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(54) **PLASMA SYNTHESIS OF HOLLOW  
NANOSTRUCTURES**

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(57) **ABSTRACT**

A method is described for the continuous production of nanotubes comprising forming a plasma jet, introducing into the plasma jet a metal catalyst or metal catalyst precursor to produce vaporised catalyst metal, directing one or more streams of quenching gas into the plasma to quench the plasma and passing the resulting gaseous mixture through a furnace, one or more nanotube forming materials being added whereby nanotubes are formed therefrom under the influence of the metal catalyst and are grown to a desired length during passage through the furnace, and collecting the nanotubes so formed.

## PLASMA SYNTHESIS OF HOLLOW NANOSTRUCTURES

[0001] The present invention relates to methods for the continuous production of carbon or other nanotubes.

[0002] Carbon nanostructures, and nanotubes in particular, are very promising candidates for a wide range of applications. One of the major limitations to further development is the volume of material that can presently be produced. A number of different synthesis routes have been reported with the vast majority falling into one of the following three categories:

[0003] 1) Electric carbon arc: typically a large current is passed between carbon electrodes in a low pressure inert atmosphere, leading to the evaporation of carbon species in the high temperature arc discharge. Products may be deposited on the counter electrode or on the chamber walls. Single-wall nanotubes are grown through the introduction of catalyst metal powders (typically transition metals such as Ni, Co, or Y) into the graphite electrodes. This method yields nanotubes with a high crystallinity but the purity of the product is low due to the instability of the arc and the non-uniformity of the growth conditions. Despite improvements allowing motorised insertion of electrodes this approach is essentially a batch process yielding only a few grams of material per run, with relatively little scope of improvement.

[0004] 2) Laser ablation: a high power laser, usually pulsed, sometimes continuous is used to ablate a graphite target, containing metal catalyst particles, into an inert atmosphere. Single-wall nanotubes condense from the mixed carbon and metal vapour. This method can produce high quality material but the yields and overall energy efficiency are low. Non-uniform ablation of the target means that this approach must also be run as a batch process.

[0005] 3) Catalytic vapour deposition: hydrocarbon gas is decomposed on a transition metal catalyst at relatively low temperatures (500-1200 C). The catalyst may either be pre-produced or formed in situ by the decomposition of a metal-containing compound. A closely related process uses the disproportionation of carbon monoxide as the carbon source. Material produced via this route, can be very pure, but usually has a high concentration of crystalline defects. Radio-frequency and microwave plasmas are sometimes used to enhance the growth process at low temperatures (e.g. 500-700 C) and pressures ( $<1$  atm).

[0006] There have also been a number of proposals for the continuous production of fullerenes using a plasma torch. Thus, WO94/04461 discloses passing a particulate carbon or liquid or gaseous hydrocarbon feedstock (e.g. acetylene or naphthalene) through an induction plasma torch and quenching the vaporised carbon with a quenching gas such as helium or argon. A soot is produced containing a few percent of fullerenes. No carbon nanotube production is disclosed. The products are described as being  $C_{60}$ ,  $C_{70}$  and higher molecular weight fullerenes of similar structural configuration.

[0007] U.S. Pat. No. 5,395,496 uses carbon halides as a plasma forming gas in a plasma torch to form a vaporised

carbon cloud which is condensed to produce a soot containing fullerenes. Optionally, hydrocarbons or an inert gas are added. Again, no production of nanotubes is reported.

[0008] In WO93/23331, carbon powder is supplied to a plasma flame produced between a cathode and an anode and the reaction products are annealed as they flow down a pathway lined with a refractory insert, which may be heated. Again, the product is a fullerene containing soot.

[0009] U.S. Pat. No. 5,593,740 discloses passing metal powder (e.g. Fe, Co, Ni, Cu or Al) into an inert gas plasma jet, which extends into a region in which a carbon containing gas is present. The plasma is quenched by a feed of nitrogen and the product is collected. Rather than carbon nanotubes, the product is ultrafine metal particles encased in a shell of carbon.

[0010] The present invention now provides a method for the continuous production of nanotubes comprising forming a plasma jet, introducing into the plasma jet a metal catalyst or metal catalyst precursor to produce vaporised catalyst metal, directing one or more streams of quenching gas into the plasma to quench the plasma and passing the resulting gaseous mixture through a furnace, one or more nanotube forming materials being added whereby nanotubes are formed therefrom under the influence of the metal catalyst and are grown to a desired length during passage through the furnace, and collecting the nanotubes so formed.

[0011] The nanotube forming material may be a carbon containing material and the product is then carbon nanotubes.

[0012] Generally, the nanotube forming material may be carbon monoxide, carbon particulates, a normally liquid or gaseous hydrocarbon, or an oxygen containing hydrocarbon derivative. Suitable carbon-containing compounds for use as the carbon source include carbon monoxide and hydrocarbons, including aromatic hydrocarbons, e.g. benzene, toluene, xylene, cumene, ethylbenzene, naphthalene, phenanthrene or anthracene, non-aromatic hydrocarbons, e.g. methane, ethane, propane, butane, pentane, hexane, cyclohexane, ethylene, propylene or acetylene, and oxygen-containing hydrocarbons, e.g. formaldehyde, acetaldehyde, acetone, methanol or ethanol, or a mixture of two or more thereof. Carbon in particulate form entrained in a suitable carrier gas may be used. In preferred embodiments, the carbon-containing compound is carbon monoxide (CO), methane, ethylene or acetylene.

[0013] The carbon source may be mixed with one or more gases acting as a diluent such as inert gases, e.g. argon. It may also be mixed with non carbon containing gases which play no direct role in the nanotube forming reaction but which play a contributory role, for instance by reacting with amorphous carbon as it is formed (as a by-product) and so keeping the reaction sites on the catalyst clean and available for nanotube formation.

[0014] Gases which may be mixed with the carbon source include argon, hydrogen, nitrogen, ammonia, carbon dioxide or helium. The nanotube forming material may further comprise non-carbon dopant elements such as nitrogen (suitably as nitrogen gas) or boron (introduced using for example boranes or carboranes) or sulphur (introduced using for example thiophene).



[0015] The method is not however restricted to the production of carbon nanotubes and the nanotube forming material optionally comprises or consists of borazine, boron powder plus nitrogen gas, boranes plus nitrogen gas, tungsten oxide powder plus hydrogen disulphate gas, tungsten disulphide powder, etc.).

[0016] The nanotube forming material may be added upstream of the plasma jet or it may be introduced into the plasma jet or after the quenching gas, or at two or more of these stages. Thus, in a first mode of operation which is essentially a pure chemical vapour deposition method, the only active ingredient passed through the plasma is the metal catalyst and all of the structural material of the nanotube product is introduced with the quenching gas or thereabouts. In this case, the plasma is used to generate suitably sized clusters of catalyst metal atoms, generally with diameters equivalent to the nanotubes to be produced. The metal nanoclusters catalyse the breakdown of the nanotube forming material to allow growth of the nanotubes on the metal particles.

[0017] In an alternative mode, which might suitably be termed 'mixed mode growth', nanotube forming material is introduced with the metal catalyst to pass through the plasma so that both the metal and the structural material of the nanotube (typically carbon) are vaporised in the plasma and nanotube nuclei condense from the plume of the plasma consisting of slightly larger metal nanoparticles (typically 3-5 nm) with relatively short nanotubes or 'fullerene caps' attached that then lengthen during passage through the furnace.

[0018] The nanotube forming material may serve as the quenching gas or it may be co-added with the quenching gas, or it may be added downstream of the plasma jet separately from the quenching gas. Some of the nanotube forming material may also be added to pass through the plasma with the metal catalyst at the same time. The proportions of nanotube forming material added to pass through the plasma jet and added downstream of it may be varied as desired.

[0019] The catalyst or catalyst precursor is suitably a transition metal catalyst or precursor, particularly one comprising copper (Cu), or a Group VIB transition metal (chromium (Cr), molybdenum (Mo), tungsten (W)) or a Group VIIB transition metal (iron (Fe), cobalt (Co), nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt)) or a mixture of two or more thereof. Metals from the lanthanide and actinide series may also be used. Preferred transition metal catalysts comprise a mixture of two or more of the listed metals. Particularly preferred transition metal catalysts comprise Fe, Ni, Co, Mo or a mixture of two or more thereof such as a 50/50 mixture (by weight) of Ni and Co, or a mixture of Fe and Ni, or a mixture of Fe and Mo. Any of these transition metals individually or in combination with any of the other transition metals listed may be used as a catalyst for carbon nanotube growth.

[0020] The catalyst may be added as metal but is preferably a metal containing compound from which metal atoms are freed in the plasma. Such a precursor is preferably a plasma decomposable compound of one or more metals listed above.

[0021] Preferably, the catalyst precursor is an organometallic compound comprising a transition metal and one or

more ligands. The ligands of the catalyst precursor preferably contain the elements C, H and O only, and preferably are simple molecules which decompose without poisoning the catalyst metal or interfering with the synthesis pathway.

[0022] Ligands of the catalyst precursor may include one or more functional groups selected from carboxylates, alkoxides, ketones, diketones, amines, amides, alkyls and aryls. Suitable ligands include methyl, cyclohexyl, carbonyl, cyclopentadienyl, cyclooctadiene, ethylene beta-diketones, phosphines, organophosphorous ligands, polyethers, dithiocarbamates, macrocyclic ligands (e.g., crown ethers) or benzene ligands, or a mixture or two or more of thereof.

[0023] The catalyst precursor may be a multimetal atom cluster, such as triiron dodecylcarbonyl.

[0024] Optionally, a finely divided substrate material may be introduced at the level of the quenching gas or thereabouts. The substrate material will help to nucleate and stabilise small metal clusters. In the most straightforward case, the substrate particles are simply finely ground powders, for example of silica or alumina. Finer materials may be generated by a range of methods known to those skilled in the art, such as fuming, colloidal processing, spray-drying, hydrothermal processing and so on. Particular benefit for the production of nanotubes may be derived by, using structured substrate particles, particularly mesoporous silicas, anodised alumina membranes, or zeolites. These materials have channels of similar dimensions to nanotubes, and can further guide both the deposition of catalyst and synthesis of nanotubes.

[0025] Alternatively, substrate particles may be introduced into the furnace separately, for example in their own carrier.

[0026] A particularly preferred approach is to use so-called POSS (polyhedral oligomeric silsesquioxane) compounds as the catalyst-substrate particles. In this case the distinction between catalyst and substrate is rather blurred, as POSS compounds are themselves molecular silica-based materials. A POSS molecule can act as a site for catalyst formation in situ.

[0027] The advantages of using a POSS are numerous. They have a very high surface area. Their diameters are around 1 nm (the same size as single wall nanotubes) but are tuneable as different POSS molecules have different sizes. They can be monodisperse (have specific molecular weights) and hence have the potential to generate well-defined products. As they have molecular character, they may be liquid or may be dissolved in the supercritical fluid or a suitable liquid carrier (and may potentially even be evaporated directly) for injection into the furnace. They have excellent thermal stability in themselves. They have the potential to form well-defined derivatives that potentially add catalytic metallic particles (for example iron). Generally a single POSS molecule will constitute a particle of substrate for nanotube growth.

[0028] The finely divided substrate particles preferably have a size not smaller than 1 nm, e.g. not less than 5 nm. They may contain not less than 10 atoms, e.g. not less than 15 to 20 atoms, perhaps not less than 50 atoms or 75 atoms. The substrate is fed to the zone in which the catalyst precursor is decomposed and preferably is essentially unchanged in the step of generating supported-catalyst par-



ticles, except for the deposition thereon of the catalyst material. However, some chemical modification of the substrate particles during the formation of the supported-catalyst particles is permissible, e.g. the removal of surface chemical groups or solvating chemical side chains. Preferably, the size of the substrate particles remains substantially unchanged.

[0029] The presence of the substrate particles during the decomposition of the catalyst precursor serves to lower the nucleation energy of the catalyst atoms and to control the size and shape of the catalyst cluster so formed.

[0030] Alternatively, a substrate precursor, for example a silicon-containing material such as tetramethyl orthosilicate or tetraethyl orthosilicate, may be contained in the solution. Such a precursor will decompose in the furnace to form a finely divided substrate material.

[0031] The plasma jet may be formed by numerous methods known in the art, but preferably is an inductively coupled plasma jet. Alternatives include the use of a cathode upstream from a tubular anode as in WO93/23331 or a microwave generator as in WO94/04461. Such inductively coupled plasma torch devices are well known as means of atomising a wide range of materials and are commonly used as a means of preparing sample fragments within a mass spectrometer. They are also known as a means of producing fine powders and nanocrystalline films. Such torches consist of an inert gas stream that is passed through a cooled conducting coil which is protected by a cool gas sheath and a quartz tube. Once the plasma is ignited (usually with a spark from a piezoelectric device), high frequency alternating current flowing in the coils couples inductively with the ions in the gas, thus increasing their kinetic energy. Effective temperatures of over 10,000 K can be reached. The material to be vaporised (which can be solid, liquid or gas) is injected into the plasma where it decomposes into its constituent atoms. In the present invention, the plasma torch is used to generate a vapour containing at least the metal catalyst atoms.

[0032] The furnace provides an opportunity for the carbon or other nanotube forming material feedstock to become progressively incorporated into growing nanotubes and the residence time in the furnace and its temperature will affect the length of the nanotubes produced suitably, the temperature within the furnace is from 700 to 1200° C. It may be uniform, or may decline toward the outlet of the furnace. The introduced materials preferably have a residence time within the furnace of from 5 to 30 seconds, e.g. about 10 seconds.

[0033] To promote rapid and effective mixing said quenching gas may be directed radially into said plasma jet from multiple directions to produce uniform conditions within the mixture thereof. The quenching gas may be inert (e.g. Ar), or may be reactive (e.g. H<sub>2</sub> which can help to etch away unwanted amorphous carbon, or N<sub>2</sub> which may dope the growing nanostructures). Most preferably the quenching gas contains a carbon-containing gas (e.g. methane or CO) that can contribute to the growth of the nanotubes. Without wishing to be limited by theory, we believe that the initial quenching step particularly controls nucleation of the nanotubes, either by determining the size of the metal clusters that are produced or by determining the diameters of fullerenic caps that appear on the surface of slightly larger metal

clusters. Nanotube nuclei may be carbon-metal structures or pure metal clusters, that grow during subsequent thermal treatment.

[0034] The invention will be further described and illustrated with reference to the accompanying drawing, in which the single FIGURE shows apparatus suitable for the performance of the method of the invention.

[0035] The apparatus comprises a plasma torch formed by a tube **10** surrounded by water cooled induction coils **12** and having at its upper end a first inlet **14** for a carrier gas containing metal catalyst precursor and optionally also a carbon or other nanotube forming material containing feedstock. A second inlet **16** is provided for a plasma forming gas which suitably is an inert gas. Materials introduced through the inlets **14** and **16** pass inside an cylindrical shield **18** upstream of the coils **12** and a sheath gas is introduced into the annular space between the tube **10** and the shield **18** via an inlet **20**. As the introduced materials pass through the tube **10** within the coils **12**, a plasma jet is formed. The sheath gas functions to separate the plasma formed by the coils from the tube wall to reduce the heating of the wall of the tube **10**.

[0036] Below the coils **12**, eight radially directed inlets **22** are provided for a quenching gas. The eight inlets **22** are directed towards the centre of the tube **10** at equal angles of 45°. This ensures rapid mixing of the quenching gas with the material of the plasma jet to produce a uniform mixture from this point on.

[0037] Below the inlet **22** is provided a tubular furnace **24** comprising a heated refractory tubular wall allowing control of the temperature therein. At the outlet end of the furnace **24** is an inlet **26** for additional cooling gas. A centrifugal separator **28** is attached to the outlet of the furnace **22** and a gas exhaust outlet **30** from the separator **28** passes through a filter **32** to waste.

[0038] In optional modifications of what is shown, some of the quenching gas inlets **22** may be used to introduce carbon or other nanotube forming feedstock or a separate inlet for such feed stock may be provided just upstream or just downstream from the quenching gas inlets.

[0039] In use in the preferred embodiments of the invention, the condensation process is controlled using a rapid turbulent injection of gas to quench the material exiting the plasma torch. This injection is carefully designed in order to ensure full mixing of the plasma and the quenching gas and to ensure that uniform conditions exist throughout the plume. Conveniently, the quenching gas may be injected from a cylindrical array of angled nozzles as shown. Nanotube elongation occurs over a longer period of time and can be favoured by allowing a suitable residence time (eg 10 sec) at moderate temperatures (e.g. 700-1200 C) with the option of introducing additional carbon feedstock. To achieve the desired quenching rate and elongation temperature the flow rate and temperature of the quenching gas may be varied. The elongation temperature can be maintained by passing the gas along a tube furnace before the product is allowed to cool freely. Once sufficiently cool, the product may be collected by the centrifugal separator and filter unit. The invention is primarily aimed at the production of hollow carbon nanotubes, whether single or multiwalled, which may be doped (eg with N or B), but is also applicable to analogous cage structures formed from other elements (eg BN, WS<sub>2</sub>, etc) The following example is performed using the apparatus as illustrated.



[0040] The plasma is generated using a 2 kW three phase 27 MHz RF induction system, using Ar as the plasma and sheath gas. 10 wt % ferrocene in toluene solution is introduced into the plasma using a nebulizer at a rate of approximately 0.01 g/min. 50:50 Methane:hydrogen at 750 C is used as the quenching gas and the furnace is held at 850 C. The total flow rate of gas through the 90 cm long, 68 mm diameter tube furnace is 2 L/min. Products, including single wall nanotubes, are deposited at the cold exit to the furnace and on a fine filter placed in across the exhaust gas stream.

[0041] The approach described has a number of advantages over the existing techniques:

[0042] 1) The process uses a high temperature vapour to initiate nanotube growth, which has been shown to produce high quality materials in other approaches.

[0043] 2) The system may be operated continuously as feedstock is injected into the plasma torch and the product collected by, for example, a centrifugal separator.

[0044] 3) The option to add carbon feedstock after the plasma phase reduces running costs because the total percentage of material that must be raised to very high temperature is reduced. This option also allows independent control of nanotube length and can, for example, enable the production of very long tubes which may be useful for mechanical reinforcement.

[0045] 4) The rate of quenching is critical in determining the diameter of the nanotubes that are produced. Hence accurate control of the quenching process allows excellent control over nanotube diameter.

[0046] 5) The uniformity of mixing during the turbulent quenching phase ensures that all the material experiences similar conditions and hence a narrow diameter distribution and a high purity product can be obtained. Current high temperature methods do not include a deliberate turbulent stage and cooling is likely to be highly uneven, as evidenced by the distribution of nanotube diameters produced.

[0047] 6) The process can use of wide range of feedstocks, from graphite and metallic powders to organo-metallic molecules and simple hydrocarbons. Thus the process can make use of cheap feedstocks that are conveniently handled. The most straightforward method of introducing the required materials into the plasma is by injection of a nebulised metal-containing liquid or solution.

[0048] Many modifications and variations of the illustrated embodiments are possible within the general scope of the invention.

1. A method for the continuous production of nanotubes comprising forming a plasma jet, introducing into the plasma jet a metal catalyst or metal catalyst precursor to produce vaporised catalyst metal, directing one or more streams of quenching gas into the plasma to quench the plasma and passing the resulting gaseous mixture through a

furnace, one or more nanotube forming materials being added whereby nanotubes are formed therefrom under the influence of the metal catalyst and are grown to a desired length during passage through the furnace, and collecting the nanotubes so formed.

2. A method as claimed in claim 1, wherein the nanotube forming material is a carbon containing material and the product is carbon nanotubes.

3. A method as claimed in claim 2, wherein the nanotube forming material is carbon containing material and the product is predominantly carbon nanotubes.

4. A method as claimed in claim 1, wherein the nanotube forming material is a carbon containing material and the product contains multi wall nanotubes.

5. A method as claimed in claim 2, wherein the nanotube forming material is carbon monoxide, carbon particulates, a normally liquid or gaseous hydro carbon, or an oxygen containing hydrocarbon derivative.

6. A method as claimed in claim 1, wherein the catalyst precursor material acts as a nanotube forming material and vice versa.

7. A method as claimed in claim 2, wherein the nanotube forming material further comprises non-carbon dopant elements.

8. A method as claimed in claim 1, wherein the nanotube forming material comprises borazine, boron powder plus nitrogen gas, boranes plus nitrogen gas, tungsten oxide powder plus hydrogen disulphide gas, or tungsten disulphide powder.

9. A method as claimed in claim 1, wherein the nanotube forming material is added upstream of the plasma jet.

10. A method as claimed in claim 1, wherein the nanotube forming material is added as or with the quenching gas, or is added downstream of the plasma jet separately from the quenching gas.

11. A method as claimed in claim 1, wherein the metal catalyst or catalyst precursor is or contains copper, chromium, molybdenum, tungsten, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, yttrium, a lanthanide or an actinide, or a mixture of two or more thereof.

12. A method as claimed in claim 1, wherein the temperature within the furnace is from 700 to 1200° C.

13. A method as claimed in claim 1, wherein the introduced materials have a residence time within the furnace of from 5 to 30 seconds.

14. A method as claimed in claim 1, wherein the plasma is generated by an inductively coupled plasma torch.

15. A method as claimed in claim 1, wherein said quenching gas is directed radially into said plasma jet from multiple directions to induce full mixing of the plasma and quenching gas to produce uniform conditions within the mixture thereof.

16. A method as claimed in claim 12, where the symmetric array of nozzles are directed at an angle to the radial direction to induce a turbulent vortex where mixing of the plasma and quenching gas occurs.

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