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(54) **Title:** NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES

(57) **Abstract:** Methods of preparing metal nanowire are disclosed that employ quaternary phosphonium salts. Such processes can produce long and thin nanowires. Compositions and articles comprising such nanowires are useful in electronics applications.



WO 2012/161894 A1

NANOWIRE PREPARATION METHODS,
COMPOSITIONS, AND ARTICLES

BACKGROUND

5 The general preparation of silver nanowires (10-200 aspect ratio) is known. See, for example, *Angew. Chem. Int. Ed.*, **2009**, 48, 60, Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, which is hereby incorporated by reference in its entirety. Such preparations typically employ Fe^{2+} or Cu^{2+} ions to “catalyze” the wire formation over other morphologies. The controlled preparation of silver
10 nanowires having desired lengths and widths, however, is not known. For example, the Fe^{2+} produces a wide variety of lengths or thicknesses and the Cu^{2+} produces wires that are too thick for many applications.

 When iron or copper are used, they are typically provided as the metal halide salts FeCl_2 or CuCl_2 . See, for example, B. Wiley et al., *Nano Letters*,
15 2004, 4, 1733-1739 and K.E. Korte et al., *J. Mats. Chem.*, **2008**, 18, 437. Other metal halide salts have been used in nanowire synthesis. See, for example, J. Jiu, K. Murai, D. Kim, K. Kim, K. Suganuma, *Mat. Chem. & Phys.*, **2009**, 114, 333, which refers to NaCl , CoCl_2 , CuCl_2 , NiCl_2 and ZnCl_2 , and S. Nandikonda, “Microwave Assisted Synthesis of Silver Nanorods,” M.S. Thesis, Auburn
20 University, Auburn, Alabama, USA, August 9, 2010, which refers to NaCl , KCl , MgCl_2 , CaCl_2 , MnCl_2 , CuCl_2 , and FeCl_3 , and Japanese patent application publication 2009-155674, which discloses SnCl_4 . U.S. patent application publication 2011/0173190 discloses nanowire preparation in the presence of tetra-*n*-butylammonium chloride.

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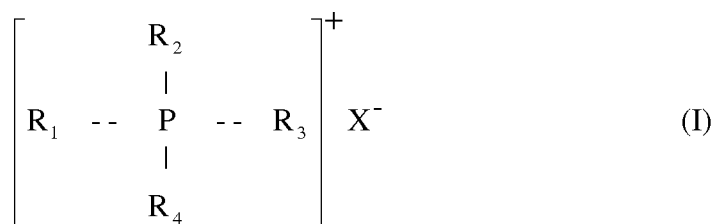
SUMMARY

 At least a first embodiment provides methods comprising providing
30 at least one first compound capable of forming at least one first halide ion, where the at least one first compound comprises at least one quaternary phosphonium salt, and reducing at least one first reducible metal ion to at least one first metal nanowire in the presence of at least one of the at least one first composition or the

at least one first halide ion. In at least some embodiments, the at least one first halide ion comprises at least one chloride ion or bromide ion.

Some such embodiments further comprise providing at least one second compound comprising the at least one reducible metal ion, wherein at least a first portion of the at least one second compound is provided prior to providing at least a second portion of the at least one first compound. Other such embodiments further comprise providing at least one second compound comprising the at least one reducible metal ion, wherein at least a first portion of the at least one second compound is provided after providing at least a second portion of the at least one first compound. Still other embodiments further comprise providing at least one second compound comprising the at least one reducible metal ion, wherein at least a first portion of the at least one second compound is provided simultaneously with at least a second portion of the at least one first compound.

In at least some embodiments, the at least one quaternary phosphonium salt may be represented by (I):



where:

R_1 , R_2 , R_3 , and R_4 each independently comprise an alkyl group, an aryl group, an alkoxy group, or an aryloxy group, and

X^- comprises a halide ion.

The at least one quaternary phosphonium salt may, for example, comprise at least one organic phosphonium halide, such as, for example, tetraphenylphosphonium chloride. The halide ion may, for example, be a chloride ion or a bromide ion.

In at least some embodiments, the at least one first metal ion may, for example, comprise at least one ion from IUPAC Group 11 or at least one coinage metal ion, such as, for example, at least one silver ion.

The at reducing may occur, in at least some cases, in the presence of at least one second metal or metal ion having an atomic number different from

that of the at least one first metal ion. In some cases, the reducing may occur in the presence of propylene glycol. Some embodiments employ reducing at at least one temperature between about 90 °C and about 150 °C.

Other embodiments provide the at least one first metal product
5 produced according to such methods. Such a first metal product may, for example, comprise at least one metal nanowire. Such metal nanowires may, in some cases, comprise at least one silver nanowire. Some embodiments provide metal nanowires comprising an average length greater than about 10 µm and an average diameter less than about 50 nm.

10 Still other embodiments provide articles comprising at least one such first metal product produced according to such methods.

These and other embodiments will be understood by the brief description of figures, description, exemplary embodiments, examples, and claims that follow.

15

BRIEF DESCRIPTION OF FIGURES

Figure 1 shows a micrograph of the silver nanowire product of Example 1.

20 Figure 2 shows a micrograph of the silver nanowire product of Example 2.

Figure 3 shows a micrograph of the silver nanowire product of Example 3.

Figure 4 shows a micrograph of the silver nanowire product of Example 4.

25 Figure 5 shows a micrograph of the silver nanowire product of Example 5.

DESCRIPTION

30 All publications, patents, and patent documents referred to in this document are incorporated by reference herein in the entirety, as though individually incorporated by reference.

U.S. Provisional Application No. 61/488,926, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, is hereby incorporated by reference in its entirety.

Reducible Metal Ions and Metal Products

Some embodiments provide methods comprising reducing at least one reducible metal ion to at least one metal. A reducible metal ion is a cation
5 that is capable of being reduced to a metal under some set of reaction conditions. In such methods, the at least one first reducible metal ion may, for example, comprise at least one coinage metal ion. A coinage metal ion is an ion of one of the coinage metals, which include copper, silver, and gold. Or such a reducible metal ion may, for example, comprise at least one ion of an IUPAC Group 11
10 element. An exemplary reducible metal ion is a silver cation. Such reducible metal ions may, in some cases, be provided as salts. For example, silver cations might, for example, be provided as silver nitrate.

In such embodiments, the at least one metal is that metal to which the at least one reducible metal ion is capable of being reduced. For example,
15 silver would be the metal to which a silver cation would be capable of being reduced.

Nanostructures, Nanostructures, and Nanowires

In some embodiments, the metal product formed by such methods
20 is a nanostructure, such as, for example, a one-dimensional nanostructure. Nanostructures are structures having at least one “nanoscale” dimension less than 300 nm, and at least one other dimension being much larger than the nanoscale dimension, such as, for example, at least about 10 or at least about 100 or at least about 200 or at least about 1000 times larger. Examples of such nanostructures
25 are nanorods, nanowires, nanotubes, nanopyramids, nanoprisms, nanoplates, and the like. “One-dimensional” nanostructures have one dimension that is much larger than the other two dimensions, such as, for example, at least about 10 or at least about 100 or at least about 200 or at least about 1000 times larger.

Such one-dimensional nanostructures may, in some cases,
30 comprise nanowires. Nanowires are one-dimensional nanostructures in which the two short dimensions (the thickness dimensions) are less than 300 nm, preferably less than 100 nm, while the third dimension (the length dimension) is greater than 1 micron, preferably greater than 10 microns, and the aspect ratio (ratio of the length dimension to the larger of the two thickness dimensions) is greater than

five. Nanowires are being employed as conductors in electronic devices or as elements in optical devices, among other possible uses. Silver nanowires are preferred in some such applications.

Such methods may be used to prepare nanostructures other than nanowires, such as, for example, nanocubes, nanorods, nanopyramids, nanotubes, and the like. Nanowires and other nanostructure products may be incorporated into articles, such as, for example, electronic displays, touch screens, portable telephones, cellular telephones, computer displays, laptop computers, tablet computers, point-of-purchase kiosks, music players, televisions, electronic games, electronic book readers, transparent electrodes, solar cells, light emitting diodes, other electronic devices, medical imaging devices, medical imaging media, and the like.

Preparation Methods

A common method of preparing nanostructures, such as, for example, nanowires, is the “polyol” process. Such a process is described in, for example, *Angew. Chem. Int. Ed.* 2009, 48, 60, Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, which is hereby incorporated by reference in its entirety. Such processes typically reduce a metal cation, such as, for example, a silver cation, to the desired metal nanostructure product, such as, for example, a silver nanowire. Such a reduction may be carried out in a reaction mixture that may, for example, comprise one or more polyols, such as, for example, ethylene glycol (EG), propylene glycol (PG), butanediol, glycerol, sugars, carbohydrates, and the like; one or more protecting agents, such as, for example, polyvinylpyrrolidinone (also known as polyvinylpyrrolidone or PVP), other polar polymers or copolymers, surfactants, acids, and the like; and one or more metal ions. These and other components may be used in such reaction mixtures, as is known in the art. The reduction may, for example, be carried out at one or more temperatures from about 90 °C to about 190 °C.

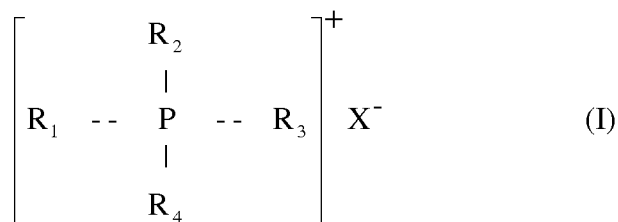
Quaternary Phosphonium Salts

Applicant has discovered that quaternary phosphonium salts may be used to provide halide ions that catalyze (or co-catalyze, with one or more metal or metal ion catalysts) the formation of one-dimensional silver nanowires.

Halide ions may thereby be produced in a controlled fashion in contrast to simply adding the halide ion to the reaction mixture in a fixed cation-to-anion ratio.

In at least some embodiments, the at least one quaternary phosphonium salt may be represented by (I):

5



where:

10

R_1 , R_2 , R_3 , and R_4 each independently comprise an alkyl group, an aryl group, an alkoxy group, or an aryloxy group, and

X^- comprises a halide ion, such as, for example, chloride, bromide, or iodide.

15

“Alkyl” refers to, for example, straight chain and branched chain alkyl groups having, for example, from about 1 to about 20 carbon atoms, or from about 1 to about 15 carbon atoms, or from about 1 to about 5 carbon atoms. Exemplary alkyl groups include methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, n-pentyl, ethylhexyl, dodecyl, isopentyl, and the like.

20

“Aryl” refers to, for example, an aromatic carbocyclic group of from about 6 to 20 carbon atoms having a single ring (e.g., phenyl) or multiple condensed rings (e.g., naphthyl or anthryl) that may or may not all themselves be condensed, provided that the point of attachment of the group is at an aromatic carbon atom. Exemplary aryl groups include phenyl, naphthyl, and the like.

25

“Alkoxy” refers to, for example, the group “RO-”, with “R” being an alkyl group. It also refers to a group comprising a sequence of two or more alkyl groups separated from each other by oxygen atoms, provided that the point of attachment of the alkoxy group is at a terminal oxygen atom, such as, for example, “ R_a -O- R_b -O-”. Exemplary alkoxy groups include methoxy, ethoxy, n-propyloxy, iso-propyloxy, n-butyloxy, t-butyloxy, n-pentyloxy, 1-ethylhex-1-

ylxy, dodecyloxy, isopentyloxy, methoxymethoxy, methoxyethoxy, ethoxyethoxy, and the like.

“Aryloxy” refers to, for example, the group “RO-”, with “R” being an aryl group. It also refers to a group comprising a sequence of two or more aryl groups separated from each other by oxygen atoms, provided that the point of attachment of the aryloxy group is at a terminal oxygen atom, such as, for example, “R_a-O-R_b-O-”. Exemplary aryloxy groups include phenoxy, naphthoxy, and the like.

The at least one quaternary phosphonium salt may, in some cases, comprise at least one organic phosphonium halide, such as, for example, tetraphenylphosphonium chloride.

Mixtures of such quaternary phosphonium salts may be used. Mixtures of such salts with other compounds capable of providing halides may also be used. Mixtures capable of providing more than one type of halide, such as both chloride and bromide, may also be used.

The metal or metal ion catalysts, if used, may be provided as metal halides, as metal cations with non-halide anions, or in any other suitable form. For example, such catalysts may be provided as alkali metal salts, alkaline earth metal salts, metalloid salts, organometallic compounds, transition metal complexes, and the like.

These methods are also believed to be applicable to reducible metal cations other than silver cations, including, for example, reducible cations of other IUPAC Group 11 elements, reducible cations of other coinage metals, and the like. The methods may also be used to prepare products other than nanowires, such as, for example, nanocubes, nanorods, nanopyramids, nanotubes, and the like. Such products may be incorporated into articles, such as, for example, transparent electrodes, solar cells, light emitting diodes, other electronic devices, medical imaging devices, medical imaging media, and the like.

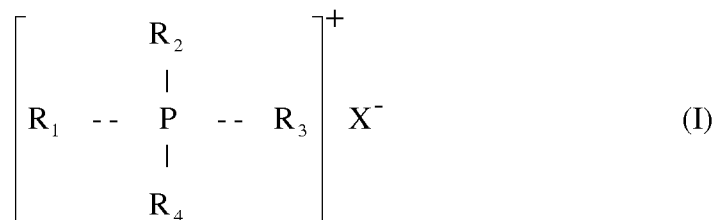
EXEMPLARY EMBODIMENTS

U.S. Provisional Application No. 61/488,926, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 12 non-limiting exemplary embodiments:

A. A method comprising:
 providing a composition capable of forming at least one first halide ion,
 said composition comprising at least one quaternary phosphonium salt; and
 reducing at least one first metal ion to at least one first metal in the

5 presence of the composition.

B. The method according to embodiment A, wherein the at least one
 quaternary phosphonium salt is represented by (I):



wherein R₁, R₂, R₃, and R₄ each independently comprise an alkyl group, an aryl

10 group, an alkoxy group, or an aryloxy group, and X⁻ comprises a halide ion.

C. The method according to embodiment A, wherein the at least one
 quaternary phosphonium salt comprises at least one organic phosphonium halide.

D. The method according to embodiment A, wherein the at least one
 quaternary phosphonium salt comprises tetraphenylphosphonium chloride.

15 E. The method according to embodiment A, wherein the at least one first
 halide ion comprises at least one chloride ion or bromide ion.

F. The method according to embodiment A, wherein the at least one first
 metal ion comprises at least one element from IUPAC Group 11.

G. The method according to embodiment A, wherein the at least one first
 20 metal ion comprises at least one coinage metal ion.

H. The method according to embodiment A, wherein the at least one first
 metal ion comprises at least one silver ion.

J. The method according to embodiment A, wherein the reducing occurs in
 the presence of at least one second metal or metal ion having an atomic number
 25 different from that of the at least one first metal ion.

K. The at least one first metal product produced according to the method of
 embodiment A.

L. The at least one first metal product according to embodiment K, said at
 least one product comprising at least one nanowire.

M. An article comprising the at least one first metal product according to embodiment K.

EXAMPLES

5 Example 1

A 500 mL reaction flask containing 280 mL ethylene glycol (EG) was stripped of at least some dissolved gases (hereafter, “degassed”) by bubbling nitrogen into the solution overnight using a TEFLON[®] fluoropolymer tube. To the EG was then added 13 mg of tetraphenylphosphonium chloride and 3.3 g of a 3 mM solution of iron (II) acetylacetonate in EG. The fluoropolymer tube was then retracted to provide nitrogen blanketing of the headspace of the reaction flask at a 0.5 L/min purge rate. Solutions of 0.77 M polyvinylpyrrolidinone (PVP) in EG and 0.25 M AgNO₃ in EG were degassed with N₂, then 20 mL syringes of each were prepared. The reaction mixture was heated to 145 °C under N₂, then the AgNO₃ and PVP solutions were added at a constant rate over 25 minutes via a 12 gauge a TEFLON[®] fluoropolymer syringe needle. The reaction was held at 145 °C for 90 minutes, and then allowed to cool to ambient temperature.

An optical microscope picture of the unpurified silver nanowire product is shown in Figure 1. Average length and diameter was determined by measuring a sample of at least 100 nanowires. The average nanowire diameter was found to be 135 ± 100 nm and the average length was found to be 20.4 ± 20.2 μ m.

Example 2

A 500 mL reaction flask containing 300 mL propylene glycol (1,2-propanediol, PG), 1.9 mg polyvinylpyrrolidinone (PVP, 55,000 molecular weight), and 61.5 mg tetraphenylphosphonium chloride was degassed overnight with N₂ using a TEFLON[®] fluoropolymer tube. The fluoropolymer tube was then retracted to provide nitrogen blanketing of the headspace of the reaction flask at a 0.5 L/min purge rate. A solution of 0.50 M AgNO₃ in PG was degassed with N₂, then a 20 mL syringe of the solution was prepared. The reaction mixture was heated to 125 °C under N₂, then the AgNO₃ solution was added at a constant rate over 25 minutes via a 12 gauge TEFLON[®] fluoropolymer syringe needle. The

reaction mixture was held at 125 °C for 60 minutes, and then allowed to cool to ambient temperature.

5 An optical microscope picture of the unpurified silver nanowire product is shown in Figure 2. Average length and diameter was determined by measuring a sample of at least 100 nanowires. The average nanowire diameter was found to be 46.4 ± 13.4 nm and the average length was found to be 9.9 ± 4.6 μ m.

Example 3

10 A 500 mL reaction flask containing 270 mL propylene glycol (1,2-propanediol, PG), 4.5 mg polyvinylpyrrolidinone (PVP, 55,000 molecular weight), and 78.3 mg tetraphenylphosphonium chloride was degassed overnight with N₂ using a TEFLON[®] fluoropolymer tube. The fluoropolymer tube was then retracted to provide nitrogen blanketing of the headspace of the reaction flask at a
15 0.5 L/min purge rate. A solution of 1.0 M AgNO₃ in PG was degassed with N₂, then a 24 mL syringe of the solution was prepared. The reaction mixture was heated to 100 °C under N₂, then the AgNO₃ solution was added at a constant rate over 120 minutes via a 12 gauge TEFLON[®] fluoropolymer syringe needle. The reaction mixture was then allowed to cool to ambient temperature.

20 An optical microscope picture of the unpurified silver nanowire product is shown in Figure 3. Average length and diameter was determined by measuring a sample of at least 100 nanowires. The average nanowire diameter was found to be 53.0 ± 6.8 nm and the average length was found to be 10.2 ± 46.4 μ m.

25

Example 4

A 500 mL reaction flask containing 280 mL propylene glycol (1,2-propanediol, PG) and 1.9 g polyvinylpyrrolidinone (PVP, 55,000 molecular weight), was degassed overnight with N₂ using a TEFLON[®] fluoropolymer tube.
30 The fluoropolymer tube was then retracted to provide nitrogen blanketing of the headspace of the reaction flask at a 0.5 L/min purge rate. Solutions of 0.50 M AgNO₃ in PG and 19.3 mM tetraphenylphosphonium chloride in PG were degassed with N₂. A 20 mL syringe of the AgNO₃ solution and a 9 mL syringe of the tetraphenylphosphonium chloride solution were prepared. The reaction

mixture was heated to 110 °C under N₂, then the AgNO₃ and tetraphenylphosphonium chloride solutions were each added at a constant rate of 0.8 mL/min via 12 gauge TEFLON[®] fluoropolymer syringe needles. The reaction mixture was held for 1 hour after completion of the tetraphenylphosphonium chloride, cooled to 100 °C, held for an additional 4 hours, then allowed to cool to ambient temperature.

An optical microscope picture of the unpurified silver nanowire product is shown in Figure 4. Average length and diameter was determined by measuring a sample of at least 100 nanowires. The average nanowire diameter was found to be 44.5 ± 5.5 nm and the average length was found to be 24.0 ± 11.5 μm.

Example 5

A 500 mL reaction flask containing 280 mL propylene glycol (1,2-propanediol, PG) and 4.5 g polyvinylpyrrolidinone (PVP, 55,000 molecular weight), was degassed overnight with N₂ using a TEFLON[®] fluoropolymer tube. The fluoropolymer tube was then retracted to provide nitrogen blanketing of the headspace of the reaction flask at a 0.5 L/min purge rate. Solutions of 1.0 M AgNO₃ in PG and 19.3 mM tetraphenylphosphonium chloride in PG were degassed with N₂. A 24 mL syringe of the AgNO₃ solution and a 24 mL syringe of the tetraphenylphosphonium chloride solution were prepared. The reaction mixture was heated to 110 °C under N₂, then the AgNO₃ solution was added at a constant rate of 0.2 mL/min via 12 gauge TEFLON[®] fluoropolymer syringe needles. 10 min after initiating the AgNO₃ solution addition, the tetraphenylphosphonium chloride solution was added via a separate syringe pump at a constant rate of 0.8 mL/min. The reaction mixture was held for 2 hrs after completion of the silver nitrate solution, then allowed to cool to ambient temperature.

An optical microscope picture of the unpurified silver nanowire product is shown in Figure 5. Average length and diameter was determined by measuring a sample of at least 100 nanowires. The average nanowire diameter was found to be 44.2 ± 8.9 nm and the average length was found to be 13.9 ± 9.7 μm.

CLAIMS:

1. A method comprising:
 providing at least one first compound capable of forming at least one first halide ion, said first compound comprising at least one quaternary phosphonium salt; and
 reducing at least one first reducible metal ion to at least one first metal nanowire in the presence of at least one of the at least one first compound or the at least one first halide ion.
2. The method according to embodiment 1, wherein the at least one quaternary phosphonium salt is represented by (I):

$$\left[\begin{array}{ccccc} & & R_2 & & \\ & & | & & \\ R_1 & \cdots & P & \cdots & R_3 \\ & & | & & \\ & & R_4 & & \end{array} \right]^+ X^- \quad (I)$$
 wherein R_1 , R_2 , R_3 , and R_4 each independently comprise an alkyl group, an aryl group, an alkoxy group, or an aryloxy group, and X^- comprises a halide ion.
3. The method according to claim 1, wherein the at least one quaternary phosphonium salt comprises at least one organic phosphonium halide.
4. The method according to claim 1, wherein the at least one quaternary phosphonium salt comprises tetraphenylphosphonium chloride.
5. The method according to claim 1, wherein the at least one first halide ion comprises at least one chloride ion or bromide ion.
6. The method according to claim 1, wherein the at least one first reducible metal ion comprises at least one of an ion from IUPAC Group 11, a coinage metal ion, or a silver ion.
7. The method according to claim 1, further comprising providing at least one second compound comprising the at least one reducible metal ion,

wherein at least a first portion of the at least one second compound is provided prior to providing at least a second portion of the at least one first compound.

8. The method according to claim 1, further comprising providing at
5 least one second compound comprising the at least one reducible metal ion,
wherein at least a first portion of the at least one second compound is provided
after providing at least a second portion of the at least one first compound.
9. The at least one first metal nanowire produced according to the
10 method of claim 1.
10. The at least one first metal nanowire according to claim 9
comprising an average length greater than about 10 μm and an average diameter
less than about 50 nm.

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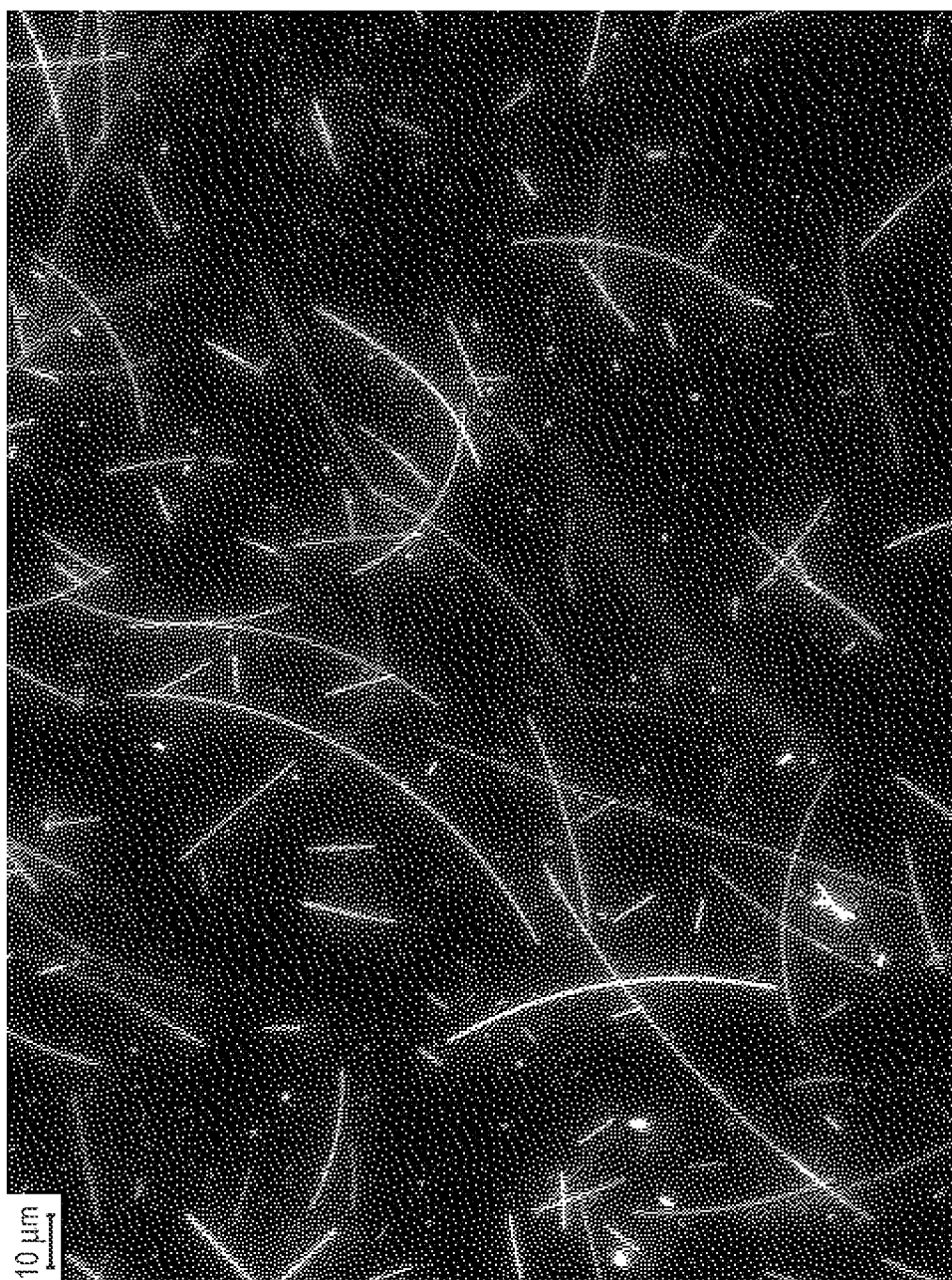


FIG. 1

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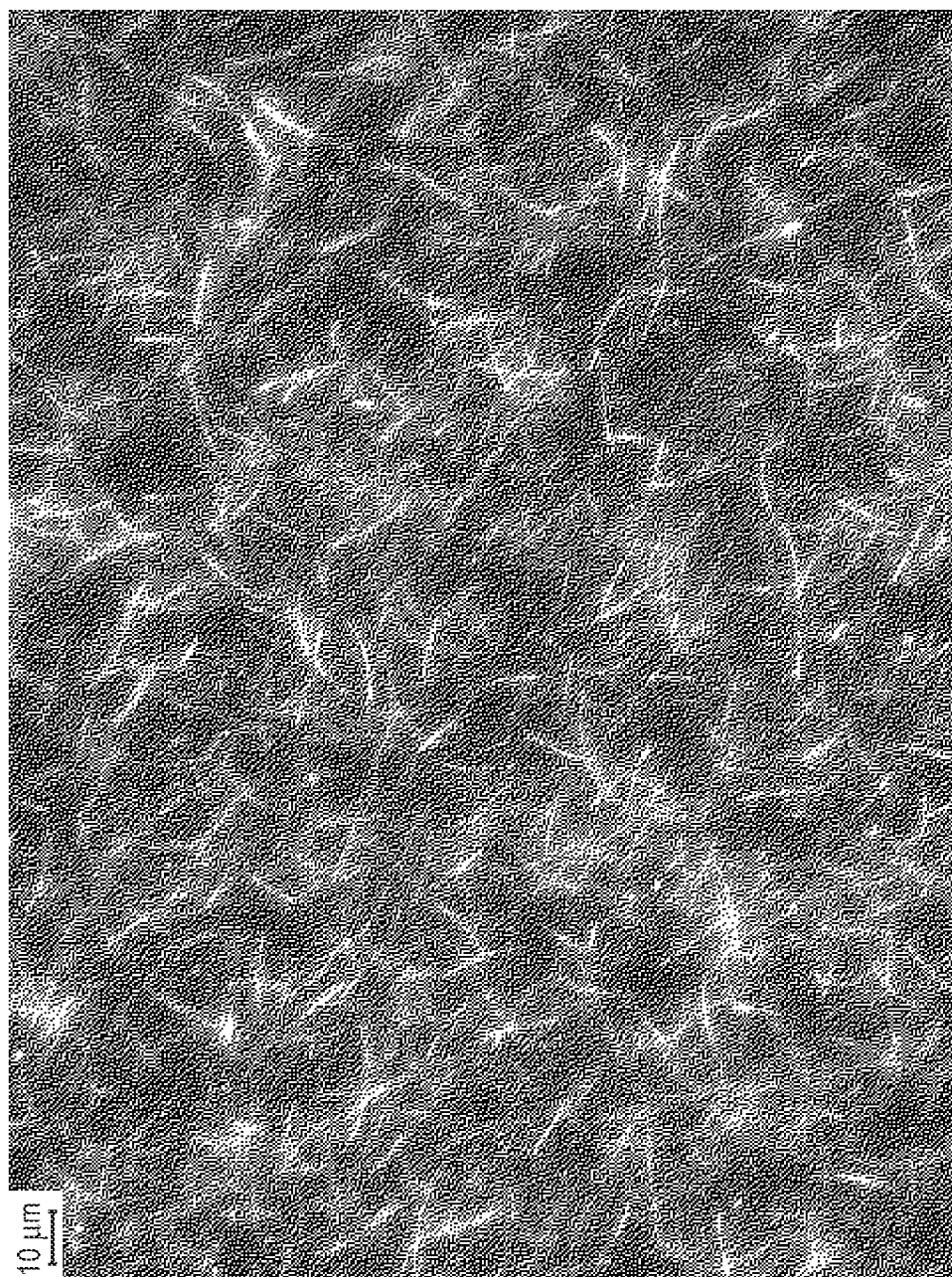


FIG. 2

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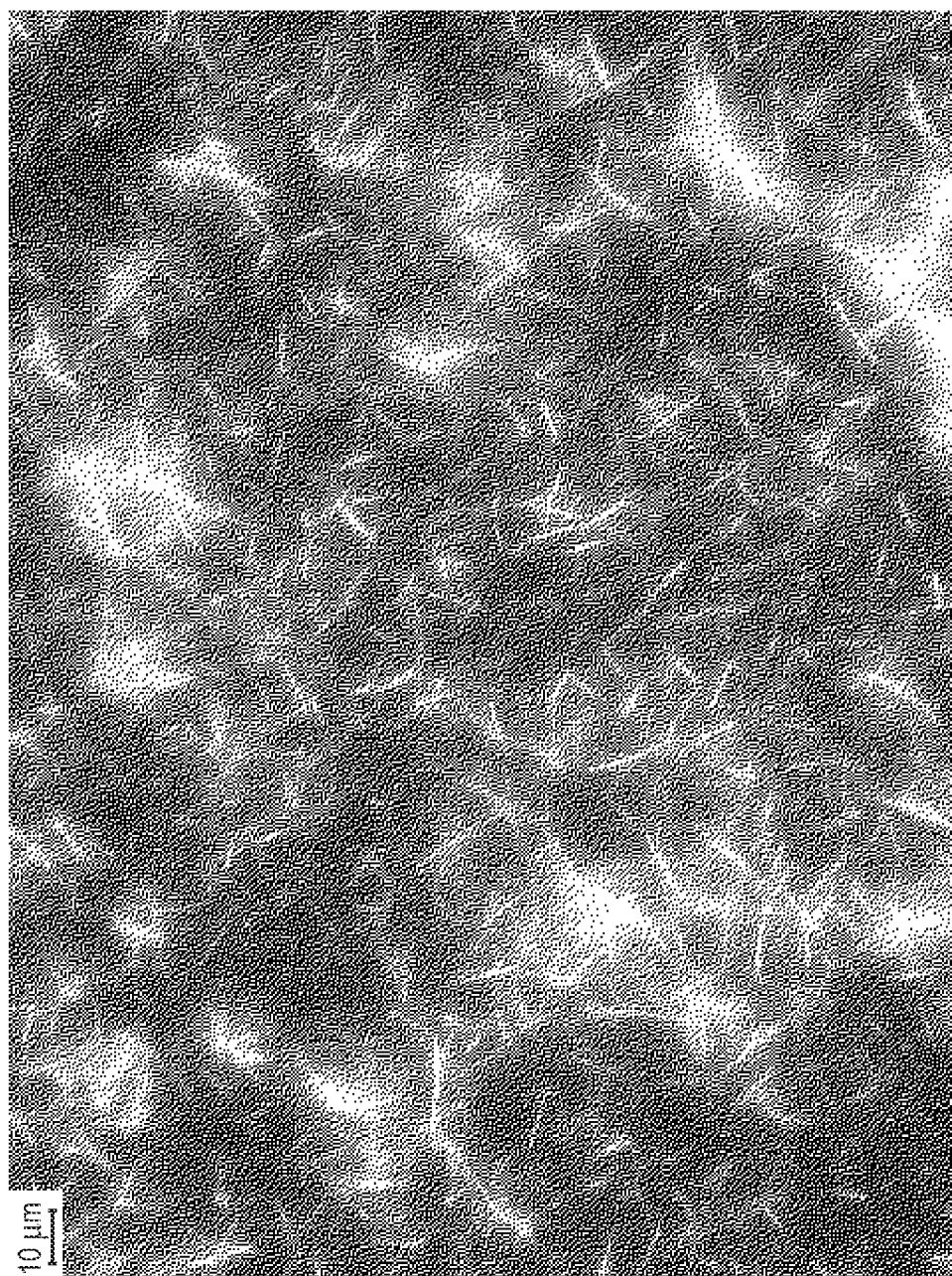


FIG. 3

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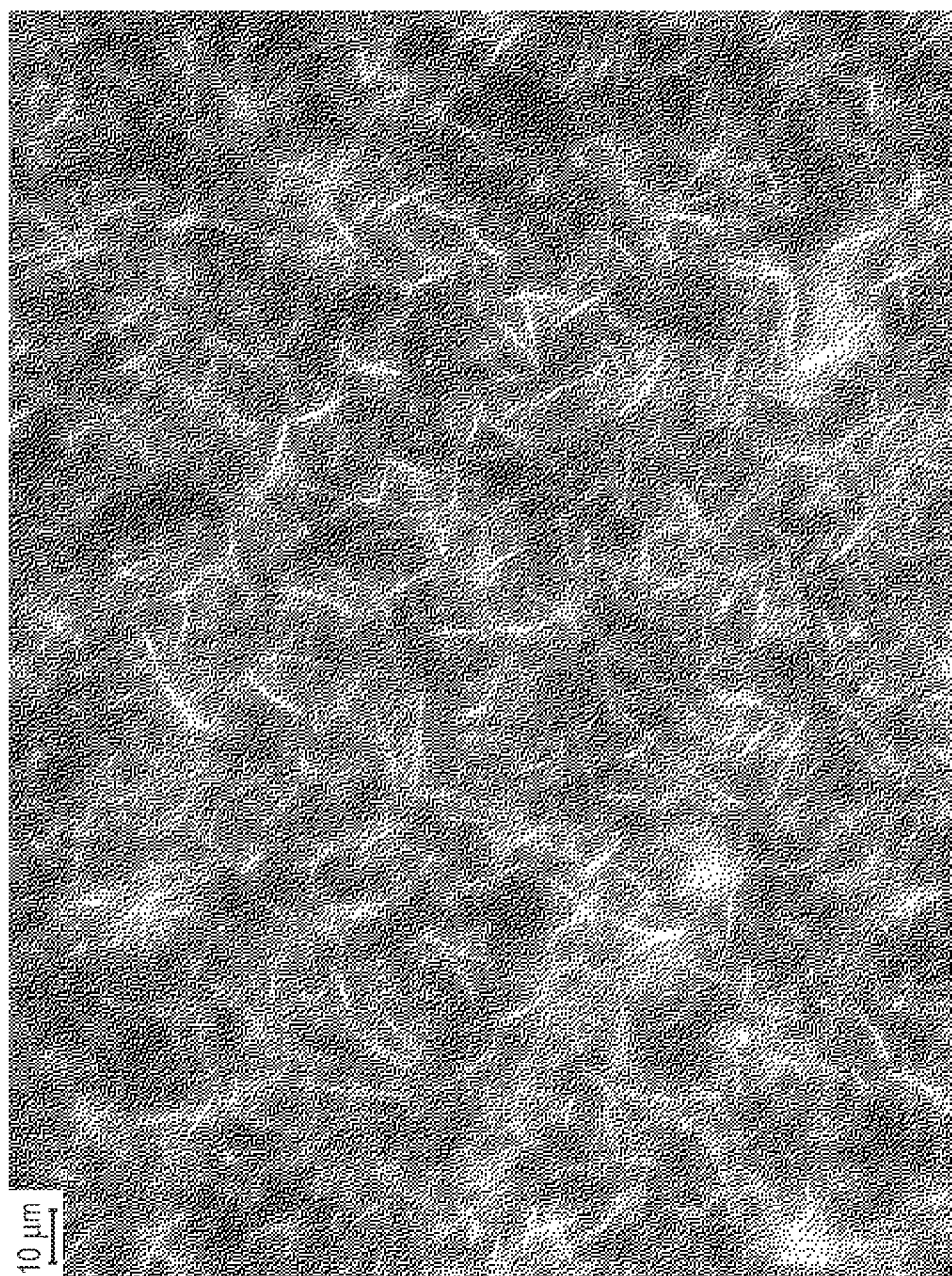


FIG. 4

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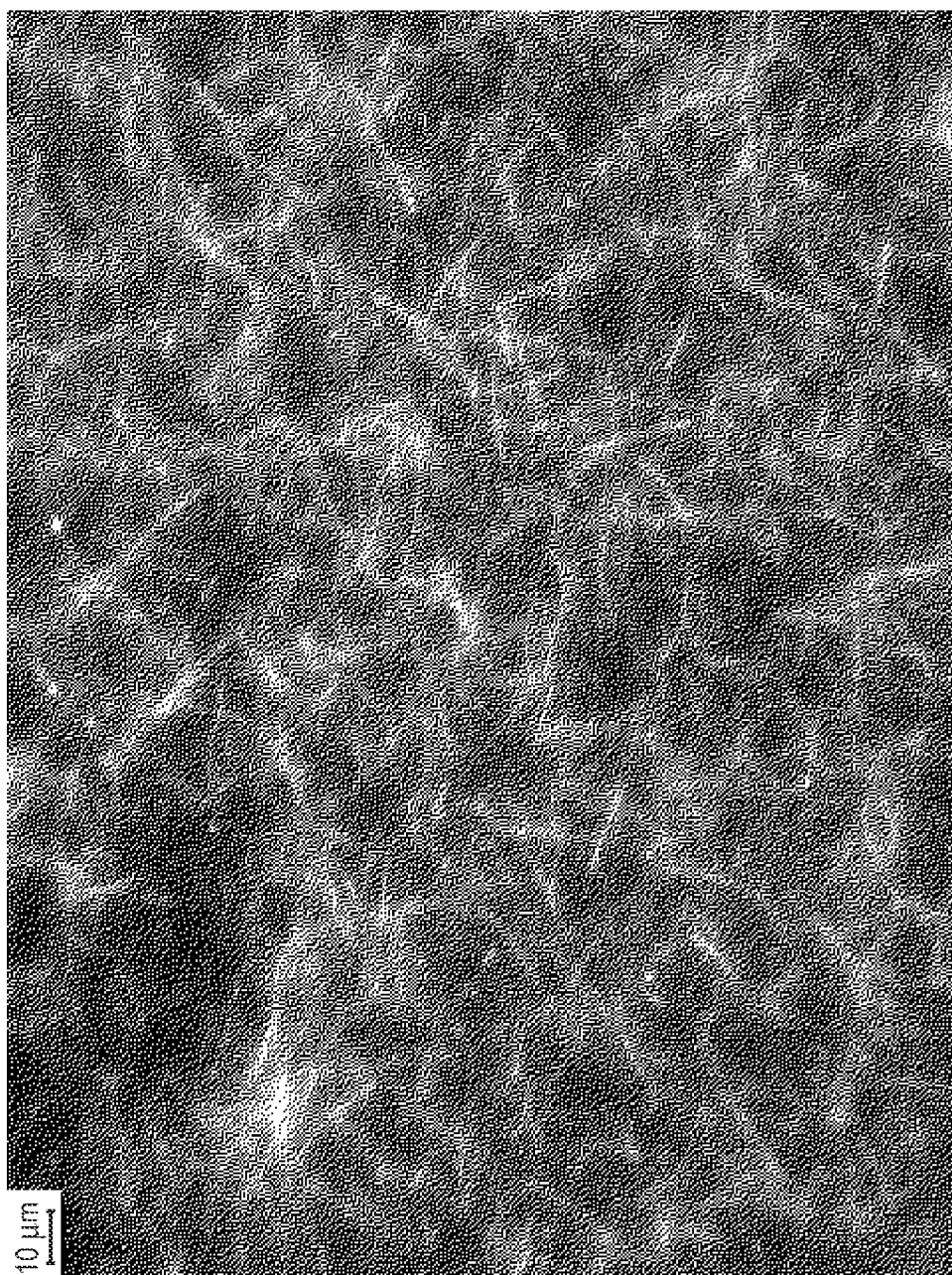


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/034143

A. CLASSIFICATION OF SUBJECT MATTER

INV. B22F9/24 C30B7/14 C30B29/60
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)
B22F C30B

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, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/297388 A1 (XIA YOUNAN [US] ET AL) 3 December 2009 (2009-12-03) paragraph [0049] - paragraph [0063] paragraph [0087]	1-10
X	----- US 2010/078197 A1 (MIYAGISHIMA NORI [JP] ET AL) 1 April 2010 (2010-04-01)	9,10
A	examples tables 1-1 ----- -/--	1-8

☒ 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

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"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

5 July 2012

Date of mailing of the international search report

12/07/2012

Name and mailing address of the ISA/

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Authorized officer

Morra, Valentina

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/034143

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KYLEE E. KORTE ET AL: "Rapid synthesis of silver nanowires through a CuCl- or CuCl2-mediated polyol process", JOURNAL OF MATERIALS CHEMISTRY, vol. 18, no. 4, 1 January 2008 (2008-01-01), page 437, XP55010797, ISSN: 0959-9428, DOI: 10.1039/b714072j cited in the application	9,10
A	Methods Results and discussion -----	1-8
X	HONG-YAN SHI 1 ET AL: "Ordering of Disordered Nanowires: Spontaneous Formation of Highly Aligned, Ultralong Ag Nanowire Films at Oil-Water-Air Interface", ADVANCED FUNCTIONAL MATERIALS, WILEY - V C H VERLAG GMBH & CO. KGAA, DE, vol. 20, no. 6, 24 March 2010 (2010-03-24), pages 958-964, XP001554277, ISSN: 1616-301X, DOI: 10.1002/ADFM.200901668	9
A	Experimental Results and discussion -----	1-8,10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/034143

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.: 1-10(partially)
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:
see FURTHER INFORMATION sheet PCT/ISA/210
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:

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 an 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.:

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-10(partially)

Present claims 1-10 relate to an extremely large number of possible methods and products. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the methods and products claimed, i.e. for methods of producing silver nanowires, see Examples. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1-10 (PCT Guidelines 9.19 and 9.23). The search of claims 1-10 was restricted to those claimed methods and products which appear to be supported and a generalisation of their composition, i.e. to methods of producing Ag, Au or Cu nanowires.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/034143

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009297388	A1	03-12-2009	NONE

US 2010078197	A1	01-04-2010	JP 2010084173 A 15-04-2010
		US 2010078197 A1	01-04-2010
