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60/867,085 22 November 2006 (22.11.2006) US
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- (74) **Agents:** CARON, R'Sue P. et al.; Ernest Orlando Lawrence Berkeley National Lab., Technology Transfer & Intellectual Property Mgmt., (patent Group) One Cyclotron Road, Ms 90b-0104, Berkeley, CA 94720 (US).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
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26 March 2009



WO 2008/140583 A3

(54) **Title:** FUNCTIONALIZED BORON NITRIDE NANOTUBES

(57) **Abstract:** A plasma treatment has been used to modify the surface of BNNTs. In one example, the surface of the BNNT has been modified using ammonia plasma to include amine functional groups. Amine functionalization allows BNNTs to be soluble in chloroform, which had not been possible previously. Further functionalization of amine-functionalized BNNTs with thiol-terminated organic molecules has also been demonstrated. Gold nanoparticles have been self-assembled at the surface of both amine- and thiol-functionalized boron nitride Nanotubes (BNNTs) in solution. This approach constitutes a basis for the preparation of highly functionalized BNNTs and for their utilization as nanoscale templates for assembly and integration with other nanoscale materials.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 07/85383

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-10 and 13-32, directed to a boron nitride nanotube functionalized with an organic molecule, and a means of producing such a molecule.

Group II: claims 11-12, directed to a boron nitride nanotube functionalized with self-assembled nanoparticles.

Group III: claim 33, directed to a stable solution comprising functionalized boron nitride nanotubes in an organic solvent.

- Please see extra sheet for continuation -

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-10 and 13-32

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 07/85383

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - B28B 1/00 USPC - 423/284 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) USPC - 423/284; 977/734 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 423/286, 290; 977/822. IPC(8) - B82B 1/00; C01B 21/064, 35/00, 35/14 (2008.04) (Term search-- see search terms below). Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST(USPT,PGPB,EPAB,JPAB); Google Patents; Google Scholar; USPTO online (Term search-- see search terms below). Search terms: nanotube, nanopipe, nanosleeve, nanocylinder, nanosock, boron, nitride, functionalized, derivatized, amine, thiol, mercapto, nanoparticle, gold, plasma, ammonia, methane, nitrogen, imine, nitrile																												
C. DOCUMENTS CONSIDERED TO BE RELEVANT																												
<table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>Wu, et al. Chemical Functionalization of Boron-Nitride Nanotubes with NH and Amino Functional Groups. Journal of the American Chemical Society, 13 September 2006 (13.9.2006); 128(36): 12001-12006. Abstract; Introduction; p. 12003, col. 2, first sentence of first full paragraph; p. 12004, col. 2, first full paragraph, continuing onto p. 12005.</td> <td>1-4</td> </tr> <tr> <td>Y</td> <td>US 2006/0058360 A1 (BOULET, et al.) 16 March 2006 (16.03.2006), paras [0117], [0120].</td> <td>5-10</td> </tr> <tr> <td>Y</td> <td>US 2006/0058360 A1 (BOULET, et al.) 16 March 2006 (16.03.2006), paras [0117], [0120].</td> <td>5, 20, 25</td> </tr> <tr> <td>Y</td> <td>Ellis, et al. Hydrophobic Anchoring of Monolayer-Protected Gold Nanoclusters to Carbon Nanotubes. Nano Letters, March 2003 (31.03.2003); 3(3): 279-282. p. 281, col. 2, first sentence of last paragraph; FIG. 4.</td> <td>6-10</td> </tr> <tr> <td>Y</td> <td>Wang, et al. Low Temperature Growth of Boron Nitride Nanotubes on Substrates. Nano Letters, December, 2005 (31.12.2005); 5(12): 2528-2532. p. 2528, col. 2, first paragraph.</td> <td>13-32</td> </tr> <tr> <td>Y</td> <td>Zhi, et al. Covalent Functionalization: Towards Soluble Multiwalled Boron Nitride Nanotubes. Angewandte Chemie International Edition, 9 December 2005 (09.12.2005); 44(48): 7932-7935. p. 7933, col. 2; p. 7933, col. 1, second and fourth paragraphs.</td> <td>13-32</td> </tr> <tr> <td>Y</td> <td>US 6,875,274 B2 (WONG, et al.) 5 April 2005 (05.04.2005), abstract; col. 2, ln 42-44; col. 2, ln 50-61.</td> <td>7</td> </tr> <tr> <td>Y</td> <td>US 2006/0084705 A1 (CARUSO, et al.) 20 April 2006 (20.04.2006), paras [0022], [0064], FIGS. 1, 9.</td> <td>10</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	Wu, et al. Chemical Functionalization of Boron-Nitride Nanotubes with NH and Amino Functional Groups. Journal of the American Chemical Society, 13 September 2006 (13.9.2006); 128(36): 12001-12006. Abstract; Introduction; p. 12003, col. 2, first sentence of first full paragraph; p. 12004, col. 2, first full paragraph, continuing onto p. 12005.	1-4	Y	US 2006/0058360 A1 (BOULET, et al.) 16 March 2006 (16.03.2006), paras [0117], [0120].	5-10	Y	US 2006/0058360 A1 (BOULET, et al.) 16 March 2006 (16.03.2006), paras [0117], [0120].	5, 20, 25	Y	Ellis, et al. Hydrophobic Anchoring of Monolayer-Protected Gold Nanoclusters to Carbon Nanotubes. Nano Letters, March 2003 (31.03.2003); 3(3): 279-282. p. 281, col. 2, first sentence of last paragraph; FIG. 4.	6-10	Y	Wang, et al. Low Temperature Growth of Boron Nitride Nanotubes on Substrates. Nano Letters, December, 2005 (31.12.2005); 5(12): 2528-2532. p. 2528, col. 2, first paragraph.	13-32	Y	Zhi, et al. Covalent Functionalization: Towards Soluble Multiwalled Boron Nitride Nanotubes. Angewandte Chemie International Edition, 9 December 2005 (09.12.2005); 44(48): 7932-7935. p. 7933, col. 2; p. 7933, col. 1, second and fourth paragraphs.	13-32	Y	US 6,875,274 B2 (WONG, et al.) 5 April 2005 (05.04.2005), abstract; col. 2, ln 42-44; col. 2, ln 50-61.	7	Y	US 2006/0084705 A1 (CARUSO, et al.) 20 April 2006 (20.04.2006), paras [0022], [0064], FIGS. 1, 9.	10	<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/>
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* 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 1 January 2009 (01.01.2009)	Date of mailing of the international search report 21 JAN 2009																											
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774																											

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 07/85383

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Cummings, et al. Mass-Production of Boron Nitride Double-Wall Nanotubes and Nanococoons. Chemical Physics Letters, 14 January 2000 (14.01.2000); 316: 211-216. p. 212, Synthesis section.	14-19, 23, 24, 27-31
Y	US 6,495,258 B1 (CHEN, et al.) 17 December 2002 (17.12.2002), col. 8, ln 53 to col. 9, ln 4.	15
Y	Azamian, et al. Directly Observed Covalent Coupling of Quantum Dots to Single-Wall Carbon Nanotubes. Journal of the Chemical Society Chemical Communications, 5 February 2002 (05.02.2002); 2002(4): 366-367. Scheme 1.	32
Y	US 6,882,094 B2 (DIMITRIJEVIC, et al.) 19 April 2005 (19.04.2005), col. 14, ln 59-63.	18, 19
Y	US 7,105,553 B2 (FISCHER, et al.) 12 September 2006 (12.09.2006), col. 29, Example 15.	21, 26
Y	US 6,676,851 B1 (BUCHECKER, et al.) 13 January 2004 (13.01.2004), cols. 6 and 8, last reactions of Schemes 1 and 2.	21, 26
Y	C. Tang, et al. A Novel Precursor for Synthesis of Pure Boron Nitride Nanotubes. Journal of the Chemical Society Chemical Communications, 21 May 2002 (21.05.2002); 2002(12): 1290-1291. p. 1290, second paragraph.	24, 27-31
Y	US 2005/0008561 A1 (FISCHER et al.) 13 January 2005 (13.01.2005) abstract, para [0040], [0029], [0035]	28, 29
Y	US 2006/0239891 A1 (NIU, et al.) 26 October 2006 (26.10.2006), paras [0079], [0080], [0082], [0085].	30
Y	US 2,375,016 A (MARPLE, et al.) 1 May 1945 (01.05.1945), col. 1, ln 38 to col. 2, ln 2.	31
X, P	T. Ikuno, et al. Amine-Functionalized Boron Nitride Nanotubes. Solid State Communications, June 2007 (30.06.2007); 142: 643-646. Entire document.	13-17, 20, 22-25, 27
X, P	T. Sainsbury, et al. Self-Assembly of Gold Nanoparticles at the Surface of Amine- and Thiol-Functionalized Boron Nitride Nanotubes. Journal of Physical Chemistry C, 6 September 2007 (06.09.2007); 111(35): 12992-12999. Entire document.	1-4, 6-10

Continuation of Box III:

The inventions listed as Groups I - II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The special technical feature of the Group I claims is providing a boron nitride nanotube comprising a surface organic moiety and a means of producing such a functionalized nanotube - not required by the claims of Groups II or III. The special technical feature of the Group II claims is a boron nitride nanotube comprising a surface monolayer of self-assembled nanostructures - not required by the claims of groups I or III. The special technical feature of the Group III claims is a stable solution comprising functionalized boron nitride nanotubes in an organic solvent, not required by the claims of Groups I or II.

The only common technical element shared by the above groups is that they are related to boron nitride nanotubes having surface modifications. While it may be possible to produce a nanotube dispersible in organic solvent, as described in Group III, using a process according to the claims of Group I, the invention of the Group I claims is not the only means to obtain such a boron nitride nanotube, as indicated by the prior art of US 2006/0041104 A1 to Ait-Haddou et al. (see para [0002], [0014], [0026], [0027]). The common technical element of the above groups does not represent an improvement over the prior art of Ait-Haddou et al. Therefore, the inventions of Group I and Group II lack unity of invention under PCT Rule 13 because they do not share a same or corresponding special technical feature.