



(51) International Patent Classification:
C01B 31/02 (2006.01)

(21) International Application Number:
PCT/IB2016/056290

(22) International Filing Date:
19 October 2016 (19.10.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/243,695 20 October 2015 (20.10.2015) US

(71) Applicant: KING ABDULLAH UNIVERSITY OF SCIENCE AND TECHNOLOGY [SA/SA]; 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 (SA).

(72) Inventors: BASSET, Jean-Marie; 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 (SA). ZHOU, Lu; 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 (SA). SAIH, Youssef; 4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900 (SA).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: CARBON NANOTUBES AND METHODS OF MAKING CARBON NANOTUBES

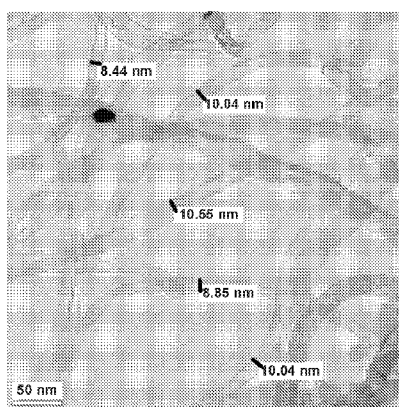


Fig. 1

(57) Abstract: Embodiments of the present disclosure provide for methods that can be used to produce carbon nanotubes (herein-after CNT) having an inner diameter about 5-55 nm, methods of tuning the inner diameter of CNTs (e.g., by adjusting reaction pressure), CNTs having an inner diameter of greater than 20 nm or more, and the like.



CARBON NANOTUBES AND METHODS OF MAKING CARBON NANOTUBES**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of and priority to U.S. Provisional Application Serial No. 62/243,695, having the title "CARBON NANOTUBES AND METHODS OF MAKING CARBON NANOTUBES," filed on October 20, 2015, the disclosure of which is incorporated herein in by reference in its entirety.

BACKGROUND

CNT has been the research focus over a decade due to its unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. In particular, owing to their extraordinary thermal conductivity and mechanical and electrical properties, CNT finds applications as additives to various structural materials.

Presently, CNT can be produced in large quantities by these following dominant techniques: chemical vapor deposition, high-pressure carbon monoxide process, arc discharge, and laser ablation. Hydrocarbons decomposition over Ni, Fe, or Co catalysts has been recently investigated by some researchers to produce CNT. It has been reported that multiwalled CNT with inner diameters 5 nm to 10 nm can be formed during ethylene decomposition at 700 °C, atmospheres pressure over Co and Fe catalysts. In addition, multi-walled carbon nanotubes have been produced that have 5 to 20 nm inner diameter and 60 to 413 nm in length, which were synthesized over nickel supported on a zeolite by the decomposition of methane in the relatively low temperature range 400–550°C. Nevertheless, almost all produced CNTs have an inner diameter from 5-20 nm.

SUMMARY

Embodiments of the present disclosure provide for methods that can be used to produce carbon nanotubes (hereinafter CNT) having an inner diameter about 5-50 nm, methods of tuning the inner diameter of CNTs (e.g., by adjusting reaction pressure), CNTs having an inner diameter of greater than 20 nm or more, and the like.

In an embodiment, a method for hydrocarbon catalytic decomposition, among others, includes: heating a catalyst to about 400 to 1000° C under an inert gas; flowing a hydrocarbon across the catalyst; and decomposing the hydrocarbon to produce carbon nanotubes (CNTs) having an inner diameter of about 5 to 55 nm. In an embodiment, the inner diameter is about 25 to 55 nm and an outer diameter of about 10 to 130 nm. In an embodiment, the hydrocarbon can be methane. In an embodiment, the catalyst can be a supported fused Fe catalyst (e.g., a fused Fe/Al₂O₃ catalyst). An embodiment of the method may also include: heating the supported fused Fe catalyst to the reduction temperature of the supported fused Fe catalyst; and flowing H₂ over the supported fused Fe catalyst to reduce the supported fused Fe catalyst. In an embodiment, the method can also include: adjusting a reaction pressure to select the inner diameter of the CNT. In an embodiment, the reaction pressure is about 5 to 50 bar.

In an embodiment, a composition, among others, includes: a CNT having an inner diameter of about 25 to 55 nm. In an embodiment, the CNT can have an outer diameter of about 10 to 130 nm.

In an embodiment, a hydrocarbon catalytic decomposition system, among others, includes: a carbon nanotube (CNT) having an inner diameter of about 25 to 55 nm that replaces commercial catalyst supports.

Other compositions, systems, methods, features, and advantages will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional compositions, systems, methods, features and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Further aspects of the present disclosure will be more readily appreciated upon review of the detailed description of its various embodiments, described below, when taken in conjunction with the accompanying drawings.

Figure 1 shows carbon nanotubes produced at 1 bar.

Figure 2 shows carbon nanotubes produced at 2 bar.

Figure 3 shows carbon nanotubes produced at 5 bar.

Figure 4 shows carbon nanotubes produced at 30 bar.

Figure 5 shows carbon nanotubes produced at 30 bar.

Figure 6 shows carbon nanotubes produced at 50 bar.

DETAILED DESCRIPTION

Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit (unless the context clearly dictates otherwise), between the upper and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, material science, inorganic chemistry, and the

like, which are within the skill of the art. Such techniques are explained fully in the literature.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, *etc.*), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is in bar. Standard temperature and pressure are defined as 0 °C and 1 bar.

Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a support" includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

General Discussion

Embodiments of the present disclosure provide for methods that can be used to produce carbon nanotubes (hereinafter CNT) having an inner diameter about 5-55 nm, methods of tuning the inner diameter of CNTs (*e.g.*, by adjusting reaction pressure), CNTs having an inner diameter of greater than 20 nm or more, and the like. In particular, embodiments of the present disclosure provide for methods to produce CNTs having large inner diameters through hydrocarbon catalytic decomposition. In addition, embodiments of the present disclosure provide for the ability to tune the CNT inner pore size by changing the hydrocarbon decomposition conditions (*e.g.*, reaction pressure).

CNTs having a large inner diameter (e.g., high inner pore volume) may be valuable in areas such as biology, catalysis, and material science. For example, CNTs can be used in biological applications to provide large channels for biomimetic platforms for developing cell interfaces. In catalysis CNTs having a large inner diameter have a crystallinity that can allow single site catalysis. In an embodiment, the CNTs can be used as catalyst supports to replace commercial supports (e.g., MCM41).

Embodiments of the present disclosure use a catalyst (e.g., a fused Fe catalyst) to produce CNTs with tunable inner pore sizes (e.g., diameters). In an embodiment, the CNT can have an inner diameter of about 5 to 55 nm and an outer diameter of about 10 to 130 nm, where for both the inner and outer diameter, any range between and including about 5 to 55 nm and about 10 to 130 nm, respectively, is intended to be included in about 1 nm or more increments in those ranges.

Methods of the present disclosure can use reaction conditions to tune the method to produce CNTs having desired dimensions including control to produce a desired inner diameter. In an embodiment, the method can be used to produce CNTs having an inner diameter of about 5 nm, about 10 nm, about 20 nm, about 22 nm, about 24 nm, about 26 nm, about 28 nm, about 30 nm, about 35 nm, about 40 nm, or about 45 nm to about 10, about 20 nm, about 25 nm, about 30 nm, about 35 nm, about 40 nm, about 45 nm, about 50 nm, or about 55 nm, where all possible integer values including and within the various inner diameter values is contemplated (e.g., about 22 to 55 nm, about 30 to 45 nm, about 10 to 30 nm, and the like).

Embodiments of the present disclosure can use catalysts made from inert oxides (e.g., Al_2O_3 , silica, silica-alumina, zirconia, titania, zinc oxide, magnesia, zeolite, mesoporous zeolite, CeO_2 , and/or SiO_2 that support one or more a combination of Fe, Ni, Cu, Co, Ru, Rh, Pt, or Pd, or the like). In an embodiment, the catalyst is a fused Fe catalyst (e.g., a fused Fe- Al_2O_3 catalyst). The fused Fe catalyst can be used for the industrialization of methane catalytic decomposition processes, which form the CNTs as well as other gases (e.g., H_2). In particular, the supported fused Fe catalyst is a fused Fe/ Al_2O_3 catalyst. In an embodiment, the Fe content in the supported fused Fe catalyst can be about 5 to 65 wt% of the supported fused Fe catalyst. In an embodiment, the alumina support can be replaced with one or more of the following: silica, silica-alumina, zirconia, titania, zinc

oxide, magnesia, zeolite, mesoporous zeolite, and the like, and a combination thereof.

An embodiment of the method can use a hydrocarbon as the source for decomposition to produce CNTs. In an embodiment, the hydrocarbon can include saturated and unsaturated hydrocarbons such as C1-C20 alkanes, C2-C20 alkenes, C2-C20 alkynes, and a mixture thereof, where each can be linear, branched, cyclic, aromatic, or a mixture thereof. In an embodiment, the hydrocarbon can be 100% pure hydrocarbon, a mixture of hydrocarbons at various concentrations, or a mixture with another gas(es) that does not interfere with the production of the CNTs. In an embodiment, the hydrocarbon can be methane.

In the following illustrative embodiment, the hydrocarbon is methane, but other hydrocarbons or mixtures can be used. In an embodiment, the catalytic reaction to produce the CNTs can be conducted in a PID microreactor or similar reactor equipped with a long stainless tube reactor (e.g., ID 9 mm, length 305 mm), which can be heated by a furnace (e.g., an electrical furnace) under a pressure of about 1 to 50 bar and a temperature of about 550 to 900°C, where the pressure and temperature can be adjusted to produce CNTs having a desired inner diameter and other dimensions. The catalyst was loaded into the reactor, while the reaction temperature was controlled by a thermocouple placed into the middle of the catalyst layer. The loaded catalyst was directly heated to the reaction temperature under an inert gas (e.g., Ar gas), and then the gas was switched to methane to begin the methane decomposition reaction for a time frame of about 10 min to 10 h. The reaction produces CNTs and other gases (e.g., H₂). Additional details regarding the decomposition of the hydrocarbon are provided in the Example.

EXAMPLES

Now having described the embodiments of the disclosure, in general, the examples describe some additional embodiments. While embodiments of the present disclosure are described in connection with the example and the corresponding text and figures, there is no intent to limit embodiments of the disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

Example 1:

The present example discloses a method that is used to prepare CNT with inner diameter ranged from about 5-55 nm through hydrocarbons decomposition at selected conditions. The present example further discloses a relationship between the pore size and reaction conditions.

Materials and general consideration:

Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received. The hard reduced oxides like Al_2O_3 , CeO_2 , SiO_2 and etc. supported Fe, Ni, Cu, Co, Ru, Rh, Pt, Pd and etc. catalysts are effect for this methane decomposition. In this present example, the methane decomposition over alumina supported iron catalyst (hereinafter $\text{Fe}/\text{Al}_2\text{O}_3$) is selected as the representative example. Iron nitrate nonahydrate (98%) and aluminum nitrate nonahydrate (99.997%) were purchased from Sigma-Aldrich and used as received. $\text{Fe}/\text{Al}_2\text{O}_3$ can be synthesized by several methods including impregnation, sol-gel, precipitation and so on. In the present example, $\text{Fe}/\text{Al}_2\text{O}_3$ materials were prepared according to the procedure named as fusion method; a typical procedure is described as follows:

- Physically grinding and mixing Fe nitrate and support nitrate
- Calcining under static air from R.T. to 350°C for 3 h with a 5°C/min
- Going down to RT under air flow, and then grinding the final sample to fine powder

Its Fe loading ranges from 5-65 wt.%, as determined by elemental analysis. Some catalysts properties are shown in Table 1.

Elemental analyses were obtained from the service of Mikroanalytisches Labor Pascher (Remagen, Germany). XRD patterns were recorded on a Bruker D8 Advanced A25 diffractometer using a Bragg–Brentano geometry with a copper tube operating at 40 kV and 40 mA. N_2 adsorption–desorption isotherms were obtained on a Micromeritics ASAP2420. Prior to these measurements, the samples were degassed for 2 h at 300°C. The surface areas of the samples were determined by a multi-point BET analysis method, and pore volumes were estimated at $P/P_0 = 0.99$. Scanning electron microscope (SEM) images were taken by the FEI Quanta 200 or

600 FEG environmental scanning electron microscope (ESEM). TEM images were taken on a Titan G2 transmission electron microscope (FEI, Hillsboro, OR, USA), operating at 80–300 kV and equipped with a 4 k × 4 k charge-coupled device (CCD) camera (US4000) and energy filter (GIF Tridiem, Gatan Inc., Pleasanton, CA, USA). The specimens were prepared by ultrasonically suspending the sample in ethanol. A drop of the suspension was then applied onto clean holey copper grids and dried in air.

Table 1 Properties of catalysts A to G

Catalysts	Fe loading [wt%]	BET [m ² /g]	Pore volume [cc/g]	Pore size [nm]
A	5	145	0.15	3.68
B	10	162	0.16	3.47
C	20	203	0.24	4.07
D	35	184	0.23	4.00
E	40	174	0.26	4.83
F	50	116	0.19	5.07
G	65	57	0.20	11.77

In an embodiment, any hydrocarbon can be selected as the source for decomposition to produce CNT. In this present example, the methane decomposition was selected as the representative example of hydrocarbon. A typical methane decomposition test is described as follows: The catalytic reaction was conducted in a PID micro reactor equipped with a long stainless tube reactor (ID 9 mm, length 305 mm), which was heated by an electrical furnace under different pressure from 1 to 50 bar and different temperatures from 550 to 900°C. In this present example, the 750°C was selected as the representative reaction temperature, while the catalyst E was selected as the representative sample. The catalyst was loaded into the reactor, while the reaction temperature was controlled by a thermocouple placed into the middle of the catalyst layer. The CH₄ used for the MCD can be at any concentration. In this present example, a pure methane gas was used. The loaded catalyst was directly heated to reaction temperature under Ar gas, and then the gas was switched to CH₄ to begin the methane decomposition reaction. The outlet gases were analyzed by an online GC (Varian 450-GC) and micro GC (Soprane MicroGC 3000).

The reaction results are summarized in Table 2.

Table 2 Summarization of the methane decomposition results over catalysts

Catalysts	Reaction temp. [°C]	Reaction GHSV [L/h·g _{cat}]	Reaction Pressure [bar]	CNT inner pore size [nm]
E	750	7.5	1	8-10
E	750	7.5	2	8-10
E	750	7.5	5	15-22
E	750	7.5	10	25-29
E	750	7.5	30	42-50
E	750	7.5	50	46-52

The CNT size of different samples in Table 2 was confirmed with TEM in Figures 1-6.

It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1% to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also include individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term "about" can include traditional rounding according to significant figures of the numerical value. In addition, the phrase "about 'x' to 'y'" includes "about 'x' to about 'y'".

It should be emphasized that the above-described embodiments of the present disclosure are merely possible examples of implementations, and are set forth only for a clear understanding of the principles of the disclosure. Many variations and modifications may be made to the above-described embodiments of the disclosure without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure.

CLAIMS

We claim at least the following:

1. A method for hydrocarbon catalytic decomposition, comprising:
heating a catalyst to about 400 to 1000° C under an inert gas;
flowing a hydrocarbon across the catalyst; and
decomposing the hydrocarbon to produce carbon nanotubes (CNTs) having an inner diameter of about 5 to 55 nm.
2. The method of claim 1, wherein the inner diameter is about 25 to 55 nm and an outer diameter of about 10 to 130 nm.
3. The method of claim 1 or 2, wherein the hydrocarbon is methane.
4. The method of claim 1, 2, or 3, wherein the catalyst is a supported fused Fe catalyst, wherein flowing a hydrocarbon across the supported fused Fe catalyst reduces the supported fused Fe catalyst.
5. The method of claim 4, wherein the supported fused Fe catalyst is a fused Fe/Al₂O₃ catalyst.
6. The method of claim 1, wherein the catalyst is a supported fused Fe catalyst, and further comprising:
heating the supported fused Fe catalyst to the reduction temperature of the supported fused Fe catalyst; and
flowing H₂ over the supported fused Fe catalyst to reduce the supported fused Fe catalyst.
7. The method of claim 1, 2, or 3, wherein the catalyst is a reduced oxide.
8. The method of claim 1, 2, 3, or 7, adjusting a reaction pressure to select the inner diameter of the CNT.

9. The method of claim 8, wherein the reaction pressure is about 5 to 50 bar.
10. The method of claim 8, wherein the reaction pressure is about 5 bar.
11. The method of claim 10, wherein the inner diameter is about 15 to 22 nm.
12. The method of claim 8, wherein the reaction pressure is about 10 bar.
13. The method of claim 12, wherein the inner diameter is about 25 to 29 nm.
14. The method of claim 8, wherein the reaction pressure is about 30 bar.
15. The method of claim 13, wherein the inner diameter is about 42 to 50 nm.
16. The method of claim 8, wherein the reaction pressure is about 50 bar.
17. The method of claim 16, wherein the inner diameter is about 46 to 52 nm.
18. A composition, comprising a carbon nanotube (CNT) having an inner diameter of about 25 to 55 nm.
19. The composition of claim 18, wherein the inner diameter is about 15 to 22 nm.
20. The composition of claim 18, wherein the inner diameter is about 25 to 29 nm.
21. The composition of claim 18, wherein the inner diameter is about 42 to 50 nm.
22. The composition of claim 18, wherein the inner diameter is about 46 to 52 nm.
23. The composition of claim 18, 19, 20, 21, or 22, wherein the CNT has an outer diameter of about 10 to 130 nm.

24. A hydrocarbon catalytic decomposition system, comprising a carbon nanotube (CNT) having an inner diameter of about 25 to 55 nm that replaces commercial catalyst supports.

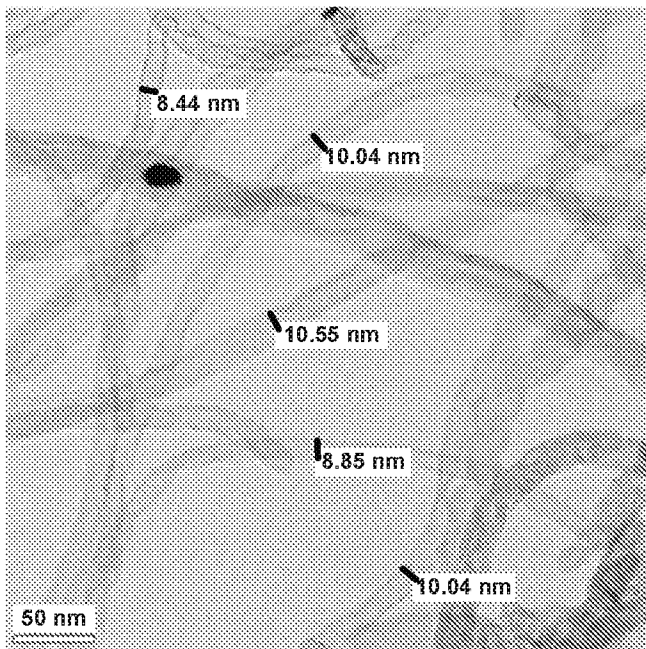


Fig. 1

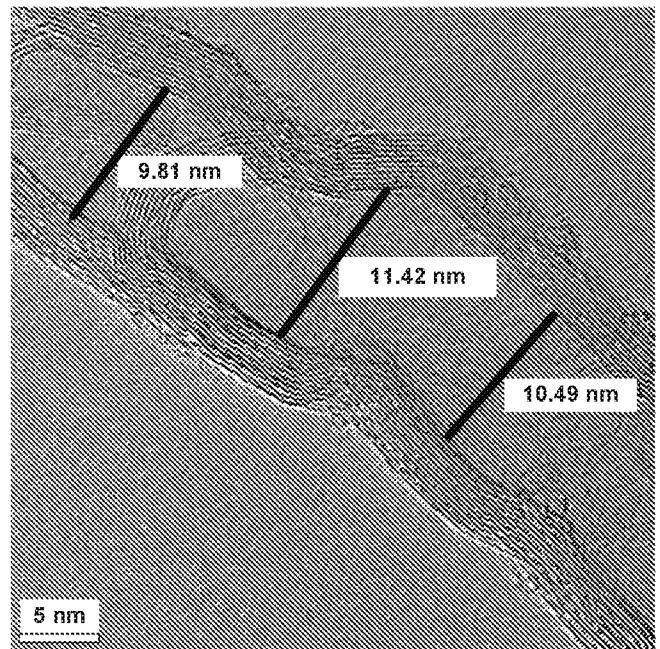


Fig. 2

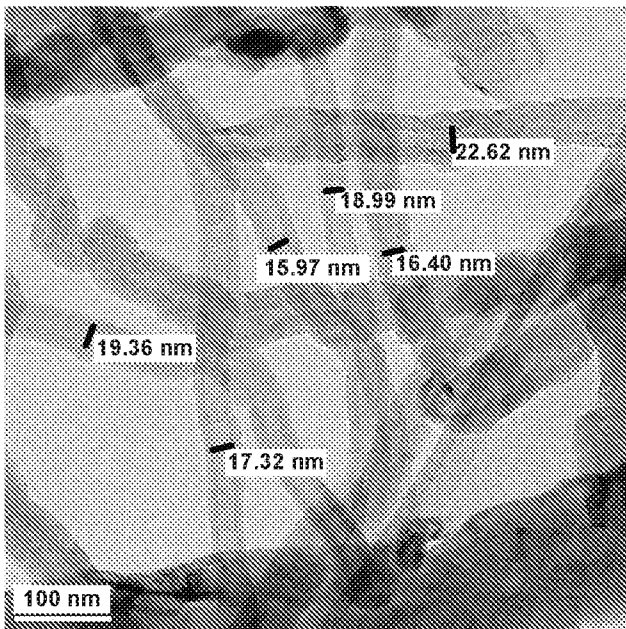


Fig. 3

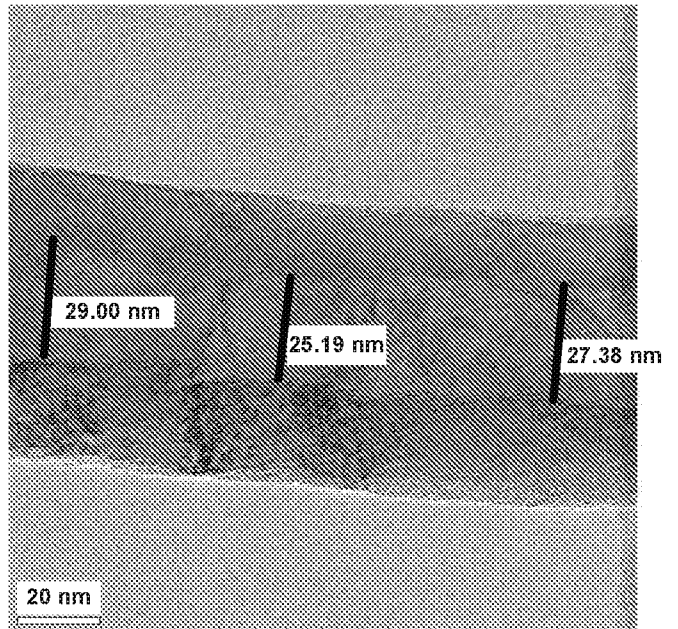


Fig. 4

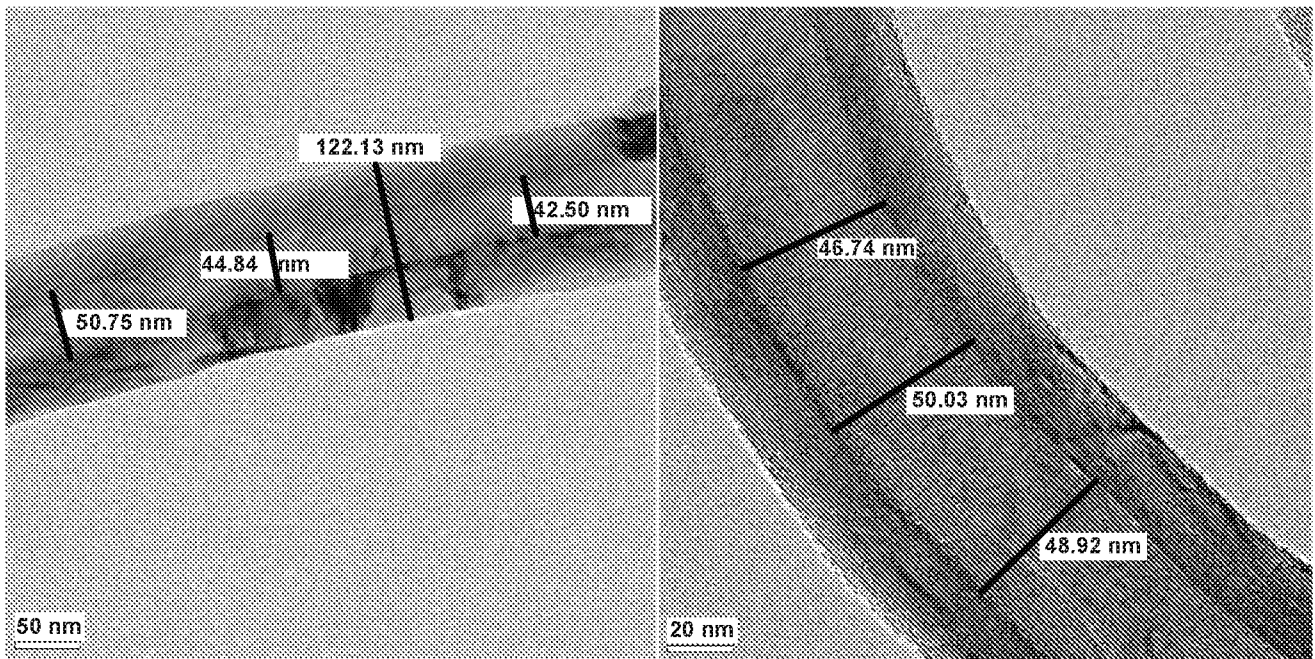


Fig. 5

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/056290

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B31/02
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CORRIAS Massimiliano: "Nouvelle Classe de catalyseurs pour la production massive en lit fluidisé de nanotubes de carbone multi parois", INTERNET CITATION, 27 September 2011 (2011-09-27), pages 111-164, XP002714865, Retrieved from the Internet: URL: http://ethesis.inp-toulouse.fr/archive/00001686/ [retrieved on 2013-10-15]	1-7,19, 23
Y	Chapitres 2 et 3;	24
A	figures 3.23, 3.26 ----- -/--	8-18, 20-22

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 November 2016

Date of mailing of the international search report

19/12/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Corrias, M

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/056290

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	M. K. SINGH ET AL.: "High density of multiwalled carbon nanotubes observed on nickel electroplated copper substrates by microwave plasma chemical vapor deposition", CHEMICAL PHYSICS LETTERS, vol. 354, 2002, pages 331-336, XP002764775,	18-20,23
Y	Results and discussion; figure 2 -----	24
X	Y. HUANG ET AL.: "Synthesis of rigid and stable large-inner-diameter multiwalled carbon nanotubes", RCS ADVANCES, vol. 2012, no. 2, 25 January 2012 (2012-01-25), pages 2685-2687, XP002764776,	18-21
Y	page 2685 - page 2686; figures 1-3 -----	24
X	F. WEI ET AL.: "The mass production of carbon nanotubes using a nano-agglomerate fluidized bed reactor: A multiscale space-time analysis", POWDER TECHNOLOGY, vol. 183, 24 November 2007 (2007-11-24), pages 10-20, XP002764777,	18,21-23
Y	3.2 MWCNT catalyst design -----	24
Y	SERP P ET AL: "Carbon nanotubes and nanofibers in catalysis", APPLIED CATALYSIS A: GENERAL, vol. 253, no. 2, 28 October 2003 (2003-10-28), pages 337-358, XP004467607, ELSEVIER, AMSTERDAM, NL ISSN: 0926-860X, DOI: 10.1016/S0926-860X(03)00549-0 "4 Catalytic performances of CNT and GNF based catalysts" "4.4 catalytic decomposition of hydrocarbon" -----	24