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(54) Title: CARBON NANOSTRUCTURES AND NETWORKS PRODUCED BY CHEMICAL VAPOR DEPOSITION

(57) Abstract: The invention pertains to a method for manufacturing crystalline carbon nanostructures and/or a network of crystalline carbon nanostructures, comprising: (i) providing a bicontinuous micro-emulsion containing metal nanoparticles having an average particle size between 1and 100nm;(ii) bringing said bicontinuous micro-emulsion into contact with a substrate; and (iii) subjecting said metal nanoparticles and a gaseous carbon source to chemical vapor deposition, thus forming carbon nanostructures and/or a network of carbon nanostructures. Therewith, it is now possible to obtain crystalline carbon nanostructures networks, preferably carbon nanotubes networks.

Carbon nanostructures and networks produced by chemical vapor deposition

FIELD OF THE INVENTION

The present invention relates to nanostructures of carbon such as carbon nanotubes (CNTs), fullerenes and graphenes. More particularly, the invention pertains to networks of carbon nanostructures, particular CNT networks, the production thereof, and the use of such networks in composite materials. The invention also pertains to compositions suitable for use in nanostructures network production.

BACKGROUND OF THE INVENTION

Carbon nanotubes are tubular structures formed by one or more layers of graphene. Since the discovery of a synthetic process to make carbon nanotubes in the early nineties, lot of attention has been concentrated on CNTs because of their excellent electrical, thermal and mechanical properties and large specific surface. Based thereon, all kinds of applications have been suggested, ranging from microelectronic components, displays, radio communication to fuel cells.

There are three main approaches for the synthesis of single- and multi-walled carbon nanotubes, including electric arc discharge of graphite rod, laser ablation of carbon, and chemical vapor deposition of hydrocarbons. However, the most cost-effective methods for synthesizing carbon nanotubes have been based on chemical vapor deposition (CVD). Metal catalyzed thermal CVD typically uses a cheap feedstock and has relatively low energy requirements, and has therefore attracted interest for the purpose of bulk synthesis. In CVD methods, a carbon-containing gas is decomposed at high temperatures and under the influence of a finely divided catalyst (usually iron, nickel, cobalt or other transition metals or alloys) the carbon atoms are bonded to form CNTs. Catalyst particles may be manufactured *in situ* by the decomposition of metalloorganic compounds or may be inserted into the CVD furnace on a fixed substrate.

EP 1952467 is directed to nanowire structures and interconnected, porous nanowire networks comprising such structures. The nanowire serves as a core for a template for the growth of carbon networks. To maximize catalyst accessibility and utilization, for instance in fuel cell applications, EP'467 teaches to deposit a thin film or layer of metal catalyst onto the surface of the nanowires. However, the intimate

linkages between nanowire support and the catalyst particles deposited thereon reflects on the limited catalyst efficacy and conductivity properties. Additionally, the catalyst particles located on top of the carbon structure makes those more vulnerable to desorption. Also, the nanostructures thus obtained are non-crystalline, which would render these structures less suited for many applications. The contents of EP'467 is herein incorporated by reference.

It is widely recognized in the art that CVD typically results in a large amount of impurities due to little control over catalyst properties besides other reasons. US 2006/0104889 teaches catalysts of small average particle sizes with narrow size distribution, otherwise difficult to synthesize. US'889 proposes catalyst particles having a size between 1 to 50 nm supported on a powdered oxide at a 1:1 – 1:50 particles to support weight ratio. The contents of US'889 is herein incorporated by reference.

EP 1334064 discloses a process for preparing carbon nanotubes, which comprises suspending nanometer-sized fine metal particles in a gaseous phase. It enables control of the shape and structure of the carbon nanotubes. The metal nanoparticles have an average size in the order of a few to several hundred nanometers. It is attempted to control CNT purity through the use of surfactant, which should prevent cohesion of the colloidal metal particles. The contents of EP'064 is herein incorporated by reference.

EP 2123602 discloses nanotubes grown using CVD process in which an S-layer of proteins is generated on a substrate and used as a mask where inorganic nanoparticles are deposited on through the incubation and and reduction of the correspodning metal salt solution. It suggests a physical assembly of discrete nanostructures in figures 1 and 2, without any chemical interconnectivity between those structures. The contents of EP 2123602 is herein incorporated by reference.

However, the narrow size distributions of metal catalyst particles applied in the art such as the above can only be provided in low densities. Even if use is made of a micro-emulsion to stabilize the metal particles, metal particle concentrations are typically of about few mM, on the penalty of break-up. For that particular example in EP 1334064, the maximum concentration of metal particles is 10 mM. Hitherto, at these kinds of concentrations however networks of carbon nanostructures have not been observed in the art.

Also, regardless of the above attempts to control particle size in CVD, Takenaka *et al.* "*Formation of carbon nanotubes through ethylene decomposition over supported Pt catalysts and silica-coated Pt catalysts*" Carbon 47 (2009) 1251 – 1257, shows that an initially controlled size of metal particles is no warrant for success, because without any preventative measures the metal particles seriously aggregate during the actual carbon decomposition.

Hence, the art strives for better control of catalyst aggregation, and consequently, the purity and uniformity of the carbon nanostructures. There is also a need for simple CVD-based methods to produce chemically interconnected carbon nanostructure networks.

SUMMARY OF THE INVENTION

The inventors have found a cost-effective method for manufacturing carbon nanostructures (such as CNTs), by forming and growing nanostructures around a monodisperse distribution of nanosized metal particles. In particular a network of chemically interconnected carbon nanostructures can be synthesized by this method, which is unprecedented. The networks when used as fillers in composites impart electrical properties, mechanical strength, thermal properties and chemical resistance unprecedented in the prior art. Examples of some of these properties are given in the accompanying examples.

Use is made of technology disclosed in WO 2010/041937, outside the field of carbon nanostructures, providing a high density and narrow size distribution of controlled size metal particles, which are grown in bicontinuous micro-emulsions. The contents of WO'937 is herein incorporated by reference. The micro-emulsion character enables good control of particle size and monodispersity. The inventors' insights render it possible to drastically reduce impurities during CVD while allowing the growth of virtually any nanostructure. Deposition of catalyst is avoided.

Key in the process of the invention is that the nanostructures are grown around the catalyst particles prepared in the bicontinuous micro-emulsion. Surprisingly, while the bicontinuous micro-emulsion character is lost in the elevated temperature CVD environment, the metal particle size is maintained, and aggregation is –unlike in the art for other stabilizing systems – less likely to occur. Although the inventors do not wish to be tied down to any theory, the reason is believed to rest in the micro-emulsion

carbonizing around the particles above 770 K, thus preventing these from sintering during carbon decomposition.

Moreover, through the use of a bicontinuous micro-emulsion for manufacturing the metal particles it is possible to reach particle concentrations higher than with any other system, including droplet-type (water-in-oil, L2 phase) micro-emulsions such as disclosed in WO 81/02688. In the field, the term 'L2' is reserved for emulsions consisting of small water surfactant aggregates in a continuous oil phase. For sake of completeness, it is confirmed in the accompanying examples that the use of the L2-type micro-emulsion in for instance the CVD process of EP 2123602 does not yield any networks. It is however noted that WO'688 itself is outside the field of carbon nanotubes, and lacks any pointer to the CVD process.

Although the inventors do not wish to be tied down to any theory, it is their belief that the increased particle concentrations may be attributed to the control of the kinetics of the production precursor atoms, nucleii and subsequently the particles via the intricate nanostructure of the bicontinuous micro-emulsion. In addition, the high surfactant concentrations available in the bicontinuous micro-emulsion stabilize the huge surface created by many small particles. It is therewith possible to increase metal particle concentrations orders of magnitude over droplet type micro-emulsions. The authors hypothesize that by having a high concentration of catalyst nanoparticles several nucleation centres are created which further grow to form the branches that form the basis of the carbon nanotube network. The art is silent on such networks.

Product-wise, the carbon nanostructures and their networks thus obtained are distinguishable from those nanostructures produced according to the prior art, in terms of structure and porosity, but also in terms of their chemical, electrical and mechanical properties (such as conductivity and permittivity) which can readily be verified without undue burden by the skilled person using conventional spectroscopic techniques (e.g. dielectric spectroscopy). These properties may benefit applications such as in catalysis (e.g. heterogenous, electrocatlysis), metallurgy (e.g. anodes for aluminum production), electronics (e.q. storage devices, processors), sensors (e.g. for biomolecules, toxic ions in water) and frameworks for utility items (e.g. aircraft or automobile parts, sports goods). Details on these properties are discussed in the accompanying examples.

LIST OF FIGURES

Figure 1 compares platinum nanoparticles produced using (a) droplet type micro-emulsion ('L2') and (b) bicontinuous micro-emulsion;

Figure 2 shows the particle size distribution of the nanoparticles produced in a bicontinuous micro-emulsion measured by dynamic light scattering. This particular batch involves 5 nm particles corresponding to the recipe in example 1;

Figure 3a shows a transmission electron microscopy image of a carbon nanotubes networks. The thicker and longer structures are clusters of smaller nanotubes;

Figure 3b highlights on the nodes where the carbon nanotubes network with illustrated overlays;

Figure 4 shows that the nanotubes are chemically interconnected. The black spots are nanoparticles catalysts that were used to grow the tubes;

Figure 5 shows a multi-walled carbon nanotube having a capped end. The lighter sheath around a dark core of the nanotubes could be due to an amorphous layer or due to aberration because of the curvature of the nanotube;

Figure 6 shows the discrepancy in shape and structure between state-of-the-art nanotubes (b) and the CNT networks (a) according to the invention. Figure 6a shows a 'sponge-like' chemically linked CNT network according to the invention. Figure 6b illustrates typical, commercially available CNTs unorganized in clumps;

Figure 7a-d: CNT networks that have chemically linked CNTs according to the invention show new types of junctions;

Figure 8 shows carbon nanotube networks grown using (a) iron and (b) silver catalyst nanoparticles;

Figure 9: (a) electrical conductivities of polymethylmethacrylate and composite comprising CNT networks and PMMA; (b) storage modulus of polyimide and composite comprising CNT networks and PI polyimides; (c) storage modulus and tan delta of polyethylene and composite comprising CNT networks and PE; and (d) storage modulus and tan delta of epoxy and composite comprising CNT networks and epoxy;

Figure 10 compares the Raman spectrum of (a) multi-walled carbon nanotubes and (b) CNT networks;

Figure 11 compares the porosity of (a) multi-walled carbon nanotubes and (b) CNT networks;

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Figure 12: Polarisation curve of the fuel cell constructed with carbon nanotube networks as the electrode and Nafion® as the electrolyte.

DETAILED DESCRIPTION

According to one aspect, the invention pertains to a method for manufacturing crystalline carbon nanostructures, preferably nanotubes, comprising (i) providing a bicontinuous micro-emulsion containing metal nanoparticles having an average particle size from 1 to 100 nanometers, (ii) bringing said bicontinuous micro-emulsion into contact with a substrate and (iii) subjecting said metal nanoparticles and a gaseous carbon source to chemical vapor deposition, thus forming said crystalline carbon nanostructures.

Advantageously, the uniformity of the metal particles is controlled in said bicontinuous micro-emulsion by mixing a first bicontinuous micro-emulsion in which the aqueous phase contains a metal complex salt capable of being reduced to the ultimate metal particles, and a second bicontinuous micro-emulsion in which the aqueous phase contains a reductor capable of reducing said metal complex salt; upon mixing the metal complex is reduced, thus forming metal particles.

The controlled bicontinuous environment stabilizes the particles against sintering or Ostwald ripening. Size, concentrations and durability of the catalyst particles are readily controlled. It is considered routine experimentation to tune the average metal particle size within the above range, for instance by amending the molar ratio of metal precursor vs. the reducing agent. An increase in the relative amount of reducing agent yields smaller particles. The metal particles thus obtained are monodisperse, deviations from the average particle size are preferably within 10 %, more preferably within 5 %. In the method of the present invention, deviations from the average particle size are less than 10%.

Also, the present technology provides no restraint on the actual metal precursor, provided it can be reduced. Unlike in the art, there is no need to subsequently deposit layers of active catalyst materials onto the metal particles thus formed. In the catalytic CVD the known effective catalyst species are the noble metals (Pt, Pd, Au, Ag), iron-family elements (Fe, Co and Ni), Ru, and Cu. Suitable metal complexes are but are not limited to (i) platinum precursors such as H_2PtCl_6; $H_2PtCl_6.xH_2O$; K_2PtCl_4;

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$K_2PtCl_4.xH_2O$; $Pt(NH_3)_4(NO_3)_2$; $Pt(C_5H_7O_2)_2$, (ii) ruthenium precursors such as $Ru(NO)(NO_3)_3$; $Ru(dip)_3Cl_2$ [dip = 4,7-diphenyl-1,10-fenanthroline]; $RuCl_3$, or (iii)

palladium precursors such as $Pd(NO_3)_2$, or (iv) nickel precursors such as $NiCl_2$ or $NiCl_2.xH_2O$; $Ni(NO_3)_2$; $Ni(NO_3)_2.xH_2O$; $Ni(CH_3COO)_2$; $Ni(CH_3COO)_2.xH_2O$; $Ni(AOT)_2$ [AOT = bis(2-ethylhexyl)sulphosuccinate].

Non-limiting suitable reducing agents are hydrogen gas, sodium boron hydride, sodium bisulphate, hydrazine or hydrazine hydrate, ethylene glycol, methanol and ethanol. Also suited are citric acid and dodecylamine.

The type of metal precursor is not an essential part of the invention, as evidenced in the accompanying examples. In one aspect, the metal of the particles of the bicontinous micro-emulsion is selected, preferably from the group consisting of Pt, Pd, Au, Ag, Fe, Co, Ni, Ru and Cu, in order to control morphology of the carbon nanotube networks ultimately formed.

The term "carbon nanostructures" are understood to comprise crystalline sp2- based carbon allotropes, i.e. substances in which a carbon atom is bonded to neighboring three carbon atoms in a hexagonal pattern, including graphene, fullerene and carbon nanotubes. Advantageously, through the use of the bicontinuous micro-emulsions and therewith the ability to provide uniform and high metal particle concentrations, the skilled person can prepare any crystalline carbon nanostructure desired, dependent on the actual metal particle size and density applied.

Carbon nanotubes are the preferred nanostructure, i.e. cylindrical carbon molecules having a diameter ranging from several angstroms to several nanometers, with the length ranging from ten-folds to thousand-folds of the diameter. With the present invention it is possible to produce both single-walled and multi-walled (e.g. double-walled) CNTs, referring to the number of carbon layers making up to the wall of the nanotube.

The method of the invention allows for the growth of crystalline carbon nanostructure networks of multiple carbon nanostructures, which are chemically interconnected, through all kinds of junctions, including Y- and H-junctions (see Figure 7).

The reaction processes of the present invention to form carbon nanotubes using chemical vapor deposition are described in the prior art. Therefore, without being particularly limited in the present invention, the process parameters for carrying out the

present invention, such as the temperature, time and pressure, may be readily determined by a person having ordinary skill in the art from the prior art. Merely as a guideline, the reaction conditions in step (iii) of using the active metal catalyst, which is deposited on a support or carrier, to catalyze a carbon accumulation reaction for forming carbon nanotubes include: introducing an inert gas (e.g. He, Ar or N_2), hydrogen and a carbon source gas into a reactor at a high temperature and a pressure of 1 – 5 bars for a reaction time of 1 – 360 minutes. The high temperature environment ranges from 750 to 1100 K, preferably 800 K or higher, more preferably at least 850 K, particularly at least 900 K. Upon completion of the reactions, the support is removed in order to recover carbon nanotubes.

The process is preferably a batch process, wherein the carbon-containing gas and metallic catalytic particles are disposed within the reactor cell and held therein for the duration of the reaction period. Alternatively, the process may be continuous, wherein the metallic catalytic particles and carbon-containing gas are continuously fed and mixed within the reactor.

The gaseous carbon source includes aliphatic hydrocarbons, both saturated and unsaturated, such as methane, ethane, propane, butane, hexane, ethylene, acetylene and propylene; carbon monoxide, oxygenated hydrocarbons such as acetone and methanol; aromatic hydrocarbons such as toluene, benzene and naphthalene; and mixtures of the above, for example carbon monoxide and methane. Use of acetylene promotes formation of multi-walled carbon nanotubes, while CO and methane are preferred gases for formation of single-walled carbon nanotubes. The gaseous carbon source may optionally be mixed with a diluents gas such as nitrogen, helium, argon or hydrogen.

The support is selected such that it will not react with the active metal catalyst inadvertently during a heating process, so that the active metal catalyst can catalyze a synthesis reaction of the carbon nanotubes as desired. The support is preferably selected from titanium, copper, stainless steel, molybdenum and inert oxides such as silica (glass, quartz), ceramics and exotic materials such as diamond. Excellent structures are obtained with zeolite for support. With the bicontinuous emulsion-based metal catalyst particles, the type of support did not have any detrimental effect on the grown nanostructures.

As a result of the process according to the invention, uniform crystalline nanostructures are obtained in which the metal nanoparticles are embedded inside and physically attached to the carbon nanostructures, which form and grow around these particles. Upon analysis it is found that metal aggregation during CVD is minimal, the singular character is maintained.

In one aspect, the invention pertains to networks of chemically linked, i.e. covalently linked, carbon nanostructures, preferably CNTs, obtained or obtainable by the method as detailed above. The minimum concentration of metal particles at which networks are formed depends on a range of parameters all readily controlled by the skilled person. Although the density of metal particles is a pronounced factor, other contributing parameters are the type of bicontinuous emulsion including its organic phase and surfactant, and their relative amounts. Examples are provided in the accompanying examples. It is considered within the skilled person's ambits to provide a metal particles density sufficient to enable network formation, the use of bicontinuous emulsions advantageously puts no restraints to this process.

In order to arrive at nanostructures networks, it is however preferred to subject metal particles in a bicontinuous micro-emulsion to the CVD process in an active metal concentration of at least 15 mM, more preferably at least 20 mM, particularly at least 25 mM, especially 30 mM. Excellent networks are obtained at concentrations higher than 40 mM. These are concentrations of the catalyst relative to the amount of the aqueous phase in the bicontinuous micro-emulsion. At high catalyst particle densities carbon nanotube networks are obtained in which the carbon nanotubes are chemically linked (Figure 3). These relative amounts are preferably based on the sum of contributing metal particles. In this aspect, the carbon nanostructures thus formed are distinguished from the prior art.

This is also reflected in the properties of the carbon nanostructure networks, which do not correspond to the behavior found for non-carbon networks. The carbon nanostructures in the prior art, which are not chemically connected, show completely different behavior. According to one embodiment, these networks may be characterized by Raman spectroscopy, exhibiting two partly overlapping signals (but yet distinguishable) in the wavelength region of 1000 – 2000 cm^{-1}, and a broad third signal in the wavelength region of 1800 – 3500 cm^{-1}; a signal is typically identified by having

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a signal-to-noise ratio of at least 5, more preferably at least 10, more preferably at least 20. The broad signal may be characterized having a signal width at half-height of at least 100 cm^{-1}, preferably 100 – 800 cm^{-1}, more preferably 100 – 400 cm^{-1}. In one embodiment, the signal width at half-height is at least 300 cm^{-1}, preferably up to 1000 cm^{-1}. An example of the distinction between CNTs and CNT networks is shown in figure 10.

Additionally or alternatively, according to embodiments of the invention the carbon nanostructure networks or CNT networks may be distinguished from CNTs unorganized and not chemically linked to one another by a (second) transition at a temperature higher than 160 °C, preferably higher than 175 °C. The presence of that second transition state is indicative of the network rather than the individual tubes. An example is shown in figure 9c.

The invention also pertains to a composite composition comprising carbon nanotube networks according to the invention, further comprising a polymer, for instance for adding mechanical strength to said polymer-based composite. It may thus be added in any amount, e.g. 0.1 – 10 wt%, more preferably 0.5 – 8 wt%, even more preferably at least 1 wt%, based on the total polymer weight in the composite.

Also disclosed herein is a bicontinuous micro-emulsion containing metal nanoparticles having an average particle size between 1 and 100 nm, wherein deviations in particle size from the average particle size are less than 10 %, preferably less than 5 %. The concentration of metal particles is preferably as described above, rendering the micro-emulsion suitable for providing crystalline nanostructures networks. The invention also pertains to the use of these bicontinuous micro-emulsions in manufacturing carbon nanostructures and networks thereof, as explained in detail here above.

EXAMPLES

Example 1. Carbon Nanotube Synthesis on Platinum Nanoparticles by CVD

Example 1a. Synthesis of Platinum Nanocatalysts

Two micro-emulsions were prepared after adding a mixture of a fluorocarbon surfactant [perfluoro(4-methyl-3,6-dioxaoctane)sulphonate] and n-hexanol to an

aqueous solution. The first micro-emulsion contained the platinum precursor hexachloroplatinic acid. To the second micro-emulsion the reducing agent hydrazine was added. The amount of reducing agent was set at ten times the concentration of the platinum complex in order to obtain complete reduction upon mixing. The synthesis of nanoparticles was carried out by mixing equal amounts of the two micro-emulsions:

$$H_2PtCl_6\ (aq) + N_2H_4\ (aq) \dashrightarrow Pt(s) + 6H^+ + 6Cl^- + N_2$$

The platinum nanoparticles were characterized using transmission electron microscopy (TEM) and dynamic light scattering (DLS). Transmission electron microscopy (TEM) was accomplished using a Philips CM30T electron microscope with a lanthanum hexaboride (LaB6) filament operated at 300 kV as the source of electrons. Samples were mounted on a Quantifoil® microgrid carbon polymer supported on a copper grid by dropping sample suspension on the grid. The particles showed an average particle size of about 5 nm, as shown in Figure 1b and 2. The variations in size were analyzed being within 10 % of the average size.

Comparitive example 1a.1. L2-phase micro-emulsion

Figure 1a shows an example of an L2-phase micro-emulsion. The figure is copied from D.-H. Chen, J.-J. Yeh and T.-C. Huang, J. Coll. Int. Sci., 215, (1999), 159–166. It stands model for the micro-emulsion applied in WO 81/02688. The nanoparticles in Figure 1a that were generated in droplet type micro-emulsions were about 9 nm in size, and quite well separated from one another.

Clearly, the bicontinuous micro-emulsion shown in Figure 1b has a higher density of uniformly sized and shaped nanoparticles than the L2-phase micro-emulsion of Figure 1a. In the bicontinuous micro-emulsion the nanoparticles seem to be clustered in pools, which are connected by channels containing nanoparticles, possibly be the result of the motif of the bicontinuous structure, which is not visible as it has no contrast with the background. It is believed that the high density of catalyst nanoparticles result in the CVD process in a high degree of branching for the carbon nanotube networks therewith forming a chemically-linked network structure.

Example 1b. Synthesis of Carbon Nanotubes

The micro-emulsion containing 10mM Pt precipitate was poured on a Copper grid, which was placed at the bottom of a reactor. After increasing the temperature to 973K (10 K /min) under a flow of nitrogen at 100 ml/min, ethylene gas (C_2H_4) was introduced at 10 ml/min into the reactor. The gas mixture passed through the reactor over the nanoparticles for 30 minutes at a constant temperature of 973K. Once the dwell step was over, the synthesis gas flow was stopped, and the reactor was cooled down to room temperature under nitrogen flow at 100 ml/min.

The carbon nanotubes thus obtained were characterized using electron microscopy (Figures 3 - 8), energy dispersive x-ray spectroscopy, dielectric spectroscopy (Figure 9a), mechanical spectroscopy (Figure 9b), Raman spectroscopy (Figure 10) and nitrogen sorption (Figure 11).

The tubes could be tuned to have a diameter from 5 to 50 nm and lengths from 100 nm to 3 microns. Each experiment resulted in nanotubes uniform in length and diameter as observed under electron microscopy (Figure 3). The variations were 18 % in diameter, and 7 % in length.

Example 2. Carbon Nanotube Network

Example 1 was repeated, with the difference that a high catalyst concentration of 100 mM was used. The resulting nanotube networks were characterized by the same techniques as mentioned in example 1. The networks had dimensions from 50 μm to 1 mm (Figure 6).

Example 3. Absorption spectroscopy

Raman spectroscopy was performed on the nanotubes network according to the invention using a Renishaw Raman Imaging Microscope, system 2000, with a 20 mW Ar laser (514 nm). The Ramascope was calibrated using a silicon wafer. The results were compared with those obtained from a graph for carbon nanotubes was obtained from: F. Inoue, A. R. Ando and P. Corio, J. Raman Spectrosc., 42, (2011), 1379-1383.

The Raman absorption spectrum of multi-walled carbon nanotubes and carbon nanotube networks is shown in Figure 10. The I_D/I_G for carbon nanotubes is 0.92 which is higher than that of nanotube networks, this is probably due to more defects during

the production of the nanotubes. The 2D band is broader for nanotube networks, which implies multiple layers or walls.

Example 4. Nitrogen sorption

A Quantachrome Autosorb-1c instrument was used for nitrogen adsorption experiments carried out on on the nanotubes network according to the invention. All samples were outgassed at 350°C for 17 hours in vacuum. The results were compared with those obtained from a graph for carbon nanotubes obtained from: M. Chen, H.-W. Yu, J.-H. Chen and H.-S. Koo, Diamond & Related Materials, 16, (2007), 1110-1115.

The specific surface area obtained by nitrogen sorption on multi-walled carbon nanotubes and carbon nanotube networks as shown in Figure 11, proves the nanotube networks to be more active. The mean pore sizes of nanotubes and nanotube networks are comparable, however the networks have a broad distribution owing to inter-particulate voids.

Example 5. Mechanical strength

A clear difference between carbon nanotubes and carbon nanotube networks is observed when added to other materials. In composite with polyimides (PI) the nanotube networks impart more mechanical stiffness on an average than carbon nanotubes as shown in Figure 9b. The graph for carbon nanotubes was obtained from: X. Jiang, Y. Bin and M. Matsuo, *Polymer*, **46**, (2005), 7418-7424.

In the case of ultra-high molecular weight polyethylene the carbon nanotube networks imparted strength that not only resulted in a longer plateau in the storage modulus after the first transition at 150 °C but also gave a new transition at 190 °C, which further yielded to a longer plateau afterwards. All is plotted in Figure 9c.

Adding 2 % by weight of carbon nanotube networks to epoxy polymer caused the strength to become almost three times better, which was maintained over a broad thermal range between 50 and 200 °C: Figure 9d.

A Pyris Diamond DMTA from Perkin Elmer Incorporated was used for the dynamic mechanical analysis. Three different frequencies of 0.1, 1 and 10 Hz were probed for each sample in the bending mode.

Example 6. Electrical properties

The electrical conductivity of polymethylmethacrylate (PMMA) composites with carbon nanotube networks as shown in Figure 9a shows that it is independent of frequency regardless of the concentration, which is an indication of percolation. This behaviour is not seen in the pure or neat PMMA. In literature: D. O. Kim et al, Organic Electronics, 9, (2008), 1-13, it is found that 3 wt. % carbon nanotubes composited PMMA has a conductivity of 0.01 Scm^{-1} which is two orders of magnitude lower than for nanotube networks composited PMMA.

A broadband dielectric spectrometer from Novocontrol GmbH equipped with a HP 4284A precision LCR meter was used to perform the dielectric analysis. The maximum applied voltage was 0.9 V.

Example 7. Thermal properties

When mixed with silicone polymer in 2 wt. % CNT networks enhanced the thermal conductivity from 0.64 to 0.7 $Wm^{-1}K^{-1}$ at 298 K.

The Isomet model 104 from Isomet Corporation was used to determine the thermal conductivity. All samples were placed on a thermally insulating mat during measurement. The conductivities reported are an average value of the top and bottom surface of the samples.

Example 8. Catalytic properties

Carbon nanotube networks based electrodes gave a peak power output of 10 $mWcm^{-2}$ using hydrogen and oxygen as the fuel and oxidant respectively. A power curve is shown in Figure 12.

An electrode area of 7 cm^2 was used. The H_2:O_2 pressure ratios were 1.5:1 and the flow rates of both gases were 50 ml/min. A Nafion® 117 membrane was used as the electrolyte.

Example 9. Other metals

Different types of surfactant, oil and metal precursor that will be combined to create a bicontinuous micro-emulsion will lead to different values for the minimum concentration of catalyst particles required to form carbon nanotubes networks.

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In the table here below a list of various bicontinuous micro-emulsions incorporating various concentrations of metal particles are listed; in each and every case a carbon nanostructures network was obtained.

Catalyst	Surfactant	Oil	Reaction Temperature	Catalyst Support
Pt (20 mM)	AOT	n-heptane	973K	Titanium
Pt (750 mM)	AOT	n-dodecane	973 K	Diamond
Pt (50 mM)	Fluorosurfactant	Hexanol	973 K	Stainless steel
Pt (50 mM)	Fluorosurfactant	Hexanol	873 K	Molybdenum
Au (20 mM)	AOT	n-heptane	973 K	Titanium
Au (40 mM)	Fluorosurfactant	Hexanol	973 K	Molybdenum
Ag (50 mM)	AOT	n-heptane	923 K	Stainless Steel
Cu (25 mM)	AOT	n-heptane	973 K	Titanium
Cu (50 mM)	Fluorosurfactant	Hexanol	873 K	Stainless Steel
Fe (100 mM)	AOT	n-heptane	973 K	Ceramic
Co (50 mM)	AOT	n-heptane	973 K	Quartz
Pt (10 mM) + Ni (10 mM)	AOT	n-heptane	973 K	Ceramic

The presented catalyst concentrations are relative to the amount of the aqueous phase in the micro-emulsion.

Using the method according to the invention, carbon nanotube networks were obtained independent of the catalyst material in the bicontinuous micro-emulsion. However, the type of catalyst material may have an effect on the morphology of the carbon nanotube networks. For instance, iron catalyst nanoparticles yield more bundled nanotube networks whose branches are undulating as seen in Figure 8a whereas silver catalyst nanoparticles yield more linear and thicker branches (Figure 8b).

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

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In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

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CLAIMS

1. A method for manufacturing crystalline carbon nanostructures and/or a network of crystalline carbon nanostructures, comprising
   (i) providing a bicontinuous micro-emulsion containing metal nanoparticles having an average particle size between 1 and 100 nm, and wherein deviations in particle size from the average particle size are less than 10 %;
   (ii) bringing said bicontinuous micro-emulsion into contact with a substrate; and
   (iii) subjecting said metal nanoparticles and a gaseous carbon source to chemical vapor deposition, thus forming carbon nanostructures and/or a network of carbon nanostructures.

2. The method according to claim 1, wherein the bicontinuous micro-emulsion contains at least 15 mM metal nanoparticles calculated on the aqueous phase.

3. A network of chemically interconnected crystalline carbon nanostructures, said network obtainable by the method according to claim 1 or 2.

4. The network according to claim 3, wherein metal nanoparticles having an average size between 1 and 100 nm are embedded in said network.

5. The network according to any one of claims 3 – 4, being a carbon nanotubes network.

6. A method for manufacturing crystalline carbon nanostructures and/or a network of crystalline carbon nanostructures, substantially as herein described with reference to the Examples, excluding Comparative Examples.

7. A network of chemically interconnected crystalline carbon nanostructures substantially as herein described with reference to the Examples, excluding Comparative Examples.

8. Crystalline carbon nanostructures manufactured by the method of claim 1 or 2.

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9. A network of chemically interconnected crystalline carbon nanostructures manufactured by the method of claim 1 or 2.

Fig 1a

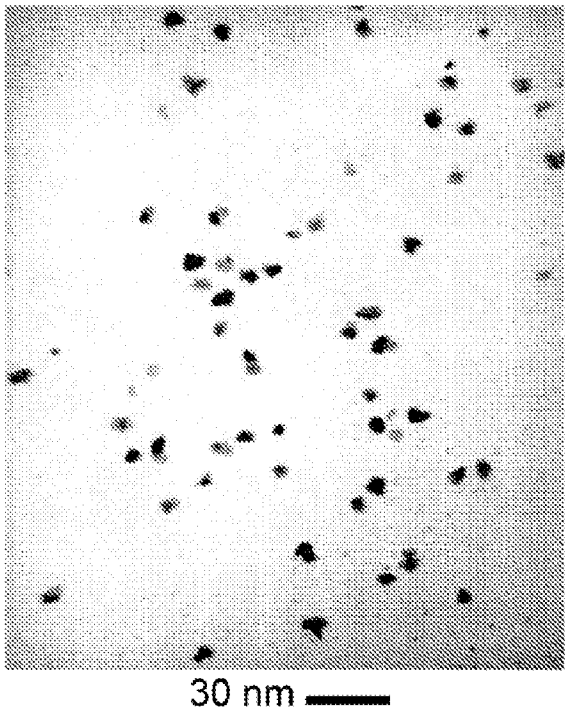


Fig 1b

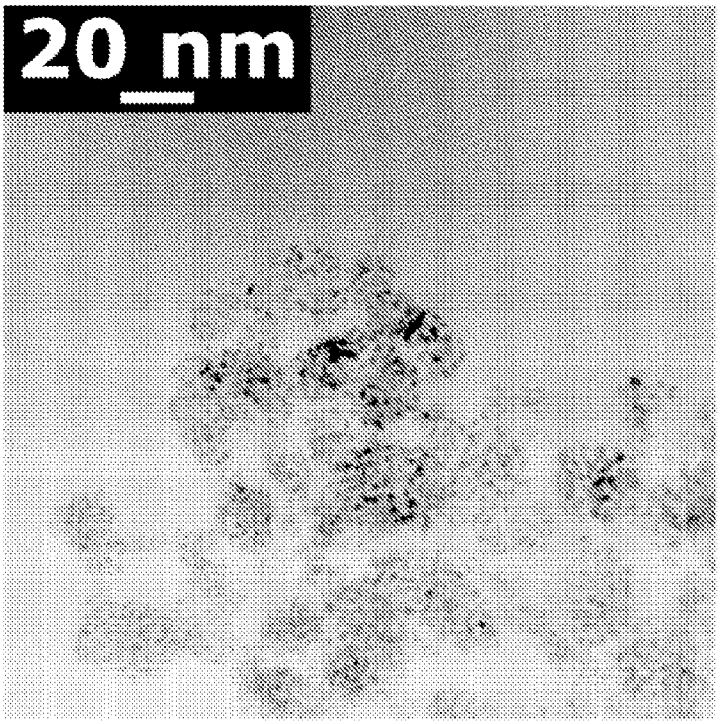


Fig 2

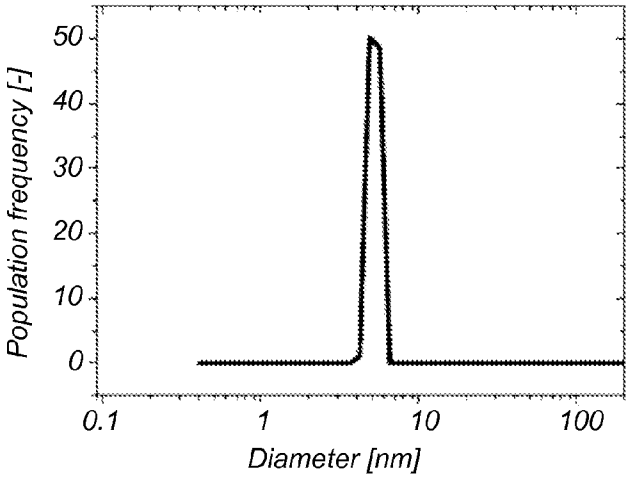


Fig 3a

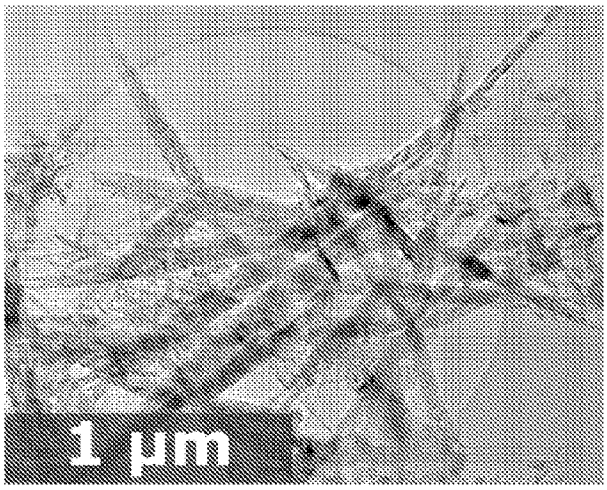


Fig 3b

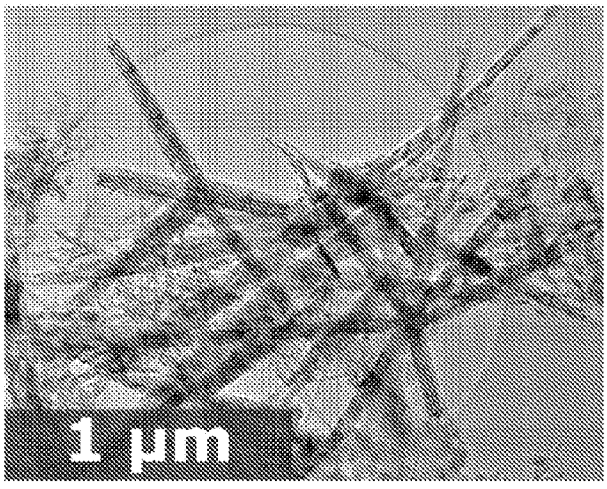


Fig 4

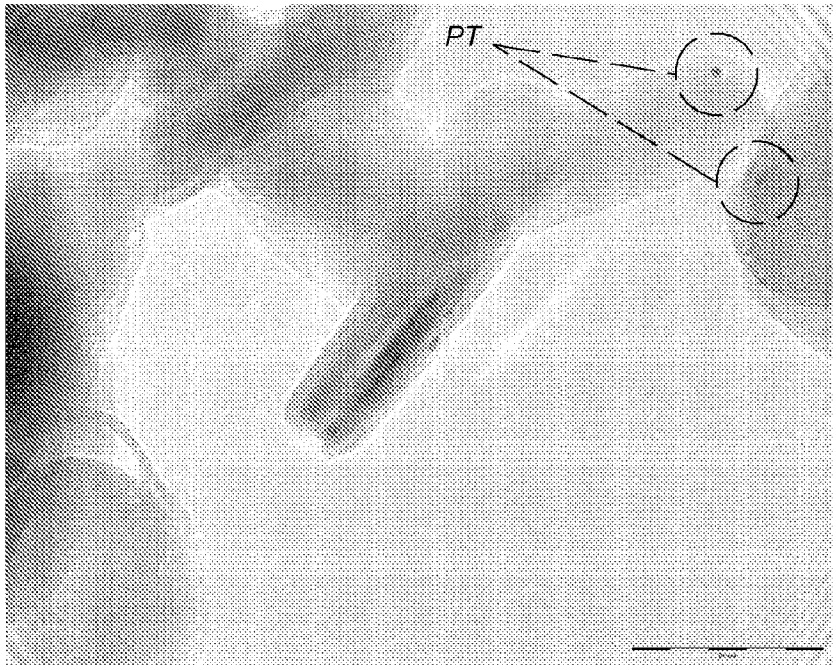


Fig 5

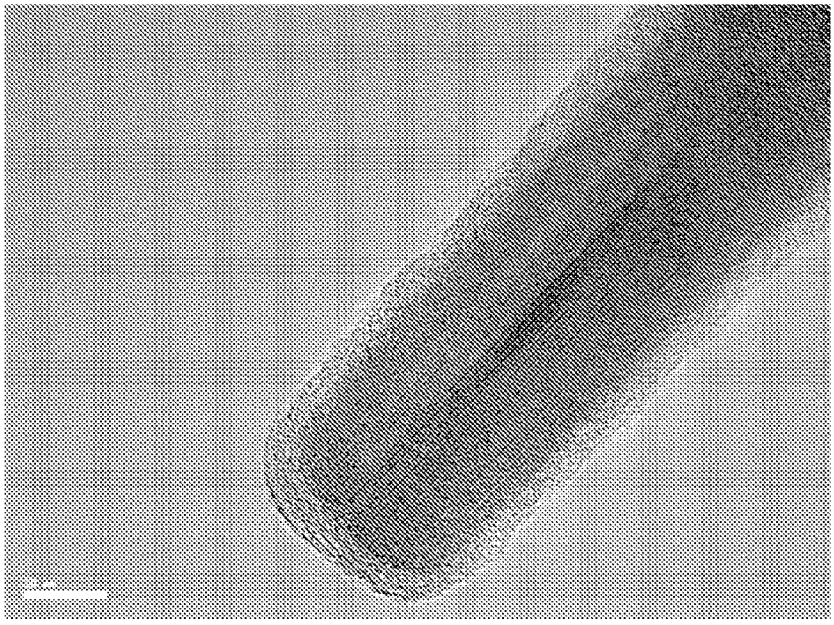


Fig 6a

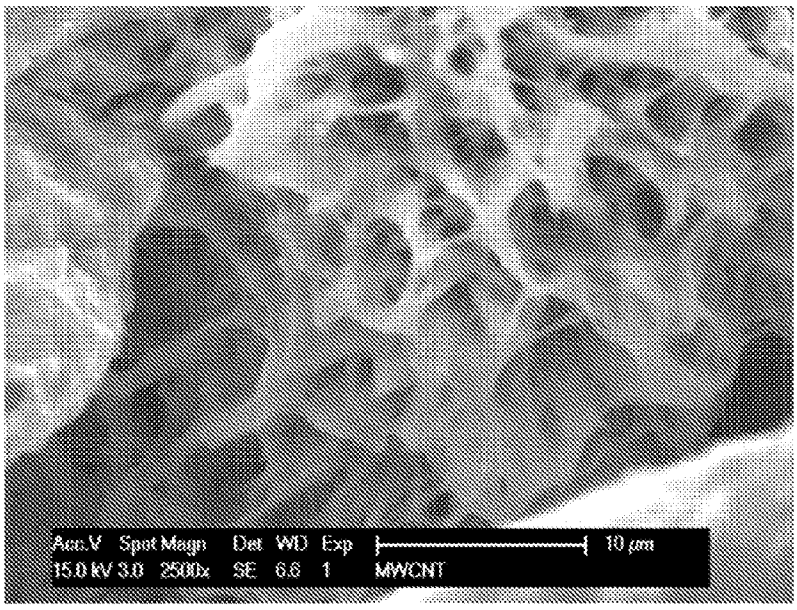

Acc.V Spot Magn Det WD Exp 10 µm
15.0 kV 3.0 2500x SE 6.6 1 MWCNT

Fig 6b

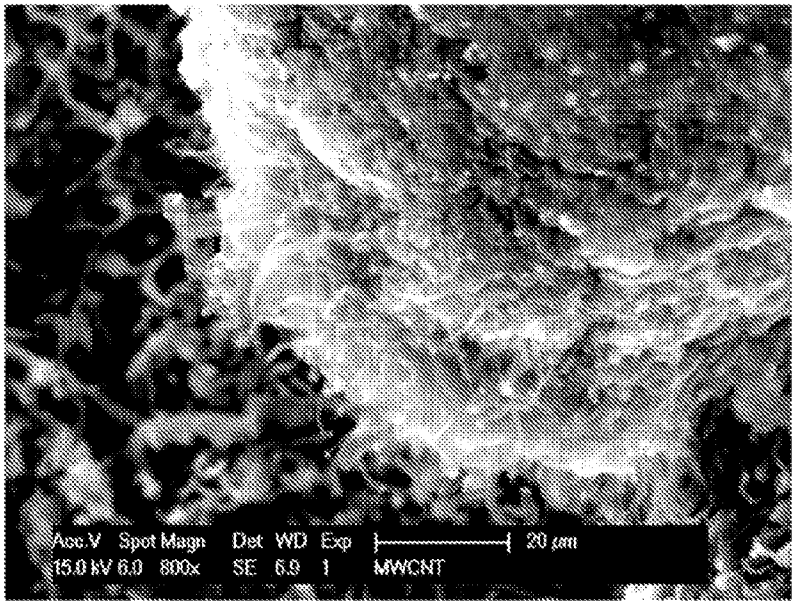

Acc.V Spot Magn Det WD Exp 20 µm
15.0 kV 6.0 800x SE 6.9 1 MWCNT

Fig 7a

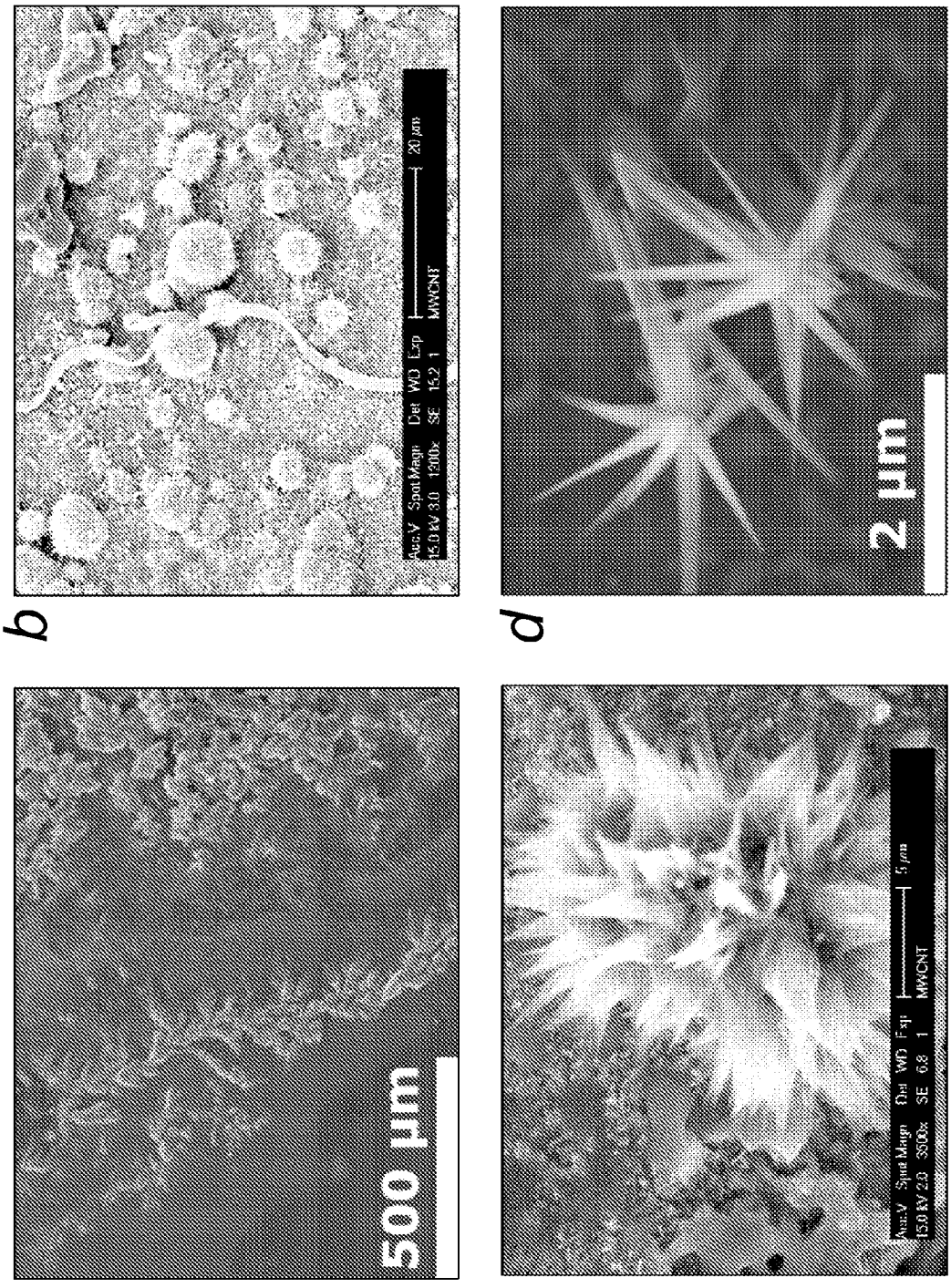

500 µm
b
Acc.V Spot Magn Det WD Exp
15.0 kV 3.0 1500x SE 15.2 1
20 µm
MWCNT
d
2 µm
c
Acc.V Spot Magn Det WD Exp
15.0 kV 2.0 3000x SE 6.8 1
5 µm
MWCNT

Fig 8a

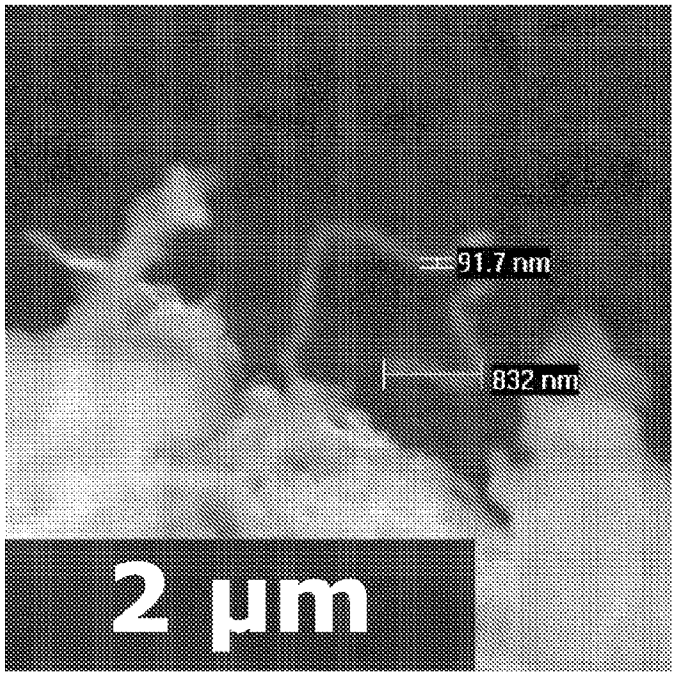


Fig 8b

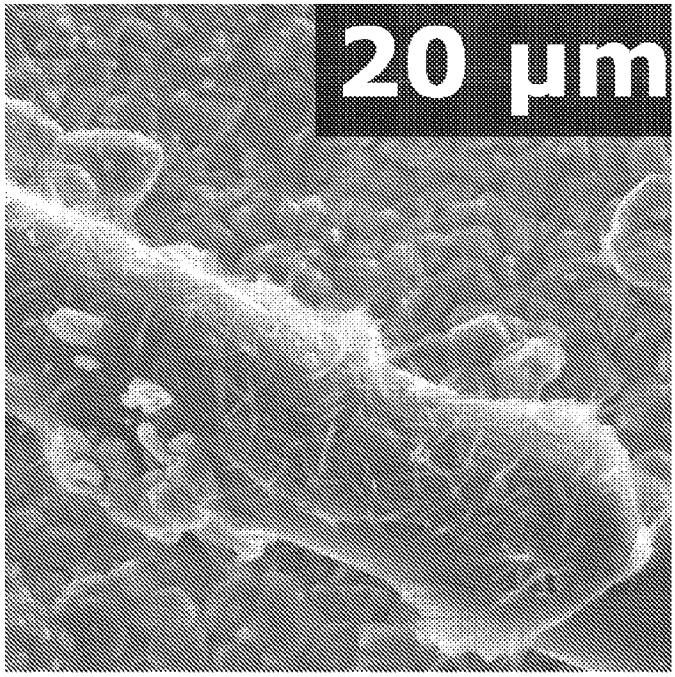


Fig 9a

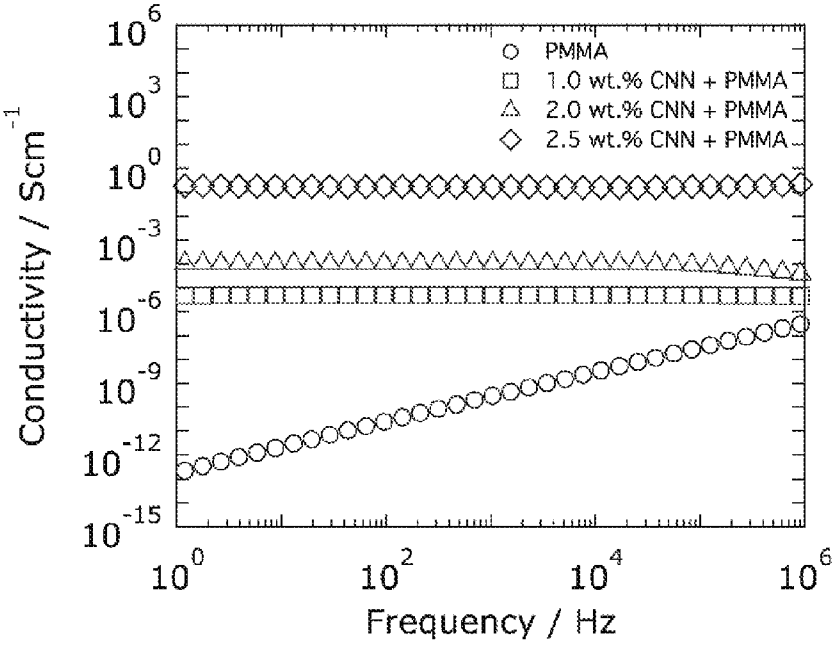

PMMA
1.0 wt.% CNN + PMMA
2.0 wt.% CNN + PMMA
2.5 wt.% CNN + PMMA
Conductivity / Scm-1
Frequency / Hz

Fig 9b

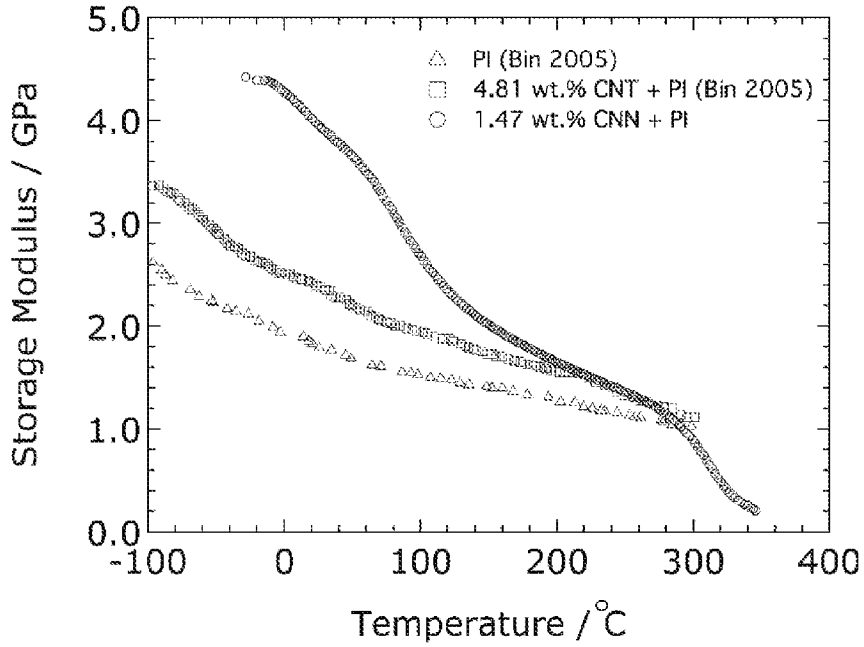

PI (Bin 2005)
4.81 wt.% CNT + PI (Bin 2005)
1.47 wt.% CNN + PI
Storage Modulus / GPa
Temperature / °C

Fig 9c

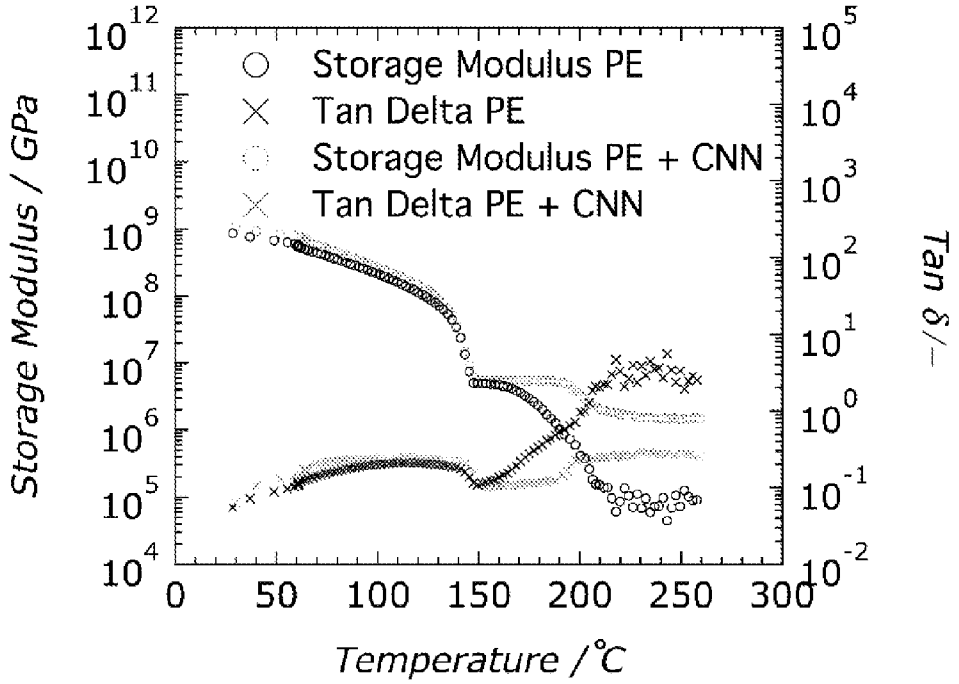

Storage Modulus PE
Tan Delta PE
Storage Modulus PE + CNN
Tan Delta PE + CNN
Storage Modulus / GPa
Tan δ / –
Temperature / °C
0
50
100
150
200
250
300

Fig 9d

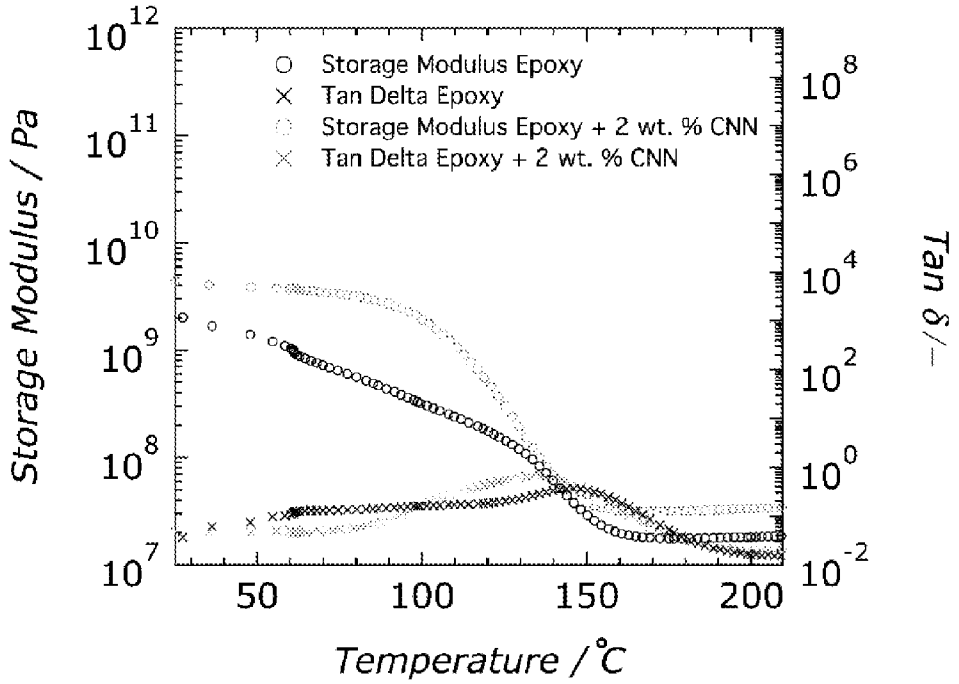

Storage Modulus Epoxy
Tan Delta Epoxy
Storage Modulus Epoxy + 2 wt. % CNN
Tan Delta Epoxy + 2 wt. % CNN
Storage Modulus / Pa
Tan δ / –
Temperature / °C
50
100
150
200

Fig 10a

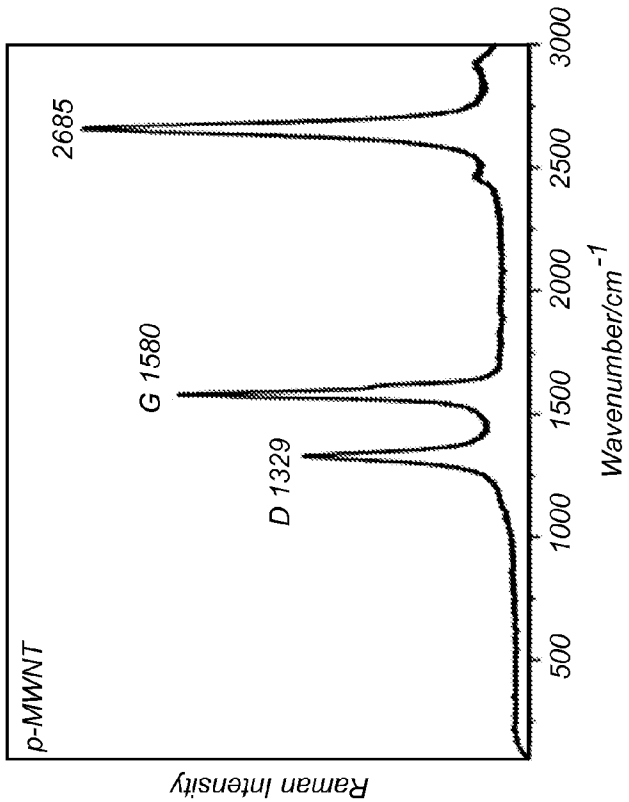


Fig 10b

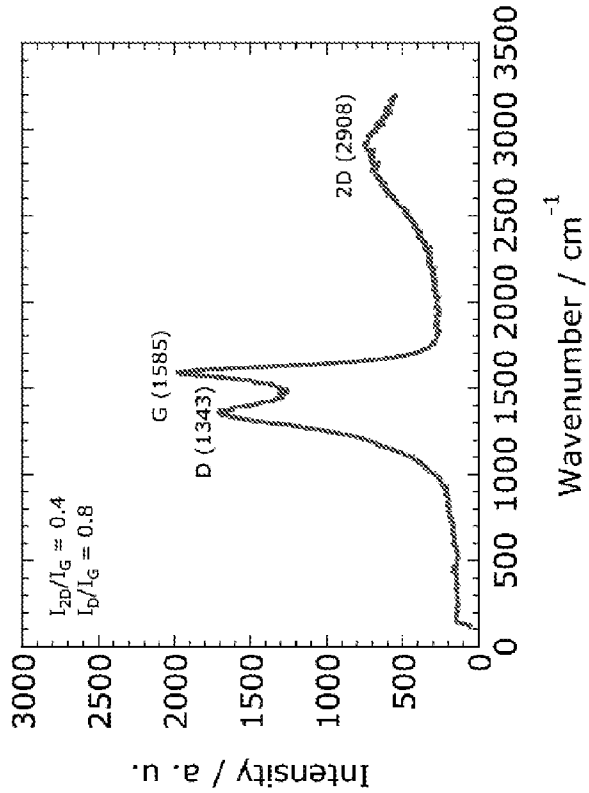


Fig 11a

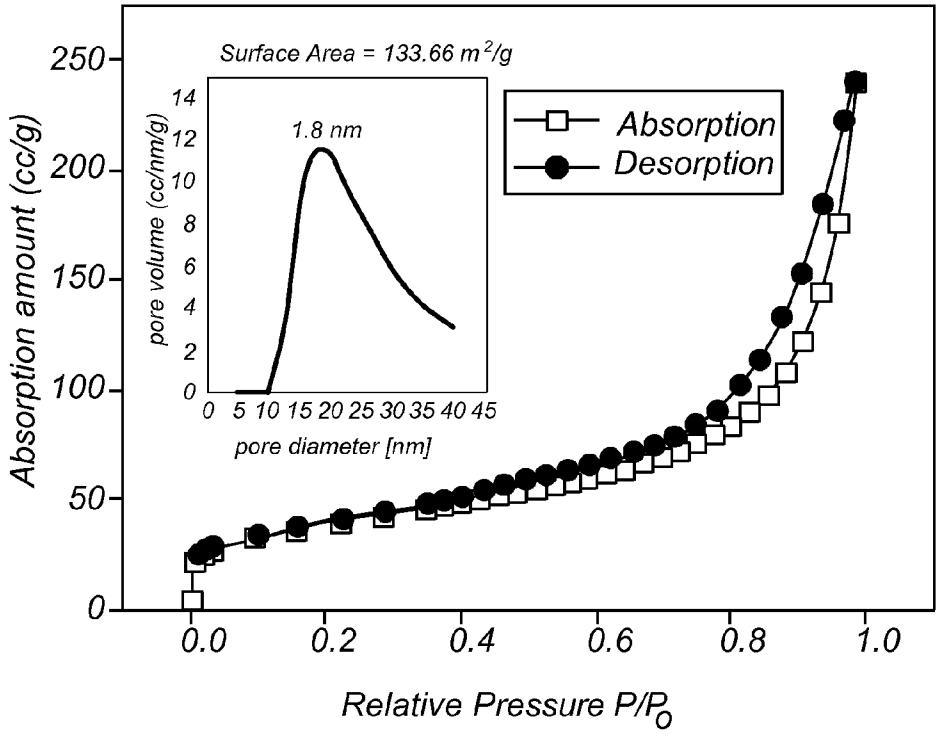


Fig 11b

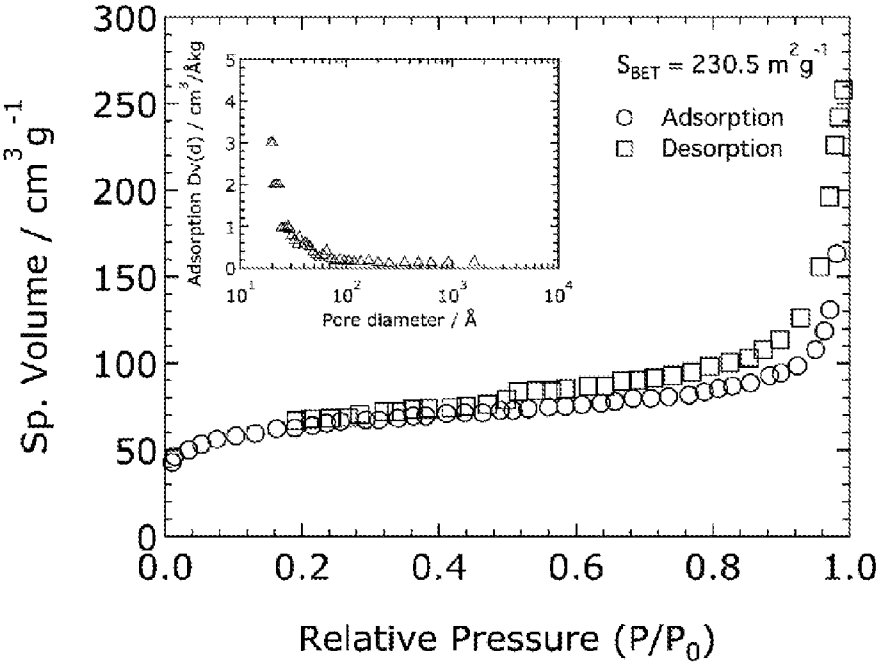
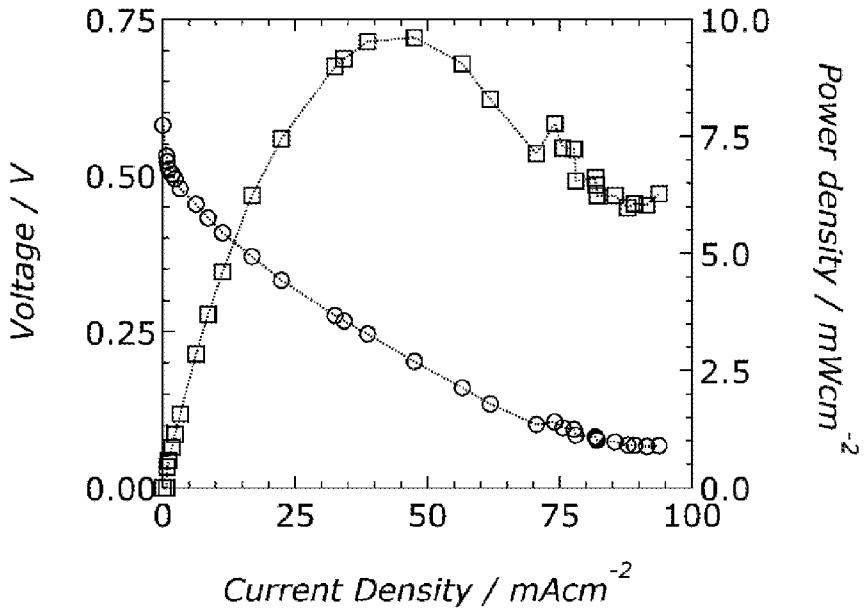


Fig 12


0.75
0.50
0.25
0.00
0
25
50
75
100
10.0
7.5
5.0
2.5
0.0
Voltage / V
Power density / mWcm-2
Current Density / mAcm-2