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Chapter 9

Recent Progress on Electrochemical Capacitors Based on Carbon Nanotubes

Emilia Grądzka and Krzysztof Winkler

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Abstract

This review is focused on the theoretical and practical aspects of electrochemical capacitors based on carbon nanotubes. In particular, recent improvements in the capacitance properties of the systems are discussed. In the first part, the charge storage mechanisms of the electrochemical capacitors are briefly described. The next part of the review is devoted to the capacitance properties of pristine single- and multi-walled carbon nanotubes. The major portion of the review is focused on the capacitance properties of modified carbon nanotubes. The electrochemical properties of nanotubes with boron, nitrogen, and other atoms incorporated into the carbon network structure as well as nanotubes modified with different functional groups are discussed. Special attention is paid to the composites of carbon nanotubes and conducting polymers, transition metal oxides, carbon nanostructures, and carbon gels. In all cases, the influences of different parameters such as porosity, structure of the electroactive layer, conductivity of the layer, nature of the heteroatoms, solvent and supporting electrolyte on the capacitance performance of hybrid materials are discussed. Finally, the capacitance properties of different systems containing carbon nanotubes are compared and summarized.

Keywords: carbon nanotubes, carbon nanoparticles, conducting polymers, composites, electrochemical capacitors, charge storage materials

1. Introduction

The last two decades can be considered a nanotechnology revolution. With each passing day, increasing attention is paid to the discovery of new nanoscale materials due to the miniaturization of devices in many areas. Nanomaterials are everywhere, from cosmetics and clothes to medicine and electronic devices. At the same time, the increased development of electronic devices requiring energy storage systems, such as batteries and supercapacitors, is starting to play a crucial role in everyday life. Supercapacitors, also called electrochemical capacitors, are

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energy saving units that can provide a huge amount of energy in a short time. Compared with batteries, electrochemical capacitors offer great advantages of high power capability, high rates of charge and discharge, high cycle life, flexible packaging and low weight [1–4].

An interesting class of nanomaterial for storage devices is carbon nanotubes due to their large open surface that is completely exposed to electrolyte ions, good electrical conductivity, high surface area, mechanical strength, good corrosion resistance, chemical stability and low mass density [4–8]. However, so far, pristine CNTs have not met the commercial requirements for energy storage devices applications due to their poor dispersion in solvents, low electrochemical characteristics in the electrolytes, and low specific capacitance [7, 8]. The capacitance properties of carbon nanotubes may be improved by surface functionalization or by the formation of composites with redox-active systems such as conducting polymers or metal oxides. On the other hand, carbon nanotubes are excellent conducting supports to improve the properties of materials with poor conductivity, stability, and capacitance performance. Hence, carbon nanotubes-based nanocomposites or nanohybrids have recently been intensively developed because of their superior properties compared to the individual component alone. Much research on supercapacitors has aimed at increasing power and energy densities as well as lowering fabrication cost [8–18].

The objective of this review is to highlight theoretical and practical aspects of the capacitance properties of carbon nanotubes and their composites. In particular, recent progress in improving the capacitance properties of systems based on carbon nanotubes is discussed. In the first part, the charge storage mechanisms in electrochemical capacitors are briefly described. The next part of the review is devoted to the capacitance properties of pristine carbon nanotubes and carbon nanotubes modified by heteroatoms or functional groups. Special attention is paid to the composites of carbon nanotubes with conducting polymers, carbon nanostructures, transition metal oxides, and carbon gels.

2. Principles and mechanism of charge storage

Electrochemical energy storage may be classified as encompassing either batteries or electrochemical capacitors (ECs), which are also known as supercapacitors, ultracapacitors, electrical double-layer capacitors, pseudocapacitors, gold capacitors or power coaches [19–21]. Supercapacitors fill the gap between batteries that exhibit high energy density and high power density conventional capacitors, covering several orders of magnitude both in energy and in power density. Batteries compared to supercapacitors store and deliver more energy with slower charge and discharge times. In the case of conventional capacitors, they have very high energy density in comparison to supercapacitors. Supercapacitors also exhibit low heating level, safety, long-term operation stability, low weight, and flexible packaging [4, 22, 23]. Due to these properties of semiconductors, they can be applied in many fields of electrotechnology. They can be used in electric and hybrid vehicles [3, 24, 25], high-energy pulsed lasers [26], mobile phones [26–28], laptops [27], and cameras [27, 28].

The charge-storage mechanism of electrochemical capacitors is controlled by two principal mechanisms: (i) a non-Faradaic electrostatic interaction resulting from ion adsorption at the

electrode/electrolyte interface defined as electric-double layer capacitance (EDLC) (**Figure 1a**) and (ii) an electrochemical oxidation/reduction reaction in electroactive materials accompanied with Faradaic charge transfer named pseudocapacitance (**Figure 1b**) [4, 29–32].

Typical supercapacitors consist of two electrodes separated by a dielectric material or electrolyte solution. In the case of EDLC, where the capacitance comes from the electrostatic charge accumulated at the electrode/electrolyte interface and strongly depends on the surface area of the electrode accessible to the electrolyte ions, mostly porous carbons are used as electrode materials due to their low price, facile synthesis, and sustainability. They are prepared by heat treatment and subsequent chemical activation with organic materials or, in the case of "carbide-derived carbons" (CDCs), by extracting metal atoms in metal carbides. More exotic materials, such as carbon nanotubes (CNTs) and graphene, are also being developed for supercapacitor applications. The operating voltage of supercapacitors depends on the solvent and electrolytes separating both electrodes. Tetraethylammonium tetrafluoroborate is often used as the supporting electrolyte in organic solvents. This salt offers a relatively high operating voltage of approximately 2.5 V and a high ionic conductivity of 20–60 mS cm^{-1}. In aqueous solutions, a maximum potential of 1.2 V can be obtained. Moreover, room-temperature ionic liquids with an operating voltage as high as 4 V could also be used as electrolyte systems. However, supercapacitors based on ionic liquids have poor device power performance due to their low ionic conductivity, i.e., below 20 mS cm^{-1} [23, 30, 33].

The specific capacitance for EDLC is assumed to follow that of a parallel-plate capacitor:

$$C = \frac{\varepsilon_r \varepsilon_0}{dA} \tag{1}$$

where ε_r is the electrolyte dielectric constant, ε_0 is the permittivity of vacuum, A is the specific surface area of the electrode, and d is the effective thickness of the EDLC. Depending on the pore size of the electrode material, two models are proposed: an electric double cylinder capacitor (EDCC) model that describes mesoporous carbon electrodes (**Figure 2a**) and an electric

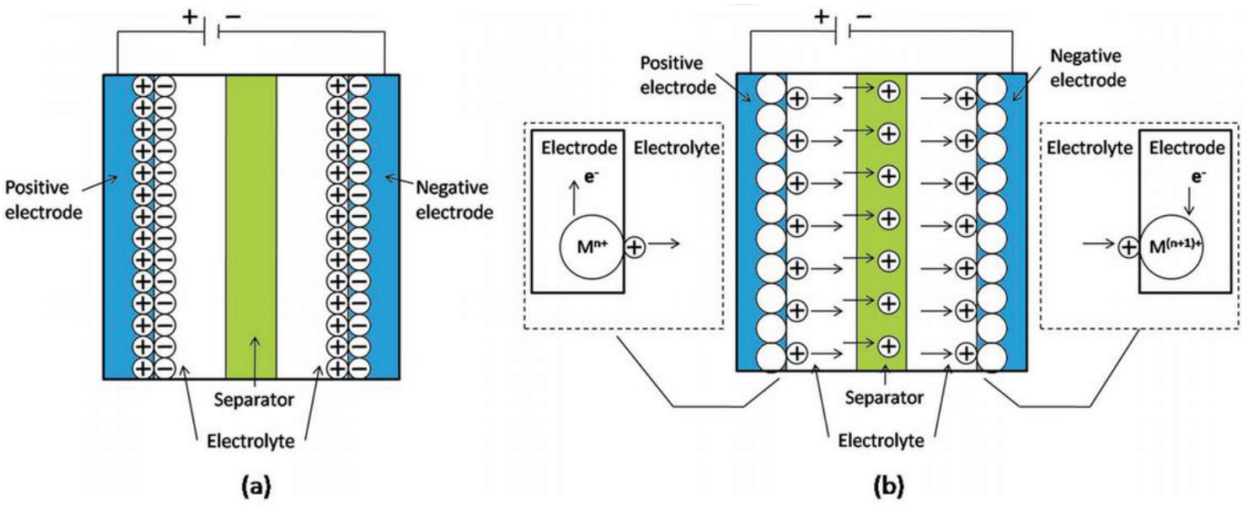


Figure 1. Schematic diagram of supercapacitors: (a) EDLC and (b) pseudocapacitor (M represents the metal atom). Reproduced with permission from Ref. [32]. Copyright 2014 The Royal Society of Chemistry.

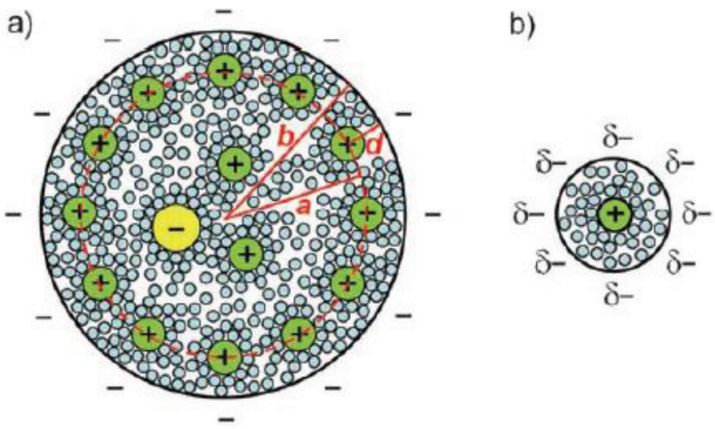


Figure 2. Schematic diagrams (top views) of (a) a negatively charged mesopore with solvated cations approaching the pore wall to form an electric double-cylinder capacitor and (b) a negatively charged micropore of radius b with cations lining up along the pore axis to form an electric wire-in-cylinder capacitor. Reproduced with permission from Ref. [34]. Copyright 2008 Wiley-VCH Verlag.

wire-in-cylinder capacitor (EWCC) model corresponding to microporous carbon electrodes (**Figure 2b**). The equation describing the capacitance in these two models can be written as:

$$C = \frac{\varepsilon_r \varepsilon_0}{bln\left[\frac{b}{b-d}\right]} A \tag{2}$$

$$C = \frac{\varepsilon_r \varepsilon_0}{bln\left(\frac{b}{a_0}\right)} A \tag{3}$$

where b is the pore radius, d is the distance of approaching ions to the surface of the carbon electrode, and a_0 is the effective size of counterions. When the pores are large enough and the pore curvature is no longer significant, the EDCC model is reduced to the traditional planar EDLC model described by Eq. (1) [30, 34].

In contrast to EDLC, pseudocapacitance results from faradaic fast reversible redox reactions involving electrode material. During electrochemical reactions, the electrode material is reduced or oxidized and doped with counterions from the electrolyte solution. In this case, conducting polymers and metal oxides or hydroxides as electrode materials are used [30]. High-area carbon electrodes also exhibit a small pseudocapacitance component due to electrochemically active redox functionalities [22]. Pseudocapacitance is described by the following equation:

$$C = \frac{d(\Delta q)}{d(\Delta V)} \tag{4}$$

where Δq is the charge related to the faradaic process in the potential range ΔV. The pseudocapacitance can reach higher values than the EDLC capacitance. However, redox capacitors exhibit lower power density due to poor electrical conductivity and lack of stability during the cycle.

The maximum energy stored in supercapacitors is given by

$$E = \frac{1}{2} CV^2 \tag{5}$$

where C is the capacitance and V is the operating voltage limited by the thermodynamic stability of the electrolyte solution. The total power of a supercapacitor is described by the following equation:

$$P = \frac{V^2}{4R} \tag{6}$$

where R is the internal resistance of the capacitor coming from the various types of resistances associated with the intrinsic electronic properties of the electrode material and electrolyte solution, mass transfer resistance of the ions in the electrode material, and contact resistance between the current collector and the electrode [22, 23, 30, 31].

The electrode is one of the most important components for charge storage and plays a crucial role in determining the energy and power density of supercapacitors [29]. In EDLC, the high surface area resulting from the highly microporous structure of carbon electrode materials such as carbon aerogels, carbon black or carbon cloth is unfavorable for electrolyte wetting and rapid ionic motions, especially at high current loads [22]. The most frequently used activated carbon electrodes exhibit low electrolyte accessibility and poor electrical conductivity. These two effects are responsible for limited energy density and high internal resistance. For this reason, carbon nanotubes (CNTs) with nanoscale size, controllable size distribution, large surface area, high mesoporosity, electrolyte accessibility, and good electrical properties are very promising candidates for replacing carbon materials as the electrode materials in high-performance capacitors. Because of this fact, an extended part of this work will focus on supercapacitors based on carbon nanotubes [4, 29].

3. Capacitance properties of single- and multi-walled carbon nanotubes

Carbon nanotubes exhibit large open surface area, excellent mechanical strength, chemical stability, low mass density, and relatively good electrical conductivity. All these properties make them a very good candidate for the electroactive material in charge storage devices. In these capacitors, the ions of electrolyte are adsorbed on the charged surface of carbon nanotubes, producing a Helmholtz layer. The capacitance properties of these systems depend on the number of graphene walls (single-, double-, or multi-wall), the nature of the electrode material, the composition of the electrolyte solution, and the structure of the carbon nanotube layer. The specific capacitance of pristine CNTs is relatively low and ranges from 2 to 45 F g^{-1} for SWCNTs [35–42] and 3 to 80 F g^{-1} for MWCNTs [36–38, 42–44]. The capacitance properties of thin films of CNTs are collected in **Table 1**.

Such a large scattering of reported specific capacitance values is mainly related to the different procedures of CNT deposition on the conducting electrode surface and, therefore, different structures of CNTs films. Carbon nanotubes can be attached to electrodes by direct growth [45], manual manipulation [46], random spreading [47], deposition in a dc current electric field [48], or gas flow [49]. Specially designed substrates are used for film formation of vertically oriented CNTs [50–53]. Two of the most common orientations of CNTs are displayed schematically in **Figure 3**. In general, films of vertically oriented carbon nanotubes exhibit much better

Carbon nanostructure	Specific capacitance (F g^{-1})	Experimental conditions	Reference
SWCNTs	2	0.1 M Na_2SO_4	[39]
	17	1 M NaCl	[40]
	18	1 M NaCl	[35]
	19	5 M KOH	[35]
	20	6 M KOH	[41]
	21	1 M NaCl	[35]
	24	7 M H_2SO_4	[35]
	40	6 M KOH	[38]
	64	1 M H_2SO_4	[42]
MWCNTs	3	7 M KOH	[43]
	9	7 M KOH	[43]
	14	1 M H_2SO_4	[42]
	14	6 M KOH	[38]
	17	4 M H_2SO_4	[43]
	26	4 M H_2SO_4	[43]
	30	1 M H_2SO_4	[44]
	36	6 M KOH	[38]
	38	1 M Na_2SO_4	[44]
	62	6 M KOH	[38]
	78	1 M H_2SO_4	[38]
	80	6 M KOH	[38]

PC, propylene carbonate.

Table 1. Selected values of specific capacitances obtained for thin films of carbon nanotubes.

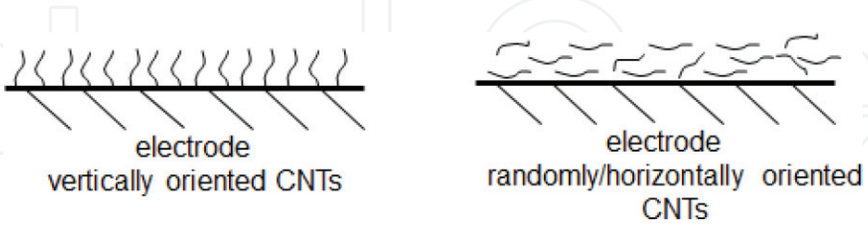


Figure 3. Schematic representation of nanotubes orientation at the electrode surface.

electrical and capacitance properties in comparison to films formed from randomly oriented nanotubes [6, 50, 54–57]. **Figure 4** shows the structure of the SWCNT layer formed under CVD growth procedure. The highest specific capacitance of 52 F g^{-1} and excellent electrochemical stability were reported for such vertical structures of SWCNTs [55].

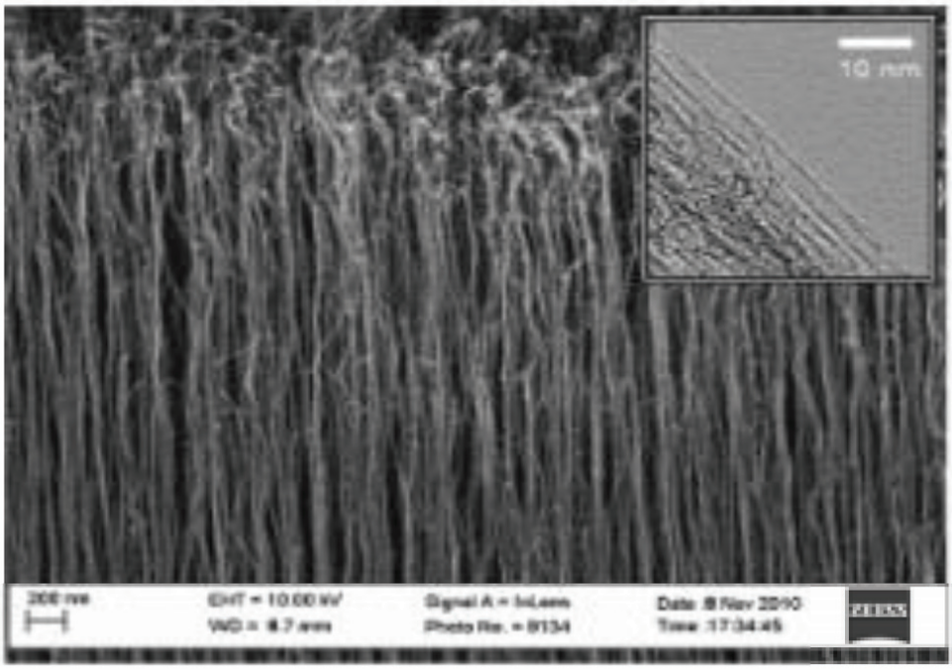


Figure 4. SEM image of the aligned carbon nanotubes formed under CVD procedure. Reproduced with permission from Ref. [6]. Copyright 2011 American Chemical Society.

4. Covalent modification of carbon nanotubes and their capacitance properties

The covalent functionalization of carbon nanotubes provides modification of their physicochemical properties. Insertion of functional groups to the carbon network solves the problem of their poor dispersion capability. Stable dispersions of modified carbon nanotubes are particularly important in the formation of thin films of capacitors or capacitive devices. Moreover, tethering electron-donating or electron-withdrawing groups on CNT surfaces changes their electronic properties by the doping effect [22, 58–62]. Such groups exhibit electrochemical activity resulting in a pseudo-Faradaic capacitance effect.

Park and co-workers showed the relationship between the electrochemical activity of functional groups attached to the CNT surface and their capacitive characteristics [58]. They found that MWCNTs covalently functionalized by carboxylic, sulfonic, and amine groups (**Figure 5**) showed a two- to fourfold increase in capacitance over that of pristine MWCNTs due to pseudocapacitive charging-discharging arising from the presence of functional groups. Functionalized CNTs also form more stable dispersions in deionized water and polar organic solvents. Such dispersions can be used in the formation of mechanically stable and uniform capacitor films. Functionalized CNTs, however, exhibit a lower surface area due to the reduction in the average pore size as a consequence of the presence of surface functional groups [58].

Figure 6 shows the effect of the addition of oxygen redox-active molecules on the electrochemical performance of CNTs. Nanotubular materials can be treated (CNTs-T) chemically [62–70],

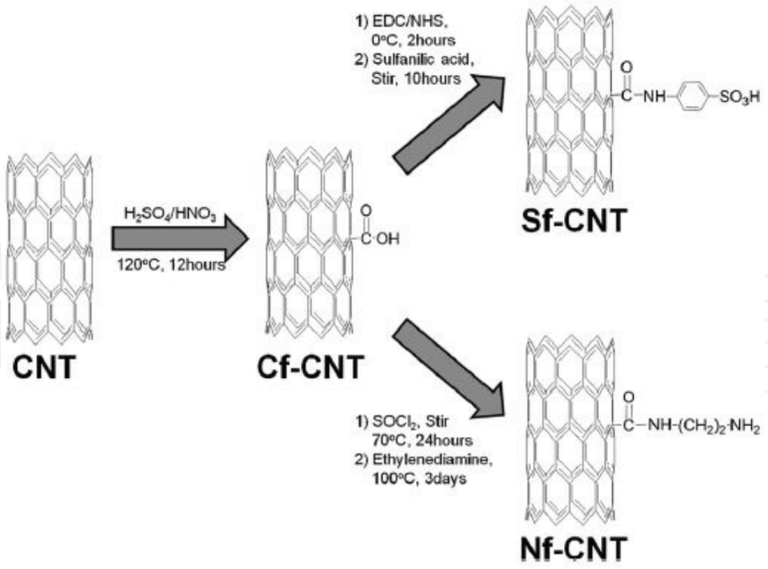


Figure 5. Schematic illustration of the covalent functionalization of CNTs. Reproduced with permission from Ref. [58]. Copyright 2013 The Royal Society of Chemistry.

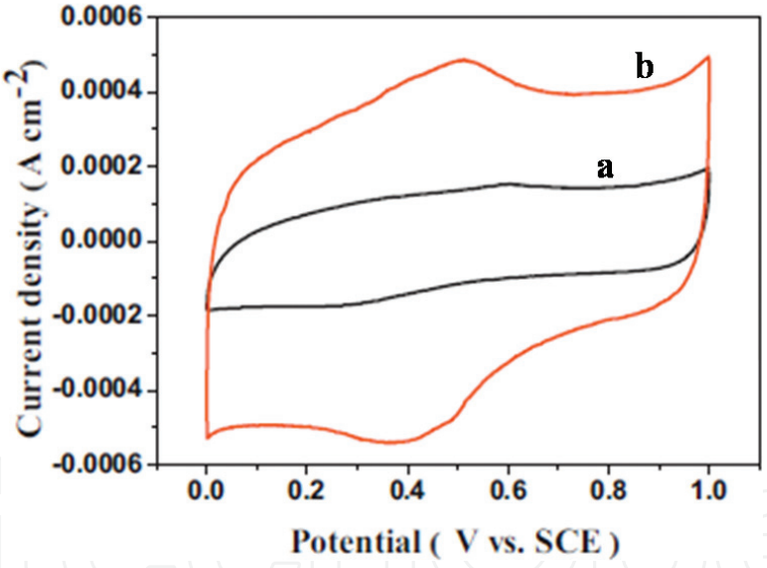


Figure 6. Cyclic voltammograms of (a) raw CNTs and (b) CNTs-T electrodes in 1 M H_2SO_4. Reproduced with permission from Ref. [62]. Copyright 2014 Elsevier.

electrochemically [59, 71, 72], photochemically [73, 74], and using plasma-induced techniques [75, 76]. The chemical modifications are usually performed in concentrated nitric acid or in a mixture of nitric and sulfuric acids. Cyclic voltammograms recorded for raw CNTs exhibit pseudorectangular cathodic and anodic profiles, which are the characteristics of ideal capacitors. In the case of CNTs-T, a pair of voltammetric peaks is observed. They are related to the redox reactions of functional groups on the CNTs-T surface:

$$>C\text{-}OH \rightleftharpoons >C{=}O + H^+ + e^- \quad (7)$$

$$>C{=}O + e^- \rightleftharpoons >C\text{-}O^- \quad (8)$$

$$\text{-}COOH \rightarrow CO_2 + H^+ + e^- \quad (9)$$

A higher current observed for CNTs-T suggests that their surface area is larger compared to that of raw CNTs. The surface of oxygen-containing functional groups also decreases surface resistivity and enhances surface wettability, offering more accessible sites for the physisorption of electrolyte ions and increasing the ionic conductivity at the electrode/electrolyte interface. In the procedure proposed by Wang and co-workers [62], the specific capacitance was increased from 28 F g^{-1} for raw CNTs to 85 F g^{-1} for CNTs-T in H_2SO_4 solution. Changing the electrolyte to H_2SO_4/hydroquinone mixture provides a drastic improvement of the specific capacitance to 508 and 3199 F g^{-1} for CNTs and CNTs-T, respectively [62].

The distribution and type of oxygen-containing functional groups depend on the type (**Figure 7a**) and concentration (**Figure 7b**) of the oxidizing agent [66, 67].

The oxidation of CNTs is a principle reaction for further functionalization of the carbon network. The combination of CNTs with graphene oxide in a lamellar graphene-CNT structure, r[GO/CNT], shown in **Figure 8** causes an increase in the electrolyte-accessible surface area due to the intercalation of CNTs between the stacked GO sheets with associated large electrochemical active sites, thus improving conductivity through the formation of a 3D network aided by CNTs. Such a covalently linked CNTs-graphene system exhibits capacitance performance much superior than that of other carbon-based electrodes [77].

The high specific capacitance of CNTs could also be obtained with the incorporation of heteroatoms such as N [61, 78–87], B [86–89], P [86, 90], and F [91]. The type of defect created by the heteroatom influences the kind of conduction generated ranging from n-type transport

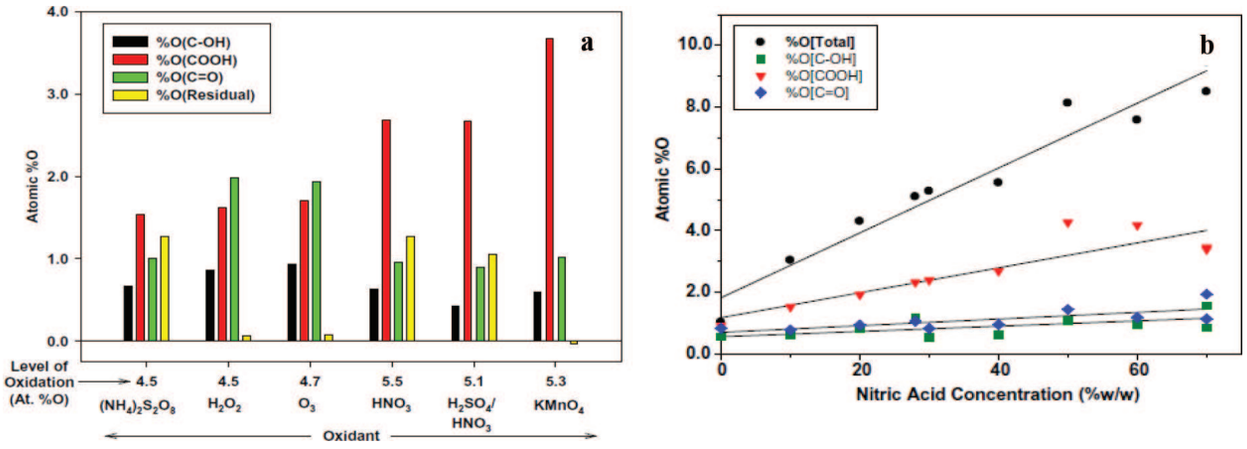


Figure 7. (a) Influence of the oxidant on the distribution of oxygen-containing functional groups, measured on MWCNTs. (b) Influence of % w/w HNO_3 on the level of oxidation, as well as the distribution of oxygen-containing functional groups. Reproduced with permission from Ref. [66]. Copyright 2011 Elsevier.

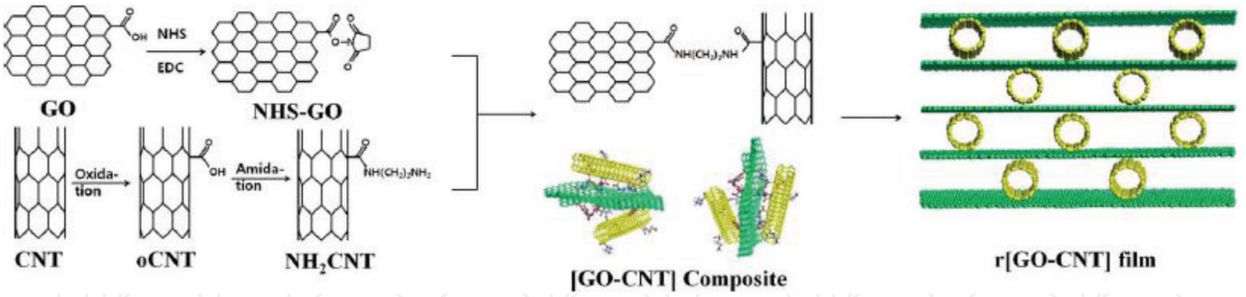


Figure 8. Synthesis scheme depicting the reaction between a GO layer and a CNT and a view of the fabricated r[GO-CNT] film. Reproduced with permission from Ref. [77]. Copyright 2013 Wiley-VCH Verlag.

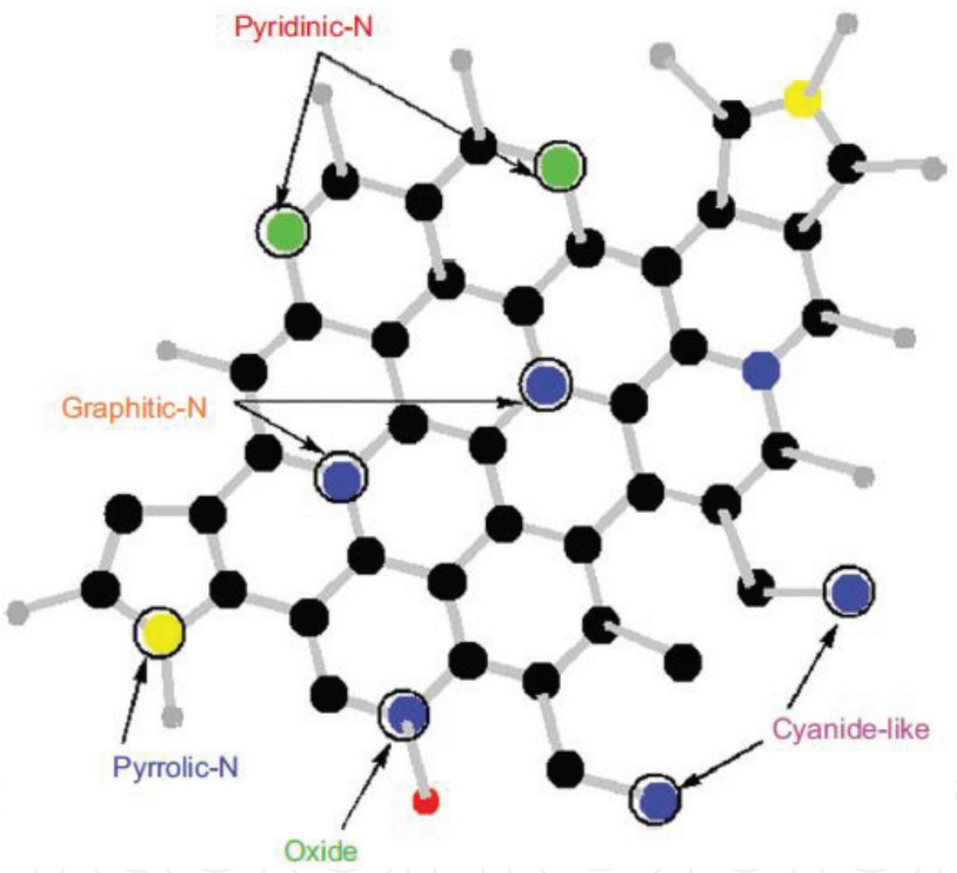


Figure 9. Schematic representation of N doping in the carbon nanomaterial. Reproduced with permission from Ref. [92]. Copyright 2013 De Gruyter.

(N substitution doping) to p-type conduction (B substitution of boron in lattice) [92]. The existence of heteroatoms significantly enhances the specific capacitance values of carbon materials by the pseudocapacitance effect [83, 88]. Gueon and co-workers found that nitrogen-doped carbon nanotubes have a specific capacitance three times higher compared to undoped carbon nanomaterial [79]. Nitrogen-containing pentagons (**Figure 9**) can induce strong bending of the nanotubes and affect the alignment of the CNT lattice, resulting in the creation of donor states near the Fermi level and hence the specific capacitance [79, 80]. The effect of B-doping on the

capacitance can be explained by modification of the space charge layer in carbon. The presence of boron leads to the enhancement of the space-charge layer capacitance through increasing the number of holes as a charge carrier or the DOS change at the Fermi level [88].

Thermal oxidation [88] or acid treatment [81] of doped CNTs improves the specific surface area and, as a consequence, the capacitance due to the tube end opening process. Coaxial supercapacitors based on hollow carbon nanotubes synthesized by chemical vapor deposition (CVD) exhibit high rate capacitance, long cycle life, and good flexibility [93].

The combination of synergetic effects in boron carbonitride nanotubes (BCNs) resulting from the combined co-doping of B and N in CNTs and their well-aligned vertical structure (VA) also provides a significant enhancement of specific capacitance performance. Vertically aligned boron carbonitride nanotubes (VA-BCNs) were synthesized on a Ni-Fe-coated SiO_2/Si substrate using the chemical vapor deposition method with a melamine diborate precursor. In this case, nitrogen atoms are bonded to carbons in both graphitic and pyridinic forms, and the resultant VA-BCNs show high specific capacitance (321 F g^{-1}) with an excellent rate capability and high durability compared to nonaligned BCNs (167 F g^{-1}) and undoped multi-walled carbon nanotubes (117 F g^{-1}) [94].

5. Hybrid materials of carbon nanotubes for energy storage

Carbon nanotubes are combined with carbon nanostructures, conducting polymers or metal oxides to form nanocomposite materials that display favorable electronic and mechanical properties [95]. Composites containing carbon nanotubes and an electroactive phase exhibit pseudocapacitive properties like metal oxide or conducting polymers and represent an important breakthrough for developing a new generation of supercapacitors based on three reasons: (i) the percolation of the electroactive particles is more efficient with nanotubes than with other carbon materials; (ii) the open mesoporous network formed by the entanglement of nanotubes allows ions to diffuse easily to the active surface of the composite components; and (iii) since the nanotubular materials are characterized by a high resiliency, the composite electrodes can easily adapt to the volumetric changes during the charging/discharging process, which improves drastically the cycling performance [22]. However, capacitors fabricated from inorganic pseudocapacitive materials typically suffer from higher internal resistance and lower lifetimes. The combination of carbon nanotubes with other carbon nanostructures results in an enhancement of energy density and lowering of the internal resistance [96].

5.1. Capacitors based on carbon nanotubes and different carbon nanostructures

The continued technological progress has led to the miniaturization of electronic devices with large volumetric energy densities. Most fabricated micro-supercapacitors based on carbon nanostructures exhibit excellent rate capabilities and stability, but low volumetric energy density. In general, increased volumetric energy density is obtained by the application of porous conductive electrode materials with sufficiently high packing density. The most popular electrode material is graphene sheets because of their ultrahigh surface area and excellent

conductivity as well as high mechanical and chemical stability. However, various interesting structures of graphene, such as one-dimensional fibers, two-dimensional films, and three-dimensional foams, in spite of high gravimetric capacitance exhibit poor volumetric performance due to strong intersheet π-π interactions, which, while increasing the packing density, do not allow high ion accessibility. To solve this problem, the synergistic effect of graphene and carbon nanotubes is utilized by the preparation of graphene-carbon nanotubes composites. In most cases, graphene oxide is used due to its hydrophilic character. However, its conductivity is low, and hence, it is doped by carbon nanotubes with very high conductivity [97]. Numerous synthesis methods have been used and a large family of hybrid composites based on graphene oxide and carbon nanotubes with the specific capacitance in the range of 120–222 F g^{-1} depending on the preparation procedure has been discovered [77, 98–104].

Ternary carbon composites containing carbon nanotubes, graphene, and activated carbon exhibit much better capacitance performance. Such systems have specific capacitances several times higher than those of their components (**Figure 10a**). The excellent electrochemical properties of ternary composites can be attributed to the high surface area and low equivalent series resistance, demonstrating that they improve the electrochemical performance for supercapacitor applications [97]. Among the multicomponent composites, a novel type of highly flexible and all-solid state supercapacitor utilizing hybrid aerogels exhibits promising properties (**Figure 10b**) [105].

Recently, much attention has been paid to 3D pillared vertically aligned carbon nanotubes (VACNTs)—graphene architectures with a controllable nanotube length (PL)/intertube distance (MIPD) as electrode materials for energy-related devices (**Figure 11**). Theoretical

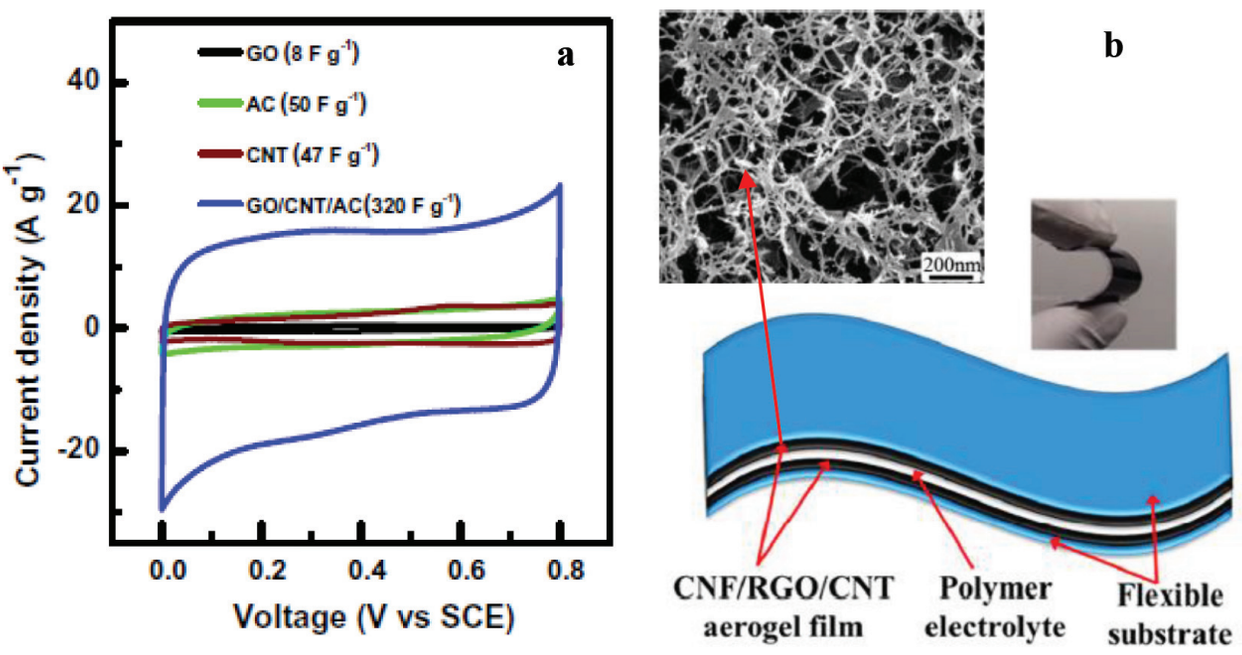


Figure 10. (a) Cyclic voltammograms of different carbon particles (GO, CNT, AC) and their composite recorded in 1 M H_2SO_4. Reproduced with permission from Ref. [97]. Copyright 2017 Elsevier. (b) Schematic diagram of the all-solid-state supercapacitor where the polymer-gel electrolyte serves as the electrolyte and the separator. Insets show the flexibility of the device and SEM image of aerogel hybrid film. Reproduced with permission from Ref. [105]. Copyright 2015 American Chemical Society.

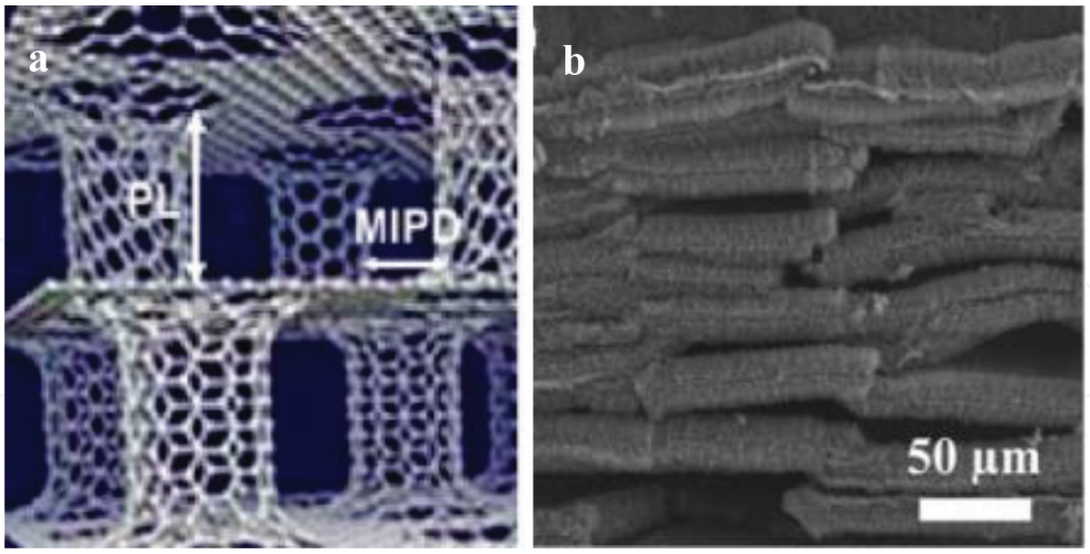


Figure 11. (a) Schematic diagram of a 3D pillared VACNT graphene nanostructure. (b) SEM images of the 3D pillared VACNT graphene architectures. Reproduced with permission from Ref. [102]. Copyright 2011 American Chemical Society.

studies have indicated that 3D pillared architectures, consisting of parallel graphene layers supported by vertically aligned carbon nanotubes (VACNTs) in between, possess desirable out-of-plane transport and mechanical properties while maintaining the excellent properties of their building blocks [102].

An ultrafast compact capacitor based on free-standing, flexible, and highly conducting films consisting of stacked nanoporous graphene layers pillared with single-walled carbon nanotubes (SWCNTs) was obtained by Pham and co-workers [109]. **Figure 12** shows the carbon nanotube (CNT)-bridged graphene 3D building blocks via the Coulombic interaction between positively charged CNTs grafted by cationic surfactants and negatively charged graphene oxide sheets, followed by KOH activation. Such a structure enhances the accessible surface area and allows for fast ion diffusion. Due to this unique 3D porous structure, a remarkable electrochemical performance with a maximum capacitance as high as 199 F g^{-1} was achieved [99].

The electrodeposition of nickel hydroxide on such hybrid nanostructures results in pseudocapacitance due to the Faradaic reaction associated with the $Ni(OH)_2$ coating. The specific capacitance is increased from 110 F g^{-1} obtained for VACNT-graphene architectures to 1384 F g^{-1} for $Ni(OH)_2$-coated VACNT graphene electrode [102].

Pristine carbon nanotubes usually provide unsatisfactory specific capacitance due to their relatively low surface area, which still needs to be enhanced. Composites containing hollow carbon nanospheres anchored to the surface of carbon nanotubes, CNT-HCS, (**Figure 13**) are synthesized via the hard template method following this trend. Disordered pores (~2 nm) observed in the shells of the carbon spheres facilitate the penetration of electrolyte ions and favor the rapid charge propagation during the charge/discharge process [106]. The electrochemical performance of capacitors based on the composites of carbon nanotubes and different carbon nanostructures are collected in **Table 2**.

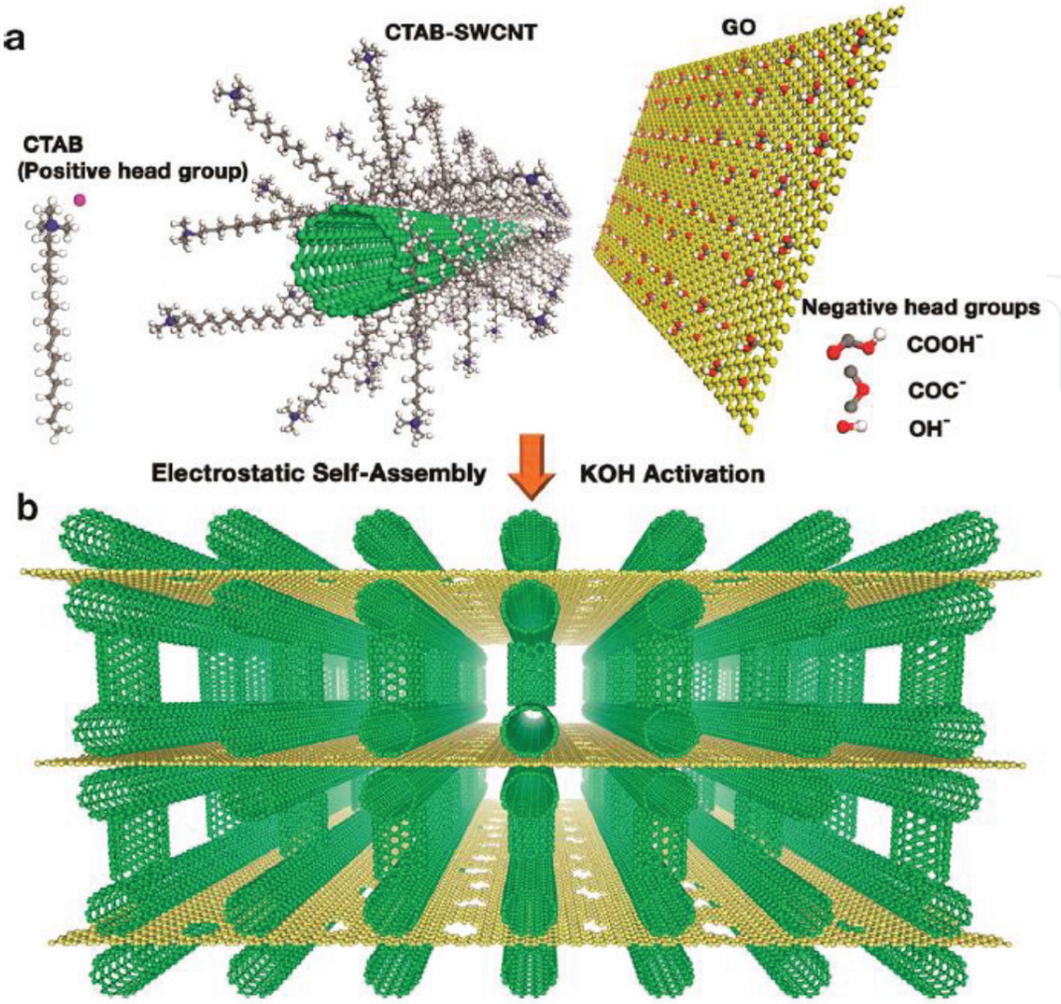


Figure 12. Schematic for fabricating the ac-Gr/SWCNT hybrid nanostructure. (a) The CTAB-grafted SWCNTs are positively charged, and the GO layers are negatively charged due to their functional groups. (b) Schematic of the 3D SWCNT-bridged graphene block. Reproduced with permission from Ref. [99]. Copyright 2015 American Chemical Society.

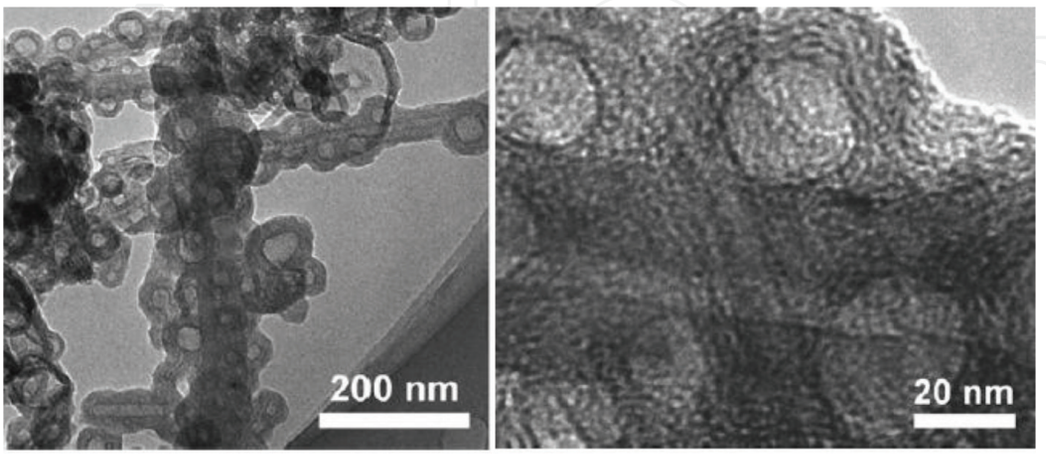


Figure 13. TEM images of CNT-HCS composite with different magnifications. Reproduced with permission from Ref. [106]. Copyright 2013 Elsevier.

Composite	Specific capacitance ($F\ g^{-1}$)	Capacitance	Power density	Energy density	Capacitance retention	Reference
CNF/rGO/CNT	252	216 mF cm^{-2}	9.5 mW cm^{-2}	28.4 mW cm^{-2}	99.5%	[105]
HCS/CNT	201.5	30.1 F cm^{-3}	11.8 kW kg^{-1}	11.3 Wh kg^{-1}	90%	[106]
SWCNT/GO	–	305 F cm^{-3}	1.085 mW cm^{-3}	6.3 mWh cm^{-3}	93%	[98]
SWCNT/GO	199	211 mF cm^{-3}	400 kW kg^{-1}	110.6 Wh kg^{-1}	98.2%	[99]
GO/CNT/AC	636	–	550 W kg^{-1}	16 Wh kg^{-1}	99.8%	[97]
Graphene/CNT	–	3.93 mF cm^{-3}	115 W cm^{-3}	2.42 mWh cm^{-3}	86%	[107]
SWCNT/CNH	43	–	3.50 kW kg^{-1}	6.03 Wh kg^{-1}	–	[96]

CNF, carbon nanofibril; rGO, reduced graphene oxide; HCS, hollow carbon spheres; AC, activated carbon; CNH, carbon nanohorns.

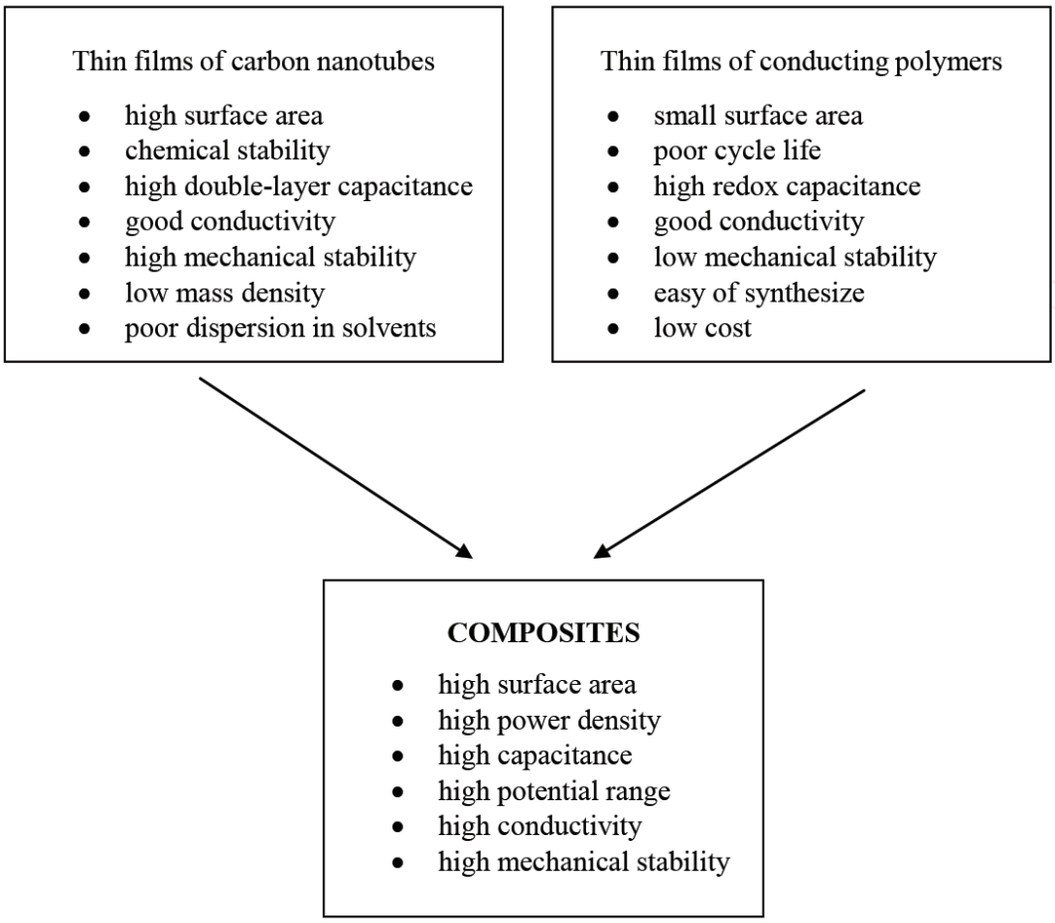
Table 2. Selected values of electrochemical performance of capacitors based on composites of carbon nanotubes and different carbon nanostructures.

5.2. Capacitors based on carbon nanotubes and conducting polymers

Composites of conducting polymers with carbon nanotubes are promising electrode materials as supercapacitors because of their good conductivity, high surface area, and excellent ability to store energy [7, 108–117]. The composites combine the large pseudocapacitance of conducting polymers with the fast charging/discharging double-layer capacitance and excellent mechanical properties of carbon nanotubes [118]. In **Scheme 1**, the properties of carbon nanostructures, conducting polymers, and the composite materials are compared.

CNTs/conducting polymer composites can be prepared by chemical [7, 13, 108, 113, 114, 118–121] or electrochemical [14, 16, 95, 110–112, 115, 118, 119, 121] polymerization. This process can be carried out on pristine CNTs or CNTs modified with functional groups or heteroatoms as a non-covalent deposition polymeric layer onto the nanotubular surface or covalent functionalization of carbon walls by polymeric chains. In the case of covalent functionalization, two approaches can be used: first, when the monomer is attached to CNTs and, in the next step, when it is polymerized via chemical or electrochemical methods [122, 123], and second, in situ chemical polymerization in the presence of dopant and self-organizing agent [7, 124]. For noncovalently modified CNTs with polymers, several strategies have been developed. Currently, they involve physical mixing in solution, in situ polymerization of monomers in the presence of CNTs, surfactant- and template-assisted processing of composites, chemical functionalization of the incorporated nanotubular material, and electrochemical polymerization carried out on an electrode surface modified with carbon nanostructures or electrochemical co-polymerization [118, 125, 126]. In **Figure 14**, exemplary procedures of nanocomposites formation are schematically presented. In most cases, electrochemical synthesis provides homogenous films [16, 118]. However, chemical polymerization generates polymers with a more porous morphology [118, 127].

Figure 15 shows the SEM images of SWCNTs/PPy composites prepared by deposition of PPy on pristine SWCNTs (**Figure 15a**) and on functionalized SWCNTs (**Figure 15b**). In the case of functionalized SWCNTs, an incomplete coverage of SWCNTs by PPy is observed [14].



Scheme 1. Properties of carbon nanostructures, conducting polymers and the composite materials.

A comparison of the electrochemical behavior of PPy, SWCNTs/PPy, and PPy/functionalized SWCNTs composites is shown in **Figure 16**. PPy films at a low scan rate exhibits a rectangular shape, which indicates an ideal capacitance behavior, while for higher scan rates, the curves are not rectangle-shaped, which indicates resistance-like electrochemical behavior due to the slow doping/dedoping process of the compact PPy layer. However, a pseudorectangular shape of the recorded cyclic voltammograms in all of the scan rates (up to 200 $mV \cdot s^{-1}$) is observed for the composites based on pristine SWCNTs (**Figure 16b**) and functionalized SWCNTs (**Figure 16c**). The PPy/functionalized SWCNTs composite exhibits also better capacitance properties compared to PPy/SWCNTs and pristine PPy (**Figure 17**).

Another way to form composites based on CNTs and conducting polymers is covalent functionalization of CNTs with monomeric units. In the next step, the composite is obtained by copolymerization of the monomer with monomer units grafted on the CNTs surface using controlled potential electrolysis. **Figure 18a** shows the electrochemical behavior of polypyrrole/CNTs (PPY/CNTs) composites obtained at different charge densities. The broad peaks observed in the voltammograms are related to the redox process within the polypyrrole component. The composites exhibit higher currents than the pure polymeric material due to higher porosity (**Figure 18c**) compared to pristine PPy (**Figure 18b**) and as a consequence of the higher capacitance of PPy/CNTs [122].

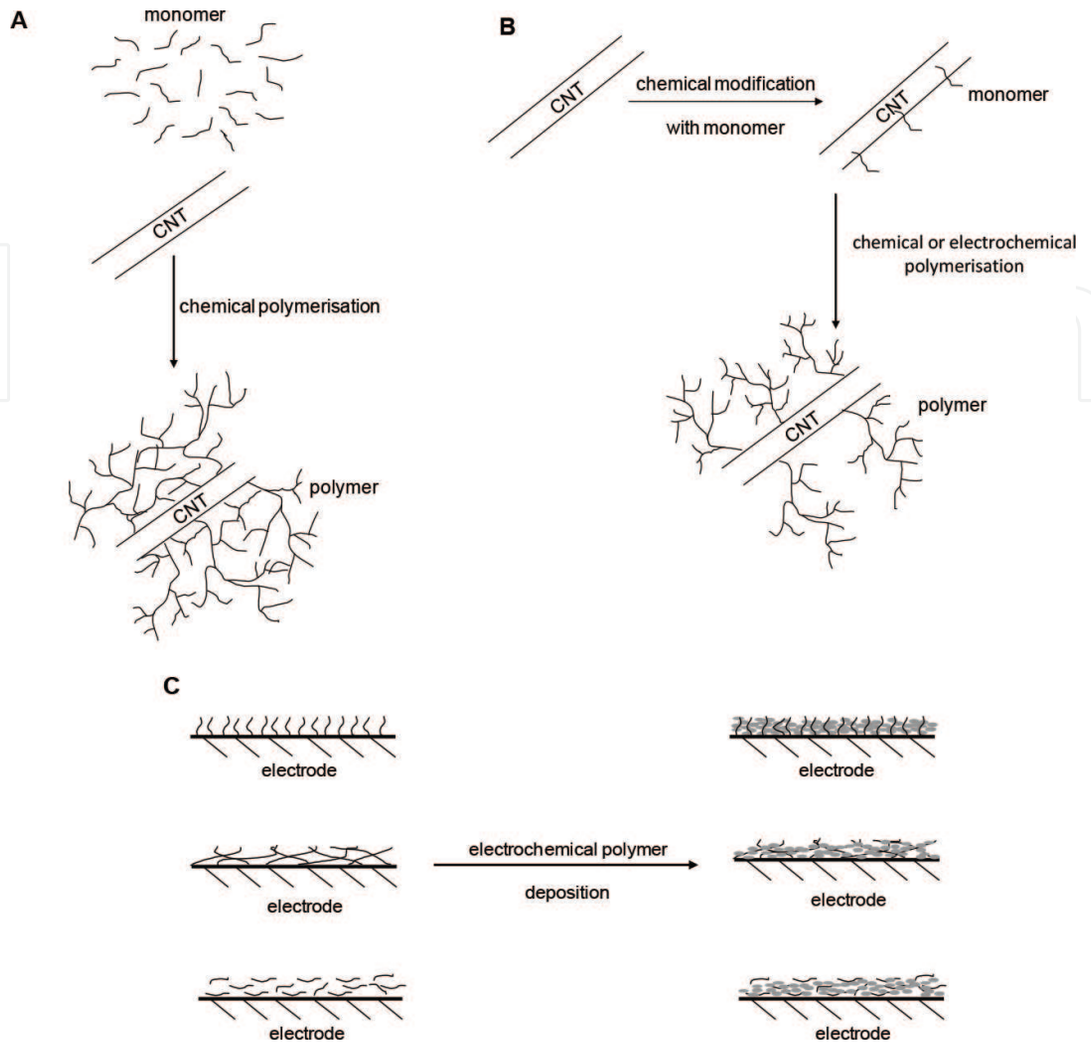


Figure 14. A schematic representation of exemplary procedures of nanocomposites formation for electrochemical measurements. (A) *in situ* chemical polymerization, (B) chemical polymerization of monomers attached to carbon nanostructure, (C) electrochemical polymerization carried out on an electrode surface modified with carbon nanostructures.

The presence of CNT components results in an increase in the practical range of electrical conductivity of the material. For example, C_{60}-Pd polymer demonstrates pseudocapacitance behavior due to faradaic reduction of C_{60} in the negative potential range (**Figure 19a**); at potentials lower than this threshold, the material exhibits very high resistance. In the CNTs/C_{60}Pd composite, the potential range of electrochemical activity increases. At negative potentials, the pseudocapacitive behavior of the polymeric component is still observed. However, the material also shows double-layer capacitance, mainly attributed to the conducting CNTs, in a less negative potential range (**Figure 19b**). Composites based on C_{60}-Pd polymers and SWCNTs or MWCNTs exhibit specific capacitance equal to 994 F g^{-1} or 758 F g^{-1} for SWCNTs/C_{60}-Pd and MWCNTs/C_{60}-Pd composites, respectively [119].

A very promising energy storage behavior was reported for 3D structure composite based on aligned carbon nanotubes (ACNTs) offering a large specific surface area, superior electronic transfer ability through individual nanotubes, and chemical inertness [95]. Three-dimensional

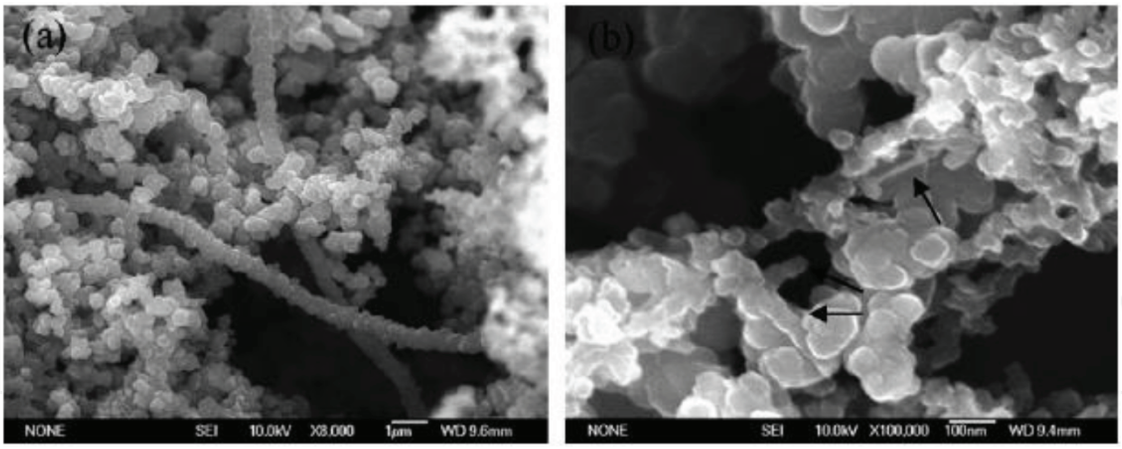


Figure 15. SEM images of (a) SWCNTs/PPy and (b) functionalized SWCNTs/PPy. Reproduced with permission from Ref. [14]. Copyright 2007 Elsevier.

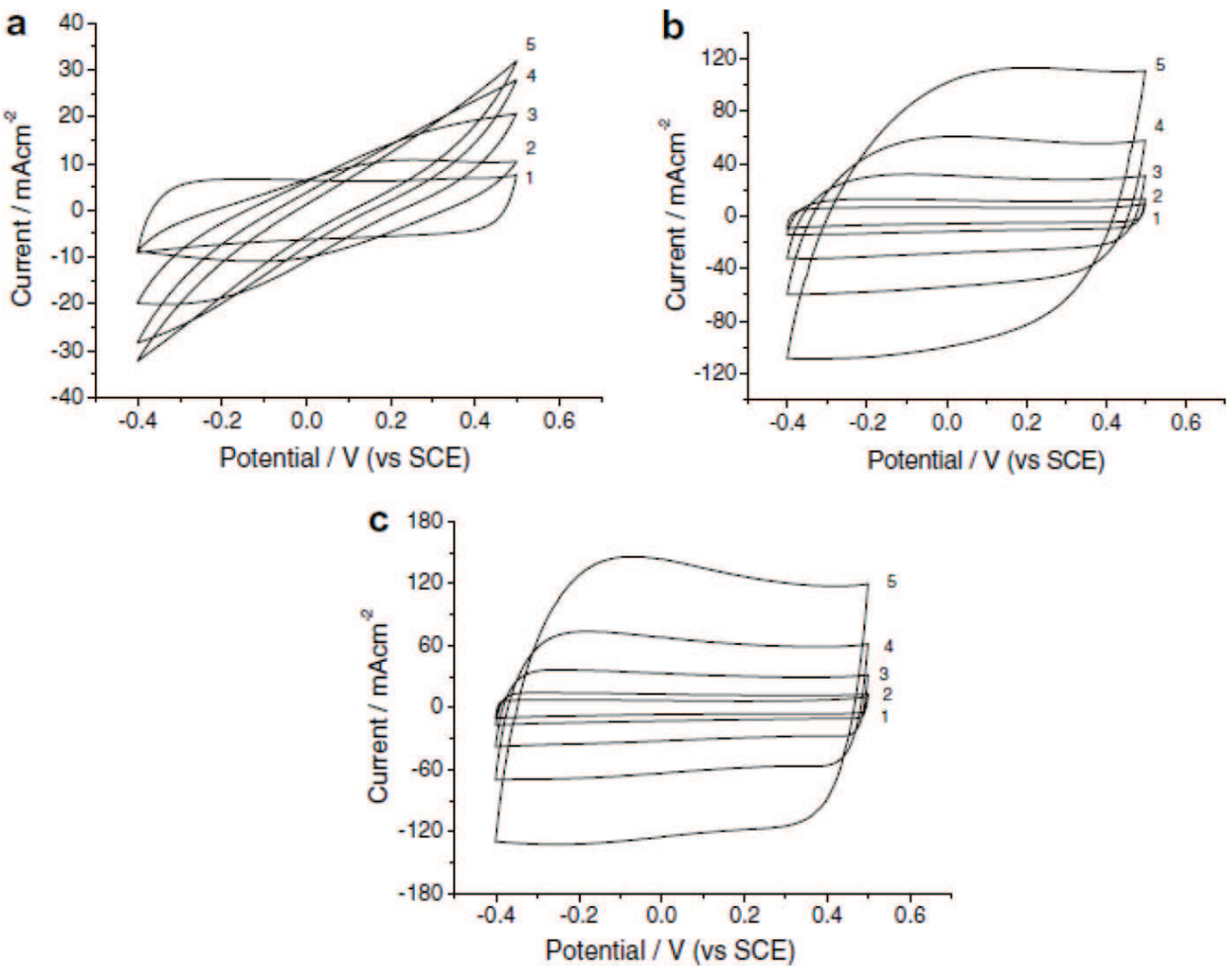


Figure 16. Cyclic voltammograms recorded for pristine (a) PPy, (b) SWCNTs/PPy and (c) functionalized SWCNTs/PPy composite films at different scan rates: (1) 10, (2) 20, (3) 50, (4) 100 (5) 200 mV s^{-1} in 1M KCl solution. Reproduced with permission from Ref. [14]. Copyright 2007 Elsevier.

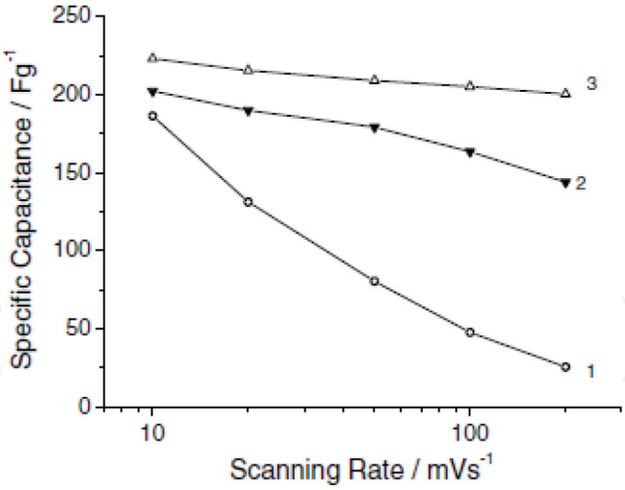


Figure 17. The specific capacitance of (1) pristine PPy film, (2) PPy/SWCNTs composite film and (3) PPy/functionalized SWCNTs composite film at various scanning rates solution. Reproduced with permission from Ref. [14]. Copyright 2007 Elsevier.

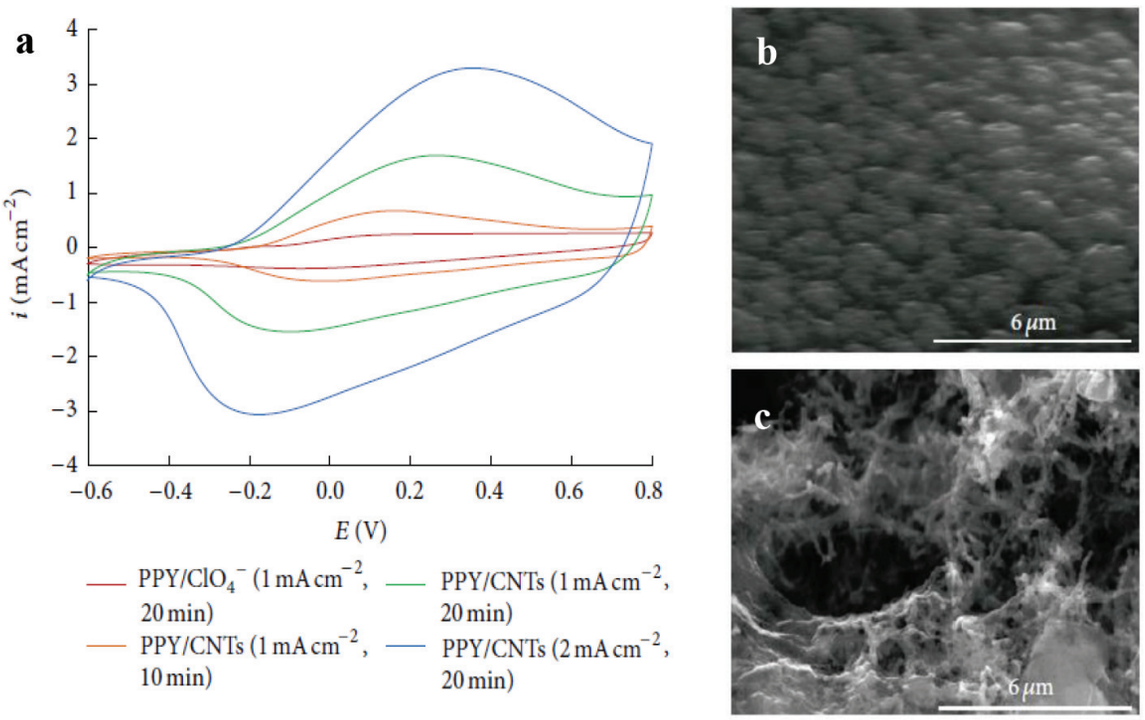


Figure 18. (a) Cyclic voltammograms recorded in propylene carbonate containing 0.1 M $LiClO_4$ for the PPY/CNTs composite films and pure polypyrrole obtained in galvanostatic conditions at different charge densities. SEM images of (b) PPY and (c) PPY/CNTs composite. Reproduced with permission from Ref. [122]. Copyright 2013 Hindawi.

hybrid composite material composed of 2D fish scale-like polyaniline nanosheet arrays on graphene oxide sheets and carbon nanotubes exhibiting high specific capacitance of 589 F g^{-1} compared to 397 F g^{-1} for pristine PANI was also investigated [18]. Moreover, ternary composite systems containing carbon nanotubes, graphene, and conducting polymers were also

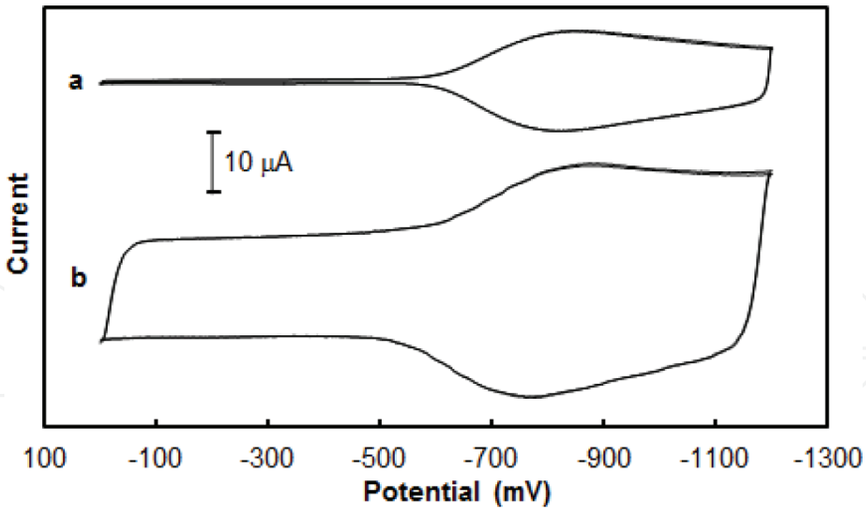


Figure 19. Cyclic voltammogram of (a) C_{60}-Pd polymer and (b) MWCNT/C_{60}-Pd composite at 100 mV/s in acetonitrile containing 0.1 M $(n\text{-}C_4H_9)_4NClO_4$. Reproduced with permission from Ref. [119]. Copyright 2013 Elsevier.

Carbon nanostructure	Composite	Specific capacitance (F g^{-1})	Reference
SWCNT	SWCNT/PPy	200	[14]
	SWCNT/PPy	305	[132]
	SWCNT/PANI	247	[129]
	SWCNT/PANI	485	[111]
	SWCNT/PANI	707	[133]
	SWCNT/PANI	1000	[134]
	SWCNT/C_{60}-Pd	994	[119]
MWCNT	MWCNT/PANI	50	[120]
	MWCNT/PANI	500	[112]
	MWCNT/PANI	670	[130]
	MWCNT/PPy	70	[120]
	MWCNT/PPy	268	[7]
	MWCNT/PPy	243	[16]
	MWCNT/PPy	506	[130]
	MWCNT/PPy	554	[126]
	MWCNT/C_{60}-Pd	758	[119]
	MWCNT/PEDOT:PSS	30	[120]
	MWCNT/PEDOT	237	[126]
Graphene/CNT	Graphene/CNT/PPy	453	[132]
GO/CNT	GO/CNT/PANI	413	[18]

Table 3. Capacitance properties of selected composites containing carbon nanostructure and conducting polymer.

investigated [128, 131]. The capacitance properties of selected composites of carbon nanotubes and conducting polymers are reported in **Table 3**.

5.3. Composites containing carbon nanotubes and metal oxides

To overcome the low energy density of supercapacitors, pseudocapacitors based on transition metal oxides have been developed [135]. The most promising among them is manganese dioxide MnO_2 because of its low cost, environmental compatibility, natural abundance, high energy density, and excellent capacitive performance in aqueous electrolytes [32, 135–143]. In aqueous electrolytes, the charging mechanism of MnO_2 may be described by the following reaction:

$$MnO_2 + M^+ + e \rightleftharpoons MnOOM \tag{10}$$

where M represents protons (H^+) and/or alkali cations such as K^+, Na^+, and Li^+. The charge storage is based either on the adsorption of cations at the surface of the electrode material or on the intercalation of cations in the bulk of the electrode material. However, the reported specific capacitance values for the various structures of MnO_2 electrodes are still far from the theoretical one [144], which may be attributed to the intrinsically poor electronic conductivity of MnO_2. To improve the capacitive performance of MnO_2, composites with carbon nanotubes characterized by high conductivity and high surface area are formed [143]. The surface morphology of CNTs/MnO_2 composite and its components is shown in **Figure 20**. **Figure 21a**

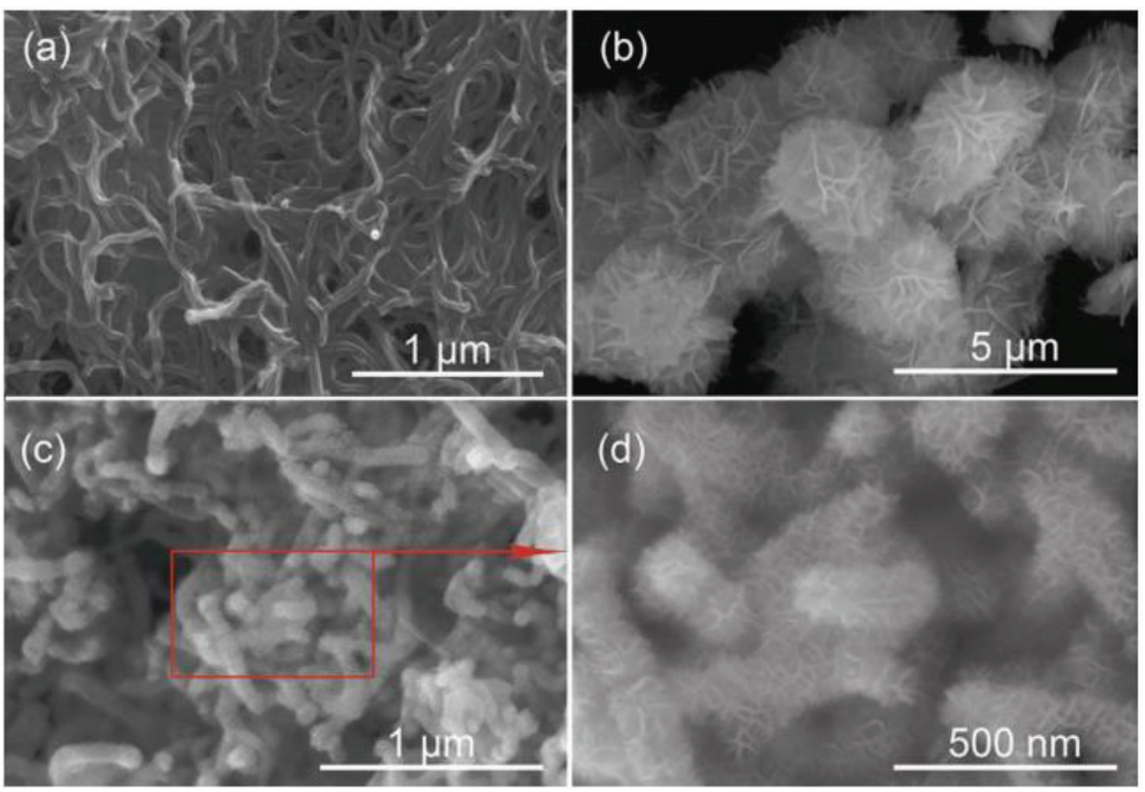


Figure 20. SEM images of (a) pristine CNTs, (b) flower-like MnO_2, (c and d) MnO2/CNT nanocomposite. Reproduced with permission from Ref. [143]. Copyright 2012 Springer.

shows the comparison of the specific capacitances of pristine CNTs, pure MnO_2 and a composite where CNTs are decorated by MnO_2 nanoflakes. CNTs exhibit the best rate capability, but their capacitance is the lowest due to the charge storage mechanism typical for double layer capacitors. The low rate capability of MnO_2 is associated with its poor electronic conductivity and low specific surface area. The combination of MnO_2 and CNTs provides the formation of a MnO_2/CNT nanocomposite exhibiting good rate capability and high specific capacitance. The results obtained by electrochemical impedance spectroscopy (**Figure 21b**) show that the MnO_2/CNT composite has a much lower diffusive resistance compared to pure MnO_2 because the slope of the low-frequency straight line representing the diffusive resistance of electrolyte in the electrode pores and cation diffusion in the host materials is similar to the line obtained for the CNTs but much larger than that of the pure MnO_2. Additionally, the charge transfer resistance, R_{ct}, localized between R_{ct} observed for CNTs and MnO_2 suggests high specific surface area for the unique hierarchy architecture of the CNTs/MnO_2 composite where the 3D electron path network constructed by the CNT cores and the nanoporous sheath composed of tiny MnO_2 nanoflakes facilitate fast electron and ion transport [143].

Apart from MnO_2 [9, 17, 135, 136, 143, 145–150], other metal oxides such as hydrous RuO_2 [151–154], NiO [155, 156], Fe_2O_3 [157], Co_3O_4 [158], MoO_3 [10, 135, 159], V_2O_5 [160], CeO_2 [161], and $NiCo_2O_4$ [162], In_2O_3 [149], TiO_2 [153], SnO_2 [153], and $(Sn + Mn)O_x$ [163] are also utilized for the formation of composite electrodes. In the case of the expensive hydrous ruthenium oxide ($RuO_2 \cdot xH_2O$) exhibiting excellent capacitance performance [164], relatively high conductivity and exceptional electrochemical reversibility, composites based on carbon nanotubes are formed to reduce its cost and enhance its capacitance properties [151–154].

So far, most studies have been devoted to the deposition of the pseudocapacitance phase onto carbon nanostructures. However, it is also possible to encapsulate metal oxides with CNTs. The MnO_2@CNTs material exhibits a significantly higher specific capacitance compared to MnO_2 outside of carbon nanotubes (**Table 4**). The difference in the electrochemical behaviors of MnO_2 enclosed in CNTs (MnO_2-*in*-CNT) and MnO_2 deposited on CNTs surface (MnO_2-*out*-CNT) is

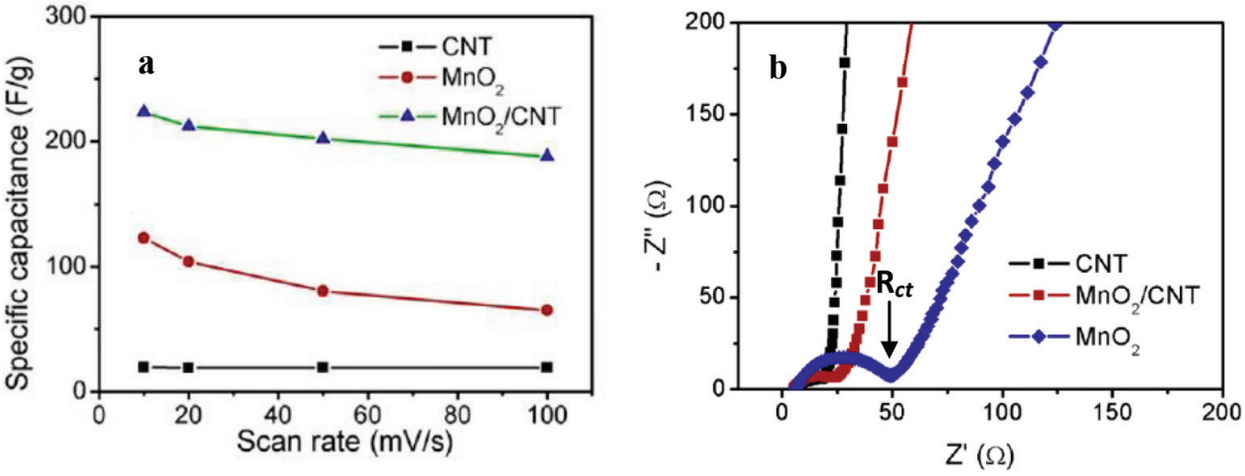


Figure 21. (a) Dependence of specific capacitance on the sweep rate and (b) Nyquist plots for pristine CNTs, pure MnO_2, and MnO_2/CNT nanocomposite electrodes. Reproduced with permission from Ref. [143]. Copyright 2012 Springer.

shown in **Figure 22**. In such a system, the former stores charge electrostatically, and the latter stores charge in virtue of highly reversible redox reactions of MnO_2. The broad anodic peak at 0.72–0.84 and 0.59–0.80 V for the samples MnO_2-*in*-CNT and MnO_2-*out*-CNT, respectively, is associated with the oxidation process of Mn(III) to Mn(IV) according to the reaction:

$$MnO_2 + 4H^+ + e \rightleftharpoons Mn^{3+} + 2H_2O \quad (11)$$

The oxidation potential of MnO_2-*in*-CNT is shifted to higher values compared to that of MnO_2-*out*-CNT because CNT-confined manganese oxide particles can easily form lower oxidation-state species compared to exterior particles. The double-layer capacitance of MnO_2-*in*-CNT is increased due to both the formation of Mn(IV)/Mn(III) redox couple and the desolvation of electrolyte ions inside the channels of CNTs blocked by MnO_2 nanoparticles [9].

Carbon nanostructure	Composite	Specific capacitance (F g^{-1})	Reference
SWCNT	SWCNT/In_2O_3	201	[149]
	SWCNT/MnO_2	253	[149]
	SWCNT/NiC_2O_4	1642	[162]
MWCNT	MWCNT/MoO_3	70	[159]
	MWCNT/MoO_3	178	[10]
	MWCNT/MnO_2	250	[147]
	MWCNT/MnO_2	944	[145]
	MWCNT/RuO_2	138	[153]
	MWCNT/RuO_2	953	[151]
	MWCNT/RuO_2	1050	[154]
	MWCNT/SnO_2	93	[153]
	MWCNT/NiO	160	[155]
	MWCNT/NiO	523	[156]
	MWCNT/TiO_2	160	[153]
	MWCNT/Co_3O_4	201	[158]
	MWCNT/(Sn+Mn)O_x	337	[163]
	MWCNT/MC/MnO_2	351	[165]
	MWCNT@MnO_2@PPy	273	[12]
CNT	MnO_2-*out*-CNT	790	[9]
	MnO_2-*in*-CNT	1250	[9]
	CNT/MnO_2	199	[150]
	CNT/MnO_2	214	[148]

MC, mesoporous carbon.

Table 4. Capacitance properties of selected composites containing carbon nanostructure and metal oxide.

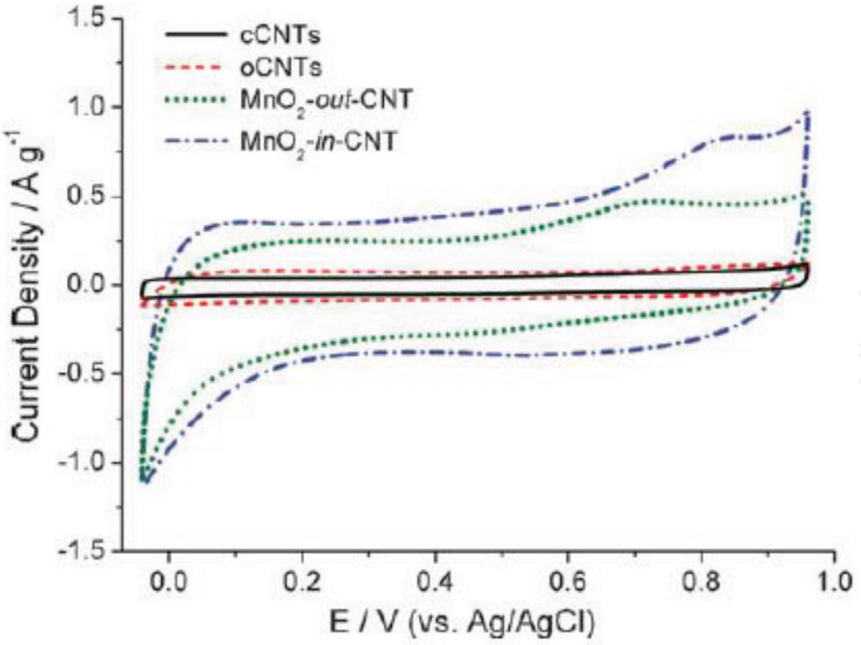


Figure 22. Cyclic voltammogram of blank cCNTs (CNTS with closed tips), oCNTs (CNTs with open tips), MnO_2-*out*-CNT and MnO_2-*in*-CNT in 1 M Na_2SO_4. Reproduced with permission from Ref. [9]. Copyright 2010 The Royal Society of Chemistry.

Moreover, hybrid materials such as carbon nanotubes/mesoporous carbon/MnO_2 [165], carbon nanotubes/3D graphene/MnO_2 [11], and carbon nanotube@MnO_2@polypyrrole [12] have been developed. **Table 4** shows the capacitance of exemplary composites based on carbon nanostructures and metal oxides.

5.4. Capacitors based on carbon nanotubes and carbon gels

Recently, much attention has been paid to novel ultralight mesoporous carbon materials named carbon aerogels (CAGs) [15, 166–173] or carbon xerogels [8, 174–178]. Carbon aerogels exhibit many interesting properties such as low mass density, continuous porosity, high surface area, and high electrical conductivity. These properties are characteristic of the aerogel microstructure, which is a network of interconnected primary particles with diameters between 3 and 25 nm (**Figure 23a**). However, aerogels consist of agglomerate particles linked by covalent bridges with a ladder structure. The contact between these particles and the space due to the pores unfortunately introduces a high internal resistance within the aerogel which limits their practical applications. To overcome this problem, composites of carbon aerogels with carbon nanotubes are formed (**Figure 23b**). CNTs with their high electrical conductivity work as nanopathways for charges and thus improve the intrinsic conductivity of the CAGs and their mechanical integrity as well [166].

The main problem in the case of composite formation is the agglomeration of carbon nanotubes within the CAG's pore network. A very useful approach for the formation of binderless carbon nanotube aerogel (CNAG) composites proposed by Bordjiba and co-workers [166, 172] provides a significant improvement in the dispersion of carbon nanotubes within the aerogel matrix and

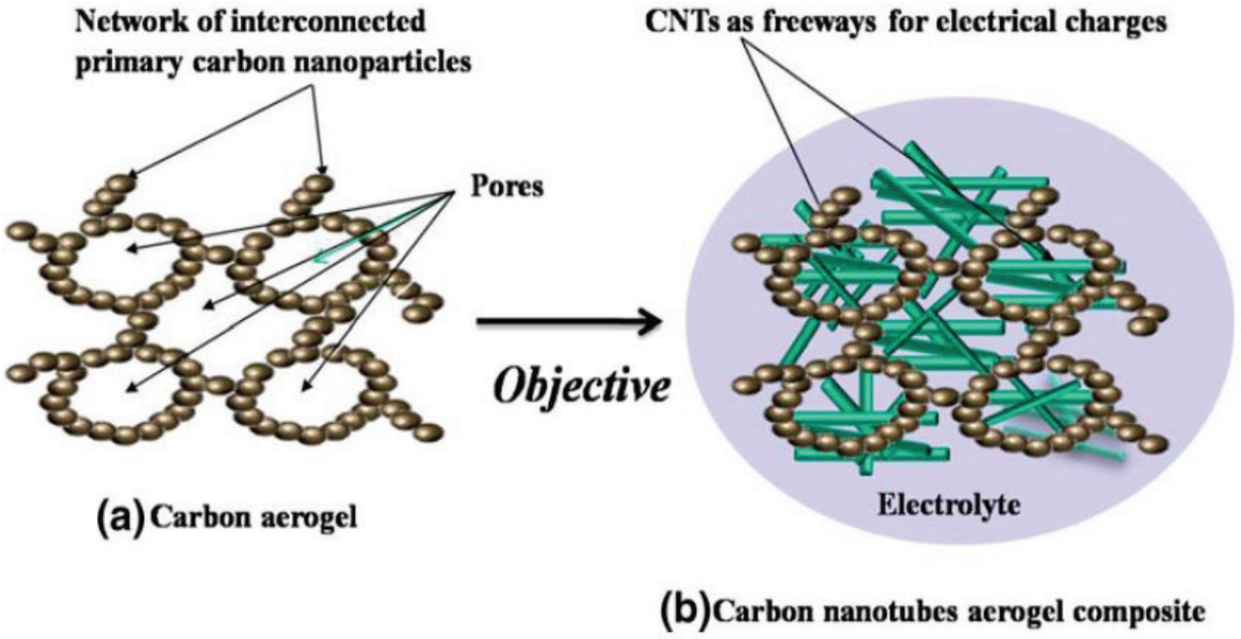


Figure 23. (a) Representation of the carbon aerogel internal structure and (b) targeted carbon nanotube aerogel composite. Reproduced with permission from Ref. [166]. Copyright 2011 Springer.

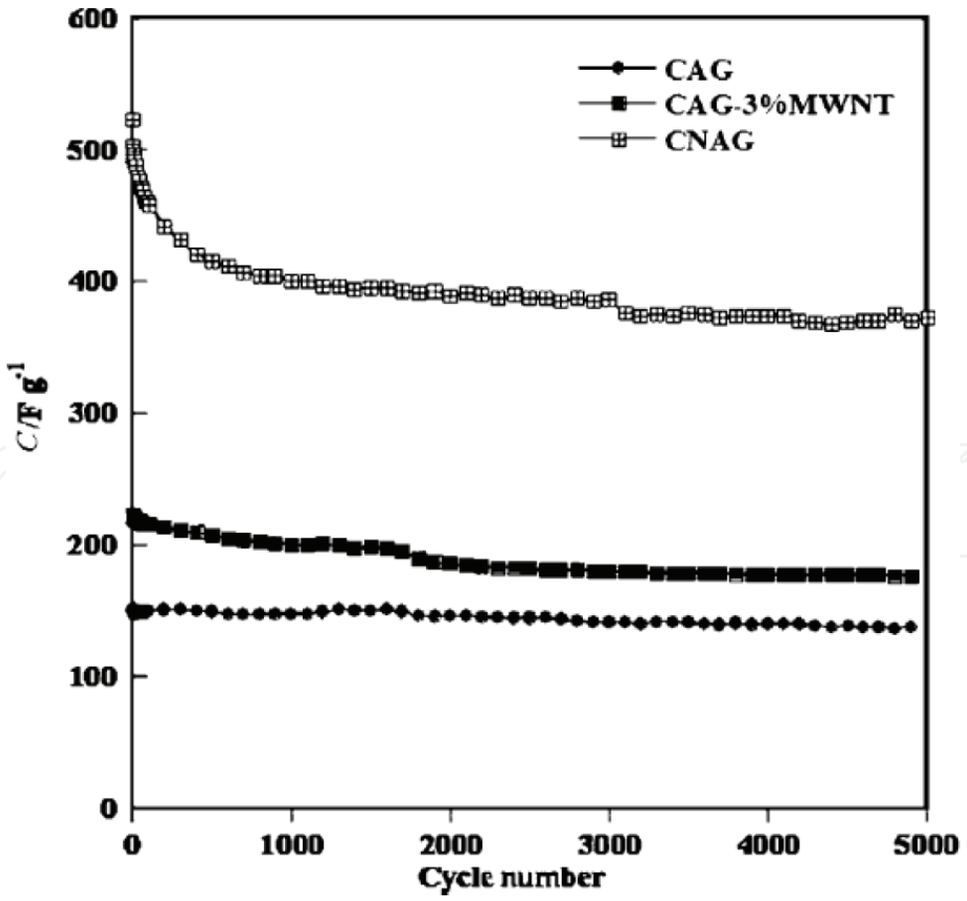


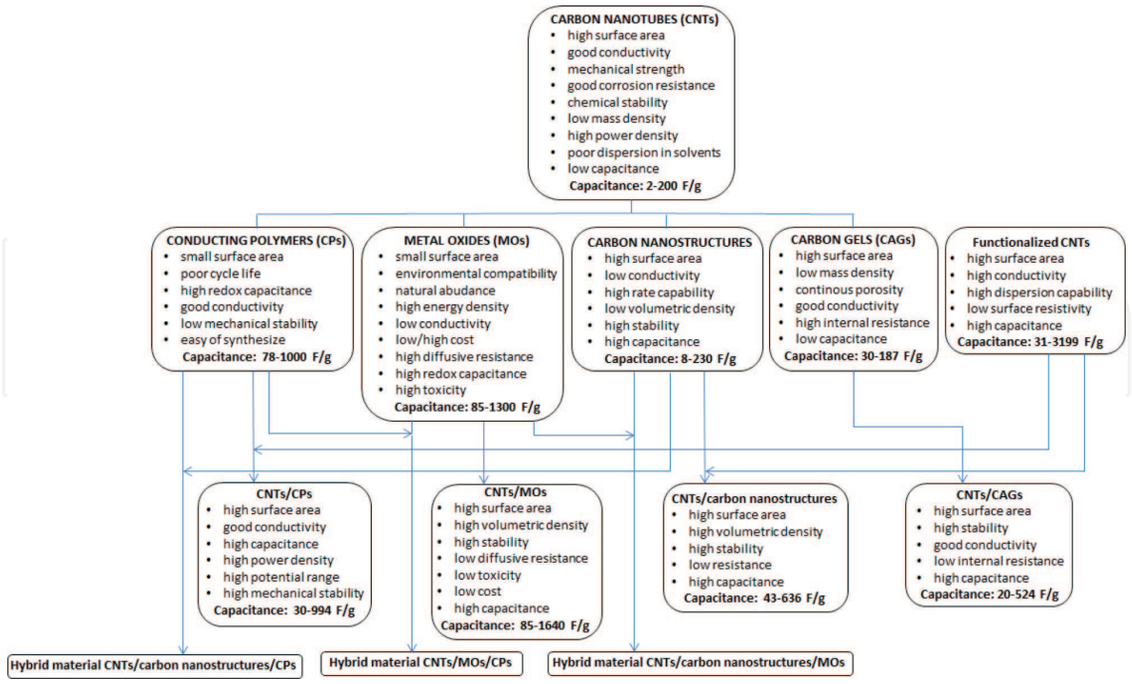
Figure 24. Cycle life of CAG, CAG-3%MWNT and CNAG composites in 5 M KOH. Reproduced with permission from Ref. [166]. Copyright 2011 Springer.

better interfacial coating. The CNAG material was prepared by a molding procedure, i.e., synthesis by a chemical vapor deposition method to grow carbon nanotubes directly onto a microfibrous carbon paper substrate. In the next step, the carbon aerogel was synthesized on the carbon nanotubes. The key feature of this method is eliminating the need to control the carbon nanotube concentration, which permits optimized dispersion processes to reinforce the aerogel's networks. The CNAG electrode delivered very high specific capacitances equal to 524 F g^{-1}. Furthermore, better integration of carbon nanotubes in the matrix of carbon aerogel improves its resistance to attack by the electrolyte and assures excellent cycle life. Such a system exhibits significantly higher capacitance and stability compared to the composite processed from the dispersion of its components in liquid phase, CAG-3%MWNT (**Figure 24**). Apart from the capacitance performance, binderless nanostructured electrodes also reduce the cost of manufacturing and avoid complicated interferences of the binders and conductivity enhancers used in practical electrodes [166, 172].

The research on CNTs and carbon aerogel composites is relatively new because their very promising properties are still being developed. The composites that have been prepared so far exhibit excellent capacitance properties [8, 166, 170–172, 177, 178]. A large progress in this area of study can be expected in the near future.

6. Conclusion and outlook

Supercapacitors have been developed to close the gap between conventional capacitors and batteries because of their high energy density and power density. In the development of electrochemical capacitors, carbon nanotubes and their composites have been widely used as electrode materials. The specific capacitance of pristine carbon nanotubes is relatively low and depends on many factors such as the kind of carbon nanotubular material, i.e., single- or multi-walled, its orientation, i.e., open or closed tips, surface area, synthesis method, solvent and supporting electrolyte. Compared with pristine carbon nanotubes, functionalized carbon nanotubes by heteroatoms or functional groups attached to nanotubes walls are expected to display improved capacitance performance. The formation of composites based on carbon nanotubes provides especially high surface area due to the presence of CNTs which is very important in the case of storage systems. Moreover, it enhances the properties of both the carbon nanotubes and the second component. Apart from the improvement in capacitance performance, the addition of CNTs reduces cost compared to metal oxide, improves stability compared to conducting polymers which exhibit rapid degradation in performance after repetitive cycles because of their swelling and shrinking, and improves the poor volumetric performance of supercapacitors based on other carbon nanomaterials. The capacitance properties strongly depend on the localization of the redox system. It was found that encapsulation of the redox phase inside a nanotubular material provides higher specific capacitance compared to a redox system situated outside of carbon nanotubes. Recently, a new generation of cheap storage systems based on mesoporous carbon aerogels was discovered. However, in this case, there is a problem with the non-homogeneous spread of carbon nanotubes within the whole network of carbon aerogel. Hence, increasing



Scheme 2. Comparison of properties of composites based on carbon nanotubes and their components.

attention is needed to solve this problem because this system could be the future for storage devices. A very promising system seems to be the attachment of redox-active nanoparticles to carbon nanotubes. Compared to bulk materials, they exhibit unique properties arising from their nanoscale sizes, such as high electrical conductivity, large surface area, short path lengths for the transport of ions and high electrochemical activity. Ultrafast compact capacitors based on 3D hybrid structures that increase the accessible surface area and allow fast ion diffusion are introducing a new class of electrode materials for storage devices. A comparison of the properties of composites based on carbon nanotubes and their components is summarized in **Scheme 2**.

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Author details

Emilia Grądzka* and Krzysztof Winkler

*Address all correspondence to: emilia@uwb.edu.pl

Institute of Chemistry, University of Bialystok, Poland

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