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## Carbon Nanotube Supercapacitors

IntechOpen

Wen Lu

*ADA Technologies Inc.*

*8100 Shaffer Parkway, Littleton, CO 80127*

*USA*

Liming Dai

*Department of Chemical Engineering*

*Case Western Reserve University*

*10900 Euclid Avenue, Cleveland, Ohio 44106*

*USA*

### 1. Introduction

Supercapacitors (aka, electrochemical capacitors or ultracapacitors) are electrochemical energy storage devices that combine the high energy-storage-capability of conventional batteries with the high power-delivery-capability of conventional capacitors (Burke, 2000; Conway, 1999). Able to achieve higher power and longer cycle life than batteries, supercapacitors have been developed to provide power pulses for a wide range of applications including electric transportation technology (e.g., hybrid electric vehicles (HEVs) and plug-in HEVs), electric utility industry (e.g., emergency backup power and grid system stability improvement), consumer electronics (e.g., laptops, cell phones, pagers, and video cameras), medical electronics (e.g., portable defibrillators, drug delivery units, and neurological stimulators), and military / defense devices (e.g., communication devices, unmanned aerial vehicles, spacecraft probes, and missile systems) (Miller & Burke, 2008; Miller & Simon, 2008). In advanced electric transportation technologies, for example, supercapacitors are being developed as power assists for HEVs and plug-in HEVs, where the supercapacitor is operated to provide peak power during acceleration and hill-climbing, and it can be recharged during regenerative braking (Ehsani et al., 2005). This is extremely useful in achieving better fuel economy, decreasing harmful emissions, and reducing the reliance on petroleum sources. A recent report prepared by the US Department of Energy indicated that supercapacitors have been paid equal attention as to batteries as the future energy storage technologies (US DoE, 2007). The world market for supercapacitors has been growing steadily and rapidly. Nevertheless, in order to improve the performance of the state-of-the-art supercapacitors to satisfy the rapidly increasing performance demands for the applications mentioned above, new electrode materials having superior properties over those of the currently used activated carbon electrodes are needed. This chapter summarizes the recent research and technology in developing carbon nanotube (CNT)-based materials as a new type of electrode materials for supercapacitors.

### 1.1 Supercapacitors and currently used supercapacitor electrode materials

The supercapacitor concept was first described in a patent filed in 1957 by Becker, who utilized a high-surface-area carbon electrode and an aqueous  $\text{H}_2\text{SO}_4$  electrolyte to fabricate the supercapacitors (Kötz & Carlen, 2000). In 1971, NEC (Japan) developed aqueous electrolyte-based supercapacitors under the energy company SOHIO's license for powersaving units in electronics. This activity was considered as the initial commercialization application of supercapacitors (Kötz & Carlen, 2000).

Typically, a supercapacitor consists of three essential components, namely the electrodes, the electrolyte, and the separator. The electrodes are an essential component for charge storage / delivery and play an important role in determining energy and power densities of a supercapacitor. Supercapacitors have been realized using three principal types of electrode materials, namely high-surface-area activated carbons (Frackowiak & Béguin, 2001), transition metal oxides (Zheng et al., 1995), and electroactive polymers (Rudge et al., 1994). Fig.1 illustrates the basic structure of a supercapacitor based on high-surface-area and porous carbon electrodes. In such a capacitor, energy is stored as charge separation in the double-layer (i.e., double layer capacitance) formed at the interface between the solid electrode surface and the liquid electrolyte. The ions displaced in forming the double-layers are transferred between the electrodes by diffusion through the electrolyte.

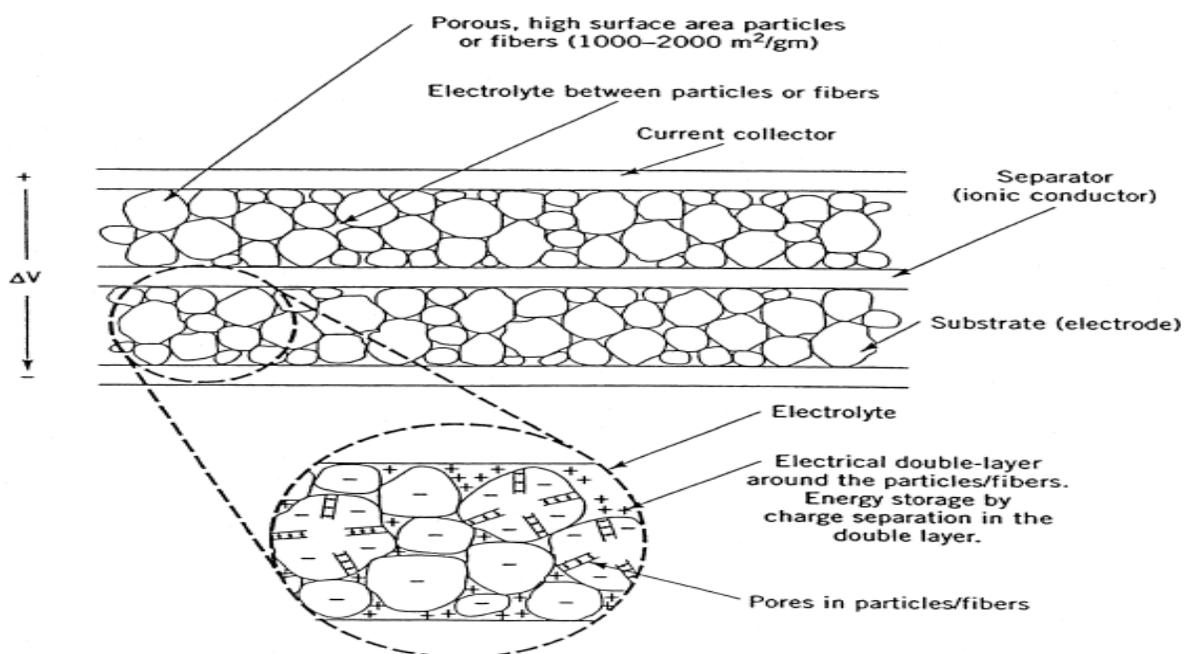


Fig. 1. Schematic of an electrical double-layer supercapacitor (Burke, 2000).

Transition metal oxides and electroactive polymers are redox materials. Faradaic reactions within the bulk of these materials provide additional charge storage, i.e., a pseudocapacitance, resulting in higher energy densities for the capacitors (i.e., pseudocapacitors or redox capacitors). However, the application of transition metal oxides (usually noble metal oxides, e.g.,  $\text{RuO}_2$ ) has been limited by their high cost and that of electroactive polymers by their limited stability. High-surface-area activated carbons are still the predominant electrode materials for commercial supercapacitors.

The maximum energy ( $E_{\max}$ ) and maximum power ( $P_{\max}$ ) of a supercapacitor are given by:

$$E_{\max} = (CU^2)/2 \quad (1)$$

$$P_{\max} = U^2/(4R) \quad (2)$$

where  $C$  is capacitance,  $U$  is cell voltage, and  $R$  is total equivalent series resistance (ESR) of the capacitor (Conway, 1999). Overall performance of the supercapacitor is determined by the physical properties of both the electrode and the electrolyte materials. Having the advantages of relatively low cost, commercial availability, and well-established electrode production technologies, high-surface-area activated carbons (specific surface area: 1000 ~ 2000 m<sup>2</sup>/g) have been the major electrode materials for commercial supercapacitors (Burke & Arulepp, 2001). Charge storage capability of these materials is usually evaluated by their capacitance, which is associated with the electrode / solution interface which varies with the type of carbon and its conditions of preparation and usually has a value of 20 ~ 50 μF/cm<sup>2</sup> (Conway, 1999). Taking a specific surface area of 1000 m<sup>2</sup>/g for carbon as an example, its ideal attainable capacitance would be 200 ~ 500 F/g. However, the practically obtained values are of only a few tens of F/g. Poor accessibility of carbon surface to electrolyte (i.e., electrolyte accessibility) has been confirmed to be the most important reason for the absence of proportionality between specific capacitance and surface area of these materials.

According to the IUPAC classification, there are three classes of pore sizes: micropores (< 2 nm), mesopores (2 ~ 50 nm), and macropores (> 50 nm) (Conway, 1999). It is known that most of the surface area of activated carbon electrode materials resides in the scale defined as micropores (Frackowiak & Béguin, 2001). Pores of this scale are often poorly or non-accessible for electrolyte ions (especially for organic electrolytes) and thus are incapable of supporting an electrical double layer. In principle, the pores greater than 0.5 nm are electrochemically accessible for aqueous electrolytes. However, larger pores are required for organic electrolytes because of their larger size of solvated ions. Having wider electrochemical windows, organic electrolytes ensure higher energy density and power density, and are being employed in commercial supercapacitors. Unfortunately, these advantages have been limited by the reduced electrolyte accessibility associated with the currently used activated carbon electrode materials. Although developed surface area is preferable for the capacitance of a carbon material, increase in the surface area is usually accompanied with the decrease of the pore size. On the other hand, it is known that mesopores contribute the most to the capacitance in an electrical double-layer capacitor (Kastening & Sprinzig, 1986; Mayer et al., 1993; Tanahashi et al., 1990). Thus, an appropriate balance between the surface area and the mesoporosity of a carbon material is the key to achieve high capacitance. Currently available activated carbon materials have high surface area but unfortunately low mesoporosity, resulting in their low electrolyte accessibility and thus limited capacitance (Frackowiak & Béguin, 2001). This translates to the limited energy density of the resultant supercapacitors (Equation 1). Moreover, along with their poor electrical conductivity, the low electrolyte accessibility of activated carbons produces a high ESR (Frackowiak & Béguin, 2001) and hence a poor power density for the capacitors (Equation 2). Consequently, fabricated from these activated carbon electrodes, currently available supercapacitors possess a limited energy density (4 ~ 5 Wh/kg) and a limited power density (1 ~ 2 kW/kg) (Burke & Arulepp, 2001).

Therefore, in order to overcome the drawbacks of the presently used activated carbon electrode materials, high surface area, high electrical conductivity, high mesoporosity, and high electrolyte accessibility should be the important properties desired for an ideal electrode material. CNTs have been utilized to develop new electrode materials to meet these requirements.

## 1.2 Carbon nanotubes

Since their discovery by Iijima in 1991 (Iijima, 1991), carbon nanotubes (CNTs) have attracted considerable attention as a family of novel electronic and electrochemical materials. CNTs can be viewed as a graphene sheet rolled up into a nanoscale tube form to produce the so-called single-wall carbon nanotubes (SWNTs, Fig.2a). There may be additional graphene tubes around the core of a SWNT to form multi-wall carbon nanotubes (MWNTs, Fig.2b), including double wall carbon nanotubes (DWNTs) (Fig.2c) (Harris, 1999). These elongated nanotubes usually have a diameter in the range from a few angstroms to tens of nanometers and a length of several micrometers up to centimeters (allowing the fabrication of mesopore electrodes) with both ends of the tubes normally capped by fullerene-like structures containing pentagons. Morphologically, CNTs can be realized in randomly entangled and in highly aligned forms (Fig.3).

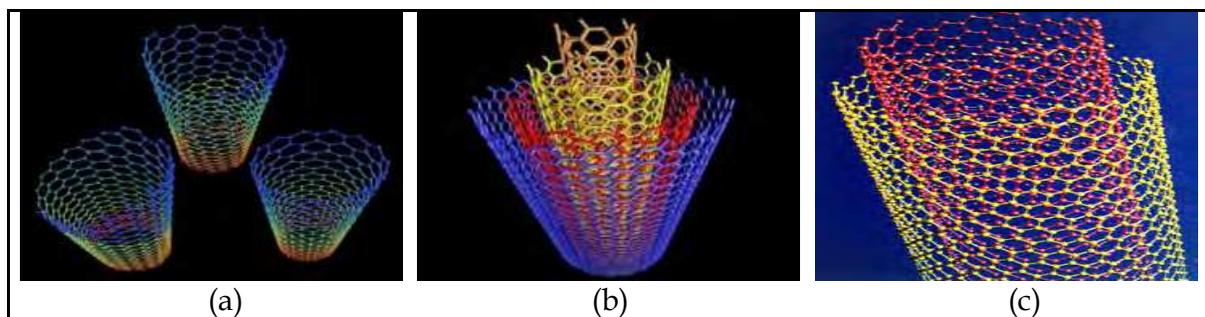


Fig. 2. (a): SWNTs with different helicities, (b): MWNT, and (c): DWNT (Harris, 1999).

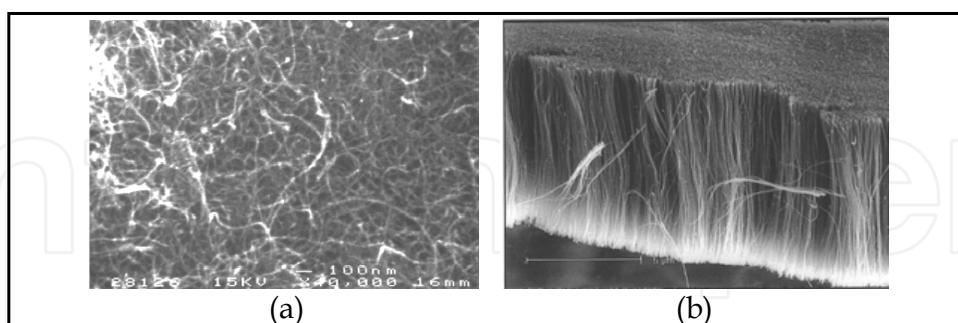


Fig. 3. Scanning electron microscopic (SEM) images of (a): randomly entangled CNTs (Niu et al., 1997), and (b): vertically aligned CNTs (Huang et al., 1999).

A wide range of approaches have been developed to synthesize CNTs including, for example, carbon arc-discharge (Ebbesen & Ajayan, 1992) and pyrolysis of hydrocarbons (Harris, 1999) for MWNTs, carbon arc-discharge (Harris, 1999), pulsed laser vaporization (Journet et al., 1997; Thess et al., 1996) and pyrolysis of hydrocarbons or carbon monoxide (Zheng et al., 2002) for SWNTs, chemical vapor deposition for aligned MWNTs (Dai, 2006;

Dai et al., 2003; Harris, 1999), and plasma-enhanced chemical vapor deposition (Qu & Dai, 2007) for aligned SWNTs. Depending on their diameter and helicity of the arrangement of carbon atoms in the walls, CNTs can exhibit semiconducting or metallic behavior (Dai, 2006; Harris, 1999), with an electrical conductivity as high as 5000 S/cm (Dresselhaus, 1996). CNTs also possess a high thermal conductivity (6000 W/mK), high thermal stability (stable up to 2800 °C in vacuum), and good mechanical properties (tensile strength 45 billion pascals) (Collins & Avouris, 2000). SWNTs have a high theoretical specific surface area of 1315 m<sup>2</sup>/g, while that of MWNTs would be lower and is determined by the diameter of the tubes and the number of the graphene walls (Peigney et al., 2001). A reasonably high surface area (~ 400 m<sup>2</sup>/g) has been obtained for a CNT “paper” electrode (Fig.3a) (Niu et al., 1997). These interesting properties make CNTs very attractive for a variety of potential applications, for example, sensors (Dai et al., 2002), hydrogen storage (Dillon et al., 1997), organic photovoltaic cells (Dai, 2006), energy storage (Che et al., 1998), and supercapacitors (Baughman et al., 2002).

## 2. Carbon nanotube supercapacitors

Specifically, owing to their novel properties of high electrical conductivity, high specific surface area, high charge transport capability, high mesoporosity, and high electrolyte accessibility, CNTs are attractive electrode materials for developing high-performance supercapacitors (Baughman et al., 2002). Like a conventional activated carbon-based supercapacitor (Fig.1), electrodes and electrolyte are two important components for a CNT supercapacitor. Research has been performed to develop different types of CNT electrode materials and combine them with various electrolytes (in different cell configurations) to improve the performance, safety, and lifetimes for supercapacitors.

### 2.1 Carbon nanotube electrodes for supercapacitors

Due to their relative ease of fabrication, randomly entangled CNTs are the first type of CNT materials that were studied for supercapacitor applications. Comparing with high-surface-area activated carbons, CNTs possess a moderate specific surface area. Nevertheless, higher capacitance has been demonstrated for CNTs, e.g., 102 F/g for MWNTs (Niu et al., 1997) and 180 F/g for SWNTs (An et al., 2001), in contrast to that of only tens of F/g for activated carbons. Based on the commonly realizable charge densities of 20 ~ 50 μF/cm<sup>2</sup> suggested for electrical double-layer capacitors (Conway, 1999), An *et al.* estimated the theoretical capacitance for their CNTs (specific surface area: 357 m<sup>2</sup>/g) (An et al., 2001). The result of 71~178 F/g was in good agreement with the observed values (180 F/g) in the upper bound, indicating the perfect electrolyte accessibility of the CNTs. It has been widely accepted that it is their unique mesoporosity (presence and large population of mesopores) induced by the tube entanglement that makes CNTs highly accessible to the electrolyte, i.e., high electrolyte accessibility and thus high capacitance (An et al., 2001; Frackowiak & Béguin, 2001; Niu et al., 1997). This conclusion coincides with the importance of mesopores that has been pointed out previously for activated carbons, confirming that the poor mesoporosity of activated carbons is a major reason responsible for their low capacitance.

High capacitance of CNTs has been utilized to improve performance for supercapacitors. An supercapacitor fabricated from SWNT electrodes and KOH electrolyte showed a promising power density of 20 kW/kg with a maximum energy density of ~10 Wh/kg (performance

based on the mass of SWNTs) (An et al., 2001). The ESR, consisting of the resistance of the electrode itself, the resistance of the electrolyte within the porous layer of the electrode, and the contact resistance between the electrode and the current collector, of the capacitor, was very small, indicating fast delivery of the stored charge and thus a very high power density as expected (Equation 2). Excellent electrical conductivity, high mesoporosity, and high electrolyte accessibility of CNTs, resulting in a high charge transport capability, are responsible for this significance. Multiplying by a factor of 0.35 (Mastragostino et al., 2000), these active material-based performances can be roughly estimated as 7 kW/kg and ~3.5 Wh/kg for a packaged capacitor. Indeed, a power density of > 8 kW/kg (with a maximum energy density of ~ 1 Wh/kg) has been realized for a packaged supercapacitor fabricated from MWNTs electrodes and H<sub>2</sub>SO<sub>4</sub> electrolyte (Niu et al., 1997). These power densities are higher than those attainable by activated carbon-based commercial capacitors (Burke & Arulepp, 2001), but the energy densities still need to improve.

It is well known that the capacitance of conventional carbon electrodes will decrease gradually with increasing discharging current density. This is because currents which are too large may block the entrances of the micropores. Therefore, the energy stored can be withdrawn only at limited discharge rates and at low frequencies or by dc techniques. In contrast, due to their high charge transport capability, fast charge injection and withdrawal are feasible for CNTs, meaning high capacitance at high frequencies (An et al., 2001; Frackowiak & Béguin, 2001; Niu et al., 1997). A frequency “knee” in the impedance spectrum (Nyquist plot) is usually used to evaluate the frequency dependence of a capacitor. At a frequency higher than the “knee”, the real part of the impedance is frequency dependent and very small capacitance will be obtained. At a frequency below this value, the resistance changes weakly with frequency and the capacitor behavior tends to approach that of a pure capacitance. The knee frequency of most commercially available supercapacitors, including those specially designed for high power applications, is < 1 Hz (Miller, 1996). In contrast, a very high “knee” frequency of 100 Hz has been realized for CNT supercapacitors (Niu et al., 1997), suggesting that most of the stored energy of the capacitor is accessible at frequencies as high as 100 Hz. A larger frequency response means better power performance in demand applications.

In the recent years, aligned CNTs have also been studied for supercapacitor applications. It has been stressed that, for electrochemical applications, it is highly desirable to have aligned / patterned structures for CNTs so that their structure / property can be easily accessed and so that they can be effectively incorporated into devices (Dai et al., 2003). Recent research demonstrated that vertically aligned CNTs are advantageous over their randomly entangled counterparts for supercapacitor applications.

First, aligned CNTs are better-structured materials for supercapacitors. Unlike the irregular pore structures of randomly entangled CNTs (Fig.3a), the vertically aligned and unbundled structures and the well spacing between tubes of the aligned CNTs (Fig.3b) provide a more mesoporous and more accessible surface (Zilli et al., 2006). The aligned structures should provide improved charge storage / delivery properties as each of the constituent aligned tubes can be connected directly onto a common electrode, i.e., participation of each tube during the charge / discharge process of the capacitor. This indicates a combined charge capacity from all individual tubes of the aligned CNT electrode, and thus enhanced energy density for the capacitor. In turn, the stored energy can be delivered rapidly through each tube of the electrode, that is, excellent power density for the capacitor.

Second, aligned CNTs have enhanced effective surface area. Surface area of randomly entangled CNTs is determined by the open space between entangled fibrils (Fig.3a). Similarly, that of aligned CNTs is determined by the open space between aligned tubes. The open space between tubes of aligned CNTs is in the range of tens of nanometers (Fig.4). This provides a well-defined surface area for each of the constituent tubes to be accessible to the electrolyte ions, resulting in enhanced effective surface area for aligned CNTs. Moreover, under appropriate conditions (e.g., plasma etching (Huang & Dai, 2002), the top end-caps of aligned CNTs can be properly opened (Fig.4). The end-cap-opening then allows the electrolyte access to the inner cavity of the tubes (Frackowiak & Béguin, 2002). The well-defined alignment, in conjunction with the tip-opened structure, makes the aligned CNTs to possess a higher accessible surface area than that of randomly entangled CNTs. Therefore, the overall enhanced surface area (from both internal and external walls of tubes) translates to an increased capacitance for the aligned CNT electrode and thus an enhanced energy density for the capacitors.

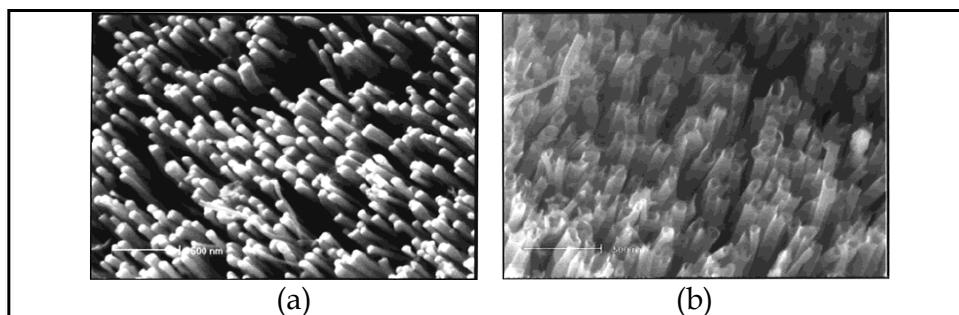


Fig. 4. SEM images of aligned CNTs before (a) and after (b) the plasma-treatment to open the top end-caps of tubes (Huang & Dai, 2002).

Recent research has demonstrated the improved rate capability for aligned CNTs over randomly entangled CNTs (Du et al., 2005; Futaba et al., 2006; Honda et al., 2007; Zhang et al., 2007; Zhang et al., 2008 (*Nano Lett*)). Also, a high capacitance has been obtained in 1 M  $\text{H}_2\text{SO}_4$  for an aligned CNT array electrode (365 F/g) prepared by chemical vapor deposition in the template of porous anodic aluminum oxide (Chen et al., 2004) and in ionic liquid electrolytes for an aligned CNT electrode (440 F/g) prepared by a template-free chemical vapor deposition approach (Lu et al., 2009).

In addition to the pure tube electrodes as discussed above, CNTs have also been employed to fabricate electrodes in nanocomposite forms (e.g., with activated carbons, electroactive polymers, or metal oxides) to improve the performance for supercapacitors.

As mentioned earlier, comparing to activated carbons, CNTs have a relatively lower specific surface area but a higher electrical conductivity, higher charge transport capability, higher mesoporosity, and higher electrolyte accessibility. It is then desirable to combine activated carbons with CNTs to fabricate composites having the combined advantages from these two components. The resultant nanocomposites would possess an improved conductivity and an appropriate balance between the specific surface area and the mesoporosity, resulting in a higher capacitance than CNTs and a higher rate capability than activated carbons. Portet *et al.* blended activated carbons (80 wt. %), DWNTs (15%), and a polymer binder (3% carboxymethylcellulose and 2% polytetrafluoroethylene) to synthesize CNT / activated carbon composites (Portet et al., 2005). Improved capacitive behavior (lower ESR, lower

capacitance loss at high frequencies, and faster charge / discharge process) has been demonstrated for supercapacitors fabricated from these composite electrodes over those from conventional activated carbon electrodes. An appropriate balance between the surface area and the mesoporosity is believed to be the key to ensure the high performance of these activated carbon- and CNT- incorporated composites.

Liu *et al.* mixed SWNTs with a polyacrylonitrile (PAN) dimethylformamide solution at the weight ratio of SWNT to PAN of 40 : 60 to fabricate a SWNT / PAN composite film electrode (Fig.5b) (Liu *et al.*, 2003). Previously, physical or chemical activation of polyacrylonitrile or its copolymers is generally used for producing activated carbon with high specific surface area and high porosity (Addoun *et al.*, 2002; Molina-Sabio, 1996). Liu *et al.* utilized this approach to convert their SWNT / PAN composite films into SWNT / activated carbon composite electrodes (with CO<sub>2</sub> activation). The specific capacitance of the resultant SWNT / activated carbon composites was significantly higher than that of a pure SWNT bucky paper electrode, which has been confirmed to be due to the higher specific surface area of the former than that of the latter. This resulted in the significantly improved power and energy densities of the SWNT / activated carbon composite electrode over those of the SWNT bucky paper electrode. For comparison, Fig.5c also plots power and energy densities of heat-treated SWNT/PAN composite film without CO<sub>2</sub> activation. The authors noticed that, although the specific capacitance of the heat-treated SWNT / PAN composite film without activation was similar to that of the bucky paper, the power density of the former is much higher than that of the latter.

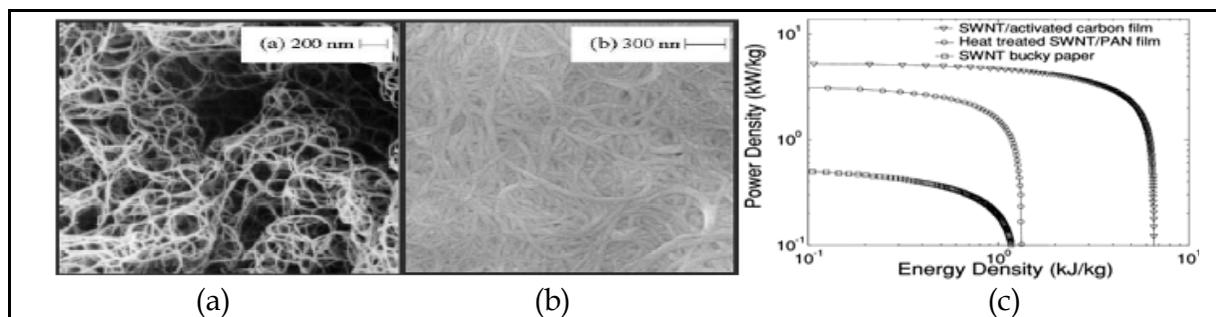


Fig. 5. SEM images of (a): as-produced HiPco SWNT powder, and (b): as-produced SWNT / PAN composite film. (c): Ragone plots for various electrodes evaluated at a discharging current of 0.01 A (Liu *et al.*, 2003).

In order to improve energy density for commercially available activated carbon-based supercapacitors, new electrode materials with high capacitance are always desired (Frackowiak & Béguin, 2001). Able to undergo Faradaic reactions within the bulk of the materials, electroactive polymers and transition metal oxides can provide additional charge storage (i.e., pseudocapacitance) to satisfy this requirement (Burke, 2000). Furthermore, in the recent years, there is a research trend combining the high-energy-storage capability of these redox materials with the high-power-delivery capability of CNTs to fabricate new composite electrode materials with improved capacitance and rate capability.

Since their discovery in 1977 (Shirakawa *et al.*, 1977), electroactive polymers (e.g., polyaniline, polypyrrole, polythiophene) have attracted considerable attention as a family of novel organic electrochemical materials. Able to store and release charge during their redox processes, electroactive polymers have been investigated for energy storage technologies

including supercapacitors (Abrizzini et al., 1996; Rudge et al., 1994). The pseudocapacitance effects connected with the Faradaic reactions enhance the overall capacitance of electroactive polymers (up to  $\sim 500$  F/g) (Burke, 2000). Electroactive polymers possess the advantages of low cost, light weight, and good processibility over transition metal oxides and high energy storage capability over high-surface-area activated carbons. In order to improve the electrochemical utilization (and hence capacitance) and rate capability of electroactive polymers, nanostructures have been developed in these electrode materials. Specifically, incorporating CNTs and electroactive polymers to fabricate nanocomposites is an efficient approach to fulfill this goal. The composites can be obtained both electrochemically and chemically. Combining the pseudocapacitance of electroactive polymers with the high electrical conductivity and high mesoporosity of CNTs, the resultant CNT / electroactive polymer nanocomposites possess enhanced capacitance and rate performance.

Using electropolymerization, CNT / electroactive polymer nanocomposites can be readily deposited from a monomer-containing solution onto a CNT preform or from a CNT / monomer-containing solution onto a traditional conductive substrate. Jurewicz *et al.* electrochemically coated polypyrrole onto a MWNT bucky paper electrode to fabricate CNT / polypyrrole composites (Jurewicz et al., 2001). After a 5 nm-thick polypyrrole coating, capacitance of the MWNTs increased substantially from 50 F/g to 163 F/g. The open entangled network of the nanocomposite was believed to favor the formation of a three-dimensional electrical double layer allowing a more effective contribution of the pseudofaradaic properties of polypyrrole. From an aqueous polymerization solution consisting of 0.5 M pyrrole and 0.5 M KCl, Hughes *et al.* potentiostatically grew polypyrrole onto aligned MWNTs to fabricate the nanocomposites (Hughes, et al., 2002 (*Adv. Mater.*)). The resulting polypyrrole layer was uniformly coated on the aligned nanotubes (Fig.6). With the well-aligned and conductive nanostructures of the MWNTs, the MWNT / polypyrrole composite showed a much larger capacitance ( $2.55$  F/cm<sup>2</sup> vs.  $0.62$  F/cm<sup>2</sup>) and higher knee frequency than a pure polypyrrole film electrode.

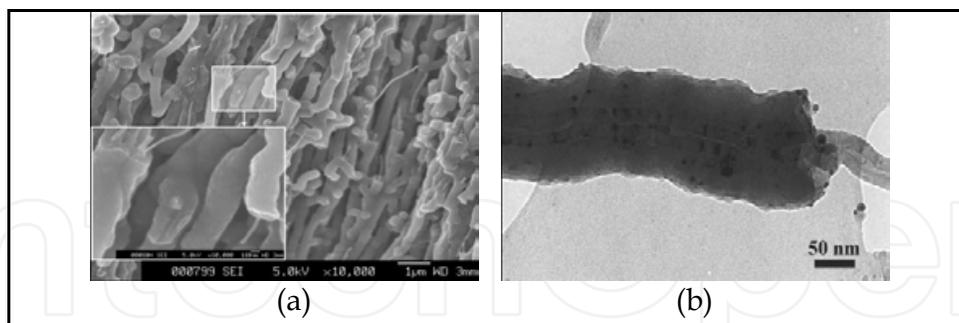


Fig. 6. Polypyrrole coated aligned MWNTs (polymerization charge  $\sim 40$  C/cm<sup>2</sup>, nanotube length  $\sim 100$   $\mu$ m). (a): SEM image of the fractured film cross section illustrating the thickness of the polypyrrole coating relative to the uncoated MWNTs, exposed by fiber-pullout, as well as the channels available to the electrolyte between the coated nanotubes. (b): TEM image showing good interaction between the polypyrrole and MWNT (Hughes, et al., 2002 (*Adv. Mater.*)).

Onto a graphite working electrode, Hughes *et al.* electrochemically (either galvanostatically or potentiostatically) grew polypyrrole from an aqueous polymerization solution consisting of 0.5 M pyrrole monomer and 0.4 wt % of suspended oxidized MWNTs (Hughes et al., 2002

(*Chem. Mater.*). Oxidation of MWNTs via an acid treatment attached functional groups such as hydroxyl, carbonyl, and carboxylic groups to the MWNT surface, facilitating their suspension in water. Thus, the negatively charged MWNTs acted both as a supporting electrolyte during polymerization and as a dopant in the polypyrrole deposited on the working electrode. The nanoporous three-dimensional arrangement of polypyrrole-coated MWNTs facilitated improved electron and ion transfer relative to pure polypyrrole films, resulting in a higher capacitance (192 F/g or 1.0 F/cm<sup>2</sup>) and a higher knee frequency for the composites than pure polypyrrole films.

The CNT / electroactive polymer nanocomposites can also be prepared chemically by an oxidant. Frackowiak *et al.* deposited polypyrrole on MWNTs by chemical polymerization with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as oxidant in an acidic solution (0.1 M HCl). The electrode was prepared by blending the resultant polypyrrole-coated MWNTs with acetylene black and PVdF binder (Frackowiak *et al.*, 2001). The capacitance obtained from nanotubes coated by polypyrrole reached 170 F/g, about twice that given by either pure nanotubes (ca. 80 F/g) or pure polypyrrole (ca. 90 F/g). The open entangled network of the nanocomposite seems to favor a better efficiency for formation of the electrical layer in polypyrrole. An *et al.* used FeCl<sub>3</sub> as oxidant to polymerize polypyrrole and deposit it on SWNTs (An *et al.*, 2002). The electrode was then prepared by mixing the SWNT / polypyrrole composite with acetylene black and PVdF binder. Due to the uniform polypyrrole coating on the porous and conductive support of SWNTs (Fig.7), the SWNT / polypyrrole nanocomposite electrode showed a much higher capacitance (265 F/g) than pure polypyrrole and pure SWNT electrodes.

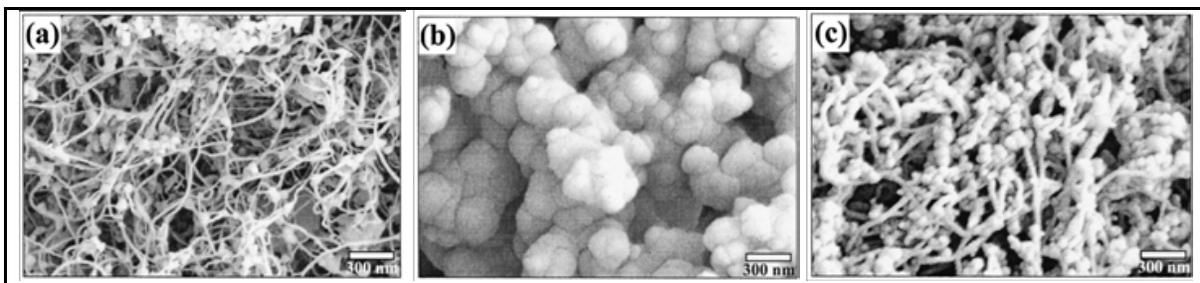


Fig. 7. SEM images of (a): as-grown SWNT, (b): pure polypyrrole, and (c): SWNT / polypyrrole composite (An *et al.*, 2002).

Noble metal oxides, such as RuO<sub>2</sub> and IrO<sub>2</sub>, have been identified as the promising electrode materials for supercapacitors due to their remarkable specific capacitance, good electrical conductivity, and high chemical stability (Zheng *et al.*, 1995). However, the high cost and scarce source of these materials retard their commercial acceptance. Recent researches have been focused on cheap transition metal oxides (e.g., vanadium oxide (V<sub>2</sub>O<sub>5</sub>), manganese oxide (MnO<sub>2</sub>), and nickel oxide (Lee, J.Y. *et al.*, 2005). Combining these metal oxides with CNTs to fabricate nanocomposites is able to improve the capacitive performance of these materials. Among them, V<sub>2</sub>O<sub>5</sub> and MnO<sub>2</sub> are two important examples.

V<sub>2</sub>O<sub>5</sub> has the advantages of non-toxicity, low cost, and high theoretical capacity (590 mAh/g) (Le *et al.*, 1996). However, the major disadvantages of V<sub>2</sub>O<sub>5</sub> are its intrinsically low electronic conductivity (10<sup>-6</sup> ~ 10<sup>-7</sup> S/cm) (Benmoussa *et al.*, 1995) and the slow Li<sup>+</sup> diffusion within the host matrix (diffusion coefficient: ~ 10<sup>-13</sup> cm<sup>2</sup>/s) (Passerini *et al.*, 1999). One effective approach to addressing these issues is to combine V<sub>2</sub>O<sub>5</sub> with CNTs to fabricate

nanocomposites. The resultant high-capacity and high-rate composite electrodes have been utilized for lithium-ion (Li-ion) battery and supercapacitor applications.

SWNTs have been introduced as conductive additives into the  $V_2O_5$  aerogels to develop  $V_2O_5$  / SWNT nanocomposites (Sakamoto & Dunn, 2002). The SWNTs have a similar morphological character and dimensional scale as the  $V_2O_5$  ribbons that compose the aerogel. Thus, there is an opportunity to exploit the high conductivity of SWNTs and have them provide electronic conduction without blocking electrolyte access to the active material. The  $V_2O_5$  / SWNT composite possesses a high pore volume that ensures electrolyte access throughout the electrode, while contact between the two phases is established at the nanometer level, and occurs at multiple points along the  $V_2O_5$  ribbons. This nanocomposite electrode shows a high specific capacity of 452 mAh/g and retains up to 65% of this capacity when the discharge rate is increased from 112 mA/g (0.2C) to 2800 mA/g (5C). Electronically conducting network developed from the SWNTs within the  $V_2O_5$  / SWNT nanocomposite is believed to contribute to this significance.

Kim *et al.* electrochemically deposited  $V_2O_5$  thin film onto a preformed CNT film substrate to prepare the  $V_2O_5$  / CNT composite electrodes (Kim *et al.*, 2006). Without the addition of a polymer binder as employed in conventional electrodes (Mandal *et al.* 2001), the electrochemically prepared  $V_2O_5$  / CNT electrode has high conductivity. With a thin  $V_2O_5$  film coating ( $\sim 6$  nm), the  $V_2O_5$  / CNT electrode shows a very high capacity of 680 mAh/g (based on the mass of  $V_2O_5$ ) at a current density of 5 A/g and retained 67% of this capacity even at a current density of as high as 100 A/g. This improved capacity is believed to be due to the combined contribution from the increased loading of  $V_2O_5$  in the  $V_2O_5$  / CNT electrode (due to high surface area of the CNTs), the improved electrochemical utilization of the  $V_2O_5$  thin film (due to its very small thickness), and the double layer capacitance of the electrode (due to high surface area of the CNTs), while the high rate performance of the  $V_2O_5$  / CNT electrode is believed to be due to the short diffusion time of  $Li^+$  in the  $V_2O_5$  thin film on the highly conductive CNT substrate. The porous and accessible structures of  $V_2O_5$  at a CNT substrate (Fig.8), in contrast to the compact structures of a dense  $V_2O_5$  film at a conventional Pt electrode, are responsible for these improvements.

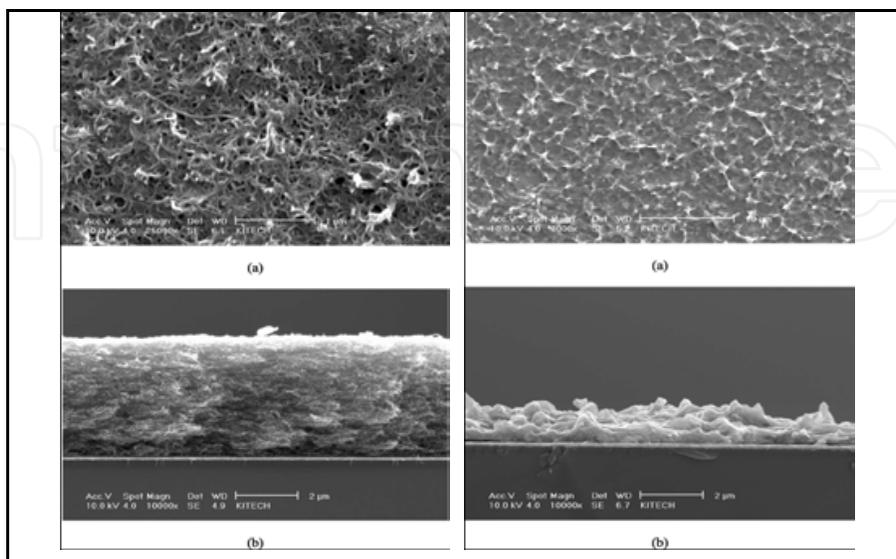


Fig. 8. SEM images ((a): plain, (b): cross-section) of electrochemically prepared  $V_2O_5$  on a CNT electrode (LEFT) and on a Pt electrode (RIGHT) (Kim *et al.*, 2006).

MnO<sub>2</sub> is also a non-toxic, low-cost, and high-capacity (theoretical: 616 mAh/g) meta oxide. In order to improve its electrochemical utilization, capacity, and rate capability for energy storage applications, MnO<sub>2</sub> has been combined with CNTs to fabricate nanocomposites. Different approaches have been investigated to synthesize the composites.

Lee *et al.* first deposited CNTs on a Ni substrate by electrophoresis from a 0.5 mg CNT/1 ml dimethylformamide solution, and then synthesized MnO<sub>x</sub> onto the resultant CNTs / Ni electrode by anodic deposition in a 0.16 M manganese sulfate pentahydrate aqueous solution (Lee, C.Y. *et al.*, 2005). In a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte, upon the increase in scan rate from 5 to 100 mV/s, the specific capacitance of the MnO<sub>x</sub> / CNT nanocomposite electrode decreased slightly from 415 to 388 F/g, retaining up to 94%. After 1000 cycles of operation, this electrode maintained 79% of its original capacitance. These indicate the good electrochemical reversibility, high capacitance, and high rate of the MnO<sub>x</sub> / CNT nanocomposites.

Using thermal decomposition of manganese nitrates, Fan *et al.* synthesized and dispersed MnO<sub>2</sub> onto a CNT matrix that was prepared by directly growing CNTs on a graphite disk (Fan *et al.*, 2006). With a MnO<sub>2</sub> loading of 36.9 μg/cm<sup>2</sup>, a high specific capacitance of 568 F/g was achieved for the resultant MnO<sub>2</sub> / CNT composite (based on MnO<sub>2</sub> mass) in a 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte and at the charge/ discharge current density of 1 mA/cm<sup>2</sup>. Excellent cycle stability (ca. 88% value of specific capacitance remained after 2500 charge / discharge cycles) and power characteristics have been obtained for this composite.

Upon the direct redox reaction between the CNTs and permanganate ions (MnO<sub>4</sub><sup>-</sup>), the resultant MnO<sub>2</sub> can be in-situ coated on the CNTs. Using this method, Ma *et al.* deposited birnessite-type MnO<sub>2</sub> on CNTs (Fig.9) (Ma *et al.*, 2008). In a 1 M LiClO<sub>4</sub> / propylene carbonate organic electrolyte, the resultant MnO<sub>2</sub> /CNT nanocomposite showed a large specific capacitance of 250 F/g even at a large current density of 1 A/g. This is equivalent to 139 mAh/g based on the total weight of the electrode material that includes the electroactive material, conducting agent, and binder. The specific capacitance of MnO<sub>2</sub> in the MnO<sub>2</sub> / CNT nanocomposite was as high as 580 F/g (320 mAh/g), indicating the excellent electrochemical utilization of the MnO<sub>2</sub> due to the use of highly conductive and porous CNT support. Further, the addition of CNTs as a conducting agent in the electrode considerably improved the rate capability of the MnO<sub>2</sub> / CNT nanocomposite.

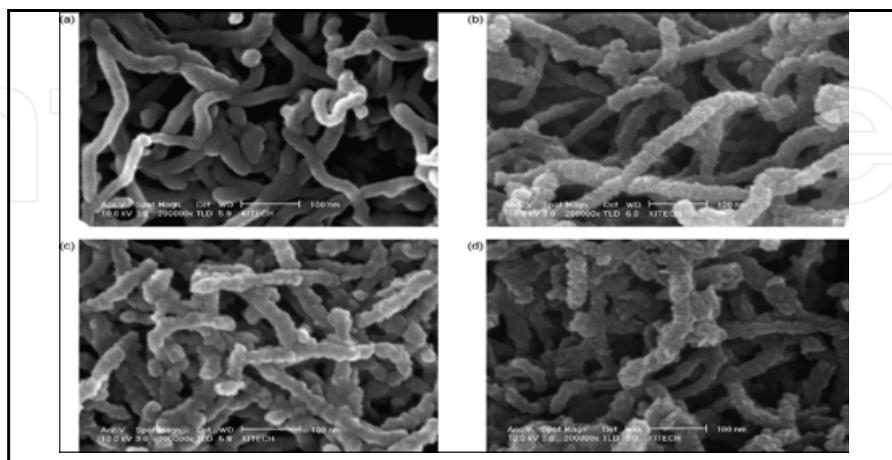


Fig. 9. SEM images of pristine CNT (a) and MnO<sub>2</sub>/CNT nanocomposites prepared in 0.1 M KMnO<sub>4</sub> containing 1.0 g CNT at 70°C under (b): pH 7, (c): pH 2.5, and (d): pH 1 of initial solution (Ma *et al.*, 2008).

Adopting a conventional slurry procedure commonly employed in fabricating electrode materials in energy storage industry, Wang *et al.* prepared their MnO<sub>2</sub> / CNT nanocomposites by simply blending MnO<sub>2</sub> with 25 wt. % MWNTs by ultrasonic vibration in ethanol and then mixing the resultant composite thoroughly with 5 wt. % poly(tetrafluoroethylene) (PTFE) binder to make a slurry. The slurry was then coated onto an aluminum current collector to make a MnO<sub>2</sub> / CNT nanocomposite sheet electrode (Wang *et al.*, 2005), which has been used for supercapacitors as discussed below.

## 2.2 Capacitor design for carbon nanotube supercapacitors

Along with their synthesis and characterization as discussed above, CNT nanocomposites have been utilized to fabricate supercapacitors in various configurations. Specifically, using a same electrode material for both the positive and negative electrodes (i.e., symmetric configuration, similar to that shown in Fig.1), the CNT / activated carbon composites are used to fabricate electric double layer supercapacitors and the electroactive polymer / CNT or metal oxide / CNT composites to fabricate pseudo-capacitors (aka, redox capacitors). With the improved capacitance and rate capability of the CNT / activated carbon composites, the capacitors fabricated from these composites showed enhanced energy and power densities than the conventional activated carbon-based capacitors. With the additional pseudocapacitance attainable from the electroactive polymer- or metal oxide-incorporated CNT composites, the pseudo-capacitors fabricated these materials showed a higher energy density than that of a carbon-based electric double layer capacitor. Further, introducing CNTs in these electroactive electrode materials improved the power performance for these new pseudo-capacitors.

Moreover, combining different electrode materials as the positive and negative electrodes (i.e., asymmetric configuration), the electroactive polymer / CNT and metal oxide / CNT composites have been employed to develop asymmetric supercapacitors (aka, hybrid supercapacitors) with further improved performance. Currently available commercial supercapacitors are fabricated in a symmetric configuration where two identical capacitive electrodes (usually activated carbon) are used as both the positive and negative electrodes (Fig.1). In this design, the capacitor utilizes only one half (on an area basis, F/ cm<sup>2</sup>) or one fourth (on a mass basis, F/g) of one electrode's capacitance, resulting in a low energy density for the capacitors (Burke & Arulepp, 2001). Recently, an asymmetric design has been developed to address this issue (Naoi & Simon, 2008). Typically, an asymmetric supercapacitor is constructed by replacing one of the capacitive carbon electrodes of a symmetric capacitor with a Faradic electrode made of electroactive materials including, for example, electroactive polymers (Fabio *et al.*, 2001), metal oxides (Bélanger *et al.*, 2008), or battery electrode materials (Pasquier *et al.*, 2003). Due to the infinite capacitance of the Faradic electrode comparing to that of the capacitive electrode, an asymmetric capacitor utilizes all (on an area basis) or half (on a mass basis) of the capacitive electrode's capacitance. Plus a high cell voltage deduced from the asymmetric configuration, high energy densities have been achieved for asymmetric capacitors. Ideally, such a system offers the advantages of both the capacitors (high power density and long cycle life) and the batteries (high energy density).

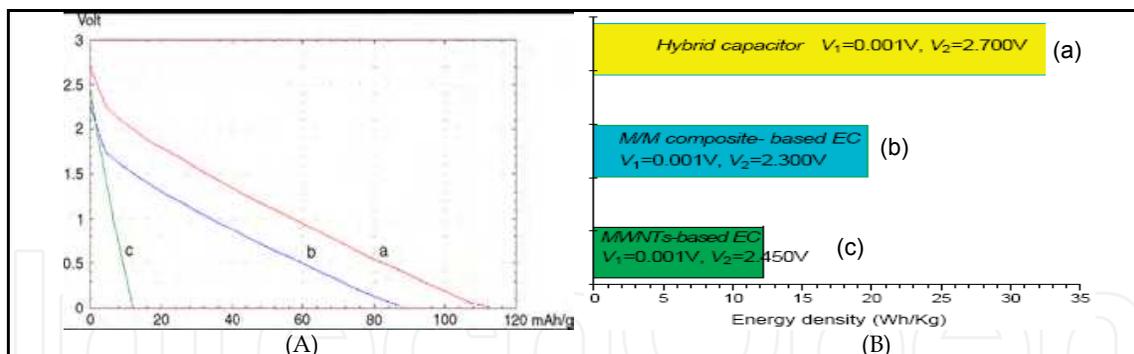


Fig. 10. Galvanostatic discharge curves (A) and energy density at 10 mA/cm<sup>2</sup> current density (B) of (a): MnO<sub>2</sub> / MWNT - MWNT asymmetric capacitor, (b): MnO<sub>2</sub> / MWNT - MnO<sub>2</sub> / MWNT symmetric capacitor, and (c): MWNT - MWNT symmetric capacitor (Wang et al., 2005).

Using their MnO<sub>2</sub> / CNT nanocomposites and a 1.0 M LiClO<sub>4</sub>/ethylene carbonate - diethyl carbonate (1:1 in vol) electrolyte, Wang *et al.* fabricated and evaluated a MnO<sub>2</sub> / MWNT - MWNT asymmetric capacitor against two symmetric capacitors incorporating the same electrode materials, i.e., MnO<sub>2</sub> / MWNT - MnO<sub>2</sub> / MWNT capacitor and MWNT - MWNT capacitor (Wang et al., 2005). The asymmetric capacitor showed the highest cell voltage and highest capacity (Fig.10A). Indeed, due to its unique configuration, the asymmetric capacitor showed a maximum specific capacitance of 56 F/g, 1.3 times that of the MnO<sub>2</sub> / MWNT - MnO<sub>2</sub> / MWNT capacitor and 3.4 times that of the MWNT - MWNT capacitor. Thus, as can be expected by Equation 1, the asymmetric capacitor showed an energy density (32.91 Wh/kg) higher than that of the symmetric ones (Fig.10B). Finally, with the high rate capability deduced from the nanostructures of both the positive and negative electrodes, the nano-nano asymmetric capacitors would be able to achieve a higher power density than the current supercapacitor technology.

### 2.3 Electrolytes for carbon nanotube supercapacitors

The electrolyte is an essential component for charge transport between the positive and negative electrodes and plays an important role in determining the performance, safety, and lifetimes of a supercapacitor. Currently used electrolytes include aqueous, mostly H<sub>2</sub>SO<sub>4</sub> and KOH, and organic, mostly propylene carbonate (PC) and acetonitrile (ACN) electrolytes. Aqueous electrolytes have the advantage of high ionic conductivity but the disadvantage of small electrochemical window (~ 1.2 V), i.e., the potential over which the electrolyte is neither reduced nor oxidized at an electrode. Organic electrolytes are advantageous over aqueous ones mainly due to their larger electrochemical windows, resulting in a larger cell voltage (2 ~ 3 V) and thus potentially higher energy (Equation 1) and power (Equation 2) densities for the capacitor. However, some organic electrolytes suffer from serious health and safety problems as they are inherently volatile, flammable, and toxic (Xu, 2004), leading to a narrow operational temperature range and potential for explosion during outlying circumstances. In addition, electrolyte depletion is another limitation of the currently used electrolytes. Upon charge, ions of the electrolyte are transported into the double layers at the electrode/electrolyte interfaces, resulting in the decrease of salt concentration in the electrolyte (the so-called electrolyte depletion) and hence the limit of energy density of the capacitor (Zheng et al., 1997). Also, this electrolyte depletion increases the cell resistance and

thus lowers the power density achievable for the capacitor. In order to overcome the limitations of currently used electrolytes, environmentally friendly electrolytes with large electrochemical windows are needed. Ionic liquids have been investigated as new electrolytes to satisfy these requirements.

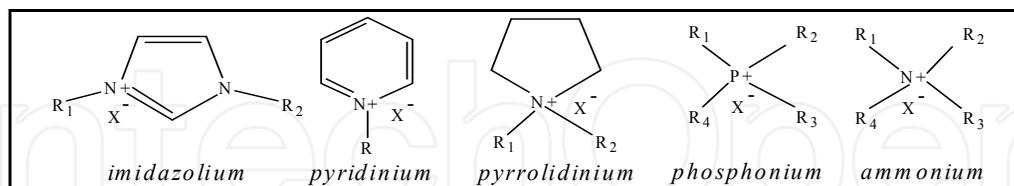


Fig. 11. Structures of ionic liquids. Combination of different cations and anions results in various ionic liquids.  $R$  = methyl, ethyl, butyl, octyl, etc.  $X^-$  =  $BF_4^-$ ,  $PF_6^-$ ,  $CF_3SO_3^-$ ,  $N(CF_3SO_2)_2^-$ ,  $(C_4F_9)_3PF_3^-$ , etc.

Typically, ionic liquids consist of nitrogen (or phosphorus)-containing organic cations and inorganic anions. Categorized by the cation, ionic liquids can be divided into five groups (Fig.11). Since the first ionic liquid, ethyl ammonium nitrate, was described in 1914 (Walden, 1914), ionic liquids have been used in a range of different applications such as chemical synthesis, catalysis, separation, and electrochemical devices (Freemantle, 2000). Unlike conventional solid salts, ionic liquids are salts that are fluid over a wide temperature range, including room temperature, with higher viscosities than either aqueous or organic electrolytes at room temperature. Ionic liquids are inherently conductive, making them good electrolytes. Certain unique properties of ionic liquids, including high ionic conductivity (up to  $10^{-2}$  S/cm), large liquid phase range ( $-100 \sim 400$  °C), wide electrochemical window (4 ~ 6 V), non-volatility, non-flammability, and non-toxicity, have made them an excellent electrolyte for various electrochemical systems including supercapacitors (Buzzeo, et al., 2004).

Given that the performance of a supercapacitor is directly proportional to the square of its cell voltage, Equations 1 & 2, the use of large-electrochemical-window ionic liquids would significantly boost the performance for supercapacitors. Compared to conventional electrolytes, ionic liquids have a unique property that they are both 100% solvents and also 100% salts. It is unnecessary to add other salts into an ionic liquid to achieve ionic conductivity. The very high ionic concentration of ionic liquids would be able to eliminate the electrolyte depletion problem as encountered with conventional electrolytes and therefore enhance the capacitor performances. Further, the superior chemical and environmental stability of ionic liquids ensures safe operation and long lifetimes for capacitors.

Conventional aqueous (An et al., 2001; Niu et al., 1997; Talapatra et al., 2006) and organic (Emmenegger et al., 2003; Futaba et al., 2006; Honda et al., 2007) electrolytes have been employed for the development of CNT supercapacitors. The aqueous electrolyte - based supercapacitors showed reasonably high power densities ( $> 7$  kW/kg) but their energy densities ( $\sim 4$  Wh/kg) are still limited. Narrow electrochemical window of the aqueous electrolytes used, and hence small cell voltages of the capacitors, is a major reason for this drawback. Thus, the advantage of the use of organic electrolytes is mainly associated with their relatively large electrochemical windows.

Electrolytes also influence the performance of asymmetric capacitors.  $MnO_2$  - Activated carbon is a frequently studied aqueous asymmetric capacitor system and shows a

reasonably high energy density (Hong et al., 2002). Unfortunately, most of the  $\text{MnO}_2$  - based capacitors show a limited cycle life (100 to 1000 charge/discharge cycles) (Naoi & Simon, 2008) largely due to manganese dissolution and oxygen evolution (associated with the small electrochemical window of aqueous electrolytes). Use of organic electrolytes having a larger electrochemical window can improve performance for asymmetric capacitors. For example, using a  $\text{LiBF}_4/\text{ACN}$  organic electrolyte, the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  - Activated carbon capacitors showed a cell voltage of about 3 V and an energy density higher than 10 Wh/kg (based on package weight) (Amatucci et al., 2001). Wang *et al.* reported a cell voltage of 1.8 V and an energy density of 35 Wh/kg (based on active electrode material mass) for their aqueous  $\text{LiMn}_2\text{O}_4$  - Activated carbon capacitors (Wang & Xia, 2005). When the aqueous electrolyte was replaced with an organic one, a higher cell voltage (2.5 V) and a higher energy density (56 Wh/kg) have been achieved for a similar capacitor ( $\text{LiMn}_2\text{O}_4$  -  $\text{MnO}_2$ ) (Ma et al., 2007).

To this end, in order to further enhance the capacitor performance, new electrolytes having even larger electrochemical windows are needed. Ionic liquids have been studied for this purpose. Initial study was performed to investigate electrochemical behavior of randomly entangled CNTs in ionic liquid electrolytes, showing a large potential window but with a limited capacitance for the CNTs (Barisci et al., 2004; Xu et al., 2006). It is likely that a facilitated access of the ionic liquid ions could not take place within the CNTs due to the mismatch between the irregular pore structures of the randomly entangled CNTs and the relatively high viscosity of the ionic liquid electrolytes (comparing to conventional aqueous and organic electrolytes). Recent research demonstrated that vertically aligned CNTs are advantageous over their randomly entangled counterparts for supercapacitor applications. Specifically, in ionic liquid electrolytes, improved rate capability has been achieved for CNTs when vertically aligned structures were employed (Zhang et al., 2008 (*J. Electrochem. Soc.*)).

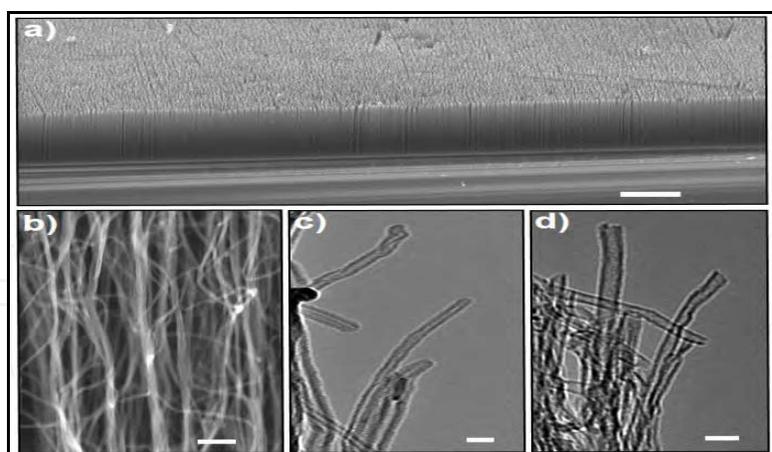


Fig. 12. (a): SEM image of a plasma-etched, vertically aligned CNT electrode (scale bar: 100  $\mu\text{m}$ ). (b): Higher magnification view of the electrode (scale bar: 100 nm). TEM images of the CNTs before (c) and after (d) plasma etching (scale bar: 20 nm). The multi-walled CNT array is highly aligned with the tube length of  $\sim 150 \mu\text{m}$  and an outer and inner diameter of approximately 10 and 5 nm, respectively (Lu et al., 2009).

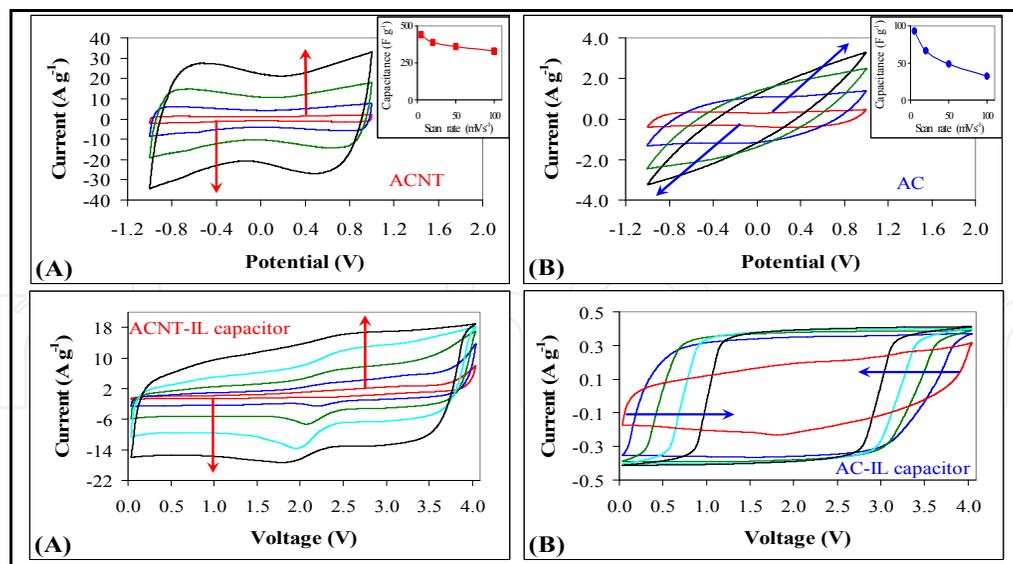


Fig. 13. TOP: CVs obtained in  $[\text{EMIM}][\text{Tf}_2\text{N}]$  for an aligned CNT electrode (A) and an activated carbon electrode (B) at 5, 20, 50, 100 mV/s as indicated by arrows. Insets show capacitance change of the electrodes upon the increase of scan rate. BOTTOM: CVs obtained for an aligned CNT capacitor (A) and an activated carbon capacitor (B), both fabricated from ionic liquid (IL)  $[\text{EMIM}][\text{Tf}_2\text{N}]$ , at the scan rate increasing from 5, 20, 50, 100, to 200 mV/s as indicated by arrows (Lu et al., 2009).

Our recent work investigated the electrochemical behavior of plasma-etched, vertically aligned CNTs (Fig.12) in ionic liquid electrolytes (Lu et al., 2007; Lu et al., 2009). In ionic liquid 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ( $[\text{EMIM}][\text{Tf}_2\text{N}]$ ), the aligned CNT electrode showed a butterfly-shape cyclic voltammogram (CV) (Fig.13. TOP (A)). At 5 mV/s, capacitance of the electrode was found to be 440 F/g, which then decreased slightly upon the increase of scan rates. The capacitance retained up to 75% when the scan rate increased from 5 to 100 mV/s. This indicates the high charge storage ability and high rate capability of the aligned CNT electrode and hence suggests that the plasma-etched aligned CNTs are appropriate electrode materials to overcome the previously perceived disadvantage of high viscosity of the ionic liquids by providing a highly accessible pathway to the ionic liquid ions. It has been pointed out previously that the ability for charge accumulation in the electrode - electrolyte interface of CNTs strongly depends on the mesoporosity, electrolyte accessibility, diameters, and surface nature (e.g., defects and functionalization) of the CNTs (Frackowiak & Béguin, 2002). Unique properties of plasma-etched, vertically aligned CNTs developed in our work are believed to be responsible for their superior capacitance in the ionic liquid.

First, the vertically aligned and unbundled structures and well spacing between tubes of the aligned CNTs (Fig.12) provide a mesoporous and accessible surface (Zilli et al., 2006), resulting in a high electrolyte accessibility, a large effective surface area, and thus a strong capacitive behavior for the aligned CNTs. Second, plasma etching can effectively open the end tips of the nanotubes (Fig.12d) (Huang et al., 1999; Huang & Dai, 2002). The importance of the internal-wall-deduced access to introduce additional surface area and hence additional capacitance has been reported for tip-opened randomly entangled CNTs (Frackowiak & Béguin, 2002). With their highly aligned and unbundled structures and thus superior electrolyte accessibility over the randomly entangled CNTs, this additional

capacitive contribution from the internal surfaces of our aligned CNTs would be more effective. Further, inner diameters of the nanotubes play an important role in determining the charge storage from the tubes' internal surfaces. It has been suggested that optimized CNTs for a supercapacitor should possess a great number of graphene layers and an open central canal with diameter below 5 nm (Frackowiak & Béguin, 2002). Our aligned CNTs have an inner diameter of about 5 nm (Fig.12c, d) and thus can expect a superior charge storage contribution from the tubes' internal surfaces. Previously, a high capacitance of 365 F/g was reported for a template-synthesized aligned CNT electrode (with an inner diameter of 110 nm), which has been attributed to the contribution of the double-layer capacitance (from both the external and internal surfaces) and the pseudocapacitance of the nanotubes (Chen et al., 2004). To this end, a higher capacitance would be achievable for our aligned CNTs due to their much smaller inner diameters (5 nm vs. 110 nm). Third, formation of defects on the aligned CNTs by plasma etching further improves the capacitive behavior of the aligned CNT electrode. It has been pointed out that the presence of a dense pyrolytic carbon outer layer on the nanotubes would decrease the nanotube's electrolyte accessibility. Destroy of this layer by defects (and thus the formation of wall roughness and the improvements in electrolyte accessibility and overall active surface area on the nanotubes) is very favorable for charging the double layer on the CNTs (Frackowiak & Béguin, 2002). Broadly, structural defects of CNTs are important to facilitate the electrochemical processes occurring on the CNTs (Wildgoose et al., 2006). Therefore, this supports that, upon plasma etching, introduction of defects on our aligned CNTs can further improve their capacitive behavior. Finally, oxygenated functionalization of the aligned CNTs by plasma etching introduces additional pseudocapacitance to the aligned CNT electrode. Capacitance of a carbon-based electrode consists of two major components (Conway, 1999), i.e., the electrical double layer capacitance due to the electrostatic attraction of charged carbon surfaces to electrolyte ions and the pseudocapacitance due to the Faradic reactions of electroactive species on the carbon surfaces. The latter arises from the surface functionalization of the CNTs. Usually, presence of oxygenated functional groups on the nanotubes and their Faradic reactions upon charge / discharge of the capacitor has been considered to be an important type of pseudocapacitance for carbon-based electrode materials (Frackowiak et al., 2000; Kim et al., 2005). Upon plasma etching, large amount of oxygenated fictionalization groups was observed on our aligned CNTs. Electrochemically, the Faradic contribution from the redox reactions of these electroactive surface groups can be evidenced by the butterfly-shape CV of the aligned CNT electrode (Fig.13. TOP (A)). Similarly, a recent work attributed the butterfly-shape CV of SWNTs to the electrochemical doping of semiconducting nanotubes and pointed out the importance of this unique mechanism in enhancing energy storage capability for CNT supercapacitors (Kimizuka et al., 2008). As a result, combining the enhanced double-layer capacitance (due to the vertical alignment and well spacing of aligned CNTs and the plasma-etch-deduced end-tip-opening and defect formation) and the additional pseudocapacitance (due to the plasma-etch-deduced oxygenated functionalization), our aligned CNTs showed a remarkable capacitance (440 F/g) in the ionic liquid electrolyte. Previously, with the combined contribution of double-layer capacitance and pseudocapacitance, a high capacitance has been obtained for a template-synthesized aligned CNT electrode (365 F/g) (Chen et al., 2004) and a tubes-in-tube CNT electrode (315 F/g) (Pan et al., 2007) in an aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte. The improved

capacitance of our aligned CNT electrode is believed to be due to its unique properties deduced from the plasma etching as discussed above.

Under the same conditions, a conventional high-surface-area activated carbon electrode showed a much smaller capacitance of about 90 F/g (Fig.13. TOP (B)). Increasing the scan rate from 5 to 100 mV/s, this capacitance decreased sharply to 32 F/g (capacitance retention: 33%), accompanying with the disappearance of the rectangle shape of the CV. This indicates the slower charge / discharge kinetics of activated carbons in the ionic liquid electrolyte and suggests that, in order to explore the large electrochemical windows of ionic liquids to improve performance for supercapacitors, CNTs (rather than traditional activated carbons) are appropriate electrode materials.

Combining the highly capacitive behavior of plasma-etched aligned CNT electrodes with the large electrochemical window of ionic liquid electrolytes, the resultant capacitor showed a high cell voltage (4 V) and superior performance. The excellent charge storage / discharge capability of the capacitor can be seen by its continuously increasing current whilst retaining the rectangular CV upon the increase of scan rates (Fig.13. BOTTOM (A)). In contrast, an activated carbon capacitor showed a fairly unchanged current and a "shrunk" CV (shown by arrows in Fig.13. BOTTOM (B)) due to the poor capacitive behavior of activated carbons in the ionic liquid. Superior capacitive behavior of the aligned CNT capacitor was also confirmed by a very high knee frequency of 54.3 Hz, indicating the ability of the capacitor to react to fast charging /discharging events. These aligned CNT- and ionic liquid-incorporated supercapacitors showed an excellent energy density (148 Wh/kg) and power density (315 kW/kg) (based on the mass of the active electrode materials), significantly outperforming those fabricated from aqueous electrolytes (An et al., 2001; Niu et al., 1997; Talapatra et al., 2006). The combination of the unique properties of plasma-etched aligned CNTs with the large electrochemical window of ionic liquids should be responsible for this significance.

### 3. Summary and outlook

In summary, CNTs have been explored as a new type of electrode materials for supercapacitors. Both randomly entangled and highly aligned CNTs have been investigated. The former is relatively easier to fabricate while the latter has a better capacitor performance. Combining the unique properties of CNTs with the high surface area of activated carbons or the additional pseudocapacitance of redox materials (electroactive polymers and metal oxides), high-capacitance and high-rate nanocomposites are being studied to improve the performance for CNT supercapacitors. CNTs and their composites have been assembled into supercapacitors with different configurations. In addition to the conventional symmetric configuration, an asymmetric design utilizing different materials as the positive and negative electrodes has attracted considerable attention due to its feasibility in improving the energy density for capacitors. While CNT supercapacitors are extensively investigated with traditional aqueous and organic electrolytes, the initial work has been begun with a relatively new electrolyte system (i.e., ionic liquids). The large electrochemical window and the chemical and environmental stability of ionic liquids make them very attractive for improving the performance, safety, and lifetimes for supercapacitors. Nevertheless, the high viscosity of ionic liquids is disadvantageous for their electrochemical applications. Thus, in the use of ionic liquids for supercapacitors, a consideration about the

electrode selection should be taken into account to ensure an appropriate match between the structures of the electrode and the properties of the ionic liquid electrolyte. The unique porous structures of CNTs make them appropriate electrode materials for developing high-performance supercapacitors with ionic liquid electrolytes.

Use of CNTs for supercapacitors has been an exciting research topic. The developments in large-scale synthesis of CNTs (Ebbesen et al., 1992; Journet et al., 1997) are accelerating these applications. Moreover, the recent research has been performed to design new CNT electrodes for fabricating practically useful capacitors and for developing high-energy and high-power energy storage technologies.

### 3.1 New design of carbon nanotube electrodes for supercapacitors

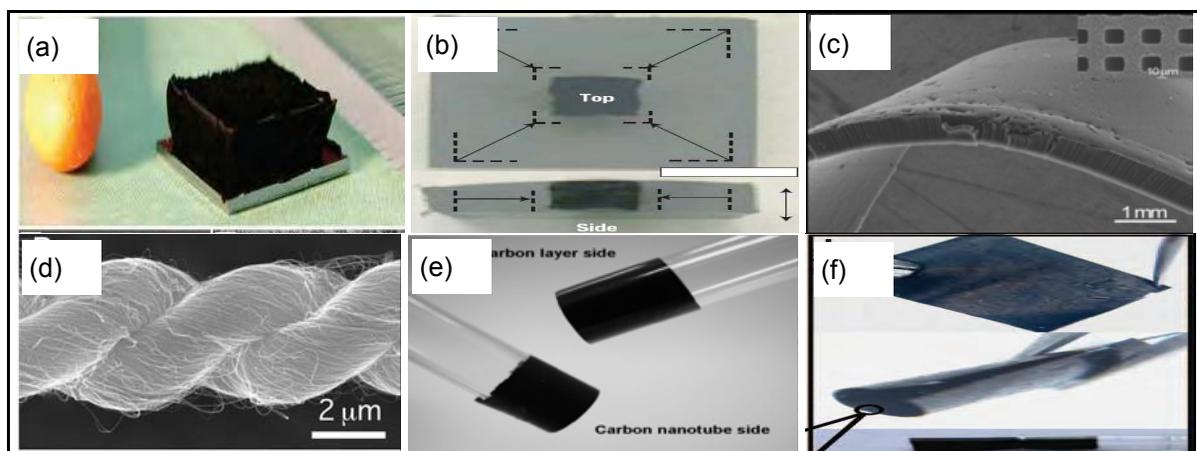


Fig. 14. Examples of some most recently developed CNT electrode materials. (a): picture of a 2.5-mm-tall super-long SWNT forest on a 7-mm by 7-mm silicon wafer. A matchstick on the left and ruler with millimeter markings on the right are for size reference (Hata et al., 2004). (b): overlaid pictures illustrating the decrease in lateral dimensions before (grey) and after (black) collapse of a highly densely packed SWNT film (Futaba et al., 2006). (c): SEM image of a freestanding ultrathick CNT film with patterned square holes (Ci et al., 2007). (d): SEM image of a two-ply MWNT yarn (Zhang et al., 2004). (e): image of a flexible CNT/Carbon layer paper rolled onto glass rods, indicating the flexibility and mechanical robustness of both sides of the composite paper (Chen et al., 2008). (f): photographs of a nanoporous cellulose paper composite electrode embedded with MWNTs and ionic liquids, demonstrating mechanical flexibility. Flat sheet (top), partially rolled (middle), and completely rolled up inside a capillary (bottom) (Pushparaj et al., 2007).

In order to make CNT materials more suitable for electrochemical device applications, there is a need to directly grow CNTs onto conductive substrates to fabricate the electrodes. The resulting CNT / substrate assemblies can be directly used to fabricate supercapacitors without a subsequent CNT transfer, ensuring a high electrical conductivity for the electrodes and hence a low internal resistance for the capacitors. A range of conductive substrates have been employed for this purpose including, for example, aluminum (Chen et al., 2008; Emmenegger et al., 2000), copper (Chen et al., 2008), nickel-containing alloys (Chen et al., 2008; Talapatra et al., 2006), and carbon (Chen et al., 2008). Furthermore, in order to make CNT supercapacitors more practically useful, it is necessary to improve

their volumetric performance. To do this, CNT materials need to be fabricated / packed in a high-loading format. This, for example, can be fulfilled by increasing the length (e.g., super-long CNTs) (Hata et al., 2004), packing density (e.g., highly densely packed CNTs) (Futaba et al., 2006), film thickness (e.g., ultrathick CNT films) (Ci et al., 2007), and multifilaments (e.g., CNT fibers and yarns) (Zhang et al., 2004) of the CNTs. Moreover, in order to improve the shape flexibility and manufacturing integrity for CNT supercapacitors, flexible CNT electrodes have been developed, for example, by directly growing CNTs on flexible carbon layers and meta foils (Chen et al., 2008) or by embedding flexible nanoporous cellulose papers with aligned CNTs (Pushparaj et al., 2007). Fig.14 shows the examples of some of these CNT electrode materials.

### 3.2 Use of carbon nanotubes for high-energy and high-power energy storage technologies

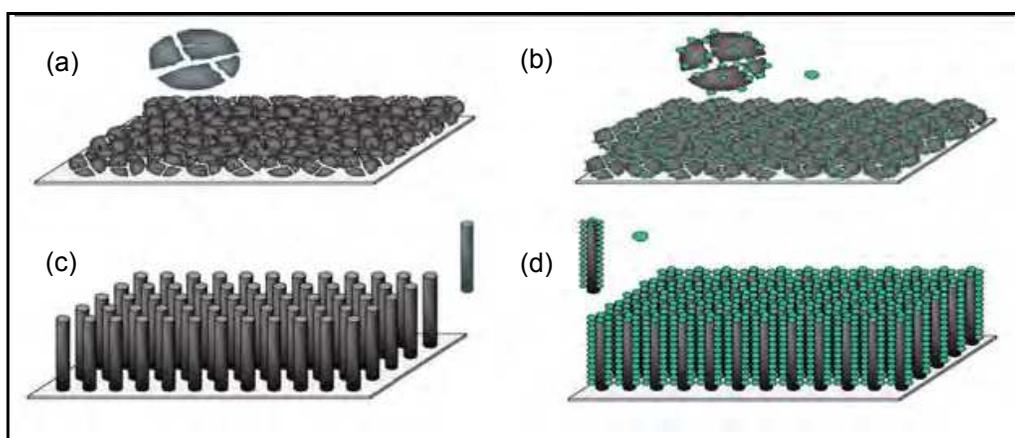


Fig. 15. Possible strategies to improve both energy and power densities for supercapacitors. a, b, Decorating activated carbon grains (a) with pseudo-capacitive materials (b). c, d, Achieving conformal deposit of pseudo-capacitive materials (d) onto highly ordered high-surface-area carbon nanotubes (c) (Simon & Gogotsi, 2008).

Achieving both high energy and high power densities for a same energy storage device has attracted considerable attention in energy storage community (Kang et al., 2006; Taberna et al., 2006). Supercapacitors have a higher power density but a lower energy density than a battery. It is then desirable to combine the high-capacity-capability of batteries with the high-rate-capability of supercapacitors to achieve a high-energy and high-power energy storage device. As discussed earlier (Section 2.1), depositing an electroactive material (electroactive polymers or metal oxides) onto the surfaces of CNTs has been investigated towards this goal. Regarding electrode architectures, vertically aligned structures of a substrate electrode have been demonstrated to be important for this requirement (Taberna et al., 2006). To this end, with their high alignment, well spacing, high effective surface area, and high electrolyte accessibility, vertically aligned CNTs have been a favorable substrate material, in conjunction with the deposition of electroactive materials, to synthesize high-capacity and high-rate electrode materials. Fig.15 illustrates the obvious advantages of vertically aligned CNTs, in contrast to traditional activated carbons, for this application. A variety of materials, e.g., electroactive polymers (Hughes et al., 2002 (*Adv. Mater.*)),

manganese oxide (Zhang et al., 2008 (*Nano Lett.*)), and vanadium oxide (Fang et al., 2008), have been deposited onto aligned CNTs towards this goal. Moreover, further research will be needed to investigate the scaling-up feasibility and the electrolyte compatibility (with an appropriate electrolyte system) of these new electrode materials in order to fabricate high-energy and high-power energy storage devices with high safety and long lifetimes.

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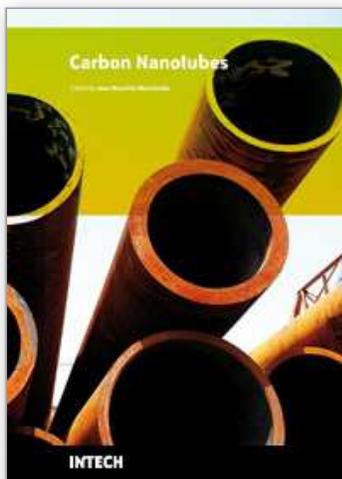
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## **Carbon Nanotubes**

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This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

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