Methods for dispersing carbon nanotubes for nanotechnology applications: liquid nanocrystals, suspensions, polyelectrolytes, colloids and organization control

Sergio Manzetti, Jean Christophe Gabriel

REVIEW

CrossMark

Methods for dispersing carbon nanotubes for nanotechnology applications: liquid nanocrystals, suspensions, polyelectrolytes, colloids and organization control

Sergio Manzetti[1,2] · Jean-Christophe P. Gabriel[3,4]

Abstract

Carbon nanotubes (CNTs) are a central part of advanced nanomaterials and are used in state-of-the-art technologies, based on their high tensile strength, excellent thermal transfer properties, low-band gaps and optimal chemical and physical stability. Carbon nanotubes are also intriguing given their unique π-electron-rich structures, which opens a variety of possibilities for modifications and alterations of their chemical and electronic properties. In this review, a comprehensive survey of the methods of solubilization of carbon nanotubes is presented, forming the methodological foundation for synthesis and manufacturing of modified nanomaterials. The methods presented herein show that solubilized carbon nanotubes have a great potential in being applied as reactants and components for advanced solar cell technologies, nanochemical compounds in electronics and as parts in thermal transfer management. An example lies in the preservation of the aromatic chemistry in CNTs and ligation of functional groups to their surfaces, which confers CNTs with an optimal potential as tunable Schottky contacts, or as parts in nanotransistors and nano-resistances. Future nanoelectronic circuits and structures can therefore depend more and more on how carbon nanotubes are modified and functionalized, and for this, solubilization is often a critical part of their fabrication process. This review is important, is in conjecture with the latest developments in synthesis and modification of CNTs, and provides the know-how for developing new CNT-based state-of-the-art technologies, particularly with emphasis on computing, catalysis, environmental remediation as well as microelectronics.

Keywords Carbon nanotubes · Nanochemistry · Modification · Organic · Reactions · Nanoelectronics · Chemical · Nanotechnology

Introduction

Chemical functionalization of carbon nanotubes (CNT) is perhaps one of the most important challenges in organic chemistry and chemical nanotechnology in present time. Not only does functionalization of carbon nanotubes play a critical role for achieving new variants of these organic nanomaterials for state-of-the-art nanotechnologies and bio-nanotechnologies [1–7]. It can also pave the way for achievements in functionalizing similar nanomaterials such as nano-cones, bucky-balls, graphene sheets and other nanomaterials composed entirely of carbon and expand the knowledge in organic chemistry and chemical nanotechnology. Modification of carbon nanotubes can furthermore be a critical part of tailoring their properties for other applications as well, such as environmental remediation [8], catalysis [9–11], battery components [12–17], or also as fuel sources [17]. Functionalization and modification of the carbon nanotube is

✉ Sergio Manzetti
  sergio.manzetti@fjordforsk.no
  http://www.fjordforsk.no

[1] Fjordforsk A/S, Nanofactory, Midtun, 6894, Vangsnes, Norway

[2] Department of Molecular and Cellular Biology, Biomedical Center, Uppsala University, Husargatan 3, 751 23 Uppsala, Sweden

[3] Nanoscience and Innovation for Materials, Biomedicine and Energy (NIMBE), CEA/CNRS/Univ. Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France

[4] Energy Research Institute @ NTU (ERI@N), 50 Nanyang Av., Singapore 639798, Singapore

Springer

essential also because it gives completely new nanomaterials as starting base for developing new components in nano-electronics and nanophotonics [5, 18–27] and can provide unique spintronic properties for particularly photonic applications and in bionanosensors [28–39], as well as function as nanoswitches [18] and nanoresistors [33, 40].

In order to achieve an ideal functionalization basis for carbon nanotubes, solubilization, dispersion and poly-electrolyzation represent the starting phase of modifying CNTs. These three fundamental approaches for modifying carbon nanotubes, without disruption of the carbon cage structure, or without excessive loss of the aromatic density of the surface of the CNTs, are selected because they can form a basis for modifying CNTs to work in various applications, particularly with reference towards microelectronics, where modification is required and plays a role for the CNTs as Schottky contacts [41–45], biosensors [23, 46, 47] and nanotransistors (Fig. 1) [48–51] and also for environmental sciences [8, 52, 53]. There CNTs have a formidable sorptive character [54] and can be tailored to fit various functions such as superhydrophobicity, metal-sorption [55–58], aromatic compounds removal [59, 60] and other parts of environmental sciences [61]. Modifications are also critical for polymers and resins [62–65], fortified materials [66–68], sensors [69–71] and also computational processing units [72].

This work is novel in that it combines the recent and older literature from chemical approaches for functionalizing nanotubes with a spectrum of methodological details and particularly a consistent applicability of the given methodologies towards recent and industrially relevant sciences. It described also the electronic properties that lie behind the modifications made on nanotubes, in a pedagogical manner, particularly for the student audience in the field of nanosciences. Combined altogether, the presented data is intended to stimulate the nanoscientist to develop new materials and composites and enhance the importance of modified nanotubes, for their applications in nanotechnology.

Suspension of carbon nanotubes

Solvent suspension and dispersion of CNTs

Functionalization of a nanomaterial implies the ability to change its chemical and physical properties by means of chemical reactions. Functionalization requires an optimal interface contact between the nanomaterial and the reactants, to reach a good chemical interaction and a high reproducible yield of the chemical reaction products. For this, a series of solvents (Fig. 2) which merge reactants with the aromatic surfaces of carbon nanotubes [54, 73, 74] are required. However, solvation of pristine carbon nanotubes is virtually impossible, as their surface has a highly unique electrostatic character arranged in a non-periodic manner. CNTs are neither regarded as ordinary aromatic, lipophilic,
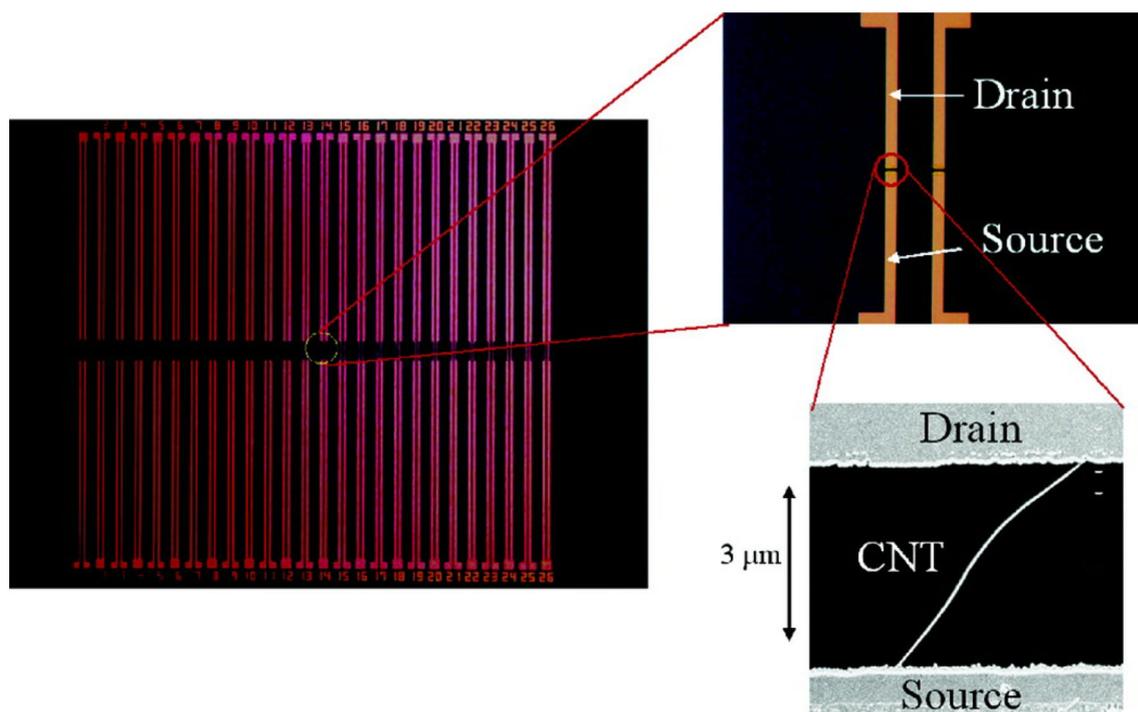

Fig. 1 Biochip composed of 26 arrayed CNT-FET. The arrayed CNTs are based on aptamer-modified carbon nanotubes. Reproduced with permissions from Ref. [50]. Copyright© 2013 American Chemical Society

or polar, given their population of π-electrons which is not counter-balanced by aromatic hydrogens, as found in the main reference aromatic compound—benzene, its cousins naphthalene, anthracene and other liquid aromatic compounds. This can be seen in the illustration in Fig. 3, which shows the unique π-electronic surface of CNTs and the reference surfaces of the aromatic structures of benzene, naphthalene and anthracene.

Pristine CNTs can however be suspended in solution and their surface of interaction be made more accessible to various reactants by devising the right solvents for chemical reactions between the carbon nanotube and a chemical compound. A set of compounds are required for this and bear often aromatic/hydrophobic and ionic properties.

N-N-Dimethylformamide (DMF) has been used for suspending CNTs in microdroplets for nanoelectronic purposes and leads to the formation of suspended bundles of CNTs [75]. DMF has also been used as a solvent for other nanomaterials similar to the carbon nanotube, such as graphene oxide nanoparticles [76]. However, being a volatile solvent, DMF may be unsuitable for reactions of exothermic character, and a solvent with lower heats of vaporization is preferred when undertaking modifications of pristine carbon nanotubes for functionalization. Gojny et al. [77] used

acetone to disperse a suspension of oxidized carbon nanotubes by ultrasonication, where acetone formed a solubilizing phase in contact with the hydroxylated side-chains of the modified CNT surface.

CNTs can also be dispersed in diethyl ether [78] during a process for fluorination of carboxylated multiwall CNTs (MWCNT-COOH). The process for solvation of the carboxylated nanotubes is applied after a modification of the MWCNTs surface, where 1 g of MWCNT-COOH is mixed with 10 mL of diethylene glycol dimethyl ether (DGDE) and 3.1 g 4-fluoroaniline in a flame-dried bottleneck flask under an inert atmosphere of nitrogen. 4 mL of amyl nitrate is then added to the mixture, which is at last diluted with diethyl ether. The function of 4-fluoroaniline and DGDE lies in transferring the fluorine to the CNT surface for covalent bond formation. The final step of diluting modified CNTs in diethyl ether is made given that diethyl ether has a very high heat capacity (Table 1). Its boiling point is however very low (34.6 °C) and can therefore be unsuitable for many reactions which release heat, such as oxidation reaction of pristine CNTs. Diethyl ether is nevertheless a very suitable solvent for storing modified CNTs over long periods of time as it protects the added side-chains on the surface of the CNTs from reacting with one CNT and another.

Fig. 2 2D structures of selected solvents for carbon nanotubes. From top left: DMF; acetone; diethyl ether; ethanol; propanol; methanol; DMSO; polyether; phenol; catechol; pyrogallol. Refer to Table 1 for details
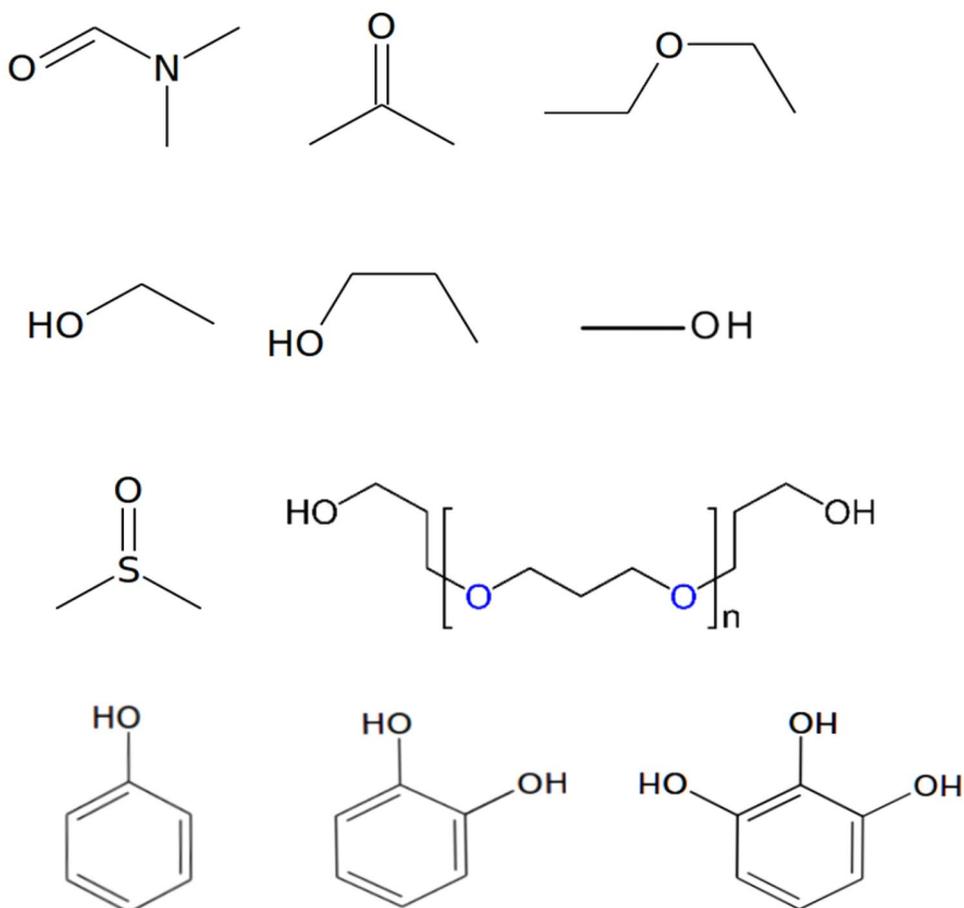
Table 1 A list of selected solvents for carbon nanotubes (Fig. 2)

Solvent	Character	C (J/K mol)	Boiling point (°C)	ΔH_{vap} (kJ/mol)	Dipole moment (Debye)	References of use with CNTs
DMF	Amphiphilic	146.05	153	47.6	3.86	[75, 76]
Acetone	Amphiphilic	125.45	56	31.30	2.91	[77]
Diethyl ether	Amphiphilic	172.50	34.6	26.17	1.15	[78]
Ethanol	Amphiphilic	111.46	78.1 (95.5%)	38.56	1.69	[127]
Propanol	Amphiphilic	0.21	82.6	44	1.63	[128]
PDDA						[134]
Polyvinyl alcohol	Amphiphilic	57–67	228	60–300[a]	7.34[b]	[132]
Methanol	Amphiphilic	79.50	64.70	38.28	1.69	[133]
DMSO	Amphiphilic/aprotic	149.40	189	52.50	3.96	[82, 118, 122]
1-Naphthol	Aromatic-polar	172.80 (gas)	285	59.70	1.56	[74]
Catechol (1,2-benzenediol)	Aromatic-polar	186.33 (gas)	513	61.2	2.64	[74]
Pyrogallol	Aromatic-polar	552.97 (gas)	309	62.13	1.97[c]	[74]
Tetracene	Aromatic (linear geometry)	468 (gas)	704.82	106.20	NA	[81]
Ionic PAHs	Aromatic/ionic	–	–	–	–	[126]
Polyethers	Polymeric, polyglycerol/polyethylene oxide, amphiphilic	–	–	–	–	[203]
PAMI	Polymeric, polyimide, amphiphilic	–	–	–	–	[82]

C heat capacity, ΔH_c std. enthalpy of combustion, ΔH_{vap} heat of vaporization at room temperature

[a][201]

[b][202]

[c]Calculated computationally with Amsterdam Density Functional [199]

In order to preserve the chemical surface of modified CNTs, a careful selection of right solvents must be made. Lin and Xing [74] have compared several solvents for interaction with CNT surfaces, using pristine CNTs. Their results showed that pyrogallol and 1-naphthol had a particularly high affinity of binding to the CNTs in multiple layers as well as at higher binding coefficients than other tested solvents (phenol, cyclohexanol, catechol, phenylphenol). The binding coefficient for naphthol increased threefold when the diameter of the CNT was reduced from 100 to 10 nm [74], a feature that was also observed in a separate study via molecular simulations [79]. It showed that two relatively large planar polycyclic aromatic hydrocarbons (PAHs), perylene and retene, interact well with the surface of CNTs in multiple layers (Fig. 4). This pattern of aromatic plane-to-CNT interaction, which also occurs between aromatic molecules [80], favors aromatic solvents for dispersing pristine CNTs in a liquid media and forms a basis of nanochemistry approaches where aromatic properties are essential components, either as individual compounds and reactants or as functional groups in selected reactants. Gotovac et al. reported also interesting results and showed that the linear four-ringed aromatic compounds tetracene has a superior sorption coefficient to the CNT surface compared to phenanthrene (three-ringed non-linear) and toluene (single-ringed

with methyl group) [81]. Interestingly, the curvature of the surface of the CNT is also critical for sorption and dispersion potential of the CNT in a media, and high-curvature CNTs (small diameter) are expected to have a lower sorption efficiency compared to lower curvature CNTs (large diameter) towards large planar aromatic compounds, given the increasing planarity of the surface of larger CNTs, as also shown in the simulation study mentioned [54]. However, for smaller polycyclic aromatic hydrocarbons, the higher surface curvature (smaller diameter) has a favorable effect for increasing sorption to the CNT surface [74]. This relationship between curvature and aromatic sorption capacity forms also a basis for dilution and dispersion methods for CNTs, where pristine CNTs can possibly solubilize to a diluted/liquid state at 900 °C if vaporized tetracene is gradually cooled slightly below its boiling point of 704 °C (Table 1) or by using other PAHs of several rings in their liquid state (such as pyrene).

Another similar group of CNT dispersants are phenolic solvents which have a good binding capacity towards CNTs. Lin and Xing showed this by comparing the relative sorption capacity of pristine CNTs to phenol, catechol and pyrogallol, which increases in order by the number of OH groups provided by the solvating compound (phenol < catechol < pyrogallol) [74]. The aromatic hydroxyl-containing compounds
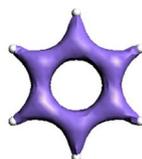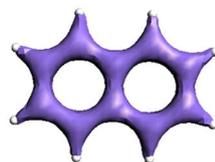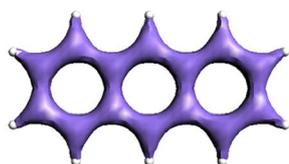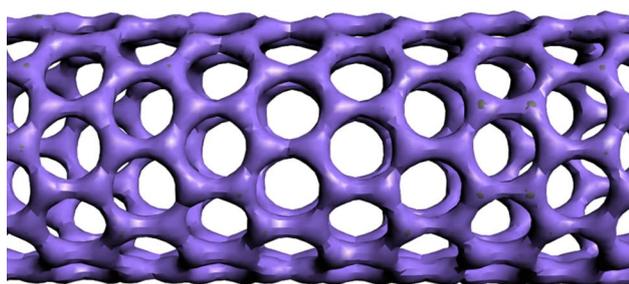
Fig. 3 Electron density plots for CNT, anthracene, naphthalene and benzene (from top to bottom). The comparison of the ED plots shows how the CNTs lack the weakly acidic hydrogens, making them completely insoluble in virtually any solvent. ED maps generated with Amsterdam Density Functional [199]

provide a particularly polarized bond at the C–OH junction, which interacts extra strongly with the carbon moieties from the hexagonal carbon geometries (Fig. 5). This type of non-covalent interaction generates more flexible interactions, than plane-to-plane interactions as for aromatic compounds, and can therefore be more suitable when CNTs are already partly modified or oxidized.

CNTs can also be suspended by adding emulgating moieties to their surfaces. Chang and Liu prepared two suspensions of MWCNTs by reversibly attaching furfuryl alcohol (FA) and *N*-(4-hydroxylphenyl)maleimide (NMHI) separately to the surface of the MWCNTs in a dimethyl sulfoxide (DMSO) solution [82]. MWCNTs acted as dienophiles in the polar aprotic environment provided by the solvent DMSO, while the FA and NMHI donated sp2 electrons to form reversible bonds with the MWCNTs. Both suspensions were prepared at 50 °C over 96 h by mixing 20 mmol of furfuryl alcohol (and 20 mmol NMHI for the

second suspension) dissolved in 15 mL DMSO with 0.05 g MWCNT. In a similar manner to DMSO, other related solvents such as DMF (dimethylformamide) and hexamethylphosphoramide (HMPA) provide also intermediate dielectric environments and hydrogen-bonding groups, which are particularly suitable in forming appropriate chemical and molecular environments for facilitating reactions between CNTs and electron donors/acceptors. Other similar types of aprotic solvents are tetrahydrofuran (THF), ethyl acetate acetone and acetonitrile.

Surfactant-assisted suspensions of CNTs

Surfactants have been used very early on to help in the dispersion and purification of CNTs in aqueous solutions [83–86]. One of the interest of surfactants is that they are theoretically easy to remove by washing, although some prove difficult to rinse off completely, which can to be a problem, especially when making electronic devices, such as gas sensors [87]. Early reports used easy to access surfactants such as sodium dodecyl sulfate (SDS), benzalkonium chloride, sodium dodecylbenzene sulfonate or nonionic ones such as polyglycol ether of high weight [83–86]. Since then, a multitude of surfactants have been used to various outcomes and to enable a wide range of applications. This has, however, already be the subject on recent reviews [88–91], we are therefore not developing further this approach beyond a few highlights presented in the following sections.

At this point it is timely to make a side note regarding the use of ultrasounds (US) that are commonly used to help disperse CNT bundles into solutions or suspensions of individual CNTs. Indeed, the use of US is far from neutral, especially when high-energy US are being used (US horns). One can cite at least three major effects associated with the use of US. First, they can induce local defects on their structure [92–97]. Green et al. reported that defects ranging from bending and buckling up to breakage of small pieces of graphitic layers were reported early on via TEM studies. When dealing with MWCNT, this could lead to the thinning of the nanotube by removal of one or more of the outer graphitic walls. They also reported that the effect was solvent dependent with a reduction of the amount of damages when using water or ethanol [92]. Secondly, as defects multiply, US can induce the breaking or shortening of CNTs [98–107]. Finally, an indirect effect is that the US horn used when applying high-energy US is itself affected by them and hence releases nanoparticles of the alloy forming the horn, usually stainless steel or titanium [108, 109]. This can be very detrimental to subsequent work performed using such polluted CNT suspensions [109]. A typical example of such side effect was reported in the field of hydrogen storage [110], where high storage capacity was reported
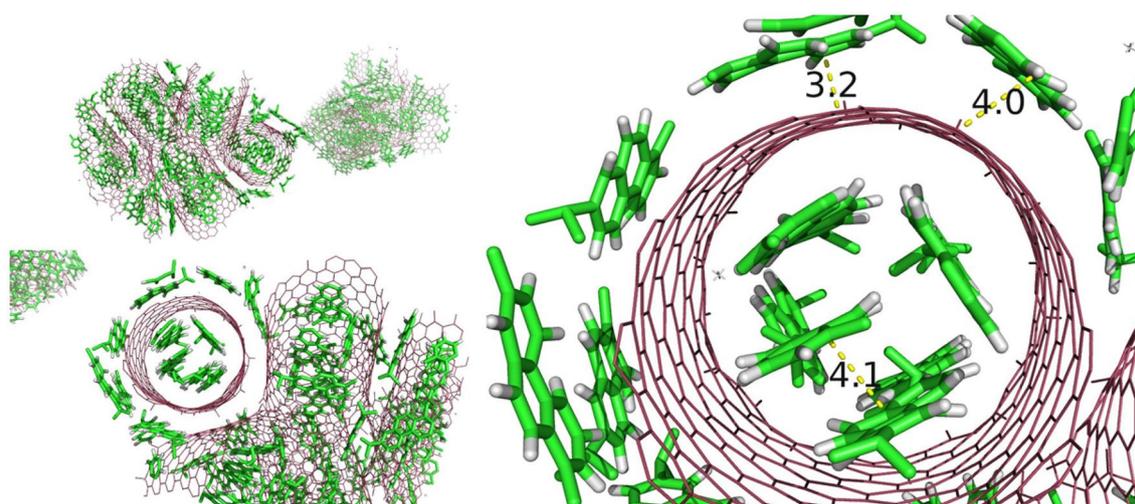
Fig. 4 van der Waals attraction between retene and perylene molecules onto the surface of carbon nanotubes. Depicted by measured distances. Adapted with permissions from Ref. [54]

for carbon nanotubes [111]. This capacity, together with the difficulty to reproduced the published result, were later attributed to the significant amount metallic nanoparticles impurities present in the material tested and arising from the horn [108]. Such large amounts were induced by using long and powerful exposures to ultrasounds to produce as high specific surface area materials as possible in order to increase the overall amount of hydrogen adsorption onto the CNTs [111]. In order to seek as reproducible processes as possible, when dealing with US and CNTs suspensions, we therefore strongly suggest (1) to closely monitor the amount of US used to treat the solution; (2) to characterize each batch to verify the morphologies, length distribution and other characteristic of the CNTs used. When suspensions are not stable on the long term, a good practice is therefore to make a new suspension from the original source of CNTs for each process batch [33, 112].

Ionic liquid suspensions of CNTs

One must wait 2003 to see first reports of dispersion of CNTs in room-temperature ionic liquids (RTIL) [113]. In this report pristine CNTs can be dispersed into imidazolium ion-based RTIL after grounding, thus forming a gel in which they form much finer bundles than initial ones. As per the authors, these gels are formed by physical cross-linking of the bundles, associated to a local molecular ordering of the ionic liquids. Typically, when single-walled carbon nanotubes (SWCNTs) in 1-alkyl-3-methylimidazolium tetrafluoroborate (AMIBF$_4$–alkyl = ethyl, n-butyl, n-hexyl) were ground and then centrifugated, a black lower highly viscous gel of SWCNTs in AMIBF$_4$ (0.5–2.5 wt% depending on the SWCNT source and RTIL used) was obtained. These gels present interesting features: (1) with both an electronic conduction arising from the percolation path via SWCNTs and ionic conduction thanks to the RTIL; (2) they behave as quasi-solid materials, hence enabling the fabrication of electrode materials. This explained the numerous reports that were subsequently published where such gels were used as electrodes in electrochemical energy storage capacitors or batteries [114, 115].

The dispersion mechanism of SWCNTs in RTIL was investigated by various spectroscopic and molecular modeling approaches by Wang et al., which shows that they interact via weak van der Waals interaction rather than "cation–pi" interaction. This keeps SWCNT's electronic structure intact. Dispersion of SWCNTs in ionic liquids having very high dielectric constants is made possible thanks to the shielding of the pi–pi stacking interaction [116].

Overall, if pristine SWCNTs are thus dispersed, hence enabling many applications, the viscosity of these suspensions can be further tuned by modifying the RTIL as well as making aqueous solution of the gel. Such work has been reported by Flahaut et al. in which imidazolium-based ionic liquids with a long hydrocarbon chain enable high concentration dispersion of pristine double-walled carbon nanotubes (DWCNTs) in water, having a low viscosity (similar to the one of water) and thus even at low IL concentration (1 mM) [117]. It should be noted that dispersibility of DWC-NTs increased with as the length of the hydrocarbon chain increased. The suspensions of partially de-bundled DWC-NTs proved to be stable for over a month. Typically, concentrated aqueous suspensions of DWCNT (50 mg/L) were first prepared on one hand as well as other aqueous solutions of the IL (1–10 mM—4 h of stirring) on the other. The two stock solutions were then mixed in an ultrasonic bath for

10 min followed by 30 min using an ultrasonic probe (25% amplitude with a pulse of 5 s on and 5 s off).

Overall, the RTIL approach appears to be a very promising and versatile tool for application requiring as pristine as possible CNTs whether it requires strong mechanically intrinsic properties or on the other extreme, low-viscosity suspensions for applications such as ink jet or spray deposition.

Polyelectrolytic solutions of CNTs

A stable dispersion of pristine and isolated CNTs is, as mentioned above, nearly impossible to achieve, as strong van der Waal interactions between individual nanotubes in colloidal suspension or solution prohibit the full individualization of the CNTs to form soluble individual macromolecules [118]. Also, their aromatic surface does not completely match with aromatic solvents [54, 74]). However, several groups have recently achieved a liquid state of this otherwise solid nanomaterial by converting SWCNTs into polyelectrolytes, composed of charged CNTs ($SWCNT^{n-}$) dissolved in a strong polar aprotic solvent, such as DMSO. Hence, Penicaud's group obtained a polyelectrolytic solution of SWCNTs by tuning their Fermi level [119]. The addition of positive charges to carbon nanotubes was performed using solid lithium or sodium as a reductant [120–123]. Thus the formed solutions contained up to 2 mg SWCNT/g DMSO and 4.2 mg SWCNT/g sulfolane and were found to be indefinitely stable in inert atmospheric conditions [122]. Metastable carbon nanotube suspensions, or solvated state of CNTs, were made up of $A(THF)C_{10}$ (A = Na, Li) where one negative charge was subdivided across 10 carbon atoms (one charge subdivided across 144 $Å^2$) [121]. Jiang et al. prepared more concentrated solutions of alkali reduced CNTs by adding crown-ether (16-crown-6) molecules (Fig. 6) as cation sequesters on SWCNT polyelectrolytes. SWCNTs' concentration was high enough to enable the observation of a liquid-crystalline phase of pristine SWCNTs and a peak "solubility" of 9.4 mg/ml in DMSO [118]. The preparation of SWCNTs is performed by reducing the nanotubes using
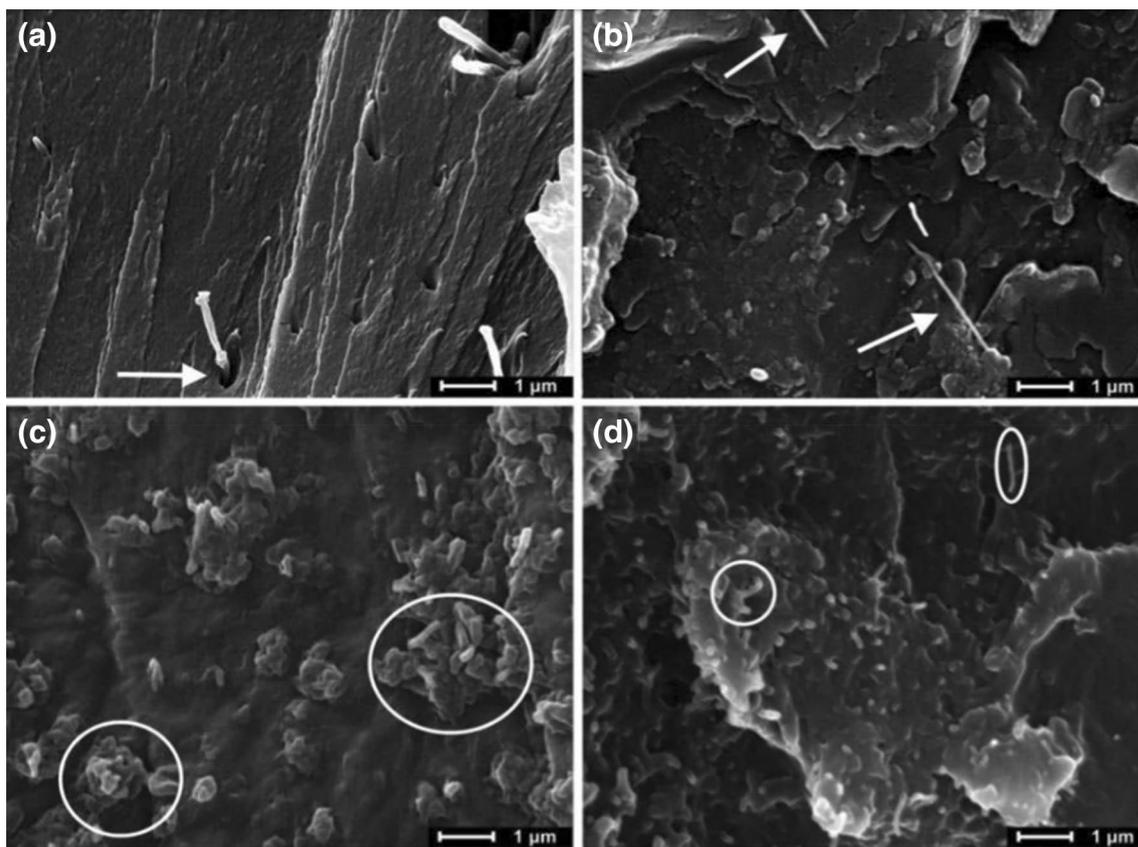

Fig. 5 Increased dispersion of functionalized CNTs. SEM micrographs show how polycarbonate-based (PC) nanocomposites loaded with 1% of different forms of modified CNTs display different dispersion levels of the CNTs. From top left to bottom right PC-composites with: **a** CNTs subjected to acid treatment: 45 wt% H_2SO_4 150 min; **b** CNTs subjected to acid treatment at 45 wt% H_2SO_4 150 min plus plasma treatment; **c** CNTs subjected to acid treatment at 70 wt% H_2SO_4 for 150 min and no plasma treatment; **d** CNTs subjected to acid treatment with 70 wt% H_2SO_4 for 150 min plus plasma treatment. Adapted with permissions from Ref. [136]. ©Copyright 2014 Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim
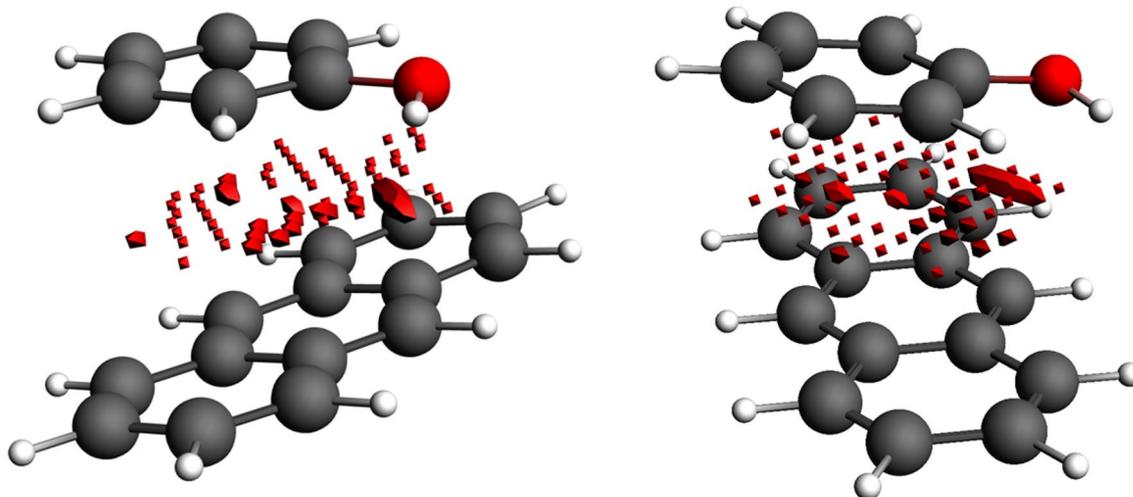
Fig. 6 Non-covalent interactions between phenol and anthracene. Left and right: the non-covalent interaction index [200] between a pyrogallol and an anthracene molecule, calculated by quantum chemical calculations using Amsterdam Density Functional [199] is shown by red dots of various proportions. The area of interaction between the C–OH bond from pyrogallol and the carbon atoms of anthracene is particularly significant (large red cluster)

alkali metals, which formed negatively charged pristine SWCNTs (as noted above). The formed negatively charged CNTs repel one another in DMSO and the alkali ions are sequestered by the 18-crown-6 molecules which together form a liquid-crystalline phase at high concentration [118]. When the concentration of the liquid-crystalline phase exceeded 9.4 mg/mL it went from solution to a viscous gel. The procedure for preparing liquid-crystalline SWCNTs is done by mixing 69.6 mg potassium metal, 163.2 mg naphthalene and 56 mL of distilled THF stirred for 24 h. After achieving a green solution, 150 mg of pristine SWCNTs is added to the mixture and stirred for 2 days at room temperature. The solution is then filtered on 0.45 μm PFTE membranes to obtain the black solid SWCNT polyelectrolyte. The dried polyelectrolytes is then mixed in DMSO and stirred for 14 h to fully disperse the polyelectrolyte SWCNTs and finally centrifuged under 9900 *g* for 45 min. The liquid-crystalline phase forms in the supernatant [118].

Moya and colleagues prepared a negatively charged polyelectrolytic solution of carbon nanotubes using polystyrene sodium sulfonate (PSS), as well as a positively charged polyelectrolyte solution of SWCNTs using polyallylamine hydrochloride (PAA) [124]. In either case, SWCNTs were retained in their pristine form, and not modified on their surface. This method is a hybrid approach between generating polyelectrolyte suspension of CNTs and solvating the CNTs in a polymeric molecule (as described in the next section). It involves the preparation of a 75–25% ethanol–water solution, in which either of the two charged polymers (PAA or PSS) is added to, in order to reach a polymer concentration of 1 mg/mL. From this point, the two separate solutions of the polymers in ethanol and water are mixed with an equal volume of SWCNTs dispersed in pure ethanol at a concentration of 0.5 mg/mL. Following which the suspensions are centrifuged, replaced of their supernatant, ultrasonicated and immersed in water. The final water-solutions of coated SWCNTs is stable for several months and display a zeta potential of −60 mV and +40 mV, respectively, for the PSS and PAA-coated nanotube polyelectrolytic solutions [124].

Han et al. synthesized water-soluble MWCNTs with polyelectrolytes attached covalently to their surface, for CNT-based dye-sensitized solar cells [125]. The followed procedure is quite different from the aforementioned studies on polyelectrolytic preparations, and involved mixing sodium styrenesulfonate (194 mmol) and 2,2,6,6-tetramethyl-1-piperidinyloxy (18.9 mmol) in 200 mL ethylene glycol. A solution of potassium persulfate (9.6 mmol) in 45 mL of double-distilled H_2O and a second solution of sodium metabisulfite (7.2 mmol) in 15 mL double-distilled H_2O are both added to the ethylene glycol solution and stirred at 130 °C under nitrogen atmosphere for 6 h. 0.4 g of MWCNTs are then added to the solution and allowed to react for 24 h with rigorous stirring, generating the surface-coated polyelectrolytes of CNTs. This procedure generates functionalized polyelectrolytes of CNTs, rather than polyelectrolytes of pristine CNTs. The generated solution is then sprayed to form a cover layer for dye-sensitized solar cells over a layer of fluorine-doped tin oxide, with various layer thicknesses ranging from 0.08 μm to 2.57 μm [125].

Paloniemi et al. prepared water-soluble polyelectrolyte SWCNTs by non-covalent modifications using ionic pyrene and naphthalene derivatives [126]. Seven different
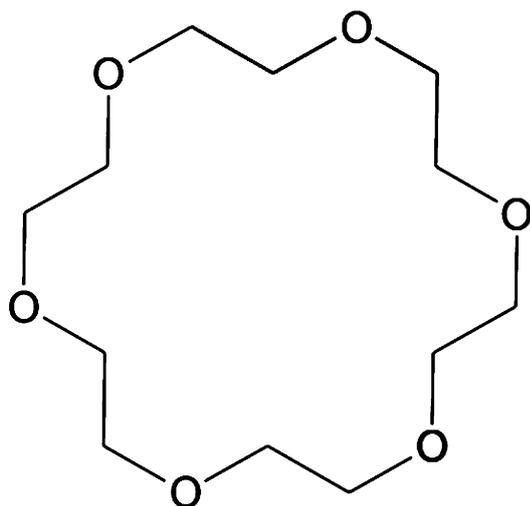
Fig. 7 18-Crown-6, a cyclic polyether with cation-sequestering properties, used for generating polyelectrolytes of Li/Na-reduced SWCNTs

ionic polycyclic aromatic compounds (Fig. 7) were used to disperse oxidized SWCNTs separately: 6-amino-4-hydroxynaphthalene-2-sulfonic acid, 5-aminonaphthalene-1-sulfonic acid, and 5-aminonaphthalene-2-sulfonic acid, which were recrystallized from boiling water, and another four: 2,5-dihydroxy-1,4-benzenedisulfonic acid, 4,5-dihydroxynaphthalene-2,7-disulfonate, 5-(dimethylamino)-1-naphthalenesulfonic and 1-pyrenemethylamine hydrochloride which were used as purchased. Only 4,5-dihydroxynaphthalene-2,7-disulfonate showed reduced solvation effects and was not considered further by the authors. For all other compounds, the procedure includes solvation of each separate compound in water at concentration (0.5–2.5 mM for 1-pyrenemethylamine hydrochloride) and an equivalent amount of NaOH is added to deprotonate the sulfonate groups. 1–3 mg of oxidized SWCNTs is then immersed in 10–15 mL of the solutions described above and sonicated for 1–1.5 h. The non-dispersed SWCNTs are then allowed to sediment overnight, and a dialysis run is performed to remove excess solvent molecules. Dialysis of the SWCNTs dispersed with 1-pyrenemethylamine hydrochloride is performed with tubes pretreated with poly(diallyldimethylammonium)chloride to prevent sorption of cationic SWCNTs on the tubing walls [126].

In general, all these polyelectrolyte methods generate macromolecular solutions of CNTs, as they gain charge and interact with the environment either by electrostatic repulsion to other CNTs or by steric interaction with some bulky solubilized ionic counterpart. In each case however, the CNTs can be traced by TEM imaging, and still appear as nanomaterials (Fig. 8). However, their chemical state is charged, and is closer to a solute rather than a material or solid, forming an excellent platform for liquid electronics and nanoenergetic suspensions for nanoelectronics, solar cells and also computing devices.

Polymeric solvation of CNT

CNTs can also be dispersed in specific polymer solutions, which form non-covalent bonds to the surfaces of the nanotubes, dispersing them in the polymeric gel. Wang and colleagues used Nafion® (sulfonated tetrafluoroethylene-based fluoropolymer-copolymer) to disperse SWCNTs and MWCNTs for preparation of amperometric biosensors and obtained a CNT solution after 36 h of suspension in a phosphate buffer or in ethanol, but no further detail is available [127]. Nafion® has also been used by Guzmán et al. by dispersing MWCNTs with 2-isopropanol for the attachment onto glassy carbon electrodes as a substrate [128]. This procedure includes the reduction and dispersion of MWCNTs by nitric acid followed by a functionalization by sulphuric acid (70%) and hydrogen peroxide (30%). This procedure, however, abolishes the unique electronic properties of the π-system in CNTs [129]. Acids and strong oxidants should therefore be avoided whenever structurally pristine CNTs are of interest in the suspension.

Zhang and Silva developed a method for dispersing MWCNTs by saturation of CNTs in organic dyes. The organic dyes used are of considerable higher molecular weight compared to the list of solvents in Table 1, and are composed of poly-ringed moieties functionalized with sulphonic, amide, carboxyl, ethoxy or hydroxyl groups. The poly-ringed dyes (such as Direct Yellow [130]) give a debundling effect of MWCNT clusters, and saturate the surfaces of the MWCNTs by chemical interaction between the CNTs and the amide and carboxyl groups of the dyes, which form MWCNT-adducts [131]. The procedure is carried out by mixing 10 mg of dye and 10 mg of MWCNTs (inner diameter 5–10 nm, outer diameter 10–20 nm and length 0.5–200 μm) in an ultrasonication bath for 40 min. This represents a cost- and time-efficient protocol compared to many of the other approaches described above.

Pan and colleagues prepared a polymeric solution of MWCNT + polyvinyl alcohol (PVA) as a polyelectrolyte solution for use in direct methanol alkaline fuel cells. They prepared a solution of PVA in water (1 g with 30 mL water) at 70 °C which was purged with ozone for 15 min. The solution was then purged with argon gas to remove free peroxide formed in the oxidation reaction of PVA, and 500 mg of CNTs was added to the mixture. The mixture is stirred for 3 h at 80 °C before used in the preparation of the electrolyte cells [132]. Shieh et al. applied a different approach and dispersed MWCNTs in methanol and obtained a good dispersion [133]. Methanol has also been used with fuel cells
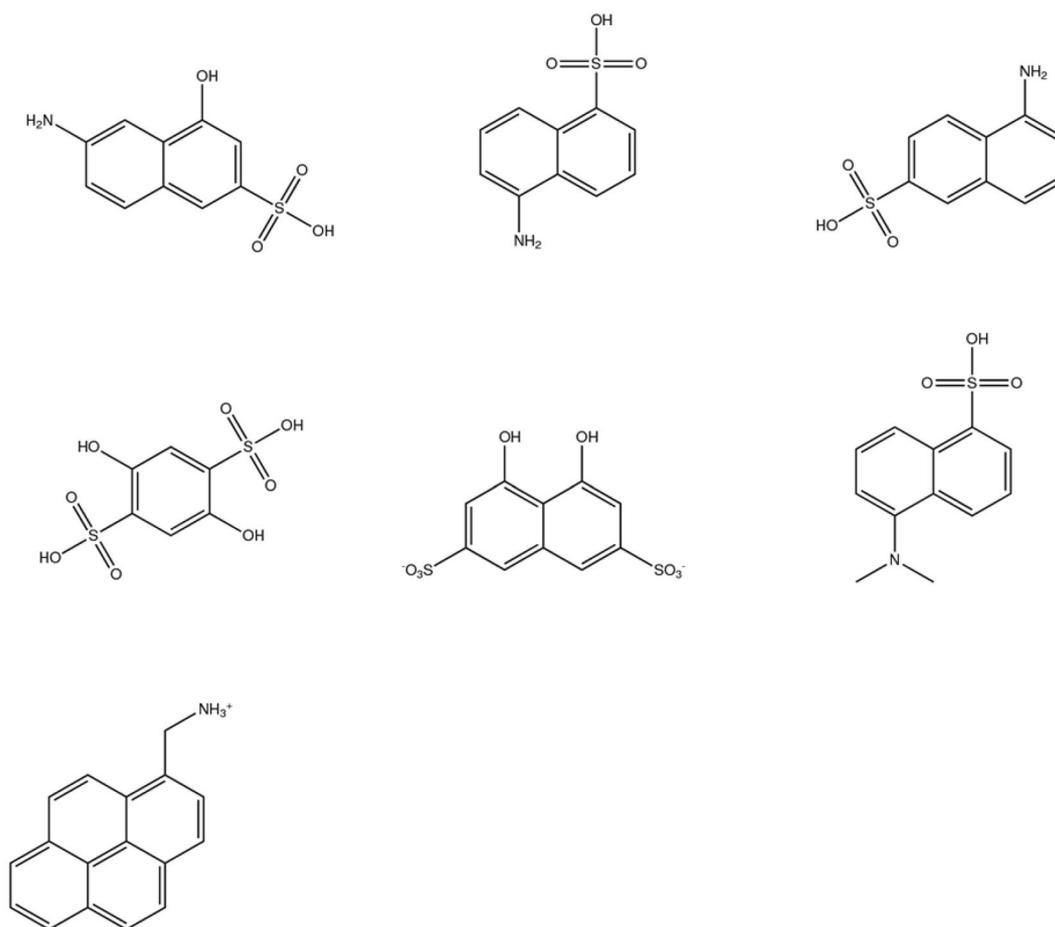
Fig. 8 Ionic PAHs used by [126] for solubilizing SWCNTs. From top left to bottom: 6-amino-4-hydroxynaphthalene-2-sulfonic acid, 5-aminonaphthalene-1-sulfonic acid, and 5-aminonaphthalene-2-sul- fonic acid, 2,5-dihydroxy-1,4-benzenedisulfonic acid, 4,5-dihydrox- ynaphthalene-2,7-disulfonate, 5-(dimethylamino)-1-naphthalenesul- fonic and 1-pyrenemethylamine hydrochloride

and CNTs in advanced fuel-source studies, for instance Liu et al. [134] prepared methanol-fuel cells based on MWCNTs as catalysts, in combination with palladium hollow nano- spheres. The MWCNTs are sonicated and dispersed in 0.5% poly(diallyldimethylammonium chloride) (PDDA) solution [134]. This generates a PDDA-coated MWCNTs, by non- covalent Coulomb interactions and forms a dispersion of MWCNTs. It is therefore particularly useful for generating a surface of positive charges on the MWCNTs, which readily binds to cations or metal nanoparticles. If the functional- ity of CNTs with a positively charged-polymer coating is intriguing, it however masquerades the nanotube surface, rendering it unsuitable as a preparation method for func- tionalization of CNTs.

Chang and Liu [82] dispersed MWCNTs with polyam- ide maleimide (PAMI) pendent groups, which were used for the first time in 2006 by Liu et al. [135]. The polymeric solvation of MWCNTs is carried out by dissolving 0.25 g of PAMI in 25 mL N,N-dimethylacetamide (DMAc). 0.05 g of MWCNTs are then added to the solution and heated at 50 °C for 96 h. The resulting suspension of MWCNTs contained MWCNTs inter-winded with PAMI molecules, formed a PAMI layer of ~ 50 nm outside the CNTs. The imide groups from PAMI formed covalent bonds to the MWCNTs surface which can be dissolved by heating the suspension at 160 °C for 20 h [82].

The following report is mentioned here, even though the structure of the CNTs are quite modified by the procedure, as it proves that means can be found to further improve CNTs dispersion. It is therefore noteworthy to mention a study by Maio et al. who performed surface functionali- zation plasma treatment [136]. In their study, they found that plasma-treated CNTs subjected to acid treatment in a 45 wt% with H_2SO_4 for 150 min, gives a better dispersion than CNTs subjected to acid treatment at 70 wt% H_2SO_4 for 150 min without prior plasma treatment. They showed in SEM images (Fig. 9) how this is visible with fewer and fewer CNTs sticking out of the composites. Depending on the nature of the composite, the CNTs can therefore be increasingly dispersed by plasma-functionalization.
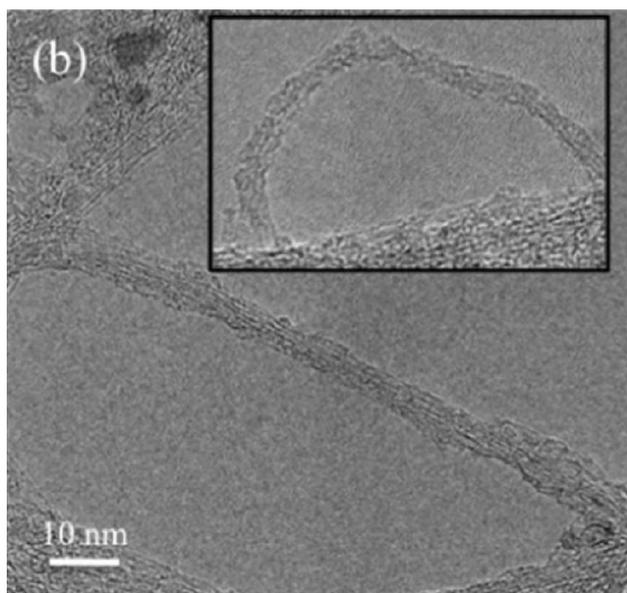
Fig. 9 TEM image of solubilized polyelectrolytes of SWCNTs imaged. Image reproduced with permissions from Ref. [118] Copyright© 2013 American Chemical Society

The procedure causes a decrease in CNT diameter, but apparently does not affect the CNT structures to a critical extent [136]. Increased dispersion of CNTs has also been achieved using surface modifications with various chemical groups, among Ferreira et al. who linked dodecylamine to the surface of CNTs [137].

Finally, macromolecule wrapping around SWCNT has proved to be a very powerful method not only to obtained stable dispersion of CNTs in aqueous solutions, but it also enabled for the bulk sorting of SWCNTs by diameter by using density gradients and ultracentrifugation of Deoxyribonucleic Acid (DNA) wrapped SWCNTs [138, 139]. This approach not only keeps the SWCNT pristine, but it also enables to obtain suspensions of SWCNT having fairly narrow disperse physical properties (for example band gap). The wrapping of SWCNT with single strand DNA molecule was first reported by Zeng et al. [140] and modified as follow to enable such separation. Typically, it is reported that decreasing aqueous dilutions of iodixanol were used and superposed to make a density gradient media (in pH 8.5 buffer). SWCNT were layered on top of the gradient. Sedimentation of SWCNT was performed at $174,000g$ for up to 10.5 h, when they reached their respective isopycnic points within the gradient. For HiPCO™ material, various bands could be observed (purple, green, and orange) indicating a rough separation of the SWCNT as a function of their intrinsic structure. Since these early reports, the approach has been fine-tuned and high-purity semiconductor or metallic SWCNT suspensions of SWCNTs are now commercially available from Nanointegris.

Anisotropic colloidal suspensions of CNTs

To further enable some applications, not only is it necessary to control the dispersion of the CNTs, but it can also be paramount to control the nanotube organization within the suspension [141]. We have already seen such a role in a previous section regarding the work of Poulin and co-workers and the making of highly oriented fibers of CNT/polymer composites [67, 142, 143], but we will develop this feature more specifically here. Such organization is indeed possible thanks to the intrinsic high anisotropy of CNTs, whether SWCNTs or MWCNTS. Such very high aspect ratio, somewhat similar to those of $Li_2Mo_6Se_6$ nanowires [144, 145] or imogolite nanotubes [146–148], or other mineral liquid crystals [149, 150], allow to anticipate that some anisotropy can be observed in such colloidal fluids/suspensions. Anisotropy can simply be induced by physical methods such as flow, electric or magnetic field. It is therefore not a permanent state and the induced organization usually disappears when the stimulus is stopped.

Flow alignment is usually induced by the shearing forces created by speed flow gradient existing in the fluid, just like tree trunks which tend to self-align along the flow on a river. This simple effect has been used by many groups to enable great achievements [67, 151–157].

An intrinsically and permanently anisotropic fluid, thus making these suspensions true lyotropic liquid crystals, otherwise called mesophases, can however be obtained when sufficiently high concentrations are reached. Although the potential existence of such a mesophase was easily intuited thanks to the occurrence of an Onsager transition [158–160], it was more precisely predicted theoretically in 2001 [161]. The biggest issue at the time was to reach a CNT suspension concentration that was high enough to enable such a transition. One therefore had to wait for the work of Windle and co-workers who used highly modified (oxidized) and charged MWCNTs to observe an isotropic–nematic transition at of 4.8% by volume [162, 163]. The latter reference [163] reports however results where the CNTs were initially strongly oxidized. It is therefore of interest to highlight the use of DNA, that can wrap around CNTs to enable SWCNT separations. Poulin et al. also succeeded to observe an isotropic/nematic typical phase transition. With the coexistence of both the isotropic and the nematic phase when SWCNT concentration was between 2 and 4 wt%, and a pure nematic phase above. This is likely to have been the first report of such a transition for aqueous suspension of pristine nanotubes [164].

If a nematic orientational ordering is now well established, higher order organization (positional) could be also expected, such as for example a rectangular, hexagonal or smectic ones, which have already been observed in the case of few other inorganic systems [165–172]. To our

knowledge, such ordered phases for pure lyotropic phase of pristine CNTs still remain to be discovered. However, a hexagonal mesophase has been obtained by using some surfactants, hence enabling an intercalated SWNT/surfactant hexagonal binary superlattice to be obtained [173]. In this first report, such ordering was obtained when hydrophilically functionalized single-walled carbon nanotubes (p-SWNTs with controlled diameters to be above that of the surfactants Pentaethylene glycol monododecyl ether (C12E5) cylindrical micelles. Highly oriented single domains could further be obtained by using an oscillatory shear field [173]. A hexagonal phase in a binary SWCNT/SDS system was also reported by Vijayaraghavan [174].

In order to obtain a smectic phase of CNTs, one would likely need to enable both (1) reaching even higher concentration suspensions as well as; (2) use CNTs having a very narrow disperse distribution of their length and with an average length that would be on the order or smaller than the radius of curvature of the CNT considered. Such requirements might prove feasible by combining the above-mentioned high concentration dispersion methods of either Windle or Poulin together with either the cutting method reported by Lustig et al. [175], or CNT obtained from suspensions of CNTs issued of a very thin CNT turf [176–178].

Finally, an elegant means of deposition of highly oriented and densely packed monolayers of CNTs was reported by Benattar et al. using 2D confinement of a Newton black film [179], a method that was also successful for the deposition of graphene oxide [180, 181].

Conclusion

Overall, more than 1400 publications can be found with titles on the functionalization of carbon nanotubes. These reports sometimes enable to increase even further CNTs suspension's concentrations when compared to the article reviewed above [129, 182–193], but as a consequence they often involve burying or modifying the tubular structures of the CNTS. Depending upon the application targeted, this can be a critical issue as such modification methods can indeed induce changes in their aromaticity [194] and their morphologies [195] and even destroy the tubular structures of CNTs [196–198]. These morphological and aromaticity changes are generally not an obstacle for polymer-based science and material-synthesis where the CNTs are required as bulk-, filling- and fortifying material; however, in specific applications towards nanoelectronics, thermal applications, memory-devices and solar-panel technologies, the attribution of CNTs to the given applications requires these to be as untouched/pristine as possible, in terms of their electronic properties and structural morphology. This review has therefore been formed as much as possible towards preserving CNTs as single entities in a dispersed or solvated state by any means possible.

References

1. Zeng, H.L., Gao, C., Yan, D.Y.: Poly(epsilon-caprolactone)-functionalized carbon nanotubes and their biodegradation properties. Adv. Func. Mater. **16**(6), 812–818 (2006). https://doi.org/10.1002/adfm.200500607

2. Zhong, J., Song, L., Meng, J., Gao, B., Chu, W.S., Xu, H.Y., Luo, Y., Guo, J.H., Marcelli, A., Xie, S.S., Wu, Z.Y.: Bio-nano interaction of proteins adsorbed on single-walled carbon nanotubes. Carbon **47**(4), 967–973 (2009). https://doi.org/10.1016/j.carbon.2008.11.051

3. Behabtu, N., Young, C.C., Tsentalovich, D.E., Kleinerman, O., Wang, X., Ma, A.W.K., Bengio, E.A., ter Waarbeek, R.F., de Jong, J.J., Hoogerwerf, R.E., Fairchild, S.B., Ferguson, J.B., Maruyama, B., Kono, J., Talmon, Y., Cohen, Y., Otto, M.J., Pasquali, M.: Strong, light, multifunctional fibers of carbon nanotubes with ultrahigh conductivity. Science **339**(6116), 182–186 (2013). https://doi.org/10.1126/science.1228061

4. Cao, Q., Han, S.J., Tulevski, G.S., Zhu, Y., Lu, D.D., Haensch, W.: Arrays of single-walled carbon nanotubes with full surface coverage for high-performance electronics. Nat. Nanotechnol. **8**(3), 180–186 (2013). https://doi.org/10.1038/nnano.2012.257

5. De Volder, M.F.L., Tawfick, S.H., Baughman, R.H., Hart, A.J.: Carbon nanotubes: present and future commercial applications. Science **339**(6119), 535–539 (2013). https://doi.org/10.1126/science.1222453

6. Shulaker, M.M., Hills, G., Patil, N., Wei, H., Chen, H.Y., Philip-Wong, H.S., Mitra, S.: Carbon nanotube computer. Nature **501**(7468), 526 (2013). https://doi.org/10.1038/nature12502

7. Wang, K., Meng, Q.H., Zhang, Y.J., Wei, Z.X., Miao, M.H.: High-performance two-ply yarn supercapacitors based on carbon nanotubes and polyaniline nanowire arrays. Adv. Mater. **25**(10), 1494–1498 (2013). https://doi.org/10.1002/adma.201204598

8. Manzetti, S.: Remediation technologies for oil-drilling activities in the Arctic: oil-spill containment and remediation in open water. Environ Technol Rev **3**(1), 49–60 (2014). https://doi.org/10.1080/21622515.2014.966156

9. Serp, P., Corrias, M., Kalck, P.: Carbon nanotubes and nanofibers in catalysis. Appl Catal Gen **253**(2), 337–358 (2003). https://doi.org/10.1016/s0926-860x(03)00549-0

10. Matsumoto, T., Komatsu, T., Arai, K., Yamazaki, T., Kijima, M., Shimizu, H., Takasawa, Y., Nakamura, J.: Reduction of Pt usage in fuel cell electrocatalysts with carbon nanotube electrodes. Chem Commun. **1**, 1 (2004). https://doi.org/10.1039/b400607k

11. Yoo, E., Gao, L., Komatsu, T., Yagai, N., Arai, K., Yamazaki, T., Matsuishi, K., Matsumoto, T., Nakamura, J.: Atomic hydrogen storage in carbon nanotubes promoted by metal catalysts. J. Phys. Chem. B **108**(49), 18903–18907 (2004). https://doi.org/10.1021/jp047056q

12. Landi, B.J., Dileo, R.A., Schauerman, C.M., Cress, C.D., Ganter, M.J., Raffaelle, R.P.: Multi-walled carbon nanotube paper anodes for lithium ion batteries. J. Nanosci. Nanotechnol. **9**(6), 3406–3410 (2009). https://doi.org/10.1166/jnn.2009.NS09

13. Landi, B.J., Ganter, M.J., Cress, C.D., DiLeo, R.A., Raffaelle, R.P.: Carbon nanotubes for lithium ion batteries. Energy Environ. Sci. **2**(6), 638–654 (2009). https://doi.org/10.1039/b904116h

14. Pol, V.G., Thackeray, M.M.: Spherical carbon particles and carbon nanotubes prepared by autogenic reactions: evaluation as anodes in lithium electrochemical cells. Energy Environ. Sci. **4**(5), 1904–1912 (2011). https://doi.org/10.1039/c0ee00256a

15. Dai, L.M., Chang, D.W., Baek, J.B., Lu, W.: Carbon nanomaterials for advanced energy conversion and storage. Small **8**(8), 1130–1166 (2012). https://doi.org/10.1002/smll.201101594

16. Evanoff, K., Khan, J., Balandin, A.A., Magasinski, A., Ready, W.J., Fuller, T.F., Yushin, G.: Towards ultrathick battery electrodes: aligned carbon nanotube—enabled architecture. Adv. Mater. **24**(4), 533 (2012). https://doi.org/10.1002/adma.201103044

17. Tseng, S.H., Tai, N.H., Hsu, W.K., Chen, L.J., Wang, J.H., Chiu, C.C., Lee, C.Y., Chou, L.J., Leou, K.C.: Ignition of carbon nanotubes using a photoflash. Carbon **45**(5), 958–964 (2007). https://doi.org/10.1016/j.carbon.2006.12.033

18. Rueckes, T., Kim, K., Joselevich, E., Tseng, G.Y., Cheung, C.L., Lieber, C.M.: Carbon nanotube-based nonvolatile random access memory for molecular computing. Science **289**(5476), 94–97 (2000). https://doi.org/10.1126/science.289.5476.94

19. van der Veen, M.H., Barbarin, Y., Kashiwagi, Y., Tokei, Z: IEEE: electron mean-free path for CNT in vertical interconnects approaches Cu. In: 2014 IEEE International Interconnect Technology Conference/Advanced Metallization Conference (2014)

20. van der Veen, M.H., Vereecke, B., Sugiura, M., Kashiwagi, Y., Ke, X.X., Cott, D.J., Vanpaemel, J.K.M., Vereecken, P.M., De Gendt, S., Huyghebaert, C., Tokei, Z: IEEE: electrical and structural characterization of 150 nm CNT contacts with cu damascene top metallization. In: 2012 IEEE International Interconnect Technology Conference (2012)

21. Gimenez-Lopez, M.D., La Torre, A., Fay, M.W., Brown, P.D., Khlobystov, A.N.: Assembly and magnetic bistability of Mn_3O_4 nanoparticles encapsulated in hollow carbon nanofibers. Angew. Chem. Int. Ed. **52**(7), 2051–2054 (2013). https://doi.org/10.1002/anie.201207855

22. Manzetti, S.: Molecular and crystal assembly inside the carbon nanotube: encapsulation and manufacturing approaches. Adv. Manuf. **1**(3), 198–210 (2013). https://doi.org/10.1007/s40436-013-0030-5

23. Manzetti, S., Vasilache, D., Francesco, E.: Emerging carbon-based nanosensor devices: structures, functions and applications. Adv. Manuf. **3**(1), 63–72 (2015). https://doi.org/10.1007/s40436-015-0100-y

24. Gabriel, J.C.P. (2003) Large scale production of carbon nanotube transistors: a generic platform for chemical sensors. In: Velev, O.D., Bunning, T.J., Xia, Y., Yang, P. (eds.) Unconventional Approaches to Nanostructures with Applications in Electronics, Photonics, Information Storage and Sensing, vol. 776. Materials Research Society Symposium Proceedings, pp. 271–277

25. Star, A., Bradley, K., Gabriel, J.C.P., Gruner, G.: Nano-electronic sensors: chemical detection using carbon nanotubes. Abstr. Pap. Am. Chem. Soc. **226**, U479–U479 (2003)

26. Star, A., Gabriel, J.C.P., Bradley, K., Gruner, G.: Electronic detection of specific protein binding using nanotube FET devices. Nano Lett. **3**(4), 459–463 (2003). https://doi.org/10.1021/nl0340172

27. Bradley, K., Davis, A., Gabriel, J.C.P., Gruner, G.: Integration of cell membranes and nanotube transistors. Nano Lett. **5**(5), 841–845 (2005). https://doi.org/10.1021/nl050157v

28. Kimmel, D.W., LeBlanc, G., Meschievitz, M.E., Cliffel, D.E.: Electrochemical sensors and biosensors. Anal. Chem. **84**(2), 685–707 (2012). https://doi.org/10.1021/ac202878q

29. Esser, B., Schnorr, J.M., Swager, T.M.: Selective detection of ethylene gas using carbon nanotube-based devices: utility in determination of fruit ripeness. Angew Chem Int Ed **51**(23), 5752–5756 (2012). https://doi.org/10.1002/anie.201201042

30. Stetter, J.R., Bradley, K., Cumings, J., Gabriel, J.C., Gruner, G., Star, A.: Nano-electronic sensors; practical device designs for sensors. Nanotech **3**, 313–316 (2003)

31. Star, A., Han, T.R., Joshi, V., Gabriel, J.C.P., Gruner, G.: Nano-electronic carbon dioxide sensors. Adv. Mater. **16**(22), 2049 (2004). https://doi.org/10.1002/adma.200400322

32. Star, A., Joshi, V., Skarupo, S., Thomas, D., Gabriel, J.C.P.: Gas sensor array based on metal-decorated carbon nanotubes. J. Phys. Chem. B **110**(42), 21014–21020 (2006). https://doi.org/10.1021/jp064371z

33. Star, A., Tu, E., Niemann, J., Gabriel, J.C.P., Joiner, C.S., Valcke, C.: Label-free detection of DNA hybridization using carbon nanotube network field-effect transistors. Proc. Natl. Acad. Sci. USA **103**(4), 921–926 (2006). https://doi.org/10.1073/pnas.0504146103

34. Gabriel, J.C.P.: 2d Random networks of carbon nanotubes. C R Phys. **11**(5–6), 362–374 (2010). https://doi.org/10.1016/j.crhy.2010.07.016

35. Snow, E.S., Perkins, F.K., Houser, E.J., Badescu, S.C., Reinecke, T.L.: Chemical detection with a single-walled carbon nanotube capacitor. Science **307**(5717), 1942–1945 (2005). https://doi.org/10.1126/science.1109128

36. Keefer, E.W., Botterman, B.R., Romero, M.I., Rossi, A.F., Gross, G.W.: Carbon nanotube coating improves neuronal recordings. Nat. Nanotechnol. **3**(7), 434–439 (2008). https://doi.org/10.1038/nnano.2008.174

37. Liu, Z., Tabakman, S., Welsher, K., Dai, H.J.: Carbon nanotubes in biology and medicine: in vitro and in vivo detection, imaging and drug delivery. Nano Res. **2**(2), 85–120 (2009). https://doi.org/10.1007/s12274-009-9009-8

38. Bondavalli, P., Legagneux, P., Pribat, D.: Carbon nanotubes based transistors as gas sensors: state of the art and critical review. Sens. Actuators B Chem. **140**(1), 304–318 (2009). https://doi.org/10.1016/j.snb.2009.04.025

39. Michelis, F., Bodelot, L., Bonnassieux, Y., Lebental, B.: Highly reproducible, hysteresis-free, flexible strain sensors by inkjet printing of carbon nanotubes. Carbon **95**, 1020–1026 (2015). https://doi.org/10.1016/j.carbon.2015.08.103

40. Manzetti, S., Enrichi, F.: State-of-the-art developments in metal and carbon-based semiconducting nanomaterials: applications and functions in spintronics, nanophotonics, and nanomagnetics. Adv Manuf **5**(2), 105–119 (2017). https://doi.org/10.1007/s40436-017-0172-y

41. Zhang, L.H., Jia, Y., Wang, S.S., Li, Z., Ji, C.Y., Wei, J.Q., Zhu, H.W., Wang, K.L., Wu, D.H., Shi, E.Z., Fang, Y., Cao, A.Y.: Carbon nanotube and CdSe nanobelt schottky junction solar cells. Nano Lett. **10**(9), 3583–3589 (2010). https://doi.org/10.1021/nl101888y

42. Chen, W.C., Rinzler, A.G., Guo, J.: Modeling and simulation of carbon nanotube-semiconductor heterojunction vertical field effect transistors. J. Appl. Phys. **113**(23), 234501 (2013). https://doi.org/10.1063/1.4811295

43. Bradley, K., Cumings, J., Star, A., Gabriel, J.C.P., Gruner, G.: Influence of mobile ions on nanotube based FET devices. Nano Lett. **3**(5), 639–641 (2003). https://doi.org/10.1021/nl025941j

44. Bradley, K., Gabriel, J.C.P., Briman, M., Star, A., Gruner, G.: Charge transfer from ammonia physisorbed on nanotubes. Phys. Rev. Lett. **91**(21), 218301 (2003). https://doi.org/10.1103/physrevlett.91.218301

45. Bradley, K., Gabriel, J.C.P., Star, A., Gruner, G.: Short-channel effects in contact-passivated nanotube chemical sensors. Appl. Phys. Lett. **83**(18), 3821–3823 (2003). https://doi.org/10.1063/1.1619222

46. Mahmoud, K.A., Hrapovic, S., Luong, J.H.T.: Picomolar detection of protease using peptide/single walled carbon nanotube/gold nanoparticle-modified electrode. ACS Nano **2**(5), 1051–1057 (2008). https://doi.org/10.1021/nn8000774

47. Mahmoud, K.A., Luong, J.H.T.: Impedance method for detecting HIV-1 protease and screening for its inhibitors using ferrocene-peptide conjugate/Au nanoparticle/single-walled carbon nanotube modified electrode. Anal. Chem. **80**(18), 7056–7062 (2008). https://doi.org/10.1021/ac801174r

48. Aguirre, C.M., Levesque, P.L., Paillet, M., Lapointe, F., St-Antoine, B.C., Desjardins, P., Martel, R.: The role of the oxygen/water redox couple in suppressing electron conduction in field-effect transistors. Adv. Mater. **21**(30), 3087 (2009). https://doi.org/10.1002/adma.200900550

49. Tao, Y., He, J., Zhang, X., Man, T.Y., Chan, M.: Full-band quantum transport based simulation for carbon nanotube field effect transistor from chirality to device performance. Mol. Simul. **34**(1), 73–80 (2008). https://doi.org/10.1080/08927020701730377

50. Maehashi, K., Katsura, T., Kerman, K., Takamura, Y., Matsumoto, K., Tamiya, E.: Label-free protein biosensor based on aptamer-modified carbon nanotube field-effect transistors. Anal. Chem. **79**(2), 782–787 (2007). https://doi.org/10.1021/ac060830g

51. Fang, Y., Hou, J.F., Fang, Y.: Flexible bio-interfaced nanoelectronics. J. Mater. Chem. C **2**(7), 1178–1183 (2014). https://doi.org/10.1039/c3tc32322f

52. Pan, B., Xing, B.S.: Adsorption mechanisms of organic chemicals on carbon nanotubes. Environ. Sci. Technol. **42**(24), 9005–9013 (2008). https://doi.org/10.1021/es801777n

53. Yang, K., Wu, W., Jing, Q., Zhu, L.: Aqueous adsorption of aniline, phenol, and their substitutes by multi-walled carbon nanotubes. Environ. Sci. Technol. **42**(21), 7931–7936 (2008). https://doi.org/10.1021/es801463v

54. Manzetti, S., Andersen, O., Garcia, C., Campos, E.: Molecular simulation of carbon nanotubes as sorptive materials: sorption effects towards retene, perylene and cholesterol to 100 degrees celsius and above. Mol. Simul. **42**(14), 1183–1192 (2016). https://doi.org/10.1080/08927022.2016.1155212

55. Yang, S.T., Li, J.X., Shao, D.D., Hu, J., Wang, X.K.: Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: Effect of contact time, pH, foreign ions and PAA. J. Hazard. Mater. **166**(1), 109–116 (2009). https://doi.org/10.1016/j.jhazmat.2008.11.003

56. Gupta, V.K., Agarwal, S., Saleh, T.A.: Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. Water Res. **45**(6), 2207–2212 (2011). https://doi.org/10.1016/j.watres.2011.01.012

57. Ren, X.M., Chen, C.L., Nagatsu, M., Wang, X.K.: Carbon nanotubes as adsorbents in environmental pollution management: a review. Chem. Eng. J. **170**(2–3), 395–410 (2011). https://doi.org/10.1016/j.cej.2010.08.045

58. Ren, X.M., Shao, D.D., Yang, S.T., Hu, J., Sheng, G.D., Tan, X.L., Wang, X.K.: Comparative study of Pb(II) sorption on XC-72 carbon and multi-walled carbon nanotubes from aqueous solutions. Chem. Eng. J. **170**(1), 170–177 (2011). https://doi.org/10.1016/j.cej.2011.03.050

59. Wang, X.L., Lu, J.L., Xing, B.S.: Sorption of organic contaminants by carbon nanotubes: influence of adsorbed organic matter. Environ. Sci. Technol. **42**(9), 3207–3212 (2008). https://doi.org/10.1021/es702971g

60. Yu, J.G., Zhao, X.H., Yang, H., Chen, X.H., Yang, Q., Yu, L.Y., Jiang, J.H., Chen, X.Q.: Aqueous adsorption and removal of organic contaminants by carbon nanotubes. Sci. Total Environ. **482**, 241–251 (2014). https://doi.org/10.1016/j.scitotenv.2014.02.129

61. Gong, J.L., Wang, B., Zeng, G.M., Yang, C.P., Niu, C.G., Niu, Q.Y., Zhou, W.J., Liang, Y.: Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent. J. Hazard. Mater. **164**(2–3), 1517–1522 (2009). https://doi.org/10.1016/j.jhazmat.2008.09.072

62. Ma, P.C., Mo, S.Y., Tang, B.Z., Kim, J.K.: Dispersion, interfacial interaction and re-agglomeration of functionalized carbon nanotubes in epoxy composites. Carbon **48**(6), 1824–1834 (2010). https://doi.org/10.1016/j.carbon.2010.01.028

63. Ma, P.C., Siddiqui, N.A., Marom, G., Kim, J.K.: Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. Compos. Part Appl. Sci. Manuf. **41**(10), 1345–1367 (2010). https://doi.org/10.1016/j.compositesa.2010.07.003

64. Sahoo, N.G., Rana, S., Cho, J.W., Li, L., Chan, S.H.: Polymer nanocomposites based on functionalized carbon nanotubes. Prog. Polym. Sci. **35**(7), 837–867 (2010). https://doi.org/10.1016/j.progpolymsci.2010.03.002

65. Choi, S.J., Kwon, T.H., Im, H., Moon, D.I., Baek, D.J., Seol, M.L., Duarte, J.P., Choi, Y.K.: A polydimethylsiloxane (PDMS) Sponge for the selective absorption of oil from water. ACS Appl. Mater. Interfaces. **3**(12), 4552–4556 (2011). https://doi.org/10.1021/am201352w

66. Zhang, H.L.: Electrospun poly (lactic-*co*-glycolic acid)/multi-walled carbon nanotubes composite scaffolds for guided bone tissue regeneration. J. Bioact. Comp. Polym. **26**(4), 347–362 (2011). https://doi.org/10.1177/0883911511413450

67. Vigolo, B., Penicaud, A., Coulon, C., Sauder, C., Pailler, R., Journet, C., Bernier, P., Poulin, P.: Macroscopic fibers and ribbons of oriented carbon nanotubes. Science **290**(5495), 1331–1334 (2000). https://doi.org/10.1126/science.290.5495.1331

68. Polizu, S., Savadogo, O., Poulin, P., Yahia, L.: Applications of carbon nanotubes-based biomaterials in biomedical nanotechnology. J. Nanosci. Nanotechnol. **6**(7), 1883–1904 (2006). https://doi.org/10.1166/jnn.2006.197

69. Goldsmith, B.R., Coroneus, J.G., Khalap, V.R., Kane, A.A., Weiss, G.A., Collins, P.G.: Conductance-controlled point functionalization of single-walled carbon nanotubes. Science **315**(5808), 77–81 (2007). https://doi.org/10.1126/science.1135303

70. Khalap, V.R., Sheps, T., Kane, A.A., Collins, P.G.: Hydrogen sensing and sensitivity of palladium-decorated single-walled carbon nanotubes with defects. Nano Lett. **10**(3), 896–901 (2010). https://doi.org/10.1021/nl9036092

71. Olive-Monllau, R., Esplandiu, M.J., Bartroli, J., Baeza, M., Cespedes, F.: Strategies for the optimization of carbon nanotube/polymer ratio in composite materials: applications as voltammetric sensors. Sens Actuators B Chem **146**(1), 353–360 (2010). https://doi.org/10.1016/j.snb.2010.02.017

72. Wong, H.S.P., Salahuddin, S.: Memory leads the way to better computing. Nat. Nanotechnol. **10**(3), 191–194 (2015). https://doi.org/10.1038/nnano.2015.29

73. Matsuo, Y., Tahara, K., Nakamura, E.: Theoretical studies on structures and aromaticity of finite-length armchair carbon

nanotubes. Org. Lett. **5**(18), 3181–3184 (2003). https://doi.org/10.1021/ol0349514

74. Lin, D.H., Xing, B.S.: Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups. Environ. Sci. Technol. **42**(19), 7254–7259 (2008). https://doi.org/10.1021/es801297u

75. Li, J., Lu, Y.J., Ye, Q., Cinke, M., Han, J., Meyyappan, M.: Carbon nanotube sensors for gas and organic vapor detection. Nano Lett. **3**(7), 929–933 (2003). https://doi.org/10.1021/nl034220x

76. Cai, D.Y., Song, M., Xu, C.X.: Highly conductive carbon-nanotube/graphite-oxide hybrid films. Adv. Mater. **20**(9), 1706 (2008). https://doi.org/10.1002/adma.200702602

77. Gojny, F.H., Nastalczyk, J., Roslaniec, Z., Schulte, K.: Surface modified multi-walled carbon nanotubes in CNT/epoxy-composites. Chem. Phys. Lett. **370**(5–6), 820–824 (2003). https://doi.org/10.1016/s0009-2614(03)00187-8

78. Theodore, M., Hosur, M., Thomas, J., Jeelani, S.: Influence of functionalization on properties of MWCNT-epoxy nanocomposites. Mater. Sci. Eng. Struct. Mater. Prop. Microstruct. Proces **528**(3), 1192–1200 (2011). https://doi.org/10.1016/j.msea.2010.09.095

79. Manzetti, S., Andersen, O.: A molecular dynamics study of nanoparticle-formation from bioethanol-gasoline blend emissions. Fuel **183**, 55–63 (2016). https://doi.org/10.1016/j.fuel.2016.06.049

80. Manzetti, S.: Chemical and electronic properties of polycyclic aromatic hydrocarbons: a review. In: Meneses, B.A. (ed.) Handbook of Polycyclic Aromatic Hydrocarbons: Chemistry, Occurrence and Health Issues, vol. 423–435. Nova Sciences Publishers, New York (2012)

81. Gotovac, S., Honda, H., Hattori, Y., Takahashi, K., Kanoh, H., Kaneko, K.: Effect of nanoscale curvature of single-walled carbon nanotubes on adsorption of polycyclic aromatic hydrocarbons. Nano Lett. **7**(3), 583–587 (2007). https://doi.org/10.1021/nl0622597

82. Chang, C.M., Liu, Y.L.: Functionalization of multi-walled carbon nanotubes with furan and maleimide compounds through Diels-Alder cycloaddition. Carbon **47**(13), 3041–3049 (2009). https://doi.org/10.1016/j.carbon.2009.06.058

83. Bonard, J.M., Stora, T., Salvetat, J.P., Maier, F., Stockli, T., Duschl, C., Forro, L., deHeer, W.A., Chatelain, A.: Purification and size-selection of carbon nanotubes. Adv. Mater. **9**(10), 827 (1997). https://doi.org/10.1002/adma.19970091014

84. Bandow, S., Rao, A.M., Williams, K.A., Thess, A., Smalley, R.E., Eklund, P.C.: Purification of single-wall carbon nanotubes by microfiltration. J. Phys. Chem. B **101**(44), 8839–8842 (1997). https://doi.org/10.1021/jp972026r

85. Islam, M.F., Rojas, E., Bergey, D.M., Johnson, A.T., Yodh, A.G.: High weight fraction surfactant solubilization of single-wall carbon nanotubes in water. Nano Lett. **3**(2), 269–273 (2003). https://doi.org/10.1021/nl025924u

86. Jiang, L.Q., Gao, L., Sun, J.: Production of aqueous colloidal dispersions of carbon nanotubes. J. Colloid Interface Sci. **260**(1), 89–94 (2003). https://doi.org/10.1016/S0021-9797(02)00176-5

87. Ndiaye, A.L., Varenne, C., Bonnet, P., Petit, E., Spinelle, L., Brunet, J., Pauly, A., Lauron, B.: Elaboration of SWNTs-based gas sensors using dispersion techniques: evaluating the role of the surfactant and its influence on the sensor response. Sens. Actuators B Chem. **162**(1), 95–101 (2012). https://doi.org/10.1016/j.snb.2011.12.041

88. Fatemi, S.M., Foroutan, M.: Recent developments concerning the dispersion of carbon nanotubes in surfactant/polymer systems by MD simulation. J. Nanostruct. Chem. **6**(1), 29–40 (2016). https://doi.org/10.1007/s40097-015-0175-9

89. Park, S.H., Bae, J.: Tailoring environment friendly carbon nanostructures by surfactant mediated interfacial engineering. J. Ind. Eng. Chem. **30**, 1–9 (2015). https://doi.org/10.1016/j.jiec.2015.05.005

90. Wang, H.: Dispersing carbon nanotubes using surfactants. Curr. Opin. Colloid Interface Sci. **14**(5), 364–371 (2009). https://doi.org/10.1016/j.cocis.2009.06.004

91. Hilding, J., Grulke, E.A., Zhang, Z.G., Lockwood, F.: Dispersion of carbon nanotubes in liquids. J. Dispers. Sci. Technol. **24**(1), 1–41 (2003). https://doi.org/10.1081/dis-120017941

92. Lu, K.L., Lago, R.M., Chen, Y.K., Green, M.L.H., Harris, P.J.F., Tsang, S.C.: Mechanical damage of carbon nanotubes by ultrasound. Carbon **34**(6), 814–816 (1996). https://doi.org/10.1016/0008-6223(96)89470-x

93. Jedrzejewska, A., Kalenczuk, R.J., Mijowska, E.: Systematic study on synthesis and purification of double-walled carbon nanotubes synthesized via CVD. Mater. Sci. Poland **29**(4), 292–298 (2011). https://doi.org/10.2478/s13536-011-0043-3

94. Lukaszczuk, P., Mijowska, E., Kalenczuk, R.: Selective oxidation of metallic single-walled carbon nanotubes. Chem. Pap. **67**(9), 1250–1254 (2013). https://doi.org/10.2478/s11696-013-0345-5

95. Liang, S.L., Li, G.F., Tian, R.: Multi-walled carbon nanotubes functionalized with a ultrahigh fraction of carboxyl and hydroxyl groups by ultrasound-assisted oxidation. J. Mater. Sci. **51**(7), 3513–3524 (2016). https://doi.org/10.1007/s10853-015-9671-z

96. Bibi, S., Yasin, T., Nawaz, M., Price, G.J.: Comparative study of the modification of multi-wall carbon nanotubes by gamma irradiation and sonochemically assisted acid etching. Mater. Chem. Phys. **207**, 23–29 (2018). https://doi.org/10.1016/j.matchemphys.2017.12.047

97. Price, G.J., Nawaz, M., Yasin, T., Bibi, S.: Sonochemical modification of carbon nanotubes for enhanced nanocomposite performance. Ultrason. Sonochem. **40**, 123–130 (2018). https://doi.org/10.1016/j.ultsonch.2017.02.021

98. Heller, D.A., Mayrhofer, R.M., Baik, S., Grinkova, Y.V., Usrey, M.L., Strano, M.S.: Concomitant length and diameter separation of single-walled carbon nanotubes. J. Am. Chem. Soc. **126**(44), 14567–14573 (2004). https://doi.org/10.1021/ja046450z

99. Liu, P., Wang, T.M.: Ultrasonic-assisted chemical oxidative cutting of multiwalled carbon nanotubes with ammonium persulfate in neutral media. Appl. Phys. Mater. Sci. Process. **97**(4), 771–775 (2009). https://doi.org/10.1007/s00339-009-5314-z

100. Liu, Y.Q., Gao, L., Sun, J., Zheng, S., Jiang, L.Q., Wang, Y., Kajiura, H., Li, Y.M., Noda, K.: A multi-step strategy for cutting and purification of single-walled carbon nanotubes. Carbon **45**(10), 1972–1978 (2007). https://doi.org/10.1016/j.carbon.2007.06.009

101. Luong, J.H.T., Hrapovic, S., Liu, Y.L., Yang, D.Q., Sacher, E., Wang, D.S., Kingston, C.T., Enright, G.D.: Oxidation, deformation, and destruction of carbon nanotubes in aqueous ceric sulfate. J. Phys. Chem. B **109**(4), 1400–1407 (2005). https://doi.org/10.1021/jp0454422

102. Park, H.J., Park, M., Chang, J.Y., Lee, H.: The effect of pretreatment methods on morphology and size distribution of multi-walled carbon nanotubes. Nanotechnology **19**(33), 335702 (2008). https://doi.org/10.1088/0957-4484/19/33/335702

103. Shelimov, K.B., Esenaliev, R.O., Rinzler, A.G., Huffman, C.B., Smalley, R.E.: Purification of single-wall carbon nanotubes by ultrasonically assisted filtration. Chem. Phys. Lett. **282**(5–6), 429–434 (1998). https://doi.org/10.1016/s0009-2614(97)01265-7

104. Shuba, M.V., Paddubskaya, A.G., Kuzhir, P.P., Maksimenko, S.A., Ksenevich, V.K., Niaura, G., Seliuta, D., Kasalynas, I., Valusis, G.: Soft cutting of single-wall carbon nanotubes by low temperature ultrasonication in a mixture of sulfuric and nitric

acids. Nanotechnology **23**(49), 495714 (2012). https://doi.org/10.1088/0957-4484/23/49/495714

105. Wang, Y., Gao, L., Sun, J., Liu, Y.Q., Zheng, S., Kajiura, H., Li, Y.M., Noda, K.: An integrated route for purification, cutting and dispersion of single-walled carbon nanotubes. Chem. Phys. Lett. **432**(1–3), 205–208 (2006). https://doi.org/10.1016/j.cplett.2006.10.054

106. Zhang, M., Yudasaka, M., Koshio, A., Jabs, C., Ichihashi, T., Iijima, S.: Structure of single-wall carbon nanotubes purified and cut using polymer. Appl. Phys. Mater. Sci. Process. **74**(1), 7–10 (2002). https://doi.org/10.1007/s003390100983

107. Zhang, M.F., Yudasaka, M., Koshio, A., Iijima, S.: Effect of polymer and solvent on purification and cutting of single-wall carbon nanotubes. Chem. Phys. Lett. **349**(1–2), 25–30 (2001). https://doi.org/10.1016/s0009-2614(01)01181-2

108. Tibbetts, G.G., Meisner, G.P., Olk, C.H.: Hydrogen storage capacity of carbon nanotubes, filaments, and vapor-grown fibers. Carbon **39**(15), 2291–2301 (2001). https://doi.org/10.1016/s0008-6223(01)00051-3

109. Jones, C.P., Jurkschat, K., Crossley, A., Compton, R.G., Riehl, B.L., Banks, C.E.: Use of high-purity metal-catalyst-free multi-walled carbon nanotubes to avoid potential experimental misinterpretations. Langmuir **23**(18), 9501–9504 (2007). https://doi.org/10.1021/la701522p

110. Jhi, S.H., Kwon, Y.K., Bradley, K., Gabriel, J.C.P.: Hydrogen storage by physisorption: beyond carbon. Solid State Commun. **129**(12), 769–773 (2004). https://doi.org/10.1016/j.ssc.2003.12.032

111. Dillon, A.C., Jones, K.M., Bekkedahl, T.A., Kiang, C.H., Bethune, D.S., Heben, M.J.: Storage of hydrogen in single-walled carbon nanotubes. Nature **386**(6623), 377–379 (1997). https://doi.org/10.1038/386377a0

112. Joiner, C., Gabriel, J.-C., Gruner, G., Star, A.: Nanotube sensor devices for DNA detection USA Patent (2007)

113. Fukushima, T., Kosaka, A., Ishimura, Y., Yamamoto, T., Takigawa, T., Ishii, N., Aida, T.: Molecular ordering of organic molten salts triggered by single-walled carbon nanotubes. Science **300**(5628), 2072–2074 (2003). https://doi.org/10.1126/science.1082289

114. Fukushima, T., Aida, T.: Ionic liquids for soft functional materials with carbon nanotubes. Chem. Eur. J. **13**(18), 5048–5058 (2007). https://doi.org/10.1002/chem.200700554

115. Barisci, J.N., Wallace, G.G., MacFarlane, D.R., Baughman, R.H.: Investigation of ionic liquids as electrolytes for carbon nanotube electrodes. Electrochem. Commun. **6**(1), 22–27 (2004). https://doi.org/10.1016/j.elecom.2003.09.015

116. Wang, J.Y., Chu, H.B., Li, Y.: Why single-walled carbon nanotubes can be dispersed in imidazolium-based ionic liquids. ACS Nano **2**(12), 2540–2546 (2008). https://doi.org/10.1021/nn800510g

117. Raiah, K., Djalab, A., Hadj-Ziane-Zafour, A., Soula, B., Galibert, A.M., Flahaut, E.: Influence of the hydrocarbon chain length of imidazolium-based ionic liquid on the dispersion and stabilization of double-walled carbon nanotubes in water. Colloids Surf. Physicochem. Eng. Asp. **469**, 107–116 (2015). https://doi.org/10.1016/j.colsurfa.2015.01.015

118. Jiang, C., Saha, A., Xiang, C., Young, C.C., Tour, J.M., Pasquali, M., Marti, A.A.: Increased solubility, liquid-crystalline phase, and selective functionalization of single-walled carbon nanotube polyelectrolyte dispersions. ACS Nano **7**(5), 4503–4510 (2013). https://doi.org/10.1021/nn4011544

119. Petit, P., Mathis, C., Journet, C., Bernier, P.: Tuning and monitoring the electronic structure of carbon nanotubes. Chem. Phys. Lett. **305**(5–6), 370–374 (1999). https://doi.org/10.1016/s0009-2614(99)00399-1

120. Penicaud, A., Poulin, P., Anglaret, E., Petit, P., Roubeau, O., Enouz, S., Loiseau, A.: Dissolution douce of single walled carbon nanotubes. In: Kuzmany, H., Fink, J., Mehring, M., Roth, S. (eds.) Electronic Properties of Novel Nanostructures, vol. 786. AIP Conference Proceedings, pp. 266–270 (2005)

121. Penicaud, A., Poulin, P., Derre, A., Anglaret, E., Petit, P.: Spontaneous dissolution of a single-wall carbon nanotube salt. J. Am. Chem. Soc. **127**(1), 8–9 (2005). https://doi.org/10.1021/ja0443373

122. Voiry, D., Drummond, C., Penicaud, A.: Portrait of carbon nanotube salts as soluble polyelectrolytes. Soft. Matter. **7**(18), 7998–8001 (2011). https://doi.org/10.1039/c1sm05959a

123. Penicaud, A., Hsu, J., Reed, C.A., Koch, A., Khemani, K.C., Allemand, P.M., Wudl, F.: C60.-with coordination-compounds—(tetraphenylporphinato)chromium(III) fulleride. J. Am. Chem. Soc. **113**(17), 6698–6700 (1991). https://doi.org/10.1021/ja00017a066

124. Moya, S.E., Ilie, A., Bendall, J.S., Hernandez-Lopez, J.L., Ruiz-Garcia, J., Huck, W.T.S.: Assembly of polyelectrolytes on CNTs by Van der Waals interactions and fabrication of LBL polyelectrolyte/CNT composites. Macromol. Chem. Phys. **208**(6), 603–608 (2007). https://doi.org/10.1002/macp.200600530

125. Han, J., Kim, H., Kim, D.Y., Jo, S.M., Jang, S.Y.: Water-soluble polyelectrolyte-grafted multiwalled carbon nanotube thin films for efficient counter electrode of dye-sensitized solar cells. ACS Nano **4**(6), 3503–3509 (2010). https://doi.org/10.1021/nn100574g

126. Paloniemi, H., Aaritalo, T., Laiho, T., Liuke, H., Kocharova, N., Haapakka, K., Terzi, F., Seeber, R., Lukkari, J.: Water-soluble full-length single-wall carbon nanotube polyelectrolytes: preparation and characterization. J. Phys. Chem. B **109**(18), 8634–8642 (2005). https://doi.org/10.1021/jp0443097

127. Wang, J., Musameh, M., Lin, Y.H.: Solubilization of carbon nanotubes by Nafion toward the preparation of amperometric biosensors. J. Am. Chem. Soc. **125**(9), 2408–2409 (2003). https://doi.org/10.1021/ja028951v

128. Guzman, C., Orozco, G., Verde, Y., Jimenez, S., Godinez, L.A., Juaristi, E., Bustos, E.: Hydrogen peroxide sensor based on modified vitreous carbon with multiwall carbon nanotubes and composites of Pt nanoparticles-dopamine. Electrochim. Acta **54**(6), 1728–1732 (2009). https://doi.org/10.1016/j.electacta.2008.09.072

129. Banerjee, S., Hemraj-Benny, T., Wong, S.S.: Covalent surface chemistry of single-walled carbon nanotubes. Adv. Mater. **17**(1), 17–29 (2005). https://doi.org/10.1002/adma.200401340

130. Porter, J.J., Perkins, W.S.: A study of thermodynamics of sorption of 3 direct dyes on cellophane film. Text. Res. J. **40**(1), 81 (1970). https://doi.org/10.1177/004051757004000112

131. Zhang, W., Silva, S.R.P.: Reversible functionalization of multiwalled carbon nanotubes with organic dyes. Scripta Mater. **63**(6), 645–648 (2010). https://doi.org/10.1016/j.scriptamat.2010.05.037

132. Pan, W.H., Lue, S.J., Chang, C.M., Liu, Y.L.: Alkali doped polyvinyl alcohol/multi-walled carbon nano-tube electrolyte for direct methanol alkaline fuel cell. J. Membr. Sci. **376**(1–2), 225–232 (2011). https://doi.org/10.1016/j.memsci.2011.04.026

133. Shieh, Y.T., Liu, G.L., Wu, H.H., Lee, C.C.: Effects of polarity and pH on the solubility of acid-treated carbon nanotubes in different media. Carbon **45**(9), 1880–1890 (2007). https://doi.org/10.1016/j.carbon.2007.04.028

134. Liu, Z.L., Zhao, B., Guo, C.L., Sun, Y.J., Shi, Y., Yang, H.B., Li, Z.A.: Carbon nanotube/raspberry hollow Pd nanosphere hybrids for methanol, ethanol, and formic acid electro-oxidation in alkaline media. J. Colloid Interface Sci. **351**(1), 233–238 (2010). https://doi.org/10.1016/j.jcis.2010.07.035

135. Liu, Y.L., Li, S.H., Lee, H.C., Hsu, K.Y.: Selective reactivity of aromatic amines toward 5-maleimidoisophthalic acid for preparation of polyamides bearing *N*-phenylmaleimide moieties. React. Funct. Polym. **66**(9), 924–930 (2006). https://doi.org/10.1016/j.reactfunctpolym.2005.12.005

136. Maio, A., Botta, L., Tito, A.C., Pellegrino, L., Daghetta, M., Scaffaro, R.: Statistical study of the influence of CNTs purification and plasma functionalization on the properties of polycarbonate-CNTs nanocomposites. Plasma Process Polym. **11**(7), 664–677 (2014). https://doi.org/10.1002/ppap.201400008

137. Ferreira, F.V., Francisco, W., de Menezes, B.R.C., Cividanes, L.D., Coutinho, A.D., Thim, G.P.: Carbon nanotube functionalized with dodecylamine for the effective dispersion in solvents. Appl. Surf. Sci. **357**, 2154–2159 (2015). https://doi.org/10.1016/j.apsusc.2015.09.202

138. Arnold, M.S., Stupp, S.I., Hersam, M.C.: Enrichment of single-walled carbon nanotubes by diameter in density gradients. Nano Lett. **5**(4), 713–718 (2005). https://doi.org/10.1021/nl050133o

139. Hersam, M.C.: Materials science nanotubes sorted using DNA. Nature **460**(7252), 186–187 (2009). https://doi.org/10.1038/460186a

140. Zheng, M., Jagota, A., Strano, M.S., Santos, A.P., Barone, P., Chou, S.G., Diner, B.A., Dresselhaus, M.S., McLean, R.S., Onoa, G.B., Samsonidze, G.G., Semke, E.D., Usrey, M., Walls, D.J.: Structure-based carbon nanotube sorting by sequence-dependent DNA assembly. Science **302**(5650), 1545–1548 (2003). https://doi.org/10.1126/science.1091911

141. Xie, X.L., Mai, Y.W., Zhou, X.P.: Dispersion and alignment of carbon nanotubes in polymer matrix: A review. Mater. Sci. Eng. R-Rep. **49**(4), 89–112 (2005). https://doi.org/10.1016/j.mser.2005.04.002

142. Vigolo, B., Penicaud, A., Coulon, C., Sauder, C., Pailler, R., Journet, C., Bernier, P., Poulin, P.: A simple method to make carbon nanotubes fibers. In: Kuzmany, H., Fink, J., Mehring, M., Roth, S. (eds.) Electronic Properties of Molecular Nanostructures, vol. 591. AIP Conference Proceedings, pp. 562–567. (2001)

143. Vigolo, B., Launois, P., Lucas, M., Badaire, S., Bernier, P., Poulin, P.: Fibers of carbon nanotubes. In: Bernier, P., Ajayan, P., Iwasa, Y., Nikolaev, P. (eds.) Making Functional Materials with Nanotubes, vol. 706. Materials Research Society Symposium Proceedings, pp. 3–8 (2002)

144. Davidson, P., Gabriel, J.C., Levelut, A.M., Batail, P.: A new nematic suspension based on all-inorganic polymer rods. Europhys. Lett. **21**(3), 317–322 (1993). https://doi.org/10.1209/0295-5075/21/3/011

145. Davidson, P., Gabriel, J.C., Levelut, A.M., Batail, P.: Nematic liquid-crystalline mineral polymerS. Adv. Mater. **5**(9), 665–668 (1993). https://doi.org/10.1002/adma.19930050916

146. Donkai, N., Hoshino, H., Kajiwara, K., Miyamoto, T.: Lyotropic mesophase of imogolite. 3. Observation of liquid-crystal structure by scanning electron and novel polarized optical microscopy. Makromolekulare Chemie Macromol. Chem. Phys. **194**(2), 559–580 (1993)

147. Gabriel, J.C.P., Batail, P.: Liquid crystals with a mineral core. Actual. Chim. **12**(8–9), 13–21 (1999)

148. Gabriel, J.C.P., Davidson, P.: New trends in colloidal liquid crystals based on mineral moieties. Adv. Mater. **12**(1), 9 (2000). https://doi.org/10.1002/(sici)1521-4095(200001)12:1%3c9:aid-adma9%3e3.0.co;2-6

149. Davidson, P., Batail, P., Gabriel, J.C.P., Livage, J., Sanchez, C., Bourgaux, C.: Mineral liquid crystalline polymers. Prog. Polym. Sci. **22**(5), 913–936 (1997). https://doi.org/10.1016/s0079-6700(97)00012-9

150. Gabriel, J.C.P., Davidson, P.: Mineral liquid crystals from self-assembly of anisotropic nanosystems. In: Antonietti, M. (ed.) Colloid Chemistry 1, vol. 226. Topics in Current Chemistry-Series, pp. 119–172 (2003)

151. Ajayan, P.M., Stephan, O., Colliex, C., Trauth, D.: Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite. Science **265**(5176), 1212–1214 (1994). https://doi.org/10.1126/science.265.5176.1212

152. Arjmand, M., Mahmoodi, M., Gelves, G.A., Park, S., Sundararaj, U.: Electrical and electromagnetic interference shielding properties of flow-induced oriented carbon nanotubes in polycarbonate. Carbon **49**(11), 3430–3440 (2011). https://doi.org/10.1016/j.carbon.2011.04.039

153. Dror, Y., Salalha, W., Khalfin, R.L., Cohen, Y., Yarin, A.L., Zussman, E.: Carbon nanotubes embedded in oriented polymer nanofibers by electrospinning. Langmuir **19**(17), 7012–7020 (2003). https://doi.org/10.1021/la034234i

154. Haggenmueller, R., Gommans, H.H., Rinzler, A.G., Fischer, J.E., Winey, K.I.: Aligned single-wall carbon nanotubes in composites by melt processing methods. Chem. Phys. Lett. **330**(3–4), 219–225 (2000). https://doi.org/10.1016/s0009-2614(00)01013-7

155. Huang, Y., Duan, X.F., Wei, Q.Q., Lieber, C.M.: Directed assembly of one-dimensional nanostructures into functional networks. Science **291**(5504), 630–633 (2001). https://doi.org/10.1126/science.291.5504.630

156. Potschke, P., Bhattacharyya, A.R., Janke, A.: Melt mixing of polycarbonate with multiwalled carbon nanotubes: microscopic studies on the state of dispersion. Eur. Polym. J. **40**(1), 137–148 (2004). https://doi.org/10.1016/j.eurpolymj.2003.08.008

157. Lanticse, L.J., Tanabe, Y., Matsui, K., Kaburagi, Y., Suda, K., Hoteida, M., Endo, M., Yasuda, E.: Shear-induced preferential alignment of carbon nanotubes resulted in anisotropic electrical conductivity of polymer composites. Carbon **44**(14), 3078–3086 (2006). https://doi.org/10.1016/j.carbon.2006.05.008

158. Onsager, L.: The effects of shape on the interaction of colloidal particles. Ann. N. Y. Acad. Sci. **51**(4), 627–659 (1949). https://doi.org/10.1111/j.1749-6632.1949.tb27296.x

159. Vroege, G.J.: The isotropic-nematic phase-transition and other properties of a solution of semiflexible poly-electrolytes. J. Chem. Phys. **90**(8), 4560–4566 (1989)

160. Vroege, G.J., Lekkerkerker, H.N.W.: Phase-transitions in lyotropic colloidal and polymer liquid-crystals. Rep. Prog. Phys. **55**(8), 1241–1309 (1992). https://doi.org/10.1088/0034-4885/55/8/003

161. Somoza, A.M., Sagui, C., Roland, C.: Liquid-crystal phases of capped carbon nanotubes. Phys. Rev. B **63**(8), 081403 (2001). https://doi.org/10.1103/physrevb.63.081403

162. Song, W.H., Kinloch, I.A., Windle, A.H.: Nematic liquid crystallinity of multiwall carbon nanotubes. Science **302**(5649), 1363 (2003). https://doi.org/10.1126/science.1089764

163. Song, W.H., Windle, A.H.: Isotropic-nematic phase transition of dispersions of multiwall carbon nanotubes. Macromolecules **38**(14), 6181–6188 (2005). https://doi.org/10.1021/ma047691u

164. Badaire, S., Zakri, C., Maugey, M., Derre, A., Barisci, J.N., Wallace, G., Poulin, P.: Liquid crystals of DNA-stabilized carbon nanotubes. Adv. Mater. **17**(13), 1673 (2005). https://doi.org/10.1002/adma.200401741

165. Camerel, F., Gabriel, J.C.P., Batail, P., Davidson, P., Lemaire, B., Schmutz, M., Guilk-Krzywicki, T., Bourgaux, C.: Original single walled nanotubules based on weakly interacting covalent mineral polymers, (1)(infinity) Nb2PS10- in *N*-methylformamide. Nano Lett. **2**(4), 403–407 (2002). https://doi.org/10.1021/nl010090l

166. Paineau, E., Krapf, M.E., Amara, M.S., Matskova, N.V., Dozov, I., Rouziere, S., Thill, A., Launois, P., Davidson, P.: A liquid-crystalline hexagonal columnar phase in highly-dilute

suspensions of imogolite nanotubes. Nat. Commun. **7**, 10271 (2016). https://doi.org/10.1038/ncomms10271

167. Gabriel, J.C.P., Camerel, F., Lemaire, B.J., Desvaux, H., Davidson, P., Batail, P.: Swollen liquid-crystalline lamellar phase based on extended solid-like sheets. Nature **413**(6855), 504–508 (2001). https://doi.org/10.1038/35097046

168. Davidson, P., Penisson, C., Constantin, D., Gabriel, J.C.P.: Isotropic, nematic, and lamellar phases in colloidal suspensions of nanosheets. Proc. Natl. Acad. Sci. USA **115**(26), 6662–6667 (2018). https://doi.org/10.1073/pnas.1802692115

169. Kleshchanok, D., Holmqvist, P., Meijer, J.M., Lekkerkerker, H.N.: Lyotropic smectic B phase formed in suspensions of charged colloidal platelets. J. Am. Chem. Soc. **134**(13), 5985–5990 (2012). https://doi.org/10.1021/ja300527w

170. Wensink, H.H.: Columnar versus smectic order in systems of charged colloidal rods. J. Chem. Phys. **126**(19), 194901 (2007). https://doi.org/10.1063/1.2730819

171. Vroege, G.J., Thies-Weesie, D.M.E., Petukhov, A.V., Lemaire, B.J., Davidson, P.: Smectic liquid-crystalline order in suspensions of highly polydisperse goethite nanorods. Adv. Mater. **18**(19), 2565 (2006). https://doi.org/10.1002/adma.200601112

172. Miyamoto, N., Nakato, T.: Liquid crystalline nature of K4Nb6O17 nanosheet sols and their macroscopic alignment. Adv. Mater. **14**(18), 1267 (2002). https://doi.org/10.1002/1521-4095(20020916)14:18%3c1267:aid-adma1267%3e3.0.co;2-o

173. Lim, S.H., Jang, H.S., Ha, J.M., Kim, T.H., Kwasniewski, P., Narayanan, T., Jin, K.S., Choi, S.M.: Highly ordered and highly aligned two-dimensional binary superlattice of a SWNT/cylindrical-micellar system. Angew. Chem. Int. Ed. **53**(46), 12548–12554 (2014). https://doi.org/10.1002/anie.201403458

174. Vijayaraghavan, D.: Self-assembled ordering of single-walled carbon nanotubes in a lyotropic liquid crystal system. J. Mol. Liq. **199**, 128–132 (2014). https://doi.org/10.1016/j.molliq.2014.08.022

175. Lustig, S.R., Boyes, E.D., French, R.H., Gierke, T.D., Harmer, M.A., Hietpas, P.B., Jagota, A., McLean, R.S., Mitchell, G.P., Onoa, G.B., Sams, K.D.: Lithographically cut single-walled carbon nanotubes: controlling length distribution and introducing end-group functionality. Nano Lett. **3**(8), 1007–1012 (2003). https://doi.org/10.1021/nl034219y

176. Kamalakaran, R., Terrones, M., Seeger, T., Kohler-Redlich, P., Ruhle, M., Kim, Y.A., Hayashi, T., Endo, M.: Synthesis of thick and crystalline nanotube arrays by spray pyrolysis. Appl. Phys. Lett. **77**(21), 3385–3387 (2000). https://doi.org/10.1063/1.1327611

177. Mayne, M., Grobert, N., Terrones, M., Kamalakaran, R., Ruhle, M., Kroto, H.W., Walton, D.R.M.: Pyrolytic production of aligned carbon nanotubes from homogeneously dispersed benzene-based aerosols. Chem. Phys. Lett. **338**(2–3), 101–107 (2001). https://doi.org/10.1016/s0009-2614(01)00278-0

178. Mayne, M., Grobert, N., Terrones, M., Kamalakaran, R., Ruhle, M., Walton, D.R.M., Kroto, H.W.: Pure and aligned carbon nanotubes produced by the pyrolysis of benzene-based aerosols. In: Kuzmany, H., Fink, J., Mehring, M., Roth, S. (eds.) Electronic Properties of Molecular Nanostructures, vol. 591. AIP Conference Proceedings, pp. 204–207 (2001)

179. Tang, G.L., Zhang, X.F., Yang, S.H., Derycke, V., Benattar, J.J.: New confinement method for the formation of highly aligned and densely packed single-walled carbon nanotube monolayers. Small **6**(14), 1488–1491 (2010). https://doi.org/10.1002/smll.201000212

180. Sridi, N., Lebental, B., Merliot, E., Cojocaru, C.S., Azevedo, J., Benattar, J.J., Nowodzinski, A., Gabriel, J.C.P., Ghis, A.: Mechanical properties of suspended few layers graphene sheets. Nanotechnology 2012, vol. 1: Advanced Materials, Cnts, Particles, Films and Composites (2012)

181. Sridi, N., Lebental, B., Azevedo, J., Gabriel, J.C.P., Ghis, A.: Electrostatic method to estimate the mechanical properties of suspended membranes applied to nickel-coated graphene oxide. Appl. Phys. Lett. **103**(5), 051907 (2013). https://doi.org/10.1063/1.4817301

182. Dyke, C.A., Tour, J.M.: Solvent-free functionalization of carbon nanotubes. J. Am. Chem. Soc. **125**(5), 1156–1157 (2003). https://doi.org/10.1021/ja0289806

183. Tasis, D., Tagmatarchis, N., Georgakilas, V., Prato, M.: Soluble carbon nanotubes. Chem. Eur. J. **9**(17), 4001–4008 (2003). https://doi.org/10.1002/chem.200304800

184. Balasubramanian, K., Burghard, M.: Chemically functionalized carbon nanotubes. Small **1**(2), 180–192 (2005). https://doi.org/10.1002/smll.200400118

185. Burghard, M.: Electronic and vibrational properties of chemically modified single-wall carbon nanotubes. Surf. Sci. Rep. **58**(1–4), 1–109 (2005). https://doi.org/10.1016/j.surfrep.2005.07.001

186. Hirsch, A., Vostrowsky, O.: Functionalization of carbon nanotubes. In: Schluter, A.D. (ed.) Functional molecular nanostructures, vol. 245. Topics in Current Chemistry-Series, pp. 193–237 (2005)

187. Prato, M., Kostarelos, K., Bianco, A.: Functionalized carbon nanotubes in drug design and discovery. Acc. Chem. Res. **41**(1), 60–68 (2008). https://doi.org/10.1021/ar700089b

188. Coleman, J.N.: Liquid-phase exfoliation of nanotubes and graphene. Adv. Func. Mater. **19**(23), 3680–3695 (2009). https://doi.org/10.1002/adfm.200901640

189. Meng, L.J., Fu, C.L., Lu, Q.H.: Advanced technology for functionalization of carbon nanotubes. Prog. Nat. Sci. **19**(7), 801–810 (2009). https://doi.org/10.1016/j.pnsc.2008.08.011

190. Peng, X.H., Wong, S.S.: Functional covalent chemistry of carbon nanotube surfaces. Adv. Mater. **21**(6), 625–642 (2009). https://doi.org/10.1002/adma.200801464

191. Singh, P., Campidelli, S., Giordani, S., Bonifazi, D., Bianco, A., Prato, M.: Organic functionalisation and characterisation of single-walled carbon nanotubes. Chem. Soc. Rev. **38**(8), 2214–2230 (2009). https://doi.org/10.1039/b518111a

192. Karousis, N., Tagmatarchis, N., Tasis, D.: Current progress on the chemical modification of carbon nanotubes. Chem. Rev. **110**(9), 5366–5397 (2010). https://doi.org/10.1021/cr100018g

193. Wepasnick, K.A., Smith, B.A., Bitter, J.L., Fairbrother, D.H.: Chemical and structural characterization of carbon nanotube surfaces. Anal. Bioanal. Chem. **396**(3), 1003–1014 (2010). https://doi.org/10.1007/s00216-009-3332-5

194. Ferreira, F.V., Francisco, W., Menezes, B.R.C., Brito, F.S., Coutinho, A.S., Cividanes, L.S., Coutinho, A.R., Thim, G.P.: Correlation of surface treatment, dispersion and mechanical properties of HDPE/CNT nanocomposites. Appl. Surf. Sci. **389**, 921–929 (2016). https://doi.org/10.1016/j.apsusc.2016.07.164

195. Scaffaro, R., Maio, A., Agnello, S., Glisenti, A.: plasma functionalization of multiwalled carbon nanotubes and their use in the preparation of nylon 6-based nanohybrids. Plasma Process. Polym. **9**(5), 503–512 (2012). https://doi.org/10.1002/ppap.201100140

196. Mawhinney, D.B., Naumenko, V., Kuznetsova, A., Yates, J.T., Liu, J., Smalley, R.E.: Infrared spectral evidence for the etching of carbon nanotubes: ozone oxidation at 298 K. J. Am. Chem. Soc. **122**(10), 2383–2384 (2000). https://doi.org/10.1021/ja994094s

197. Banerjee, S., Wong, S.S.: Rational sidewall functionalization and purification of single-walled carbon nanotubes by solution-phase ozonolysis. J. Phys. Chem. B **106**(47), 12144–12151 (2002). https://doi.org/10.1021/jp026304k

198. Simmons, J.M., Nichols, B.M., Baker, S.E., Marcus, M.S., Castellini, O.M., Lee, C.S., Hamers, R.J., Eriksson, M.A.: Effect

of ozone oxidation on single-walled carbon nanotubes. J. Phys. Chem. B **110**(14), 7113–7118 (2006). https://doi.org/10.1021/jp0548422

199. te Velde, G., Bickelhaupt, F.M., Baerends, E.J., Guerra, C.F., Van Gisbergen, S.J.A., Snijders, J.G., Ziegler, T.: Chemistry with ADF. J. Comput. Chem. **22**(9), 931–967 (2001). https://doi.org/10.1002/jcc.1056

200. Saleh, G., Gatti, C., Lo Presti, L.: Non-covalent interaction via the reduced density gradient: Independent atom model vs experimental multipolar electron densities. Comput. Theor. Chem. **998**, 148–163 (2012). https://doi.org/10.1016/j.comptc.2012.07.014

201. Sochava, I.V., Trapeznikova, O.N.: The specific heat of chain structures at low temperatures. Dokl. Akad. Nauk. SSSR **113**(4), 784–786 (1957)

202. Umoren, S.A., Obot, I.B., Madhankumar, A., Gasem, Z.M.: Effect of degree of hydrolysis of polyvinyl alcohol on the corrosion inhibition of steel: theoretical and experimental studies. J. Adhes. Sci. Technol. **29**(4), 271–295 (2015). https://doi.org/10.1080/01694243.2014.985281

203. Wurm, F., Hofmann, A.M., Thomas, A., Dingels, C., Frey, H.: Alpha, omega(*n*)-heterotelechelic hyperbranched polyethers solubilize carbon nanotubes. Macromol. Chem. Phys. **211**(8), 932–939 (2010). https://doi.org/10.1002/macp.200900652