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(71) Applicant *(for all designated States except US)*: **PURDUE RESEARCH FOUNDATION** [US/US]; 1281 Win Hentschel Blvd., West Lafayette, IN 47906 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **WU, Yue** [CN/US]; 3151 Litchfield Ln., West Lafayette, IN 47906 (US). **YADAV, Gautam G.** [US/US]; 101 Andrew Place, Apt. E5, West Lafayette, IN 47906 (US). **ZHANG, Genqiang** [CN/MY]; Blk 911 Jurong West St. 91#12-293, singapore Malaysia (MY).

(74) Agent: **WHITE, Ryan O.**; Taft Stettinius & Hollister LLP, One Indiana Square, Ste. 3500, Indianapolis, IN 46204 (US).

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*[Continued on next page]*

(54) Title: SYNTHESIS OF METAL OXIDE-BASED THERMOELECTRIC MATERIALS FOR HIGH TEMPERATURE APPLICATIONS

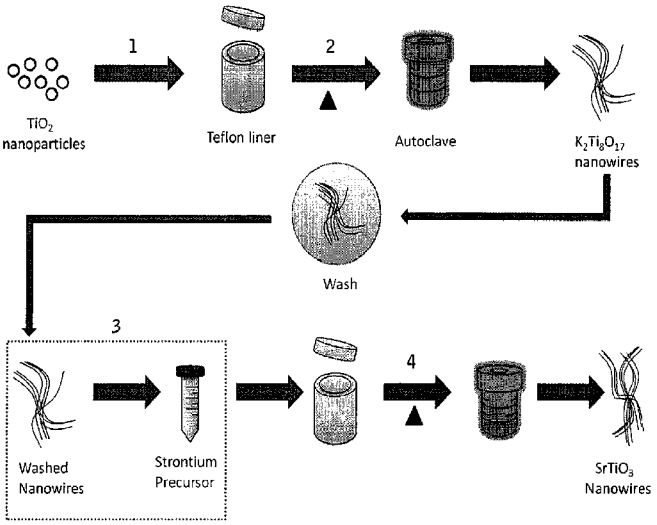


FIG. 1

(57) Abstract: Nanowire synthesis and one dimensional nanowire synthesis of titanates and cobaltates. Exemplary titanates and cobaltates that are fabricated and discussed include, without limitation, strontium titanate ($SrTiO_3$), barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), calcium cobaltate ($Ca_3Co_4O_9$) and sodium cobaltate ($NaCo2O_4$).

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PATENT COOPERATION TREATY APPLICATION
Docket No. PRF04-00480

Title: Synthesis of Metal Oxide-Based Thermoelectric Materials for High Temperature Applications

## CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** The present application claims priority to United States provisional patent application entitled, "Synthesis of Metal Oxide-Based Thermoelectric Materials for High Temperature Applications," having U.S. Serial No. 61/445,178 and filed on February 22, 2011, the disclosure of which is hereby incorporated by reference.

## INTRODUCTION TO THE INVENTION

**[0002]** The present disclosure is directed to nanowire synthesis and, more specifically, to one dimensional nanowire synthesis of titanates. Exemplary titanates that will be discussed include, without limitation, strontium titanate ($SrTiO_3$), barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), calcium cobaltate ($Ca_3Co_4O_9$) and sodium cobaltate ($NaCo_2O_4$). In exemplary form, synthesis of each of the foregoing titanates follows the same generic method for the respective titanate synthesis precursors. The instant disclosure also discloses synthesis of calcium and sodium cobaltate. These cobaltates also follow an analogous generic procedure.

**[0003]** The titanate nanowires are fairly elongated with an average diameter of around 10 nm and fibrous in structure. The cobalt oxide ($Co_3O_4$) nanowires which are precursors in the synthesis of calcium and sodium cobalt oxide are free standing and have an average diameter of 530 nm.

**[0004]** The performance of a thermoelectric device is evaluated by a metric known as the figure of merit, (ZT). The figure of merit can be expressed as an equation:

$$ZT = S^2 \cdot \sigma \cdot T / \kappa$$

where:

S is the Seebeck coefficient,

$\sigma$ is the electrical conductivity of the thermoelectric material,

T is the temperature, and

$\kappa$ is the thermal conductivity.

Greater values of ZT indicate greater thermodynamic efficiency and better device performance. More specifically, figure of merit values of at least three are considered to be important in order for a thermoelectric device to be competitive with current mechanical generation and refrigeration methods.

**[0005]** One dimensional (1D) nanowire structure assist in the transfer of charge carriers and scattering of phonons which ultimately lead to an increase in electrical conductivity ($\sigma$) and decrease in thermal conductivity ($\kappa$) respectively. The electronic density of states undergoes a dramatic change and becomes sharper near the band edge for a 1D system, which results in a higher power factor for a given carrier concentration. This is the main reason behind tailoring the titanates and cobaltates into nanowire structures which in turn would increase ZT. Cobaltates are known to have high S and low thermal conductivity due to their strongly-correlated electronic structures and layered crystal structures.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0006]** FIG. 1 is an exemplary process flow for forming strontium/barium/lead titanate nanowires in accordance with the instant disclosure.

**[0007]** FIG. 2 is an image from a transmission electron microscope showing $TiO_2$ nanoparticles.

**[0008]** FIG. 3 are images from a transmission electron microscope showing the transformation of $TiO_2$ nanoparticles to $K_2Ti_8O_{17}$ nanowires.

**[0009]** FIG. 4 is a high resolution image from a transmission electron microscope showing $K_2Ti_8O_{17}$ nanowires.

**[0010]** FIG. 5 is an image from a transmission electron microscope showing $K_2Ti_8O_{17}$ nanowires.

**[0011]** FIG. 6 is an image from a transmission electron microscope showing $SrTiO_3$ nanowires.

**[0012]** FIG. 7 is an image from a transmission electron microscope showing $BaTiO_3$ nanowires.

**[0013]** FIG. 8 is an image from a transmission electron microscope showing $PbTiO_3$ nanowires.

**[0014]** FIG. 9 is a high resolution image from a transmission electron microscope showing $SrTiO_3$ nanowires.

**[0015]** FIG. 10 is a high resolution image from a transmission electron microscope showing $BaTiO_3$ nanowires.

**[0016]** FIG. 11 is a high resolution image from a transmission electron microscope showing $PbTiO_3$ nanowires.

**[0017]** FIG. 12 is an X-ray diffraction of a titanium oxide raw material and potassium, strontium, lead and barium titanates fabricated in accordance with the instant disclosure.

**[0018]** FIG . 13 are thermal diffusivity, specific heat, and thermal conductivity of $SrTiO_3$ as a function to temperature.

**[0019]** FIG. 14 includes an image and a high resolution image from a scanning electron microscope of $Co_3O_4$ nanowires grown on a glass substrate.

**[0020]** FIG. 15 is an X-ray diffraction of $Co_3O_4$ on a glass substrate.

## DETAILED DESCRIPTION

**[0021]** The exemplary embodiments of the present disclosure are described and illustrated below to encompass nanowire synthesis and, more specifically, to one dimensional nanowire synthesis of titanates. Of course, it will be apparent to those of ordinary skill in the art that the preferred embodiments discussed below are exemplary in nature and may be reconfigured without departing from the scope and spirit of the present invention. However, for clarity and precision, the exemplary embodiments as discussed below may include optional steps, methods, and features that one of ordinary skill should recognize as not being a requisite to fall within the scope of the present invention.

**[0022]** Referencing FIG. 1, an exemplary process for synthesizing strontium titanate, barium titatate, and lead titanate includes a hydrothermal reaction. The exemplary synthesis process is carried out in two steps, the first of which involves production of potassium titanate nanowires prior to addition of a metal precursor that leads to formation of the respective titanates. Moreover, the reactions are carried out in the presence of potassium hydroxide solution with varying concentrations.

**[0023]** An exemplary process for forming potassium titanate nanowires includes using 0.08g of commercially available titanium oxide ($TiO_2$) nanoparticles 10 less than 25 nanometers in size (see FIG. 2) that are added to a container (e.g., a glass vial) containing 6.8g of potassium hydroxide (KOH) dissolved in 12ml of deionized (DI) water. The mixture is then thoroughly mixed and later poured into a second container 20, in exemplary form, having a non-stick liner (e.g., a Teflon liner). The second container 20 is placed inside an autoclave 30 and heated at 200°C at atmospheric pressure for at least two days (e.g., three days) to transform substantially all of the particles into nanowires 40. FIG. 3 shows images from a transmission electron microscope of titanium particles and of potassium titanate nanowires. FIGS. 4 and 5 show high resolution images from a transmission electron microscope of potassium titanate nanowires.

**[0024]** Referring back to FIG. 1, after the reaction has ended, the autoclave is allowed to cool down to room temperature and the contents from the second container are

transferred to a third container (e.g., a plastic tube) where the contents are thoroughly washed 50 with DI water to remove any potassium salts present.

**[0025]** An exemplary process for forming the strontium/barium/lead titanates includes, depending upon the precursor desired, using: (i) 0.16g of strontium nitrate; (ii) 0.131g of barium nitrate; or (iii) 0.166g of lead nitrate. The chosen nitrate is then mixed with a solution of 0.7g of KOH dissolved in 10ml of DI water in a container (e.g., a glass vial). The mixture is thoroughly mixed until the strontium/barium/lead nitrate is well dispersed in the solution. The solution is then added to well-washed potassium titanate nanowires and mixed 60 thoroughly before addition to a second container, in this circumstance having a non-stick liner (e.g., Teflon liner) 70. The second container and its contents are then placed in an autoclave 80 and heated at 200°C for at least one day. After the reaction has ended, the autoclave is allowed to cool down to room temperature and the contents from the second container are transferred to a third container (e.g., a plastic tube) where the contents are thoroughly washed with DI water to remove any potassium salts present. The end product is the formation of the respective strontium/barium/lead titanate nanowires 90.

**[0026]** FIGS. 6-8 show images from a transmission electron microscope of strontium titanate nanowires, barium titanate nanowires, and lead titanate nanowires, respectively.

**[0027]** FIGS. 9-11 show high resolution images from a transmission electron microscope of strontium titanate nanowires, barium titanate nanowires, and lead titanate nanowires, respectively.

**[0028]** FIG. 12 are X-ray diffraction plots of barium titanate, lead titanate, strontium titanate, potassium titanate, and titanium oxide.

**[0029]** FIG. 13 are plots of thermal diffusivity, specific heat, and thermal conductivity of strontium titanate nanowires fabricated in accordance with the instant disclosure, as a function of temperature.

**[0030]** An exemplary process for synthesizing calcium cobaltate and sodium cobaltate includes a hydrothermal synthesis carried out in two steps. The first step includes the formation of cobalt oxide ($Co_3O_4$) nanowires. The second step involves forming the cobalt and sodium precursors that are ultimately used to form the respective cobaltates.

**[0031]** An exemplary process for forming cobalt oxide ($Co_3O_4$) nanowires includes growing $Co_3O_4$ nanowires on a substrate (e.g., glass). The substrate, in this case glass, is cut into several pieces and kept inside a sealed container (e.g., Petri dish) before the reaction. To obtain the reaction, 10 mmols of cobalt nitrate hexahydrate is first dissolved in 10ml of DI water and stirred for approximately two minutes. 40 ml of 27wt% of ammonia is then added to the dissolved mixture and then stirred for approximately thirty minutes. Afterwards, sealed container is heated at 90°C for approximately fourteen hours. During this time, the container remains sealed to prevent any ammonia from escaping during the reaction.

**[0032]** After the reaction has been completed, the glass pieces are recovered from the sealed container and washed in DI water. The washed glass pieces reveal a dark surface that is indicative of nanostructure growth. The glass pieces are then dried at room temperature, after which the glass pieces are heated inside a tube furnace at 250°C using a thermal progression rate of 60°C/hour for approximately four hours. Thereafter, the nanowires are removed from the glass pieces.

**[0033]** FIG. 14 shows images from a scanning electron microscope of cobalt oxide nanowires grown on the glass substrate.

**[0034]** FIG. 15 is an X-ray diffraction plot of the cobalt oxide nanowires grown on the glass substrate.

**[0035]** An exemplary process for forming the calcium/sodium cobaltates includes, depending upon the precursor desired, using: (i) 0.16g of calcium nitrate; or (ii) 0.16g of sodium nitrate, which is mixed with a solution of 0.7g of KOH dissolved in 10ml of DI water in a container (e.g., a glass vial). The mixture is thoroughly mixed until the calcium/sodium nitrate is well dispersed in the solution. The solution is then added to

well-washed cobalt oxide nanowires and mixed thoroughly before addition to a second container, in this circumstance having a non-stick liner (e.g., Teflon liner). The second container and its contents are then placed in an autoclave and heated at 200°C for at least one day. After the reaction has ended, the autoclave is allowed to cool down to room temperature and the contents from the second container are transferred to a third container (e.g., a plastic tube) where the contents are thoroughly washed with DI water. The end product is the formation of the respective calcium/sodium cobaltates.

**[0036]** The syntheses of the respective titanates and cobaltates ultimately produce thermoelectric materials that may be used for high temperature applications. Since these thermoelectric materials are oxide based materials, the materials are able to withstand high temperatures and have high efficiencies at high and very high temperatures.

**[0037]** Following from the above description and disclosure summaries, it should be apparent to those of ordinary skill in the art that, while the methods and apparatuses herein described constitute exemplary embodiments of the present disclosure, the invention contained herein is not limited to this precise embodiment and that changes may be made to such embodiments without departing from the scope of the invention as defined by the claims. Additionally, it is to be understood that the invention is defined by the claims and it is not intended that any limitations or elements describing the exemplary embodiments set forth herein are to be incorporated into the interpretation of any claim element unless such limitation or element is explicitly stated. Likewise, it is to be understood that it is not necessary to meet any or all of the identified advantages or objects of the disclosure in order to fall within the scope of any claims, since the invention is defined by the claims and since inherent and/or unforeseen advantages of the present invention may exist even though they may not have been explicitly discussed herein.

**[0038]** What is claimed is:

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1. A nanowire comprising at least one of the following: strontium titanate ($SrTiO_3$), barium titanate ($BaTiO_3$), lead titanate ($PbTiO_3$), calcium cobaltate ($Ca_3Co_4O_9$) and sodium cobaltate ($NaCo_2O_4$).

2. The nanowire of claim 1, wherein the nanowire comprises strontium titanate ($SrTiO_3$).

3. The nanowire of claim 1, wherein the nanowire comprises sodium cobaltate ($NaCo_2O_4$).

4. The nanowire of claim 1, wherein the nanowire comprises barium titanate ($BaTiO_3$).

5. The nanowire of claim 1, wherein the nanowire comprises lead titanate ($PbTiO_3$).

6. The nanowire of claim 1, wherein the nanowire comprises calcium cobaltate ($Ca_3Co_4O_9$).

7. A process for forming nanowires, the process comprising:

forming alkali metal titanate nanowires; and,

combining the alkali metal titanate nanowires with at least one of a strontium nitrate solution, a barium nitrate solution, a lead nitrate solution, a calcium nitrate solution, a sodium nitrate solution, and a potassium nitrate solution to create a combination; and,

processing the combination.

8. The method of claim 7, wherein processing the combination comprises:

heating the combination at a temperature above 200°C for at least one day to form an end product; and,

washing the end product after the heating step, where the washing includes rinsing the end product with deionized water.

9. The method of either claim 7 or 8, wherein forming alkali metal titanate nanowires comprises:

mixing nanoparticles containing titanium with an alkali solution to create a precursor mixture; and,

heating the precursor mixture at a temperature above 200°C for at least two days.

10. The method of claim 8, wherein processing the combination further comprises separating the end product from solution.

11. A process for forming nanowires, the process comprising:

forming alkali metal cobaltate nanowires; and,

combining the alkali metal cobaltate nanowires with at least one of a strontium nitrate solution, a barium nitrate solution, a lead nitrate solution, a calcium nitrate solution, a sodium nitrate solution, and a potassium nitrate solution to create a combination; and,

processing the combination.

12. The method of claim 11, wherein processing the combination comprises:

heating the combination at a temperature above 200°C for at least one day to form an end product; and,

washing the end product after the heating step, where the washing includes rinsing the end product with deionized water.

13. The method of either claim 11 or 12, wherein forming alkali metal cobaltate nanowires comprises:

mixing nanoparticles containing cobalt with an alkali solution to create a precursor mixture; and,

heating the precursor mixture at a temperature above 200°C for at least two days.

14. The method of claim 12, wherein processing the combination further comprises separating the end product from solution.

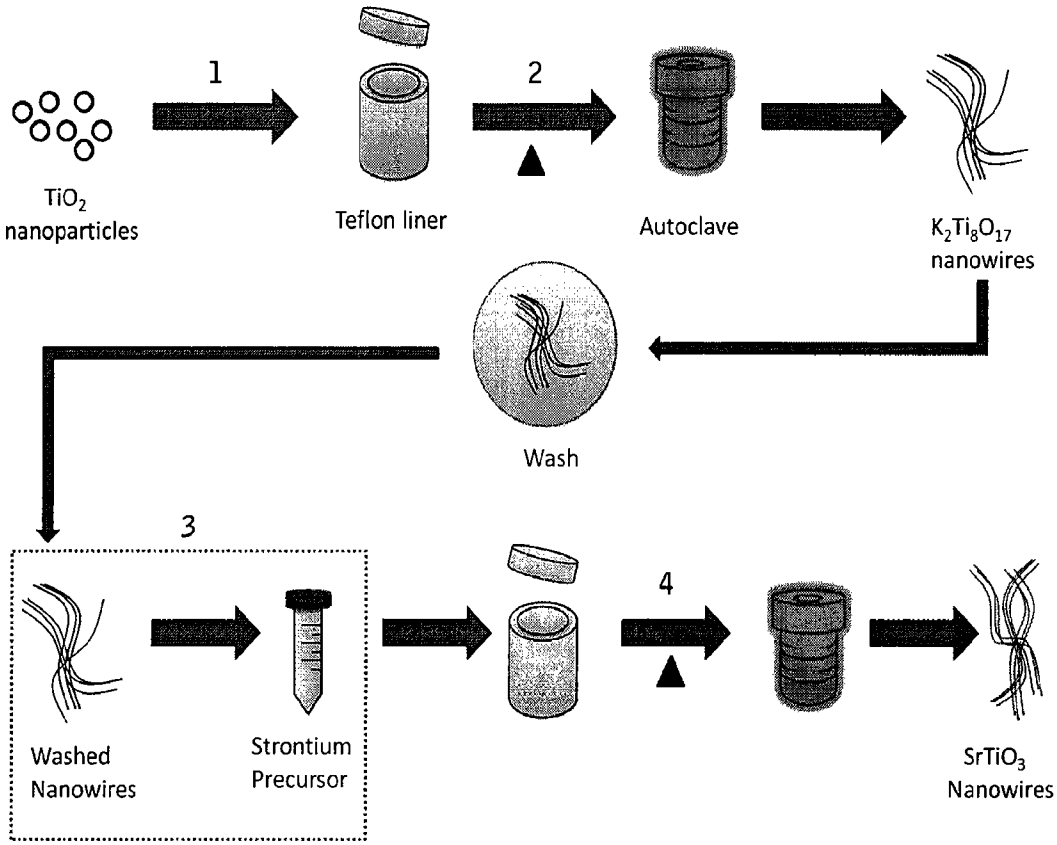
1
2
$TiO_2$ nanoparticles
Teflon liner
Autoclave
$K_2Ti_8O_{17}$ nanowires
Wash
3
4
Washed Nanowires
Strontium Precursor
$SrTiO_3$ Nanowires

FIG. 1

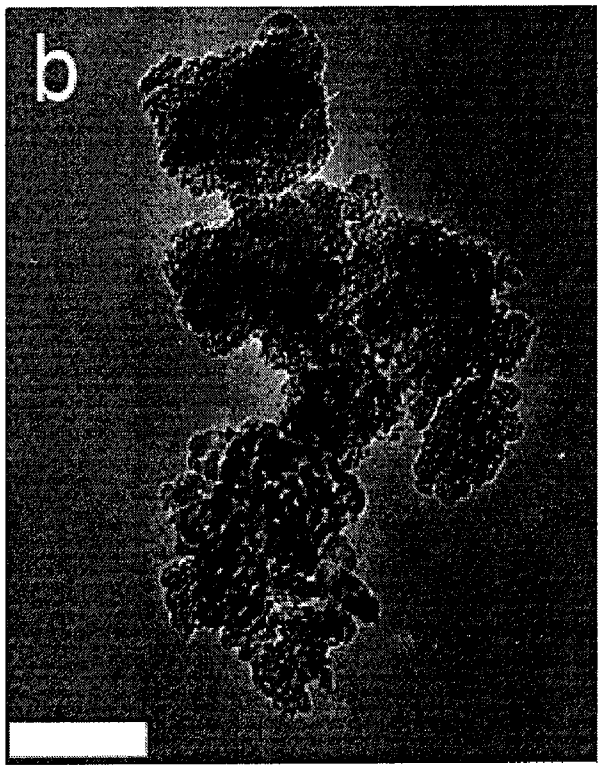


FIG. 2

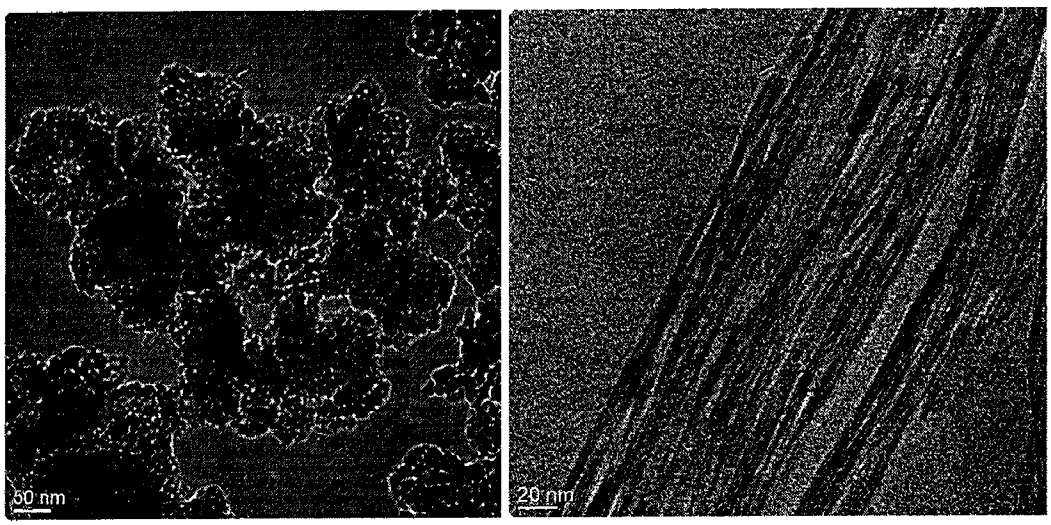


FIG. 3

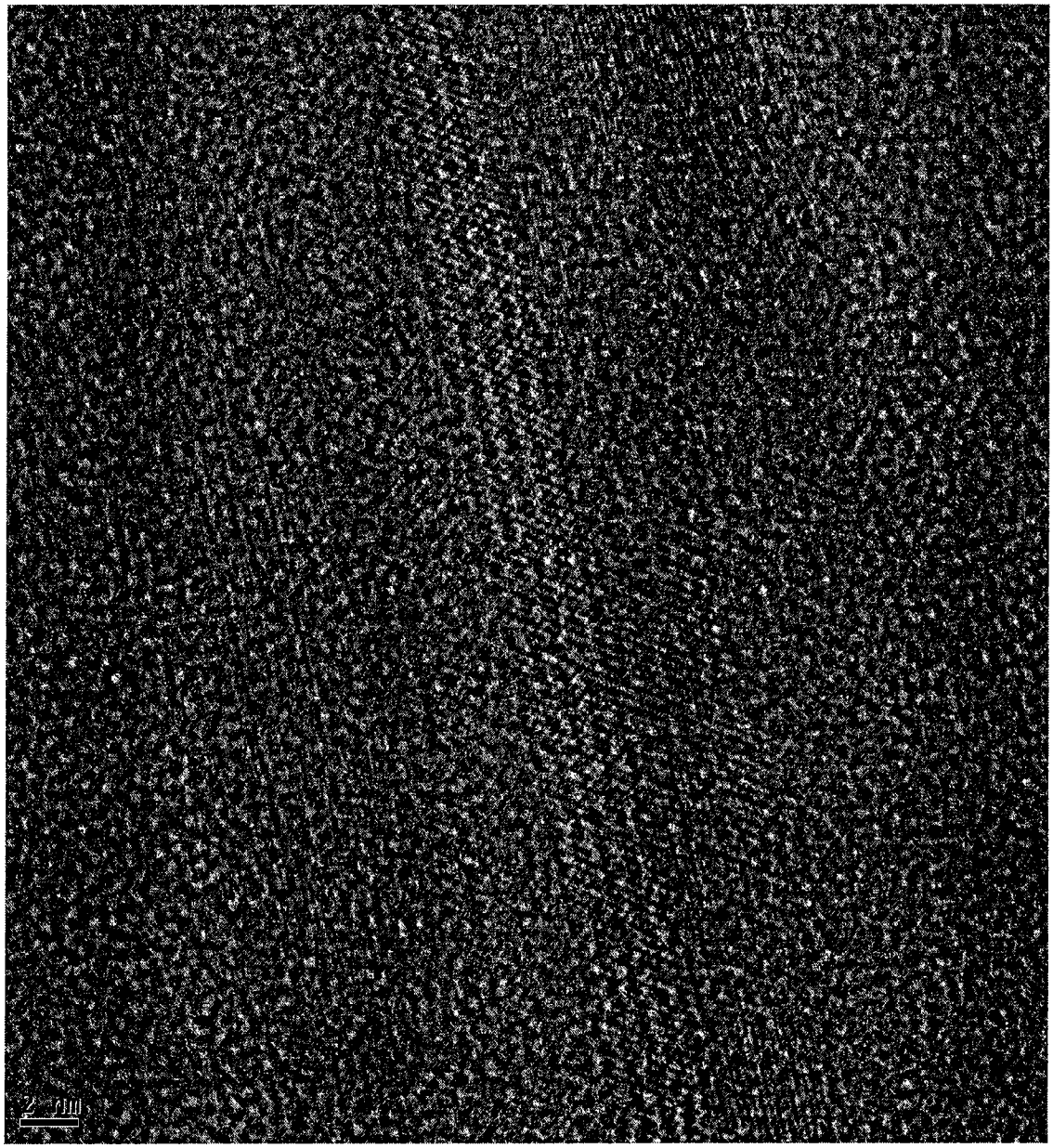

FIG. 4

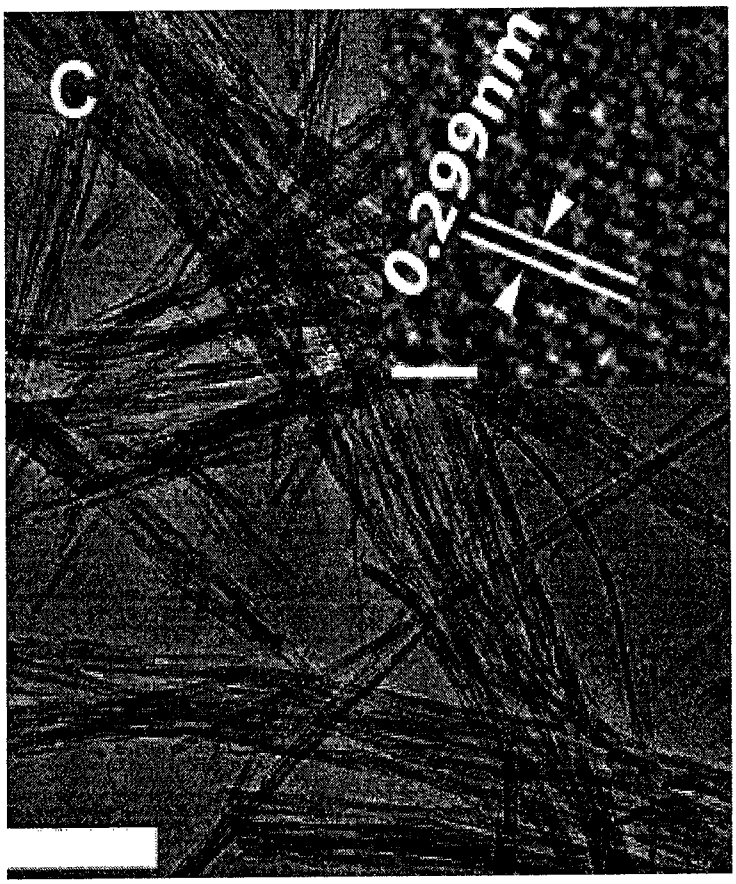


FIG. 5

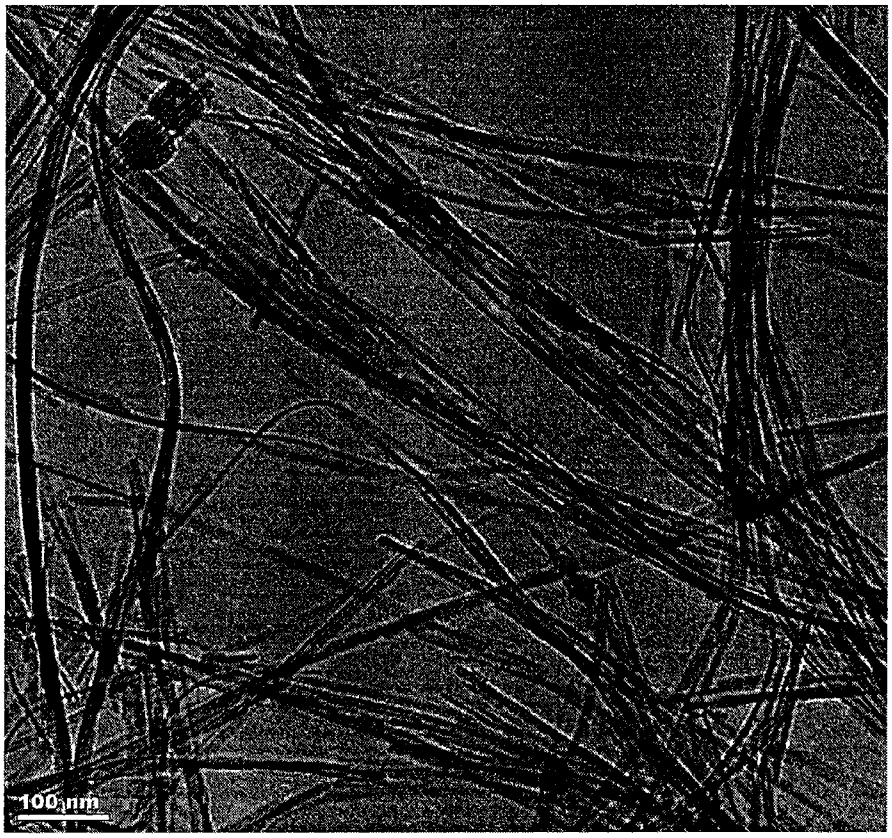


FIG. 6

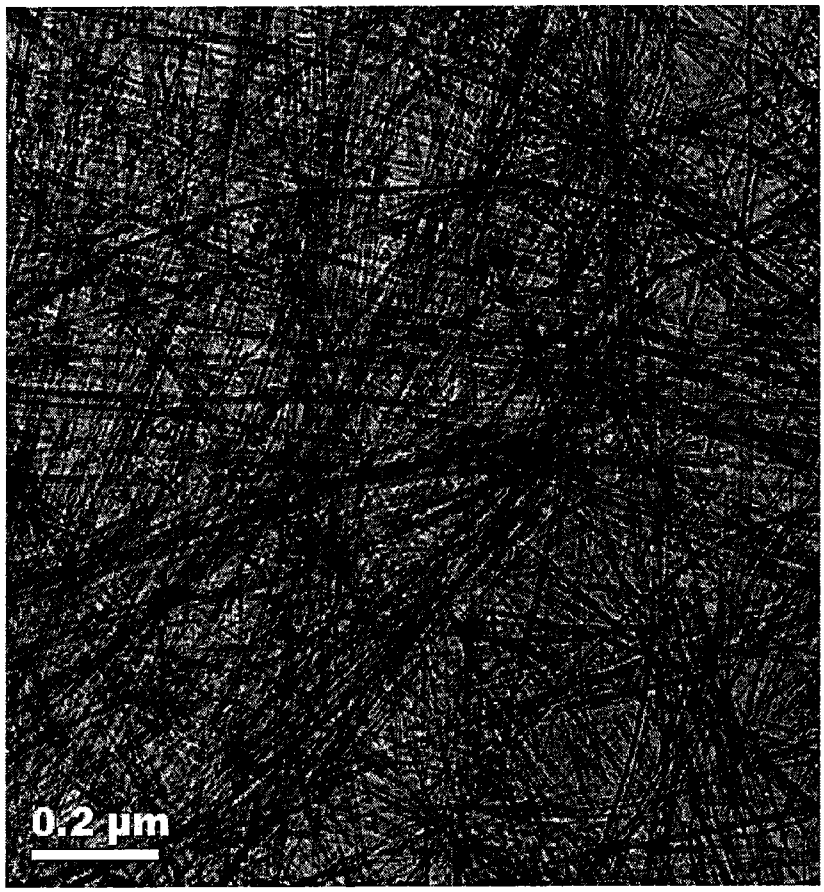


FIG. 7

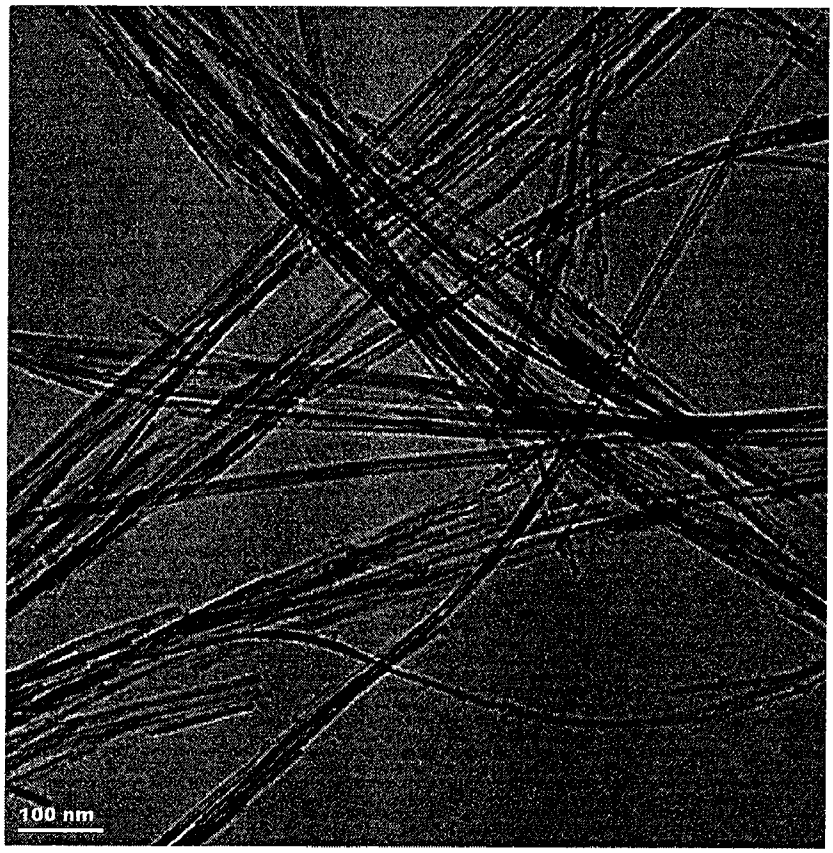


FIG. 8

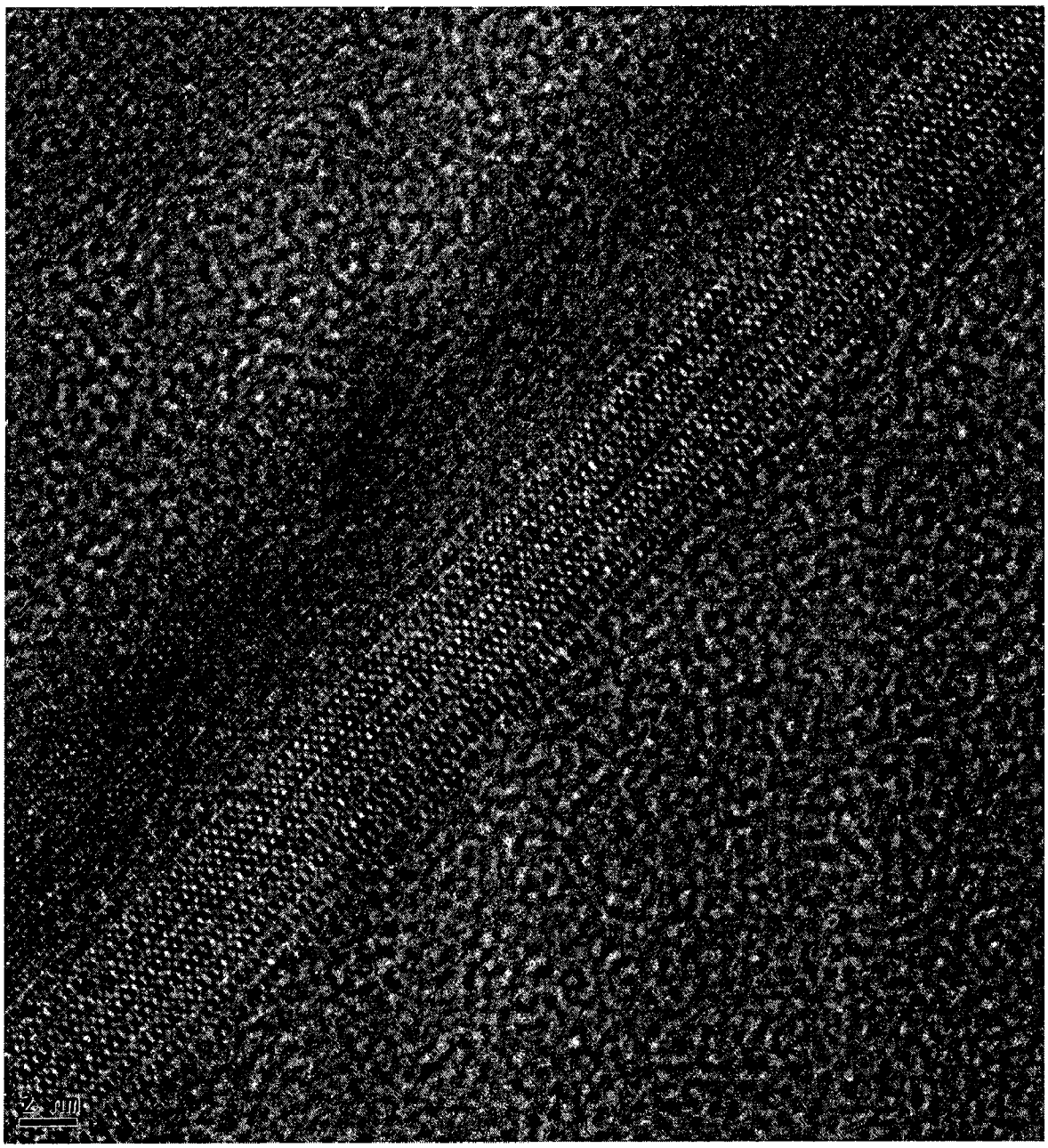

FIG. 9

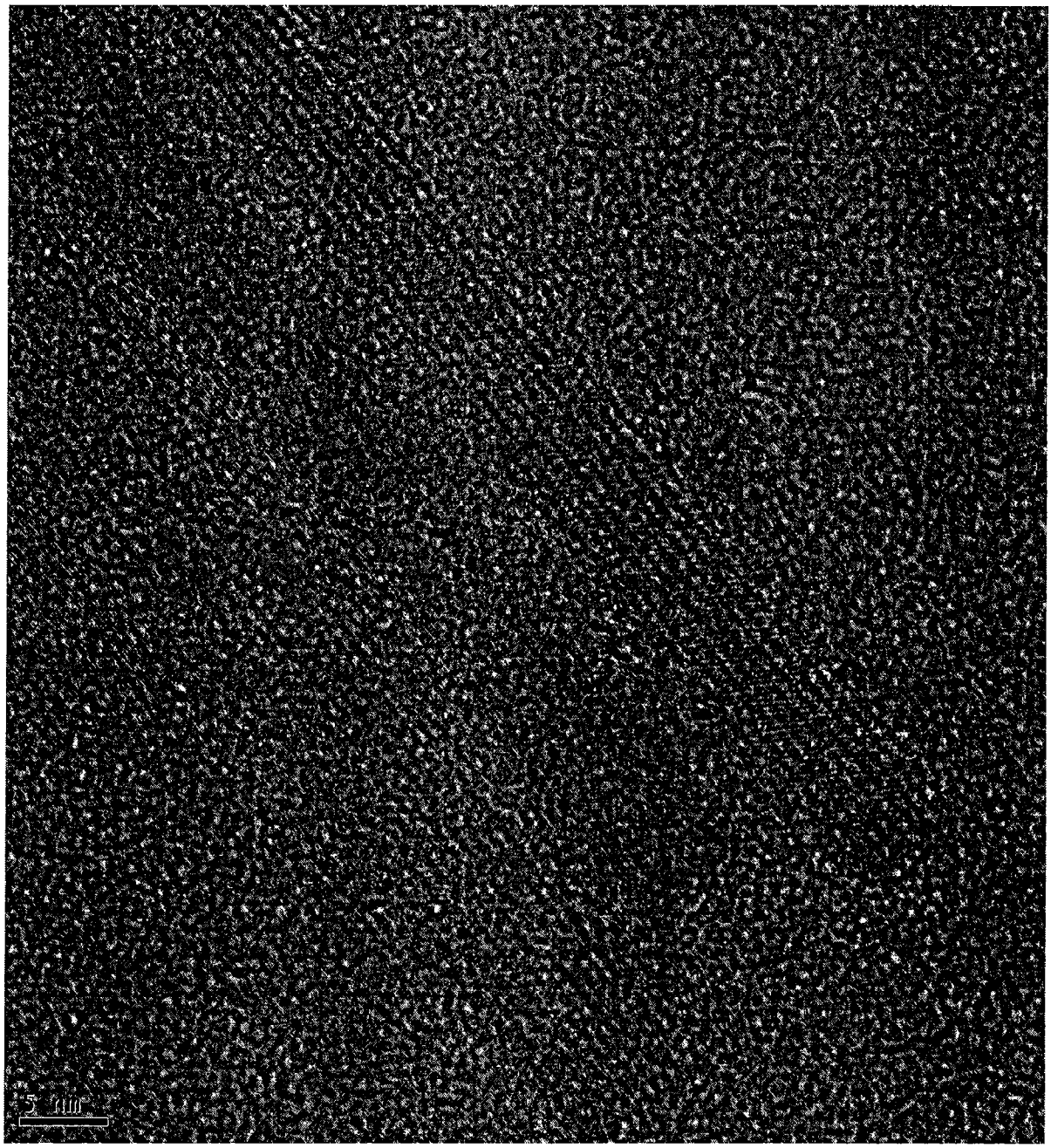


FIG. 10

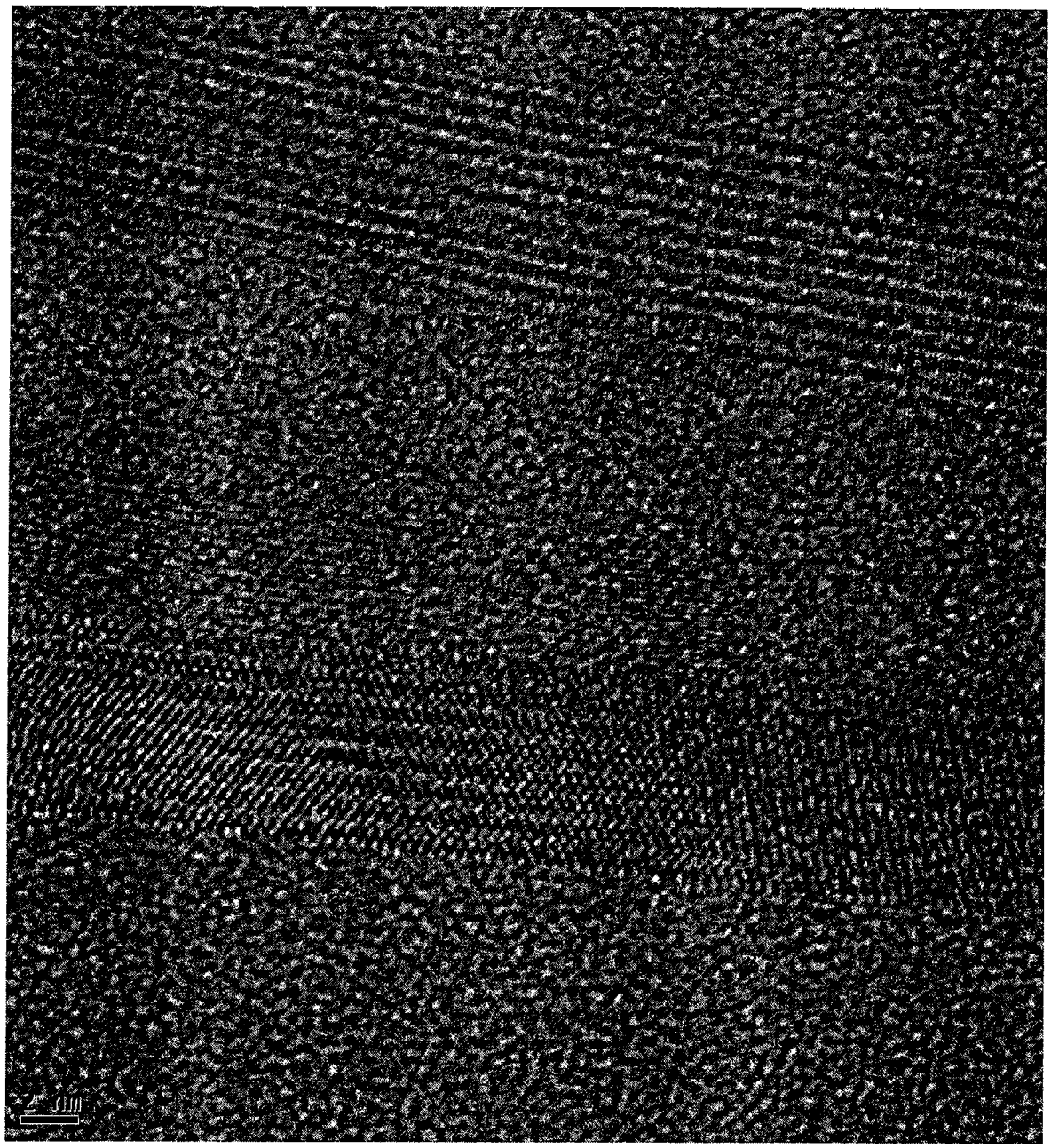

FIG. 11

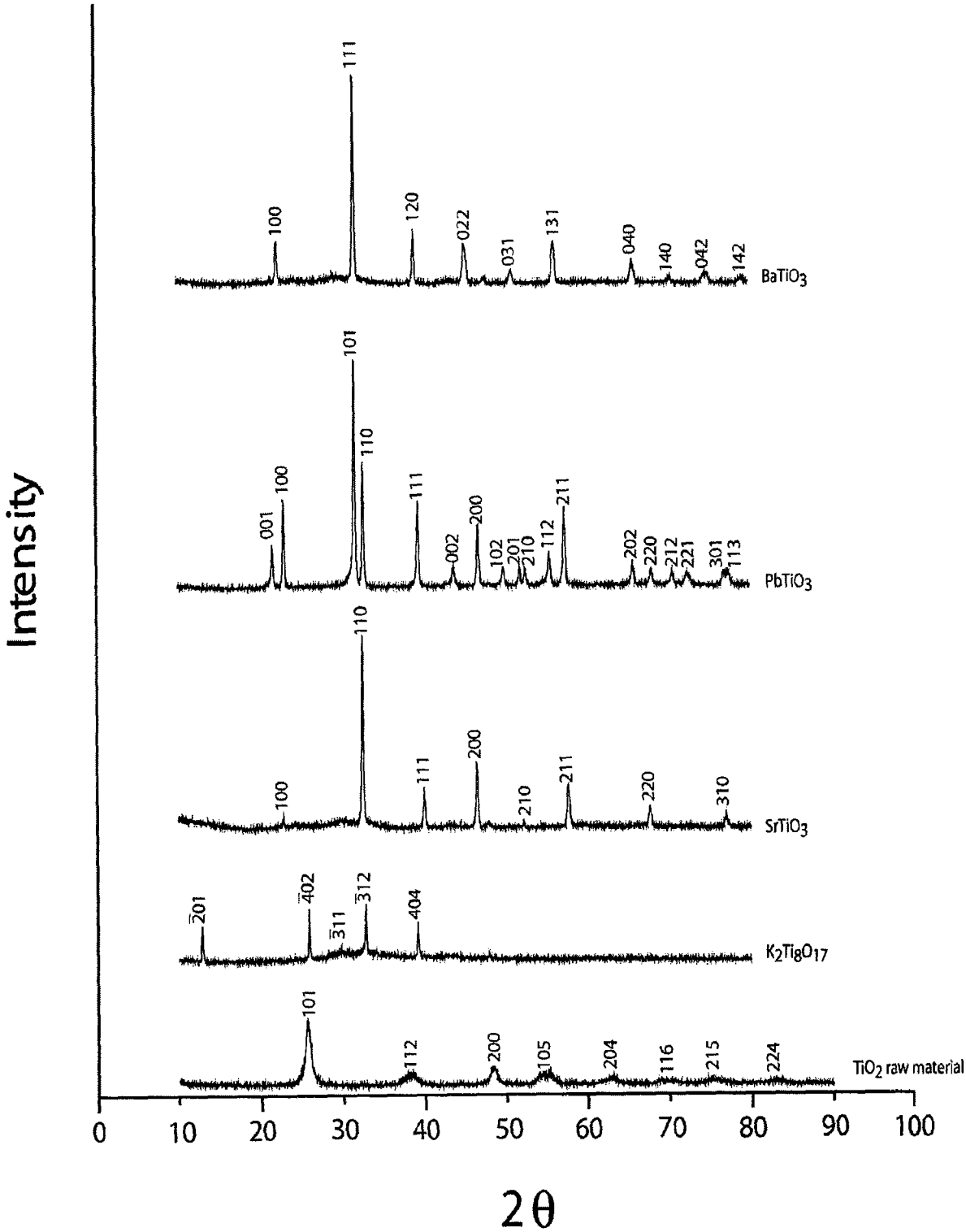
Intensity
100
111
120
022
031
131
040
140
042
142
BaTiO3
001
100
101
110
111
002
200
102
201
210
112
211
202
220
212
221
301
113
PbTiO3
100
110
111
200
210
211
220
310
SrTiO3
201
402
311
312
404
K2Ti8O17
101
112
200
105
204
116
215
224
TiO2 raw material
0
10
20
30
40
50
60
70
80
90
100
2θ

**FIG. 12**

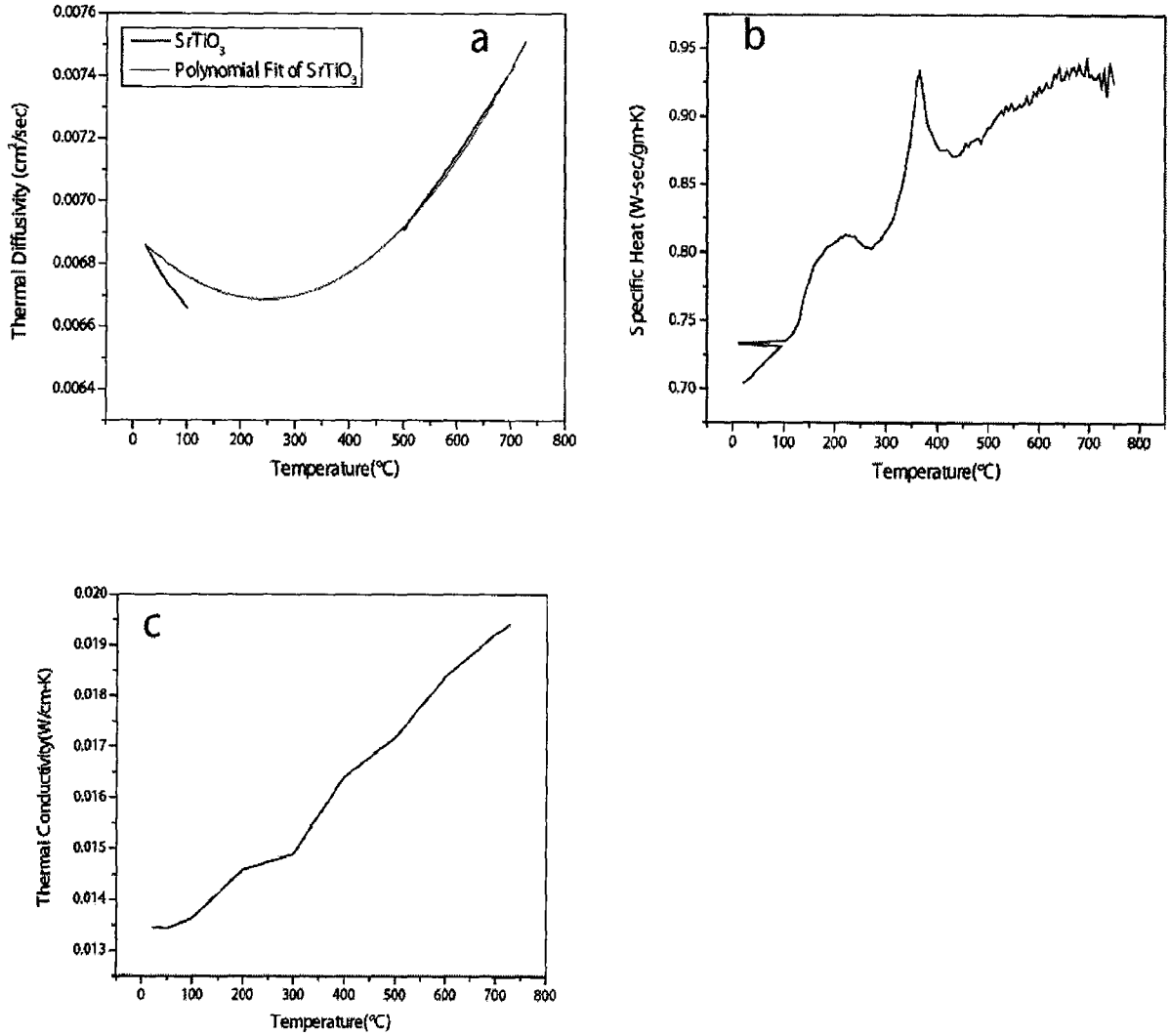
a
$SrTiO_3$
Polynomial Fit of $SrTiO_3$
Thermal Diffusivity ($cm^2$/sec)
Temperature(°C)
b
Specific Heat (W-sec/gm-K)
Temperature(°C)
c
Thermal Conductivity(W/cm-K)
Temperature(°C)

**FIG. 13**

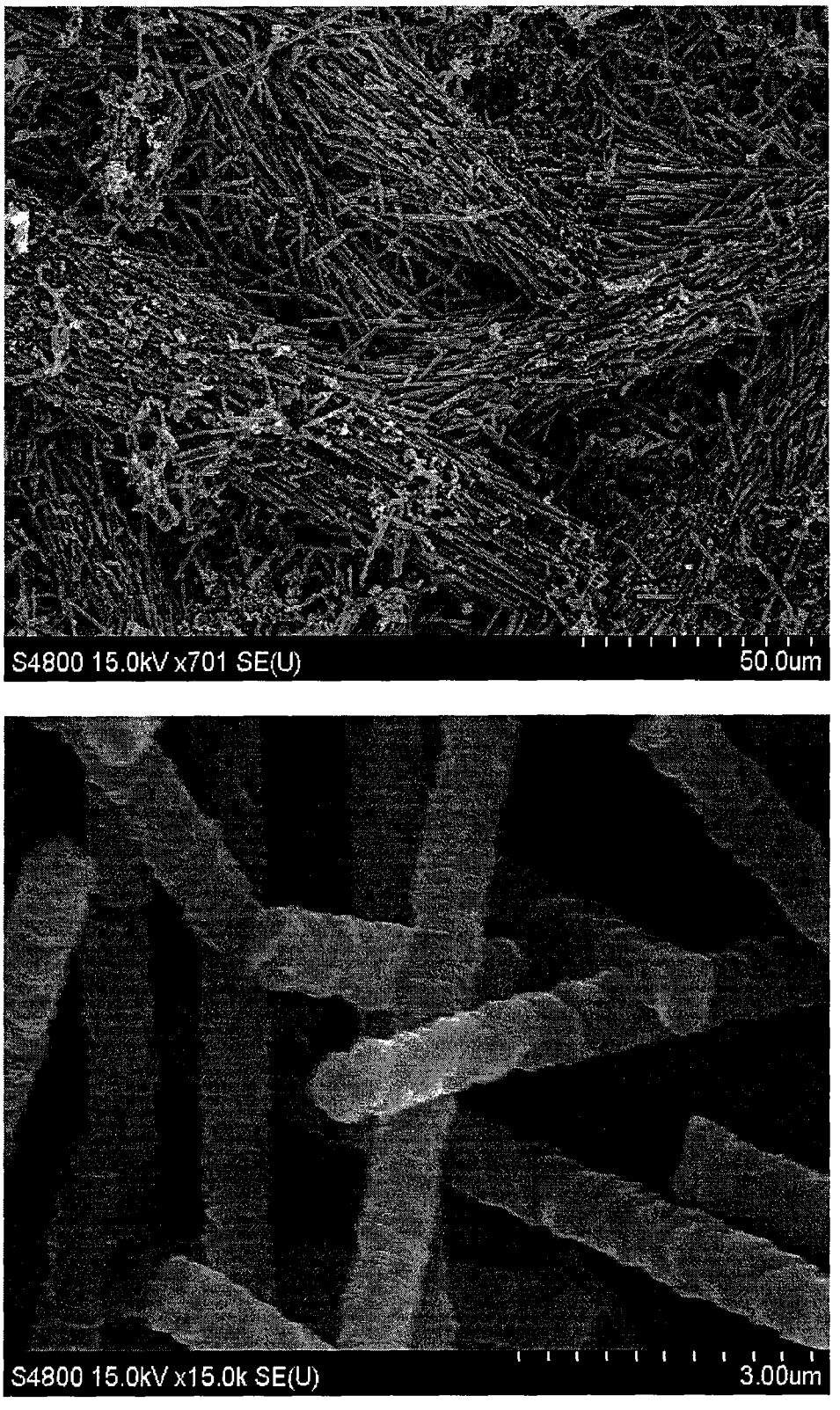


FIG. 14

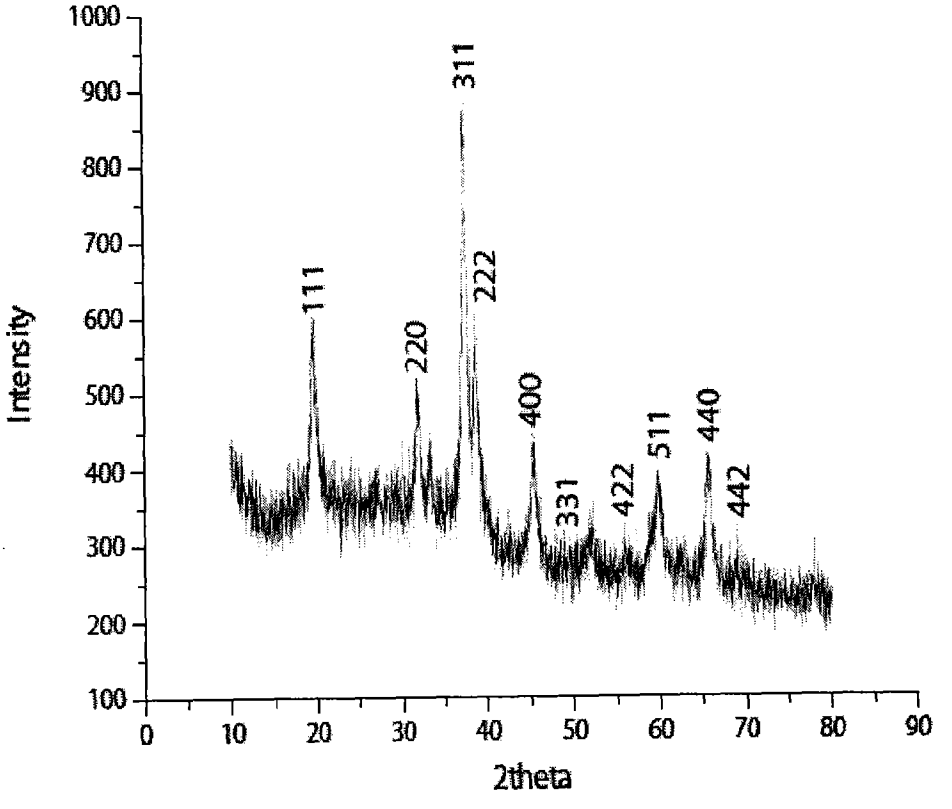
Intensity
2theta
111
220
311
222
400
331
422
511
440
442
1000
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
60
70
80
90

FIG. 15

# INTERNATIONAL SEARCH REPORT

PCT/US2012/025872

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 51/00 (2012.01)

USPC - 977/811

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)

IPC(8) - B32B 37/00, 37/14, 38/10; H01L 21/02, 29/00, 29/12, 35/00, 51/00 (2012.01)

USPC - 257/12, 40, 295, 383, 763, 770, E21.002; 438/582, 685; 977/700, 762, 773, 778, 780, 785, 790, 810-812, 823, 883

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)

MicroPatent, Google Patents, WIPO, Public PatFT and AppFT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br>–<br>Y | US 7,744,717 B2 (ANDREWS et al) 29 June 2010 (29.06.2010) entire document | 1, 2, 4, 5<br>---<br>3, 6 |
| Y | US 2009/0302306 A1 (YUN et al) 10 December 2009 (10.12.2009) entire document | 7-10, 12-14 |
| Y | US 7,585,474 B2 (WONG et al) 08 September 2009 (08.09.2009) entire document | 7-14 |
| Y | US 6,756,154 B2 (MAEDA et al) 29 June 2004 (29.06.2004) entire document | 11-14 |
| Y | US 2006/0118158 A1 (ZHANG et al) 08 June 2006 (08.06.2006) entire document | 3 |
| Y | US 2008/0003487 A1 (TAKIZAWA) 03 January 2008 (03.01.2008) entire document | 6 |

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:

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