

A METHOD FOR PRODUCING CARBON NANOTUBES

Field of the Invention

- 5 This invention relates to a method for producing carbon nanotubes. More particularly, this invention relates to a method for producing carbon nanotubes using induction heating with simultaneous levitation of catalyst.

Background

10

Carbon nanomaterials are allotropes of carbon such as carbon nanotubes (CNTs), graphene, fullerene, carbon nanowalls, carbon nanofibres, graphite, diamond and diamond-like carbon. Among them, carbon nanotubes are classified as crystalline carbon or graphitic structure and they can exist as single-walled carbon nanotubes and multi-walled carbon nanotubes. Carbon nanotubes have very high tensile strength, excellent electrical conductivity, and the ability to bear high working temperatures. Their physical, electrical and thermal properties make them special materials for a number of applications.

15

- 20 Currently, the synthesis of carbon nanotubes are typically carried out by three different methods, namely, arc discharge, laser ablation and chemical vapour deposition over metallic catalysts. Chemical vapour deposition method is reported to be more selective and has been used most extensively. Arc discharge and laser ablation methods are relatively less selective, leading to mixtures of different carbon materials and lower purity of carbon nanotubes. Arc discharge method produces many by-products. As a result, the process requires complicated and well controlled purification steps. Laser ablation method has several shortcomings and high equipment cost is one of them.

25

- 30 The most common scalable procedure for large scale production of carbon nanotubes is one that uses a suitable reactor coupled with catalytic chemical vapour deposition process. However, during the growth of the carbon nanotubes, the solid volume in the reactor steadily increases in a fixed reactor space. This leads to a large drop in pressure within the reactor and causes blockage in the

reactor. This poses a serious problem, especially in large scale production of carbon nanotubes.

The conventional methods used for producing carbon nanotubes have another
5 shortcoming. The methods often include the use of conventional ovens for heating the carbon source and the catalyst. This method of heating consumes large amounts of energy, and heat inefficiently. This adversely affects the efficiency of the overall production process.

10 Some of the conventional methods used for producing carbon nanotubes involve a wet chemical process for separating the carbon nanotubes from unused catalyst. In such methods, the catalyst is first dissolved in an acidic medium to form a solution. The carbon nanotubes which are insoluble in the liquid medium are recovered by sedimentation, filtration, cleaning and drying. The catalyst which
15 formed a salt solution with the acidic medium is then recovered by a multi-step processing involving electrolysis, thermal reduction, and thermal decomposition, etc. to the size or form required for the intended function of the catalyst. Although wet chemical process has the advantage of removing amorphous or non-graphitic carbons, the medium often causes damage to the crystallinity and morphology of
20 the carbon nanotubes produced from the process. This results in the deterioration of the mechanical and electrical properties of the carbon nanotubes. The effective removal of unused catalyst while preserving the carbon nanotubes structure thus poses a challenge.

25 Carbon nanotubes are the fastest growing segment in nanomaterial technology market across the globe. The global carbon nanotubes market is divided into submarkets for carbon nanotube types and its applications. The product types include single-walled carbon nanotube and multi-walled carbon nanotubes. The application areas include electronics and semiconductors, chemicals and polymers,
30 batteries and capacitors, energy and utilities, medical applications, composites, aerospace and defense, and others. The other areas include water applications, cosmetics, fast moving consumer goods products, and so on. Currently, most of the carbon sources for production of carbon nanotubes are derived from pure hydrocarbon gasses or fossil fuel. As there has been an increasing demand for

carbon nanotubes, many researchers are constantly looking for other carbon sources for production of better quality carbon nanotubes to meet the increasing demand.

- 5 It is therefore desirable to provide a method for producing carbon nanotubes that seeks to address at least one of the problems described hereinabove, or at least to provide an alternative.

Summary of Invention

10

The above and other problems are solved and an advance in the art is made by a method in accordance with this invention. A first advantage of a method in accordance with this invention is that the method allows for an efficient way of producing high quality and high purity carbon nanotubes. A second advantage of a
15 method in accordance with this invention is that the method is cost effective.

15

In accordance with one embodiment of this invention, a method for producing carbon nanotubes is provided. The method comprises heating a catalyst in a fluidized bed reactor by induction heating. The catalyst is cooled and waste
20 materials containing carbon source are added to the catalyst. The waste materials containing the carbon source and the catalyst in the reactor are heated by induction heating while a DC bias is applied to the catalyst and the catalyst is levitated simultaneously by magnetic means to mix the catalyst with the waste materials containing the carbon source to form carbon nanotubes.

20

25

In accordance with another embodiment of this invention, the method further comprises heating the waste materials containing the carbon source in a separate enclosure by induction heating to depolymerize the waste materials containing the carbon source prior to adding the waste materials containing the carbon source to
30 the catalyst.

30

In accordance with an embodiment of this invention, the waste materials containing the carbon source may be selected from the group consisting of plastic wastes,

rubber wastes, wood wastes, paper wastes, textile wastes and organic chemical wastes.

In accordance with an embodiment of this invention, the catalyst may be selected from the group consisting of a ferromagnetic element, a combination of ferromagnetic elements, an alloy comprising one or a combination of ferromagnetic elements, an alloy comprising a combination of ferromagnetic elements with one or more non-ferromagnetic elements and any such element, alloy or combination mixed with non-reactive support structures.

In accordance with an embodiment of this invention, the induction heating is carried out using induction coils. Preferably, the induction coils are wound proximate to and around the external wall of the fluidized bed reactor. In accordance with some embodiments of this invention, the induction heating is carried out by applying an AC power output having a frequency in the range of 50Hz to 14MHz to the induction coils.

In accordance with an embodiment of this invention, the catalyst is heated in presence of a reducing gas. In accordance with other embodiment of this invention, the catalyst is heated to a temperature between 400°C and 650°C.

In accordance with an embodiment of this invention, the waste materials containing the carbon source and the catalyst are heated to a temperature between 600°C and 1100°C.

Brief Description of the Drawings

The above advantages and features of a method and apparatus in accordance with this invention are described in the following detailed description and are shown in the drawings:

Figures 1(a) to 1(c) show the results of the carbon nanotubes produced in accordance with an embodiment of the first aspect of the present invention which used plastic wastes as the carbon source, with the plastic wastes heated on the

catalyst. Figure 1(a) is a Field Emission Scanning Electron Microscopy (FESEM) showing the vertically aligned and high density carbon nanotubes of a length of about 10 μ m obtained in accordance with the embodiment of the present invention. Figure 1(b) is a Transmission Electron Microscopy (TEM) showing a multi-walled carbon nanotube having an external diameter of 40-50nm and with the nanocatalyst encapsulated at the tip of the carbon nanotube. Figure 1(c) is a Raman spectrum showing the crystalline or graphitic carbon at 1580cm⁻¹.

Figures 2(a) to 1(c) show the results of the carbon nanotubes produced in accordance with an embodiment of the second aspect of the present invention which uses plastic wastes as the carbon source, wherein the carbon source are depolymerized prior to adding to the catalyst. Figure 1(a) is a FESEM showing the vertically aligned and high density carbon nanotubes of a length of about more than 20 μ m. Figure 1(b) is a TEM showing a multi-walled carbon nanotube having an external diameter of 16-18nm and with the nanocatalyst encapsulated at the tip of the carbon nanotube. Figure 1(c) is a Raman spectrum showing the high intensity of the crystalline or graphitic carbon at 1580cm⁻¹.

Figure 3 is a graph showing the crystal planes of non-magnetized nickel before induction heating and magnetized nickel before induction heating.

Detailed Description

This invention relates to a method for producing carbon nanotubes. More particularly, this invention relates to a method for producing carbon nanotubes using induction heating with simultaneous levitation of catalyst.

In accordance with one aspect of the present invention, carbon nanotubes are formed by preheating a catalyst in a fluidized bed reactor by induction heating. The catalyst is cooled and waste materials containing carbon source are added to catalyst. The waste materials containing the carbon source and the catalyst in the reactor are heated by induction heating while a DC bias is applied to the catalyst and the catalyst is levitated simultaneously by magnetic means to mix the catalyst with the waste materials containing the carbon source to form carbon nanotubes.

The waste materials suitable for use in the present invention are materials containing carbon source. Such materials include, but are not limited to, plastic wastes, rubber wastes, wood wastes, paper wastes, textile wastes and organic chemical wastes. Preferably, the waste materials are plastic wastes. The plastic wastes may comprise polyethylene terephthalate, polyethylene, polypropylene, polystyrene, styrene butadiene rubber and/or other plastic materials.

The catalyst suitable for use in the present invention can be any material that can be levitated and is electrically conducting. Examples of such catalyst include a ferromagnetic element, a combination of ferromagnetic elements, an alloy comprising one or a combination of ferromagnetic elements, an alloy comprising a combination of ferromagnetic elements with one or more non-ferromagnetic elements or any such element, alloy or combination mixed with non-reactive support structures. Preferably, the ferromagnetic element includes iron, nickel and cobalt. One skilled in the art will recognize that other electrically conducting catalyst may be used without departing from the scope of the present invention. The catalyst can be of any suitable shape or form. For example, it can be in a form of particle, wool, wire, mesh, plate, pellet, tablet and the like and combinations thereof. In one embodiment of the present invention, the catalyst is in the form of particles. In another embodiment of the present invention, the catalyst is coated or impregnated onto non-reactive particles.

The carbon nanotubes produced in accordance with the present invention are either single-walled or multi-walled, depending on the types of catalyst and waste materials used in the method.

Any suitable type of fluidized bed reactor can be used in the present invention. In an exemplary embodiment of the invention, the fluidized bed reactor consists of a vertical quartz tube with a diameter of about 200 mm, and a length of about 1200 mm. Catalyst in the form of stainless steel wool is packed within the centre zone of the column where induction coil is wound to the external wall of the quartz column.

In accordance with the method of the present invention, the energy for preheating the catalyst and heating the waste materials containing the carbon source with the catalyst is supplied by high-frequency alternating current (AC). A device for using AC to generate a magnetic field in close proximity to or around the catalyst is
5 provided.

The magnetic field generated by the device penetrates the reactor and passes through the catalyst in the reactor. The alternating magnetic field induces eddy currents in the reactor which in turns heat the catalyst and the waste materials in
10 the reactor. The frequency of the AC used in the method of the present invention is dependent on various factors including, but not limited to, the size of the catalyst, the penetration depth into the reactor and coupling between the device and the catalyst to be heated. The frequency of the AC supplied to the device must be sufficient for the device to generate a magnetic field that allows induction heating
15 to take place within the reactor. Any suitable range of AC frequency may be employed. In one embodiment of the invention, the frequency of the AC supplied to the device is in the range of 50 Hz to 14 MHz.

In one embodiment of the present invention, the device includes coils which are
20 adapted to generate magnetic field to inductively heat the reactants in the reactor. The coils are provided at close proximity to but external to the wall of the reactor. In a preferred embodiment of the invention, the coils are wound around the external wall of the reactor, proximate to the reaction zone of the reactor. One skilled in the art will recognize that other configurations may be employed without departing from the scope of the present invention. In this embodiment, the coils
25 may be made of copper tubing or any good conductor of electricity equivalent to copper. The shape, diameter and number of turns of the coils around the external wall of the reactor may influence the efficiency and pattern of the magnetic field generated by the coils. In any case, the strength of the magnetic field generated
30 by the device should be high enough to induce sufficient eddy currents to inductively heat the catalyst and the waste materials containing the carbon source to desired temperatures and maintaining the temperatures for a predetermined period if necessary.

In the method of the present invention, the catalyst in the reactor is levitated by magnetic means provided in close proximity to but external to the reactor. The levitation of the catalyst provides more efficient fluidization of the reactants in the reactor and facilitates flow of the reactants in the reactor. It provides a more homogenous mixing of the catalyst with the waste materials containing the carbon source. All these in turns result in the production of carbon nanotubes with enhanced quality and purity.

Any magnetic means capable of generating a constant magnetic field at or near the catalyst can be used in the present invention. Such magnetic means include, but not limited to, permanent magnet, magnetizer, electromagnet, equivalents thereof or a combination thereof. A single or a plurality of same magnetic means or a combination thereof may be used in the present invention, depending on the strength of the magnetic field required to levitate the catalyst in the reactor. In any case, the strength of the magnetic field generated by the magnetic means should be high enough to levitate the catalyst in the reactor and to maintain the levitation of the catalyst in the reactor. The magnetic means may be positioned anywhere proximate to the reactor, at a distance sufficient for the magnetic field generated thereto to penetrate through the reactor to levitate the catalyst in the reactor. One skilled in the art will recognize that any arrangements of the magnetic means may be employed without departing from the scope of the present invention. The levitation of the catalyst is carried out simultaneously while the waste materials containing the carbon source and the catalyst are inductively heated in the reactor. In a preferred embodiment, a plurality of electromagnets is used.

In an embodiment of the present invention, direct positive or negative current (DC) bias is applied to the catalyst to generate an electric field in the catalyst during the heating process. The amount of DC bias applied to the catalyst are dependent on various factors including, but not limited to, the shape and form of the catalyst and whether there are any interfering structures nearby that may affect the electric field in the catalyst. In any case, the DC bias applied to the catalyst should be sufficient to generate an electric field in the catalyst to cause and/or increase inter-particle repulsion of the catalyst within the reactor.

In accordance with the embodiment of the present invention, the catalyst is preheated in presence of a reducing gas. This is to activate the reactivity of the surface of the catalyst, and to enhance the growth of the carbon nanotubes. The reducing gas can be pure hydrogen, ammonia or nitrogen or a mixture thereof. In an embodiment of the present invention, the catalyst is heated to a temperature in the range of 400°C to 650°C. The catalyst is maintained at this temperature for a period sufficient for the activation of the reactivity of the catalyst to take place. In a preferred embodiment of the invention, the catalyst is maintained at the predetermined temperature for about 10 minutes or longer. The catalyst is then allowed to cool to room temperature in the same environment.

In the present invention, the waste materials containing the carbon source may be added to the catalyst by mixing the waste materials containing the carbon source with the catalyst or simply placing the waste materials containing the carbon source in contact with the catalyst without any mixing. In the latter embodiment, mixing can take place when the catalyst in the reactor is levitated. In one embodiment of the invention, the waste materials containing the carbon source and the catalyst are inductively heated in a vacuum or under inert gas condition. Inert gas such as nitrogen or argon may be used, although one skilled in the art will recognize that other inert gases may be used without departing from the scope of the present invention. Preferably, the waste materials containing the carbon source and the catalyst are heated to a temperature in the range of 600°C to 1100°C for a desired duration to form carbon nanotubes. The dwell time is minimum 1 minute at the temperature set point to allow the time for nucleation of the carbon nanotubes. The dwell time may be prolonged as desired to obtain more carbon nanotubes as they grow with time.

In another embodiment of the present invention, reducing gas such as pure hydrogen or ammonia or a mixture thereof may optionally be introduced into the reactor during the production process. This is to activate the catalyst for continuous growth of the carbon nanotubes. It is also to prevent the catalyst from being poisoned by amorphous carbons which deactivate the catalyst. Other suitable reducing gas may be used without departing from the scope of the present invention.

In accordance with the embodiments of this aspect of the invention, carbon nanotubes are formed intermixed with the catalyst. The carbon nanotubes are densely grown and vertically aligned on the substrate, as illustrated in Figure 1(a).

5 Muti-walled carbon nanotubes with catalyst encapsulated may also be formed and this is illustrated in Figure 1(b). The carbon nanotubes formed in accordance with this aspect of the invention have high intensity of crystalline or graphitic structure at 1580 cm^{-1} (see Figure 1(c)), and defective sites and amorphous carbon structure at 1350 cm^{-1} .

10 In another aspect of the present invention, the waste materials containing the carbon source are depolymerized prior to adding them to the catalyst. This is carried out by heating the waste materials containing the carbon source separately in another enclosure under vacuum or inert gas condition. In a preferred
15 embodiment, the heating is carried out via induction heating. The waste materials containing the carbon source are introduced into a metal chamber or a metal container that can be electromagnetized, and heated to a temperature in the range of 350°C to 450°C . Suitable inert gas such as nitrogen or argon may be used, although one skilled in the art will recognize that other inert gases may be used
20 without departing from the scope of the present invention. Gaseous distillate from the depolymerisation process is then fed to the reactor containing the catalyst. The catalyst in this embodiment may or may not be pre-treated. In an embodiment of the present invention, the catalyst is pre-treated according to the steps as described hereinabove. The AC frequency used for the induction heating has a
25 range from 50 Hz to 1 kHz.

In this aspect of the invention, the gaseous distillate and the catalyst in the reactor are heated to a temperature in the range of 650°C to 1100°C . Carbon nanotubes formed thereto are intermixed with the catalyst. The average external diameter of
30 the carbon nanotubes obtained in the temperature range of 650°C to 1100°C is between 20 nm and 60nm. In the same temperature range, the carbon nanotubes formed thereto are multi-walled and the number of walls decreases with increasing growth temperature. The number of walls can range from 6 to 30. The carbon nanotubes produced in this embodiment of the invention are not wavy (see Figure

2(a)) as compared to the carbon nanotubes produced in accordance with the embodiment of the first aspect of the invention as described hereinabove. The carbon nanotubes are also more dense and narrower in diameter (see Figure 2(b)) as compared to the carbon nanotubes formed in accordance with the embodiment
5 of the first aspect of the invention. As illustrated in Figure 2(c), the carbon nanotubes have higher intensity of crystalline or graphitic structure at 1580 cm^{-1} as compared to the embodiment of the first aspect of the invention. The difference is primarily due to reduced contamination from using the waste materials feedstock that has been depolymerized prior to use. In one embodiment of this aspect of the
10 invention, additives such as antioxidant, neutralizing reagents and/or other inhibitors may be added to the waste materials to pre-treat the waste materials before use.

The gaseous by-products produced in the method of the present invention can be
15 collected or combusted to supplement heating, or partly recycled. The gaseous by-products may include primarily hydrogen and a small amount of light hydrocarbons.

The waste materials used in the present invention provide a low-cost carbon
20 source as compared to high-cost pure hydrocarbons used in conventional methods. This makes the method of the present invention relatively more cost effective as compared to the conventional methods. The valuable by-products, such as hydrogen, produced in the method of the present invention are a good source for clean energy. The method allows waste materials to be recycled and this helps to
25 improve the recycling rate of waste materials substantially.

The method in accordance with the present invention is efficient as it uses induction heating in heating the waste materials containing the carbon source and the catalyst. Induction heating provides a higher heating efficiency as compared to
30 conventional heating where heating is carried out by burning of fuel. Induction heating involves localized heating. There is no requirement for advanced cooling. Induction heating also provides a higher geometrical flexibility and there are also environmental gains such as lower energy consumption.

The attachment of an external magnetic means to the reactor coupled with a DC bias applied to the catalyst helps to facilitate fluidization of the reagents in the reactor through levitation and inter-particle repulsion of the catalyst, respectively, in the reactor. The magnetic field generated by the magnetic means and the electric field generated by the DC bias increase inter-particle repulsion of the catalyst and this in turns enhances the fluidization of the catalyst in the reactor. The facilitated fluidization leads to production of carbon nanotubes with enhanced quality and purity. It also results in a higher conversion rate of the raw carbon source to carbon nanotubes.

The use of fluidized bed reactor in the method of the present invention has the advantage of providing a large surface area between the waste materials and the catalyst. In the fluidized bed reactor, the catalyst particles are mobile within a fixed space and are made to move freely. It provides sufficient space for growth of the carbon nanotubes and good mixing between the waste materials and the catalyst particles. The fluidization of catalyst makes heat and mass transfer more efficient and creates uniform distributions of temperature and concentration. Furthermore, fluidization reduces stagnant film formation at solid surface, which acts as a heat and mass transfer barrier.

The following examples illustrate various embodiments of this invention. One skilled in the art will recognize that the examples set out below are not an exhaustive list of the embodiments of this invention.

Example 1

The following example shows the different results obtained using non-magnetized catalyst versa magnetized catalyst in accordance with the method of the present invention.

During the heating or annealing and magnetization of the catalyst, the electronic spins of all domains align in the same direction with the formation of specific axes and planes of magnetization. At the same time during heating or annealing, the grain size of the catalyst grows but the crystal axes and planes are preserved

despite the changes in domain sizes and the randomization of the directions of electronic spins within the magnetic domains. Overall, the effect of heating or annealing and magnetization of the catalyst is to achieve the specific crystal axis and planes such that the quality of the carbon nanotubes grown on the catalyst is consistent and well defined. This is achieved by heating the catalyst inductively to arrive at the specific or preferred crystal plane.

Due to ferromagnetic coupling, induction heating is 70% more efficient than the resistive and fuel-fired heating employed in conventional methods. The direction of growth of the carbon nanotubes is dependent on the axes and planes of magnetization. Table 1 below shows the hard axes and hard planes of magnetization for the directional growth of the carbon nanotubes on ferromagnetic catalysts.

Table 1: The crystal axes and planes for preferential growth of the carbon nanotubes for three ferromagnetic elements.

Ferromagnetic Catalyst	Carbon nanotubes growth orientation	
	Preferred Growth Direction wrt Crystal Axis	Preferred Growth Direction wrt Crystal Plane
Nickel	$\perp <110>$	// (110)
Iron	$\perp <100>$	// (100)
Cobalt	$\perp <0001>$	// (0001)

The symbols $\perp$ and // denote normal to and parallel to respectively. The crystal axes and planes also apply to the alloys of the ferromagnetic elements.

From Table 1, we can see that the preferential growth of the carbon nanotubes is normal to the hard axes of magnetization and parallel to the hard planes of magnetization. X-Ray diffraction (XRD) confirmed that the crystal axes and planes are preserved after annealing prior to the growth of the carbon nanotubes as annealing only affect the grain sizes, despite the changes in magnetic domain sizes and directions of electronic spins. Using magnetized nickel catalyst as an

example, the carbon nanotubes grow uniformly and at normal to the hard axis of magnetization $\langle 110 \rangle$ and parallel to the hard plan of magnetization (110). On the contrary, the carbon nanotubes grown on non-magnetized nickel have wide distribution in sizes, morphology, and electrical conductivity (see Figure 3).

5

Figure 3 shows the crystal planes of non-magnetized nickel before induction heating and magnetized nickel before induction heating. During XRD analysis, Si(100) substrate was used as the support to hold the nickel sample.

- 10 For growth temperature in the range of 900°C to 1100°C, the carbon nanotubes are conducting with an average resistance per length of 850Ω per μm. For growth temperature in the range of 650°C to 900°C, the carbon nanotubes are semiconducting with a resistance per length of at least 10⁴Ω per μm.
- 15 The purity of the carbon nanotubes as measured by the total crystalline carbon content is between 90% and 96%.

Example 2

- 20 This example serves to illustrate the growth of carbon nanotubes using conventional methods: (i) pyrolysis of acetylene (C₂H₂) over the catalyst of nickel thin film coated onto silicon substrate; and (ii) microwave plasma chemical vapour deposition (MPCVD).
- 25 In this experiment, pyrolysis was carried out at 900°C for a period of 30 minutes in a furnace which was heated by resistive heating element. The ratio of the flow rates of the carbon source from acetylene and the reducing gas, hydrogen was 1:4. The average growth rate of the carbon nanotubes was 2.5 μm/min.
- 30 In a separate experiment, the growth of the carbon nanotubes was carried out at 800°C for a period of 30 minutes in a microwave plasma chemical vapour reactor. The carbon source and the sample used in this method were the same as that used in the pyrolysis method described hereinabove. The average growth rate of the carbon nanotubes was 1.2 μm/min, and the ratio of the flow rate of acetylene

and hydrogen was 1:4. Both experiments resulted in multi-walled carbon nanotubes having 8 to 10 walls and 18 to 22 walls using resistive heating method and MPCVD method, respectively.

	Resistive heating method	MPCVD method
Growth rate of CNTs	2.5 $\mu\text{m}/\text{min}$	1.2 $\mu\text{m}/\text{min}$
No. of walls in CNTs	8 to 10 walls	18 to 22 walls

5

Example 3

This example serves to illustrate the growth of carbon nanotubes on catalytic support of steel wire (catalyst) using plastic wastes as carbon source and induction heating. The plastic wastes consist of polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP), polystyrene (PS), styrene butadiene rubber (SBR) and other plastics materials, and were subjected to the following conditions/procedures:

10

15

Prior to contacting the plastic wastes, the catalyst (i.e. the steel wire) was pretreated in a reducing gas of pure hydrogen and heated at a temperature of 600°C for 10 minutes. The induction heating was effected by AC frequency of 40 kHz at a power of 1 kW.

20

The catalyst was then cooled to room temperature in the same environment after the pretreatment process.

25

Plastic wastes were mixed or placed in contact with the pretreated catalyst and were heated in a vacuum or under inert gas of nitrogen or argon, at a temperature of 950°C for 30 minutes. At this stage, reducing gas of pure or mixture of hydrogen and ammonia can optionally be introduced to the environment. For the purpose of this experiment, reducing gas of pure hydrogen was introduced to the environment. Carbon nanotubes were formed intermixed with the catalyst. The induction heating was effected by AC frequency of 40 kHz at a power of 1 kW.

30

The carbon nanotubes formed by this method were densely grown on the catalyst. The average growth rate of the carbon nanotubes was 2.8 $\mu\text{m}/\text{min}$. This experiment resulted in multi-walled carbon nanotubes with 10 to 15 walls and an external wall thickness of 25 μm to 30 μm .

5

	Method involving induction heating
Growth rate of CNTs	2.8 $\mu\text{m}/\text{min}$
No. of walls in CNTs	10 to 15 walls
Thickness of external wall	25 to 30 μm

In this method, the gaseous by-product, hydrogen produced thereto can be collected, or combusted to supplement heating, or partly recycled and mixed with the feed in the reactor.

10

Example 4

This example serves to illustrate the growth of carbon nanotubes on catalytic support of steel wire (catalyst) using plastic wastes as carbon source, and induction heating with levitation of catalyst. The plastic wastes used in this example are the same as those used in Example 3.

15

Prior to contacting the plastic wastes, the catalyst was pretreated in a reducing gas of pure hydrogen and heated at a temperature of 600°C for 10 minutes. Induction heating was effected by AC frequency of 40 kHz at a power of 1 kW.

20

An external hard magnet was attached in close proximity to the furnace to provide a constant magnetic field to the catalyst such that the catalyst was levitated in the heating process. The levitation of the catalyst provided more efficient fluidization within the furnace and facilitated mass transport of the reactants and products within the furnace. The fluidization of the catalyst was supplemented by applying a positive DC bias of +100 volts to the electrically conducting catalyst.

25

The catalyst was cooled to room temperature in the same environment after the pretreatment process.

In the same setup, plastic wastes were mixed or placed in contact with the pretreated catalyst and were heated in vacuum or under inert gas of nitrogen or argon, at a temperature of 950°C for 30 minutes. At this stage, reducing gas of pure or mixture of hydrogen and ammonia may optionally be introduced to the environment. For the purpose of this experiment, reducing gas of pure hydrogen was introduced to the environment. The induction heating was effected by AC frequency of 40 kHz at a power of 1 kW.

The fluidization of the catalyst was supplemented by applying a positive DC bias of +100 volts to the electrically conducting catalyst.

The carbon nanotubes obtained in this example were densely grown on the catalyst. The average growth rate of the carbon nanotubes was 3 µm/min. The experiment resulted in multi-walled carbon nanotubes with 8 to 15 walls and an external wall thickness of 20 µm to 25 µm.

	Method involving induction heating & levitation of catalyst
Growth rate of CNTs	3.0 µm/min
No. of walls in CNTs	8 to 15 walls
Thickness of external wall	20 to 25 µm

Example 5

The example serves to illustrate the growth of carbon nanotubes on catalytic support of steel wire (catalyst) using plastic wastes as carbon source, induction heating, levitation of catalyst and depolymerization of plastic wastes prior to adding the plastic wastes to the catalyst. The plastic wastes used in this example are the same as those used in Example 3.

In this example, the catalyst was pretreated in a reducing gas of pure hydrogen and heated at temperature of 600°C for 10 minutes prior to contacting the catalyst to plastic wastes. Induction heating was effected by AC frequency of 40 kHz at a power of 1 kW.

5

An external hard magnet was attached in close proximity to the furnace to provide a constant magnetic field to the catalyst such that the catalyst was levitated in the heating process. The levitation of catalyst provided more efficient fluidization within the furnace and facilitated mass transport of the reactants and the products.

10 The fluidization of the catalyst was supplemented by applying a positive DC bias of +100 volts to the electrically conducting catalyst.

The pretreated catalyst was heated to 950°C. The plastic wastes were then mixed with antioxidant and neutralization reagent and was depolymerized by heating
15 separately in another vacuum chamber at a temperature of 400°C for 60 minutes. The induction heating was effected by AC frequency of 50 Hz at a power of 1 kW.

The gaseous distillate from the depolymerisation process was fed to the vacuum chamber containing the pretreated catalyst at 950°C for a period of 30 minutes.

20

The carbon nanotubes obtained in this experiment were densely grown on the catalyst. The average growth rate of the carbon nanotubes was 3.2 µm/min. The experiments resulted in multi-walled carbon nanotubes with 6 to 12 walls and an external wall thickness of 15 µm to 22 µm.

25

	Method involving induction heating, levitation of catalyst & depolymerization of plastic wastes
Growth rate of CNTs	3.2 µm/min
No. of walls in CNTs	6 to 12 walls
Thickness of external wall	15 to 22 µm

The above examples show that relatively good growth rate of carbon nanotubes can be achieved by the method in accordance with the present invention as compared to methods known in the art.

- 5 The above is a description of the subject matter the inventors regard as the invention and is believed that those skilled in the art can and will design alternative embodiments that include of this invention as set forth in the following claims.

Claims:

1. A method for producing carbon nanotubes, comprising:
heating a catalyst in a fluidized bed reactor by induction heating;
5 cooling the catalyst in the fluidized bed reactor;
adding waste materials containing carbon source to the catalyst;
heating the waste materials containing the carbon source and the catalyst
by induction heating;
applying a DC bias to the catalyst; and
10 levitating the catalyst simultaneously by magnetic means to mix the catalyst
with the waste materials containing the carbon source to form carbon nanotubes.
2. The method according to claim 1, further comprising:
heating the waste materials containing the carbon source in a separate
15 enclosure by induction heating to depolymerize the waste materials containing the
carbon source prior to adding the waste materials containing the carbon source to
the catalyst.
3. The method according to claim 1, wherein the magnetic means include one
20 or more electromagnets.
4. The method according to claim 1, wherein the waste materials containing
the carbon source are selected from the group consisting of plastic wastes, rubber
wastes, wood wastes, paper wastes, textile wastes and organic chemical wastes.
25
5. The method according to claim 1, wherein the catalyst is selected from the
group consisting of a ferromagnetic element, a combination of ferromagnetic
elements, an alloy comprising one or a combination of ferromagnetic elements, an
alloy comprising a combination of ferromagnetic elements with one or more non-
30 ferromagnetic elements and any such element, alloy or combination mixed with
non-reactive support structures.
6. The method according to claim 5, wherein the ferromagnetic element is
selected from the group consisting of iron, nickel and cobalt.

7. The method according to claim 1, wherein the catalyst is in a form selected from the group consisting of particle, wool, wire, mesh, plate, pellet and tablet.

5 8. The method according to claim 1 or 2, wherein the induction heating is carried out using induction coils.

9. The method according to claim 8, wherein the induction coils are wound proximate to and around the external wall of the fluidized bed reactor.

10 10. The method according to claim 8, wherein the induction heating is carried out by applying an AC power output having a frequency in the range of 50 Hz to 14 MHz to the induction coils.

15 11. The method according to claim 1, wherein the catalyst is heated in presence of a reducing gas.

12. The method according to claim 11, wherein the reducing gas is selected from the group consisting of hydrogen, ammonia, nitrogen or a mixture thereof.

20 13. The method according to claim 1, further comprising:
introducing a second reducing gas into the reactor while heating the waste materials containing the carbon source and the catalyst in the reactor.

25 14. The method according to claim 13, wherein the second reducing gas is selected from the group consisting of hydrogen, ammonia or a mixture thereof.

15. The method according to claim 1, wherein the catalyst is heated to a temperature between 400°C and 650°C.

30 16. The method according to claim 1, wherein the waste materials containing the carbon source and the catalyst is heated to a temperature between 600°C and 1100°C.