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Review

Emerging Applications of Carbon Nanotubes[†]

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On the basis of their unique electrical and mechanical properties, carbon nanotubes (CNTs) have attracted great attention in recent years. A diverse array of methods has been developed to modify CNTs and to assemble them into devices. On the basis of these innovations, many applications that include the use of CNTs have been demonstrated. Transparent electrodes for organic light-emitting diodes (OLEDs), lithium-ion batteries, supercapacitors, and CNT-based electronic components such as field-effect transistors (FETs) have been demonstrated. Furthermore, CNTs have been employed in catalysis and sensing as well as filters and mechanical and biomedical applications. This review highlights illustrative examples from these areas to give an overview of applications of CNTs.

1. Introduction

Carbon nanotubes (CNTs) possess a unique set of electrical and mechanical properties which have been stimulating increasing interest in their applications.[1−5] Structurally, CNTs can be described as a sheet of graphene rolled into a tube. Depending on the orientation of the tube axis relative to the carbon network, different types of CNTs, described by the indices of the their chiral vector, n and m, can be obtained. The CNTs that are formed by connection of the head and tail of the chiral vector are referred to by their respective indices (i.e., see the 14,0 and 8,8 structures in Figure 1). Armchair CNTs ($n = m$) usually show metallic conductivity while zigzag ($m = 0$) or chiral ($n \neq m$) CNTs are semiconducting (Figure 1a).

Additionally, CNTs can vary by the number of carbon-layers in their sidewalls. Single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and multiwalled CNTs (MWCNTs) have been synthesized and are commercially available (Figure 1b).[6−9] Indeed, this variety opens the field to many different applications. Whereas semiconducting SWCNTs have, for example, been used in field-effect transistor (FET)-based sensors[10] metallic conducting MWCNTs have found their way into electrodes for electrocatalysis.[11]

Even though CNTs are depicted as open-ended tubes for simplicity, their ends are usually capped by fullerene-type hemispheres. The higher curvature at these end groups compared to the sidewalls of the CNTs leads to a difference in chemical reactivity that can be exploited to selectively functionalize the ends of CNTs.[12] In addition to covalent functionalization, the properties of CNTs can be modified by deposition of metal or metal oxide particles[13] or by the noncovalent attachment of polymers[14] or small molecules.[15] These different options add another level to the structural variety of CNTs and render them a highly customizable material.

In addition to their electrical properties, CNTs possess a very high strength that can be exploited in mechanical applications. Their high aspect ratio allows them to be fabricated into ropes analogous to spinning yarns from macroscopic fibers.[16] Utilized in a different context, this feature also enables the use of single CNTs as electrodes in nanoelectronic components.[17] Finally, their high surface area to mass ratio has played a major role in CNT-based applications. This is a particularly important advantage in electrocatalytic processes wherein metal catalysts are immobilized on the surface of CNTs.[18]

This review provides an overview of a variety of applications that are based on the unique properties of pristine as well as functionalized CNTs. The intense research on CNT applications creates a dynamic situation with new discoveries being made constantly, hence it is impossible to cover all published and noteworthy work. As a result, we highlight illustrative examples from the main areas of CNT-based applications.

2. CNT-based Electrodes

Several properties of CNTs make them promising candidates for use as electrodes. Besides their good conductivity, they have a high surface per mass ratio. Furthermore, they can be used in a variety of shapes—as individual nanotube electrodes, as a layer on top of an existing electrode, or as a free-standing electrode without any additional support.[19] As discussed in the Introduction, CNTs are known to interact with a variety of metal and metal oxide nanoparticles and can be covalently and noncovalently functionalized. Such modifications have been used to tune the properties of the CNT electrode to better suit the desired application.

Transparent Electrodes. Optically transparent electrodes (OTEs) are essential components of organic solar cells

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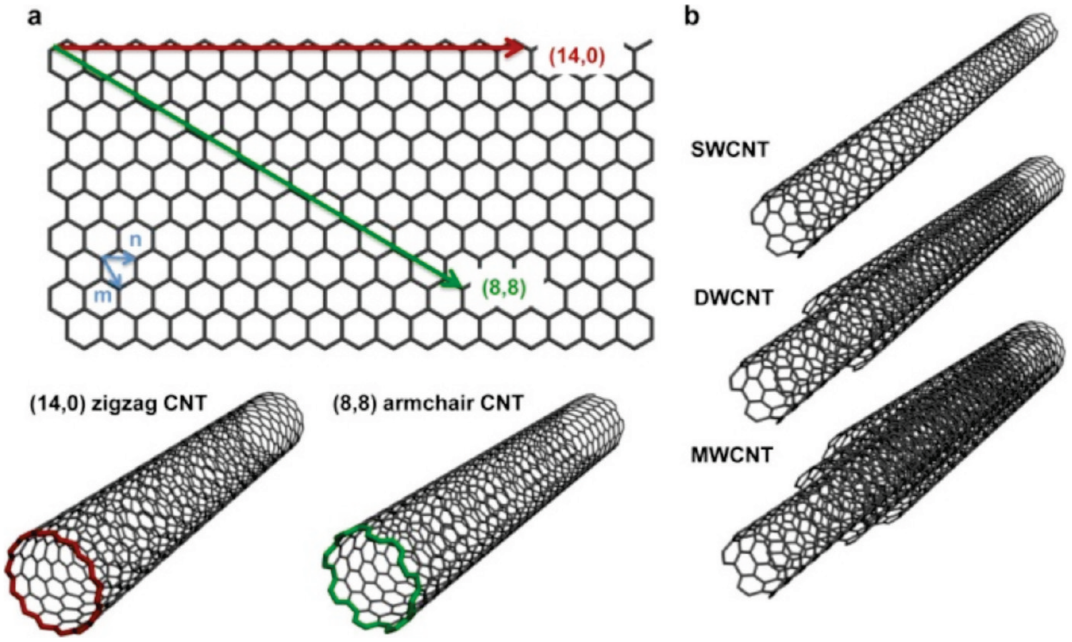

Figure 1. Structural variety of CNTs. (a) Orientation of the carbon network in armchair (*n*, *n*) and zigzag (*n*, 0) CNTs. (b) Single, double, and multiwalled CNTs.

as well as organic light-emitting diodes (OLEDs). Thin layers of CNTs, instead of the commonly used metal oxide conductive films like indium tin oxide, offer the advantage of more flexible electrodes and an alternative to rare metals such as indium. Depending on the desired application, CNT-OTEs must be processed into a thin film with strong (low resistivity) CNT-CNT junctions. Free standing thin films can be assembled by collecting dispersed CNTs on a filter[20,21] or by solution casting of high quality dispersions followed by doping or extraction of polymer.[22] These thin films can then be transferred onto the substrate. An alternative method involves direct spray-coating onto final substrates.[23−25] The superior suitability of CNTs for flexible electrodes becomes particularly obvious when low bending radii are desired. OLEDs with CNT electrodes operate almost identically under bending, whereas the sheet resistance of ITO-based electrodes dramatically increases because of cracks in their surface.[24]

An important aspect when utilizing CNTs as transparent electrodes is finding the proper balance between transparency and sheet resistance. Although ITO is not well-suited for flexible OTEs, it offers a low sheet resistance at good transparencies compared to CNTs. Nevertheless, by optimizing these parameters, it is possible to assemble CNT-containing organic photovoltaic devices that come close to controls using ITO in terms of quantum efficiency and fill factor.[23] The film morphology of the CNT electrode is another important determinate of performance. When using CNT-OTEs in electroluminescent devices inhomogeneous films can limit the brightness and cause electric short circuits. Depositing CNTs onto substrates functionalized with amine groups suitable for interaction with the CNTs addresses this issue in part and leads to significantly better device performance,[21] but it remains necessary to develop techniques that yield homogeneous CNT films reproducibly. Another important contributor toward the performance of CNT-based electrodes is the effect of doping. The Stevenson group systematically studied the effect of different amounts of nitrogen doping on the density of states and the electrical conductivity of CNT electrodes.[26] It would be expected that an increasing nitrogen content with the resulting higher density of states results in higher conductivities of the CNT electrodes. In the presented study, this trend could not be observed, however. The authors attribute this to differences in CNT length (and the resulting increased junction resistance for films of shorter CNTs) and morphology of the fabricated films. This underlines that CNT-based electrodes present a complex system and the careful control of a variety of factors is necessary on the way toward applications. Furthermore, the difference between mixtures of different types of SWCNTs (i.e., metallic and semiconducting) and purely metallic SWCNTs plays a role with regard to the stability of the sheet resistance of SWCNT thin films.[27] Whereas the sheet resistance of a film consisting of a mixture of metallic and semiconducting SWCNTs dropped from 19.6 to 0.99 kΩ/sq after air exposure and doping with H_2SO_4, a sample of 99% metallic SWCNTs showed only a change from 1.03 kΩ/sq to 0.65 kΩ/sq after the same treatment.

Electrodes for Lithium Ion Batteries. Their high surface area and similarity to currently used graphite makes CNTs promising candidates for use in lithium ion batteries. Calculations suggest that SWCNT bundles can intercalate Li on the interior wall of the CNTs and in interstitial spaces up to a density of about one Li per two carbon atoms, which is significantly higher than graphite.[28] Furthermore, a theoretical study of the interaction between Li/Li^+ and the CNT sidewall suggests that Li/Li^+ transport is energetically favored along the interior

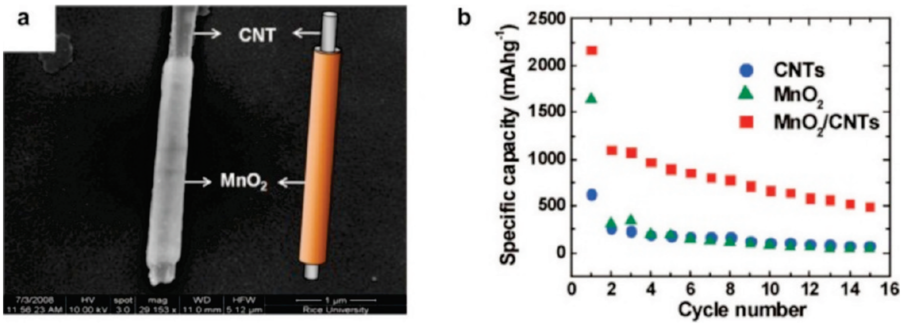

Figure 2. CNT-containing MnO_2 nanotubes for use in lithium ion batteries. (a) SEM image and schematic representation of the coaxial structure. (b) Discharge capacity vs cycle number for MnO_2/CNT coaxial nanotubes, MnO_2 nanotubes, and CNTs. Reprinted with permission from ref 35. Copyright 2009 American Chemical Society.

walls of CNTs while the energy surface of lithium on the exterior wall suggests that the metal is localized above the centroid of the six membered rings.[29] Experimentally, the use of CNTs as electrodes for lithium batteries has been demonstrated by several laboratories.[19,30−35] Examples include metal oxide modified CNTs that further improve the properties of the CNTs. Reddy et al. demonstrate that the synthesis of CNTs inside MnO_2 nanotubes leads to a composite electrode material that is superior to both individual components in terms of the specific charge storage capacity (Figure 2).[35]

Other studies demonstrate a high rate of Li intercalation for TiO_2/CNT composites,[33] enhanced air stability and improved safety in dichalcogenide/CNT based Li^+ batteries,[32] and greater reversibility of Sb/CNT and $SnSb_{0.5}$/CNT based batteries compared to their CNT-free counterparts.[31] CNTs in the form of aligned CNT arrays can be used as electrodes in battery applications without the need of an additional metal or metal oxide. However, achieving good electrical contacts between the aligned nanotubes has presented challenges. This can be overcome by using a conducting polymer such as PEDOT as a back contact.[30] The resulting electrode shows stable performance during a large number of cycles and is of considerably lower weight compared to conventional electrodes.

Another aspect that is important in the fabrication of batteries is the complexity of the electrode. Conventional electrodes usually consist of a metal substrate onto which a mixture of active material, binder, and electrical conductor is deposited. In contrast, CNTs can be fabricated into "buckypaper" electrodes by collection of surfactant-dispersed CNTs on a filter.[19] Even though the discharge capacity of devices based on these electrodes is slightly lower than what can be obtained with conventional electrodes, the more facile fabrication is a clear advantage.

In addition to the illustrated examples, CNT-containing electrodes can be used in a variety of other applications. As will be discussed (vide infra), they can serve as components in sensors,[12,36,37] fuel cells,[38−42] dielectrophoretic trapping of DNA molecules,[43] and as superior electrodes in cyclic voltammetry for trace level detection.[44]

3. Supercapacitors

Electrochemical double-layer capacitors (EDLCs), are considered a superior alternative to lithium batteries in applications that require high peak power for short periods of time. They store energy in the charged double layer that develops when a voltage is applied between electrodes that are immersed in an electrolyte. The capacitance of EDLCs scales with the active surface area of the electrode. In commercial EDLCs, carbon electrodes are rendered highly porous by thermal treatment to improve the surface area. In contrast, CNTs, offer intrinsically high surface areas and have thus been studied extensively as a material for EDLC applications. Extrapolation of experimental results has led Signorelli et al. to suggest that CNT-based EDLCs can achieve approximately seven times higher energy densities than current activated carbon-based devices.[45]

Capacitors Based on Pristine CNTs. There are several ways to produce CNT-based supercapacitors. Pristine CNTs can be deposited onto a charge collector by electrophoretic deposition from a CNT suspension,[46] or they can be grown directly on a Ni support or a graphitic foil.[47,48] Another method demonstrated by Futaba et al. is the liquid-induced collapse of SWCNT forests to give a densified material ($0.57\ g\ cm^{-3}$ compared to $0.029\ g\ cm^{-3}$ for as-grown CNTs) that maintains a high Brunauer−Emmett−Teller (BET) surface area similar to the "as-grown" CNTs (Figure 3).[49]

In addition to these methods, it is possible to use binders such as poly(vinylidene chloride) for EDLCs.[50] Using this latter approach, a specific capacitance of 180 F/g has been obtained.

Further improvement of the capacitance of an EDLC can be accomplished by the introduction of defect sites on the CNTs which add a redox pseudocapacitance to the double-layer capacitance. This can be achieved by plasma etching,[51] argon irradiation,[52] or by simply heating the CNTs in CO_2 or dry air.[53] Following this approach, Lu et al. were able to achieve energy densities of $148\ W\ h\ kg^{-1}$, which is close to energy densities of Li ion batteries.[51]

Metal/CNT Capacitors. The combination of CNTs with metals or metal oxides is another route to improve the performance of EDLCs as a result of pseudocapacitance that originates from redox processes.[54,55] The deposition of Ag nanoparticles has been shown to improve the specific capacitance of SWCNT based capacitors from 47 to $106\ F\ g^{-1}$.[54] In this context, it is notable that the capacitance increases with decreasing diameter of the utilized Ag nanoparticles in the observed range of 13 to 1 nm. An even larger increase in

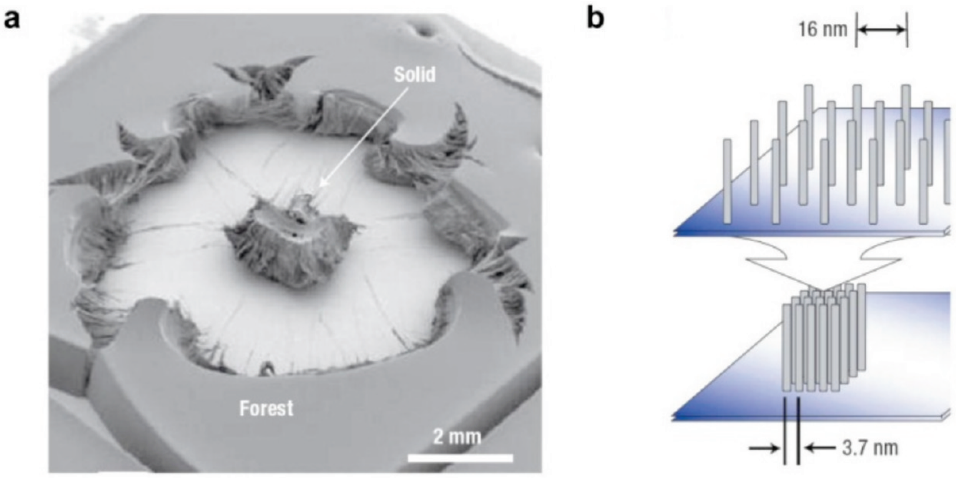

Figure 3. Fabrication of a high-density SWCNT material by liquid-induced collapse of CNT forests. (a) SEM image of high-density SWCNT ("solid") and the surrounding SWCNT forest (b) Schematic diagram of the liquid-induced collapse process. Reprinted with permission from ref 49. Copyright 2006 Nature Publishing Group.

capacitance from 29.8 to 250.5 F g^{-1} has been achieved when pristine MWCNTs were modified with MnO_2.[56]

Polymer/CNT Composite Capacitors. Although the MnO_2-induced increase in capacitance discussed above is remarkable, only the fraction of the Mn moieties that are within a thin, electrochemically active layer at the surface of the material are electrochemically active.[57] To achieve high loadings of electrochemically active MnO_2 in a supercapacitor, ternary composites of CNTs, polypyrrole (PPy), and MnO_2 have been investigated.[58] These composites exhibit high cyclability, retaining 88% of the initial charge after 10 000 cycles. Sivakkumar et al. attribute this performance to the CNTs ability to disperse high loads of MnO_2 in the conductive polymer. In those studies, the ternary composite outperforms CNT/MnO_2 as well as PPy/MnO_2 composites in terms of specific capacitance.

The use of conducting polymers in CNT-based supercapacitors is not limited to devices that contain metal oxides. Composites of polyaniline (PANI) and SWCNTs have been shown to have superior performance compared to capacitors that use either material individually.[59] Khomenko et al. demonstrated the use of two different types of conducting polymers, PPy and PANI, in a CNT-containing supercapacitor. Using PPy/MWCNT as the negative and PANI/MWCNT as the positive electrode, they have achieved a capacitance of 320 F g^{-1}.[60]

4. CNT-based Electronic Components

CNTs promise to be essential parts of many future electronic components such as nanowires, transistors, and switches. Assemblies of metallic as well as semiconducting CNTs can be used to produce macroscopic devices, but methods are also being developed that allow for individual tubes to be used as nanoelectronic components.

Nanowires. The high aspect ratio and electronic transport capabilities of CNTs make them promising candidates for use in nanowires. These assertions are supported by both calculations and experimental results[61,62] that demonstrate excellent performance even at temperatures up to 250 °C and high current densities of up to 1×10^9 to 1×10^{10} A cm^{-2}.[63] In nanowire performance, CNTs of typical dimensions (8.6 nm diameter and 2.6 μm in length) have been found to be comparable to the calculated properties of Au nanowires with the same dimensions.[64] In addition to individual CNTs, composites of CNTs and conducting polymers have many potential applications. Wang et al. have demonstrated a template method wherein pyrrole is electropolymerized in the presence of CNTs to produce highly conductive nanowires.[65]

Use of CNTs as Contacts in Organic Transistors. Aromatic organic molecules and conjugated polymers can interact with the surface of CNTs to give low contact resistance when CNTs are used as the electrodes in organic field-effect transistors (organic FETs or OFETs).[66] The contact resistance of poly(3-hexylthiophene) (P3HT) thin-film FETs produced using spray-coated CNT array contacts was found to be similar to devices using Au bottom contacts. For pentacene-based transistors the CNT array contact resistance was found to be lower than that of the corresponding Au contacts.[66] In addition to deposition by spray-coating, CNT arrays can also be applied by spin-coating of CNTs that were previously dispersed in water by wrapping with poly(4-styrene sulfonate) (PSS). Pentacene FETs, so created, displayed field-effect mobilities that were four times higher than analogous FETs with Au bottom contacts.[67]

In addition to this enhanced performance, pentacene-based FETs can be efficiently miniaturized when individual CNTs instead of CNT arrays are used as the source/drain electrodes. Qi et al. recently demonstrated an FET in which pentacene bridges a sub-10 nm gap cut into a SWCNT.[17] In an example published by Aguirre et al., individual CNTs proved to be well-suited contacts for charge injection into pentacene transistors, outperforming metal-based electrodes by an order of magnitude.[68]

CNT-based Field Effect Transistors. While metallic conducting CNTs are a good material for the source/drain electrodes of OFETs, semiconducting SWCNTs themselves are an attractive active material for FETs. In addition to creating simplified structures for FETs, the use of SWCNTs has also led to the development of CNT-based sensors (vide infra).[69,70] In an early example, Tans et al. were able to fabricate a back-gated FET based on an individual semiconducting SWCNT that spanned the gap between two Pt electrodes on an Si/SiO_2 substrate.[71] One challenge for early SWCNT FETs was the contact resistance at the interface between the CNTs and the metal electrodes, which limited the conductance in the "on" state. This problem was overcome by using Pd to contact the CNTs, as this material exhibits stronger interactions with the nanotubes. The resulting FETs have been shown to behave as ohmically contacted ballistic conductors when in the "on" state.[72] To fabricate more complex devices, it is necessary to employ methods to create arrays of individual CNT-based devices. Franklin et al. demonstrated that arrays can be produced by catalytically growing SWCNTs between Mo contacts upon which catalyst particles had been deposited.[73] The yield of contacts that are bridged by individual SWCNTs was up to 30% with a majority of the CNTs having the prerequisite semiconducting properties to produce high-quality FETs.

Other uses of CNTs in electronic components. CNTs can be used as other active electronic components, including bistable molecular switches. Many examples of molecular switches have been demonstrated[74,75] but in order to incorporate these switches into individually addressable electronic circuits, efficient contacts to discrete devices are necessary. CNTs are good candidates for this purpose because they provide good conductivity on the nanoscale and can also be attached covalently to molecular switching units. Recent theoretical studies suggest the feasibility of this concept for optically as well as nanomechanically induced switching mechanisms.[76−78]

A particularly interesting application of CNTs has been demonstrated by Jensen et al.,[79] wherein they describe a radio receiver based on a single MWCNT. In their setup, the MWCNT simultaneously acts as the antenna, tuner, amplifier, and demodulator—functions that are usually performed by individual components. The field emission from the tip of the MWCNTs in an electric field was monitored. When a radio signal, tuned to the resonance frequency of the MWCNTs, was broadcasted, the CNTs vibrate and the field emission changed as a function of the modulation of the radio signal (Figure 4). By connecting a sensitive speaker to this device, transmitted songs could be easily recognized by the human ear.

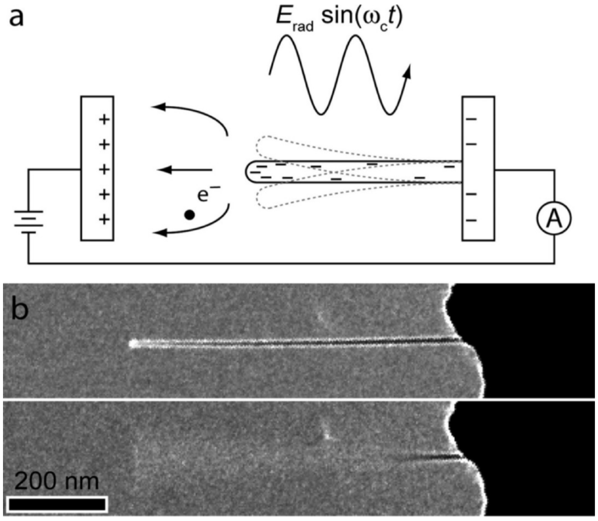

Figure 4. Nanotube radio. (a) Schematic representation. Upon excitation by radio transmissions, the MWCNT tip resonates and emits electrons that are detected via the resulting current. (b) Transmission electron micrographs of the MWCNT radio off and on resonance. Reprinted with permission from ref 79. Copyright 2007 American Chemical Society.

5. Catalysis

Because of their conductivity, high surface area, and facile functionalization to give catalytically active sites, CNTs are promising candidates for catalysis. One important aspect that needs to be considered in this context is the purity of the CNTs. Commercial CNTs usually contain residual metal catalyst particles from the synthesis and typical washing procedures such as the use of nitric acid at elevated temperatures cannot always completely remove these impurities.[80] Purity is especially important in cases wherein electrocatalytic activity is attributed to pristine CNTs, because metal impurities can contribute toward the observed catalytic behavior.[81]

Fuel Cells. In the interest of developing clean, sustainable, and mobile power sources, much attention has been focused on proton exchange membrane fuel cells (PEMFCs) in general, and direct methanol fuel cells (DMFCs) in particular.[82−85] One limitation of these fuel cells is the high cost of the Pt catalyst. By depositing catalyst nanoparticles on the surface of CNTs with high active surface areas, reduced amounts of Pt are needed to get high catalytic activity. Other carbon-based materials such as high-surface-area carbon black can also be used for this purpose, but several studies demonstrate that MWCNT catalyst supports produce higher activities.[82,83,86] There are multiple methods to synthesize Pt/MWCNT composites. CNTs are first oxidized by refluxing in HNO_3 or H_2SO_4/HNO_3 and subsequently mixed with a Pt nanoparticle precursor such as H_2PtCl_6. The latter salt is either reduced chemically with $NaBH_4$[83,87] or reduced under thermal conditions using intermittent microwave irradiation to give MWCNT/Pt nanoparticle composites.[88] An alternative is the electrodeposition of the metal catalyst onto pristine CNTs.[86] Although the use of CNT/Pt composites reduces the required amount of the noble metal, it is still desirable to replace it with a more earth-abundant alternative. The use of covalent linkages has been demonstrated in MWCNT materials containing cobalt porphyrins, and these materials have superior oxygen reduction performance as compared to other related systems.[89] More recently, another alternative has been demonstrated in which nickel bisdiphosphine units are covalently attached to MWCNTs via diazonium chemistry.[84] The active nickel center is a mimic of the active site of hydrogenase enzymes and showed excellent catalytic activity and stability.

Organic Reaction Catalysis. Metal-modified SWCNTs and MWCNTs have been reported to catalyze organic reactions. The aldehyde group in prenal (3-methyl-2-butenal) has been hydrogenated using a Pt/SWCNT system yielding the unsaturated alcohol prenol (3-methyl-2-butenol) in good selectivity relative to common side products 3-methylbutyraldehyde and 3-methyl-butanol.[90] When compared to Al_2O_3 and SiO_2, CNTs display superior catalytic performance as supports for Pt or Pd catalysts in the hydrogenation of o-chloronitrobenzene to o-chloroaniline.[91] Beyond the reduction of olefins and aldehydes, CNT-supported group 9 and 10 metal catalysts (Pt, Rh, PtPd, and PdRh) have been investigated for the hydrogenation of aromatic molecules. In the hydrogenation of toluene and naphthalene, MWCNT-supported PtPd exhibited particularly high initial turnover frequencies compared to $SiO_2-Al_2O_3$ or ZrPSi-supported catalysts.[18] The authors conclude that the low steric hindrance of metals adsorbed onto the external sidewall of the CNTs, as compared to the alternative supports, contributes to this effect. Furthermore, MWCNT-supported PdRh, Pt, and Rh catalysts have been shown to hydrogenate benzene at room temperature, a process that is not possible with commercial carbon-based Pd and Rh catalysts.[92] Beyond these examples, CNTs have been used as metal support for the oxidation of cellobiose[93] and in Suzuki coupling reactions.[94]

Immobilization of Biomacromolecules. A prerequisite for the use of CNTs in biocatalysis is the successful immobilization of catalytically active biomacromolecules on the surface of the CNTs, ideally with an electrical interconnection that can lead to electrocatalytic activity. Enzymes such as horseradish peroxidase,[95] glucose oxidase,[96] or hydrogenase[97] have been successfully immobilized on CNT-modified electrodes and their electrocatalytic activity has been confirmed by cyclic voltammetry (CV). Several methods for the connection of CNTs and enzymes have been utilized. A facile way to immobilize enzymes is to drop-cast a suspension of CNTs onto an electrode and subsequently immerse this modified electrode in a solution of the enzyme.[97] The biocompatibility of the CNTs in this process is improved by covalently attaching pol(ethylene glycol) (PEG) chains.[98] This functionalization also increases the water solubility and thus facilitates the device fabrication. Alternatively, CNTs and enzymes can be deposited onto an electrode by successive spray-casting from the respective dispersions.[96] In addition to these noncovalent immobilization methods, it has been shown that covalently cross-linked networks of CNTs and enzymes can be formed and linked to Au electrodes using electropolymerizable aniline moieties.[99] These resulting bioelectrocatalytic systems are able to oxidize glucose at a turnover rate of ca. 1025 s^{-1}, thereby showing that the incorporation of the functionalization does not lead to degradation of the enzyme's activity.

6. Filters and Membranes

The interactions of the CNT surface with target molecules, in addition to the inherent porosity resulting from their tubular structure, renders them interesting materials for the formation of filters and membranes. For these applications, CNTs can be easily assembled onto a larger pore size supporting filter or networks of nanotubes can be created to produce all-CNT membranes.[100]

Transport of Small Molecules through CNTs. The internal diameter of CNTs varies depending on the conditions that are used to synthesize the CNTs, with typical diameters ranging from 1 nm for SWCNTs and several nanometers for MWCNTs. With diameters on the same order of magnitude as most single molecules, CNTs are well-suited as pores for molecular transport. Simulations have shown that water transport within the tubes is facile, which is at first glance remarkable considering that the nonpolar surface of the CNTs does not interact well with polar water molecules.[101] Water molecules inside the tubes are energetically stabilized by hydrogen-bond interaction with their neighboring molecules. Subsequent theoretical investigations have built upon this and explored the possibility of using SWCNTs for water desalination.[102] Although water can pass through armchair type SWCNTs with chiral vectors ranging between (5,5) and (8,8), the diffusion of sodium ions is energetically too high for the smaller (5,5) and (6,6) SWCNTs. This effect has been demonstrated experimentally in the direct contact membrane distillation (DCMD) of salt water utilizing self-supporting CNT membranes.[103] In these experiments, 99% salt rejection could be achieved at flux rates of ca. 12 kg m^{-2} h^{-1}.

Functionalization of the CNT end-groups, which are the entrances to the CNT pores, can also be used to influence the transport. In an early example, Hinds et al. oxidized the end groups of the membrane-forming CNTs and subsequently covalently attached biotin to the terminal carboxylate groups which were then bound to streptavidin.[104] After streptavidin binding, the flux of $Ru(NH_3)_6^{3+}$ across the membrane was reduced by a factor of 15 showing the successful change of the transport through the pores. This approach has been extended to include functionalizing the end groups of CNTs with aliphatic groups of different chain lengths as well as anionically charged dye molecules.[105] The flux of cationic ruthenium trisbipyridine and methyl viologen was demonstrated to be significantly higher for the membranes that were functionalized with the anionic dye, as compared to those functionalized by nonpolar groups.

Although these examples are interesting for applications that require the permanent preference for the transport of a certain species, it is also desirable to have the ability to dynamically switch the transporting ability of membranes. This can be accomplished by modulating the water wettability of the CNTs in a membrane with external stimuli. Increasing the temperature of a CNT-membrane from 293 to 306 K, or exposing it to sonication, led to a significant increase in the diffusion of ionic compounds such as HCl, Na_2SO_4, or KCl, thereby demonstrating the feasibility of this concept.[106]

Substrate-Supported Filters Based on CNT Networks. CNT-based membranes are not only interesting candidates to discriminate between compounds that have a size on the Å scale, but can also be used to remove bacteria and viruses from water or to filter aerosols from air. A particular advantage of CNTs in this context is that the resulting filters can be easily cleaned by ultrasonication and autoclaving, which allows for repeated use with full filtering efficiency.[107] For these applications, the CNTs are typically deposited onto a membrane such as polytetrafluoroethylene,[108] poly(vinylidene fluoride),[109] polyamide, or polypropylene for structural support.[110] In these schemes, SWCNTs as well as MWCNTs have been shown to exhibit excellent retention of bacteria and viruses. An additional benefit of this approach is that SWCNT-based filters exhibit high antimicrobial activity.[109]

7. Sensors

CNTs are widely viewed as natural sensing elements that deliver a key nanowire architecture that had been previously identified as providing high sensitivity.[111] Several aspects of CNT properties that have been discussed earlier in the context of other applications can be exploited to create sensory responses. Specifically, CNTs that are functionalized with molecular units imparting specificity can be used to make resistive or FET sensory devices. Electrical-based sensor schemes have the potential for facile integration into other electronic circuits, miniaturization, low power consumption, and low cost.

CNTs have been used in their pristine form to create sensory systems exploiting their high surface area and adsorptive properties. Alternatively, they can be functionalized with metal or metal oxide particles, coated with polymers, or covalently linked to DNA or enzymes to provide specifity.

Sensors Based on Pristine CNTs. Numerous examples of sensors employing pristine (unfunctionalized) SWCNTs have been reported. In these devices CNTs can interact directly with analytes via van der Waals or donor−acceptor interaction between the target molecule and the SWCNT sidewall. Additionally, sensitivity to specific classes of chemicals have been attributed to the presence of defect sites on the SWCNTs as well as residual metal catalyst that is left from the CNT fabrication process.

SWCNT-based sensors for reactive gases such NO_2 and NH_3 have been studied and in this case the respective oxidizing and reducing nature of the analytes allows for them to be distinguished with transistor type sensors using individual semiconducting SWCNTs.[112,113] Under a gate voltage of +4 V exposure to 200 ppm NO_2 resulted in an increase in conductivity by 3 orders of magnitude.[113] Randomly grown networks of SWCNTs were used to create sensors for the nerve agent simulant dimethyl methylphosphonate (DMMP).[112] Sub-ppb levels of DMMP could be detected with minimal response to potentially interfering molecules, such as hydrocarbons or water. CNTs can also be fabricated into sensors by dispersion in a solvent such as DMF and subsequent drop-casting onto electrodes. A conductance-based sensor obtained in this fashion was able to detect NO_2 at a concentration of 44 ppb and nitrotoluene at 262 ppb.[114]

As a result of their fabrication and purification processes, CNTs contain defect sites and residual metal catalyst that can contribute to the sensing response. Purposely introducing defect sites by partial oxidation of CNTs increased their electrical response to various chemical vapors, presumably by creating stronger CNT−analyte interacations.[115] As oxidative treatment is a common CNT purification method, this effect needs to be considered when utilizing "pristine" CNTs in a sensor. Iron oxide particles that are often present in unpurified CNT samples provide another source that can induce a sensing response that does not stem intrinsically from the carbon network. The Compton group investigated this effect by comparing the cyclovoltammetric response of a CNT-modified basal plane pyrolytic graphite (BPPG) electrode with a Fe(III) oxide modified BPPG electrode to H_2O_2.[36] Based on their findings, they suggest that residual Fe_2O_3 particles on the CNT surface are the main cause for the response of CNT films to H_2O_2.

Metal and Metal Oxide Particles. Beyond being a potential contaminant in CNT-based sensing devices, the aforementioned metal oxide particles can be introduced purposefully in order to create more pronounced or more specific sensing responses. A CuO/MWCNT-modified electrode showed a significantly higher current response to glucose compared to a MWCNT electrode.[13] Using a standard three-electrode cell with the CuO/MWCNT electrode as the working electrode, this sensor was able to determine the glucose concentration in human blood serum samples. The response time was ca. 1 s and the sensor recovered almost completely after the measurement (≥95%). In another example, an MWCNT-carrying glassy carbon electrode (GCE) was modified with a porous ZnO film.[116] This sensor was used to detect hydroxylamine with a very low detection limit of 0.12 μM and exhibited a quick sensing response of < 3 s, as well as complete recovery. In addition to metal oxides, metal nanoparticles have been used in CNT sensors. An electrode composed of MWCNTs, gold nanoparticles, and glucose oxidase was used as an amperometric biosensor for glucose achieving a detection limit of 20 μM.[117]

Coating with Polymers or Biomacromolecules. Polymers have been utilized to increase the sensitivity and selectivity of CNT-based sensors and Snow et al. described a capacitive SWCNT sensor for a variety of chemical vapors.[14] Coating the sensor with a thin layer of a strong hydrogen-bonding polycarbosilane (HC) increased the response to acetone ca. 100 fold, and a self-assembled monolayer (SAM) coating containing hexafluoroisopropanol moieties significantly decreased the response time for the nerve agent mimic DMMP (Figure 5).

In another example, an SWCNT-based FET type sensor was coated with either the electron donating polymer polyethyleneimine (PEI) or the strongly acidic polymer Nafion.[118] PEI lowered the detection limit for the oxidizing gas NO_2 from 10−50 ppb to 100 ppt as compared to an uncoated device. The PEI coated sensor did not react to NH_3 vapor (100 ppm in air), however Nafion coatings enabled NH_3-detection while at the same time eliminating the response to NO_2. Other recent examples of polymer

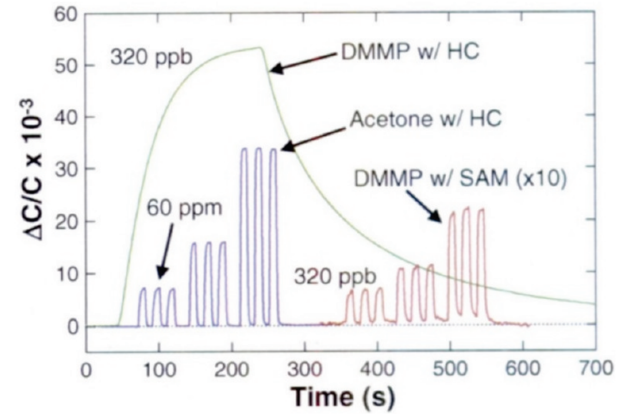

Figure 5. Decrease in response time to DMMP from a CNT sensor coated with a strong hydrogen-bonding polycarbosilane (HC) (green curve) to one coated with a self-aligned monolayer (SAM) coating of hexafluoroisopropanol moieties (red curve). Reprinted with permission from ref 14. Copyright 2005 American Association for the Advancement of Science.

enhanced selectivity include response to DMMP and xylene isomers by wrapping SWCNTs with functionalized polythiophenes.[119,120] In the case of xylene detection, the latter method demonstrated the ability of sophisticated molecular recognition to create differential sensory responses based solely on the isomeric composition of an analyte.

Blending MWCNTs with functionalized poly(olefin sulfone)s (POSs), polymers that degrade upon exposure to radiation, led to devices which show a 5-fold increase in conductivity when exposed to 5×10^3 rad of γ radiation.[121] The effects were optimized by creating polymers with affinities to the MWCNTs and heavy elements (bismuth) to create enhanced γ-ray absorption. The increased conduction stems from spontaneous depolymerization and the resulting increased interconnections of the conductive MWCNTs to create conductive pathways between electrodes.

DNA or other biomacromolecules can also be used to improve the performance of CNT-based sensors. Drop-casting a solution of single-stranded DNA (ss-DNA) onto an SWCNT FET sensor increased its response to several vapors including methanol, trimethylamine, and DMMP.[10] Furthermore, ss-DNA-modified SWCNTs can be used to electrochemically detect the hybridization with a target ss-DNA strand.[122] The polysaccharide chitosan was used to wrap MWCNTs and provided functional groups for the attachment of glucose dehydrogenase to create a glucose sensor.[123] Enzymes can also be incorporated in sensors by drop-casting directly onto an SWCNT electrode and subsequent coating with a nafion layer.[124] Another fabrication method for creating a biocomposite electrode is the mixing of tyrosinase, epoxy resin, and MWCNTs and subsequent curing at 40 °C for 1 week.[125] Using this electrode, catechol could be detected at a detection limit of 0.01 mM, a value about half of that obtainable with an analogous graphite sensor.

Noncovalent Attachment of Small Molecules. The noncovalent interactions of small molecules with the SWCNT surface have been used to provide functionality to increase sensor selectivity. An early approach involved sensors created by depositing hematoxylin onto an MWCNT-modified GCE.[37] Utilizing differential pulse voltammetry (DPV), the resulting electrode could be used to detect adrenaline with good sensitivity and selectivity over ascorbic acid, and uric acid.

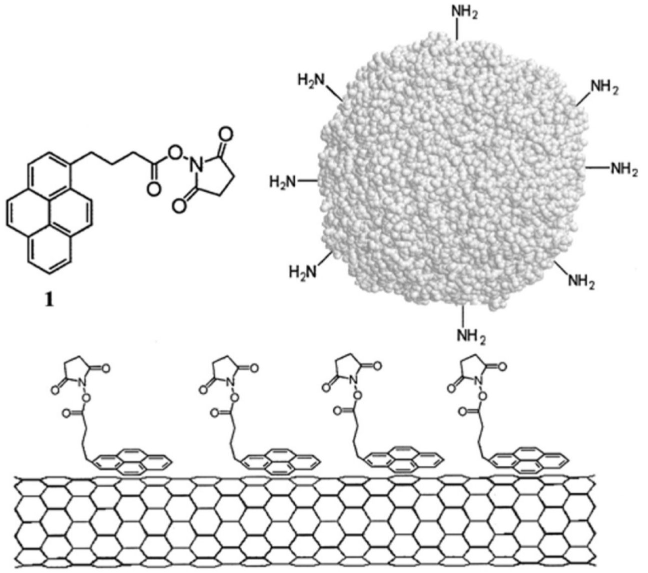

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Figure 6. 1-Pyrenebutanoic acid succinimidyl ester is adsorbed onto the CNT surface providing a chemically reactive anchor for the immobilization of proteins. Reprinted with permission from ref 15. Copyright 2001 American Chemical Society.

As a result of the strong interaction between the π network of the CNT surface and pyrene, this group has been widely used for the noncovalent attachment of functional groups to CNTs. Chen et al. exploited this by incubating CNTs in a solution of 1-pyrenebutanoic acid succinimidyl ester to create a precursor to biological functionalization. Subsequently, they immobilized various proteins on the CNT by reaction of the succinimidyl ester with amine groups (Figure 6).[15]

This method has further been utilized to incorporate glucose oxidase into an SWCNT sensor.[126] The same pyrene linker was reacted with a functionalized aniline to bind hexafluoroisopropanol (HFIP) to SWCNTs.[127] FET-type sensors based on these modified SWCNTs showed a very low detection limit of 50 ppb for the nerve agent mimic DMMP, as well as good selectivity over other chemical vapors such as ethanol, water, toluene, or hexane.

Chemical Modification. Another possibility for the connection of sensing units onto CNTs is to use covalent attachment of functional groups. Because of its simplicity, the oxidation of CNTs to yield carboxylic acid groups has been the dominant method for this purpose. The carboxylic acid groups can be used to attach oligonucleotides via carbodiimide chemistry.[12,128] By combining electrodes obtained in this fashion with $\mathrm{Ru(bpy)_3}^{2+}$-mediated guanine oxidation, Li et al. achieved detection limits of only a few attomoles in a DNA sensor.[12] The same strategy can also be used to attach the enzyme glucose oxidase for the detection of glucose.[129] Although less common, other covalent functionalization methods have been employed in order to fabricate CNT based sensors. SWCNTs have been covalently functionalized by phenyl boronic acid moieties for glucose sensing by both wrapping with poly(aminophenylboronic acid) or the covalent attachment of phenyl boronic acid using diazonium chemistry.[69]

8. Biomedical Applications

With the development of covalent[130] and noncovalent[131] methods to achieve water-soluble CNTs as well as procedures to attach biomolecules to CNTs,[10] the development of biomedical applications of CNTs became possible.[132] An interesting field in this context is the use of CNTs for bioelectronic applications. The Kotov group demonstrated that it is possible to grow neuronal cells on an SWCNT-based lbl film and subsequently excite the cells by passing a current through the CNT network.[133] While a synthetic polymer (poly(acrylic acid)) was used for the anionic layers in this example, it is also possible to fabricate multilayer films using poly(styrene sulfonate) wrapped SWCNTs and laminin, a component of the human extracellular matrix.[134] Neural networks could be grown and electrically excited on this substrate. The interfacing of CNTs and neural cells can be an important step toward the development of bioelectronic components such as neural prosthetic devices. Nevertheless, other challenges have to be overcome on the way to real-world applications. One such challenge is the formation of CNT-based nerve mimics that contain a sufficiently high density of separately addressable conductive channels. One way to achieve this is by repeatedly drawing and bundling CNT-filled glass fibers.[135] Starting from a single channel with a diameter of 150 μm after the first draw, a bundle of 19600 channels with an individual channel diameter of 0.39 μm was obtained after three drawing and bundling cycles. The process also improves the CNT alignment inside the channels resulting in an increased conductivity after each drawing step. The conductivity is however still low (1.21×10^{-4} S/m) compared to other CNT-based electronic components and it would be desirable to increase this value.

Another field of research in the context of CNT-based biomedical applications is the use of CNTs for therapeutic applications. Several examples have been reported such as the CNT-assisted delivery of platinum anticancer drugs[136] or as molecular transporters for human T cells.[137] Even though the cytotoxicity of the CNTs was tested and shown to be low in both studies, the toxicity of CNTs remains a complex question and might limit their use in biomedical applications.[138]

9. Mechanical Applications

As a result of their covalent carbon networks, CNTs are exceptionally strong materials and exhibit Young's moduli on the order of 1 TPa for SWCNTs and low defect density MWCNTs grown by arc-discharge.[139,140]

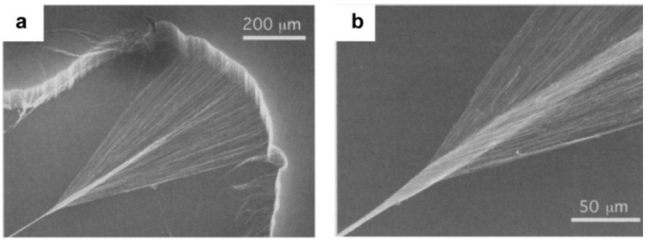

Figure 7. Spinning of CNT yarns from MWCNT forests. (a and b) SEM images of the spinning process. Reprinted with permission from ref 16. Copyright 2004 American Association for the Advancement of Science.

High Strength Applications. CNTs strongly interact with each other via van der Waals forces and unless specially treated after their synthesis, they form bundles. Separating these bundles can be a challenge when individual CNTs are desired. In high strength applications, however, these bundles or ropes allow for the realization of the CNT mechanical properties on a macroscopic scale. By manipulating ropes consisting of tens to hundreds of SWCNTs with an atomic force microscope tip (AFM tip), the tensile strength of these bundles has been determined to be on the order of 45 GPa.[141] The synthesis of CNTs can be optimized to achieve ropes of macroscopic dimensions. Zhu et al. fabricated SWCNT strands with lengths up to several centimeters by catalytic pyrolysis of n-hexane.[142] These strands showed metallic conductance above 90 K and a Young's modulus of 49−77 GPa. By spinning MWCNTs from nanotube forests while introducing twist, CNT equivalents of cotton or wool yarns could be obtained (Figure 7).[16]

The MWCNT yarns have a density of ca. 0.8 g cm^{-3} and a tensile strength of 460 MPa when combined into two-ply yarns. Yarns fabricated by this procedure have been assembled into sheets that were several centimeters wide and one meter long.[143] These hydrophobic sheets could support water droplets with a mass that was approximately 50 000 times higher than the mass of the area of the MWCNT sheet they contacted.

CNT-containing Actuators. CNTs in pristine form or in combination with polymers have been fabricated into electromechanical actuators. In these actuators, a voltage is applied to CNTs immersed in an electrolyte and the charge injected into the CNTs is compensated by the formation of a double-layer. At low charge injection, this results in expansion of the material for electron injection and contraction for hole injection. In an early example, Baughman et al. demonstrated this effect using sheets of SWCNTs that were immersed in NaCl solutions as well as other electrolytes.[144] Higher strain rates and amplitudes could be achieved by using resistance compensation.[145] On the basis of the same principle, a ply actuator has been demonstrated by forming a layered material of CNTs and an epoxy film.[146] CNTs can also be used in Nafion-based actuators wherein an applied voltage causes swelling, because the induced charge is compensated by uptake of ions from a surrounding electrolyte. Landi et al. demonstrated that Nafion composites with high purity SWCNTs showed actuation with CNT contents as low as 0.5% w/w, which is an indication of the high conductivity and large aspect ratio of the CNTs.[147]

10. Challenges for Applications of CNTs

CNTs are good candidates for a variety of applications. Nevertheless, there are several challenges associated with their synthesis, purification, processing, and fabrication into devices. CNTs are usually synthesized by either chemical vapor deposition (CVD),[148] laser ablation,[149] or arc discharge.[3] Although the use of a metal catalyst in these processes can be avoided in some cases such as the arc discharge production of MWCNTs, it is required in most synthetic processes. As a result, residual metal particles are a common impurity in CNT samples. If not removed properly, these impurities can significantly change the behavior of a CNT-based device as illustrated by the Compton group and described previously.[36] In addition to metal particles, as synthesized CNTs commonly contain amorphous carbon, fullerenes and carbon nanoparticles.[150] Several purification procedures have been suggested such as the gas[151] and liquid phase[152] as well as electrochemical oxidation[153] of impurities and high purities of over 99% (with respect to metal content) have been achieved. It has to be noted, however, that some of these methods significantly alter the properties of the CNTs. The treatment with H_2SO_4/HNO_3 for example is known to cut long CNTs into smaller fragments introducing carboxylic acid groups at their ends.[154] Although this can be desirable for the subsequent attachment of functional groups, it can be a disadvantage when defect-free CNTs with high aspect ratios are required in electronic applications. Physical methods such as filtration,[155] centrifugation[156] or high-temperature annealing[157] can avoid CNT shortening and oxidation, but they are less effective in removing impurities compared to oxidative methods and in some cases require dispersible CNT samples. Therefore, the combination of chemical and physical methods has been attempted. Li et al. reported a procedure in which SWCNT bundles were purified by washing with benzene and HCl as well as ultrasonic and freezing treatment.[158] A purity of 95% was achieved while no damage to the SWCNT bundles was observed by SEM and Raman measurements.

Despite these advances, the purification of CNTs remains challenging. It is therefore desirable to develop CNT synthesis conditions that result in low amounts of impurities. Hata et al. have been able to synthesize SWCNT forests with a carbon purity of over 99.98%.[159] They observed that water activates the metal catalyst in ethylene CVD. By optimizing the water and ethylene level during the reaction, they were able to increase the SWCNT product to catalyst ratio by 2 orders of magnitude compared to the high-pressure carbon monoxide (HiPCO) process, which led to the observed very high purities. Optimizing the CNT synthesis conditions can lead to other advantages such as the formation of CNTs with narrow diameter distribution[160] or the preferred synthesis of metallic SWCNTs (up to 91%).[161]

Besides synthesis and purification, the processing of CNTs is a key challenge on the way to applications. The major limiting factor in this context is the low solubility of CNTs.[162] Several attempts have been made in order to overcome this limitation including the noncovalent attachment of solubilizing units[131,163] as well as the oxidation of defect sites[164] or sidewall functionalization using azomethine ylides[130] or diazonium chemistry.[165] Although pristine CNTs are essentially insoluble, especially in polar solvents such as water, aqueous solubilities of up to 20 mg/mL have been reported using the mentioned methods. This has enabled the use of solution processing techniques such as drop-casting, spin-casting, or spraying, which facilitates the fabrication of CNT-based devices and opens the field for new applications. Nevertheless, it has to be noted that many of the reported high CNT solubilities rely on high-density covalent sidewall-functionalization. When SWCNTs are used, this functionalization results in a drastically reduced conductivity and is therefore not a viable option for many electronic applications. The development of novel methods that facilitate the processing of CNTs while having little impact on their electrical properties or providing the option to restore the conductivity in a subsequent step would therefore be desirable.

11. Conclusions

We have summarized the many applications of pristine and modified SWCNTs and MWCNTs that have emerged since their discovery about 20 years ago. The broad scope of these applications suggests that a multitude of CNT-based technologies will be the result of their unique properties of high electrical conductivity, mechanical strength, high aspect ratio, and nanoscale diameter. Many methods have been developed to modify carbon nanotubes including the deposition of metal nanoparticles or metal oxides, the noncovalent attachment of polymers, biomacromolecules and small aromatic compounds as well as various methods for the covalent functionalization. Additionally, various ways to fabricate CNT-based devices such as drop-casting, spin-casting, spraying, or deposition onto a filter support have been developed. A combination of these functionalization and fabrication methods has made it possible to use CNTs in electrodes, capacitors and other electronic components, sensors, filters, and membranes, and in catalysis, biomedical, and mechanical applications. A prerequisite for further progress will be an increased availability of high-quality CNTs combined with newly developed modification and fabrication methods that overcome challenges that are currently limiting some applications of CNTs. Amazing progress has been made in all areas of CNT applications in the recent past and based on the amount of research that is being done on CNTs as well as the scientific community's fascination, significant further progress can be expected to create dramatic technological advances.

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References

(1) Mintmire, J. W.; Dunlap, B. I.; White, C. T. *Phys. Rev. Lett.* **1992**, *68*, 631.

(2) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. B.* **1992**, *46*, 1804.
(3) Iijima, S. *Nature* **1991**, *354*, 56.
(4) Falvo, M. R.; Clary, G. J.; Taylor, R. M., II; Chi, V.; Brooks, F. P., Jr; Washburn, S.; Superfine, R. *Nature* **1997**, *389*, 582.
(5) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.
(6) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787.
(7) Ebbesen, T. W.; Ajayan, P. M. *Nature* **1992**, *358*, 220.
(8) Hutchison, J. L.; Kiselev, N. A.; Krinichnaya, E. P.; Krestinin, A. V.; Loutfy, R. O.; Morawsky, A. P.; Muradyan, V. E.; Obraztsova, E. D.; Sloan, J.; Terekhov, S. V.; Zakharov, D. N. *Carbon* **2001**, *39*, 761.
(9) Flahaut, E.; Bacsa, R.; Peigney, A.; Laurent, C. *Chem. Commun.* **2003**, 1442.
(10) Staii, C.; Johnson, A. T., Jr.; Chen, M.; Gelperin, A. *Nano Lett.* **2005**, *5*, 1774.
(11) Banks, C. E.; Davies, T. J.; Wildgoose, G. G.; Compton, R. G. *Chem. Commun.* **2005**, 829.
(12) Li, J.; Ng, H. T.; Cassell, A.; Fan, W.; Chen, H.; Ye, Q.; Koehne, J.; Han, J.; Meyyappan, M. *Nano Lett.* **2003**, *3*, 597.
(13) Jiang, L.-C.; Zhang, W.-D. *Biosens. Bioelectron.* **2010**, *25*, 1402.
(14) Snow, E. S.; Perkins, F. K.; Houser, E. J.; Badescu, S. C.; Reinecke, T. L. *Science* **2005**, *307*, 1942.
(15) Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. *J. Am. Chem. Soc.* **2001**, *123*, 3838.
(16) Zhang, M.; Atkinson, K. R.; Baughman, R. H. *Science* **2004**, *306*, 1358.
(17) Qi, P.; Javey, A.; Rolandi, M.; Wang, Q.; Yenilmez, E.; Dai, H. *J. Am. Chem. Soc.* **2004**, *126*, 11774.
(18) Pawelec, B.; La Parola, V.; Navarro, R. M.; Murcia-Mascarós, S.; Fierro, J. L. G. *Carbon* **2006**, *44*, 84.
(19) Ng, S. H.; Wang, J.; Guo, Z. P.; Chen, J.; Wang, G. X.; Liu, H. K. *Electrochim. Acta* **2005**, *51*, 23.
(20) Chien, Y.-M.; Lefevre, F.; Shih, I.; Izquierdo, R. *Nanotechnology* **2010**, *21*, 134020.
(21) Kim, M. J.; Shin, D. W.; Kim, J.-Y.; Park, S. H.; Han, I. T.; Yoo, J. B. *Carbon* **2009**, *47*, 3461.
(22) Gu, H.; Swager, T. M. *Adv. Mater.* **2008**, *20*, 4433.
(23) Feng, Y.; Ju, X.; Feng, W.; Zhang, H.; Cheng, Y.; Liu, J.; Fujii, A.; Ozaki, M.; Yoshino, K. *Appl. Phys. Lett.* **2009**, *94*, 123302.
(24) Hu, L.; Li, J.; Liu, J.; Grüner, G.; Marks, T. *Nanotechnology* **2010**, *21*, 155202.
(25) Vasilyeva, S. V.; Unur, E.; Walczak, R. M.; Donoghue, E. P.; Rinzler, A. G.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2288.
(26) Wiggins-Camacho, J. D.; Stevenson, K. J. *J. Phys. Chem. C.* **2009**, *113*, 19082.
(27) Miyata, Y.; Yanagi, K.; Maniwa, Y.; Kataura, H. *J. Phys. Chem. C.* **2008**, *112*, 3591.
(28) Zhao, J.; Buldum, A.; Han, J.; Lu, J. P. *Phys. Rev. Lett.* **2000**, *85*, 1706.
(29) Udomvech, A.; Kerdcharoen, T.; Osotchan, T. *Chem. Phys. Lett.* **2005**, *406*, 161.
(30) Chen, J.; Liu, Y.; Minett, A. I.; Lynam, C.; Wang, J.; Wallace, G. G. *Chem. Mater.* **2007**, *19*, 3595.
(31) Chen, W. X.; Lee, J. Y.; Liu, Z. *Carbon* **2003**, *41*, 959.
(32) Dominko, R.; Arčon, D.; Mrzel, A.; Zorko, A.; Cevc, P.; Venturini, P.; Gaberscek, M.; Remskar, M.; Mihailovic, D. *Adv. Mater.* **2002**, *14*, 1531.
(33) Moriguchi, I.; Hidaka, R.; Yamada, H.; Kudo, T.; Murakami, H.; Nakashima, N. *Adv. Mater.* **2006**, *18*, 69.
(34) Morris, R. S.; Dixon, B. G.; Gennett, T.; Raffaelle, R.; Heben, M. J. *J. Power Sources* **2004**, *138*, 277.
(35) Reddy, A. L. M.; Shaijumon, M. M.; Gowda, S. R.; Ajayan, P. M. *Nano Lett.* **2009**, *9*, 1002.
(36) Šljukić, B.; Banks, C. E.; Compton, R. G. *Nano Lett.* **2006**, *6*, 1556.
(37) Zare, H. R.; Nasirizadeh, N. *Sensor Actuator, B* **2010**, *143*, 666.
(38) Somani, S. P.; Somani, P. R.; Sato, A.; Umeno, M. *Diamond Relat. Mater.* **2009**, *18*, 497.
(39) Tang, Z.; Chua, D. H. C. *J. Electrochem. Soc.* **2010**, *157*, B868.
(40) Tang, Z.; Ng, H. Y.; Lin, J.; Wee, A. T. S.; Chua, D. H. C. *J. Electrochem. Soc.* **2010**, *157*, B245.
(41) Yang, J.; Liu, D.-J. *Carbon* **2007**, *45*, 2845.
(42) Yun, Y. S.; Bak, H.; Jin, H.-J. *Synth. Met.* **2010**, *160*, 561.
(43) Tuukkanen, S.; Toppari, J. J.; Kuzyk, A.; Hirviniemi, L.; Hytönen, V. P.; Ihalainen, T.; Törmä, P. *Nano Lett.* **2006**, *6*, 1339.
(44) Bertoncello, P.; Edgeworth, J. P.; Macpherson, J. V.; Unwin, P. R. *J. Am. Chem. Soc.* **2007**, *129*, 10982.
(45) Signorelli, R.; Ku, D. C.; Kassakian, J. G.; Schindall, J. E. *Proc. IEEE* **2009**, *97*, 1837.
(46) Du, C.; Pan, N. *J. Power Sources* **2006**, *160*, 1487.
(47) Yoon, B.-J.; Jeong, S.-H.; Lee, K.-H.; Kim, H. S.; Park, C. G.; Han, J. H. *Chem. Phys. Lett.* **2004**, *388*, 170.
(48) Chen, J. H.; Li, W. Z.; Wang, D. Z.; Yang, S. X.; Wen, J. G.; Ren, Z. F. *Carbon* **2002**, *40*, 1193.
(49) Futaba, D. N.; Hata, K.; Yamada, T.; Hiraoka, T.; Hayamizu, Y.; Kakudate, Y.; Tanaike, O.; Hatori, H.; Yumura, M.; Iijima, S. *Nat. Mater.* **2006**, *5*, 987.
(50) An, K. H.; Kim, W. S.; Park, Y. S.; Choi, Y. C.; Lee, S. M.; Chung, D. C.; Bae, D. J.; Lim, S. C.; Lee, Y. H. *Adv. Mater.* **2001**, *13*, 497.
(51) Lu, W.; Qu, L.; Henry, K.; Dai, L. *J. Power Sources* **2009**, *189*, 1270.
(52) Hoefer, M.; Bandaru, P. R. *Appl. Phys. Lett.* **2009**, *95*, 183108.
(53) Yamada, Y.; Kimizuka, O.; Machida, K.; Suematsu, S.; Tamamitsu, K.; Saeki, S.; Yamada, Y.; Yoshizawa, N.; Tanaike, O.; Yamashita, J.; Don, F.; Hata, K.; Hatori, H. *Energ. Fuel* **2010**, *24*, 3373.
(54) Wee, G.; Mak, W. F.; Phonthammachai, N.; Kiebele, A.; Reddy, M. V.; Chowdari, B. V. R.; Gruner, G.; Srinivasan, M.; Mhaisalkar, S. G. *J. Electrochem. Soc.* **2010**, *157*, A179.
(55) Zhang, W.-D.; Chen, J. *Pure Appl. Chem.* **2009**, *81*, 2317.
(56) Xie, X.; Gao, L. *Carbon* **2007**, *45*, 2365.
(57) Toupin, M.; Brousse, T.; Bélanger, D. *Chem. Mater.* **2004**, *16*, 3184.
(58) Sivakkumar, S. R.; Ko, J. M.; Kim, D. Y.; Kim, B. C.; Wallace, G. G. *Electrochim. Acta* **2007**, *52*, 7377.
(59) Zhou, Y.-k; He, B.-l; Zhou, W.-j; Huang, J.; Li, X.-h; Wu, B.; Li, H.-l *Electrochim. Acta* **2004**, *49*, 257.
(60) Khomenko, V.; Frackowiak, E.; Béguin, F. *Electrochim. Acta* **2005**, *50*, 2499.
(61) Tans, S. J.; Devoret, M. H.; Dai, H.; Thess, A.; Smalley, R. E.; Geerligs, L. J.; Dekker, C. *Nature* **1997**, *386*, 474.
(62) White, C. T.; Todorov, T. N. *Nature* **1998**, *393*, 240.
(63) Wei, B. Q.; Vajtai, R.; Ajayan, P. M. *Appl. Phys. Lett.* **2001**, *79*, 1172.
(64) Kreupl, F.; Graham, A. P.; Duesberg, G. S.; Steinhögl, W.; Liebau, M.; Unger, E.; Hönlein, W. *Microelectron. Eng.* **2002**, *64*, 399.
(65) Wang, J.; Dai, J.; Yarlagadda, T. *Langmuir* **2005**, *21*, 9.
(66) Southard, A.; Sangwan, V.; Cheng, J.; Williams, E. D.; Fuhrer, M. S. *Org. Electron.* **2009**, *10*, 1556.
(67) Hong, K.; Nam, S.; Yang, C.; Kim, S. H.; Chung, D. S.; Yun, W. M.; Park, C. E. *Org. Electron.* **2009**, *10*, 363.
(68) Aguirre, C. M.; Ternon, C.; Paillet, M.; Desjardins, P.; Martel, R. *Nano Lett.* **2009**, *9*, 1457.
(69) Vlandas, A.; Kurkina, T.; Ahmad, A.; Kern, K.; Balasubramanian, K. *Anal. Chem.* **2010**, *82*, 6090.
(70) Goldoni, A.; Petaccia, L.; Lizzit, S.; Larciprete, R. *J. Phys.-Condens. Mat.* **2010**, *22*, 013001.
(71) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, *393*, 49.
(72) Javey, A.; Guo, J.; Wang, Q.; Lundstrom, M.; Dai, H. *Nature* **2003**, *424*, 654.
(73) Franklin, N. R.; Wang, Q.; Tombler, T. W.; Javey, A.; Shim, M.; Dai, H. *Appl. Phys. Lett.* **2002**, *81*, 913.
(74) Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172.
(75) Dulić, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; Jong, J. J. D. de; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. J. *Phys. Rev. Lett.* **2003**, *91*, 1.
(76) Li, X.-F.; Wang, L.; Chen, K.-Q.; Luo, Y. *Appl. Phys. Lett.* **2009**, *95*, 232118.
(77) Zhao, P.; Fang, C. F.; Wang, Y. M.; Zhai, Y. X.; Liu, D. S. *Physica E* **2009**, *41*, 474.
(78) Zhao, P.; Wang, P.; Zhang, Z.; Fang, C.; Wang, Y.; Zhai, Y.; Liu, D. *Solid State Commun.* **2009**, *149*, 928.
(79) Jensen, K.; Weldon, J.; Garcia, H.; Zettl, A. *Nano Lett.* **2007**, *7*, 3508.
(80) Pumera, M. *Carbon* **2007**, 6453.
(81) Banks, C. E.; Crossley, A.; Salter, C.; Wilkins, S. J.; Compton, R. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2533.
(82) Li, W.; Liang, C.; Zhou, W.; Qiu, J.; Zhou, Z.; Sun, G.; Xin, Q. *J. Phys. Chem. B* **2003**, *107*, 6292.
(83) Prabhuram, J.; Zhao, T. S.; Tang, Z. K.; Chen, R.; Liang, Z. X. *J. Phys. Chem. B* **2006**, *110*, 5245.
(84) Le Goff, A.; Artero, V.; Jousselme, B.; Tran, P. D.; Guillet, N.; Métayé, R.; Fihri, A.; Palacin, S.; Fontecave, M. *Science* **2009**, *326*, 1384.
(85) Wang, C.; Waje, M.; Wang, X.; Tang, J. M.; Haddon, R. C.; Yan, Y. *Nano Lett.* **2004**, *4*, 345.
(86) Tang, H.; Chen, J. H.; Huang, Z. P.; Wang, D. Z.; Ren, Z. F.; Nie, L. H.; Kuang, Y. F.; Yao, S. Z. *Carbon* **2004**, *42*, 191.
(87) Golikand, A. N.; Lohrasbi, E.; Maragheh, M. G.; Asgari, M. *J. Appl. Electrochem.* **2009**, *39*, 2421.
(88) Tian, Z. Q.; Jiang, S. P.; Liang, Y. M.; Shen, P. K. *J. Phys. Chem. B* **2006**, *110*, 5343.
(89) Zhang, W.; Shaikh, A. U.; Tsui, E. Y.; Swager, T. M. *Chem. Mater.* **2009**, *21*, 3234.
(90) Lordi, V.; Yao, N.; Wei, J. *Chem. Mater.* **2001**, *13*, 733.
(91) Jiang, L.; Gu, H.; Xu, X.; Yan, X. *J. Mol. Catal. A: Chem.* **2009**, *310*, 144.
(92) Yoon, B.; Pan, H.-B.; Wai, C. M. *J. Phys. Chem. C* **2009**, 1520.
(93) Tan, X.; Deng, W.; Liu, M.; Zhang, Q.; Wang, Y. *Chem. Commun.* **2009**, 7179.
(94) Sullivan, J. A.; Flanagan, K. A.; Hain, H. *Catal. Today* **2009**, *145*, 108.
(95) Chen, H.; Dong, S. *Biosens. Bioelectron.* **2007**, *22*, 1811.
(96) Zhao, H.-Z.; Sun, J.-J.; Song, J.; Yang, Q.-Z. *Carbon* **2010**, *48*, 1508.
(97) Luo, X.; Brugna, M.; Tron-Infossi, P.; Giudici-Orticoni, M. T.; Lojou, É. *J. Biol. Inorg. Chem.* **2009**, *14*, 1275.
(98) Wen, Y.; Wu, H.; Chen, S.; Lu, Y.; Shen, H.; Jia, N. *Electrochim. Acta* **2009**, *54*, 7078.

(99) Baravik, I.; Tel-Vered, R.; Ovits, O.; Willner, I. *Langmuir* **2009**, *25*, 13978.

(100) López-Lorente, A. I.; Simonet, B. M.; Valcárcel, M. *Anal. Chem.* **2010**, *82*, 5399.

(101) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188.

(102) Corry, B. *J. Phys. Chem. B* **2008**, *112*, 1427.

(103) Dumée, L. F.; Sears, K.; Schütz, J.; Finn, N.; Huynh, C.; Hawkins, S.; Duke, M.; Gray, S. *J. Membr. Sci.* **2010**, *351*, 36.

(104) Hinds, B. J.; Chopra, N.; Rantell, T.; Andrews, R.; Gavalas, V.; Bachas, L. G. *Science* **2004**, *303*, 62.

(105) Majumder, M.; Chopra, N.; Hinds, B. J. *J. Am. Chem. Soc.* **2005**, *127*, 9062.

(106) Yu, M.; Funke, H. H.; Falconer, J. L.; Noble, R. D. *J. Am. Chem. Soc.* **2010**, *132*, 8285.

(107) Srivastava, A.; Srivastava, O. N.; Talapatra, S.; Vajtai, R.; Ajayan, P. M. *Nat. Mater.* **2004**, *3*, 610.

(108) Brady-Estévez, A. S.; Nguyen, T. H.; Gutierrez, L.; Elimelech, M. *Water Res.* **2010**, *44*, 3773.

(109) Brady-Estévez, A. S.; Kang, S.; Elimelech, M. *Small* **2008**, *4*, 481.

(110) Guan, T.; Yao, M. *J. Aerosol Sci.* **2010**, *41*, 611.

(111) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201.

(112) Novak, J. P.; Snow, E. S.; Houser, E. J.; Park, D.; Stepnowski, J. L.; McGill, R. A. *Appl. Phys. Lett.* **2003**, *83*, 4026.

(113) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.

(114) Li, J.; Lu, Y.; Ye, Q.; Cinke, M.; Han, J.; Meyyappan, M. *Nano Lett.* **2003**, *3*, 929.

(115) Robinson, J. A.; Snow, E. S.; Badescu, S. C.; Reinecke, T. L.; Perkins, F. K. *Nano Lett.* **2006**, *6*, 1747.

(116) Zhang, C.; Wang, G.; Liu, M.; Feng, Y.; Zhang, Z.; Fang, B. *Electrochim. Acta* **2010**, *55*, 2835.

(117) Rakhi, R. B.; Sethupathi, K.; Ramaprabhu, S. *J. Phys. Chem. B* **2009**, *113*, 3190.

(118) Qi, P.; Vermesh, O.; Grecu, M.; Javey, A.; Wang, Q.; Dai, H.; Peng, S.; Cho, K. J. *Nano Lett.* **2003**, *3*, 347.

(119) Wang, F.; Yang, Y.; Swager, T. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8394.

(120) Wang, F.; Gu, H.; Swager, T. M. *J. Am. Chem. Soc.* **2008**, *130*, 5392.

(121) Lobez, J. M.; Swager, T. M. *Angew. Chem., Int. Ed.* **2010**, *49*, 95.

(122) Zhang, X.; Jiao, K.; Liu, S.; Hu, Y. *Anal. Chem.* **2009**, *81*, 6006.

(123) Zhang, M.; Smith, A.; Gorski, W. *Anal. Chem.* **2004**, *76*, 5045.

(124) Pham, X.-H.; Bui, M.-P. N.; Li, C. A.; Han, K. N.; Kim, J. H.; Won, H.; Seong, G. H. *Anal. Chim. Acta* **2010**, *671*, 36.

(125) Pérez López, B.; Merkoçi, A. *Analyst* **2009**, *134*, 60.

(126) Besteman, K.; Lee, J.-O.; Wiertz, F. G. M.; Heering, H. A.; Dekker, C. *Nano Lett.* **2003**, *3*, 727.

(127) Kong, L.; Wang, J.; Luo, T.; Meng, F.; Chen, X.; Li, M.; Liu, J. *Analyst* **2010**, *135*, 368.

(128) Cai, H.; Cao, X.; Jiang, Y.; He, P.; Fang, Y. *Anal. Bioanal. Chem.* **2003**, *375*, 287.

(129) Lin, Y.; Lu, F.; Tu, Y.; Ren, Z. *Nano Lett.* **2004**, *4*, 191.

(130) Georgakilas, V.; Tagmatarchis, N.; Pantarotto, D.; Bianco, A.; Briand, J.-P.; Prato, M. *Chem. Commun.* **2002**, 3050.

(131) Star, A.; Steuerman, D. W.; Heath, J. R.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 2508.

(132) Yang, W.; Thordarson, P.; Gooding, J. J.; Ringer, S. P.; Braet, F. *Nanotechnology* **2007**, *18*, 412001.

(133) Gheith, M. K.; Pappas, T. C.; Liopo, A. V.; Sinani, V. A.; Shim, B. S.; Motamedi, M.; Wicksted, J. P.; Kotov, N. A. *Adv. Mater.* **2006**, *18*, 2975.

(134) Kam, N. W. S.; Jan, E.; Kotov, N. A. *Nano Lett.* **2009**, *9*, 273.

(135) Hendricks, T. R.; Ivanov, I. N.; Schaeffer, D. A.; Menchhofer, P. A.; Simpson, J. T. *Nanotechnology* **2010**, *21*, 115301.

(136) Feazell, R. P.; Nakayama-Ratchford, N.; Dai, H.; Lippard, S. J. *J. Am. Chem. Soc.* **2007**, *129*, 8438.

(137) Liu, Z.; Winters, M.; Holodniy, M.; Dai, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 2023.

(138) Poland, C. A.; Duffin, R.; Kinloch, I.; Maynard, A.; Wallace, W. A. H.; Seaton, A.; Stone, V.; Brown, S.; Macnee, W.; Donaldson, K. *Nat. Nanotechnol.* **2008**, *3*, 423.

(139) Salvetat, J.-P.; Bonard, J.-M.; Thomson, N. H.; Kulik, A. J.; Forró, L.; Benoit, W.; Zuppiroli, L. *Appl. Phys. A: Mater. Sci. Process.* **1999**, *69*, 255.

(140) Ruoff, R. S.; Lorents, D. C. *Carbon* **1995**, *33*, 925.

(141) Walters, D. A.; Ericson, L. M.; Casavant, M. J.; Liu, J.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Appl. Phys. Lett.* **1999**, *74*, 3803.

(142) Zhu, H. W.; Xu, C. L.; Wu, D. H.; Wei, B. Q.; Vajtai, R.; Ajayan, P. M. *Science* **2002**, *296*, 884.

(143) Zhang, M.; Fang, S.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R.; Baughman, R. H. *Science* **2005**, *309*, 1215.

(144) Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; De Rossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* **1999**, *284*, 1340.

(145) Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Madden, J. D.; Baughman, R. H. *Smart Mater. Struct.* **2003**, *12*, 549.

(146) Yun, Y.-H.; Shanov, V.; Schulz, M. J.; Narasimhadevara, S.; Subramaniam, S.; Hurd, D.; Boerio, F. J. *Smart Mater. Struct.* **2005**, *14*, 1526.

(147) Landi, B. J.; Raffaelle, R. P.; Heben, M. J.; Alleman, J. L.; VanDerveer, W.; Gennett, T. *Nano Lett.* **2002**, *2*, 1329.

(148) Cheng, H. M.; Li, F.; Su, G.; Pan, H. Y.; He, L. L.; Sun, X.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1998**, *72*, 3282.

(149) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, *273*, 483.

(150) Hou, P.; Liu, C.; Cheng, H. *Carbon* **2008**, *46*, 2003.

(151) Chiang, I. W.; Brinson, B. E.; Huang, A. Y.; Willis, P. A.; Bronikowski, M. J.; Margrave, J. L.; Smalley, R. E.; Hauge, R. H. *J. Phys. Chem. B.* **2001**, *105*, 8297.

(152) Li, Y.; Zhang, X.; Luo, J.; Huang, W.; Cheng, J.; Luo, Z.; Li, T.; Liu, F.; Xu, G.; Ke, X.; Li, L.; Geise, H. J. *Nanotechnology* **2004**, *15*, 1645–1649.

(153) Fang, H.-T.; Liu, C.-G.; Liu, C.; Li, F.; Liu, M.; Cheng, H.-M. *Chem. Mater.* **2004**, *16*, 5744.

(154) Liu, J.; Rinzler, A.; Dai, H.; Hafner, J.; Bradley, R.; Boul, P.; Lu, a; Iverson, T.; Shelimov, K.; Huffman, C.; Rodriguez-Macias, F.; Shon, Y.; Lee, T.; Colbert, D.; Smalley, R. *Science* **1998**, *280*, 1253–6.

(155) Shelimov, K. B.; Esenaliev, R. O.; Rinzler, A. G.; Huffman, C. B.; Smalley, R. E. *Chem. Phys. Lett.* **1998**, *282*, 429.

(156) Hu, H.; Yu, A.; Kim, E.; Zhao, B.; Itkis, M. E.; Bekyarova, E.; Haddon, R. C. *J. Phys. Chem. B* **2005**, *109*, 11520.

(157) Lambert, J. M.; Ajayan, P. M.; Bernier, P.; Planeix, J. M.; Brotons, V.; Coq, B.; Castaing, J. *Chem. Phys. Lett.* **1994**, *226*, 364.

(158) Li, F.; Cheng, H. M.; Xing, Y. T.; Tan, P. H.; Su, G. *Carbon* **2000**, *38*, 2041.

(159) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science* **2010**, *306*, 1362.

(160) Dervishi, E.; Li, Z.; Watanabe, F.; Xu, Y.; Saini, V.; Biris, A. R.; Biris, A. S. *J. Mater. Chem.* **2009**, *19*, 3004.

(161) Harutyunyan, A. R.; Chen, G.; Paronyan, T. M.; Pigos, E. M.; Kuznetsov, O. a; Hewaparakrama, K.; Kim, S. M.; Zakharov, D.; Stach, E. a; Sumanasekera, G. U. *Science* **2009**, *326*, 116–20.

(162) Tasis, D.; Tagmatarchis, N.; Georgakilas, V.; Prato, M. *Chem.—Eur. J.* **2003**, *9*, 4000.

(163) Backes, C.; Schmidt, C. D.; Hauke, F.; Böttcher, C.; Hirsch, A. *J. Am. Chem. Soc.* **2009**, *131*, 2172.

(164) Asuri, P.; Karajanagi, S. S.; Sellitto, E.; Kim, D.-Y.; Kane, R. S.; Dordick, J. S. *Biotechnol. Bioeng.* **2006**, *95*, 804.

(165) Li, H.; Cheng, F.; Duft, A. M.; Adronov, A. *J. Am. Chem. Soc.* **2005**, *127*, 14518.