Advanced Physical Chemistry of Carbon Nanotubes

Jun Li and Gaind P. Pandey

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506; email: junli@ksu.edu

Annu. Rev. Phys. Chem. 2015. 66:331-56

First published online as a Review in Advance on January 12, 2015

The Annual Review of Physical Chemistry is online at physchem.annualreviews.org

This article's doi: 10.1146/annurev-physchem-040214-121535

Copyright © 2015 by Annual Reviews. All rights reserved

Keywords

nanoelectronics, transparent conductive electrode, oxygen reduction reaction, filtration membranes, electrical energy storage, solar cells

Abstract

The past decade has seen a surge of exciting research and applications of carbon nanotubes (CNTs) stimulated by deeper understanding of their fundamental properties and increasing production capability. The intrinsic properties of various CNTs were found to strongly depend on their internal microstructures. This review summarizes the fundamental structure-property relations of seamless tube-like single- and multiwalled CNTs and conically stacked carbon nanofibers, as well as the organized architectures of these CNTs (including randomly stacked thin films, parallel aligned thin films, and vertically aligned arrays). It highlights the recent development of CNTs as key components in selected applications, including nanoelectronics, filtration membranes, transparent conductive electrodes, fuel cells, electrical energy storage devices, and solar cells. Particular emphasis is placed on the link between the basic physical chemical properties of CNTs and the organized CNT architectures with their functions and performance in each application.

1. INTRODUCTION

CNT: carbon nanotube

SWNT: single-walled carbon nanotube

MWNT: multiwalled carbon nanotube

Carbon nanofiber

(CNF): a special type of carbon nanotube consisting of a stack of graphitic cones or cups along the axis and typically a large hollow core

Plasma-enhanced chemical vapor deposition

(PECVD): a process that uses energetic plasma in a reactor to accelerate commonly employed, thermally driven chemical vapor deposition reactions

Chemical vapor deposition (CVD):

a process used to deposit solid materials by thermal decomposition and chemical reaction of gas-phase precursors in a heated reactor The term carbon nanotubes (CNTs) refers to a family of seamless tube-like materials made of atomic layers of sp^2 -bonded carbon atoms. These materials were known as hollow carbon nanofibers, carbon filaments, or graphite whiskers as early as the 1950s (1, 2). However, major research and applications of CNTs were stimulated by Iijima's (3) discovery of their atomic structure in 1991. Particularly, over the past decade, the production capability of CNTs has increased by more than tenfold, reaching \sim 5 kiloton per year in 2011 (4). This enabled many commercial applications utilizing large quantities of unorganized CNTs in the form of powders, composite materials, and thin films. Although macroscopic systems are enhanced by CNTs in many ways, they are far from fully utilizing the intrinsic properties of individual CNTs. However, the rapid developments in our fundamental understanding, new characterization and modeling techniques, and novel fabrication methods have driven exciting research using organized architectures to better utilize the intrinsic properties of CNTs. This article highlights recent developments of organized CNT architectures in selected applications.

2. PHYSICAL PROPERTIES OF CARBON NANOTUBES

The CNT structure can start with a planar atomic sheet consisting of covalently bonded carbon atoms (i.e., graphene), as shown in **Figure 1***a*. All carbon atoms in graphene are in sp² form (except a small number of sp³ atoms at the edges or defects), forming a two-dimensional (2D) network with a hexagonal lattice. Graphene is a large conjugate system with delocalized π -electrons shared among the carbon atoms. As a graphene layer rolls into a seamless tube, it forms a single-walled carbon nanotube (SWNT) (**Figure 1***b*). Multiple SWNTs packed in a tight concentric structure form a multiwalled carbon nanotube (MWNT) (**Figure 1***c*).

The unique structure of graphene results in a strong interaction between atoms in the layer but little interaction between adjacent layers, leading to drastically different properties in and out of the graphene plane. This is reflected in the highly anisotropic properties of graphite, which can be viewed as a stack of graphene sheets. The electrical, thermal, mechanical, and electrochemical properties of graphite vary by orders of magnitude between in-plane and cross-plane measurements (5, 6). The properties of all traditional carbon materials can be correlated with the dimension and organization of the anisotropic graphitic domains in their internal structures (5, 6). Such highly anisotropic properties also apply to CNTs. Many extraordinary electrical, thermal, and mechanical properties of CNTs are specifically along the axial direction. Thus, it is critical to organize CNTs into proper configurations or architectures for desired high performance.

The internal microstructure of a CNT is also important in defining its physical properties. A good example is provided by carbon nanofibers (CNFs), which are special types of CNTs that consist of conically stacked graphene (or graphitic) cups (7) (**Figure 1***d*). This type of structure is common in vertically aligned CNFs grown on solid substrates by plasma-enhanced chemical vapor deposition (PECVD) (8, 9) and bulk production by catalytic chemical vapor deposition (CVD) in floating reactors (7). A large body of literature simply refers to the conically stacked CNFs as MWNTs or bamboo-like MWNTs (8, 9), but later studies discovered that the unique structure of CNFs distinguishes them from normal MWNTs in many applications (10–16), as discussed below.

All CNTs have high-aspect-ratio, fiber-like structures. SWNTs have the smallest diameter (0.8–5 nm) of all the CNTs and a variable length from tens of nanometers to millimeters, whereas MWNTs have a larger diameter (\sim 3 to >100 nm) and lengths similar to those of SWNTs. CNFs typically have an outer diameter of \sim 10–300 nm, a length up to \sim 200 µm, and a characteristic, mostly hollow core, which makes up one-third to two-thirds of the CNF's diameter. Fully dispersed



Figure 1

Schematic illustrations of the atomic structure of (*a*) a layer of graphene, (*b*) a single-walled carbon nanotube, (*c*) a multiwalled carbon nanotube, and (*d*) a carbon nanofiber consisting of a conical (or cup-like) stack of graphitic microstructure with a cone angle θ relative to the fiber axis.

short SWNTs have all atoms exposed at the surface, giving a specific surface area (SSA) up to 1,600 m²/g (17). But the SSA of SWNT bundles, MWNTs, and CNFs is much lower. The sidewall of SWNTs and MWNTs is hydrophobic and chemically inert, similar to a graphite basal plane. Chemical functionalization relies on weak interactions, such as surfactant encapsulation and π - π stacking of conjugate molecules. Strongly oxidized CNTs may present defects at the sidewall for covalent functionalization but tend to degrade other properties. In contrast, the sidewall of a hollow CNF consists of abundant broken graphitic edges, yielding a much more active surface for chemical functionalization (15) and interface with other electrochemically active materials (16, 18–20).

The electronic properties of an isolated defect-free SWNT depend on its helicity (or chirality), which is defined by the vector $\mathbf{C} = m\mathbf{a}_1 + n\mathbf{a}_2$ along which a graphene sheet is rolled into a seamless tube, where \mathbf{a}_1 and \mathbf{a}_2 are the two primary lattice vectors of the hexagonal graphene structure (**Figure 1***a*). It is known that an SWNT presents semiconducting properties, denoted as a semiconducting (s-)SWNT, if $|m - n|/3 \neq$ integer, but it presents metallic properties, denoted as a metallic (m-)SWNT, if |m - n|/3 = integer (21, 22). As a result, a typical growth process

Field-effect transistor (FET): a

transistor that uses an electric field to control the charge carrier and hence the conductivity of a semiconducting channel between a source and a drain electrode generates about two-thirds of s-SWNTs and one-third of m-SWNTs (21, 22). The band gap of an s-SWNT also depends on its diameter, d_{CNT} , with $E_g = 2d_{\text{CC}\gamma}/d_{\text{CNT}}$, where $d_{\text{CC}} = 0.142$ nm is the C–C bond length in graphene, and $\gamma = 2.5-3.2$ eV is the nearest-neighbor hopping parameter (23). Each individual tube in a small-diameter MWNT behaves similar to an SWNT, with little interaction between adjacent shells (24). But MWNTs larger than 10 nm in diameter are essentially metallic conductors at room temperature. So are CNFs.

The strong sp² bonding between the carbon atoms in CNTs yields remarkable mechanical strength, represented by a large Young's modulus of ~1 TPa and a tensile strength of ~150 GPa (25–27), comparable to the in-plane properties of graphene. The strong bonding makes CNTs one of the most resilient materials (28). The Young's modulus of a single conical shell in a CNF was predicted to be $\cos^4\theta$ (with θ the cone angle) of the equivalent SWNT (29). However, experimentally measured values from CNFs varied from 5–60 GPa (30) to 0.9–1.2 TPa (31). The dependence of the thermal conductivity on CNT structures is very similar to that of the mechanical properties. Both SWNTs and MWNTs have extremely high axial thermal conductivities, up to 3,500 W/m·K (32) and 3,000 W/m·K (33), respectively, comparable to the in-plane value of graphite. But randomly stacked SWNTs exhibit thermal conductivities of only 0.7 W/m·K (34), and aligned SWNTs have 200 W/m·K (35). CNFs have a thermal conductivity of 14 W/m·K along the axis (36).

3. CARBON NANOTUBE GROWTH, SORTING, AND ASSEMBLY

CVD is the dominant technique for CNT growth, used for high-volume production in floating catalyst reactors and device fabrication on designated substrates. Bulk-produced CNTs typically require postgrowth purification, thermal annealing, and chemical functionalization. Electronic devices require further sorting of s-SWNTs and m-SWNTs by four approaches: (*a*) preferential synthesis, (*b*) postgrowth separation, (*c*) selective deposition, and (*d*) controlled removal on the device.

Using the method of preferential synthesis by optimizing the proper precursor, catalyst, and substrate, investigators reported the successful production of 91% of m-SWNTs (37) and 95% of s-SWNTs (38). A PECVD study further demonstrated the ability to grow 96% s-SWNTs in vertically aligned arrays (39). In postgrowth processes, s-SWNTs and m-SWNTs can be separated by density-gradient ultracentrifugation after selectively wrapping SWNTs with DNA (40), surfactant (41), or block copolymer (42). Over 99% of m-SWNTs or s-SWNTs can be obtained (42). This method is quite attractive as SWNTs can be isolated within a very narrow diameter range (0.02 nm), thus providing a precise band gap. In addition, density-gradient ultracentrifugation is a scalable technique for large production. Other scalable separation techniques include ion-exchange chromatography of DNA-wrapped SWNTs (43) and gel exclusion of surfactantwrapped SWNTs (44). SWNTs with a specific chirality can be obtained by combining preferential growth and postgrowth separation (45). For special applications, AC dielectrophoresis has been demonstrated to attract m-SWNTs toward a microelectrode array, leaving surfactant-wrapped s-SWNTs in the solution (46) due to the difference in relative dielectric constant. Alternatively, modifying the device surface with amine groups has been demonstrated to induce selective adsorption of s-SWNTs, whereas phenyl groups tended to have stronger binding with m-SWNTs (47). Finally, m-SWNTs can be removed by electrical breakdown (24), selective gas-phase plasma etching (48), or UV irradiation followed by washing with surfactants (49) after the mixed SWNTs are fabricated into electronic devices such as field-effect transistors (FETs).

Organized CNTs include three configurations: (*a*) randomly stacked thin films, (*b*) horizontally aligned submonolayer films, and (*c*) vertically aligned arrays. Both random and aligned SWNT

thin films are critical components in nanoelectronics, optoelectronics, photovoltaics, and sensors, and their preparation and properties are reviewed by Cao & Rogers (50). Most random SWNT thin films are deposited from bulk-produced SWNT solutions and can be easily scaled up. A random CNT network can be tailored to be semiconducting or metallic by the collective effects of CNT density, length, percolation threshold, the composition of the starting materials, and film geometry. High-density, aligned SWNT films can be achieved using AC dielectrophoresis (46, 51) or Langmuir-Blodgett techniques (52). In a major development, low-density, aligned SWNTs can be prepared by CVD on specifically cut quartz or sapphire crystal surfaces (38, 53-55). Highlevel control of the parallel alignment and tube density (~5-60 SWNTs per micrometer) was achieved using narrow catalyst lines on the quartz surface. With proper growth processes, these aligned SWNTs can be semiconductor enriched (38, 55), fitting the needs of nanoelectronics. Furthermore, the aligned SWNTs can be transferred to a flexible plastic substrate or a silicon wafer using a gold-coated thin polyimide film as a carrier (56, 57). The gold/polyimide film adheres to the SWNTs and is removed by wet etching after transfer, leaving only SWNTs on the receiving substrate. This enables the integration of aligned SWNTs with silicon processes, leading to large-scale integrated circuits of CNT FETs (58, 59).

Most applications involving MWNTs use randomly stacked films, whose preparation is less stringent and can be achieved by solution casting, spin coating, ink printing, filtration, thermal spraying, and electrophoretic deposition. Vertically aligned SWNTs (39, 60), MWNTs (61, 62), and CNFs (10) are normally achieved by CVD or PECVD with catalysts seeded on proper substrates (8, 9, 63). Incorporating water during CVD growth was found to dramatically enhance the activity and lifetime of the catalysts, resulting in very dense and vertically aligned SWNT forests with a height up to 2.5 mm (60). Moreover, this method can be applied to grow patterned and highly organized SWNT structures. In the DC-biased PECVD process, CNTs tend to grow along the electrical field lines. By changing the local electrical field direction, CNTs can be bent to produce sophisticated zigzag structures (64).

4. APPLICATIONS OF CARBON NANOTUBES

4.1. Carbon Nanotubes in Nanoelectronics

SWNTs have been recognized as potential semiconducting materials to replace silicon in future nanoelectronics (65). Proper SWNTs have the right band gap (hundreds of milli–electron volts) as the semiconducting channel in a room-temperature FET, which was demonstrated in 1998 (66) with a platinum source and drain electrodes, and an SiO₂-covered silicon back gate. The atomic thin and smooth body makes SWNTs free of electron scattering, showing ideal ballistic transport (67, 68) and a high mobility up to ~10,000 cm²/(V·s) (69) after minimizing the metal-CNT contact resistance with palladium source and drain electrodes and further subtracting it from the total resistance. Theoretical studies predicted that an SWNT FET is superior to a silicon FET in maintaining gate control as the channel length is reduced, leading to the possibility of smaller transistors. Recently, a local-gated SWNT FET with only a 9-nm channel length demonstrated an impressively small inverse subthreshold slope of 94 mV per decade and a high on/off ratio, over 10^4 (70) (**Figure 2***a*,*b*).

Earlier studies on FETs using a single SWNT channel frequently encountered large deviceto-device variations owing to uncontrolled chirality, diameter, and placement of the SWNTs, as well as the influence of gas adsorption and dielectric surface charges (71). Recently, exciting progress toward large-scale integrated circuits has been made by increasing the statistical reliability using tens to thousands of SWNTs in the patterned channel instead of only one. Two approaches



Figure 2

(*a*) Schematic illustration of the device structure of a single-walled carbon nanotube (SWNT) field-effect transistor (FET) with a local bottom W gate, 3-nm HfO₂ dielectric, and palladium source/drain contacts that were deposited on top of a single SWNT channel. Above the schematic are a top-view scanning electron micrograph and a cross-sectional transmission electron micrograph showing the ~9-nm channel length in the SWNT FET. (*b*) The I_d - V_{gs} curve showing the characteristics of the SWNT FET. Panels *a* and *b* adapted with permission from Reference 70. Copyright 2012 American Chemical Society. (*c*) Scanning electron micrograph of aligned SWNTs grown on a Y-cut quartz surface that were transferred onto a silicon wafer in some FETs. Panel *c* adapted with permission from Reference 53. Copyright 2007 American Chemical Society. (*d*) Scanning electron micrograph of a randomly stacked SWNT network used in some FETs. Panel *d* adapted with permission from Reference 75. Copyright 2013 American Chemical Society. Abbreviation: SS, subthreshold slope.

have been employed: aligned parallel SWNT channels (**Figure 2***c*) and randomly stacked SWNT networks (**Figure 2***d*).

Using aligned SWNTs, Shulaker et al. (58) built the first computer with a central processor based entirely on 178-SWNT FETs. Three key efforts were made to overcome the inherent imperfections (mixed m- and s-SWNTs and misplacement on the surface) to enable the integration. First, with the use of CVD, high-quality, horizontally aligned, parallel SWNTs were grown on crystalline quartz substrates and then transferred to traditional SiO₂/Si substrates (56, 57). This made it possible to produce 99.5% aligned SWNTs at lithographically patterned areas at the wafer scale. Second, a misplacement-immune layout technique was used to remove SWNTs in the predefined regions by plasma etching to ensure that no incorrect connections existed. Third, selective electrical breakdown was applied to remove \sim 99.99% of m-SWNTs

in each channel to increase I_{on}/I_{off} to >10⁴. This CNT computer was able to run an operating system to simultaneously perform counting and integer sorting, as well as to take 20 different commercial MIPS instructions (58). In a following study, this group further reduced the device size from 1 µm to sub-20 nm and demonstrated the first very large-scale integration–compatible processing solution for CNT FET digital circuits (59). They also directly integrated CNT FET infrared light sensors with a circuit at a 32-nm channel length and demonstrated the capability of operating at ~100 kHz while consuming only 130 nW at 2 V (59).

The random network approach has been demonstrated in the development of medium-scale CNT thin-film integrated circuits, particularly on flexible plastic substrates (72-75). CNTs are deposited on the flexible substrate surface by transfer printing from or direct adsorption from CNT solutions. The CNT thin films are then patterned by oxygen plasma etching. These studies have taken three approaches to overcome the short-circuit problem by m-SWNTs. Cao et al. (72) patterned the random network (similar to that shown in **Figure 2**d) into parallel stripes (\sim 5 µm in width and \sim 50 µm in length) as the conducting channels for FETs. The density of the CNTs was controlled so that a typical device incorporated ~16,000 individual SWNTs. Even though about one-third of the SWNTs were metallic, the completed metallic pathways between the source and drain electrodes were avoided using proper CNT length/density and stripe geometry. The resulting SWNT FETs have shown encouraging properties, such as high mobility [80 cm²/(V·s)], a low subtreshold slope (140 mV per decade), low operating voltage (<5 V), and a high I_{on}/I_{off} ratio (>10⁵). Sun et al. (73) used a much lower CNT density to avoid forming metallic pathways and achieved comparable transistor performance. The Javey group (74, 75) avoided the m-SWNT problem by using a commercial semiconductor-enriched SWNT solution (99% s-SWNTs; NanoIntegris Inc.) as the starting material. High-performance CNT thin-film transistor (TFT) circuits on flexible substrates have been demonstrated using a printing process that is potentially applicable for roll-to-roll manufacturing of wall-size devices (75). The TFT circuit was then integrated with a conductive, pressure-sensitive rubber material and organic light-emitting diodes (OLEDs) into a user-interactive electronic skin that can provide instantaneous visual response to the local pressure. Even though the TFTs based on random CNT networks are limited by the large channel size (>50 μ m), the low cost and ease for large-scale manufacturing on flexible substrates make them attractive for certain applications.

4.2. Carbon Nanotube Membranes and Electrochemical Filters

Significant attention has been focused on CNT membranes for potential applications in programmable transdermal drug delivery, biomolecule separation, DNA translocation, natural protein channel mimicking, chemical separation, gas separation, and water desalination (76–83). Membranes based on CNT pores are attractive because of (*a*) their atomically flat graphitic planes, allowing fast fluid flow; (*b*) the ability to covalently functionalize the entrances to the CNT pores with charged groups; and (*c*) high electrical conductivity, allowing for the concentration of the electric field at the CNT tip (81).

Pioneering efforts to obtain a vertically oriented membrane structure have focused on wellordered nanoporous monoliths such as porous alumina and track-etched polycarbonate with minimal path tortuosity and nanometer-scale pore size (84). Common problems include the inability to place an effective monolayer of gatekeeper moiety at the pore entrance and the inherently slow process of fluid flow in nanometer-scale pores. The inner cores of CNTs have the potential to exhibit a fast interfacial slip velocity, as the weak van der Waals interaction and atomically flat surface at the pore wall would not scatter flowing fluids (85). The pressure-driven flow of gas, liquids, and ions has been investigated using various types of CNT membranes (76, 78). An aligned array **OLED:** organic light-emitting diode

Transdermal drug delivery: the noninvasive delivery of medication through the skin surface

Slip velocity: the difference in velocities between two phases in vertical flow

Electro-osmotic

flow: motion of liquid induced by an applied potential

Microtoming:

a process to cut materials into extremely thin slices

TCE: transparent conductive electrode

of CNTs impregnated in a polystyrene matrix has been reported to form a membrane structure with well-ordered nanometer-scale pores (average diameter \sim 7 nm) (76). Ionic and gas transport through the CNT membrane was consistent with the observed areal density of aligned CNT cores. Holt et al. (78) reported gas and water flow measurements through microfabricated membranes with aligned CNT pores of <2 nm in diameter. The gas and water permeabilities were orders of magnitude higher than those of commercial polycarbonate membranes, despite CNT pore sizes an order of magnitude smaller.

Electro-osmotic flow is the primary method to control fluid flux in lab-on-chip diagnostics, medical implants, drug delivery, and chemical separations (86). CNT membranes have been fabricated to examine this flow. Using ordered MWNTs, Majumder et al. (79) found that the conformational change of gatekeeper molecules can be utilized to effectively separate chemical species of different sizes. Functionalized MWNT membranes have been used for very power-efficient electrophoretic/osmotic pumping of nicotine through human skin at therapeutically useful doses, and extremely high Li⁺ and K⁺ mobilities were reported in SWNT channels (80). Hinds and colleagues (81) synthesized SWNTs with an average diameter of ~0.9 nm using CVD. Membranes were formed by microtoming a CNT-epoxy composite mixture to a thickness of 5 μ m (**Figure** *3a,b*). They concluded that the electrophoretic mobilities of various ions in such membranes were enhanced by a factor of two to three compared to the bulk values.

A randomly oriented CNT membrane as a flow-through electrode has been shown to be an effective electrochemically active microfilter for water treatment including virus removal/ inactivation and oxidative degradation of dyes and phenol (82, 83, 87-89). Vecitis et al. (83) demonstrated the efficacy of an anodic MWNT microfilter toward the removal and inactivation of viruses (MS2) and bacteria (Escherichia coli). In the absence of electrolysis, the MWNT filter was effective for the complete removal of bacteria by sieving and the multilog removal of viruses by depth filtration. Concomitant electrolysis during filtration results in significantly increased inactivation of influent bacteria and viruses. The electrochemical oxidation kinetics of the traditional bipolar systems with two separate electrodes is often limited by diffusional mass transfer because of the reduced reactive depth of a porous 3D CNT electrode, even at micrometer-scale depths (90). Gao & Vecitis (82) examined the reactive depth and performance of an electrochemical CNT network toward phenol removal and oxidation in the batch (conventional bipolar electrode configuration) and flow (either by tangential or through perpendicular) configurations, in which mass transport into the CNT network is predominantly via diffusion and convection, respectively (Figure 3c). They showed that the electrochemical CNT network operated in the flow configuration is superior to the batch configuration with regard to the extent of phenol extra-oxidation (up to tenfold), current efficiency (greater than twofold), and susceptibility to passivation. Depth profiles of phenol electropolymerization provided direct evidence that the convective flow through the CNT network effectively activates the internal electron-transfer sites that were inaccessible by diffusion in the batch system. The higher current efficiency in the flow configuration results from the predominance of the inherently more efficient direct (compared to indirect) phenol electro-oxidation mechanism. However, the electrochemical filtration efficiency toward aqueous phenol is reduced during extended electrolysis owing to electrode surface passivation (89). Thus, for long-term applications of this novel electrochemical technology, electrode passivation is one of the most important challenges to overcome.

4.3. Carbon Nanotube Films as Transparent Conductive Electrodes

Transparent conductive electrodes (TCEs) are necessary components in flat-panel displays, touch screens, light emitters, and photovoltaics, which currently rely on transparent conductive oxides



Figure 3

(*a*) Scanning electron micrograph of a carbon nanotube (CNT) (with \sim 7-nm diameter) membrane structure consisting of substantially dense (\sim 10^{9–10} tubes/cm²), open-ended, and vertically oriented CNTs in an impermeable material. Panel *a* adapted with permission from Reference 85. Copyright 2011 American Chemical Society. (*b*) Scanning electron micrograph showing a cross-sectional view of a membrane containing nanotubes (diameter less than 1 nm) uniformly dispersed in an epoxy resin matrix. Panel *b* adapted with permission from Reference 81. Copyright 2012 Macmillan Publishers Limited. (*c*) An electrochemical filtration apparatus. On the left is a schematic illustration of electrochemical filtration. On the right are photographs of the whole reaction cell (including the upper and bottom caps), anode components (titanium ring and CNT network with cross-sectional and aerial images), and cathode (perforated stainless steel). Panel *c* adapted with permission from Reference 89. Copyright 2013 Elsevier Ltd.

(TCOs), such as indium tin oxide (ITO) and aluminum-doped ZnO (91). However, the inherent brittleness of TCO-related films limits their applications in flexible devices. SWNT-film TCEs of-fer several benefits over traditional TCOs, such as mechanical flexibility/durability, high chemical resistance, and sustainability (92–94). They are particularly attractive as an ITO replacement for OLEDs and organic photovoltaic (OPV) devices in low-cost, roll-to-roll manufacturing (92, 95).

The factors influencing the performance of CNT TCEs are sheet resistance and visible light transmittance, which are governed by the DC conductivity (σ_{DC}) and optical conductivity (σ_{op}) of the CNT film (96). Increasing σ_{DC} is desired to achieve both high sheet conductance (low sheet resistance) and high optical transmission based on two mechanisms. Because σ_{DC} is related to the number of available charge carriers (*n*) and the mobility (μ) by $\sigma_{DC} = ne\mu$, one could either increase the carrier density by doping the material or increase the mobility. Although the intrinsic

TCO: transparent conductive oxide

ITO: indium tin oxide or tin-doped indium oxide

OPV: organic photovoltaic

Oxygen reduction reaction (ORR):

a critical reaction in the cathode of fuel cells and metal-air batteries to utilize O₂ fuels by reducing them into products values of isolated CNTs are very high, with σ_{DC} up to 200,000 S/cm and μ up to 100,000 cm²/ (V·s), the randomly oriented, undoped CNT film showed only $\sigma_{DC} < 6,600$ S/cm and $\mu = 1-10$ cm²/(V·s) (96), which was limited by the large resistance of CNT junctions.

The conductivity of a CNT film depends on the type of CNTs, mean tube/bundle length and diameter, network density, and film thickness. Other factors that influence the conductivity (or sheet resistance) are the film purity (amorphous or sp³-bonded carbon and other carbonaceous materials), tube doping level, CNT surface interactions, and m-CNT/s-CNT ratio (96). It was found that longer CNT bundles provide a higher network conductivity at the same density of CNT junctions (97). Smaller bundles led to higher conductivity at the same transparency because of the decrease in non-current-carrying tubes in the middle of CNT bundles. In addition, the orientation of the bundles affected the efficiency of the conductive network. Randomly oriented CNTs are preferred as they have a lower percolation threshold than do aligned CNTs (98). Indeed, Hecht et al. (99) reported that the $\sigma_{\rm DC}$ of CNT films varied with the tube length, following a power law ($\sigma_{\rm DC} \sim L^{1.46}$). The CNT film density is another critical scaling parameter, following a 2D percolation scaling law at very low densities (96), with the critical percolation threshold depending on the aspect ratio D (length/diameter) of the CNT bundle ($\sigma_{\rm DC} \sim D^{\beta}$, with β between 1 and 1.5). Because of the highly 1D nature of CNT bundles, the percolation threshold is typically less than 1% of the surface coverage (and is inversely proportional to the square of the tube length). Above the percolation threshold, the sheet conductance increases rapidly with the network density (tubes/area). There are several reports pushing the σ_{DC} of CNT films to higher values (100– 103). Hecht et al. (104) used chlorosulfonic superacid to deposit highly conductive, transparent CNT films from highly debundled CNT dispersions onto various surfaces by a filtration/transfer method. The sheet resistance was 60 Ω/sq ($\sigma_{DC} = \sim 12,825$ S/cm), and the transmittance (at 550 nm) was 90.9%. Graham and colleagues (105) evaluated the effectiveness of different doping procedures on the electrical stability of doped SWNT films in air and concluded that HNO3 and $SOCl_2$ were effective for hole doping SWNT films, enhancing the conductivity by more than twofold. However, all doped films were instable over time, and the HNO3-treated films were not thermally stable at temperatures below those of typical solar cell operations. A thin layer of PEDOT/PSS, typically used to planarize the anode surface or to facilitate hole collection and injection, can effectively stabilize the doped CNT films.

4.4. Carbon Nanotubes for Electrocatalysis in Fuel Cells

Oxygen reduction reaction (ORR) is an important process in the cathode of fuel cells and metal-air batteries (106). It proceeds either through a four-electron process to directly combine oxygen, electrons, and protons into water or through a less-efficient process involving two-step, two-electron pathways to form hydrogen peroxide ions as an intermediate (106, 107). To date, platinum nanoparticles (NPs) have been considered as the best ORR catalysts and are commonly used in fuel cells owing to their relatively low overpotential and high current density. However, they suffer from sluggish reaction kinetics, high cost, the susceptibility to fuel crossover from the anode, deactivation by CO, and poor stability under electrochemical conditions (108). Recently, intensive efforts have been made to develop new efficient electrocatalysts to reduce or replace platinum in fuel cells. In particular, CNT-supported metal NPs (109–113) and certain nitrogendoped carbon nanomaterials (e.g., CNTs, graphene) (114–119) have been demonstrated as efficient ORR catalysts free from CO poisoning and crossover effects, with better long-term operational stability.

CNTs can serve as catalyst supports owing to a high SSA, high electrical conductivity, and excellent electrochemical durability. Kamat and colleagues (110) found that SWNT-supported



Figure 4

(*a*) Scanning electron micrograph of platinum particles anchored on single-walled carbon nanotubes (SWNTs). (*b*) Schematic illustration of the reduction of O₂ at a platinum/SWNT electrocatalyst. Panels *a* and *b* adapted with permission from Reference 110. Copyright 2006 American Chemical Society.
(*c*) Schematic illustration of the reduction of O₂ at a nitrogen-doped carbon nanotube (CNT) electrocatalyst.
(*d*) Scanning electron micrograph of vertically aligned nitrogen-doped CNTs. Panels *c* and *d* adapted with permission from Reference 119. Copyright 2010 American Chemical Society. (*e*) Cyclic voltammetry curves [scan rate of 50 mV/s versus saturated calomel electrode (SCE)] showing electrocatalytic capabilities of boron-doped CNTs for the oxygen reduction reaction in an O₂-saturated 1-M NaOH electrolyte. Panel *e* adapted with permission from Reference 123. Copyright 2011 Wiley-VCH Verlag.

platinum NPs present a twofold-higher rate constant than traditional platinum/carbon catalysts. The high porosity of SWNT films may facilitate reactant diffusion and their interaction with the platinum surface (**Figure 4***a*,*b*). Accelerated durability tests confirmed that SWNTs also enhance the catalyst stability. A platinum/MWNT electrode also demonstrated CO-tolerance electrocatalysis. However, pristine CNTs do not have enough binding sites to anchor metal NPs. Functionalization by harsh acid oxidation introduces structural defects, which reduces the electrical conductivity and durability of CNTs (109). The effective attachment of metal NPs onto intact CNTs remains challenging. Yang et al. (111) adopted a noncovalent functionalization strategy to assemble platinum nanocubes onto a negatively charged surface of poly(sodium 4-styrenesulfonate)-wrapped CNTs via electrostatic interactions. Such an electrocatalyst showed relatively high catalytic activity for ORR.

Recently, it was demonstrated that nitrogen-containing CNTs or graphenes can be directly used as metal-free ORR catalysts (114–119). It is believed that either pyridinic or pyrrol/

pyridone-type nitrogen is responsible for the enhanced ORR activity (120) (Figure 4c). These nitrogen functional groups transform to more thermally stable structures during heat treatment. Furthermore, nitrogen is known to create defects on carbon, which may increase the edge plane exposure and thus enhance catalytic activity (116). Although the ORR activity of CNTs is significantly improved with nitrogen doping, it is still low compared to platinum NPs. Recently, Dai and colleagues (107) found that vertically aligned nitrogen-containing CNTs (VA-NCNTs) (Figure 4d) could be effective metal-free ORR electrocatalysts in a four-electron ORR process free from CO poisoning. In alkaline conditions, the authors demonstrated higher electrocatalytic activity, a smaller crossover effect, and better long-term stability for VA-NCNTs compared to platinum/carbon. The improved catalytic activity was attributed to the electron-accepting ability of the nitrogen atoms, which created a net positive charge on adjacent carbon atoms in the VA-NCNT to attract electrons from the anode and facilitated the ORR (107). Dai and colleagues (121) also prepared a vertically aligned MWNT array codoped with phosphorus and nitrogen with a relatively high phosphorus-doping level, which exhibited high ORR electrocatalytic activity, good long-term durability, and tolerance to methanol and CO compared to those doped only with phosphorus or nitrogen. Yu et al. (122) developed a simple plasma-etching technique to generate metal-free particle catalysts for efficient metal-free growth of undoped or nitrogen-doped SWNTs. They observed that metal-free, nitrogen-containing CNTs show relatively good electrocatalytic activity and long-term stability for ORR in an acidic medium compared to undoped CNTs.

Boron-doped CNTs have also been developed as metal-free electrocatalysts for ORR with high electrocatalytic activity, high stability, and immunity to methanol crossover and CO poisoning (123). Electrocatalytic performance was progressively improved by increasing the boron content (**Figure 4***e*). Based on theoretical calculations, the authors concluded that boron doping enhanced O_2 chemisorption. Electrons tend to accumulate in the vacant $2p_z$ orbital of a boron dopant from the π^* orbital of the conjugated system. Therefore, boron serves as a bridge to transfer electrons to the chemisorbed O_2 molecules and weakens the O–O bond, facilitating the ORR. The two key factors for ORR include breaking the electroneutrality of CNTs to create charged sites favorable for O_2 adsorption by either electron-rich (as nitrogen) or electron-deficient (as boron) dopants and then effectively utilizing carbon π -electrons for O_2 reduction.

CNTs codoped with boron and nitrogen atoms (BCN nanotubes), in either aligned or random forms, have band gaps that are tunable by adjusting their chemical compositions (124). Unlike pristine CNTs, the band gaps of BCN nanotubes are independent of the diameter and chirality (125, 126). Wang et al. (126) prepared vertically aligned BCN nanotubes by pyrolysis of melamine diborate as a single-compound source of carbon, boron, and nitrogen for BCN nanotube growth. Owing to a synergetic effect arising from codoping of CNTs with boron and nitrogen, the resultant vertically aligned BCN nanotube electrode has higher electrocatalytic activity for ORR in an alkaline medium than its counterparts doped with boron or nitrogen alone.

Even though significant progress has been achieved, current heteroatom-doped CNT catalysts still suffer from low activity and limited efficiency owing to inherent drawbacks, such as low activesite densities and low electrical conductivity. ORR activity is generally much higher in alkaline media than in acids. A hybrid system combining CNT and graphene was proposed to increase the number of catalytic sites. Dai and coworkers (127) developed such an ORR electrocatalyst based on few-walled CNT-graphene complexes. Under a unique oxidation condition, the outer walls were partially unzipped, creating nanoscale graphene sheets attached to the inner CNTs. The graphene sheets contained extremely small amounts of iron originating from nanotube growth and some nitrogen impurities, which facilitated the formation of catalytic sites and boosted catalytic activity. The inner walls remained intact with high electrical conductivity, facilitating charge transport during electrocatalysis. Such a hybrid structure showed good ORR catalytic activity in both acidic and alkaline media.

4.5. Carbon Nanotubes in Electrical Energy Storage

The performance of electrical energy storage devices, including electrochemical capacitors and batteries, depends on the fast electrochemical reactions at the electrode-electrolyte interfaces. The unique structure and attractive intrinsic electrical, chemical, and mechanical properties of CNTs can be used to facilitate effective electron transfer and ion diffusion through integration into proper multiscale architectures and incorporation of other active nanomaterials.

4.5.1. Electrochemical capacitors. Electrochemical capacitors, also known as supercapacitors, consist of electrical double-layer capacitors (EDLCs) and pseudocapacitors, which store electrical energy in the form of charges generated by electrochemical processes at a pair of electrodes. CNTs are ideal electrode materials for EDLCs because of relatively high SSAs, a unique pore structure, superior electrical properties, high mechanical and thermal stability, and the ability to form connected networks. Randomly stacked films of bulk-produced SWNTs and MWNTs have been explored as EDLC materials, particularly for high-power applications (128–133). However, the specific capacitance (SC) varies from \sim 4 to 160 F/g, and hence the energy density strongly depends on the sample preparation and electrical contact between CNTs. The SSA of a typical CNT film is $<500 \text{ m}^2/\text{g}$, lower than that of commercial activated carbons (1,000–3,000 m²/g). This is mainly limited by the poorly developed microporous volume in CNT films. For MWNT films, it can be increased by chemical activation (134), but SC values still cannot reach that of activated carbons. Surface functionalization through oxidation treatments leads to significant improvements in protic media (128). However, the cycle life tends to decrease. Currently, efforts are focused on the development of dense vertically aligned CNT forests to increase electrolyte accessibility and enable direct electrical contact to all CNTs from a common current collector (135-138). Such CNT-based nanoarchitectures appear to be quite promising, particularly for microelectronic applications (139, 140).

Moreover, given their high electrical conductivity, high mechanical strength, and fiber-like structure, CNTs are good structural supports for other pseudocapacitive materials (128). CNTs have been used as conductive fillers or structural frames to improve electrical access to metal oxides that are not very conductive (e.g., RuO₂, MnO₂, and V₂O₅) and as facilitators for fast surface redox reactions to make pseudocapacitors (141–147). This approach effectively combines the high electrochemical activity of metal oxides for a high SC and high energy density with the robust conductive CNT structure for better charge transport. For example, a V₂O₅·xH₂O/CNT film electrode showed a high SC of 910 F/g at a potential scan rate of 10 mV/s, approximately three times higher than that of a V₂O₅·xH₂O thin-film electrode (300 F/g) (148). Compared to randomly stacked CNT films, vertically aligned CNTs (149) and CNFs (18) are more attractive in reducing contact resistance, facilitating fast kinetics involving electron and ion transport, and providing open space for metal oxide deposition.

Electrical conductive polymers (ECPs), such as polyaniline and polypyrrole, represent another type of pseudocapacitor material. They are known to suffer from poor cycling stability and fast capacitance decay at high cycling rates owing to large volume changes and the drop in electrical conductivity accompanying the reaction. ECP-CNT composites combine the large pseudocapacitance of ECPs with the stable, highly conductive, open CNT framework so that the ECP can sustain the strains in the charging-discharging cycling process. For example, Liu et al. (150) synthesized polyaniline/SWNT films through an in situ electrochemical polymerization/degradation process and achieved a high SC of 706.7 F/g. Fang et al. (151) showed an SC of ~427 F/g by

homogeneously coating polypyrrole on a self-supported MWNT membrane using pulsed electrochemical deposition.

Lithium-ion battery (**LIB**): a rechargeable battery relying on Li⁺ reversibly moving back and forth between two host electrodes during charge and discharge

4.5.2. Lithium-ion battery materials. Graphite is the most common anode material in commercial lithium-ion batteries (LIBs), with a theoretical capacity of 372 mAh/g based on lithium intercalation between weakly bonded graphitic layers. Short, chemically cut SWNTs (with open ends and an average length of 0.5μ m) showed reversible lithium storage approximately twice this value, attributed to lithium filling of the interior space of SWNTs (152). Generally, MWNTs and SWNTs showed similar properties, with a reversible lithium insertion capacity between 220 and 780 mAh/g and a large hysteresis between insertion and extraction curves (128). Vertically aligned MWNTs have shown a high reversible specific capacity (up to 782 mAh/g at 57 mA/g), about ten times their nonaligned equivalent, which was retained at a moderate level (166 mAh/g) at a high discharge rate of 26 A/g (62). This was attributed to improved ion transport and electron collection using the vertical architecture in LIBs.

Similar to their use in pseudocapacitors, CNTs can be employed as the structural support and current collector in LIB electrodes. A good example is provided by silicon/CNT core-shell materials as LIB anodes. Silicon has an extremely high lithium storage capacity (up to \sim 3,800 mAh/g at room temperature, \sim 10 times that of graphite's capacity), has an attractively low lithiation potential (0.2–0.4 V versus Li/Li⁺, comparable to graphite), and is naturally abundant (153–155). However, when lithium is inserted into silicon, it forms alloys with up to 320% volumetric expansion and severe stress, leading to fracturing and loss of the electrical connection; consequently, the capacity fades after only tens of cycles. Nanostructured silicon materials have been employed to reduce the internal stress (due to the large surface to volume ratio) and to improve reaction kinetics (due to the short Li⁺ diffusion path) (153–155). But performance at high charge-discharge rates and its long-term stability are still not sufficient.

Hybrid materials utilizing a highly conductive and stable CNT core to support a silicon shell have recently been explored to improve the power rate while maintaining high capacity and good cycle stability (16, 61, 156–158). Vertically aligned MWNTs (61, 157) and CNFs (16, 158) are particularly advantageous because the rigid structure (due to a large diameter of 20–200 nm) can sustain the high mechanical stress during charge-discharge processes, whereas the open inter-CNT space allows silicon to be deposited along the full length of CNTs and affords faster Li⁺ diffusion in electrolytes (**Figure 5**). As a result, investigators obtained a very high specific capacity of 3,000-3,500 mAh/g at up to a 2C (or C/0.5) rate (maintaining nearly the full capacity of amorphous silicon) and much smaller insertion/extract hysteresis (**Figure 5***d*) (16). After 100 cycles, the capacity decreased only by <8%, with a Coulombic efficiency >99%,

Figure 5

⁽*a*) Schematic illustration of accommodating the volume changes of silicon during lithium insertion/ extraction by the core-shell structure on vertically aligned carbon nanofibers (VACNFs) or multiwalled carbon nanotubes (MWNTs). (*b*) Scanning electron micrograph at a 45° perspective view.
(*c*) Transmission electron micrograph of the tapered silicon shell with a nanocolumnar structure on a VACNF array. (*d*) The charge-discharge curve at different C rates. (*e*) The insertion (*gray*) and extraction (*red*) capacity and Coulombic efficiency (*blue*) over 100 cycles of this silicon-coated VACNF lithium-ion battery anode. Panels *a*–*e* adapted with permission from Reference 16. Copyright 2013 the Royal Society of Chemistry. (*f*) Scanning electron micrograph of vertically aligned MWNTs grown on an Inconel disk. (*Inset*) High-resolution transmission electron micrograph of a single MWNT. (*g*) High-resolution transmission electron micrograph of the structure of CVD-deposited silicon on the vertically aligned MWNT. Panels *f* and *g* adapted with permission from Reference 61. Copyright 2011 Elsevier Ltd.



Dye-sensitized solar cell (DSSC):

a low-cost photovoltaic device based on sensitizing light-absorbing dye molecules on the surface of a mesoporous semiconducting material to generate photo-excited charge separation

Bulk heterojunction

(**BHJ**): the large interface formed between two interpenetrating 3D porous, but continuous, phases except at the initial conditioning cycles (16). Interestingly, CVD-deposited silicon on vertically aligned MWNTs (61, 157) formed a chain of solid spheres (**Figure 5***f*,*g*), whereas ion sputtering–coated silicon on vertically aligned CNFs presented tapered silicon shells (**Figure 5***a*,*b*) (16, 158). Further inspection by transmission electron microscopy revealed that the silicon shell comprised nanocolumns anchored on the CNF surface (**Figure 5***c*), likely correlated with the graphitic edges at the CNF sidewall (**Figure 1***d*). The unique CNF structure was found to form a much better electrochemical interface with the silicon shell than MWNTs. Remarkable capacity was retained as the charge-discharge rate was raised to 8C (16, 159). It is noteworthy that such a core-shell structure may be applicable to other anode materials (e.g., SnO₂, Fe₂O₃, and TiO₂) and cathode materials (e.g., MnO₂, LiCoO₂, and LiFePO₄), as CNTs are potentially stable in a wide range, from 0 to 5 V (versus Li/Li⁺). The robust, chemically stable, and highly conductive vertical MWNTs and CNFs provide a route to realize the desired open 3D architecture for broad electrochemical energy storage applications (160, 161).

4.6. Carbon Nanotubes in Solar Cells

Along with TCEs, CNTs were also extensively explored as active photovoltaic components in OPVs and dye-sensitized solar cells (DSSCs). A key effort in increasing the efficiency of OPVs is to improve the charge separation of photogenerated excitons (bound electron-hole pairs) at the interface between an electron donor and an electron acceptor, preferably in a bulk heterojunction (BHJ) network. It was expected that CNTs (mostly SWNTs) would serve as electron acceptors, with their high mobility allowing better electron transport. The high aspect ratio may help to form a BHJ structure with a lower percolation threshold. This was confirmed by work on OPVs with $\sim 1\%$ of SWNTs blended into conjugate polymers such as poly(3-octylthiophene) (162) and poly(3-hexylthiophene) (P3HT) (163) and work reviewed by Cataldo et al. (164). Particularly, incorporating an SWNT network into organic BHJ solar cells has produced an $\sim 10\%$ higher short-circuit current (J_{SC}) and similar open-circuit voltage (V_{OC}) and fill factor, leading to an $\sim 10\%$ increase in power efficiency (163). More importantly, the optimum active layer thickness was increased from 90 nm to 110 nm, which is attributed to the enhanced charge carrier collection by SWNTs. Another study demonstrated that the strong interaction between SWNTs and conjugate polymer enhanced the crystallinity of P3HT at the SWNT sidewall and induced a higher $V_{\rm OC}$ (165). The m-SWNTs, however, may cause charge recombination and are detrimental to device performance. The use of purified s-SWNTs may be a viable solution. A recent study demonstrated that high-purity s-SWNTs can be obtained using polythiophene wrapping followed by centrifugation (166). This method can be directly used for OPV fabrication. Other studies explored a bilayer heterojunction design (167). By making direct electrical contact with individual SWNTs horizontally deposited on a quartz surface and then burying them in a thin P3HT film to form SWNT/P3HT junctions, Dissanayake et al. (167) surprisingly discovered that both s-SWNTs and m-SWTNs functioned as efficient hole acceptors instead of electron acceptors.

Both SWNTs and MWNTs were employed in DSSCs as conducting scaffolds (168) underneath the TiO₂ NP film or conductive pathway inside the TiO₂ NP film (169–173). The work function of CNTs is comparable to that of an ITO anode and matches well with the band structure of TiO₂. Hence, it is expected that CNTs should enhance the electron collection efficiency. However, the results are quite controversial, with mixed reports of enhanced photocurrent (169–171) and detrimental effects (172, 173). One varying factor is how the CNTs were encapsulated to avoid direct contact with dye molecules and electrolytes. Dang et al. (172) demonstrated that m-SWNTs generated short-circuit paths, negating the possible benefits provided by s-SWNTs. It is critical to separate m- and s-SWNTs and encapsulate them properly. The authors used a type of genetically engineered M13 virus (with a long rod shape and a small diameter of <10 nm) to bind along the SWNTs and dispersed them in solution. The viruses also aided the complete encapsulation of SWNTs with TiO₂ in later steps. The DSSCs made with $\sim0.1\%$ of such SWNTs showed increased power conversion efficiency from $\sim8.3\%$ to 10.6%.

Ideally, making direct electrical contact with each CNT would provide the best current collection efficiency. This can be achieved with vertically aligned architecture. Liu et al. (19, 20) demonstrated a core-shell structure with a 50–100-nm-thick TiO₂ shell coated on vertically aligned CNFs by CVD. The photoluminescence of TiO₂ in the CNF-TiO₂ core-shell structure was found to be completed quenched (20). The DSSC made with N719 dye on this vertical core-shell architecture has shown a $V_{\rm OC}$ of 0.64 V, comparable with that of traditional DSSCs. Other characteristics were encouraging ($J_{\rm SC} = 2.91$ mA/cm², a fill factor of 58.2%, and a power conversion efficiency of 1.09%), considering that the estimated TiO₂ surface area (and dye loading) in this architecture was at least 15 times smaller than that of traditional DSSCs (19). One possible solution to increase dye loading is to fill TiO₂ NPs in the gap between core-shell fibers to form a connected porous TiO₂ network with embedded CNFs as conductive pathways. However, the advantage of the open space for higher I⁻/I₃⁻ mediator diffusion may be lost. Photon absorption by carbon may also need to be mitigated.

4.7. Carbon Nanotubes for Biological and Biomedical Applications

The application of CNTs in biological and biomedical research, and eventually clinical use, is a very broad and extremely active area. Ongoing activities include the use of CNTs in biosensors (as charge-sensitive semiconducting channels in FET sensors or nanostructured electrodes), drug delivery (as nanostructured drug carriers with high cell-penetrating abilities), diagnosis (as contrast agents in near-infrared and Raman spectroscopy imaging), therapeutics (as electromagnetic wave absorbers in cancer hyperthermia), regenerative medicine (as nanostructured scaffolds for cell and tissue cultures), and implantable medical devices (as fillers in biocompatible composites). All these research activities are much beyond the scope of this article. More information can be found in focused review articles (174, 175) and books (176, 177).

5. PERSPECTIVE, OUTLOOK, AND FUTURE DIRECTIONS

As shown in the above discussions, the unique properties of CNTs can enhance the performance of current applications or provide new opportunities. The success strongly depends on how the proper CNTs are selected and organized into the desired configuration. A deeper understanding of the structure-property relation is key to utilizing the intrinsic properties of CNT materials.

SUMMARY POINTS

- 1. CNTs consist of a family of high-aspect-ratio, tube-like materials dominated by conjugate sp²-bonded carbon atoms. Their physical properties strongly depend on the internal microstructures.
- Different applications require organizing CNTs into proper configurations and architectures to utilize the desired properties.
- CNTs assembled with other materials into hybrids have enhanced performance in many applications.

4. Commercial technologies involving CNTs have emerged at an accelerating rate in the past decade.

FUTURE ISSUES

- The driving forces for the development of applications utilizing the intrinsic properties of CNTs continue to be new methods for synthesizing CNTs with controlled diameter, chirality, electronic properties, and internal microstructure; sorting CNTs according to size and physical properties; organizing CNTs into desired configurations/architectures; and placing CNTs in precisely defined locations with controlled alignments.
- 2. Cost reduction and production scale-up of CNT materials and devices remain critical for CNT commercialization. Scalable manufacturing techniques, such as roll-to-roll printing, are promising for future CNT electronics and energy applications.
- 3. Integrating CNTs with other technologies such as OLEDs, OPVs, biosensors, and biomedical devices and assembling CNTs with other active materials into functional hybrids are promising routes to generate new applications.
- 4. The development of theoretical/computer modeling techniques to understand the material properties of CNTs with complex internal structures and external configurations/ architectures may provide insights into practical problems.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

The authors acknowledge the support from NSF CMMI-1100830, NASA NX13AD42A, NSF EPSCoR EPS-0903806, and matching funds provided by the State of Kansas and Kansas State University.

LITERATURE CITED

- 1. Chung DDL. 1994. Carbon Fiber Composites. Newton, MA: Butterworth-Heinemann
- 2. Ebbesen TW. 1997. Carbon Nanotubes: Preparation and Properties. Boca Raton, FL: CRC
- 3. Iijima S. 1991. Helical microtubules of graphitic carbon. Nature 354:56-58
- 4. De Volder MFL, Tawfick SH, Baughman RH, Hart AJ. 2013. Carbon nanotubes: present and future commercial applications. *Science* 339:535–39
- McCreery RL. 1991. Carbon electrodes: structural effects on electron transfer kinetics. In *Electroanalytical Chemistry*, ed. AJ Bard, pp. 221–374. New York: Marcel Dekker
- McCreery RL. 2008. Advanced carbon electrode materials for molecular electrochemistry. *Chem. Rev.* 108:2646–87
- 7. Endo M, Kim YA, Hayashi T, Fukai Y, Oshida K, et al. 2002. Structural characterization of cup-stackedtype nanofibers with an entirely hollow core. *Appl. Phys. Lett.* 80:1267–69

3. Provides the first report of the helical graphitic microtubule structure of CNTs.

4. Presents a comprehensive review on present and future commercial applications of CNTs.

- 8. Ren ZF, Huang ZP, Wang DZ, Wen JG, Xu JW, et al. 1999. Growth of freestanding multiwall carbon nanotube on each nanonickel dot. *Appl. Phys. Lett.* 75:1086–88
- 9. Ren ZF, Huang ZP, Xu JW, Wang JH, Bush P, et al. 1998. Synthesis of large arrays of wellaligned carbon nanotubes on glass. *Science* 282:1105–7
- Melechko AV, Merkulov VI, McKnight TE, Guillorn MA, Klein KL, et al. 2005. Vertically aligned carbon nanofibers and related structures: controlled synthesis and directed assembly. *J. Appl. Phys.* 97:041301
- Syed LU, Liu J, Prior AM, Hua DH, Li J. 2011. Enhanced electron transfer rates by AC voltammetry for ferrocenes attached to the end of embedded carbon nanofiber nanoelectrode arrays. *Electroanalysis* 23:1709–17
- Swisher LZ, Prior AM, Shishido S, Nguyen TA, Hua DH, Li J. 2014. Quantitative electrochemical detection of cathepsin B activity in complex tissue lysates using enhanced AC voltammetry at carbon nanofiber nanoelectrode arrays. *Biosens. Bioelectron.* 56:129–36
- Swisher LZ, Syed LU, Prior AM, Madiyar FR, Carlson KR, et al. 2013. Electrochemical protease biosensor based on enhanced AC voltammetry using carbon nanofiber nanoelectrode arrays. *J. Phys. Chem. C* 117:4268–77
- Ngo Q, Yamada T, Suzuki M, Ominami Y, Cassell AM, et al. 2007. Structural and electrical characterization of carbon nanofibers for interconnect via applications. *IEEE Trans. Nanotechnol.* 6:688–95
- 15. Landis EC, Hamers RJ. 2008. Covalent grafting of ferrocene to vertically aligned carbon nanofibers: electron-transfer processes at nanostructured electrodes. *J. Phys. Chem. C* 112:16910–18
- Klankowski SA, Rojeski RA, Cruden BA, Liu J, Wu J, Li J. 2013. A high-performance lithium-ion battery anode based on the core-shell heterostructure of silicon-coated vertically aligned carbon nanofibers. *J. Mater. Chem. A* 1:1055–64
- 17. Cinke M, Li J, Chen B, Cassell A, Delzeit L, et al. 2002. Pore structure of raw and purified HiPco single-walled carbon nanotubes. *Chem. Phys. Lett.* 365:69–74
- Liu J, Essner J, Li J. 2010. Hybrid supercapacitor based on coaxially coated manganese oxide on vertically aligned carbon nanofiber arrays. *Chem. Mater.* 22:5022–30
- Liu J, Kuo Y-T, Klabunde KJ, Rochford C, Wu J, Li J. 2009. Novel dye-sensitized solar cell architecture using TiO₂-coated vertically aligned carbon nanofiber arrays. ACS Appl. Mater. Interfaces 1:1645–49
- Liu J, Li J, Sedhain A, Lin J, Jiang H. 2008. Structure and photoluminescence study of TiO₂ nanoneedle texture along vertically aligned carbon nanofiber arrays. *J. Phys. Chem. C* 112:17127–32
- Odom TW, Huang JL, Kim P, Lieber CM. 2000. Structure and electronic properties of carbon nanotubes. *7. Phys. Chem. B* 104:2794–809
- 22. Anantram M, Leonard F. 2006. Physics of carbon nanotube electronic devices. Rep. Prog. Phys. 69:507-61
- Han J. 2005. Structures and properties of carbon nanotubes. In *Carbon Nanotubes: Science and Applications*, ed. M Meyyappan, pp. 1–24. Boca Raton, FL: CRC
- 24. Collins PC, Arnold MS, Avouris P. 2001. Engineering carbon nanotubes and nanotube circuits using electrical breakdown. *Science* 292:706–9
- Salvetat-Delmotte J-P, Rubio A. 2002. Mechanical properties of carbon nanotubes: a fiber digest for beginners. *Carbon* 40:1729–34
- Ruoff RS, Qian D, Liu WK. 2003. Mechanical properties of carbon nanotubes: theoretical predictions and experimental measurements. C. R. Phys. 4:993–1008
- 27. Srivastava D. 2005. Computational nanotechnology of carbon nanotubes. In *Carbon Nanotubes: Science and Applications*, ed. M Meyyappan, pp. 25–63. Boca Raton, FL: CRC
- Srivastava D, Menon M, Cho KJ. 1999. Nanoplasticity of single-wall carbon nanotubes under uniaxial compression. *Phys. Rev. Lett.* 83:2973–76
- Wei C, Srivastava D. 2004. Nanomechanics of carbon nanofibers: structural and elastic properties. *Appl. Phys. Lett.* 85:2208–10
- Cruden BA, Cassell AM. 2006. Vertically oriented carbon nanofiber based nanoelectromechanical switch. IEEE Trans. Nanotechnol. 5:350–55
- Qi HJ, Teo KBK, Lau KKS, Boyce MC, Milne WI, et al. 2003. Determination of mechanical properties of carbon nanotubes and vertically aligned carbon nanotube forests using nanoindentation. *J. Mecb. Phys. Solids* 51:2213–37

9. Provides the first report on synthesizing large arrays of vertically aligned CNFs using PECVD.

10. Presents a comprehensive review on the structure, growth, and properties of vertically aligned CNFs.

16. Depicts highperformance silicon LIB anodes enabled by a core-shell structure on vertically aligned CNFs.

- Pop E, Mann D, Wang Q, Goodson K, Dai H. 2005. Thermal conductance of an individual single-wall carbon nanotube above room temperature. *Nano Lett.* 6:96–100
- Kim P, Shi L, Majumdar A, McEuen PL. 2001. Thermal transport measurements of individual multiwalled nanotubes. *Phys. Rev. Lett.* 87:215502
- Hone J, Whitney M, Zettl A. 1999. Thermal conductivity of single-walled carbon nanotubes. Synth. Met. 103:2498–99
- Hone J, Llaguno MC, Nemes NM, Johnson AT, Fischer JE, et al. 2000. Electrical and thermal transport properties of magnetically aligned single wall carbon nanotube films. *Appl. Phys. Lett.* 77:666–68
- Yu CH, Saha S, Zhou JH, Shi L, Cassell AM, et al. 2006. Thermal contact resistance and thermal conductivity of a carbon nanofiber. *J. Heat Transf.* 128:234–39
- 37. Harutyunyan AR, Chen G, Paronyan TM, Pigos EM, Kuznetsov OA, et al. 2009. Preferential growth of single-walled carbon nanotubes with metallic conductivity. *Science* 326:116–20
- Ding L, Tselev A, Wang J, Yuan D, Chu H, et al. 2009. Selective growth of well-aligned semiconducting single-walled carbon nanotubes. *Nano Lett.* 9:800–5
- Qu L, Du F, Dai L. 2008. Preferential syntheses of semiconducting vertically aligned single-walled carbon nanotubes for direct use in FETs. *Nano Lett.* 8:2682–87
- Arnold MS, Stupp SI, Hersam MC. 2005. Enrichment of single-walled carbon nanotubes by diameter in density gradients. *Nano Lett.* 5:713–18
- Arnold MS, Green AA, Hulvat JF, Stupp SI, Hersam MC. 2006. Sorting carbon nanotubes by electronic structure using density differentiation. *Nat. Nanotechnol.* 1:60–65
- Homenick CM, Rousina-Webb A, Cheng F, Jakubinek MB, Malenfant PRL, Simard B. 2014. Highyield, single-step separation of metallic and semiconducting SWCNTs using block copolymers at low temperatures. *7. Phys. Chem. C* 118:16156–64
- Zheng M, Jagota A, Semke ED, Diner BA, McLean RS, et al. 2003. DNA-assisted dispersion and separation of carbon nanotubes. *Nat. Mater.* 2:338–42
- Tanaka T, Urabe Y, Nishide D, Kataura H. 2011. Discovery of surfactants for metal/semiconductor separation of single-wall carbon nanotubes via high-throughput screening. *J. Am. Chem. Soc.* 133:17610– 13
- Li X, Tu X, Zaric S, Welsher K, Seo WS, et al. 2007. Selective synthesis combined with chemical separation of single-walled carbon nanotubes for chirality selection. *J. Am. Chem. Soc.* 129:15770–71
- Krupke R, Hennrich F, Löhneysen HV, Kappes MM. 2003. Separation of metallic from semiconducting single-walled carbon nanotubes. *Science* 301:344–47
- LeMieux MC, Roberts M, Barman S, Jin YW, Kim JM, Bao Z. 2008. Self-sorted, aligned nanotube networks for thin-film transistors. *Science* 321:101–4
- Zhang G, Qi P, Wang X, Lu Y, Li X, et al. 2006. Selective etching of metallic carbon nanotubes by gas-phase reaction. *Science* 314:974–77
- Chen Y, Zhang J. 2014. Chemical vapor deposition growth of single-walled carbon nanotubes with controlled structures for nanodevice applications. Acc. Chem. Res. 47:2273–81
- Cao Q, Rogers JA. 2009. Ultrathin films of single-walled carbon nanotubes for electronics and sensors: a review of fundamental and applied aspects. *Adv. Mater.* 21:29–53
- Krupke R, Linden S, Rapp M, Hennrich F. 2006. Thin films of metallic carbon nanotubes prepared by dielectrophoresis. *Adv. Mater.* 18:1468–70
- Li XL, Zhang L, Wang XR, Shimoyama I, Sun XM, et al. 2007. Langmuir-Blodgett assembly of densely aligned single-walled carbon nanotubes from bulk materials. J. Am. Chem. Soc. 129:4890–91
- Kocabas C, Kang SJ, Ozel T, Shim M, Rogers JA. 2007. Improved synthesis of aligned arrays of single-walled carbon nanotubes and their implementation in thin film type transistors. *J. Phys. Chem. C* 111:17879–86
- Zhou W, Ding L, Yang S, Liu J. 2011. Synthesis of high-density, large-diameter, and aligned singlewalled carbon nanotubes by multiple-cycle growth methods. ACS Nano 5:3849–57
- 55. Li J, Liu K, Liang S, Zhou W, Pierce M, et al. 2013. Growth of high-density-aligned and semiconductingenriched single-walled carbon nanotubes: decoupling the conflict between density and selectivity. ACS Nano 8:554–62

- Kang SJ, Kocabas C, Kim H-S, Cao Q, Meitl MA, et al. 2007. Printed multilayer superstructures of aligned single-walled carbon nanotubes for electronic applications. *Nano Lett.* 7:3343–48
- 57. Liu X, Han S, Zhou C. 2005. Novel nanotube-on-insulator (NOI) approach toward single-walled carbon nanotube devices. *Nano Lett.* 6:34–39
- Shulaker MM, Hills G, Patil N, Wei H, Chen H-Y, et al. 2013. Carbon nanotube computer. Nature 501:526–30
- Shulaker MM, Van Rethy J, Wu TF, Liyanage LS, Wei H, et al. 2014. Carbon nanotube circuit integration up to sub-20 nm channel lengths. ACS Nano 8:3434–43
- 60. Hata K, Futaba DN, Mizuno K, Namai T, Yumura M, Iijima S. 2004. Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes. *Science* 306:1362–64
- Wang W, Epur R, Kumta PN. 2011. Vertically aligned silicon/carbon nanotube (VASCNT) arrays: hierarchical anodes for lithium-ion battery. *Electrochem. Commun.* 13:429–32
- 62. Welna DT, Qu LT, Taylor BE, Dai LM, Durstock MF. 2011. Vertically aligned carbon nanotube electrodes for lithium-ion batteries. *J. Power Sources* 196:1455–60
- Meyyappan M, Delzeit L, Cassell A, Hash D. 2003. Carbon nanotube growth by PECVD: a review. *Plasma Sources Sci. Technol.* 5:205–16
- AuBuchon JF, Chen L-H, Jin S. 2005. Control of carbon capping for regrowth of aligned carbon nanotubes. *J. Phys. Chem. B* 109:6044–48
- 65. Collins PG, Avouris P. 2000. Nanotubes for electronics. Sci. Am. 283:62-69
- Tans SJ, Verschueren ARM, Dekker C. 1998. Room-temperature transistor based on a single carbon nanotube. Nature 393:49–52
- Javey A, Guo J, Wang Q, Lundstrom M, Dai H. 2003. Ballistic carbon nanotube field-effect transistors. *Nature* 424:654–57
- 68. Franklin AD, Chen Z. 2010. Length scaling of carbon nanotube transistors. Nat. Nanotechnol. 5:858-62
- 69. Zhou XJ, Park JY, Huang SM, Liu J, McEuen PL. 2005. Band structure, phonon scattering, and the performance limit of single-walled carbon nanotube transistors. *Phys. Rev. Lett.* 95:146805
- Franklin AD, Luisier M, Han S-J, Tulevski G, Breslin CM, et al. 2012. Sub-10 nm carbon nanotube transistor. Nano Lett. 12:758–62
- Franklin AD, Tulevski GS, Han S-J, Shahrjerdi D, Cao Q, et al. 2012. Variability in carbon nanotube transistors: improving device-to-device consistency. ACS Nano 6:1109–15
- Cao Q, Kim H-S, Pimparkar N, Kulkarni JP, Wang C, et al. 2008. Medium-scale carbon nanotube thin-film integrated circuits on flexible plastic substrates. *Nature* 454:495–500
- Sun D-M, Timmermans MY, Tian Y, Nasibulin AG, Kauppinen EI, et al. 2011. Flexible highperformance carbon nanotube integrated circuits. *Nat. Nanotechnol.* 6:156–61
- Wang C, Hwang D, Yu Z, Takei K, Park J, et al. 2013. User-interactive electronic skin for instantaneous pressure visualization. *Nat. Mater.* 12:899–904
- Lau PH, Takei K, Wang C, Ju Y, Kim J, et al. 2013. Fully printed, high performance carbon nanotube thin-film transistors on flexible substrates. *Nano Lett.* 13:3864–69
- Hinds BJ, Chopra N, Rantell T, Andrews R, Gavalas V, Bachas LG. 2004. Aligned multiwalled carbon nanotube membranes. *Science* 303:62–65
- Nednoor P, Chopra N, Gavalas V, Bachas LG, Hinds BJ. 2005. Reversible biochemical switching of ionic transport through aligned carbon nanotube membranes. *Chem. Mater.* 17:3595–99
- Holt JK, Park HG, Wang Y, Stadermann M, Artyukhin AB, et al. 2006. Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* 312:1034–37
- 79. Majumder M, Zhan X, Andrews R, Hinds BJ. 2007. Voltage gated carbon nanotube membranes. *Langmuir* 23:8624–31
- Lee CY, Choi W, Han J-H, Strano MS. 2010. Coherence resonance in a single-walled carbon nanotube ion channel. *Science* 329:1320–24
- Wu J, Gerstandt K, Zhang H, Liu J, Hinds BJ. 2012. Electrophoretically induced aqueous flow through single-walled carbon nanotube membranes. *Nat. Nanotechnol.* 7:133–39
- 82. Gao G, Vecitis CD. 2012. Reactive depth and performance of an electrochemical carbon nanotube network as a function of mass transport. *ACS Appl. Mater. Interfaces* 4:6096–103

58. Reports on the first computer for which the central processor is based entirely on CNTs.

81. Demonstrates that

within such membranes

are three times higher

than the bulk mobility.

the mobilities of ions

- Vecitis CD, Schnoor MH, Rahaman MS, Schiffman JD, Elimelech M. 2011. Electrochemical multiwalled carbon nanotube filter for viral and bacterial removal and inactivation. *Environ. Sci. Technol.* 45:3672–79
- Jirage KB, Hulteen JC, Martin CR. 1997. Nanotubule-based molecular-filtration membranes. Science 278:655–58
- Majumder M, Chopra N, Hinds BJ. 2011. Mass transport through carbon nanotube membranes in three different regimes: ionic diffusion and gas and liquid flow. ACS Nano 5:3867–77
- Wu J, Gerstandt K, Majumder M, Zhan X, Hinds BJ. 2011. Highly efficient electroosmotic flow through functionalized carbon nanotube membranes. *Nanoscale* 3:3321–28
- Schnoor MH, Vecitis CD. 2013. Quantitative examination of aqueous ferrocyanide oxidation in a carbon nanotube electrochemical filter: effects of flow rate, ionic strength, and cathode material. *J. Phys. Chem.* C 117:2855–67
- Zhang Q, Vecitis CD. 2014. Conductive CNT-PVDF membrane for capacitive organic fouling reduction. *J. Membr. Sci.* 459:143–56
- Gao G, Vecitis CD. 2013. Electrocatalysis aqueous phenol with carbon nanotubes networks as anodes: electrodes passivation and regeneration and prevention. *Electrochim. Acta* 98:131–38
- Milczarek G, Inganäs O. 2012. Renewable cathode materials from biopolymer/conjugated polymer interpenetrating networks. *Science* 335:1468–71
- 91. Gordon RG. 2000. Criteria for choosing transparent conductors. MRS Bull. 25:52-57
- Li J, Hu L, Wang L, Zhou Y, Grüner G, Marks TJ. 2006. Organic light-emitting diodes having carbon nanotube anodes. *Nano Lett.* 6:2472–77
- 93. Hecht DS, Thomas D, Hu L, Ladous C, Lam T, et al. 2009. Carbon-nanotube film on plastic as transparent electrode for resistive touch screens. *J. Soc. Inform. Display* 17:941–46
- Xu H, Chen L, Hu L, Zhitenev N. 2010. Contact resistance of flexible, transparent carbon nanotube films with metals. *Appl. Phys. Lett.* 97:143116
- Hu L, Li J, Liu J, Grüner G, Marks T. 2010. Flexible organic light-emitting diodes with transparent carbon nanotube electrodes: problems and solutions. *Nanotechnology* 21:155202
- Hecht DS, Hu L, Irvin G. 2011. Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures. *Adv. Mater.* 23:1482–513
- Kaskela A, Nasibulin AG, Timmermans MY, Aitchison B, Papadimitratos A, et al. 2010. Aerosolsynthesized SWCNT networks with tunable conductivity and transparency by a dry transfer technique. *Nano Lett.* 10:4349–55
- Du J, Pei S, Ma L, Cheng HM. 2014. 25th anniversary article: carbon nanotube- and graphene-based transparent conductive films for optoelectronic devices. *Adv. Mater.* 26:1958–91
- Hecht D, Hu L, Grüner G. 2006. Conductivity scaling with bundle length and diameter in single walled carbon nanotube networks. *Appl. Phys. Lett.* 89:133112–13
- 100. Zhou Y, Hu L, Grüner G. 2006. A method of printing carbon nanotube thin films. Appl. Phys. Lett. 88:123109
- 101. Hu L, Yuan W, Brochu P, Grüner G, Pei Q. 2009. Highly stretchable, conductive, and transparent nanotube thin films. *Appl. Phys. Lett.* 94:161108
- Nirmalraj PN, Lyons PE, De S, Coleman JN, Boland JJ. 2009. Electrical connectivity in single-walled carbon nanotube networks. *Nano Lett.* 9:3890–95
- Shim BS, Zhu J, Jan E, Critchley K, Kotov NA. 2010. Transparent conductors from layer-by-layer assembled SWNT films: importance of mechanical properties and a new figure of merit. ACS Nano 4:3725–34
- 104. Hecht DS, Heintz AM, Lee R, Hu L, Moore B, et al. 2011. High conductivity transparent carbon nanotube films deposited from superacid. *Nanotechnology* 22:075201
- 105. Jackson R, Domercq B, Jain R, Kippelen B, Graham S. 2008. Stability of doped transparent carbon nanotube electrodes. *Adv. Funct. Mater.* 18:2548–54
- 106. Basu S. 2007. Fuel Cell Science and Technology. New York: Springer
- 107. Gong K, Du F, Xia Z, Durstock M, Dai L. 2009. Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. *Science* 323:760–64
 - 108. Winter M, Brodd RJ. 2004. What are batteries, fuel cells, and supercapacitors? Chem. Rev. 104:4245-70

96. Provides a comprehensive review on transparent electrodes on CNTs and graphene films.

107. Demonstrates the role of nitrogen doping on vertically aligned CNTs for metal-free, efficient ORR catalysts.

- Zhang S, Shao Y, Yin G, Lin Y. 2010. Carbon nanotubes decorated with Pt nanoparticles via electrostatic self-assembly: a highly active oxygen reduction electrocatalyst. J. Mater. Chem. 20:2826–30
- Kongkanand A, Kuwabata S, Girishkumar G, Kamat P. 2006. Single-wall carbon nanotubes supported platinum nanoparticles with improved electrocatalytic activity for oxygen reduction reaction. *Langmuir* 22:2392–96
- 111. Yang W, Wang X, Yang F, Yang C, Yang X. 2008. Carbon nanotubes decorated with Pt nanocubes by a noncovalent functionalization method and their role in oxygen reduction. *Adv. Mater.* 20:2579–87
- 112. Higgins DC, Meza D, Chen Z. 2010. Nitrogen-doped carbon nanotubes as platinum catalyst supports for oxygen reduction reaction in proton exchange membrane fuel cells. *J. Phys. Chem. C* 114:21982–88
- Shaijumon MM, Ramaprabhu S, Rajalakshmi N. 2006. Platinum/multiwalled carbon nanotubesplatinum/carbon composites as electrocatalysts for oxygen reduction reaction in proton exchange membrane fuel cell. *Appl. Phys. Lett.* 88:253105
- Kundu S, Nagaiah TC, Xia W, Wang Y, Dommele SV, et al. 2009. Electrocatalytic activity and stability of nitrogen-containing carbon nanotubes in the oxygen reduction reaction. *J. Phys. Chem. C* 113:14302–10
- Chen Z, Higgins D, Chen Z. 2010. Nitrogen doped carbon nanotubes and their impact on the oxygen reduction reaction in fuel cells. *Carbon* 48:3057–65
- 116. Nagaiah TC, Kundu S, Bron M, Muhler M, Schuhmann W. 2010. Nitrogen-doped carbon nanotubes as a cathode catalyst for the oxygen reduction reaction in alkaline medium. *Electrochem. Commun.* 12:338–41
- 117. Zhong G, Wang H, Yu H, Peng F. 2014. The effect of edge carbon of carbon nanotubes on the electrocatalytic performance of oxygen reduction reaction. *Electrochem. Commun.* 40:5–8
- Qu L, Liu Y, Baek J-B, Dai L. 2010. Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells. ACS Nano 4:1321–26
- 119. Xiong W, Du F, Liu Y, Perez A Jr, Supp M, et al. 2010. 3-D carbon nanotube structures used as high performance catalyst for oxygen reduction reaction. *J. Am. Chem. Soc.* 132:15839–41
- Ozaki J-I, Anahara T, Kimura N, Oya A. 2006. Simultaneous doping of boron and nitrogen into a carbon to enhance its oxygen reduction activity in proton exchange membrane fuel cells. *Carbon* 44:3358–61
- 121. Yu D, Xue Y, Dai L. 2012. Vertically aligned carbon nanotube arrays co-doped with phosphorus and nitrogen as efficient metal-free electrocatalysts for oxygen reduction. *J. Phys. Chem. Lett.* 3:2863–70
- 122. Yu D, Zhang Q, Dai L. 2010. Highly efficient metal-free growth of nitrogen-doped single-walled carbon nanotubes on plasma-etched substrates for oxygen reduction. J. Am. Chem. Soc. 132:15127–29
- 123. Yang L, Jiang S, Zhao Y, Zhu L, Chen S, et al. 2011. Boron-doped carbon nanotubes as metal-free electrocatalysts for the oxygen reduction reaction. *Angew. Chem. Int. Ed. Engl.* 123:7270–73
- 124. Han W-Q, Cumings J, Zettl A. 2001. Pyrolytically grown arrays of highly aligned B_xC_yN_z nanotubes. Appl. Phys. Lett. 78:2769–71
- Hamada N, Sawada S-I, Oshiyama A. 1992. New one-dimensional conductors: graphitic microtubules. *Phys. Rev. Lett.* 68:1579–81
- 126. Wang S, Iyyamperumal E, Roy A, Xue Y, Yu D, Dai L. 2011. Vertically aligned BCN nanotubes as efficient metal-free electrocatalysts for the oxygen reduction reaction: a synergetic effect by co-doping with boron and nitrogen. *Angew. Chem. Int. Ed. Engl.* 50:11756–60
- 127. Li Y, Zhou W, Wang H, Xie L, Liang Y, et al. 2012. An oxygen reduction electrocatalyst based on carbon nanotube-graphene complexes. *Nat. Nanotechnol.* 7:394–400
- Frackowiak E, Beguin F. 2002. Electrochemical storage of energy in carbon nanotubes and nanostructured carbons. *Carbon* 40:1775–87
- Niu C, Sichel EK, Hoch R, Moy D, Tennent H. 1997. High power electrochemical capacitors based on carbon nanotube electrodes. *Appl. Phys. Lett.* 70:1480–82
- Frackowiak E, Metenier K, Bertagna V, Beguin F. 2000. Supercapacitor electrodes from multiwalled carbon nanotubes. *Appl. Phys. Lett.* 77:2421–23
- 131. Liu CG, Liu M, Li F, Cheng HM. 2008. Frequency response characteristic of single-walled carbon nanotubes as supercapacitor electrode material. *Appl. Phys. Lett.* 92:143108
- 132. An K, Jeon K, Heo J, Lim S, Bae D, Lee Y. 2002. High-capacitance supercapacitor using a nanocomposite electrode of single-walled carbon nanotube and polypyrrole. *J. Electrochem. Soc.* 149:A1058–62

126. Provides the first report on ORR catalysts based on vertically aligned BCN nanotubes.

- 133. Izadi-Najafabadi A, Yasuda S, Kobashi K, Yamada T, Futaba DN, et al. 2010. Extracting the full potential of single-walled carbon nanotubes as durable supercapacitor electrodes operable at 4 V with high power and energy density. *Adv. Mater.* 22:E235–41
- Frackowiak E, Delpeux S, Jurewicz K, Szostak K, Cazorla-Amoros D, Beguin F. 2002. Enhanced capacitance of carbon nanotubes through chemical activation. *Chem. Phys. Lett.* 361:35–41
- Simon P, Burke AF. 2008. Nanostructured carbons: double-layer capacitance and more. *Electrochem. Soc. Interface* 17:38–43
- 136. Futaba DN, Hata K, Yamada T, Hiraoka T, Hayamizu Y, et al. 2006. Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes. *Nat. Mater.* 5:987–94
- Lu W, Qu L, Henry K, Dai L. 2009. High performance electrochemical capacitors from aligned carbon nanotube electrodes and ionic liquid electrolytes. *J. Power Sources* 189:1270–77
- Kim B, Chung H, Kim W. 2012. High-performance supercapacitors based on vertically aligned carbon nanotubes and nonaqueous electrolytes. *Nanotechnology* 23:155401
- 139. Talapatra S, Kar S, Pal SK, Vajtai R, Ci L, et al. 2006. Direct growth of aligned carbon nanotubes on bulk metals. *Nat. Nanotechnol.* 1:112–16
- Pushparaj VL, Shaijumon MM, Kumar A, Murugesan S, Ci L, et al. 2007. Flexible energy storage devices based on nanocomposite paper. *Proc. Natl. Acad. Sci. USA* 104:13574–77
- Kim Y-T, Tadai K, Mitani T. 2005. Highly dispersed ruthenium oxide nanoparticles on carboxylated carbon nanotubes for supercapacitor electrode materials. *J. Mater. Chem.* 15:4914–21
- Lee J-K, Pathan HM, Jung K-D, Joo O-S. 2006. Electrochemical capacitance of nanocomposite films formed by loading carbon nanotubes with ruthenium oxide. *J. Power Sources* 159:1527–31
- 143. Sun Z, Liu Z, Han B, Miao S, Du J, Miao Z. 2006. Microstructural and electrochemical characterization of RuO₂/CNT composites synthesized in supercritical diethyl amine. *Carbon* 44:888–93
- 144. Ramani M, Haran BS, White RE, Popov BN, Arsov L. 2001. Studies on activated carbon capacitor materials loaded with different amounts of ruthenium oxide. *J. Power Sources* 93:209–14
- 145. Panić V, Vidaković T, Gojković S, Dekanski A, Milonjić S, Nikolić B. 2003. The properties of carbonsupported hydrous ruthenium oxide obtained from RuO_xH_y sol. *Electrochim. Acta* 48:3805–13
- 146. Yan J, Fan Z, Wei T, Cheng J, Shao B, et al. 2009. Carbon nanotube/MnO₂ composites synthesized by microwave-assisted method for supercapacitors with high power and energy densities. *J. Power Sources* 194:1202–7
- 147. Yan J, Fan Z, Wei T, Qian W, Zhang M, Wei F. 2010. Fast and reversible surface redox reaction of graphene-MnO₂ composites as supercapacitor electrodes. *Carbon* 48:3825–33
- Kim I-H, Kim J-H, Cho B-W, Lee Y-H, Kim K-B. 2006. Synthesis and electrochemical characterization of vanadium oxide on carbon nanotube film substrate for pseudocapacitor applications. *J. Electrochem. Soc.* 153:A989–96
- Zhang H, Cao GP, Wang ZY, Yang YS, Shi ZJ, Gu ZN. 2008. Growth of manganese oxide nanoflowers on vertically-aligned carbon nanotube arrays for high-rate electrochemical capacitive energy storage. *Nano Lett.* 8:2664–68
- Liu J, Sun J, Gao L. 2010. A promising way to enhance the electrochemical behavior of flexible singlewalled carbon nanotube/polyaniline composite films. *J. Phys. Chem. C* 114:19614–20
- 151. Fang Y, Liu J, Yu DJ, Wicksted JP, Kalkan K, et al. 2010. Self-supported supercapacitor membranes: polypyrrole-coated multi-walled carbon nanotube networks enabled by pulsed electrodeposition. *J. Power Sources* 195:674–79
- 152. Shimoda H, Gao B, Tang XP, Kleinhammes A, Fleming L, et al. 2002. Lithium intercalation into opened single-wall carbon nanotubes: storage capacity and electronic properties. *Phys. Rev. Lett.* 88:015502
- Zamfir MR, Nguyen HT, Moyen E, Lee YH, Pribat D. 2013. Silicon nanowires for Li-based battery anodes: a review. J. Mater. Chem. A 1:9566–86
- Arico AS, Bruce P, Scrosati B, Tarascon JM, Van Schalkwijk W. 2005. Nanostructured materials for advanced energy conversion and storage devices. *Nat. Mater.* 4:366–77
- Szczech JR, Jin S. 2011. Nanostructured silicon for high capacity lithium battery anodes. *Energy Environ.* Sci. 4:56–72

- Cui LF, Yang Y, Hsu CM, Cui Y. 2009. Carbon-silicon core-shell nanowires as high capacity electrode for lithium ion batteries. *Nano Lett.* 9:3370–74
- 157. Gohier A, Laïk B, Kim K-H, Maurice J-L, Pereira-Ramos J-P, et al. 2012. High-rate capability silicon decorated vertically aligned carbon nanotubes for Li-ion batteries. *Adv. Mater.* 24:2592–97
- Fan Y, Zhang Q, Xiao QZ, Wang XH, Huang K. 2013. High performance lithium ion battery anodes based on carbon nanotube-silicon core-shell nanowires with controlled morphology. *Carbon* 59:264–69
- 159. Klankowski SA, Pandey GP, Cruden BA, Liu J, Wu J, et al. 2014. High-rate lithium-ion battery anodes based on silicon-coated vertically aligned carbon nanofibers. In 2014 IEEE International Conference on Nanotechnology, pp. 22–23. New York: IEEE
- Long JW, Dunn B, Rolison DR, White HS. 2004. Three-dimensional battery architectures. *Chem. Rev.* 104:4463–92
- 161. Jiang J, Li Y, Liu J, Huang X, Yuan C, Lou XW. 2012. Recent advances in metal oxide-based electrode architecture design for electrochemical energy storage. Adv. Mater. 24:5166–80
- Kymakis E, Amaratunga GAJ. 2002. Single-wall carbon nanotube/conjugated polymer photovoltaic devices. *Appl. Phys. Lett.* 80:112–14
- 163. Nam C-Y, Wu Q, Su D, Chiu C-Y, Tremblay NJ, et al. 2011. Nanostructured electrodes for organic bulk heterojunction solar cells: model study using carbon nanotube dispersed polythiophene-fullerene blend devices. *J. Appl. Phys.* 110:064307
- 164. Cataldo S, Salice P, Menna E, Pignataro B. 2012. Carbon nanotubes and organic solar cells. *Energy Environ. Sci.* 5:5919–40
- Geng J, Zeng T. 2006. Influence of single-walled carbon nanotubes induced crystallinity enhancement and morphology change on polymer photovoltaic devices. J. Am. Chem. Soc. 128:16827–33
- 166. Lee HW, Yoon Y, Park S, Oh JH, Hong S, et al. 2011. Selective dispersion of high purity semiconducting single-walled carbon nanotubes with regioregular poly(3-alkylthiophene)s. *Nat. Commun.* 2:541
- Dissanayake NM, Zhong Z. 2010. Unexpected hole transfer leads to high efficiency single-walled carbon nanotube hybrid photovoltaic. *Nano Lett.* 11:286–90
- Kongkanand A, Dominguez RM, Kamat PV. 2007. Single wall carbon nanotube scaffolds for photoelectrochemical solar cells: capture and transport of photogenerated electrons. *Nano Lett.* 7:676–80
- 169. Zhang S, Niu H, Lan Y, Cheng C, Xu J, Wang X. 2011. Synthesis of TiO₂ nanoparticles on plasmatreated carbon nanotubes and its application in photoanodes of dye-sensitized solar cells. *J. Phys. Chem.* C 115:22025–34
- 170. Jang S-R, Vittal R, Kim K-J. 2004. Incorporation of functionalized single-wall carbon nanotubes in dye-sensitized TiO₂ solar cells. *Langmuir* 20:9807–10
- 171. Dembele KT, Selopal GS, Soldano C, Nechache R, Rimada JC, et al. 2013. Hybrid carbon nanotubes– TiO₂ photoanodes for high efficiency dye-sensitized solar cells. *J. Phys. Chem. C* 117:14510–17
- Dang XN, Yi HJ, Ham MH, Qi JF, Yun DS, et al. 2011. Virus-templated self-assembled single-walled carbon nanotubes for highly efficient electron collection in photovoltaic devices. *Nat. Nanotechnol.* 6:377– 84
- 173. Yang N, Zhai J, Wang D, Chen Y, Jiang L. 2010. Two-dimensional graphene bridges enhanced photoinduced charge transport in dye-sensitized solar cells. *ACS Nano* 4:887–94
- 174. Saito N, Haniu H, Usui Y, Aoki K, Hara K, et al. 2014. Safe clinical use of carbon nanotubes as innovative biomaterials. *Chem. Rev.* 114:6040–79
- 175. Liu Z, Tabakman S, Welsher K, Dai H. 2009. Carbon nanotubes in biology and medicine: in vitro and in vivo detection, imaging and drug delivery. *Nano Res.* 2:85–120
- 176. Li J, Wu NQ, eds. 2014. Biosensors Based on Nanomaterials and Nanodevices. Boca Raton. FL: CRC. 517 pp.
- 177. Klingeler R, Sim RB, eds. 2011. Carbon Nanotubes for Biomedical Applications. Heidelberg: Springer

RELATED RESOURCES

https://nanohub.org/, a resource for nanoscience and nanotechnology created by the NSFfunded Network for Computational Nanotechnology

- http://www.nanointegris.com/en/home, a commercial source for high-purity, electronically separated nanomaterials
- http://en.wikipedia.org/wiki/List_of_software_for_nanostructures_modeling, a list of software for nanostructures modeling
- http://www.jcrystal.com/products/wincnt/, Nanotube Modeler, computer software for generating *xyz* coordinates for nanotubes and nanocones
- Burton D, Lake P, Palmer A. 2014. Carbon nanofibers: properties and applications of carbon nanofibers (CNFs) synthesized using vapor-grown carbon fiber (VGCF) manufacturing technology. Tech. Rep., Sigma-Aldrich, St. Louis, MO. http://www.sigmaaldrich.com/materials-science/ nanomaterials/carbon-nanofibers.html
- http://pyrografproducts.com/carbon-nanotubes.html, a comparison of carbon nanotubes and carbon nanofibers
- Kumar A, Zhou C. 2010. The race to replace tin-doped indium oxide: Which material will win? ACS Nano 4:11–14