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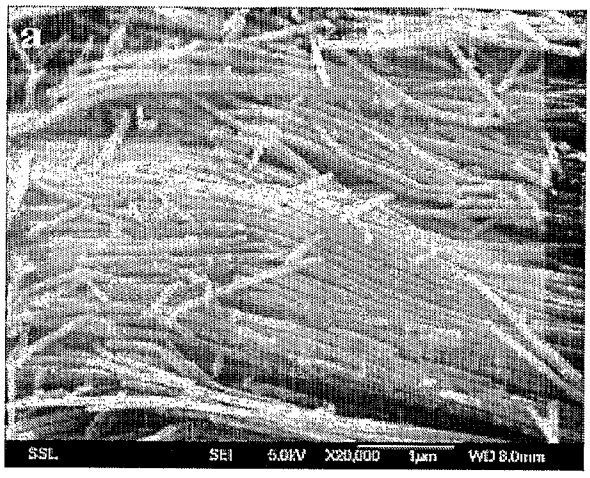
(54) Title: CARBON NANOTUBE(S) AND METHOD FOR MAKING THE SAME

(a)



(57) Abstract: The present invention provides a carbon nanotube (CNT) comprising at least one outer tube and at least one inner tube. In particular, the carbon nanotube is a tube(s)-in-tube carbon nanotube (TiT-CNT). The present invention also provides a method for preparing carbon nanotubes (CNTs) comprising the steps of: (a) providing at least one nanotemplate; (b) performing a first pyrolysis in the presence of at least one first carbon source, wherein the at least one first carbon source contacts the at least one nanotemplate; and (c) performing at least one further pyrolysis in the presence of at least one second carbon source, wherein the at least one first carbon source and the at least one second carbon source are the same or different.

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Carbon nanotube(s) and method for making the same

Field of the invention

The present invention relates to carbon nanotube(s) and to method(s) for making the same. The carbon nanotube(s) according to the invention have applications in many fields, such as hybrid power sources for electrical energy, digital telecommunication systems, uninterruptible power supply (UPS) for computers, and pulse laser technique.

Background of the invention

The power requirements for a number of portable electronic devices have exceeded the capability of conventional batteries to such an extent that great attention is being focused on supercapacitors with higher power density and less reduction in energy density.

Electrode materials for electrochemical capacitors (EC) have been extensively studied due to the increasing demand for new kind of energy storage devices with high specific power and long durability (B. E. Conway, 1999). These storage devices can be used in digital telecommunication systems, uninterruptible power supply (UPS) for computers, pulse laser technique, and the like. The electrode materials can be conducting polymers (such as, polyacetylene, polypyrrole, and polyaniline) (K. Lota et al., 2004; S. K. Ryu et al., 2003), oxides (such as RuO_2 and Co_3O_4) (K. H. Chang et al., 2004; D. Rochefort and D. J. Guay, 2005; J. N. Broughton and M. J. Brett, 2005), or their composites. Recently, carbon nanotubes (CNTs) have been studied for electrochemical supercapacitor electrodes due to their unique properties, such as large surface area, high chemical stability, flexibility and high conductivity (C. Niu et al., 1997; K. H. An et al., 2001; J. Y. Lee et al., 2003). The capacitance of CNTs strongly depends on the purity of the CNT and electrolyte (E. Frackowiak et al., 2001; J. N. Barisci et al., 2003; J. N. Barisci et al., 2004).

Functionalization of CNTs (C. Niu et al., 1997; J. Y. Lee et al., 2003; E. Frackowiak et al., 2000; B. J. Yoon et al., 2004) and modification of the CNTs with conducting polymers can also increase the capacitance of CNT supercapacitors because conducting polymers are also common electrode materials for supercapacitors and are known to create pseudocapacitance through Faradaic process (C. Zhou et al., 2005; M. Hughes et al., 2002; C. Downs et al., 1999).

Summary of the invention

The present invention seeks to address the problems above, and in particular provides tube(s)-in-tube carbon nanotubes (TiT-CNTs) for use in various applications including, but not limited to, hybrid power sources for electrical energy, digital telecommunication systems, uninterruptible power supply (UPS) for computers and pulse laser techniques. The TiT-CNTs may be prepared by a two-step pyrolysis process.

According to a first aspect, the present invention provides a method for preparing carbon nanotubes (CNTs) comprising the steps of:

(a) providing at least one nanotemplate;

(b) performing a first pyrolysis in the presence of at least one first carbon source, the at least one first carbon source contacting the at least one nanotemplate; and

(c) performing at least one further pyrolysis in the presence of at least one second carbon source,

wherein the at least one first carbon source and the at least one second carbon source are the same or different.

The CNTs may comprise at least one outer tube and at least one inner tube. CNTs comprising at least one tube may be formed after step (b). In particular, CNTs comprising at least one outer tube and at least one inner tube may be formed after step (c). The tube formed after step (b) may be the outer tube of the CNTs formed after step (c). The CNTs may be tube(s)-in-tube CNTs (TiT-CNTs). The TiT-CNTs are formed after the at least one further pyrolysis. The at least one outer tube and the at least one inner tube may be single-walled CNTs (SWCNTs) and/or multi-walled CNTs (MWCNTs).

According to a second aspect, the present invention provides a method for preparing tube(s)-in-tube carbon nanotubes (TiT-CNTs) comprising the steps of:

(a) providing at least one nanotemplate;

(b) preparing carbon nanotubes (CNTs) by performing a first pyrolysis in the presence of at least one first carbon source, the at least one first carbon source contacting at least one nanotemplate; and

(c) performing at least one further pyrolysis in the presence of at least one second carbon source,

wherein the at least one first carbon source and the at least one second carbon source are the same or different.

The CNTs formed from step (b) may be single-walled CNTs (SWCNTs) and/or multi-walled CNTs (MWCNTs). The TiT-CNTs may comprise at least one outer tube and at least one inner tube. The at least one outer tube and the at least one inner tube may be single-walled CNTs (SWCNTs) and/or multi-walled CNTs (MWCNTs).

According to a particular aspect, the average diameter of: the at least one tube of the CNTs formed after step (b) of any method of the present invention; and/or the at least one outer tube of the CNTs formed after step (c) of any method of

the present invention, may be from 30 nm to 400 nm. The average diameter of: the at least one inner tube of the CNTs formed after step (c) of any method of the present invention may be less than or equal to about 20 nm. More in particular, less than or equal to about 10 nm, and even more in particular, about 7 nm.

In the method according to any aspect of the present invention, the first pyrolysis and/or the at least one further pyrolysis may be performed in the presence of a catalyst. Any suitable catalyst may be used. For example, the catalyst may be a transition metal. The catalyst may be selected from a group consisting of: Ni, Fe, Co, Al, Mn, Pd, Mo, W, Cr and alloys thereof. The catalyst may be deposited onto and/or inside the at least one nanotemplate. The catalyst may be deposited onto the inner walls of the CNTs prepared from the first pyrolysis of step (b).

The catalyst may be deposited onto the inner walls of the CNTs formed after step (b) by immersing the at least one nanotemplate and/or CNTs into a catalyst-containing solution. Any suitable catalyst-containing solution may be used. For example, the catalyst-containing solution may comprise at least one of the catalysts described above. In particular, the catalyst-containing solution may be Ni_2SO_4. The immersion may be carried out for a suitable period of time.

The at least one nanotemplate according to any aspect of the present invention may be porous. For example, the at least one nanotemplate may be anodic aluminium oxide and/or titanium oxide. The average pore diameter of the nanotemplate may be from 10 nm to 400 nm. The average thickness of the nanotemplate may be from 0.5 to 500 μm.

Any suitable carbon source may be used for the methods according to the present invention. The carbon source may be a hydrocarbon source. The at least one first carbon source and the at least one second carbon source may be independently selected from the group consisting of: alkane, alkene, alkyne,

aromatic hydrocarbon, carbon monoxide, metal organic compound and a mixture thereof. In particular, the at least one first carbon source and the at least one second carbon source may be independently selected from the group consisting of: methane, ethylene, benzene, acetylene, carbon monoxide, $Co(CO)_5$, $Fe(C_5H_5)_2$ and a mixture thereof. Even more in particular, the at least one first carbon source and/or the at least one second carbon source is ethylene, acetylene or a mixture thereof.

According to a particular aspect, the first pyrolysis and the at least one further pyrolysis may be performed under the same or different conditions. The conditions may include temperature and time. The first pyrolysis and/or the at least one further pyrolysis may be performed at a temperature greater than 300°C. In particular, the temperature may be from 400°C to 1000°C. Even more in particular, the temperature is from 500°C to 650°C. The first pyrolysis and/or the at least one further pyrolysis may be performed from 10 to 120 minutes. In particular, the first pyrolysis and/or the at least one further pyrolysis may be performed from 30 to 80 minutes.

According to a particular aspect, the first pyrolysis and/or the at least one further pyrolysis may be performed in the presence of a mixture of gases, the mixture comprising hydrogen gas and/or an inert gas. For example, the inert gas may be argon, helium, neon, nitrogen, krypton, xenon, radon, or a mixture thereof.

According to another particular aspect, the method according to any aspect of the present invention may comprise the step of removing the CNTs formed after step (b) and/or step (c) from the at least one nanotemplate.

According to another aspect, the present invention also provides carbon nanotubes (CNTs) obtainable by any method of the present invention.

The present invention also provides a carbon nanotube (CNT) comprising at least one outer tube and at least one inner tube. The at least one outer tube

and/or the at least one inner tube may be a single-walled CNT (SWCNT) or a multi-walled CNT (MWCNT).

The average diameter of the at least one outer tube of the CNTs may be from 30 nm to 400 nm. The average diameter of the at least one inner tube of the CNTs may be less than or equal to about 20 nm. More in particular, less than or equal to about 10 nm, and even more in particular, about 7 nm.

The present invention also provides a use of carbon nanotubes (CNTs) comprising at least one outer tube and at least one inner tube in the manufacture of: electrodes; fuel cells; hydrogen storage devices; batteries; sorbents for air/water purification and/or gas separation systems; catalyst supports; and/or supercapacitors.

The present invention also provides an electrode and/or a supercapacitor comprising at least one CNT prepared according to any method of the present invention. The at least one CNT may comprise at least one outer tube and at least one inner tube.

The present invention also provides an electrode and/or a supercapacitor comprising at least one carbon nanotube (CNT), the at least one carbon nanotube comprising at least one outer tube and at least one inner tube.

Brief description of the figures

Figure 1: SEM images of the AAO-template after a first step of pyrolysis of ethylene: (a) 50 nm multi-walled carbon nanotubes (MWCNTs) are imbedded in the AAO template nanopores; and (b) after partially removing the surface of the AAO template.

Figure 2: SEM images of the tube-in-tube carbon nanotubes (TiT-CNTs) after the second step of pyrolysis of ethylene and total removal of the AAO template: (a) Sample ATM50: 50 nm outer diameter and (b) Sample ATM300: 300 nm outer diameter.

Figure 3: The cyclic voltammetry (CV) plots of five samples in 0.5M H_2SO_4 at a scan rate of 50 mV/s.

Figure 4: Pore size distribution of five samples calculated using Barrett-Joyner-Halenda (BJH) method.

Detailed description of the invention

Bibliographic references mentioned in the present specification are for convenience listed in the form of a list of references and added at the end of the examples. The whole content of such bibliographic references is herein incorporated by reference.

In this invention, it was found that high capacitance value of supercapacitors made of tube(s)-in-tube carbon nanotubes (TiT-CNTs) can be realized. The TiT-CNTs, optionally with uniform diameters, may be synthesized by a two-step chemical vapour deposition process or two-step pyrolysis of ethylene on AAO template. For example, in the first step, large-diameter multi-walled carbon nanotubes (MWCNTs) may be grown from the pyrolysis of ethylene (C_2H_4) using an anodic aluminium oxide (AAO) template which can be easily produced by a two-step anodization of aluminium foil. In the second step, the TiT-CNTs may be fabricated by the second pyrolysis of ethylene (C_2H_4). The capacitance of the supercapacitors based on TiT-CNTs are related to the diameter and structure of the TiT-CNTs, which may be controllable in the two-step process. The TiT-CNTs may comprise at least one outer tube and at least one inner tube. The diameter of the tubes formed may be controlled, as desired. This

method is simple, easy and may be suitable for large scale production. Accordingly, the present invention provides carbon nanotubes which can exhibit high capacitance. Such carbon nanotubes may have applications as hybrid power sources for electrical energy, in digital telecommunication systems, as uninterruptible power supply (UPS) for computers, and in pulse laser technique.

According to a first aspect, the present invention provides a method for preparing carbon nanotubes (CNTs) comprising the steps of:

(a) providing at least one nanotemplate;

(b) performing a first pyrolysis in the presence of at least one first carbon source, the at least one first carbon source contacting the at least one nanotemplate; and

(c) performing at least one further pyrolysis in the presence of at least one second carbon source,

wherein the at least one first carbon source and the at least one second carbon source are the same or different.

The CNTs may comprise at least one outer tube and at least one inner tube. CNTs comprising at least one outer tube and at least one inner tube may be formed after step (c). In particular, the CNTs comprising at least one outer tube and at least one inner tube formed after step (c) may be referred to as tube(s)-in-tube CNTs (TiT-CNTs). There may be a plurality of inner tubes. CNTs comprising at least one tube may be formed after step (b). The at least one tube of the CNT formed after step (b) may be the at least one outer tube of the CNT formed after step (c). The CNTs may be single-walled CNTs (SWCNTs) and/or multi-walled CNTs (MWCNTs). In particular, the at least one outer tube and/or at least one inner tube may be SWCNTs or MWCNTs. The at least one tube of the CNT formed after step (b) may be SWCNT or MWCNT.

According to a second aspect, the present invention provides a method for preparing tube(s)-in-tube carbon nanotubes (TiT-CNTs) comprising the steps of:

(a) providing at least one nanotemplate;

(b) preparing carbon nanotubes (CNTs) by performing a first pyrolysis in the presence of at least one first carbon source, the at least one first carbon source contacting at least one nanotemplate; and

(c) performing at least one further pyrolysis in the presence of at least one second carbon source,

wherein the at least one first carbon source and the at least one second carbon source are the same or different.

The CNTs formed from step (b) may be single-walled CNTs (SWCNTs) and/or multi-walled CNTs (MWCNTs). The TiT-CNTs may be SWCNTs and/or MWCNTs. The TiT-CNTs may comprise at least one outer tube and at least one inner tube. In particular, there may be a plurality of inner tubes. For example, the at least one inner tube are comprised within the at least one outer tube to form the TiT-CNTs. The at least one outer tube and the at least one inner tube may be SWCNTs and/or MWCNTs.

For the purposes of the present invention, carbon nanotubes (CNTs) are defined as a substance in which a carbon atom is bonded to neighbouring three carbon atoms, these bonded carbon atoms forming a hexagonal ring with other adjacent bonded carbon atoms and such rings being repeated in a honeycomb pattern to form a sheet which rolls into a cylindrical tube. CNTs are primarily or completely carbon in a substantially cylindrical or rod-like form. The CNTs may include both tubes and rods. The CNTs may be single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs).

SWCNTs are fullerenes consisting essentially of sp^2 -hybridized carbon typically arranged in hexagons and pentagons. These carbon cylindrical structures, known commonly as "buckytubes", have extraordinary properties, including high electrical and thermal conductivity, as well as high strength and stiffness.

MWCNTs are nested single-wall carbon cylinders and possess some properties similar to SWCNTs. However, since SWCNTs have fewer defects than MWCNTs, SWCNTs are generally stronger and more conductive. Additionally, SWCNTs have considerably higher available surface area per gram of carbon than MWCNTs. Dispersing SWCNTs, however, is much more difficult than dispersing MWCNTs because the SWCNTs can "rope" together in aligned bundles of a few to many hundreds of nanotubes and be held tightly together by van der Waals forces.

The CNTs formed according to any method of the present invention may have an average diameter of less than 500 nm. In particular, the average diameter of the at least one tube of the CNTs formed after step (b) and/or the average diameter of the at least one outer tube of the CNTs formed after step (c) may be from 30 nm to 400 nm. Even more in particular, the average diameter of the at least one tube and/or the at least one outer tube may be from 50 nm to 300 nm. For example, the average diameter of the at least one tube and/or the at least one outer tube is 50 nm or 300 nm. The average diameter of the at least one tube and/or the at least one outer tube may depend on the average pore diameter of the at least one nanotemplate.

The average diameter of the at least one inner tube of the CNTs formed after step (c) may be less than or equal to the average diameter of the at least one outer tube. In particular, the average diameter of the at least one inner tube may be less than or equal to 100 nm. The average diameter of the at least one inner tube may be less than or equal to 20 nm. More in particular, less than or equal to 10 nm, and even more in particular, about 7 nm.

For the purposes of the present invention, the term 'pyrolysis' is defined as the chemical decomposition of a compound by the action of heat. The conditions under which pyrolysis is performed may be varied, such as catalyst (if used), temperature, time, pressure and/or flow rate of the material used in the pyrolysis. The characteristics of the CNTs obtained may depend on the conditions of the first pyrolysis and/or the at least one further pyrolysis. The first pyrolysis and the at least one further pyrolysis may be performed under the same or different conditions.

According to a particular aspect, the first pyrolysis and/or the at least one further pyrolysis may be performed in the presence of a catalyst. In particular, the first pyrolysis may be performed in the presence of a catalyst. The catalyst may be deposited onto and/or inside the at least one nanotemplate. In particular, the at least one further pyrolysis may be performed in the presence of a catalyst. The catalyst may be deposited onto the inner walls of the CNTs formed after step (b). In particular, the catalyst may be deposited onto the inner walls of the at least one tube of the CNTs formed after step (b).

The catalyst may be deposited by any suitable method. The catalyst may be deposited by an impregnation process. For example, the catalyst may be deposited by immersing the at least one nanotemplate and/or CNTs into a catalyst-containing solution for a suitable period of time. The immersion of the at least one nanotemplate and/or CNTs into the catalyst-containing solution may be carried out from 30 minutes to 4 hours.

Any suitable catalyst may be used for the purposes of the present invention. The catalyst may be a transition metal. The catalyst may be selected from the group consisting of: Ni, Fe, Co, Al, Mn, Pd, Mo, W, Cr, Ti, Ru, Re, Rh, V and alloys thereof. In particular, the catalyst may be Ni or Co. The catalyst-containing solution may be Ni_2SO_4 solution.

The first pyrolysis and the at least one further pyrolysis may be carried out in the presence of a carbon source. The carbon source used for each pyrolysis may be the same or different. Any suitable carbon source may be used. The carbon source may be a hydrocarbon source. The carbon source may include but is not limited to aliphatic hydrocarbons, aromatic hydrocarbons, carbonyls, halogenated hydrocarbons, silyated hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, phenols, esters, amines, alkylnitriles, thioethers, cyanates, nitroalkyls, alkylnitrates, and/or mixtures of one or more of the above. In particular, the carbon source may be independently selected from the group consisting of: alkane, alkene, alkyne, aromatic hydrocarbon, carbon monoxide, metal organic compound and mixtures thereof. More in particular, the carbon source may be any one of the following or a mixture thereof: methane, ethane, propane, butane, ethylene, benzene, acetylene, methylsilane carbon monoxide, $Co(CO)_5$ and $Fe(C_5H_5)_2$. Even more in particular, the carbon source may be ethylene, acetylene or a mixture thereof. The type of carbon source may determine the type of CNTs formed. For example, performing pyrolysis in the presence of some carbon sources may form higher quality CNTs compared to when other carbon sources are used due to better graphitization and/or carbonization during pyrolysis. In particular, ethylene forms better graphitized CNTs compared to acetylene (H. Pan et al, J. Nanosci. Nanotech., 2004). The volumetric flow rate of the carbon source being supplied to the pyrolysis step may be controlled. For example, the volumetric flow rate may be from 1 sccm to 100 sccm. In particular, the volumetric flow rate may be from 10 sccm to 50 sccm, more in particular, 16 sccm.

The first pyrolysis and the at least one further pyrolysis may be carried out at a suitable temperature for a suitable period of time. The temperature may be greater than 300°C. In particular, the temperature may be from 400°C to 1000°C. More in particular, the temperature may be from 500°C to 650°C. The temperature at which pyrolysis is performed may depend on the carbon source

used for the pyrolysis. For example, between the use of acetylene and ethylene for the carbon source, the temperature at which pyrolysis is conducted when acetylene is used as the carbon source is much lower than when ethylene is used. The temperature required when acetylene is used may be greater than 550°C, whereas using ethylene, a temperature of greater than 850°C may be required. Methane, in turn, requires an even higher pyrolysis temperature.

The time period for which the first pyrolysis and/or the at least one further pyrolysis is carried out may be from 10 minutes to 120 minutes. In particular, pyrolysis may be carried out from 30 minutes to 80 minutes.

The first pyrolysis and/or the at least one further pyrolysis may be carried out in the presence of a gas or a mixture of gases. The gas and/or mixture of gases may include, but may not be limited to, hydrogen gas and/or an inert gas. The inert gas may be argon, helium, neon, nitrogen, krypton, xenon, radon and/or a mixture thereof. The volumetric flow rate of the gas or mixture of gases may be controlled. For example, the volumetric flow rate may be from 10 sccm to 300 sccm. In particular, the volumetric flow rate may be from 50 sccm to 200 sccm, more in particular, 100 sccm.

The at least one nanotemplate used in any aspect of the present invention may be porous. The nanotemplate may be anodic aluminium oxide (AAO) and/or titanium oxide. The nanotemplate may be formed by any suitable method. For example, the AAO nanotemplate may be formed using a modified two-step anodization method as disclosed in H. Pan et al, J. Nanosci. Nanotech., 2004. As mentioned above, the average diameter of the nanopore of the at least one nanotemplate may determine the average diameter of the diameter of the at least one tube and/or the at least one outer tube of the CNTs formed from the method according to any aspect of the present invention. Accordingly, the average diameter of the nanopores of the at least one nanotemplate may be from 10 nm to 600 nm. In particular, the average diameter may be from 30 nm

to 400 nm. Even more in particular, the average diameter may be from 50 nm to 300 nm. The average diameter may be 50 nm or 300 nm. Further, the average thickness of the at least one nanotemplate may be from 0.5 to 500 μm.

According to a particular aspect, the method of any aspect of the present invention further comprises a step of removing CNTs formed after step (b) and/or step (c) from the at least one nanotemplate. Any suitable method of removal of the CNTs may be employed for the purposes of the present invention. This may include the use of any suitable solvent(s). For example, HF acid may be used to remove the CNTs from the nanotemplate. The CNTs may then be cleaned to a pH of about 7 by using distilled water. The CNTs may be dried. For example, the CNTs may be dried to a temperature of about 120°C.

According to another aspect, the present invention provides carbon nanotubes (CNTs) obtainable by any method of the present invention. In particular, the present invention provides tube(s)-in-tube carbon nanotubes (TiT-CNTs) obtainable by any method of the present invention.

The morphology of the CNTs obtained by the method of the present invention is described in the Examples below. In particular, the average diameter, pore size (average pore diameter) and pore size distribution may be determined. Any suitable method may be used to determine the pore size and the pore size distribution. For example, the pore size distribution may be determined using the Barrett-Joyner-Halenda (BJH) method (E.P. Barrett et al, 1951; F. Rouquerol, 1999).

"Pore size" and "pore size distribution" can have different meanings. "Pore size" can be measured by (optical or electron) microscopy whereas pore size distribution and pore volume are determined statistically from counting in a field of view (of a representative portion of the material). Further, pore size of each pore usually refers to the average pore diameter. Pore size is determined by plotting pore volume (for large pore materials the volume of pores having a size

of less than 100 nm can ignored) vs. pore size and "average pore size" is the pore size at 50% of the existing pore volume (e.g., for a material that has a 40% pore volume, the "average pore size" is the size of the largest sized pore that adds with all smaller sized pores to reach 20% pore volume). Where practicable, the pore size and pore volume are measured on a cross-section of the material that may be obtained with a diamond bladed saw.

The present invention also provides a carbon nanotube (CNT) comprising at least one outer tube and at least one inner tube. The CNT may comprise at least one outer tube and a plurality of inner tubes. In particular, the CNT may be a tube(s)-in-tube CNT (TiT-CNT). The CNT may be a single-walled CNT (SWCNT) or multi-walled CNT (MWCNT). In particular, the at least one outer tube and/or the at least one inner tube may be a SWCNT and/or MWCNT.

The CNT of the present invention may have an average diameter of less than 500 nm. In particular, the average diameter of the at least one outer tube of the CNT may be from 30 nm to 400 nm. Even more in particular, the average diameter of the at least one outer tube may be from 50 nm to 300 nm. For example, the average diameter of the at least one outer tube is 50 nm or 300 nm.

The average diameter of the at least one inner tube of the CNT may be less than or equal to the average diameter of the at least one outer tube. In particular, the average diameter of the at least one inner tube may be less than or equal to 100 nm. The average diameter of the at least one inner tube may be less than or equal to 20 nm. More in particular, less than or equal to 10 nm, and even more in particular, about 7 nm.

The CNT according to the present invention may have a specific capacitance greater than 50 F/g. In particular, the specific capacitance of the CNT of the present invention is greater than 100 F/g. Even more in particular, greater than 350 F/g. Specific capacitance of a device is the measure of the ability of the

device to store energy in the form of an electrostatic field (such as charge) per unit weight of the device. Specific capacitance may be measured by any suitable method known to a person skilled in the art. An example of a method is provided in the Examples below.

The capacitance of the CNT of the present invention may be dependent on the average diameter of the CNT. In particular, the capacitance of the CNT may be dependent on the average diameter of the at least one outer tube of the CNT. For example, the capacitance of the CNT may be higher for CNTs which have a smaller average diameter. As seen in Table 1 below, the specific capacitance of CNT with an average diameter of 50 nm (ATM50) is higher than the specific capacitance of CNT with an average diameter of 300 nm (ATM300). The larger specific capacitance of the CNT with a smaller diameter may be contributed to the larger surface area, better pore size distribution and high conductivity.

Accordingly, the CNTs of the present invention may be used in digital telecommunication systems, uninterruptible power supply (UPS) for computers, pulse laser technique, and the like. The CNTs may also be used for other applications such as in the construction of devices for practical applications in many fields including electron emitters, field-emission transistors, electrodes for photovoltaic cells and light emitting diodes, optoelectronic elements, bismuth actuators, chemical and biological sensors, gas and energy storages, molecular filtration membranes and energy-absorbing materials.

According to another aspect, the present invention provides a use of carbon nanotubes (CNTs) according to any aspect of the present invention, comprising at least one outer tube and at least one inner tube in the manufacture of: electrodes; fuel cells; hydrogen storage devices; batteries; sorbents for air/water purification and/or gas separation systems; catalyst supports; and/or supercapacitors.

The present invention also provides an electrode comprising at least one carbon nanotube (CNT) as described above.

The present invention also provides an electrode comprising at least one CNT prepared by any method of the present invention. The at least one CNT may comprise at least one outer tube and at least one inner tube.

The present invention also provides a supercapacitor comprising at least one carbon nanotube (CNT) as described above.

The present invention also provides a supercapacitor comprising at least one CNT prepared by any method of the present invention. The at least one CNT may comprise at least one outer tube and at least one inner tube

Supercapacitors are electrochemical capacitors formed by two polarizable electrodes, a separator and an electrolyte. The capacitance of a supercapacitor is the sum of double layer capacitance and pseudocapacitance. Double layer capacitance arises when a charge accumulation is achieved electrostatically on either side of the electrode and electrolyte interface, while pseudocapacitance is brought about by surface redox-reaction.

Having now generally described the invention, the same will be more readily understood through reference to the following examples which are provided by way of illustration, and are not intended to be limiting of the present invention.

EXAMPLES

All chemicals and solvents used in the present example were Sigma-Aldrich chemicals.

Preparation of anodic aluminium oxide (AAO) template

Carbon nanotubes were fabricated by a two-step pyrolysis of ethylene process at high temperatures on AAO template. The AAO template was prepared using a modified two-step anodization process as described in H. Pan et al., IEEE Trans. Nanotech., 2004.

As the starting material, high purity (approximately 99.999%) aluminium foil was annealed under argon atmosphere at 500°-600°C for approximately 2 hours, in order to increase the grain size of the aluminium metal and to ensure the homogenous growth of nanopores over a large area. After being degreased with acetone and rinsed with ethanol, the aluminium foil was electrochemically polished in a mixture of perchloric acid and ethanol (1:4 in volume) under constant voltage of 20 V at 0°C for 4 minutes.

Thereafter, a two-step anodization was utilized to prepare an ordered AAO template. The first anodization of the aluminium foil was performed at 40 V in an oxalic acid solution of 3 weight% (wt%) at about 25°C for 6 hours. The AAO template was then chemically etched in a mixed solution of phosphoric acid and chromic acid (3:1 by weight) at 60°C to remove aluminium oxide formed. The second anodization was performed under the same conditions as the first anodization except for 8 hours. The average diameter of the nanopore of the AAO template obtained was about 40 nm. The average thickness of the AAO template obtained was about 100 μm. The remaining aluminium was removed in 10 wt% $CuCl_2$ solution.

A second AAO template was formed in the same manner as described above, except that the anodization was performed at 160 V instead of 40 V, and using 10 wt% phosphoric acid instead. This resulted in the formation of an AAO template with nanopores having an average diameter of about 300 nm.

Preparation of carbon nanotubes (CNTs)

(i) Multi-walled carbon nanotubes (MWCNTs)

MWCNTs were prepared following the procedure described in H. Pan et al, J. Nanosci. Nanotech., 2004. Generally, the growth of MWCNTs was carried out in a quartz tube (80 cm in length, 2.5 cm in diameter). The AAO template was placed at the centre of the quartz tube, which was inserted into a horizontal high-temperature furnace (Carbolite 2416). A flow of Ar (95%) and H_2 (5%) gas mixture at 100 sccm was introduced to the quartz tube via stainless junctions and tubes (2 mm in diameter). The temperature of the furnace was increased to 600°C at a rate of 25°C/min. After the temperature reached about 600°C, a flow of acetylene at 16 sccm was introduced into the quartz tube. Pyrolysis of acetylene was carried out for a period of 30 minutes without catalysts. This resulted in the formation of MWCNTs within the nanopores of AAO template. After the pyrolysis, the flow of acetylene was stopped and the furnace was cooled down to room temperature under the flow of the gas mixture (Ar and H_2).

The MWCNTs were removed from the AAO template using 10 wt% HF acid, cleaned to a pH of 7 using distilled water and dried at a temperature of about 120°C.

(ii) Tube-in-tube carbon nanotubes (TiT-CNTs)

MWCNTs were produced following the procedure in (i) above, without removing the MWCNTs from the AAO template. The AAO template was then immersed in Ni_2SO_4 solution for about 2 hours to enable the deposition of Ni catalyst onto the inner walls of MWCNTs. A second pyrolysis was carried out under the same conditions as the first pyrolysis, except pyrolysis of ethylene was performed instead of that of acetylene.

This step resulted in the formation of carbon nanotubes within the MWCNTs which were embedded in the nanopores of the AAO template and covered by Ni catalysts, forming TiT-CNTs.

The TiT-CNTs were removed from the AAO template using 10 wt% HF acid, cleaned to a pH of 7 using distilled water and dried at a temperature of about 120°C.

Morphology of CNTs

The morphology of the CNTs was observed by scanning electron microscope (SEM, JEOL JSM-6700F).

MWCNTs were normally confined within the nanopore channels of the AAO template because the alumina channel inner wall decomposes the hydrocarbon (H. Pan et al., J. Nanosci. Nanotech., 2004). Figure 1 shows the SEM image of MWCNTs produced on the AAO template. The average diameter of the MWCNTs is about 50 nm obtained after the first step of pyrolysis of ethylene.

Figure 1(a) clearly indicated that MWCNTs were formed within the nanopores in the AAO template. The nanopores were widened, and the MWCNTs were exposed out after the AAO template was partially etched. The exposed tips of the MWCNTs have equal length and are tangled together, as seen in Figure 1(b).

Figure 2 shows the SEM images of TiT-CNTs after totally removing the AAO template. The surface of the TiT-CNTs is rough with a lot of smaller pores. From the open ends of TiT-CNTs, smaller carbon nanotubes within the MWCNTs are observable. For TiT-CNTs with a diameter of 300 nm, it is clear that the MWCNTs of diameter of 300 nm confine a lot of smaller CNTs inside. Some TiT-CNTs (diameter of 300 nm) were broken and smaller CNTs were released from inside during the removal of the AAO template in HF acid. This can be seen in Figure 2(b). The reason is because of the CNTs poor graphitization.

The average diameter of the smaller CNTs within the MWCNTs (300 nm) is about 20 nm. For 50 nm TiT-CNTs, the smaller CNTs within the MWCNTs (50 nm) was less than 10 nm in diameter (Figure 2(a)).

Cyclic voltammetry (CV) measurements

The specific surface area of the samples was characterized by nitrogen isotherm at 77K (NOVA 3200, Quantachrome Corp) based on the Brunauer-Emmett-Teller (BET) method (S. Erunauer et al, 1938).

Cyclic voltammetry (CV) measurements were performed in an electrochemical measurement unit (Solartron SI1280B), a combined electrochemical interface and frequency response analyser (GCC 540, 724-01-004, Radiometer Analytical SAS), at room temperature with a scan rate of 50 mV/s.

Five samples were used in our experiments for comparison. They included AAO MWCNTs (50 nm in diameter), AAO MWCNTs (300 nm), AAO TiT-CNTs (50 nm), AAO TiT-CNTs (300 nm), and commercial MWCNTs (10-20 nm) (NTP, Shenzhen Nanotech Port Co. Ltd.), which were labelled as AM50, AM300, ATM50, ATM300 and CM20, respectively.

A working electrode was fabricated by casting a Nafion-impregnated sample onto a 3 mm diameter glassy carbon electrode. 4 mg of sample dispersed in 0.5 mL of aqueous ethanol solution (1:1 volume/volume) was sonicated for 15 minutes (G Li and PG Pickup, 2003). This sample ink was dropped onto the glassy carbon electrode and the cast electrode was placed in a vacuum oven until the catalyst was totally dry for the CV measurement. The cast working electrode was then immersed in 0.5 M H_2SO_4 which was de-aerated with high purity nitrogen gas for electrochemical measurement. A Pt foil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively.

The CV measurement is helpful in understanding the electrochemical performance on the electrode of the superconductor during charging and discharging processes. Figure 3 shows the CV plots of the five samples in aqueous solution of 0.5 M H_2SO_4 at a scan rate of 50 mV/s. The CV plot of the background (glassy carbon electrode) is almost a straight line, as seen in the middle of Figure 3, indicating that the contribution of the glassy electrode to the results is negligible.

There is an average of two peaks on every CV plot for each of the five samples. This indicates that supercapacitors can be realized due to the existence of Faradaic processes. The charger storage in the Faradaic process is achieved by an electron transfer that produces chemical or oxidation state changes in the electroactive materials according to Faraday's law related to the potential (B. E. Conway, 1999). In the present example, the well remarkable region with reversible Faradaic reactions is observed within the range of 0.2 to 0.4 V, as seen in Figure 3. The redox peaks on the CV plots can be ascribed to functional groups (for example oxegenated groups), such as carboxylic, OH^- and H^+ groups (E. Frackowiak et al., 2000) attached to the surface of the electrodes comprising the CNTs. Accordingly, this makes H_2SO_4 an ideal electrolyte for CV measurements. Contribution from the residual catalyst should be ruled out since the samples were washed thoroughly in HF.

Capacitance

The voltammetric charge (q) integrated from positive or negative sweeps of CV plots can be used as an effective signal in determining the pseudocapacitance in redox transitions (B. E. Conway, 1999). Accordingly, the average specific capacitance of the above-mentioned samples were estimated from the CV plots shown in Figure 3 by integrating the area under the current (per gram of the sample)-potential curve and then dividing by the sweep rate, and the potential window according to the following equation:

$$C_{ave} = q/(\Delta V \times m) = \frac{1}{1.2mv}\int_0^{1.2} i(V)dV = \frac{1}{1.2v}\int_0^{1.2} \frac{i(V)}{m}dV \qquad (1)$$

where

v is a constant of sweep rate applied for the CV measurements, i.e. $\frac{dV}{dt}$;

$i(V)$ is a current response depending on sweep voltage; and

voltammetric charge is thus estimated as $q = \int_0^{1.2} \frac{i(V)}{v}dV$.

The sweep potential is from -0.2 to 1.0 V, and thus the potential window (ΔV) is 1.2 V.

The average specific capacitance of the commercial CNTs (10-20 nm in diameter) (CM20) was about 46 F/g, which was comparable to the value reported in literature (Liu T et al., 2003). The CV plot of AM50 is very similar to that reported in Q. L. Chen et al., 2004. The average specific capacitances of the remaining four samples were 183, 57, 406 and 117 F/g for AM50, AM300, ATM50 and ATM300, respectively.

The average specific capacitance of ATM50 is about 8 times that of CM20 and about twice the mean value of oxidatively purified single-wall carbon nanotubes functionalized with arylsulfonic acid moieties and then treated with pyrrole, as reported in C. Zhou, et al., 2005. The CV plot of ATM50 is close to the rectangular shape of an ideal double layer capacitor. An electrode of ATM50 was tested by the CV measurement for 5000 cycles in aqueous solution of 0.5 M H_2SO_4. A decrease of the specific capacitance was not observed, which indicated the cycling stability of ATM50.

The capacitance of carbon based electrochemical supercapacitors depends on two kinds of accumulated energy (E. Frackowiak and F. Beguin, Carbon 2001):

(a) the electrostatic attraction in electrical double layer capacitors (EDLC); and (b) faradaic reactions inducing pseudocapacitance. The amount of electrical charge accumulated due to electrostatic attraction in EDLC depends on the area of the electrode/electrolyte interface that can be accessed by the charge carriers. Therefore, the higher surface area of the electrode material could lead to higher capacitance if the area can be fully accessed by the charge carriers. However, the surface area is hardly accessible if the electrode consists of micropores (i.e. <2 nm) (E. Frackowiak and F. Beguin, Carbon 2001). Thus, higher surface area does not always result in higher capacitance because the capacitance depends on the pore size and pore size distribution.

The average pore diameters and average specific capacitance is shown in Table 1. For the present example, the average pore diameters of all five samples were larger than 2 nm. The average pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method (E.P. Barrett et al, 1951). The results are shown in Figure 4, and summarised in Table 1.

Table 1: Specific surface area, average pore size, and capacitance of the carbon nanotubes.

	CM20	AMC50	AMC300	ATM50	ATM300
Specific area (m^2/g)	136	649	264	500	390
Average pore diameter (nm)	8.8	3.9	7.4	5.2	9.1
Capacitance (F/g)	46	183	57	406	117

From Figure 4, it can be seen that the dominant pore diameter for AM50 and ATM50 is about 3.9 nm, but is about 2 nm for other samples. It is observed that the average specific capacitance for AM50 and ATM50 is larger than those of other samples. Also, it was found that capacitance increases with the increase

of the specific surface area with the exception of ATM50. Electrical conductivity is one of the factors that affect the capacitance. It should be mentioned that the higher the specific surface area, the poorer the conductivity should be. This could be one of reasons for the capacitance of ATM50 being larger than that of AM50.

As mentioned above, pseudocapacitance induced by faradaic reactions also contributes to the capacitance, which depends on the surface functionalization of the carbon nanostructures. The redox peaks in the CV plots indicated the existence of oxygenated groups (H^+ or OH^-) on the surface of the carbon nanostructures, which leads to the remarkable pseudocapacitance (E. Frackowiak, et al., 2000). The pseudocapacitance arises from the quick faradaic charge transfer reactions. Pseudocapacitance is strongly related to the pore size, pore size distribution and the conductivity of the carbon materials, i.e. the CNTs. It is observed from Table 1 that ATM50 shows the highest average specific capacitance due to its high surface area, better pore size distribution and conductivity, as analyzed in the EDLC.

Discussion

From the above example, it can be seen that tube-in-tube carbon nanostructures (TiT-CNTs) exhibit better supercapacitance compared to commercial CNTs and AAO-based MWCNTs produced by a one-step ethylene pyrolysis process. Further, the smaller diameter of TiT-CNTs exhibit better supercapacitance than TiT-CNTs with larger diameters. The larger supercapacitance of ATM50 is contributed to their larger specific surface area, better pore size distribution and high conductivity. Accordingly, TiT-CNTs would be useful in satisfying power requirements in devices.

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Claims

1. A method for preparing carbon nanotubes (CNTs) comprising the steps of:

   (a) providing at least one nanotemplate;

   (b) performing a first pyrolysis in the presence of at least one first carbon source, wherein the at least one first carbon source contacts the at least one nanotemplate; and

   (c) performing at least one further pyrolysis in the presence of at least one second carbon source,

   wherein the at least one first carbon source and the at least one second carbon source are the same or different.

2. The method according to claim 1, wherein CNTs comprising at least one outer tube and at least one inner tube are formed after step (c).

3. The method according to claim 2, wherein the at least one outer tube and/or the at least one inner tube are single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs).

4. The method according to any of the preceding claims, wherein CNTs comprising at least one tube are formed after step (b).

5. The method according to claim 4, wherein the CNTs comprising at least one tube formed after step (b) are single-walled CNTs (SWCNTs) or multi-walled CNTs (MWCNTs).

6. The method according to any of the preceding claims, wherein the first pyrolysis and/or the at least one further pyrolysis is performed in the presence of a catalyst.

7. The method according to any of the preceding claims, wherein the first pyrolysis is performed in the presence of a catalyst, and the catalyst is deposited onto and/or inside the at least one nanotemplate.

8. The method according to any of the preceding claims, wherein the at least one further pyrolysis is performed in the presence of a catalyst, and the catalyst is deposited onto the inner walls of the CNTs formed after step (b).

9. The method according to claim 8, wherein the catalyst is deposited onto the inner walls of the CNTs formed after step (b) by immersing the at least one nanotemplate and/or CNTs into a catalyst-containing solution.

10. The method according to claim 9, wherein the catalyst-containing solution is Ni_2SO_4.

11. The method according to claim 9 or claim 10, wherein the at least one nanotemplate and/or CNTs is immersed in the catalyst-containing solution for a time period from 30 minutes to 4 hours.

12. The method according to any one of claims 6 to 11, wherein the catalyst comprises a transition metal selected from a group consisting of: Ni, Fe, Co, Al, Mn, Pd, Mo, W, Cr and alloys thereof.

13. The method according to any one of claims 6 to 12, wherein the catalyst is Ni or Co.

14. The method according to any of the preceding claims, wherein the at least one nanotemplate is porous.

15. The method according to any of the preceding claims, wherein the at least one nanotemplate is anodic aluminium oxide and/or titanium oxide.

16. The method according to any of the preceding claims, wherein the at least one first carbon source and the at least one second carbon source are

independently selected from the group consisting of: alkane, alkene, alkyne, aromatic hydrocarbon, carbon monoxide, metal organic compound and a mixture thereof.

17. The method according to claim 16, wherein the at least one first carbon source and the at least one second carbon source are independently selected from the group consisting of: methane, ethylene, benzene, acetylene, carbon monoxide, $Co(CO)_5$, $Fe(C_5H_5)_2$ and a mixture thereof.

18. The method according to claim 16 or claim 17, wherein the at least one first carbon source and/or the at least one second carbon source is ethylene or acetylene.

19. The method according to any of the preceding claims, wherein the first pyrolysis and the at least one further pyrolysis is performed under the same or different conditions.

20. The method according to any of the preceding claims, wherein the first pyrolysis and/or the at least one further pyrolysis is performed in the presence of a mixture of gases, the mixture comprising hydrogen gas and/or an inert gas.

21. The method according to claim 20, wherein the inert gas is argon, helium, neon, nitrogen, krypton, xenon, radon.

22. The method according to any of the preceding claims, wherein the first pyrolysis and/or the at least one further pyrolysis is performed at a temperature greater than 300°C.

23. The method according to claim 22, wherein the temperature is from 400°C to 1000°C.

24. The method according to claim 22 or claim 23, wherein the temperature is from 500°C to 650°C.

25. The method according to any of the preceding claims, wherein the first pyrolysis and/or the at least one further pyrolysis is performed from 10 to 120 minutes.

26. The method according to claim 25, wherein the first pyrolysis and/or the at least one further pyrolysis is performed from 30 to 80 minutes.

27. The method according to any one of the preceding claims, wherein the average pore diameter of the nanotemplate is from 10 nm to 400 nm.

28. The method according to any one of the preceding claims, wherein the average thickness of the nanotemplate is from 0.5 to 500 μm.

29. The method according to any one of claims 4 to 28, wherein the average diameter of: the at least one tube of the CNTs formed after step (b); and/or the at least one outer tube of the CNTs formed after step (c), is from 30 nm to 400 nm.

30. The method according to claim 29, wherein the average diameter is about 50 nm.

31. The method according to claim 29, wherein the average diameter is about 300 nm.

32. The method according to any one of claims 2 to 31, wherein the average diameter of: the at least one inner tube of the CNTs formed after step (c) is less than or equal to about 20 nm.

33. The method according to claim 32, wherein the average diameter is less than or equal to about 10 nm.

34. The method according to claim 32 or claim 33, wherein the average diameter is about 7 nm.

35. The method according to any of the preceding claims, wherein the method further comprises the step of removing the CNTs formed after step (b) and/or step (c) from the at least one nanotemplate.

36. Carbon nanotubes (CNTs) obtainable by the method according to any of the preceding claims.

37. A carbon nanotube (CNT) comprising at least one outer tube and at least one inner tube.

38. The CNT according to claim 37, wherein the at least one outer tube and/or the at least one inner tube is a single-walled CNT (SWCNT) or a multi-walled CNT (MWCNT).

39. The CNT according to claim 37 or claim 38, wherein the at least one outer tube has an average diameter from 30 nm to 400 nm.

40. The CNT according to claim 39, wherein the at least one outer tube has an average diameter of about 50 nm.

41. The CNT according to claim 39, wherein the at least one outer tube has an average diameter of about 300 nm.

42. The CNT according to any one of claims 37 to 41, wherein the at least one inner tube has an average diameter of less than or equal to about 20 nm.

43. The CNT according to claim 42, wherein the at least one inner tube has an average diameter of less than or equal to about 10 nm.

44. The CNT according to claim 43, wherein the at least one inner tube has an average diameter of about 7 nm.

45. Use of carbon nanotubes (CNTs) comprising at least one outer tube and at least one inner tube in the manufacture of: electrodes; fuel cells; hydrogen storage devices; batteries; sorbents for air/water purification and/or gas separation systems; catalyst supports; and/or supercapacitors.

46. An electrode comprising at least one carbon nanotube (CNT), the at least one carbon nanotube comprising at least one outer tube and at least one inner tube.

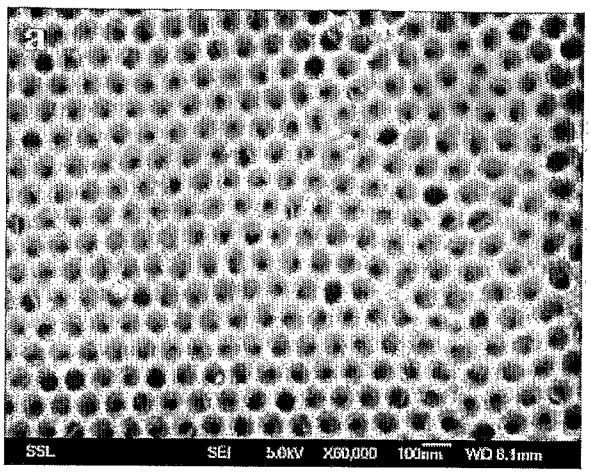
47. An electrode comprising at least one CNT prepared according to the method of claims 1 to 35, wherein the at least one CNT comprises at least one outer tube and at least one inner tube.

48. A supercapacitor comprising at least one carbon nanotube (CNT), the at least one carbon nanotube comprising at least one outer tube and at least one inner tube.

49. A supercapacitor comprising at least one CNT prepared according to the method of claims 1 to 35, wherein the at least one CNT comprises at least one outer tube and at least one inner tube.

Figure 1

(a)


a
SSL SEI 5.0kV X60,000 100nm WD 8.1mm

(b)

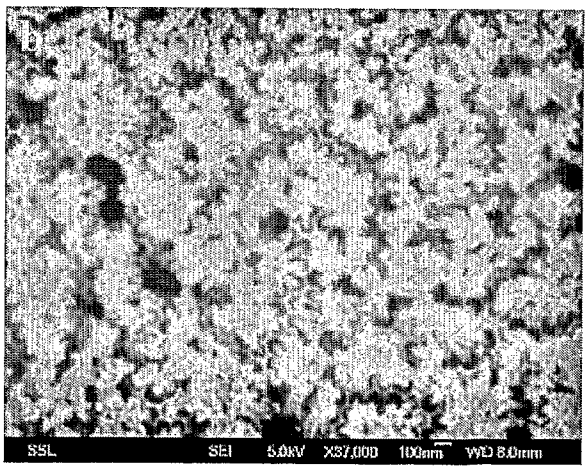

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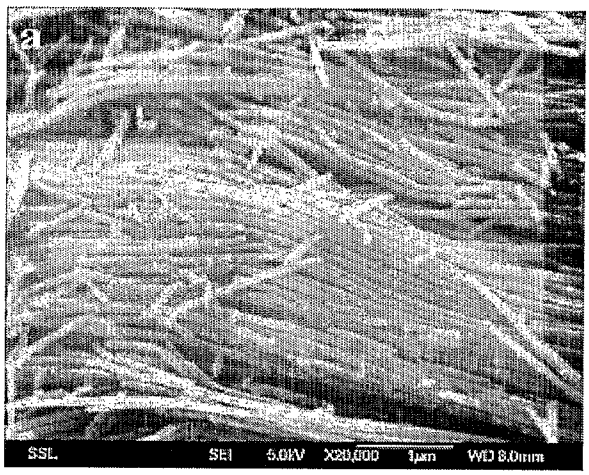
Figure 2

(a)


a
SSL SEI 5.0kV X20,000 1μm WD 8.0mm

(b)

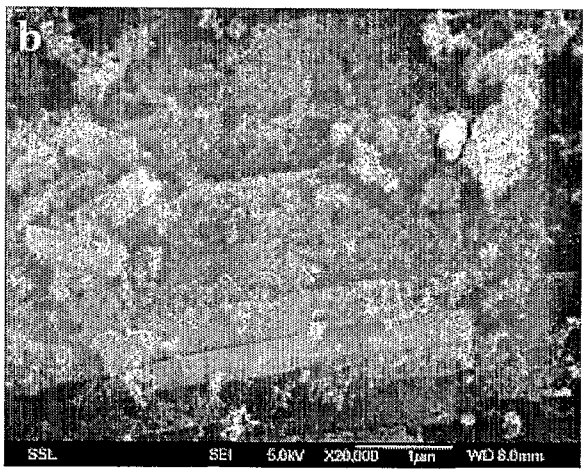

b
SSL SEI 5.0kV X20,000 1μm WD 8.0mm

Figure 3

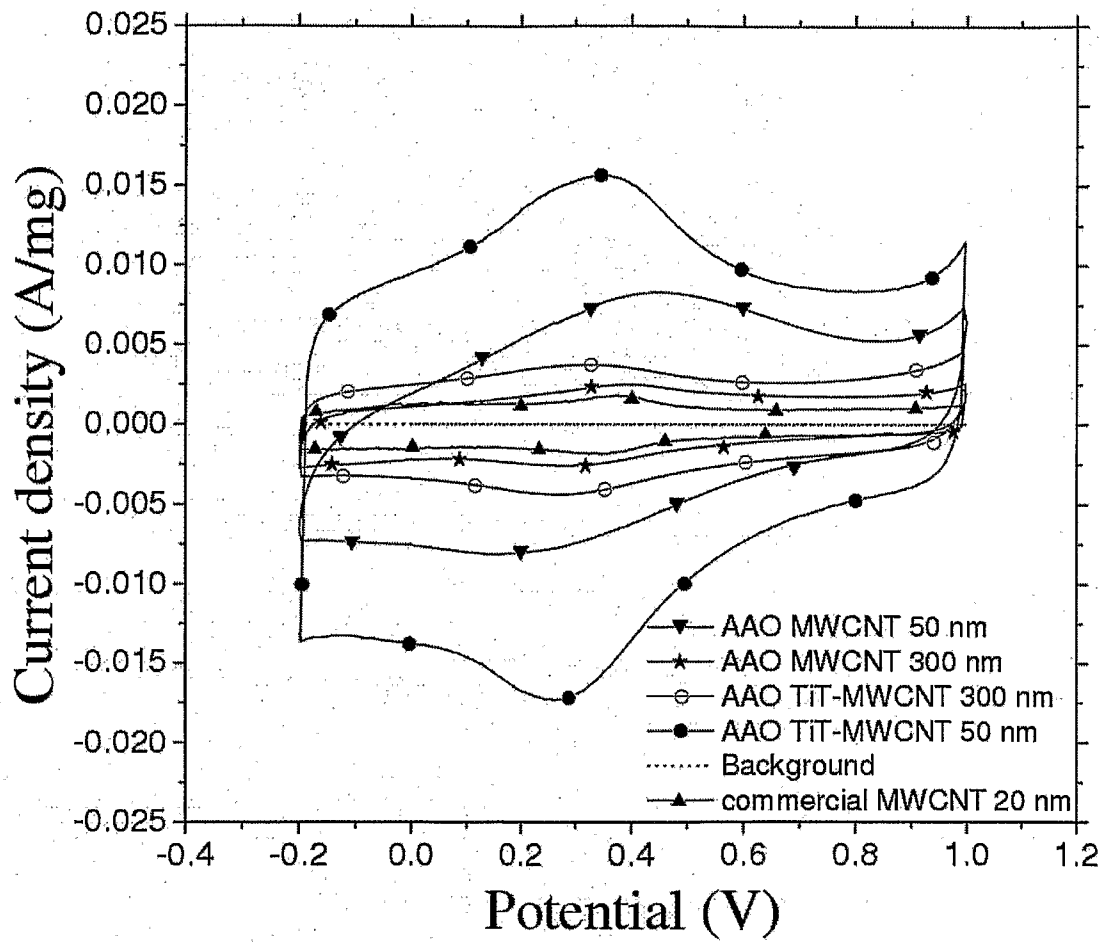
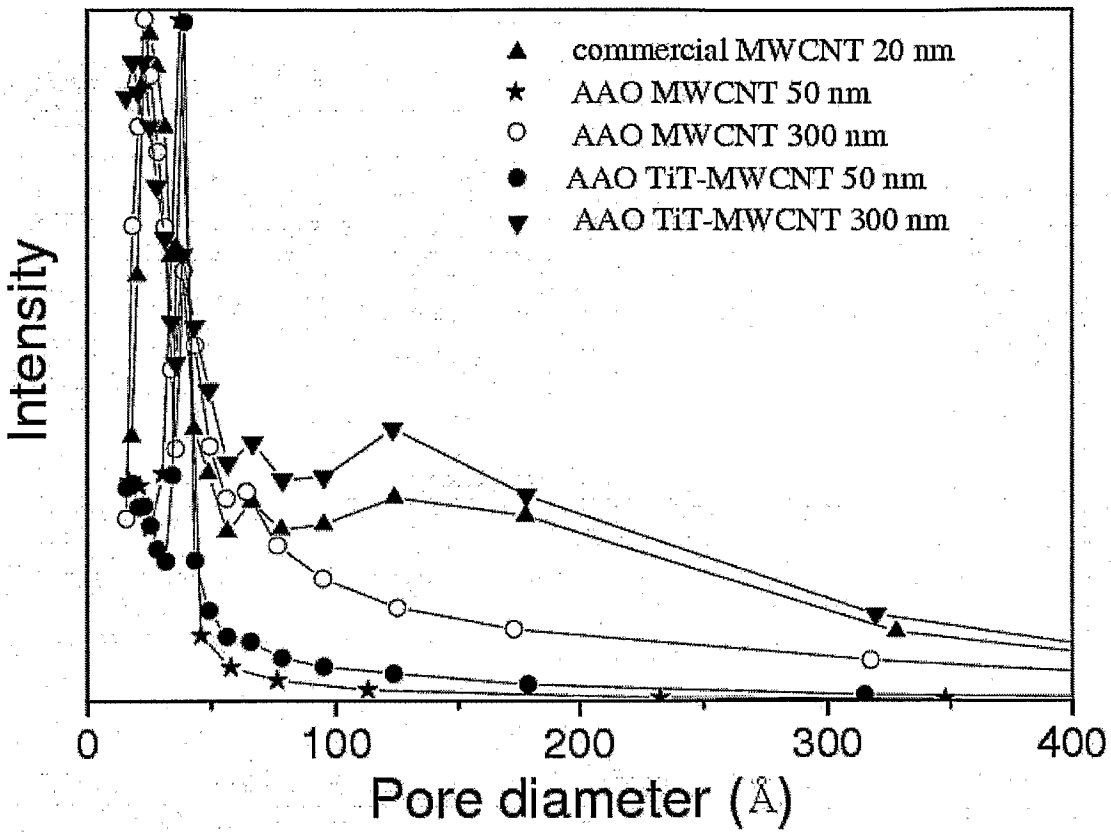

Current density (A/mg)
Potential (V)
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
-0.010
-0.015
-0.020
-0.025
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
AAO MWCNT 50 nm
AAO MWCNT 300 nm
AAO TiT-MWCNT 300 nm
AAO TiT-MWCNT 50 nm
Background
commercial MWCNT 20 nm

Figure 4


commercial MWCNT 20 nm
AAO MWCNT 50 nm
AAO MWCNT 300 nm
AAO TiT-MWCNT 50 nm
AAO TiT-MWCNT 300 nm
Intensity
0
100
200
300
400
Pore diameter (Å)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2007/000059

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

B82B 3/00 (2006.01) ***C01B 31/02*** (2006.01) ***H01M 4/96*** (2006.01)
C01B 31/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI: (Nanotube? Or buckytube? or (graphite fibril?) or (nano+(2d)tube?) or +CNT or (nano+(s)fib+) or (nano+(s)filament+)) AND (+template? or AAO or (anodic aluminium oxide)) AND (reactor or furnace or pyrolysis or CVD or (chemical vapour deposition) or ((heat+ or temperature) 3w (decompos+)) or (thermal (w) reaction?)) AND ((Carbon (w) (gas or source)) or methane or ethanol or acetylene or hydrocarbon or (carbon (w) monoxide) or ethylene or benzene) AND (electrode? Or (fuel cell?) Or battery or (hydrogen storage) or (catalyst support) or sorbent or supercapacitor or (super (w) capacitor)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHAMOING HUANG: Controllable 3D architectures of aligned carbon nanotube arrays by multi-step processes. Chemical Physics Letters 374 (2003) 157-163. Whole article	1-7, 12, 16, 19-23, 35-38
Y		1-49

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
30 April 2007

Date of mailing of the international search report
9 MAY 2007

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEN Y. *et. al.*: Patterned growth of carbon nanotubes on Si substrates without predeposition of metal catalysts. Applied Physics Letters 87, 033103 (2005) Whole article	1-3, 6, 7, 12, 16, 19-24, 29, 30, 36-40
Y		1-49
X	WO 2004/083113 A (LEE C) 30 September 2004 Whole document	37-39, 42
X	WO 2005/086982 A (EIKOS INC) 22 September 2005 Whole document	37, 45, 46
X	Derwent Abstract Accession No. 2005-380746/39 Class A85 L03 (L02) KR 2005001589 A (DPI SOLUTIONS INC) 7 January 2005 Abstract	37, 45, 46
X	Derwent Abstract Accession No. 2005-108875/12 Class L03 KR 2004084114 A (KOREA ELECTRONIC TECHNOLOGY INST) 6 October 2004 Abstract	37, 45, 46
X	Derwent Abstract Accession No. 2004-816667/81 Class A85 E36 L03 (A26) JP 2004323258 A (TORAY IND INC) 18 November 2004 Abstract	37, 45, 46
X	US 2004/0197638 A (McELRATH *et. al.*) 7 October 2004 Whole document	37, 45, 46
X	Derwent Abstract Accession No. 2003-350441/33 Class E36 L02 KR 200204644 A (DONG WOON INT CO LTD) 30 May 2002 Abstract	37, 45, 46
X	EP 1591418 A (MAX-PLANCK-GESELLSCHAFT ZUR FORDERUNG DER WISSENSCHAFTEN E.V.) 2 November 2005 Whole document	37, 45, 46
X	Derwent Abstract Accession No. 2003-458392/44 Class A85 L03 CN 1404174 A (UNIV QINGHUA) 19 March 2003 Abstract	37, 45
X	WO 2005/075663 A (THE PROVOST, FELLOWS AND SCHOLARS OF THE COLLEGE OF THE HOLY AND UNDIVIDED TRINITY OF QUEEN ELIZABETH, NEAR DUBLIN, UNIVERSITY OF WOLLONGONG) 18 August 2005 Whole document	37, 45
X	Derwent Abstract Accession No. 2002-624424/67 Class E36 J06 L03 KR 2002007237 A (NANOTECH CO LTD) 26 January 2002 Abstract	37, 45

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/085130 A (CANATU OY) 15 September 2005 Whole document	37, 45
X	Wikipedia, Free Encyclopedia: http://en.wikipedia.org/wiki/Supercapacitor (retrieved on 2 May 2007) Whole document	48
X	DU C. *et. al.*: High power density supercapacitors using locally aligned carbon nanotube electrodes. Nanotechnology 16 (2005) 350-353 Whole document	48
X	AN K.H. *et. al.*: High-capacitance supercapacitor using a nanocomposite electrode of single-walled cabon nanotube and polypyrrole. Journal of the Electrochemical Society, 149 (8) A 1058-A1062 (2002) Whole document	48
X	HU W. *et. al.*: Growth of well-aligned carbon nanotube arrays on silicon substrates using porous alumina film as a nanotemplate. Applied Physics Letters, Vol. 79, Number 19, 5 November 2001, 3083-3085 Whole document	37-39
Y	Note that HU W. et. al. can be combined with either SHAMOING HUANG or CHEN Y. *et. al.*	1-49

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2007/000059

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

[See Supplemental Box Continuation of Box III]

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box
(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: III

This International Searching Authority has found that there are different inventions as follows:

- Claims 1-36 are directed to a method of preparing carbon nano-tubes comprising the steps of (a) providing at least one nanotemplate; (b) performing a first pyrolysis in the presence of at least one first carbon source; and (c) performing at least one further pyrolysis. It is considered that performing two step pyrolysis of a carbon source in the presence of a nanotemplate comprises a first distinguishing feature.

- Claims 37-44, 45, 46, and 48 are directed to carbon nanotubes with at least one outer tube and at least one inner tube where claims 45, 46 and 48 define that they are used to manufacture electrodes or supercapacitors. It is considered that carbon nanotubes with at least one outer tube and at least one inner tube comprises a second distinguishing feature.

  Claims 47 and 49 share both technical features.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art..

Each of the abovementioned groups of claims has a different distinguishing feature and they do not share any feature which could satisfy the requirement for being a special technical feature. Because there is no common special technical feature it follows that there is no technical relationship between the identified inventions. Therefore the claims do not satisfy the requirement of unity of invention *a priori.*

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/SG2007/000059

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	2004083113	KR	2004008295	US	2006216221		
WO	2005086982	US	2005266162				
KR	20050001589						
KR	20040084114						
JP	2004323258						
US	2004197638	AU	2003304194	EP	1570539	WO	2004109837
KR	20020004644						
EP	1591418	US	2005255321				
CN	1404174						
WO	2005075663	IE	20050054				
KR	20020007237	KR	2003003281				
WO	2005085130	CA	2559070	EP	1727767	FI	20040365
		KR	2007000122				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX