United States Patent
Siochi et al.

TEMPLATED GROWTH OF CARBON NANOTUBES

Inventors: Emilie J. Siochi, Newport News, VA (US); Tarek Abdel-Fattah, Yorktown, VA (US)

Assignee: The United States of America as represented by the Administrator of the National Aeronautics and Space Administration, Washington, DC (US)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

Appl. No.: 11/129,751
Filed: May 11, 2005

Prior Publication Data

Related U.S. Application Data
Provisional application No. 60/570,964, filed on May 12, 2004.

Int. Cl.
C01B 31/02
D01F 9/12

U.S. Cl. 423/447.3; 977/742; 977/842

Field of Classification Search 423/447.3; 977/742; 842

See application file for complete search history.

References Cited
U.S. PATENT DOCUMENTS
6,129,901 A 10/2000 Moskovits et al.
6,231,744 B1 5/2001 Yang et al.
6,335,016 B1 12/2001 Reasano et al.
6,350,488 B1 2/2002 Lee et al.
6,413,487 B1 7/2002 Reasano et al.
6,602,932 B2 * 8/2003 Feldheim et al. 523/201


OTHER PUBLICATIONS

Primary Examiner—Stuart L. Hendrickson
Assistant Examiner—Alvin T. Raetzsch
Attorney, Agent, or Firm—Robin W. Edwards

ABSTRACT
A method of growing carbon nanotubes uses a synthesized mesoporous silica template with approximately cylindrical pores being formed therein. The surfaces of the pores are coated with a carbon nanotube precursor, and the template with the surfaces of the pores so-coated is then heated until the carbon nanotube precursor in each pore is converted to a carbon nanotube.

16 Claims, 1 Drawing Sheet
In accordance with the present invention, a method of growing carbon nanotubes starts by synthesizing a template made from a mesoporous silica having approximately cylindrical pores formed therein. The inner surfaces of the pores are then coated with a carbon nanotube precursor capable of being carbonized upon the heating thereof. The template with the surfaces of the pores so-coated is then heated until the carbon nanotube precursor in each pore is converted to a carbon nanotube.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects, features and advantages of the present invention will become apparent upon reference to the following description of the embodiments and to the drawings, wherein corresponding reference characters indicate corresponding parts throughout the several views of the drawings and wherein:

FIG. 1 is a top view of a hexagonal pack of hollow mesoporous silica cylinders that form a template of mesoporous silica used in the method of the present invention;

FIG. 2 is a cross-sectional view of the synthesized template of mesoporous silica taken along line 2–2 in FIG. 1;

FIG. 3 is a cross-sectional view of the synthesized template with the approximately cylindrical pores thereof coated with a carbon nanotube precursor in accordance with the method of the present invention; and

FIG. 4 is a part cross-sectional, part schematic view of the synthesized template having CNTs formed in the approximately cylindrical pores after carbonization of the carbon nanotube precursor in accordance with the method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring now to the drawings, and more particularly to a top view in FIG. 1 and a cross-sectional view in FIG. 2, a synthesized template for use in the present invention is shown and is referenced generally by numeral 10. Template 10 is formed by a close pack configuration of hollow mesoporous cylinders 11 arranged in a hexagonal pack. This arrangement of cylinders 11 defines a mesoporous silica 12 (FIG. 2) having approximately cylindrical pores 14 formed therein that serve as the mold for growing carbon nanotubes (CNTs) in accordance with the present invention. In this illustrated example, mesoporous silica 12 is of uniform thickness 'T' with individual approximately cylindrical pores 14 extending all the way therethrough. Pores 14 are straight and can be parallel to one another as shown. When it is desired to produce a quantity of CNTs having substantially uniform diameters, each of approximately cylindrical pores 14 should have the same (or nearly the same) diameter. For example, a sample template was synthesized to yield approximately cylindrical pores 14 having diameters in the range of 3.5–4.0 nanometers. This diameter range provides CNTs that are useful for a variety of applications to include mechanical reinforcement, electrical conductivity enhancement, and possibly thermal management.

As is known in the art of template construction, approximately cylindrical pores 14 are formed by the following general steps: providing approximately cylindrical rods (not shown) that are typically made from an organic material and have outside diameters equal to the desired inside diameters of approximately cylindrical pores 14, synthesizing mesoporous silica about the rods whereby the rods become "plugs" within mesoporous silica cylinders 11, and then
removing the “plugs” (e.g., via organic material degradation) to yield the structure illustrated in FIG. 1 and 2. The synthesizing of mesoporous silica (about the red plugs that will be removed to define approximately cylindrical pores 14) is known in the art. See, for example, “Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism,” Kegele et al., Nature 1992, Vol. 359, p. 710, and “A New Family of Mesoporous Molecular Sieves Prepared With Liquid Crystal Templates,” Beck et al., J. Am. Chem. Soc., Vol. 114, 1992, p. 10834.

Brieﬂy, reagents used for the synthesis of template 10 included ammonium hydroxide (NH₄OH) at 30 weight percent, tetraethylorthosilicate (TEOS), aluminum isopropoxide ([iso-pro]₃Al) and cetyltrimethylammonium bromide (CTABr). The synthesis of mesoporous silica template 10 was performed using the following reaction composition 1.0 TEOS: 0.01 ([iso-pro]₃Al): 0.2 CATHr: 0.5 NH₄OH: 150 H₂O. The resulting gel was aged for 5 days at 110º C. in TEFLO™-lined stainless steel autoclaves. The product was filtered, washed with distilled water, dried in air, and finally calcined at 650º C. for 6 hours. The 650º C. exposure step removes the organic “plugs” by degradation. The resulting aluminum mesoporous silica can then be, but is not required to be, treated with 0.1M solution of cobalt nitrate (Co(NO₃)₂) solution, iron salts, nickel salts, or any other metal salts for 4 hours to impregnate cobalt in the mesoporous silica. The product is then ﬁltered, washed with distilled water, and dried.

The next step in the present invention is to coat the surfaces of each of approximately cylindrical pores 14 with a carbon nanotube precursor 20 as shown in FIG. 3. While carbon nanotube precursor 20 is essentially any hydrocarbon that can be carbonized through the heating thereof to form a CNT (e.g., polymers, solvents such as toluene, or other aromatic hydrocarbons), one of the great advantages of the present invention is achieved when carbon nanotube precursor 20 is sugar-based. For example, carbon nanotube precursor 20 can be based on the readily-available and inexpensive table sugar or sucrose. Since carbon nanotube precursor 20 is most effective when its hydrocarbon content is optimized and since sucrose has many hydroxyl (—OH) groups, it is advantageous to reduce the number of hydroxyl groups present in sucrose prior to the carbonization thereof to form CNTs. One way of reducing sucrose’s hydroxyl groups while simultaneously coating the surface of approximately cylindrical pores 14 will now be explained by way of example. Sucrose is first mixed in solution with sulfuric acid with the resulting mixture then being impregnated into template 10. Such impregnation can be achieved in a variety of ways to include, but not limited to, immersion of template 10 into the sucrose/sulfuric acid solution, flowing the sucrose/sulfuric acid solution over/through template 10, or otherwise introducing the sucrose/sulfuric acid solution into approximately cylindrical pores 14 of template 10. The sulfuric acid removes some water from the sucrose to thereby reduce the hydroxyl group content of the sucrose to effectively convert same to an intermediate (sucrose-based) carbon black that serves as carbon nanotube precursor 20. After such impregnation with the sucrose/sulfuric acid solution, template 10 so-impregnated is dried (e.g., at 160º C. in a nitrogen atmosphere) to yield the structure illustrated in FIG. 3.

To grow CNTs, the structure illustrated in FIG. 3 is heated to bring about the carbonization of carbon nanotube precursor 20. That is, a CNT 30 (FIG. 4) grows from carbon nanotube precursor 20 coated on approximately cylindrical pores 14. For the illustrated example of a reduced hydroxyl group derivative of sucrose serving as carbon nanotube precursor 20, heating temperatures in the range of 700–900º C. were used to successfully grow CNTs 30. Time for such heating ranged from 8–12 hours. Such heating can be performed while applying a vacuum, or inert atmosphere such as nitrogen, helium, or argon to the structure illustrated in FIG. 3 in order to reduce the temperature at which CNT growth is completed. It was found that the increased hydrocarbon content of a reduced hydroxyl group derivative of sugar served to optimize the inventive method by providing the chemical structure more favorable to yielding the high hydrocarbon content of the target product, i.e., CNTs 30.

Since CNTs 30 grow from carbon nanotube precursor 20 which is constrained within approximately cylindrical pores 14, CNT growth and the resulting CNTs 30 are deﬁned by approximately cylindrical pores 14 that, in this example, are straight and have substantially uniform diameters and lengths.

Following the growth of CNTs 30 in approximately cylindrical pores 14, the resulting structure is a mesoporous carbon-silica nanocomposite 40 that can function as a semiconducting material. The shape and size of semiconducting nanocomposite 40 can be tailored during the formation of the mesoporous silica template.

If it is desired to utilize CNTs 30 by themselves, mesoporous silica 12 can be removed to thereby yield a plurality of uniform length and diameter CNTs 30. To retain the straight and parallel nature of CNTs 30 in mesoporous silica 12 after silica 12 is removed, it may be necessary to couple one or both ends of each of CNTs 30 to a support (not shown) prior to the removal of mesoporous silica 12. Removal of mesoporous silica 12 can be achieved by dissolving silica 12 through application of a solvent (e.g., hydrochloric acid) that does not react with CNTs 30.

The advantages of the present invention are numerous. By constraining CNT growth to pre-sized tubes, CNTs having uniform length and diameter can be grown easily and simply. The process yields individual and straight CNTs that will not be bundled or aggregated. Further, the ability to use readily-available, inexpensive and non-hazardous sugars as the source for the carbon nanotube precursor will greatly improve the affordability of CNTs.

Although the invention has been described relative to a specific embodiment thereof, there are numerous variations and modiﬁcations that will be readily apparent to those skilled in the art in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced other than as speciﬁcally described.

What is claimed as new and desired to be secured by Letters Patent of the United States is:
1. A method of growing carbon nanotubes, comprising the steps of:
   synthesizing a template made from a mesoporous silica such that said template has a plurality of approximately cylindrical pores formed therein;
   coating surfaces of each of said approximately cylindrical pores with a carbon nanotube precursor capable of being carbonized upon the heating thereof; and
   heating said template with said surfaces of said approximately cylindrical pores so-coated until said carbon nanotube precursor in each of said approximately cylindrical pores is converted to a carbon nanotube wherein said carbon nanotube precursor is sugar-based.
2. A method of growing carbon nanotubes, comprising the steps of:
synthesizing a template made from a mesoporous silica such that said template has a plurality of approximately cylindrical pores formed therein;
coating surfaces of each of said approximately cylindrical pores with a carbon nanotube precursor capable of being carbonized upon the heating thereof; and
heating said template with said surfaces of said approximately cylindrical pores so-coated until said carbon nanotube precursor in each of said approximately cylindrical pores is converted to a carbon nanotube;
wherein, said step of coating includes the step of impregnating said template with a solution of sucrose diluted in a liquid.

3. A method of growing carbon nanotubes, comprising the steps of:
synthesizing a template made from a mesoporous silica such that said template has a plurality of approximately cylindrical pores formed therein;
coating surfaces of each of said approximately cylindrical pores with a carbon nanotube precursor capable of being carbonized upon the heating thereof; and
heating said template with said surfaces of said approximately cylindrical pores so-coated until said carbon nanotube precursor in each of said approximately cylindrical pores is converted to a carbon nanotube;
wherein, said step of coating includes the step of impregnating said template with a solution of sucrose diluted in sulfuric acid.

4. A method for growing carbon nanotubes, comprising the steps of:
synthesizing a template made from a mesoporous silica such that said template has a plurality of approximately cylindrical pores formed therein in a parallel relationship to one another with each of said straight approximately cylindrical pores having an inside diameter in the range of approximately 3.5-4.0 nanometers;
coating surfaces of each of said straight approximately cylindrical pores with sugar-based carbon nanotube precursor; and
heating said template with said surfaces of said straight approximately cylindrical pores so-coated until said sugar-based carbon nanotube precursor in each of said straight approximately cylindrical pores is converted to a carbon nanotube.

5. A method according to claim 4 wherein said step of synthesizing includes the step of impregnating mesoporous silica with a material selected from the group consisting of cobalt, iron, nickel and any other active metal.

6. A method according to claim 4 wherein said step of coating comprises the step of impregnating said template with a solution of a sugar diluted in a liquid select to reduce a length of time associated with said step of heating.

7. A method according to claim 6 wherein said sugar is sucrose and said liquid is sulfuric acid.

8. A method according to claim 4 further comprising, during said step of heating, the step selected from the group consisting of applying a vacuum to said template and applying an inert atmosphere to said template.

9. A method according to claim 4 further comprising the steps of dissolving said template after said step of heating.

10. A method for growing carbon nanotubes, comprising the steps of:
synthesizing a template made from mesoporous silica such that said template has a plurality of approximately cylindrical pores formed therein;
impregnating said template with a solution of sucrose diluted in sulfuric acid;
drying said template so-treated wherein surfaces of each of said approximately cylindrical pores are coated with a reduced hydroxyl group derivative of sucrose; and
heating said template with said surfaces of said approximately cylindrical pores so-coated until said reduced hydroxyl group derivative of sucrose in each of said approximately cylindrical pores is converted to a carbon nanotube.

11. A method according to claim 10 wherein said step of synthesizing includes the step of impregnating mesoporous silica with a material selected from the group consist of cobalt, iron, nickel and any other active metal.

12. A method according to claim 10 further comprising, during said step of heating, the step selected from the group consisting of applying a vacuum to said template and applying an inert atmosphere to said template.

13. A method according to claim 10 further comprising the step of dissolving said template after said step of heating.

14. A method according to claim 10 wherein said step of heating is carried out at a temperature in the range of 700-900° C.

15. The method according to claim 4 further comprising, during said step of heating, the step selected from the group consisting of applying a vacuum to said template and applying an inert atmosphere to said template, wherein the inert atmosphere is selected from the group consisting of nitrogen, helium and argon.

16. The method according to claim 10 further comprising, during said step of heating, the step selected from the group consisting of applying a vacuum to said template and applying an inert atmosphere to said template, wherein the inert atmosphere is selected from the group consisting of nitrogen, helium and argon.