buoyant densities show opposite dependence on CNT diameter (Fig. 14). From a practical point of view, keeping the caps closed has a profound effect on the separation efficiency as density of water-filled CNTs becomes essentially constant at large diameters. Having the CNTs filled with water in this case may not only result in cross-contamination with unfilled CNTs of similar buoyant density, but under certain circumstances sorting may even become impossible if differences in buoyant densities are too small.



**Fig. 14.** Separation of empty and water-filled CNTs by diameter using DGU. Reproduced and modified with permission [133]. Copyright 2011, Wiley-VCH.

Bile salts (sodium cholate, sodium deoxycholate, sodium taurodeoxycholate) in general were found much more effective in individualization of CNTs than linear surfactants (sodium dodecylsulfate, sodium dodecylbenzenesulfonate) [135]. Often they also create more uniform sidewall coverage. Both these effects are crucial for successful differentiation, which is based on

very minute differences in the CNT structure. Bonaccorso gave a through analysis how various surfactants interact with CNTs and showed how that influences the course of DGU. Linear surfactants were found to have a higher capacity for CNT dispersion, but their individualization capabilities are much lower, which results in a high content of CNT bundles after dispersion rather than single CNTs wrapped with surfactant.

The resolution of DGU can be also improved by using various gradient media [130]. Prolonged centrifugation in iodixanol creates a very steep density gradient, whereas that of CsCl is moderately curved. CsCl established a different environment for selective isolation of (11,10) CNTs from a 95% pure fraction of semiconducting CNTs prepared by regular M/S prior to that.

It was reported that sucrose could be used as a gradient medium in density-gradient ultracentrifugation of CNTs [131]. The motivation was to substitute the commonly used iodixanol, which has a range of disadvantages. Such medium is very expensive and also contains iodine atoms, which can readily dope semiconducting CNTs [4]. An additional benefit from using sucrose instead of iodixanol is that it is much easier to remove it from the purified CNT material. Unfortunately, despite the fact that metallic-semiconducting enrichment did take place, the results are inferior as compared with corresponding processing in iodixanol. The obtained material gave FETs with switching ratios just in the order of  $10^2$ .

The method was also found successful in differentiation of double-wall CNTs according to the electrical character of the outer wall [129]. After coarse separation by wall number, M/S separation using SC/SDS by DGU yielded 98% pure outer-wall metallic double-wall CNT and 96% pure outer-wall semiconducting double-wall CNT. Characterization of these materials by optical absorbance and Raman spectroscopy is troublesome due to the signals coming from the inner walls.

## 2.5 Chromatography

The name chromatography is derived from a Greek word chroma, which means color. Although you probably think of pitch black when CNTs are considered, these individual tubules made of carbon can in fact give all colors of the rainbow, when they are properly resolved. Chromatography can be employed to sort CNTs according to a wide range of types (Table 5).

Table 5. Chromatographic methods of separation of CNTs.

Separation type	Method	CNTs	Eluent	Stationary phase	Ref.
l	SEC	As-made, dispersed with SDS	Aq. SDS	CPG	[136-138]
l	SEC	As-made, dispersed with DNA	Aq. buffer at pH=7 (Tris, EDTA, NaCl)	SiO <sub>2</sub>	[139]
M/S	Filtration	Diazotized, dispersed with SDS	ODCB DMF	SiO <sub>2</sub>	[140]
M/S	SEC	As made, dispersed with SDS	SDS DOC	Sepharose 2B	[141]
d, M/S	SEC	As made, dispersed with SDS	SDS DOC	Sepharose 2B	[142]
l, M/S	SEC	As made, dispersed with SC	SDS SC	Sephacryl S-200HR	[143]
d, (n,m)	SEC	As made, dispersed with SDS	SDS DOC	Sephacryl S-200HR Sephacryl S-300HR	[144, 145]
(n,m)	SEC*	As made, dispersed with SDS	SDS	Sephacryl S-200HR	[146]
(n,m)	SEC**	As made, dispersed with SDS and SC	DOC	Sephacryl S-200HR	[147]
(n,m)	SEC**	As made, dispersed with SDS	SDS	Sephacryl S-200HR	[148, 149]
(n,m), e	SEC	As made, dispersed with SDS	SDS	Sephacryl S-200HR	[150]
d, M/S	IEC	As made, dispersed with DNA	NaSCN in MES buffer at pH=7	NS1500	[32]
(n,m)	IEC	As made, dispersed with DNA	NaCl, sodium citrate, sodium benzoate EDTA, at pH=7	NS1500	[56, 151-153]

d (diameter), l (length), (n,m) chiral angle, M/S (metallic/semiconducting character), e (enantiomer form), Size Exclusion Chromatography (SEC), IEC, Controlled Pore Glass (CPG), *o*-dichlorobenzene (ODCB), dimethylformamide (DMF), sodium dodecyl sulfate (SDS), sodium cholate (SC), sodium deoxycholate (DOC), 2-(*N*-morpholino)ethanesulfonic acid (MES).

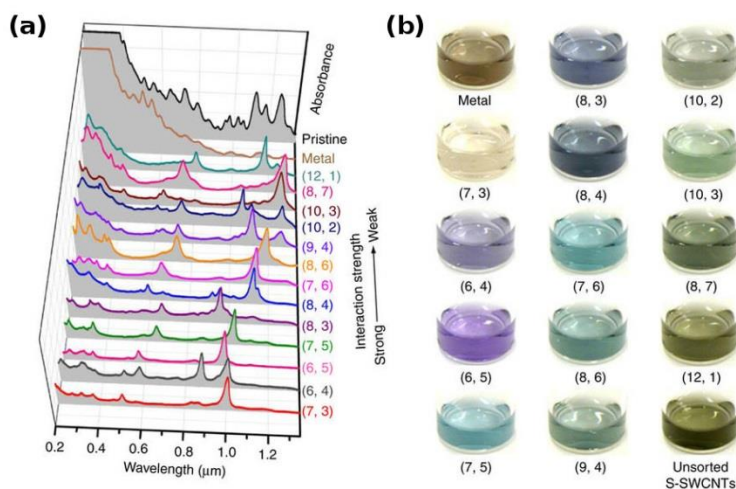
\* Temperature controlled

\*\* pH controlled



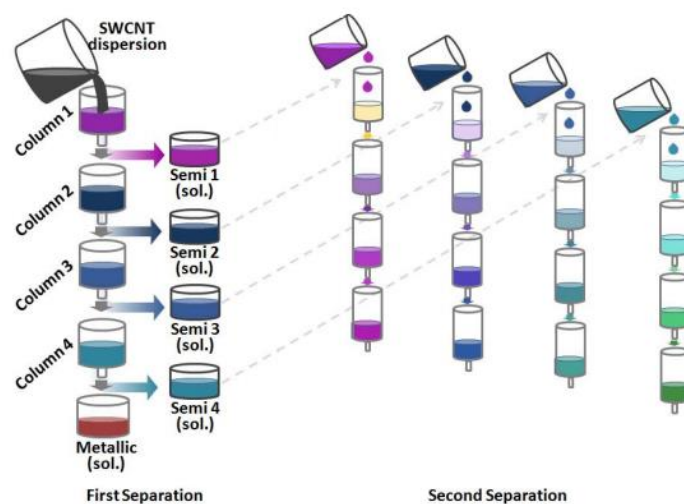
Perhaps the first reports of separation of CNTs by chromatography came from the work of Duesberg *et al.* [136-138]. The team noticed that CNTs can be separated by fractions of different length distribution using controlled pore glass (1400 Å pores). When columns of 2000, 300 and 100 Å pores were used in sequence, the average length decreased from >500 nm (2000 Å) to <100 nm (100 Å). In parallel, small particles and graphitic contaminants were removed in the process [139]. SiO<sub>2</sub> can also be used as the stationary phase, but the size of mesh is very important. 35–60 mesh of 150 Å pores was found suitable for SEC [140] to enable elution.

Initial studies using agarose gel confirmed that metallic/semiconducting CNT separation is possible, when DOC was used for elution of bound greenish semiconducting CNTs [141]. In contrast, metallic CNTs of reddish color remained unbound and readily migrated through the gel. Unfortunately, agarose gel not only requires surfactant with high dispersibility such as DOC to unbind semiconducting CNTs, but it does not offer sufficiently high resolution.



**Fig. 15.** (a) Optical absorption spectra of 13 (n, m) semiconducting CNTs separated by gel chromatography and (b) their photographs showing their distinct colors. Reproduced and modified with permission [145]. Copyright 2011, Macmillan Publishers.

It has been showed that Sephacryl gel can be much more selective [154]. It was also found that if a chromatographic column is overloaded with parent CNT dispersion, the distribution of obtained species is improved because adsorption sites become fully occupied with the CNT types, which exhibit the strongest interaction with the gel [145]. Semiconducting CNTs of smaller diameter interact with gel more strongly, and so they are adsorbed first. To elute them in sequence, a stepwise increase in surfactant concentration such as SDS can be employed [142]. Because of the same principle, single-walled CNTs can be separated from double-walled CNTs by chromatography [155]. What regards metallic CNTs, they have the highest affinity towards surfactant molecules, and so they are often fully wrapped with them. Full coating with SDS minimizes interaction with the gel and makes them most mobile among all the CNTs, therefore they are often eluted first. The use of multi-column chromatographic separation enabled differentiation between 13 major chiralities [144, 145].



**Fig. 16.** Separation of CNTs by gel chromatography according to electrical character and their optical isomers in the second round. Reproduced and modified with permission [150]. Copyright 2014, American Chemical Society.

In fact, resolution of this method is even higher and enabled separation of CNT isomers of 9 chiralities (Fig. 16) [150]. Semiconducting CNTs are first separated from metallic CNTs and initially sorted by chirality into distinct fractions. These fractions were then resolved further using a series of chromatographic columns. At this point separation of both optical isomers has been confirmed by circular dichroism. Left-handed species revealed a stronger interaction with the gel. It has been noted that CNTs of small chiral angle did not exhibit similar resolution because their interaction with the gel is not specific to the same extent. The reason is that the adsorption energy of gel on these CNT optical isomers is quite low.

Ultrahigh purity at the level of 99.9% in terms of semiconducting CNT amount was reported by Tulevski and co-workers [156] It was found difficult to quantify the extent of separation by optical absorption due to low signal-to-noise ratio, so 4212 FETs from the material were assembled evaluate the material after sorting. Out of all the manufactured FETs, only 6 were composed of metallic CNTs whereas 4206 consisted of semiconducting CNTs. Appreciable level of purity results in high on/off ratios, which reached up to  $10^5 - 10^6$  [143].

Temperature can have a very significant influence on the course of gel chromatography. It controls the interaction between the surfactant-wrapped CNTs and the gel [146]. Decreasing temperatures switch off adsorption of certain CNTs in the gel. As a consequence, a range of chromatographic columns connected in series, but kept at different temperature, in which one feeds the other, enable stepwise fractionation. CNTs of seven different chiral angles were resolved. Moreover, pH change by adding HCl [148, 149] or bubbling of the surfactant solution with CO<sub>2</sub> (pH is decreased with CO<sub>2</sub> addition) showed a significant increase in the separation resolution [147]. Under appropriate pH conditions, signals from metallic CNTs were completely removed in the resulting material after sorting. Almost monochiral (6,5) and (7,5) samples were

obtained. Decrease of pH results in p-doping of CNTs [157] and the positive charge affects how surfactant molecules assemble around CNTs. Moreover, when SDS is employed as surfactant, it can form 1-dodecanol by hydrolysis at low pH [148], which can also affect surfactant-CNT ordering.

Separation of CNTs can also be accomplished by ion-exchange chromatography (IEC) [32, 56]. It was found that the shorter the separated CNT, the better the yield. Sonication is most commonly used to accomplish this goal, because it induces cutting of CNTs. It is a result of strain forces acting on them, which scales with the square of CNT length [149]. IEC is often carried out in conjunction with SEC to narrow down length distribution for further processing [158].

The process of IEC showed that with each collected fraction dispersed with DNA there is a gradual increase in diameter for semiconducting CNTs and depletion of metallic CNTs. The effect has been explained by the difference in polarizability between these CNT types. Further investigation by Tu *et al.* demonstrated more than 20 DNA sequences, which recognize particular types of CNTs and are useful for IEC, but could also be employed to other sorting methods [151]. What regards the electrical properties of the produced material, FETs constructed from semiconducting CNTs resolved by this method reached appreciable performance with switching ratios up to  $10^5 - 10^6$  [152, 153].

Once again, the method can be extended to separation of DWCNTs by the electrical character of the outer wall [159]. Recently it has been reported that sorting is possible by both inner and outer wall type [160]. All four combinations M@M, S@M, S@S, and M@S (inner@outer wall, M – metallic, S – semiconducting) were obtained. First SWCNTs are removed by gel permeation, and then the remaining DWCNT fractions are further purified by (co)polymer isolation (next

section). Despite that the reported work was focused on DWCNTs, the mechanism presented by Li *et al.* has got very important implications for SWCNT separation by gel chromatography, DGU, ATPE, *etc.* It was found that specific surfactant wrapping on CNTs, which directly affects the shape of the hydration layer, is heavily influenced by the “oxidation state” of a CNT. Metallic CNTs are more easily oxidized by H<sub>2</sub>O/O<sub>2</sub> environment due to the presence of electrons at the Fermi level. As a consequence, the slight positive charge, which they bear on the surface, attracts surfactant such as SDS more readily. The less the CNTs are oxidized, the stronger their interaction with *e.g.* Sephacryl gel because of the lack of solubilizing SDS layer. Semiconducting CNTs with bandgap at the Fermi level behave this way at close to neutral pH. To sum up, by varying the pH one can directly affect the course of the separation even by the electronic character of the inner wall (in the case of DWCNTs).

## 2.6 (Co)polymer isolation

All CNTs are dispersible, but some types can be more dispersible than others – to paraphrase the famous quote. It has been realized that certain polymers can selectively bind with CNTs of particular length, diameter, metallic character, chirality or even handedness (Table 6). Because this makes them more “soluble”, that leads to the possibility of relatively easy differentiation between various CNT types.

Table 6. Separation of CNTs by extraction with polymers.

Separation type	Polymer	Enrichment and performance	Ref.
l	Polymethacrylate, polystyrene sulfonate	Length-sorted CNTs were enriched with semiconducting CNTs by aqueous two-phase extraction $10^5$ - $10^7$ on/off ratio	[161]
d	Poly(3-alkyl)thiophene	Material enriched with small-diameter semiconducting CNTs $10^4$ on/off ratio	[162]
d	Poly(phenylenevinylenes)	Dispersion of CNTs of particular diameter distribution (0.75 – 0.84 nm)	[163]
M/S	Pluronic, Tetricon	99% pure semiconducting CNTs 74% pure metallic CNTs	[164]
M/S	Copolymer of fluorene and thiazazole	Material enriched with semiconducting CNTs $10^4$ on/off ratio	[165]
M/S	Polyfluorene derivative	66% sorting efficiency of semiconducting CNTs	[166]
M/S	Polyfluorene derivative	99.9% pure semiconducting CNTs $10^7$ on/off ratio	[167]
M/S	Poly( <i>N</i> -decyl-2,7-carbazole)	Selectivity towards $(n - m) > 2$ semiconducting CNTs	[27]
M/S	Poly(3-dodecyl)thiophene	Material enriched with semiconducting CNTs $10^4$ on/off ratio	[168]
M/S	Poly(3-dodecyl)thiophene	Material enriched with semiconducting CNTs $10^6$ on/off ratio	[169, 170]
M/S	Poly(3-alkyl)thiophenes	Material enriched with semiconducting CNTs $>10^6$ on/off ratio	[171]
M/S	Polyvinylpyrrolidone	Semiconducting CNTs remain suspended Metallic precipitated out $10^5$ on/off ratio	[172]
(n,m)	Fluorene- and carbazole-based (co)polymers	N/A	[173]
(n,m)	DNA	Recognition of specific CNTs*	[174]
(n,m)	DNA	86% pure semiconducting CNTs of selected chirality	[175]
(n,m), e	Polyfluorene derivative	Enantiomers of different CNT chiralities	[176]

d (diameter), l (length), (n,m) chiral angle, M/S (metallic/semiconducting character), e (enantiomer form)

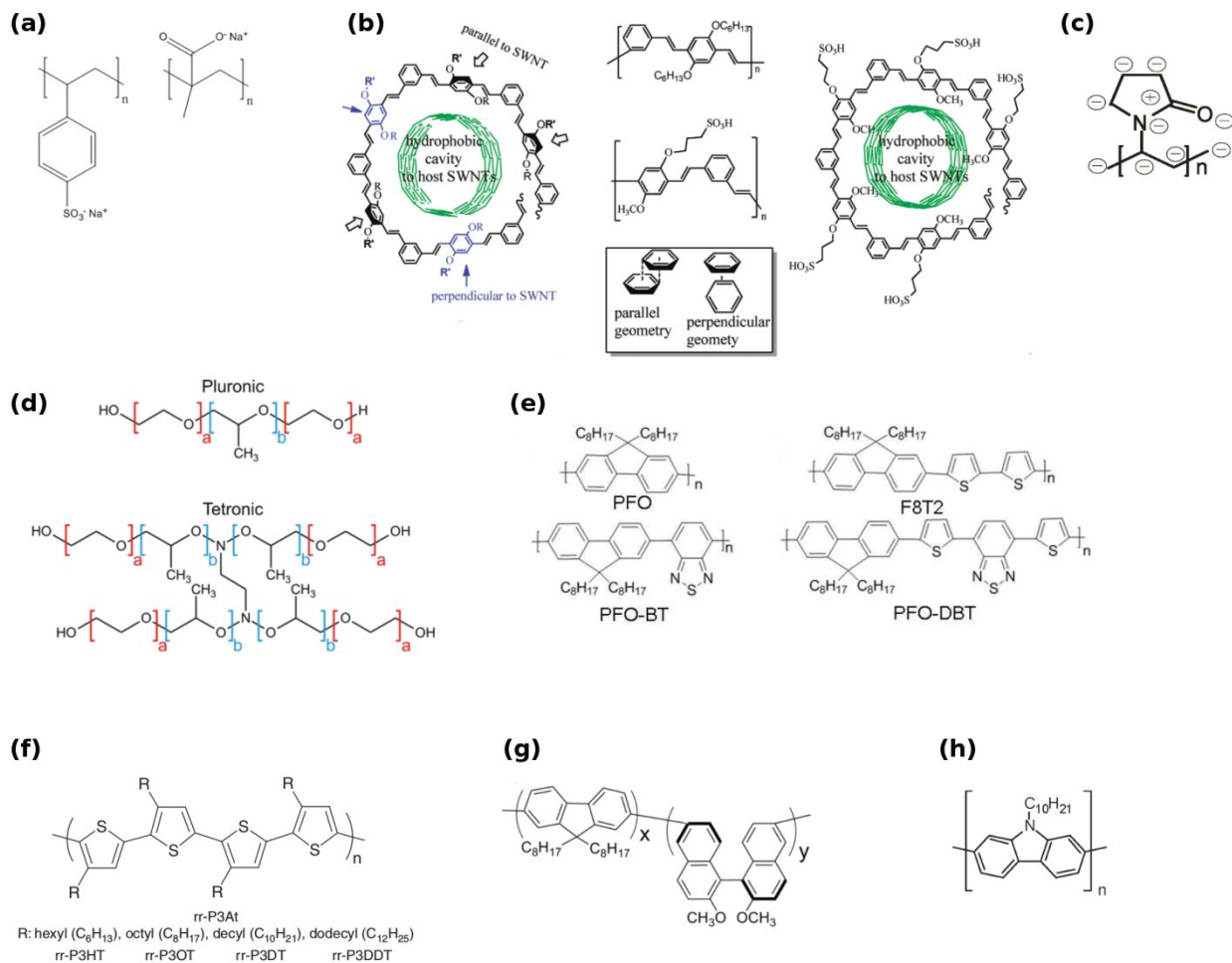
\* Modeling results

Gui *et al.* addressed the problem of CNT length sorting by the action of polymethacrylate or polystyrene sulfonate [161] (Fig. 17a). For some applications of CNTs such as drug delivery short CNTs are preferred because then the therapy based on them is more effective – on the other hand, for most electrical applications, the longer the CNTs the better to overcome the problem of contact resistance. The team found out that the aforementioned polymers were able to sort SC- or DOC-dispersed CNTs in a stepwise fashion based on their length (250 to 650 nm long CNTs were separated). With the increase in polymer concentration, shorter and shorter CNTs were precipitated out. Probably the best illustration of the viability of this technique is that FETs built from these materials reached impressive on/off switching ratios up to  $10^7$ .

Not just by length, but sorting with polymers was also capable of differentiation by diameter [162, 163]. Diameter of a semiconducting CNT is directly related to its bandgap, which opens up possibilities of tailoring the material for a particular electrical application. To isolate CNTs of small diameter, one can use poly(3-alkylthiophenes) (Fig. 17f) [162]. The longer the alkyl side chain, the higher the yield of the separation due to the enhanced interaction of the polymer with CNTs. Furthermore, it was reported that it is possible to separate certain small-diameter CNTs when an alternating copolymer of m-phenylenevinylene and p-phenylenevinylene is employed (Fig. 17b). Due to the fact that one substituent is hydrophilic and the other hydrophobic, the copolymer conforms into a helical structure, which is able to wrap (and so separate) CNTs of a 0.75 – 0.84 nm diameter distribution [163].

Co-polymers are also able to differentiate between metallic and semiconducting CNTs. Tetronic and Pluronic (Fig. 17d) are composed of hydrophobic and hydrophilic blocks, which display affinity towards respective CNT types, if the proportion between the blocks is appropriate [164].

It was demonstrated that in such case respective purities up to 74% and 99% can be attained.

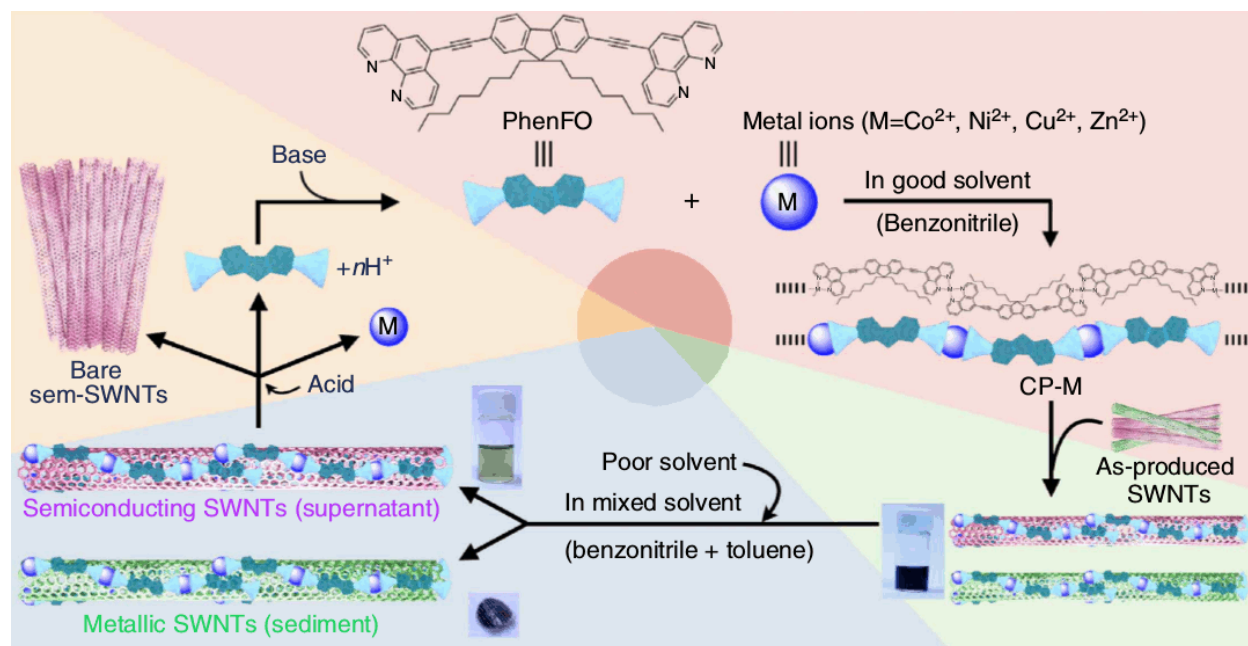


**Fig. 17.** (Co)polymers used for separation of CNTs (a) polymethacrylate and polystyrene sulfonate, (b) poly(phenylenevinylene) [163], (c) polyvinylpyrrolidone [172], (d) Pluronic and Tetronic [164], (e) polyfluorenes and their derivatives [165], (f) poly(3-alkyl)thiophenes [171], (g) polyfluorene-binaphthol [176], (h) polycarbazole [27]. Reproduced and modified with permission. Copyright, American Chemical Society (2010–2012), The Royal Society of Chemistry (2014), Macmillan Publishers (2011).

When one takes a closer look at the structure of Tetronic, it is not surprising that the copolymer binds preferentially with metallic CNTs as it contains nitrogen centers, which, as indicated before, have affinity towards this type of CNTs. What is interesting, isolated semiconducting



CNTs were found to be 25% longer than metallic. The effect was explained by the fact that metallic CNTs have larger dielectric constant, what makes their bundles stronger and so less susceptible to disintegration by sonication, which is carried out prior to sorting.



**Fig. 18.** Separation of CNTs by a metal-coordination polymer system. Reproduced and modified with permission [166]. Copyright 2014, Macmillan Publishers.

Moreover, the family of polyfluorenes (Fig. 17e) was found to offer large-diameter semiconducting CNTs (complementary to some of the methods presented above) at relatively high yield [165]. Most importantly, the polymers can provide FETs with high-performance material as switching ratios up to  $10^7$  were recorded from CNTs isolated using this method [167]. Toshimitsu and colleagues proposed interesting solution, in which the working polymer can readily be turned back into monomers, which simplifies subsequent purification of the material [166]. When metal-coordination polymers composed of fluorene and metal ions are employed as the separating macromolecule, they can be then disintegrated by simple acid treatment (Fig. 18).

What is more, under certain conditions polyfluorenes disperse preferentially semiconducting CNTs, which satisfy the following rule  $(n - m) \leq 2$  (large chiral angle), whereas *N*-decyl-2,7-carbazole (Fig. 17h) analogue is appropriate for  $(n - m) \geq 2$  (small chiral angle). Ability to enrich CNTs in terms of particular chiral angle has also been shown [173]. Perhaps the most encouraging were the results of Akazaki *et al.* who reported resolution of (6,5) and (7,6) CNTs into right- and left-handed enantiomers by using polyfluorenes with chiral bulky moieties (Fig. 17g) [176]. Interestingly, at higher content of the chiral moiety, the system showed inversion of the enantiomer recognition. Chiral and conformational interaction changes were given as a possible underlying reason for the observed effect.

As shown in the case of poly(3-alkylthiophene) (Fig. 17f) as the isolating polymers, solvent selection may have a large influence on the dispersion yield [168], which reached up to 40% when decalin or *o*-xylene was employed. Furthermore, the nature of the solvent affects the interaction between the surfactant and the CNTs, and thus the sorting yield. The poly(3-alkylthiophenes) in general are very effective in isolation of semiconducting CNTs [169-171] and also give FET material of relatively high switching ratios, some of which exceed  $10^6$  [171].

Similar to the case of selective precipitation by length, metal/semiconductor separation can also be carried out by these means. When CNT dispersion was introduced to polyvinylpyrrolidone (Fig. 17c) in DMF for a prolonged time, the semiconducting CNTs remained suspended, whereas the metallic ones precipitated out [172]. The effect was explained by surfactant unwrapping from the metallic CNTs over time. Unfortunately, the reported switching ratios of  $10^5$  are attained by a minority of produced FETs. Most of them are at the level of  $10^3$ .

Furthermore, DNA is perhaps one of the most tailorable polymers for CNT recognition [174, 175]. It was proven to have a very selective nature depending on its sequence (one may refer to a

comprehensive summary by Tu *et al.* [151]), but the obvious disadvantage is in its high cost. For instance (TAT)<sub>4</sub> sequence is very specific to the (6,5) CNTs and forms a highly ordered barrel on such CNT type. On the other hand, when DNA of the same sequence was employed on (8,7) CNTs, disordered and unstable structure was observed [174]. The shape of the wrapping helix, whether it is right- or left-handed on the surface of a CNT is also sequence dependent as proven by simulation. Escherichia coli or salmon genomic DNA can extract (6,5) CNTs with enrichment up to 75% or 86% was observed, respectively [175].

## 2.7 Aqueous two-phase extraction

Aqueous two-phase extraction (ATPE) is a popular tool used in biotechnology, which has been recently adapted for CNTs [177]. Albertsson noticed that two water soluble polymers can separate into distinct phases if critical concentrations are reached [178]. More importantly, these two phases enables partitioning of cell particles and other biomaterials such as nucleic acids, proteins, microorganisms and virus particles [179]. The method is of sufficiently high resolution to differentiate CNTs by diameter, electrical character, chiral angle and handedness (Table 7).

Table 7. Separation of CNTs by ATPE.

Separation type	CNT dispersant	ATPE system	Ref.
d, M/S	SC	PEG/DEX	[177, 180]
d, M/S	SC	PEG/DEX*	[181]
d, M/S	DOC	PEG/DEX	[182]
d, M/S	DOC	PEG/DEX**	[28]
d, M/S, (n,m)	DOC	PEG/DEX	[183, 184]
d, M/S, (n,m)	DOC	PEG/DEX*	[132]
d, M/S, (n,m)	DNA	PEG/DEX PEG/PAM (PEG+PEG-DA)/DEX PVP/DEX *	[185, 186]
d, M/S, (n,m), e	DOC	PEG/DEX PEG/PAM ***	[187]

d (diameter), (n,m) chiral angle, M/S (metallic/semiconducting character), e (enantiomer form), SC (sodium cholate), SDS (sodium dodecyl sulfate), DOC (sodium deoxycholate), poly(ethylene glycol) (PEG), poly(ethylene glycol) diamine (PEG-DA), dextran (DEX), polyacrylamide (PAM), polyvinylpyrrolidone (PVP)

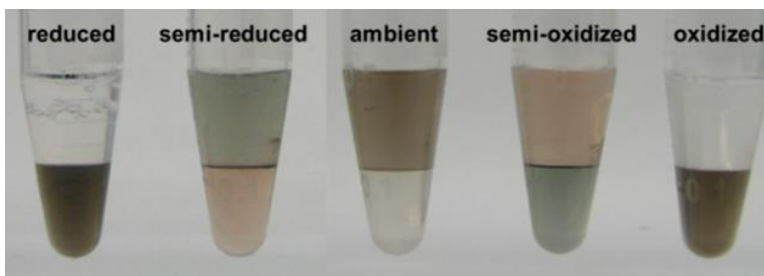
\* NaCl/NaSCN or KSCN added to modulate CNT-surfactant interaction

\*\* NaClO or BH<sub>4</sub> added to modulate redox state of CNTs

\*\*\* DOC exchanged for DNA after dispersion

When PEG and DEX solutions are mixed, two immiscible aqueous phases form spontaneously, each of which has a different affinity towards CNTs. Khripin *et al.* first reported successful separation of CNTs according to diameter and electrical character using this method [177]. It

was demonstrated that two effects are in force. In the case of small diameter CNTs (<1 nm), curvature makes smaller diameter CNTs less hydrophobic. What regards the case of large diameter CNTs (>1.2 nm), their separation is mostly based on electrical character: semiconducting CNTs are more hydrophobic due to lower polarizability. Moreover, to modulate the interaction of CNTs with the two phases and redistribute them, various parameters can be tuned. For instance, addition of SDS to SC counteracts the strong, but often nonspecific dispersing power of SC, which wraps CNT very tightly [188]. Selectivity was improved to a large extent this way. Higher temperature can in turn desorb surfactant from CNTs, which affects the partition. Lowering the temperature in this case was found to improve the separation [180, 182]. The same can be accomplished by addition of chaotropic NaSCN (pushes CNTs into more hydrophilic bottom phase) [177], or kosmotropic NaCl (shifts CNTs into more hydrophobic top phase) [132] salts, which affect the CNT-surfactant hydration later – key aspect for the end result of ATPE. The interaction of CNTs with surfactant can also be modulated by redox reactions (Fig. 19), which may be used to enhance isolation of semiconducting CNTs [28]. When all these parameters are optimized for a CNT of particular type, high-purity isolation of a given chirality can be accomplished in only two steps [132].



**Fig. 19.** Influence of redox reactions on the course of ATPE. Reproduced with permission [28].

Copyright 2015, American Chemical Society.

Fagan and co-workers extended the study by investigating a wide range of surfactant concentration to improve the resolution [183]. For instance, increase in SDS or DOC concentration resulted in a gradual shift of the components from DEX (bottom) to PEG (top) phase. SC on the other hand differentiates mostly by electrical character. Sequential separation and replacement of PEG phases with gradually higher surfactant concentration (*e.g.* SDS) enables successful fractionation by diameter. Fractions of narrow diameter distribution, but two to three chiral angles were obtained. Subsequent ATPE with SC enables separation by electrical character. Careful execution of the processes together yields CNTs fractions of high uniformity in terms of chiral angle. Herein, CNTs of certain chiral angle were isolated with >85% purity.

To improve the separation degree, highly-specific DNA can be employed [185]. Solvation energy difference of the two phases was found to have a strong influence on DNA sequence dependent partition. By changing the system phases from common PEG/DEX of smaller difference in hydrophilicity/hydrophobicity to PEG/PAM of larger difference, the course of separation can be controlled. Additional level of control can be obtained when poly(ethylene glycol) diamine (PEG-DA) is added to PEG, which bears positive charge and introduces electrostatic-based separation component. However, it has to be noted that direct dispersion of CNTs with DNA (most often accomplished by sonication) makes a negative impact on the secondary and tertiary domains of DNA. Moreover, it is not effective for dispersion of CNTs of diameter larger than 1 nm. A recently reported method showed that CNTs could be first dispersed with more powerful surfactants as bile salts, and then the surfactant was exchanged with DNA of appropriate sequence [187].

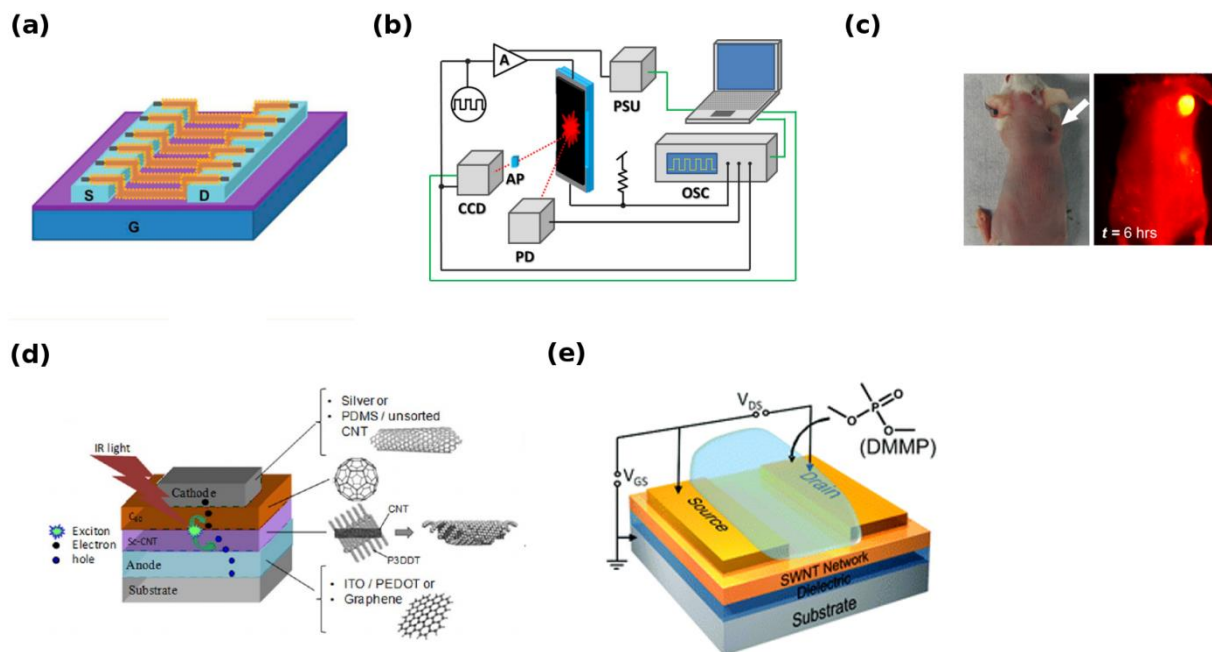
A population of large diameter CNTs is generally hard to separate into components because the differences between the members (such as curvature) are less evident. Due to this effect, CNT

species of up to 1.03 nm in diameter have been separated by gel chromatography [146]. It has been proven that ATPE is universal and can differentiate between CNTs of a wide range of diameters synthesized by four production methods [184]. The window of operation is on par with those from density-gradient ultracentrifugation ( $d=1.44$  nm) [130] or polyfluorene extraction ( $d=1.59$  nm) [127]. However, the resolution limit for optimized ATPE method may in the future be applicable to CNTs with diameters exceeding 1.7 nm [182, 184]. From a practical point of view, the method is more rapid, simpler and does not require capital investment as compared with long or energy intensive processes such as chromatography or density-gradient ultracentrifugation.

ATPE is also able to differentiate between DWCNTs [189] or right/ left-handed isomers of  $>20$  SWCNT chiralities already [186, 187]. DNA adopts two different folds on each of the forms, which enables their separation. Interestingly, such difference results in very different chemical reactivity of the two species in contact with DNA. By using NaClO, 90% of (+) (6,5) CNTs were oxidized as compared to just 10% for (–) (6,5) CNTs. The surface of the former is more exposed to the environment, and so it is more strongly oxidized by NaClO, whereas the latter is much more tightly wrapped with DNA. The hypothesis was confirmed by a large mismatch in their anhydrous density, which gives indirect information about how well a surfactant such as DNA interacted with particular CNTs. When the similar methodology was employed, but the CNTs were first dispersed with bile salts, which were then exchanged for appropriate DNA sequences, nearly 100% enantiomeric excess was attained [187]. CNT materials of such level of perfection enable production of FETs with high performance in the range of  $10^6 - 10^7$  in terms of switching ratio [181, 190]. It is important to stress that determination of purity of this order is nontrivial and Raman spectra of such enriched CNTs have to be interpreted carefully [191].

### 3. Applications

First applications of sorted CNTs have already emerged and their performance has been evaluated and compared with devices based on unsorted material (Fig. 20).



**Fig. 20.** Overview of applications (a) Field effect transistor [192], (b) electroluminescent CNT film [18], (c) optical and near-infrared image of mouse injected with (6,5) CNTs [193], (d) all-carbon solar cell, (e) aqueous chemical sensor [194]. Reproduced and modified with permission. Copyright, American Chemical Society (2009, 2012, 2013, 2016), American Institute of Physics (2014).

One of the most accurate methods to assess the extent of enrichment in semiconducting CNTs has been based on evaluation of the on/off ratio of a FET made from them (Fig. 20a). The review documents many results of this characteristic, but the highest reported switching ratio is currently at the level of  $10^8$  [192]. In this case, polyfluorene (poly(9,9-di-*n*-dodecylfluorenyl-2,7-diyl)) wrapped CNT material was additionally subjected to size-exclusion chromatography, which in



the end gave purity exceeding 99.7%. Such processing enabled separation of preferentially solubilized close-to-armchair CNTs. FETs fabricated from them by electrophoresis were well-aligned and integrated, which can explain the observed high performance. With high-purity semiconducting CNTs, the FETs can not only offer high-switching ratios, but also operating frequencies up to 80 GHz can be attained [195].

Moreover, when electric current is passed through CNTs, light emission in both near-infrared and infrared spectral regions occurs (Fig. 20b) [10]. Rich spectral response, in contrast with expected black body radiation, demonstrates big potential of these materials for optoelectronics. The emission, which is a result of excitonic  $E_{11}$  and  $E_{22}$  interband-transitions, falls within wavelengths important for telecommunication. It was later demonstrated that sorting of CNTs gives much narrower emission peaks, the wavelengths of which correlate well with the particular chiral angle [18, 196, 197]. Triplet-triplet annihilation mechanism was proposed to explain observed electroluminescence delay. The results show that light emitters of tailorable wavelength can be made from CNTs depending on the employed CNT type.

On the other hand, when irradiated with light, CNTs can be used for biological imaging (Fig. 20c). Photoluminescence of semiconducting CNTs make them promising materials in the near infrared range (1 – 1.4 $\mu$ m). It is a suitable range for biological imaging, wherein low autofluorescence of tissue and reduced photon scattering works to our advantage. It has been shown that selectively eluted (12,1) and (11,3) absorb at ~800 nm and emit near ~1200 nm with 5-fold higher photoluminescence than unsorted CNT materials. That enabled imaging of whole mouse using 6-fold lower injection dose of CNTs. The reason for the reduced dosage is that selected CNTs are in strong resonance with 808 nm excitation. From the safety point of view, it has to be noted that toxic SC and SDS have to first exchanged for phospholipid-polyethylene

glycol (PL-PEG) or other biocompatible dispersing agent. Treated mice were monitored for 4 months with no obvious health problems [198]. Further advances revealed that additional reduction in dosage is possible down to  $1/10^{\text{th}}$  of the content of corresponding unsorted CNT mixtures [193]. Injection of CNTs resulted in relatively low accumulation in the reticuloendothelial system. In that study however, (6,5) CNTs not only were used for imaging, but also for photothermal therapy. When irradiated with laser of suitable wavelength (991 nm matched the  $E_{11}$  resonance of employed (6,5) CNTs) the tumor (where CNTs were directed) was heated up to  $50^{\circ}\text{C}$ . No signs of regrowth during 1.5 months following the treatment was observed.

CNTs can also serve as solar cell components (Fig. 20d). Solar cells were fabricated using bandgap sorted CNTs of small-diameter (in conjunction with  $C_{60}$  to align energy levels and absorb complementing regions of solar spectrum) [199]. They demonstrated higher open-circuit voltage (0.44 V vs 0.39 V) and infrared external quantum efficiency (16% vs 4%) than corresponding solar cells made from unsorted CNTs. Small diameter CNTs were found to have more efficient charge transfer to  $C_{60}$ . It has to be noted that the wrapping polymer may have a strong influence on the measured open-circuit voltage and generally the performance of a solar cell [200]. Moreover, when diameter-sorted SWCNTs were coupled with phthalocyanine by  $\pi$ - $\pi$  stacking relatively high light-harvesting capacity was observed. A maximum of photon-to-current efficiency 12% was achieved. In the case of dye-sensitized solar cells, nearly monochiral semiconducting CNTs significantly increased the overall performance again as compared with unsorted material [201]. Metallic CNTs were confirmed to have a negative effect on charge extraction, so they have to be avoided with the same precision as when FETs are constructed.

It has been shown that all-carbon (anode, active layers, cathode) solar cells can be successfully fabricated [202] demonstrating that sorted CNTs have big potential for photovoltaics. [162].

Piezoresistive effect in unsorted CNTs has been documented, but as the new results show, there is a clear benefit of using chirality resolved material for this purpose [203]. Having the material of carefully defined electrical properties can improve the performance by almost an order of magnitude. The sorting process however has to be executed to such extent, so that the resulting material is of near monochiral nature. The reason is that even a small number of impurities (*e.g.* low resistance/gauge factor CNTs) can have a deleterious effect on strain sensitivity, which deteriorates the overall piezoresistive action.

Sensing abilities of CNTs improve with the purity of used semiconducting CNTs, their alignment, debundling and chirality [194]. Compounds such as dimethyl methylphosphonate (DMMP) or trinitrotoluene (TNT) can then be detected from just 2 parts per billion (ppb) (Fig. 20e). In some cases, diameter of chosen CNTs for sensing is important. CNTs of diameters larger than 1 nm are able to sense H<sub>2</sub>, but the sensitivity vanishes for smaller diameter CNTs (change of work function upon H<sub>2</sub> spillover and chemisorption) [204]. Moreover, besides other species, sorted semiconducting CNTs were confirmed to detect NO<sub>2</sub> and NH<sub>3</sub> [205]. The resistivity of the sensor decreased when it was exposed to NO<sub>2</sub>, but increased when it was in contact with NH<sub>3</sub> (NO<sub>2</sub> is preferentially chemisorbed, whereas NH<sub>3</sub> is physisorbed).

Due to high thermal conductivity of individual CNTs, they are often considered as good heat sink candidate materials. Although the dependence of electrical conductivity of CNTs on chirality has been explored to a large extent, the influence of chiral angle on thermal conductivity has not achieved the same level of attention. Lian and co-workers investigated how variation in the ratio of metallic to semiconducting CNTs affects thermal transport properties [206]. It has

been found that thermal contact resistance (number of junctions, length, alignment, presence of residual surfactant/functional groups, *etc.*) dominates how well the material conducts heat. The heat flow was found to be predominantly carried by phonons, so the transport is generally not dependent on chirality or electrical character (contrary to the published modeling results [21]).

#### 4. Conclusions and future overlook

It is very encouraging to see that new protocols are developed to produce a wider range of CNTs than just popular (6,5). With each chiral angle “mastered” we are getting a better understanding how the CNT forming machinery works, which in turn brings us closer to selective synthesis of other chiralities. Iterative progress on this front may enable full control over the CNT structure one day.

Every chiral angle gives a different set of properties: bandgap,  $E_{ii}$  emission wavelength, *etc.*, which makes it possible to match CNT type with a given application. However, as proven by the results of the reviewed studies, although CNT chirality is important, length/alignment/purity influence should not be underestimated. Even carefully extracted CNTs of a selected type may show inferior performance if they are contaminated, grafted with unwanted functional groups, too short or of isotropic distribution. The effect is most evident in the applications, which require high electrical or thermal conductivity as such modification would introduce significant junction resistance hindering electron or phonon propagation.

The most effective sorting strategies rely on CNT material synthesized with some chirality preference already at this stage because it is much easier to resolve a mixture into components if it is composed of a smaller number of individual species. It would be important to focus on the synthesis side and establish more selective protocols. It has been shown that CNTs of certain chiral angles such as (6,5) or (9,8) can be preferentially manufactured using appropriate reaction parameters. The question is if we have not found other catalysts to produce the remaining CNT types yet or some CNT types exhibit extraordinary stability. When additional compounds are introduced to the reaction mixture they were found to steer the synthesis into a different direction. It may be worthwhile to take the well-documented catalyst system such as CoMoCAT

(for preferential (6,5) synthesis) and try introducing additional species, which may enable production of other chiralities.

Because of high costs (capital investment to buy equipment or necessity to rely on expensive chemical compounds) incurred when sorting CNTs, it may be beneficial to revisit the strategy of cloning. Other expenditure-intensive sorting methods could be employed to establish a library of CNTs, which then could be employed as templates. Such approach very much resembles polymerase chain reaction used for DNA amplification. In our case *initialization* step would open and activate the master copies and *elongation* step would proceed with the synthesis. It is not hard to imagine an optimized process such as this, which could be fully automated, but at present the copying process is not accurate enough for wider application

Some chemicals engaged to sort CNTs can be considered expensive when the amount of produced CNT of a given type is taken into consideration. Significant efforts leading to obtaining CNT (n,m) concentrations on the order of  $\mu\text{g/mL}$  can be accepted at the laboratory scale for fundamental research, but currently not for applications at the commercial level. Polyfluorenes for polymer extraction, iodixanol as a density gradient medium in ultracentrifugation, dextran for two-phase extraction, *etc.* come with a rather high price tag. What is more, many fold excess of them has to be employed to obtain the product. We need to explore the alternatives and look for “a generic drug”, which would have equivalent sorting capabilities, but become available at much lower cost. Aqueous two-phase extraction is a powerful, but relatively simple technique which would greatly gain if replacements to bile salts and dextran could be obtained as they constitute more than 90% of the sorting cost. Another option would be to establish protocols, in which the used chemicals can be recycled at least to some extent. This way not only the cost of chirality sorted material would be greatly reduced, but it could be synthesized at a much larger

scale. That would enable evaluation of such materials in a wider range of applications on the real-life scale.

Although relatively expensive, using DNA for recognition of particular CNT type was found very effective. More importantly, by varying the nucleotide sequence, a nearly limitless number of DNA strands can be made. The number of combinations scales according to  $4^n$ , wherein  $n$  stands for a number of nucleotides in sequence. Each of this DNA strand has a slightly different affinity for particular CNTs. Because thorough experimental validation at this scale may be far from realistic, it would be important to establish techniques of accurate theoretical modeling of interaction of such DNA segments with various CNTs. Screening of such library by computation would select the most viable candidate segments to be verified empirically.

It is interesting to see that different sorting methods show some common findings, which gives a more insightful view into the science of nanocarbon. For example, certain surfactant combinations (SDS/SC in particular) were found very effective for sorting regardless of the method employed – DGU, ATPE, (di)electrophoresis, *etc.* It indicates that gaining more understanding of surfactant-CNT interaction can make a bigger impact than anticipated and improve the CNT resolution in general (not just optimize a selected method).

The number of developed sorting techniques and their capabilities reaching the precision level of handedness CNT resolution is very impressive. What once was thought as impossible can be currently carried out by combining a few of polymers, CNTs and water. It has taken 12 years from the discovery of CNTs to establish first sorting strategies, but the research in this area has intensified every since (Fig. 1). Even more, we are now entering the exponential “growth” phase, so further discoveries are expected to surprise us in the foreseeable future. Maybe the Holy Grail of the CNT science, the full chirality control, is close to be discovered after all?

## **Acknowledgments**

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## Biographies



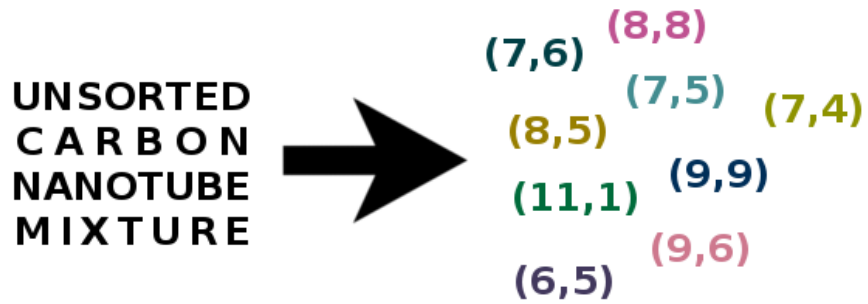
Dr Dawid Janas graduated from University of Cambridge in 2014 with a PhD degree in materials science. For the next 2 years, he held a Research Associate position in the Electric Carbon Nanomaterials group at the University of Cambridge. Since 2016, he is a Research Fellow at the Silesian University of Technology in Poland. His current research interests include manufacture of carbon nanostructures, tuning of their properties, chemical functionalization and real-life applications.

## Table of contents

### **Towards monochiral carbon nanotubes: A review of progress in sorting of single-wall carbon nanotubes**

Dawid Janas\*

This review provides an in-depth overview of the sorting methods of carbon nanotubes



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