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

(57) Abstract: Nanomaterial preparation methods, compositions, and articles are disclosed and claimed. Such methods can provide nanomaterials with improved morphologies relative to previous methods. Such materials are useful in electronic applications.



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 the 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.

The metal ions used to catalyze wire formation are generally primarily reported to be provided as a metal halide salt, usually as a metal
15 chloride, for example, FeCl_2 or CuCl_2 . 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 ; Japanese patent application publication JP2009155674, which describes SnCl_4 ; S. Nandikonda, “Microwave Assisted Synthesis of Silver Nanorods,” M.S. Thesis, Auburn University, August 9, 2010,
20 which refers to NaCl , KCl , MgCl_2 , CaCl_2 , MnCl_2 , CuCl_2 , and FeCl_3 ; S. Nandikonda and E. W. Davis, “Effects of Salt Selection on the Rapid Synthesis of Silver Nanowires,” Abstract INOR-299, 240th ACS National Meeting, Boston, MA, August 22-27, 2010, which discloses NaCl , KCl , MgCl_2 , CaCl_2 , MnCl_2 , CuCl_2 , FeCl_3 , Na_2S , and NaI ; Chinese patent application publication
25 CN101934377, which discloses Mn^{2+} ; Y. C. Lu, K. S. Chou, *Nanotech.*, **2010**, 21, 215707, which discloses Pd^{2+} ; and Chinese patent application publication CN102029400, which discloses NaCl , MnCl_2 , and Na_2S .

SUMMARY

30 At least some embodiments provide methods comprising providing at least one composition comprising at least one first reducible metal ion and at least one second metal or metal ion comprising at least one element or ion of an

element from IUPAC Group 3, IUPAC Group 4, IUPAC Group 5, IUPAC Group 6, or IUPAC Group 7, the at least one second metal or metal ion differing in atomic number from the at least one first reducible metal ion; and reducing the at least one first reducible metal ion to at least one first metal.

5 In at least some cases, the at least one first reducible metal ion may, for example, comprise one or more of at least one coinage metal ion, at least one ion of an element from IUPAC Group 11, or at least one silver ion.

 In at least some embodiments, the at least one composition may comprise at least one metal oxide compound comprising the at least one second
10 metal or metal ion. Such metal oxide compounds may, for example, comprise at least one of a metal oxide halide compound or a transition metal oxide compound. In at least some cases, the at least one second metal or metal ion may comprise an oxidation state of +4 or greater.

 The at least one second metal or metal ion may, in some cases,
15 comprise at least one element or ion of an element from IUPAC Group 3, or at least one element from IUPAC Group 4, or at least one element or ion of an element from IUPAC Group 5, or at least one element or ion of an element from IUPAC Group 6, or at least one element or ion of an element from IUPAC Group 7. The at least one second metal or metal ion may, in other cases, comprise
20 elements or ions of elements from more than one of IUPAC Groups 4, 5, 6, or 7.

 Other embodiments provide the at least one first metal produced according to such methods.

 Still other embodiments provide metal nanowires comprising the at least one first metal produced according to such methods. In some cases, such
25 metal nanowires may, for example, comprise an aspect ratio between about 50 and about 10,000. Such nanowires may, for example, comprise an average diameter of between about 10 nm and about 300 nm, or of between about 25 nm and about 60 nm, or of between about 60 nm and about 140 nm, or of between about 140 nm and about 260 nm. In some cases, such metal nanowires may comprise at least
30 one silver nanowire.

 Yet still other embodiments provide articles comprising the at least one first metal produced according to such methods. Such articles may, for

example, comprise one or more of an electronic display, a touch screen, a portable telephone, a cellular telephone, a computer display, a laptop computer, a tablet computer, a point-of-purchase kiosk, a music player, a television, an electronic game, an electronic book reader, a transparent electrode, a solar cell, a light emitting diode, an electronic device, a medical imaging device, or a medical imaging medium.

These embodiments and other variations and modifications may be better understood from the brief description of figures, description, exemplary embodiments, examples, figures, and claims that follow. Any embodiments provided are given only by way of illustrative example. Other desirable objectives and advantages inherently achieved may occur or become apparent to those skilled in the art. The invention is defined by the appended claims.

BRIEF DESCRIPTION OF FIGURES

FIG. 1 shows an optical micrograph of the silver nanowire product of Example 1.

FIG. 2 shows a scanning electron micrograph of the silver nanowire product of Example 1.

FIG. 3 shows an optical micrograph of the silver nanowire product of Example 5.

FIG. 4 shows an optical micrograph of the silver nanowire product of Example 6.

FIG. 5 shows an optical micrograph of the silver nanowire product of Example 7.

FIG. 6 shows an optical micrograph of the silver nanowire product of Example 8.

FIG. 7 shows an optical micrograph of the silver nanowire product of Example 9.

FIG. 8 shows an optical micrograph of the silver nanowire product of Example 10, at 45 min reaction time.

FIG. 9 shows an optical micrograph of the silver nanowire product of Example 10, at 60 min reaction time.

FIG. 10 shows an optical micrograph of the silver nanowire product of Example 11.

5 FIG. 11 shows an optical micrograph of the silver nanowire product of Example 12.

FIG. 12 shows an optical micrograph of the silver nanowire product of Example 13.

10 FIG. 13 shows an optical micrograph of the silver nanowire product of Example 14.

FIG. 14 shows an optical micrograph of the silver nanowire product of Example 15.

FIG. 15 shows an optical micrograph of the silver nanowire product of Example 15.

15 FIG. 16 shows an optical micrograph of the silver nanowire product of Example 16.

FIG. 17 shows an optical micrograph of the silver nanowire product of Example 16.

20 FIG. 18 shows an optical micrograph of the silver nanowire product of Example 17.

FIG. 19 shows an optical micrograph of the silver nanowire product of Example 18.

FIG. 20 shows an optical micrograph of the silver nanowire product of Example 19.

25 FIG. 21 shows an optical micrograph of the silver nanowire product of Example 20.

DESCRIPTION

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

U.S. Provisional Application No. 61/421,294, filed December 9, 2010, entitled METAL ION CATALYSIS OF METAL ION REDUCTION, METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/423,744, filed December 16, 2010, entitled METAL ION CATALYSIS
5 OF METAL ION REDUCTION, METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/488,824, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/488,834, filed May 23, 2011, entitled METAL ION CATALYSIS OF METAL ION REDUCTION,
10 METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/488,840, filed May 23, 2011, entitled METAL ION CATALYSIS OF METAL ION REDUCTION, METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/488,880, filed May 23, 2011, entitled METAL ION CATALYSIS OF METAL ION REDUCTION, METHODS,
15 COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/488,945, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/488,977, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application
20 No. 61/488,983, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/494,072, filed June 7, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/522,741, filed August 12, 2011, entitled NANOWIRE PREPARATION
25 METHODS, COMPOSITIONS, AND ARTICLES; U.S. Provisional Application No. 61/523,977, filed August 16, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES; and U.S. Provisional Application No. 61/523,987, filed August 16, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, are each
30 hereby incorporated by reference in their 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.

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
20 like. These 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.

25

Metal or Metal Ion from IUPAC Groups 3, 4, 5, 6, or 7

In some embodiments, the at least one reducible metal ion is reduced in the presence of at least one second metal or metal ion comprising at least one metal or metal ion from IUPAC Groups 3, 4, 5, 6, or 7. The at least one
30 second metal or metal ion may, in some cases, comprise at least one element or ion of an element from IUPAC Group 3, or at least one element or ion of an element from IUPAC Group 4, or at least one element or ion of an element from

IUPAC Group 5, or at least one element or ion of an element from IUPAC Group 6, or at least one element or ion of an element from IUPAC Group 7. The at least one second metal or metal ion may, in other cases, comprise elements or ions of elements from more than one of IUPAC Groups 4, 5, 6, or 7.

5 Applicants have discovered that metals or metal ions from IUPAC Groups 3, 4, 5, 6, or 7 may be used to prepare metal nanowires, such as, for example, silver nanowires, with desirable control of thickness, or length, or both, often with improved control of non-wire contamination.

10 IUPAC Group 3 metals or metal ions comprise scandium, ions of scandium, yttrium, ions of yttrium, lanthanum, and ions of lanthanum. Exemplary compounds comprising IUPAC Group 3 metals or metal ions are scandium (II) chloride hexahydrate, yttrium (III) chloride hexahydrate, and lanthanum (III) chloride heptahydrate. Various metal ion oxidation states, such as, for example, +2, +3, or +4, are thought to be useful.

15 IUPAC Group 4 metals or metal ions comprise titanium, ions of titanium, zirconium, ions of zirconium, hafnium, and ions of hafnium. Exemplary compounds comprising IUPAC Group 4 metals or metal ions are titanium (IV) chloride, zirconium tetrachloride bis(tetrahydrofuran) adduct, and hafnium tetrachloride bis(tetrahydrofuran) adduct. Various metal ion oxidation states, such as, for example, +2, +3, or +4, are thought to be useful.

20 IUPAC Group 5 metals or metal ions comprise vanadium, ions of vanadium, niobium, ions of niobium, tantalum, and ions of tantalum. Exemplary compounds comprising IUPAC Group 5 metals or metal ions are vanadium (III) chloride, niobium (V) chloride, and tantalum (V) chloride. Various metal ion oxidation states, such as, for example, +2, +3, +4, +5, or higher, are thought to be useful.

25 IUPAC Group 6 metals or metal ions comprise chromium, ions of chromium, molybdenum, ions of molybdenum, tungsten, and ions of tungsten. Exemplary compounds comprising IUPAC Group 6 metals or metal ions are chromium (III) chloride hexahydrate, molybdenum (VI) dichloride dioxide, and tungsten (IV) chloride. Various metal ion oxidation states, such as, for example, +2, +3, or +4, are thought to be useful.

IUPAC Group 7 metals or metal ions comprise manganese, ions of manganese, technetium, ions of technetium, rhenium, and ions of rhenium.

Exemplary compounds comprising IUPAC Group 7 metals or metal ions are manganese (II) chloride and rhenium (III) chloride. It is believed that other metal ion oxidation states, such as, for example, +3, +4, +5, +6, or +7, may also provide useful results.

Metals or metal ions from IUPAC Groups 3, 4, 5, 6, or 7 may also comprise metal oxide compounds, such as, for example, transition metal oxide compounds or metal oxide halide compounds, such as those comprising at least one metal atom from IUPAC Groups 3, 4, 5, 6, or 7, such as, for example, molybdenum, tungsten, vanadium, zirconium, and the like. In some cases, the metal oxide compounds may comprise metal oxide halide compounds, such as metal oxide chloride compounds. The metal oxide halide compounds may comprise transition metal oxide halide compounds, such as, for example, transition metal chloride compounds. Exemplary metal oxide compounds are MoO_2Cl_2 , MoOCl_4 , WO_2Cl_2 , WOCl_4 , and VOCl_3 .

Nanostructures, Nanostructures, Nanowires, and Articles

In some embodiments, the metal product formed by such methods is a nanostructure, such as, for example, a one-dimensional nanostructure. Nanostructures are structures having at least one “nanoscale” dimension less than 300 nm. Examples of such nanostructures are nanorods, nanowires, nanotubes, nanopyramids, nanoprisms, nanoplates, and the like. “One-dimensional” nanostructures have one dimension that is much larger than the other two nanoscale 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, comprise nanowires. Nanowires are one-dimensional nanostructures in which the two short dimensions (the thickness dimensions) are less than 300 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.

The compositions and methods of the present application allow tailoring of nanowire diameters. In some cases, nanowires may have a specific
5 range of thickness. Thinner nanowires can be useful in applications where transparency is important, while thicker nanowires can be useful in applications requiring high current densities. A medium range of thicknesses may be useful to achieve a balance of such properties. Such nanowires may, for example, comprise an average diameter of between about 10 nm and about 300 nm, or of between
10 about 25 nm and about 260 nm, or of between about 25 nm and about 60 nm, or of between about 60 nm and about 140 nm, or of between about 140 nm and about 260 nm.

Such methods may be used to prepare nanostructures other than nanowires, such as, for example, nanocubes, nanorods, nanopyramids, nanotubes,
15 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,
20 other electronic devices, medical imaging devices, medical imaging media, and the like.

Preparation Methods

A common method of preparing nanostructures, such as, for
25 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.
30 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, 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 120 °C to about 190 °C, or from about 80 °C and about 190 °C.

EXEMPLARY EMBODIMENTS

U.S. Provisional Application No. 61/421,294, filed December 9, 2010, entitled METAL ION CATALYSIS OF METAL ION REDUCTION, METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 27 non-limiting exemplary embodiments:

- A. A method comprising:
 - providing a composition comprising:
 - at least one first compound comprising at least one first reducible metal ion,
 - at least one second compound comprising at least one second metal or metal ion differing in atomic number from said at least one first reducible metal, said at least one second metal or metal ion comprising at least one element from IUPAC Group 7, and
 - at least one solvent; and
 - reducing the at least one first reducible metal ion to at least one first metal.
- B. The method of embodiment A, wherein the composition further comprises at least one protecting agent.
- C. The method of embodiment B, wherein the at least one protecting agent comprises at least one of: one or more surfactants, one or more acids, or one or more polar polymers.
- D. The method of embodiment B, wherein the at least one protecting agent comprises polyvinylpyrrolidinone.
- E. The method of embodiment B, further comprising inerting the at least one protecting agent.

- F. The method of embodiment A, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.
- G. The method of embodiment A, wherein the at least one first reducible metal ion comprises at least one ion of an element from IUPAC Group 11.
- 5 H. The method of embodiment A, wherein the at least one first reducible metal ion comprises at least one ion of silver.
- J. The method of embodiment A, wherein the at least one first compound comprises silver nitrate.
- K. The method of embodiment A, wherein the at least one second metal or
- 10 metal ion comprises manganese or an ion of manganese.
- L. The method of embodiment A, wherein the at least one second compound comprises at least one salt of said at least one second metal or metal ion.
- M. The method of embodiment L, wherein the at least one salt comprises at least one chloride.
- 15 N. The method of embodiment A, wherein the at least one solvent comprises at least one polyol.
- P. The method of embodiment A, wherein the at least one solvent comprises at least one of: ethylene glycol, propylene glycol, glycerol, one or more sugars, or one or more carbohydrates.
- 20 Q. The method of embodiment A, wherein the composition has a ratio of the total moles of the at least one second metal or metal to the moles of the at least one first reducible metal ion from about 0.0001 to about 0.1.
- R. The method of embodiment A, wherein the reduction is carried out at one or more temperatures from about 120 °C to about 190 °C.
- 25 S. The method of embodiment A, further comprising inerting one or more of: the composition, the at least one compound comprising at least one first reducible metal ion, the at least one second metal or metal ion, or the at least one solvent.
- T. The at least one first metal produced according to the method of embodiment A.
- 30 U. At least one article comprising the at least one first metal produced according to the method of embodiment A.
- V. The at least one article of embodiment U, wherein the at least one first

metal comprises one or more nanowires, nanocubes, nanorods, nanopyrramids, or nanotubes.

W. The at least one article of embodiment U, wherein the at least one first metal comprises at least one object having an average diameter of between about
5 10 nm and about 500 nm.

X. The at least one article of embodiment U, wherein the at least one first metal comprises at least one object having an aspect ratio from about 50 to about 10,000.

Y. At least one metal nanowire with an average diameter of between about 10
10 nm and about 150 nm, and with an aspect ratio from about 50 to about 10,000.

Z. The nanowire of embodiment Y, wherein the at least one metal comprises at least one coinage metal.

AA. The nanowire of embodiment Y, wherein the at least one metal comprises at least one element of IUPAC Group 11.

15 AB. The nanowire of embodiment Y, wherein the at least one metal comprises silver.

AC. At least one article comprising the at least one metal nanowire of embodiment Y.

U.S. Provisional Application No. 61/423,744, filed December 16,
20 2010, entitled METAL ION CATALYSIS OF METAL ION REDUCTION, METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 27 non-limiting exemplary embodiments:

AD. A method comprising:
25 providing a composition comprising:
at least one first compound comprising at least one first reducible metal ion,
at least one second compound comprising at least one second metal or metal ion differing in atomic number from said at least one first reducible
30 metal, said at least one second metal or metal ion comprising at least one element having an oxidation state of 4+ or greater, and
at least one solvent; and

reducing the at least one first reducible metal ion to at least one first metal.

AE. The method of embodiment AD, wherein the composition further comprises at least one protecting agent.

AF. The method of embodiment AE, wherein the at least one protecting agent
5 comprises at least one of: one or more surfactants, one or more acids, or one or more polar polymers.

AG. The method of embodiment AE, wherein the at least one protecting agent comprises polyvinylpyrrolidinone.

AH. The method of embodiment AE, further comprising inerting the at least
10 one protecting agent.

AJ. The method of embodiment AD, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.

AK. The method of embodiment AD, wherein the at least one first reducible metal ion comprises at least one ion of an element from IUPAC Group 11.

15 AL. The method of embodiment AD, wherein the at least one first reducible metal ion comprises at least one ion of silver.

AM. The method of embodiment AD, wherein the at least one first compound comprises silver nitrate.

AN. The method of embodiment AD, wherein the at least one second metal or
20 metal ion comprises niobium or an ion of niobium.

AP. The method of embodiment AD, wherein the at least one second compound comprises at least one salt of said at least one second metal or metal ion.

AQ. The method of embodiment AP, wherein the at least one salt comprises at
25 least one chloride.

AR. The method of embodiment AD, wherein the at least one solvent comprises at least one polyol.

AS. The method of embodiment AD, wherein the at least one solvent comprises at least one of: ethylene glycol, propylene glycol, glycerol, one or
30 more sugars, or one or more carbohydrates.

- AT. The method of embodiment AD, wherein the composition has a ratio of the total moles of the at least one second metal or metal to the moles of the at least one first reducible metal ion from about 0.0001 to about 0.1.
- AU. The method of embodiment AD, wherein the reduction is carried out at
5 one or more temperatures from about 120 °C to about 190 °C.
- AV. The method of embodiment AD, further comprising inerting one or more of: the composition, the at least one compound comprising at least one first reducible metal ion, the at least one second metal or metal ion, or the at least one solvent.
- 10 AW. The at least one first metal produced according to the method of embodiment AD.
- AX. At least one article comprising the at least one first metal produced according to the method of embodiment AD.
- AY. The at least one article of embodiment AX, wherein the at least one first
15 metal comprises one or more nanowires, nanocubes, nanorods, nanopyramids, or nanotubes.
- AZ. The at least one article of embodiment AX, wherein the at least one first metal comprises at least one object having an average diameter of between about 10 nm and about 500 nm.
- 20 BA. The at least one article of embodiment AX, wherein the at least one first metal comprises at least one object having an aspect ratio from about 50 to about 10,000.
- BB. At least one metal nanowire with an average diameter of between about 10 nm and about 150 nm, and with an aspect ratio from about 50 to about 10,000.
- 25 BC. The nanowire of embodiment BB, wherein the at least one metal comprises at least one coinage metal.
- BD. The nanowire of embodiment BB, wherein the at least one metal comprises at least one element of IUPAC Group 11.
- BE. The nanowire of embodiment BB, wherein the at least one metal
30 comprises silver.
- BF. At least one article comprising the at least one metal nanowire of embodiment BB.

U.S. Provisional Application No. 61/488,824, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 27 non-limiting exemplary embodiments:

- 5 BG. A method comprising:
providing a composition comprising:
at least one first compound comprising at least one first reducible metal ion,
at least one second compound comprising at least one second metal
10 or metal ion differing in atomic number from said at least one first reducible metal, said at least one second metal or metal ion comprising at least one element from IUPAC Group 7, and
at least one solvent; and
reducing the at least one first reducible metal ion to at least one first metal.
- 15 BH. The method of embodiment BG, wherein the composition further comprises at least one protecting agent.
- BJ. The method of embodiment BH, wherein the at least one protecting agent comprises at least one of: one or more surfactants, one or more acids, or one or more polar polymers.
- 20 BK. The method of embodiment BH, wherein the at least one protecting agent comprises polyvinylpyrrolidinone.
- BL. The method of embodiment BH, further comprising inerting the at least one protecting agent.
- BM. The method of embodiment BG, wherein the at least one first reducible
25 metal ion comprises at least one coinage metal ion.
- BN. The method of embodiment BG, wherein the at least one first reducible metal ion comprises at least one ion of an element from IUPAC Group 11.
- BP. The method of embodiment BG, wherein the at least one first reducible metal ion comprises at least one ion of silver.
- 30 BQ. The method of embodiment BG, wherein the at least one first compound comprises silver nitrate.
- BR. The method of embodiment BG, wherein the at least one second metal or

metal ion comprises rhenium or an ion of rhenium.

BS. The method of embodiment BG, wherein the at least one second compound comprises at least one chloride.

BT. The method of embodiment BG, wherein the at least one second
5 compound comprises rhenium(III) chloride.

BU. The method of embodiment BG, wherein the at least one solvent comprises at least one polyol.

BV. The method of embodiment BG, wherein the at least one solvent comprises at least one of: ethylene glycol, propylene glycol, glycerol, one or
10 more sugars, or one or more carbohydrates.

BW. The method of embodiment BG, wherein the composition has a ratio of the total moles of the at least one second metal or metal ion to the total moles of the at least one first reducible metal ion from about 0.0001 to about 0.1.

BX. The method of embodiment BG, wherein the reduction is carried out at
15 one or more temperatures from about 120 °C to about 190 °C.

BY. The method of embodiment BG, further comprising inerting one or more of: the composition, the at least one compound comprising the at least one first reducible metal ion, the at least one second metal or metal ion, or the at least one solvent.

20 BZ. The at least one first metal produced according to the method of embodiment BG.

CA. At least one article comprising the at least one first metal produced according to the method of embodiment BG.

CB. The at least one article of embodiment CA, wherein the at least one first
25 metal comprises one or more nanowires, nanocubes, nanorods, nanopyramids, or nanotubes.

CC. The at least one article of embodiment CA, wherein the at least one first metal comprises at least one object having an average diameter of between about 10 nm and about 500 nm.

30 CD. The at least one article of embodiment CA, wherein the at least one first metal comprises at least one object having an aspect ratio from about 50 to about 10,000.

CE. At least one metal nanowire with an average diameter of between about 10 nm and about 150 nm, and with an aspect ratio from about 50 to about 10,000.

CF. The nanowire of embodiment CE, wherein the at least one metal nanowire comprises at least one coinage metal.

5 CG. The nanowire of embodiment CE, wherein the at least one metal nanowire comprises at least one element of IUPAC Group 11.

CH. The nanowire of embodiment CE, wherein the at least one metal nanowire comprises silver.

CJ. At least one article comprising the at least one metal nanowire of
10 embodiment CE.

U.S. Provisional Application No. 61/488,834, filed May 23, 2011,
entitled METAL ION CATALYSIS OF METAL ION REDUCTION,
METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated
by reference in its entirety, disclosed the following 27 non-limiting exemplary
15 embodiments:

CK. A method comprising:

providing a composition comprising:

at least one first compound comprising at least one first reducible
metal ion,

20 at least one second compound comprising at least one second metal
or metal ion differing in atomic number from said at least one first reducible
metal, said at least one second metal or metal ion comprising at least one element
from IUPAC Group 5, and

at least one solvent; and

25 reducing the at least one first reducible metal ion to at least one first metal.

CL. The method of embodiment CK, wherein the composition further
comprises at least one protecting agent.

CM. The method of embodiment CL, wherein the at least one protecting agent
comprises at least one of: one or more surfactants, one or more acids, or one or
30 more polar polymers.

CN. The method of embodiment CL, wherein the at least one protecting agent
comprises polyvinylpyrrolidinone.

- CP. The method of embodiment CL, further comprising inerting the at least one protecting agent.
- CQ. The method of embodiment CK, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.
- 5 CR. The method of embodiment CK, wherein the at least one first reducible metal ion comprises at least one ion of an element from IUPAC Group 11.
- CS. The method of embodiment CK, wherein the at least one first reducible metal ion comprises at least one ion of silver.
- CT. The method of embodiment CK, wherein the at least one first compound
10 comprises silver nitrate.
- CU. The method of embodiment CK, wherein the at least one second metal or metal ion comprises vanadium or an ion of vanadium.
- CV. The method of embodiment CK, wherein the at least one second compound comprises at least one salt of said at least one second metal or metal
15 ion.
- CW. The method of embodiment CV, wherein the at least one salt comprises at least one chloride.
- CX. The method of embodiment CK, wherein the at least one solvent comprises at least one polyol.
- 20 CY. The method of embodiment CK, wherein the at least one solvent comprises at least one of: ethylene glycol, propylene glycol, glycerol, one or more sugars, or one or more carbohydrates.
- CZ. The method of embodiment CK, wherein the composition has a ratio of the total moles of the at least one second metal or metal ion to the total moles of the at
25 least one first reducible metal ion from about 0.0001 to about 0.1.
- DA. The method of embodiment CK, wherein the reduction is carried out at one or more temperatures from about 120 °C to about 190 °C.
- DB. The method of embodiment CK, further comprising inerting one or more of: the composition, the at least one compound comprising the at least one first
30 reducible metal ion, the at least one second metal or metal ion, or the at least one solvent.
- DC. The at least one first metal produced according to the method of

embodiment CK.

DD. At least one article comprising the at least one first metal produced according to the method of embodiment CK.

DE. The at least one article of embodiment DD, wherein the at least one first
5 metal comprises one or more nanowires, nanocubes, nanorods, nanopyrramids, or nanotubes.

DF. The at least one article of embodiment DD, wherein the at least one first metal comprises at least one object having an average diameter of between about 10 nm and about 500 nm.

10 DG. The at least one article of embodiment DD, wherein the at least one first metal comprises at least one object having an aspect ratio from about 50 to about 10,000.

DH. At least one metal nanowire with an average diameter of between about 10 nm and about 150 nm, and with an aspect ratio from about 50 to about 10,000.

15 DJ. The nanowire of embodiment DH, wherein the at least one metal nanowire comprises at least one coinage metal.

DK. The nanowire of embodiment DH, wherein the at least one metal nanowire comprises at least one element of IUPAC Group 11.

DL. The nanowire of embodiment DH, wherein the at least one metal nanowire
20 comprises silver.

DM. At least one article comprising the at least one metal nanowire of embodiment DH.

U.S. Provisional Application No. 61/488,840, filed May 23, 2011, entitled METAL ION CATALYSIS OF METAL ION REDUCTION,
25 METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 27 non-limiting exemplary embodiments.

DN. A method comprising:

providing a composition comprising:

30 at least one first compound comprising at least one first reducible metal ion,

at least one second compound comprising at least one second metal

- or metal ion differing in atomic number from said at least one first reducible metal, said at least one second metal or metal ion comprising at least one element from IUPAC Group 3, and
- at least one solvent; and
- 5 reducing the at least one first reducible metal ion to at least one first metal.
- DP. The method of embodiment DN, wherein the composition further comprises at least one protecting agent.
- DQ. The method of embodiment DP, wherein the at least one protecting agent comprises at least one of: one or more surfactants, one or more acids, or one or
- 10 more polar polymers.
- DR. The method of embodiment DP, wherein the at least one protecting agent comprises polyvinylpyrrolidinone.
- DS. The method of embodiment DP, further comprising inerting the at least one protecting agent.
- 15 DT. The method of embodiment DN, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.
- DU. The method of embodiment DN, wherein the at least one first reducible metal ion comprises at least one ion of an element from IUPAC Group 11.
- DV. The method of embodiment DN, wherein the at least one first reducible
- 20 metal ion comprises at least one ion of silver.
- DW. The method of embodiment DN, wherein the at least one first compound comprises silver nitrate.
- DX. The method of embodiment DN, wherein the at least one second metal or metal ion comprises scandium or an ion of scandium.
- 25 DY. The method of embodiment DN, wherein the at least one second compound comprises at least one salt of said at least one second metal or metal ion.
- DZ. The method of embodiment 11, wherein the at least one salt comprises at least one chloride.
- 30 EA. The method of embodiment DN, wherein the at least one solvent comprises at least one polyol.
- EB. The method of embodiment DN, wherein the at least one solvent

comprises at least one of: ethylene glycol, propylene glycol, glycerol, one or more sugars, or one or more carbohydrates.

EC. The method of embodiment DN, wherein the composition has a ratio of the total moles of the at least one second metal or metal ion to the total moles of the at least one first reducible metal ion from about 0.0001 to about 0.1.

ED. The method of embodiment DN, wherein the reduction is carried out at one or more temperatures from about 120 °C to about 190 °C.

EE. The method of embodiment DN, further comprising inerting one or more of: the composition, the at least one compound comprising the at least one first reducible metal ion, the at least one second metal or metal ion, or the at least one solvent.

EF. The at least one first metal produced according to the method of embodiment DN.

EG. At least one article comprising the at least one first metal produced according to the method of embodiment DN.

EH. The at least one article of embodiment EG, wherein the at least one first metal comprises one or more nanowires, nanocubes, nanorods, nanopyramids, or nanotubes.

EJ. The at least one article of embodiment EG, wherein the at least one first metal comprises at least one object having an average diameter of between about 10 nm and about 500 nm.

EK. The at least one article of embodiment EG, wherein the at least one first metal comprises at least one object having an aspect ratio from about 50 to about 10,000.

EL. At least one metal nanowire with an average diameter of between about 10 nm and about 150 nm, and with an aspect ratio from about 50 to about 10,000.

EM. The nanowire of embodiment EL, wherein the at least one metal nanowire comprises at least one coinage metal.

EN. The nanowire of embodiment EL, wherein the at least one metal nanowire comprises at least one element of IUPAC Group 11.

EP. The nanowire of embodiment EL, wherein the at least one metal nanowire comprises silver.

EQ. At least one article comprising the at least one metal nanowire of embodiment EL.

U.S. Provisional Application No. 61/488,880, filed May 23, 2011, entitled METAL ION CATALYSIS OF METAL ION REDUCTION,
5 METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 27 non-limiting exemplary embodiments:

ER. A method comprising:

providing a composition comprising:

10 at least one first compound comprising at least one first reducible metal ion,

at least one second compound comprising at least one second metal ion differing in atomic number from said at least one first reducible metal, said at least one second metal ion comprising at least one element from IUPAC Group 4,

15 and

at least one solvent; and

reducing the at least one first reducible metal ion to at least one first metal.

ES. The method of embodiment ER, wherein the composition further comprises at least one protecting agent.

20 ET. The method of embodiment ES, wherein the at least one protecting agent comprises at least one of: one or more surfactants, one or more acids, or one or more polar polymers.

EU. The method of embodiment ES, wherein the at least one protecting agent comprises polyvinylpyrrolidinone.

25 EV. The method of embodiment ES, further comprising inerting the at least one protecting agent.

EW. The method of embodiment ER, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.

30 EX. The method of embodiment ER, wherein the at least one first reducible metal ion comprises at least one ion of an element from IUPAC Group 11.

EY. The method of embodiment ER, wherein the at least one first reducible metal ion comprises at least one ion of silver.

- EZ. The method of embodiment ER, wherein the at least one first compound comprises silver nitrate.
- FA. The method of embodiment ER, wherein the at least one second metal ion comprises an ion of titanium.
- 5 FB. The method of embodiment ER, wherein the at least one second compound comprises at least one chloride.
- FC. The method of embodiment ER, wherein the at least one second compound comprises titanium(IV) chloride.
- FD. The method of embodiment ER, wherein the at least one solvent comprises
10 at least one polyol.
- FE. The method of embodiment ER, wherein the at least one solvent comprises at least one of: ethylene glycol, propylene glycol, glycerol, one or more sugars, or one or more carbohydrates.
- FF. The method of embodiment ER, wherein the composition has a ratio of the
15 total moles of the at least one second metal or metal ion to the total moles of the at least one first reducible metal ion from about 0.0001 to about 0.1.
- FG. The method of embodiment ER, wherein the reduction is carried out at one or more temperatures from about 120 °C to about 190 °C.
- FH. The method of embodiment ER, further comprising inerting one or more
20 of: the composition, the at least one compound comprising the at least one first reducible metal ion, the at least one second metal or metal ion, or the at least one solvent.
- FJ. The at least one first metal produced according to the method of embodiment ER.
- 25 FK. At least one article comprising the at least one first metal produced according to the method of embodiment ER.
- FL. The at least one article of embodiment FK, wherein the at least one first metal comprises one or more nanowires, nanocubes, nanorods, nanopyramids, or nanotubes.
- 30 FM. The at least one article of embodiment FK, wherein the at least one first metal comprises at least one object having an average diameter of between about 10 nm and about 500 nm.

FN. The at least one article of embodiment FK, wherein the at least one first metal comprises at least one object having an aspect ratio from about 50 to about 10,000.

5 FP. At least one metal nanowire with an average diameter of between about 10 nm and about 150 nm, and with an aspect ratio from about 50 to about 10,000.

FQ. The nanowire of embodiment FP, wherein the at least one metal nanowire comprises at least one coinage metal.

FR. The nanowire of embodiment FP, wherein the at least one metal nanowire comprises at least one element of IUPAC Group 11.

10 FS. The nanowire of embodiment FP, wherein the at least one metal nanowire comprises silver.

FT. At least one article comprising the at least one metal nanowire of embodiment FP.

U.S. Provisional Application No. 61/488,945, filed May 23, 2011,
15 entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 16 non-limiting exemplary embodiments:

FU. A method comprising:

20 providing a composition comprising at least one metal oxide compound; and

reducing at least one first metal ion to at least one first metal in the presence of the metal oxide compound.

FV. The method according to embodiment FU, wherein the at least one metal oxide compound comprises at least one metal oxide halide compound.

25 FW. The method according to embodiment FU, wherein the at least one metal oxide compound comprises at least one metal oxide chloride compound.

FX. The method according to embodiment FU, wherein the at least one metal oxide compound comprises at least one transition metal oxide compound.

30 FY. The method according to embodiment FU, wherein the at least one metal oxide compound comprises at least one transition metal halide compound.

FZ. The method according to embodiment FU, wherein the at least one metal oxide compound comprises at least one transition metal chloride compound.

- GA. The method according to embodiment FU, wherein the at least one metal oxide compound comprises at least one transition metal.
- GB. The method according to embodiment FU, wherein the at least one metal oxide compound comprises at least one molybdenum, tungsten, vanadium, or zirconium atom.
- GC. The method according to embodiment FU, wherein the at least one metal oxide compound comprises at least one of MoO_2Cl_2 , MoOCl_4 , WO_2Cl_2 , WOCl_4 , VOCl_3 , or ZrOCl_2 .
- GD. The method according to embodiment FU, wherein the at least one metal oxide compound comprises molybdenum(IV) dichloride dioxide.
- GE. The method according to embodiment FU, wherein the at least one first metal ion comprises at least one element from IUPAC Group 11.
- GF. The method according to embodiment FU, wherein the at least one first metal ion comprises at least one coinage metal ion.
- GG. The method according to embodiment FU, wherein the at least one first metal ion comprises at least one silver ion.
- GH. The at least one first metal product produced according to the method of embodiment FU.
- GJ. The at least one first metal product according to embodiment GH, said at least one product comprising at least one nanowire.
- GK. An article comprising the at least one first metal product according to embodiment GH.
- U.S. Provisional Application No. 61/488,977, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 20 non-limiting exemplary embodiments:
- GL. A method comprising:
- providing at least one first composition comprising at least one first reducible metal ion, and
- reducing the at least one first reducible metal ion to at least one first metal in the presence of at least one second metal ion comprising at least one IUPAC Group 6 element.

- GM. The method according to embodiment GL, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.
- GN. The method according to embodiment GL, wherein the at least one first reducible metal ion comprises at least one ion of an IUPAC Group 11 element.
- 5 GP. The method according to embodiment GL, wherein the at least one first reducible metal ion comprises at least one silver ion.
- GQ. The method according to embodiment GL, wherein the at least one composition comprises silver nitrate.
- GR. The method according to embodiment GL, wherein the at least one second
10 metal ion comprises a tungsten ion.
- GS. The method according to embodiment GL, wherein the at least one second metal ion comprises tungsten in its +4 oxidation state.
- GT. The method according to embodiment GL, wherein the reduction occurs in the presence of at least one protecting agent.
- 15 GU. The method according to embodiment GL, wherein the reduction occurs in the presence of at least one polyol.
- GV. A product comprising the at least one first metal produced by the method according to embodiment GL.
- GW. The product according to embodiment GV comprising at least one metal
20 nanowire.
- GX. An article comprising the product according to embodiment GV.
- GY. A composition comprising at least one metal nanowire, at least one chloride ion, and at least one ion of an IUPAC Group 6 element.
- GZ. The composition according to embodiment GY, wherein the at least one
25 metal nanowire comprises at least one silver nanowire.
- HA. The composition according to embodiment GY, wherein the at least one metal nanowire comprises an average diameter between about 10 nm and about 500 nm.
- HB. The composition according to embodiment GY, wherein the at least one
30 metal nanowire comprises an aspect ratio between about 50 and about 10,000.
- HC. The composition according to embodiment GY, wherein the at least one metal nanowire comprises an average diameter between about 10 nm and about

150 nm, and an aspect ratio between about 50 and about 10,000.

HD. A product comprising the at least one metal nanowire of the composition of embodiment GY.

HE. An article comprising the at least one product according to embodiment

5 HD.

HF. The article according to embodiment HE comprising at least one of an electronic display, a touch screen, a portable telephone, a cellular telephone, a computer display, a laptop computer, a tablet computer, a point-of-purchase kiosk, a music player, a television, an electronic game, an electronic book reader, a
10 transparent electrode, a solar cell, a light emitting diode, an electronic device, a medical imaging device, or a medical imaging medium.

U.S. Provisional Application No. 61/488,983, filed May 23, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed
15 the following 20 non-limiting exemplary embodiments:

HG. A method comprising:

providing at least one first composition comprising at least one first reducible metal ion, and

20 reducing the at least one first reducible metal ion to at least one first metal in the presence of at least one second metal ion comprising at least one IUPAC Group 6 element.

HH. The method according to embodiment HG, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.

HJ. The method according to embodiment HG, wherein the at least one first
25 reducible metal ion comprises at least one ion of an IUPAC Group 11 element.

HK. The method according to embodiment HG, wherein the at least one first reducible metal ion comprises at least one silver ion.

HL. The method according to embodiment HG, wherein the at least one composition comprises silver nitrate.

30 HM. The method according to embodiment HG, wherein the at least one second metal ion comprises a chromium ion.

HN. The method according to embodiment HG, wherein the at least one second

metal ion comprises chromium in its +3 oxidation state.

HP. The method according to embodiment HG, wherein the reduction occurs in the presence of at least one protecting agent.

HQ. The method according to embodiment HG, wherein the reduction occurs in
5 the presence of at least one polyol.

HR. A product comprising the at least one first metal produced by the method according to embodiment HG.

HS. The product according to embodiment HR comprising at least one metal nanowire.

10 HT. An article comprising the product according to embodiment HR.

HU. A composition comprising at least one metal nanowire, at least one chloride ion, and at least one ion of an IUPAC Group 6 element.

HV. The composition according to embodiment HU, wherein the at least one metal nanowire comprises at least one silver nanowire.

15 HW. The composition according to embodiment HU, wherein the at least one metal nanowire comprises an average diameter between about 10 nm and about 500 nm.

HX. The composition according to embodiment HU, wherein the at least one metal nanowire comprises an aspect ratio between about 50 and about 10,000.

20 HY. The composition according to embodiment HU, wherein the at least one metal nanowire comprises an average diameter between about 10 nm and about 150 nm, and an aspect ratio between about 50 and about 10,000.

HZ. A product comprising the at least one metal nanowire of the composition of embodiment HU.

25 JA. An article comprising the at least one product according to embodiment HZ.

JB. The article according to embodiment JA comprising at least one of an electronic display, a touch screen, a portable telephone, a cellular telephone, a computer display, a laptop computer, a tablet computer, a point-of-purchase kiosk,
30 a music player, a television, an electronic game, an electronic book reader, a transparent electrode, a solar cell, a light emitting diode, an electronic device, a medical imaging device, or a medical imaging medium.

U.S. Provisional Application No. 61/494,072, filed June 7, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, which is incorporated by reference in its entirety, disclosed the following 20 non-limiting exemplary embodiments:

- 5 JC. A method comprising:
providing at least one first composition comprising at least one first reducible metal ion, and
reducing the at least one first reducible metal ion to at least one first metal in the presence of at least one second metal ion comprising at least one lanthanide
10 element or actinide element.
- JD. The method according to embodiment JC, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.
- JE. The method according to embodiment JC, wherein the at least one first reducible metal ion comprises at least one ion of an IUPAC Group 11 element.
- 15 JF. The method according to embodiment JC, wherein the at least one first reducible metal ion comprises at least one silver ion.
- JK. The method according to embodiment JC, wherein the at least one composition comprises silver nitrate.
- JL. The method according to embodiment JC, wherein the at least one second
20 metal ion comprises at least one lanthanum ion or actinide ion.
- JM. The method according to embodiment JC, wherein the at least one second metal ion comprises lanthanum in its +3 oxidation state.
- JN. The method according to embodiment JC, wherein the reduction occurs in the presence of at least one protecting agent.
- 25 JP. The method according to embodiment JC, wherein the reduction occurs in the presence of at least one polyol.
- JQ. A product comprising the at least one first metal produced by the method according to embodiment JC.
- JR. The product according to embodiment JQ comprising at least one metal
30 nanowire.
- JS. An article comprising the product according to embodiment JQ.
- JT. A composition comprising at least one metal nanowire, at least one

chloride ion, and at least one ion of a lanthanide element or at least one ion of an actinide element.

JU. The composition according to embodiment JT, wherein the at least one metal nanowire comprises at least one silver nanowire.

- 5 JV. The composition according to embodiment JT, wherein the at least one metal nanowire comprises an average diameter between about 10 nm and about 500 nm.

JW. The composition according to embodiment JT, wherein the at least one metal nanowire comprises an aspect ratio between about 50 and about 10,000.

- 10 JX. The composition according to embodiment JT, wherein the at least one metal nanowire comprises an average diameter between about 10 nm and about 150 nm, and an aspect ratio between about 50 and about 10,000.

JY. A product comprising the at least one metal nanowire of the composition of embodiment JT.

- 15 JZ. An article comprising the at least one product according to embodiment 18.

- KA. The article according to embodiment JZ comprising at least one of an electronic display, a touch screen, a portable telephone, a cellular telephone, a computer display, a laptop computer, a tablet computer, a point-of-purchase kiosk,
20 a music player, a television, an electronic game, an electronic book reader, a transparent electrode, a solar cell, a light emitting diode, an electronic device, a medical imaging device, or a medical imaging medium.

- U.S. Provisional Application No. 61/522,741, filed August 12, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS,
25 AND ARTICLES, which is incorporated by reference in its entirety, disclosed the following 20 non-limiting exemplary embodiments:

KB. A method comprising:

providing at least one first composition comprising at least one first reducible metal ion, and

- 30 reducing the at least one first reducible metal ion to at least one first metal in the presence of at least one second metal ion comprising at least one element from IUPAC Group 3.

- KC. The method according to embodiment KB, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.
- KD. The method according to embodiment KB, wherein the at least one first reducible metal ion comprises at least one ion of an IUPAC Group 11 element.
- 5 KE. The method according to embodiment KB, wherein the at least one first reducible metal ion comprises at least one silver ion.
- KF. The method according to embodiment KB, wherein the at least one composition comprises silver nitrate.
- KG. The method according to embodiment KB, wherein the at least one second
- 10 metal ion comprises at least one yttrium ion.
- KH. The method according to embodiment KB, wherein the at least one second metal ion comprises yttrium in its +3 oxidation state.
- KJ. The method according to embodiment KB, wherein the reduction occurs in the presence of at least one protecting agent.
- 15 KK. The method according to embodiment KB, wherein the reduction occurs in the presence of at least one polyol.
- KL. A product comprising the at least one first metal produced by the method according to embodiment KB.
- KM. The product according to embodiment KL comprising at least one metal
- 20 nanowire.
- KN. An article comprising the product according to embodiment KL.
- KP. A composition comprising at least one metal nanowire, at least one chloride ion, and at least one ion of an IUPAC Group 3 element.
- KQ. The composition according to embodiment KP, wherein the at least one
- 25 metal nanowire comprises at least one silver nanowire.
- KR. The composition according to embodiment KP, wherein the at least one metal nanowire comprises an average diameter between about 10 nm and about 500 nm.
- KT. The composition according to embodiment KP, wherein the at least one
- 30 metal nanowire comprises an aspect ratio between about 50 and about 10,000.
- KU. The composition according to embodiment KP, wherein the at least one metal nanowire comprises an average diameter between about 10 nm and about

150 nm, and an aspect ratio between about 50 and about 10,000.

KV. A product comprising the at least one metal nanowire of the composition of embodiment KP.

KW. An article comprising the at least one product according to embodiment

5 KV.

KX. The article according to embodiment KW comprising at least one of an electronic display, a touch screen, a portable telephone, a cellular telephone, a computer display, a laptop computer, a tablet computer, a point-of-purchase kiosk, a music player, a television, an electronic game, an electronic book reader, a
10 transparent electrode, a solar cell, a light emitting diode, an electronic device, a medical imaging device, or a medical imaging medium.

U.S. Provisional Application No. 61/523,977, filed August 16, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS, AND ARTICLES, which is hereby incorporated by reference in its entirety,
15 disclosed the following 27 non-limiting exemplary embodiments:

KY. A method comprising:

providing a composition comprising:

at least one first compound comprising at least one first reducible metal ion,

20 at least one second compound comprising at least one second metal ion differing in atomic number from said at least one first reducible metal, said at least one second metal ion comprising at least one element from IUPAC Group 4, and

at least one solvent; and

25 reducing the at least one first reducible metal ion to at least one first metal.

KZ. The method of embodiment KY, wherein the composition further comprises at least one protecting agent.

LA. The method of embodiment KZ, wherein the at least one protecting agent comprises at least one of: one or more surfactants, one or more acids, or one or
30 more polar polymers.

LB. The method of embodiment KZ, wherein the at least one protecting agent comprises polyvinylpyrrolidinone.

- LC. The method of embodiment KZ, further comprising inerting the at least one protecting agent.
- LD. The method of embodiment KY, wherein the at least one first reducible metal ion comprises at least one coinage metal ion.
- 5 LE. The method of embodiment KY, wherein the at least one first reducible metal ion comprises at least one ion of an element from IUPAC Group 11.
- LF. The method of embodiment KY, wherein the at least one first reducible metal ion comprises at least one ion of silver.
- LG. The method of embodiment KY, wherein the at least one first compound
10 comprises silver nitrate.
- LH. The method of embodiment KY, wherein the at least one second metal ion comprises an ion of zirconium or hafnium.
- LJ. The method of embodiment KY, wherein the at least one second compound comprises at least one chloride.
- 15 LK. The method of embodiment KY, wherein the at least one second compound comprises at least one of zirconium tetrachloride bis(tetrahydrofuran) adduct or hafnium tetrachloride bis(tetrahydrofuran) adduct.
- LM. The method of embodiment KY, wherein the at least one solvent comprises at least one polyol.
- 20 LN. The method of embodiment KY, wherein the at least one solvent comprises at least one of: ethylene glycol, propylene glycol, glycerol, one or more sugars, or one or more carbohydrates.
- LP. The method of embodiment KY, wherein the composition has a ratio of the total moles of the at least one second metal or metal ion to the total moles of
25 the at least one first reducible metal ion from about 0.0001 to about 0.1.
- LQ. The method of embodiment KY, wherein the reduction is carried out at one or more temperatures from about 120 °C to about 190 °C.
- LR. The method of embodiment KY, further comprising inerting one or more of: the composition, the at least one compound comprising the at least one first
30 reducible metal ion, the at least one second metal or metal ion, or the at least one solvent.
- LS. The at least one first metal produced according to the method of

embodiment KY.

LT. At least one article comprising the at least one first metal produced according to the method of embodiment KY.

LU. The at least one article of embodiment LT, wherein the at least one first
5 metal comprises one or more nanowires, nanocubes, nanorods, nanopyramids, or nanotubes.

LV. The at least one article of embodiment LT, wherein the at least one first metal comprises at least one object having an average diameter of between about 10 nm and about 500 nm.

10 LX. The at least one article of embodiment LT, wherein the at least one first metal comprises at least one object having an aspect ratio from about 50 to about 10,000.

LY. At least one metal nanowire with an average diameter of between about 10 nm and about 150 nm, and with an aspect ratio from about 50 to about 10,000.

15 LZ. The nanowire of embodiment LY, wherein the at least one metal nanowire comprises at least one coinage metal.

MA. The nanowire of embodiment LY, wherein the at least one metal nanowire comprises at least one element of IUPAC Group 11.

MB. The nanowire of embodiment LY, wherein the at least one metal nanowire
20 comprises silver.

MC. At least one article comprising the at least one metal nanowire of embodiment LY.

U.S. Provisional Application No. 61/523,987, filed August 16, 2011, entitled NANOWIRE PREPARATION METHODS, COMPOSITIONS,
25 AND ARTICLES, which is hereby incorporated by reference in its entirety, disclosed the following 27 non-limiting exemplary embodiments:

MD. A method comprising:

providing a composition comprising:

30 at least one first compound comprising at least one first reducible metal ion,

at least one second compound comprising at least one second metal ion differing in atomic number from said at least one first reducible metal, said at

- least one second metal ion comprising at least one element from IUPAC Group 5,
and
at least one solvent; and
reducing the at least one first reducible metal ion to at least one first metal.
- 5 ME. The method of embodiment MD, wherein the composition further
comprises at least one protecting agent.
MF. The method of embodiment ME, wherein the at least one protecting agent
comprises at least one of: one or more surfactants, one or more acids, or one or
more polar polymers.
- 10 MG. The method of embodiment ME, wherein the at least one protecting agent
comprises polyvinylpyrrolidinone.
MH. The method of embodiment ME, further comprising inerting the at least
one protecting agent.
MJ. The method of embodiment MD, wherein the at least one first reducible
15 metal ion comprises at least one coinage metal ion.
MK. The method of embodiment MD, wherein the at least one first reducible
metal ion comprises at least one ion of an element from IUPAC Group 11.
ML. The method of embodiment MD, wherein the at least one first reducible
metal ion comprises at least one ion of silver.
- 20 MM. The method of embodiment MD, wherein the at least one first compound
comprises silver nitrate.
MN. The method of embodiment MD, wherein the at least one second metal ion
comprises an ion of tantalum.
MP. The method of embodiment MD, wherein the at least one second
25 compound comprises at least one chloride.
MQ. The method of embodiment MD, wherein the at least one second
compound comprises tantalum (V) chloride.
MR. The method of embodiment MD, wherein the at least one solvent
comprises at least one polyol.
- 30 MS. The method of embodiment MD, wherein the at least one solvent
comprises at least one of: ethylene glycol, propylene glycol, glycerol, one or
more sugars, or one or more carbohydrates.

- MT. The method of embodiment MD, wherein the composition has a ratio of the total moles of the at least one second metal or metal ion to the total moles of the at least one first reducible metal ion from about 0.0001 to about 0.1.
- MU. The method of embodiment MD, wherein the reduction is carried out at
5 one or more temperatures from about 120 °C to about 190 °C.
- MV. The method of embodiment MD, further comprising inerting one or more of: the composition, the at least one compound comprising the at least one first reducible metal ion, the at least one second metal or metal ion, or the at least one solvent.
- 10 MU. The at least one first metal produced according to the method of embodiment MD.
- MV. At least one article comprising the at least one first metal produced according to the method of embodiment MD.
- MW. The at least one article of embodiment MV, wherein the at least one first
15 metal comprises one or more nanowires, nanocubes, nanorods, nanopyramids, or nanotubes.
- MX. The at least one article of embodiment MV, wherein the at least one first metal comprises at least one object having an average diameter of between about 10 nm and about 500 nm.
- 20 MY. The at least one article of embodiment MV, wherein the at least one first metal comprises at least one object having an aspect ratio from about 50 to about 10,000.
- MZ. At least one metal nanowire with an average diameter of between about 10 nm and about 150 nm, and with an aspect ratio from about 50 to about 10,000.
- 25 NA. The nanowire of embodiment MZ, wherein the at least one metal nanowire comprises at least one coinage metal.
- NB. The nanowire of embodiment MZ, wherein the at least one metal nanowire comprises at least one element of IUPAC Group 11.
- NC. The nanowire of embodiment MZ, wherein the at least one metal nanowire
30 comprises silver.
- ND. At least one article comprising the at least one metal nanowire of embodiment MZ.

EXAMPLES

Example 1

To a 500 mL reaction flask was added 280 mL ethylene glycol (EG) and 1.2 g of 7.3 mM MnCl_2 in EG. This solution was stripped of at least some dissolved gases by bubbling N_2 into the solution for at least 2 hrs using a glass pipette at room temperature with mechanical stirring while at 100 rpm. (This operation will be referred to as “degassing” the solution in the sequel.) Stock solutions of 0.25 M AgNO_3 in EG and 0.77 M (based on moles of repeat units) polyvinylpyrrolidinone (PVP, 55,000 molecular weight) in EG were also degassed by bubbling N_2 into the solutions for 60 minutes. Two syringes were loaded with 20 mL each of the AgNO_3 and PVP solutions. The reaction mixture was heated to 145°C under N_2 and the AgNO_3 and PVP solutions were added at a constant rate over 25 minutes via 12 gauge Teflon syringe needles. The reaction was held at 145°C for 90 minutes then allowed to cool to room temperature. From the cooled mixture, the reaction mixture was diluted by an equal volume of acetone, and centrifuged at 500 G for 45 minutes. The supernatant was decanted, leaving a solid that was re-dispersed in 200 mL isopropanol by 10 minutes, and centrifuged again, decanted and diluted with 15 mL isopropanol.

An optical microscope picture of the silver nanowires is shown in Figure 1. A scanning electron micrograph of the silver nanowires is shown in Figure 2. Table I shows the average diameter and length of the silver nanowires.

Examples 2-4

The procedure of Example 1 was repeated, while varying the amount of MnCl_2 solution that was used. Table I summarizes shows the average diameter and length of the resulting silver nanowires.

Example 5

To a 500 mL reaction flask was added 280 mL ethylene glycol (EG), which was degassed for 2 hrs by bubbling N_2 into the solution using a glass pipette at room temperature with mechanical stirring while at 100 rpm. Stock

solutions of 0.25 M AgNO₃ in EG and 0.77 M polyvinylpyrrolidinone (PVP) in EG were also degassed by bubbling N₂ into the solutions overnight. Two syringes where loaded with 20 mL each of the AgNO₃ and PVP solutions. Immediately prior to the following heating step, 1.55 g of 11 mM NbCl₅ in EG, which was
5 freshly prepared in a glove box under N₂, was added to the degassed EG. This reaction mixture was heated to 155°C under N₂ and the AgNO₃ and PVP solutions were added at a constant rate over 25 minutes via 12 gauge Teflon syringe needles. The reaction was held at 155°C for 90 minutes then allowed to cool to room temperature. From the cooled mixture, the reaction mixture was diluted by
10 an equal volume of acetone, and centrifuged at 400 G for 45 minutes. The supernatant was decanted, leaving a solid that was re-dispersed in 200 mL isopropanol by shaking 10 minutes and centrifuged again, decanted and diluted with 15 mL isopropanol.

An optical microscope picture of the silver nanowires is shown in
15 Figure 3. The nanowires had an average diameter of 63.4 ± 18.3 nm, based on measurement of at least 100 wires.

Example 6

To a 500 mL reaction flask containing 280 mL ethylene glycol
20 (EG) was added at room temperature 1.30 g of a freshly prepared solution of 9.8 mM ReCl₃ in EG, which had been prepared under nitrogen. The resulting mixture was degassed with nitrogen through a glass pipette for 2 hours while stirring at 100 rpm. Solutions of 0.77 M polyvinylpyrrolidinone (PVP) in EG and 0.25 M AgNO₃ in EG were also degassed with nitrogen for 60 minutes, then
25 20 mL syringes of each were prepared. The reaction mixture was heated to 155 °C under nitrogen blanketing, 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 155 °C for 90 minutes, and then allowed to cool to ambient temperature.

30 An optical microscope picture of the silver nanowire product is shown in Figure 4.

Example 7

To a 500 mL reaction flask containing 280 mL ethylene glycol (EG) was added 0.74 g of a solution of 27 mM VCl_3 in EG at room temperature. This mixture was degassed with nitrogen using a glass pipette while stirring at 100 rpm for 2 hrs. Stock solutions of 0.25 M AgNO_3 in EG and 0.77 M polyvinylpyrrolidinone (PVP) in EG were also degassed with nitrogen for 60 min. Two syringes were loaded with 20 mL each of the AgNO_3 and PVP solutions. The reaction mixture was heated to 145 °C under N_2 and then the AgNO_3 and PVP solutions were added at a constant rate over 25 minutes via 12 gauge TEFLON[®] fluoropolymer syringe needles. The reaction was held at 145 °C for 90 minutes and then allowed to cool to room temperature.

An optical micrograph of the silver nanowire product, approximately 10 microns in length, with very few nanoparticles, is shown in Fig. 5. The nanowires had an average diameter of 30.2 ± 18.4 nm, based on measurement of at least 100 wires.

Example 8

To a 500 mL reaction flask containing 280 mL ethylene glycol (EG) was added 1.0 g of a freshly prepared solution of 20 mM $\text{ScCl}_2 \cdot 6\text{H}_2\text{O}$ in EG. The reaction mixture was degassed for 2 hrs by bubbling N_2 into the solution using a glass pipette at room temperature with mechanical stirring at 100 rpm. Stock solutions of 0.25 M AgNO_3 in EG and 0.77 M polyvinylpyrrolidinone (PVP) in EG were also degassed by bubbling N_2 into the solutions for 60 min. Two syringes were loaded with 20 mL each of the AgNO_3 and PVP solutions. The reaction mixture was heated to 155 °C under N_2 and then, after the reaction mixture was held for 10 min, the AgNO_3 and PVP solutions were added at a constant rate over 25 minutes via 12 gauge Teflon syringe needles. The reaction was held at 155 °C for 90 minutes and then allowed to cool to room temperature.

An optical micrograph of the silver nanowire product is shown in Fig. 6. There was minimal nanoparticle contamination. The nanowires had an average diameter of 44.1 ± 8.4 nm, based on measurement of at least 100 wires.

Example 9

A 94 mM TiCl_4 toluene/ethylene glycol (EG) emulsion was first prepared by mixing 1.0 M TiCl_4 in toluene with EG at room temperature under nitrogen with stirring. To a 500 mL reaction flask containing 280 mL EG was added 0.22 g of this emulsion at room temperature. This mixture was degassed with nitrogen while stirring at 100 rpm for 2 hrs. Stock solutions of 0.25 M AgNO_3 in EG and 0.77 M polyvinylpyrrolidinone (PVP) in EG were also degassed for 60 min by bubbling N_2 into the solutions at room temperature. Two syringes were loaded with 20 mL each of the AgNO_3 and PVP solutions. The reaction mixture was heated to 155 °C under N_2 and then the AgNO_3 and PVP solutions were added at a constant rate over 25 minutes via 12 gauge TEFLON[®] fluoropolymer syringe needles. The reaction was held at 155 °C for 90 minutes and then allowed to cool to room temperature.

An optical micrograph of the silver nanowire product is shown in Fig. 7. The nanowires had an average diameter of 32 ± 16 nm, based on measurement of at least 100 wires.

Example 10

A 500 mL reaction flask containing 280 mL ethylene glycol (EG) was degassed overnight using nitrogen introduced using a sub-surface TEFLON[®] fluoropolymer tube. To the flask as then added 0.82 g of a freshly prepared 22 mM solution of molybdenum (IV) dichloride dioxide in EG. The fluoropolymer tube was then retracted to provide nitrogen blanketing at a flow rate of approximately 0.5 L/min. The reaction mixture was heated to 145 °C while stirring at 100 rpm. Solutions of 0.84 M polyvinylpyrrolidinone (PVP) in EG and 0.25 M AgNO_3 in EG were degassed with nitrogen, then 20 mL syringes of each were prepared. The AgNO_3 and PVP solutions were then added at a constant rate over 25 minutes via a 12 gauge TEFLON[®] fluoropolymer syringe needle. The reaction was held at 145 °C for 90 minutes then allowed to cool to ambient temperature.

An optical microscope picture of the silver nanowire product at 45 min reaction time is shown in Figure 8. Figure 9 shows the product at 60 min reaction time.

5 Example 11

To a 500 mL reaction flask containing 280 mL ethylene glycol (EG), 3.3 g of a 5.9 mM solution of tungsten (IV) chloride in EG was added at room temperature. The mixture was agitated at 100 rpm and degassed with nitrogen using a glass pipette for 2 hrs. Stock solutions of 0.25 M AgNO₃ in EG and 0.77 M polyvinylpyrrolidinone (PVP) in EG were also degassed with nitrogen for 60 min, then 20 mL syringes of each were prepared. The flask was then heated to 145 °C while degassing by bubbling nitrogen through its contents. The AgNO₃ and PVP solutions were then added at a constant rate over 25 min via a 12 gauge a TEFLON[®] fluoropolymer syringe needle. The flask was then held at temperature for 60 min, after which it was allowed to cool down to ambient temperature.

The reaction product was diluted with an equal volume of acetone, then centrifuged at 500 G for 45 min. The supernatant was decanted, leaving a solid that was redispersed in 200 mL isopropanol by shaking 10 min, and then centrifuged, decanted, and redispersed in 15 mL isopropanol. An optical micrograph of the silver nanowire product is shown in Fig. 10. The nanowires had an average diameter of 54.4 ± 12.6 nm, based on measurement of at least 100 wires.

25 Example 12

To a 500 mL reaction flask containing 280 mL ethylene glycol (EG), 1.0 g of a 7.8 mM solution of chromium (III) chloride hexahydrate in EG was added at room temperature. The mixture was agitated at 100 rpm and degassed with nitrogen using a glass pipette for 2 hrs. Stock solutions of 0.25 M AgNO₃ in EG and 0.77 M polyvinylpyrrolidinone (PVP) in EG were also degassed with nitrogen for 60 min, then 20 mL syringes of each were prepared.. The flask was then heated to 145 °C while degassing by bubbling nitrogen

through its contents. The AgNO_3 and PVP solutions were then added at a constant rate over 25 min via a 12 gauge a TEFLON[®] fluoropolymer syringe needle. The flask was then held at temperature for 90 min, after which it was allowed to cool down to ambient temperature.

5 The reaction product was diluted with an equal volume of acetone, then centrifuged at 500 G for 45 min. The supernatant was decanted, leaving a solid that was redispersed in 200 mL isopropanol by shaking 10 min, and then centrifuged, decanted, and redispersed in 15 mL isopropanol. A scanning electron micrograph of the silver nanowire product is shown in Fig. 11. The silver
10 nanowires had an average diameter of 47 ± 14 nm.

Example 13

A 500 mL reaction flask containing 280 mL ethylene glycol (EG) was agitated at 100 rpm and degassed overnight at room temperature using
15 nitrogen that was introduced below the liquid surface through a TEFLON[®] fluoropolymer tube. Afterwards, 15 mg of lanthanum (III) chloride heptahydrate was added to the reaction flask. Stock solutions of 0.25 M AgNO_3 in EG and 0.84 M polyvinylpyrrolidinone (PVP, 55,000 weight-average molecular weight) in EG were also degassed with nitrogen for 60 min, then 20 mL syringes of each
20 were prepared. The flask was then heated to 145 °C while blanketing the reaction flask headspace with nitrogen. The AgNO_3 and PVP solutions were then added at a constant rate over 25 min via a 12 gauge a TEFLON[®] fluoropolymer syringe needle. The flask was then held at temperature for 90 min, after which it was allowed to cool down to ambient temperature.

25 Figure 12 shows a 400-power optical micrograph of the silver nanowire product, which had an average nanowire diameter of 58.3 ± 27.8 nm, where the indicated average diameter and standard deviation were calculated from measurements of at least 100 wires.

30

Example 14

The procedure according to Example 13 was repeated, except that 59 mg of lanthanum (III) chloride heptahydrate was used and the reaction was carried out for 150 min before cooling. Figure 13 shows a 400-power optical micrograph of the silver nanowire product, which had an average nanowire diameter of 88.2 ± 33.8 nm.

Example 15

A 500 mL reaction flask containing 280 mL ethylene glycol (EG), 2.4 g polyvinylpyrrolidinone (PVP, 55,000 weight-average molecular weight), and 7.1 mg of yttrium (III) chloride hexahydrate was degassed overnight at room temperature using nitrogen that was introduced below the liquid surface through a TEFLON[®] fluoropolymer tube. The tube was then retracted from the liquid to provide nitrogen blanketing of the reaction flask headspace at approximately 0.5 L/min, after which the flask was then heated to 145 °C. A stock solution of 0.50 M AgNO₃ in EG was also degassed with nitrogen, then a 40 mL syringe of the solution was prepared. The AgNO₃ solution was then added at a constant rate over 25 min via a 12 gauge TEFLON[®] fluoropolymer syringe needle. The flask was then held at temperature for 60 min, after which it was allowed to cool down to ambient temperature.

Figures 14 and 15 show optical micrographs of the silver nanowire product. The nanowires had an average diameter of 88.9 ± 17.1 nm, based on measurement of at least 100 wires.

Example 16

The procedure of Example 15 was repeated using 3.3 mg 7.1 mg of yttrium (III) chloride hexahydrate. Figures 16 and 17 show optical micrographs of the silver nanowire product. The nanowires had an average diameter of 89.4 ± 18.7 nm, based on measurement of at least 100 wires.

Example 17

A 500 mL reaction flask containing 300 mL ethylene glycol (EG), 2.2 g polyvinylpyrrolidinone (PVP, 55,000 weight-average molecular weight), and 9.2 mg of hafnium tetrachloride bis(tetrahydrofuran) adduct, was degassed overnight at room temperature using nitrogen that was introduced below the liquid surface through a TEFLON[®] fluoropolymer tube. The tube was then retracted from the liquid to provide nitrogen blanketing of the reaction flask headspace at approximately 0.5 L/min, after which the agitated flask was then heated to 145 °C. A stock solution of 0.50 M AgNO₃ in EG was also degassed with nitrogen, and then a 20 mL syringe of the degassed solution was prepared. The AgNO₃ solution was then added at a constant rate over 25 min via a 12 gauge TEFLON[®] fluoropolymer syringe needle. The flask was then held at temperature for 60 min, after which it was allowed to cool down to ambient temperature.

Figure 18 shows an optical micrograph of the nanowire product, which had an average diameter of 253.5 ± 133.0 nm and an average length of 8.7 ± 5.5 μm, based on measurement of 100 wires.

Example 18

The procedure of Example 17 was repeated using 6.9 mg of zirconium tetrachloride bis(tetrahydrofuran) adduct in place of the hafnium-containing adduct. Figure 19 shows an optical micrograph of the silver nanowire product, which had an average diameter of 147.3 ± 50.0 nm and an average length of 15.6 ± 12.0 μm, based on measurement of 100 wires.

Example 19

A 500 mL reaction flask containing 300 mL ethylene glycol (EG), 2.2 g polyvinylpyrrolidinone (PVP, 55,000 weight-average molecular weight), and 4.3 mg of tantalum (V) chloride, was degassed overnight at room temperature using nitrogen that was introduced below the liquid surface through a TEFLON[®] fluoropolymer tube. The tube was then retracted from the liquid to provide nitrogen blanketing of the reaction flask headspace at approximately 0.5 L/min,

after which the agitated flask was then heated to 145 °C. A stock solution of 0.50 M AgNO₃ in EG was also degassed with nitrogen, and then a 20 mL syringe of the degassed solution was prepared. The AgNO₃ solution was then added at a constant rate over 25 min via a 12 gauge TEFLON[®] fluoropolymer syringe needle.

- 5 The flask was then held at temperature for 60 min, after which it was allowed to cool down to ambient temperature.

Figure 20 shows an optical micrograph of the nanowire product, which had an average diameter of 83.1 ± 11.9 nm and an average length of 13.2 ± 3.6 μm, based on measurement of 100 wires.

10

Example 20

The procedure of Example 19 was repeated using 9.9 mg of tantalum (V) chloride. Figure 21 shows an optical micrograph of the silver nanowire product, which had an average diameter of 215 ± 119 nm and an average length of 10.6 ± 6.5 μm, based on measurement of 100 wires.

15

Example 21 (Comparative)

A 500 mL reaction flask containing 200 mL ethylene glycol (EG), 1.28 mL of a 0.006 M solution of FeCl₂ in ethylene glycol (EG) was degassed using a subsurface glass pipette. The agitated flask was then heated to 135 °C, continuing the nitrogen bubbling for 1 hr, followed by nitrogen blanketing of the headspace thereafter. Stock solutions of 0.094 M AgNO₃ in EG and 0.282 M polyvinylpyrrolidone (PVP) in EG were also degassed with nitrogen. 60 mL syringes of the degassed AgNO₃ and PVP solutions were then prepared and then added at a constant rate over 10 min via a 12 gauge TEFLON[®] fluoropolymer syringe needle. The flask was then held at temperature for 2.5 hr, after which it was quenched in an ice bath to cool to room temperature.

25

The resulting nanowires had an average diameter of 121 ± 27 nm, based on measurement of at least 100 wires.

30

Example 22 (Comparative)

A 500 mL reaction flask containing 300 mL ethylene glycol (EG), 2.2 g polyvinylpyrrolidinone (PVP, 55,000 weight-average molecular weight), and 1.4 g of a 6.9 mM solution of tin (II) chloride in EG, was degassed for 2 hrs at room temperature using nitrogen that was introduced below the liquid surface through a glass pipette. The tube was then retracted from the liquid to provide nitrogen blanketing of the reaction flask headspace, after which the agitated flask was then heated to 145 °C. Stock solutions of 0.28 M AgNO₃ in EG and 0.84 M PVP in EG were also degassed with nitrogen, and then 20 mL syringes of the degassed solutions were prepared. The AgNO₃ and PVP solutions were then added at a constant rate of 0.8 mL/min via a 12 gauge TEFLON[®] fluoropolymer syringe needle. The flask was then held at temperature for 120 min, after which it was allowed to cool down to ambient temperature.

The resulting nanowires had an average diameter of 75.9 ± 17.1 nm and an average length of 7.4 ± 3.3 μm, based on measurement of at least 100 wires.

Example 23

The procedure of Example 19 was repeated, using 18.7 mg of hafnium tetrachloride bis(tetrahydrofuran) adduct in place of the tantalum (V) chloride. The resulting nanowire product had an average diameter of 238.1 ± 102.7 nm and an average length of 11.0 ± 7.6 μm, based on measurement of 100 wires.

Example 24

The procedure of Example 19 was repeated, using 16.2 mg of , zirconium tetrachloride bis(tetrahydrofuran) adduct in place of the tantalum (V) chloride. The resulting nanowire product had an average diameter of 241 ± 95 nm and an average length of 10.4 ± 6.6 μm, based on measurement of 100 wires.

TABLE I

ID	Mole Ratio Mn²⁺:Ag⁺	Average Diameter (nm)	Average Length (micron)
Example 1	1:632	63 ± 15	6.3 ± 2.0
Example 2	1:213	55 ± 15	9.0 ± 4.0
Example 3	1:93	60 ± 14	11 ± 5.0
Example 4	1:213	25 ± 15	10.6 ± 3.7

CLAIMS:

1. A method comprising:
providing at least one composition comprising at least one
first reducible metal ion and at least one second metal or metal ion comprising at
least one element or ion of an element from IUPAC Group 3, IUPAC Group 4,
IUPAC Group 5, IUPAC Group 6, or IUPAC Group 7, the at least one second
metal or metal ion differing in atomic number from the at least one first reducible
metal ion; and
reducing the at least one first reducible metal ion to at least
one first metal.
2. The method according to claim 1, wherein the at least one
first reducible metal ion comprises one or more of at least one coinage metal ion,
at least one ion of an element from IUPAC Group 11, or at least one silver ion.
3. The method according to claim 1, wherein the at least one
composition comprises at least one metal oxide compound comprising the at least
one second metal or metal ion.
4. The method according to claim 3, wherein the at least one
metal oxide compound comprises at least one of a metal oxide halide compound
or a transition metal oxide compound.
5. The method according to claim 1, wherein the at least one
second metal or metal ion an oxidation state of +4 or greater.
6. The method according to claim 1, wherein the at least one
second metal or metal ion comprises at least one element or ion of an element
from IUPAC Group 3.

7. The method according to claim 1, wherein the at least one second metal or metal ion comprises at least one element f or ion of an element from IUPAC Group 4.
- 5 8. The method according to claim 1, wherein the at least one second metal or metal ion comprises at least one element or ion of an element from IUPAC Group 5.
9. The method according to claim 1, wherein the at least one
10 second metal or metal ion comprises at least one element or ion of an element from IUPAC Group 6.
10. The method according to claim 1, wherein the at least one second metal or metal ion comprises at least one element or ion of an element
15 from IUPAC Group 7.
11. The at least one first metal produced according to the method of claim 1.
12. At least one metal nanowire comprising the at least one first metal produced according to the method of claim 1.
13. The at least one metal nanowire according to claim 12, comprising an aspect ratio between about 50 and about 10,000.
- 25 14. The at least one metal nanowire according to claim 12, comprising an average diameter of between about 10 nm and about 300 nm.
15. The at least one metal nanowire according to claim 12,
30 comprising an average diameter of between about 25 nm and about 60 nm.

16. The at least one metal nanowire according to claim 12,
comprising an average diameter of between about 60 nm and about 140 nm.
17. The at least one metal nanowire according to claim 12,
5 comprising an average diameter of between about 140 nm and about 260 nm.
18. The at least one metal nanowire according to claim 12,
comprising at least one silver nanowire.
- 10 19. An article comprising the at least one first metal produced
according to the method of claim 1.
20. The article according to claim 19, comprising at least one of
an electronic display, a touch screen, a portable telephone, a cellular telephone, a
15 computer display, a laptop computer, a tablet computer, a point-of-purchase kiosk,
a music player, a television, an electronic game, an electronic book reader, a
transparent electrode, a solar cell, a light emitting diode, an electronic device, a
medical imaging device, or a medical imaging medium.

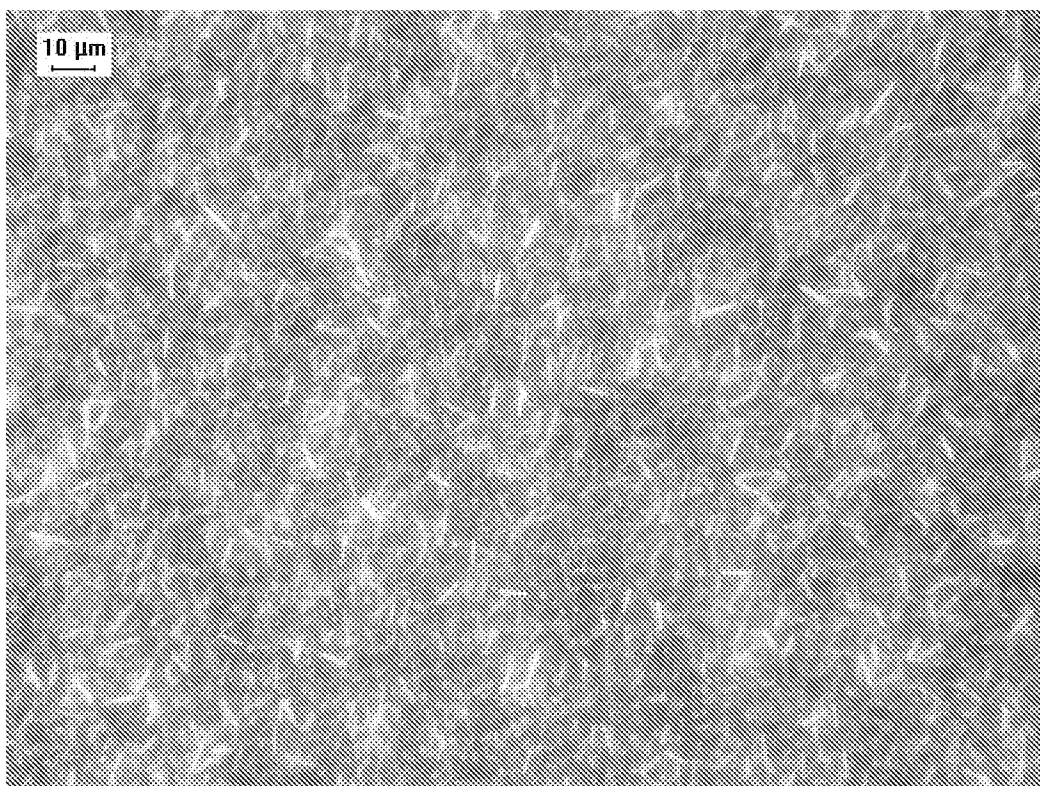
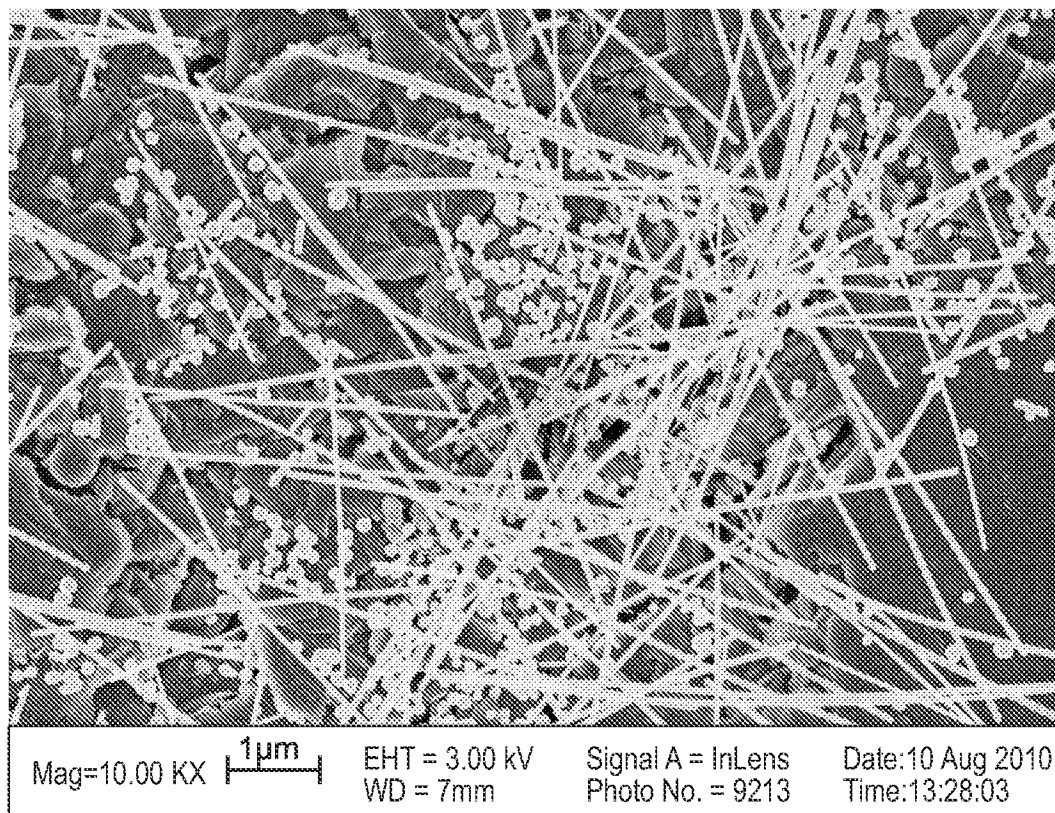


FIG. 1

2/21

**FIG. 2**

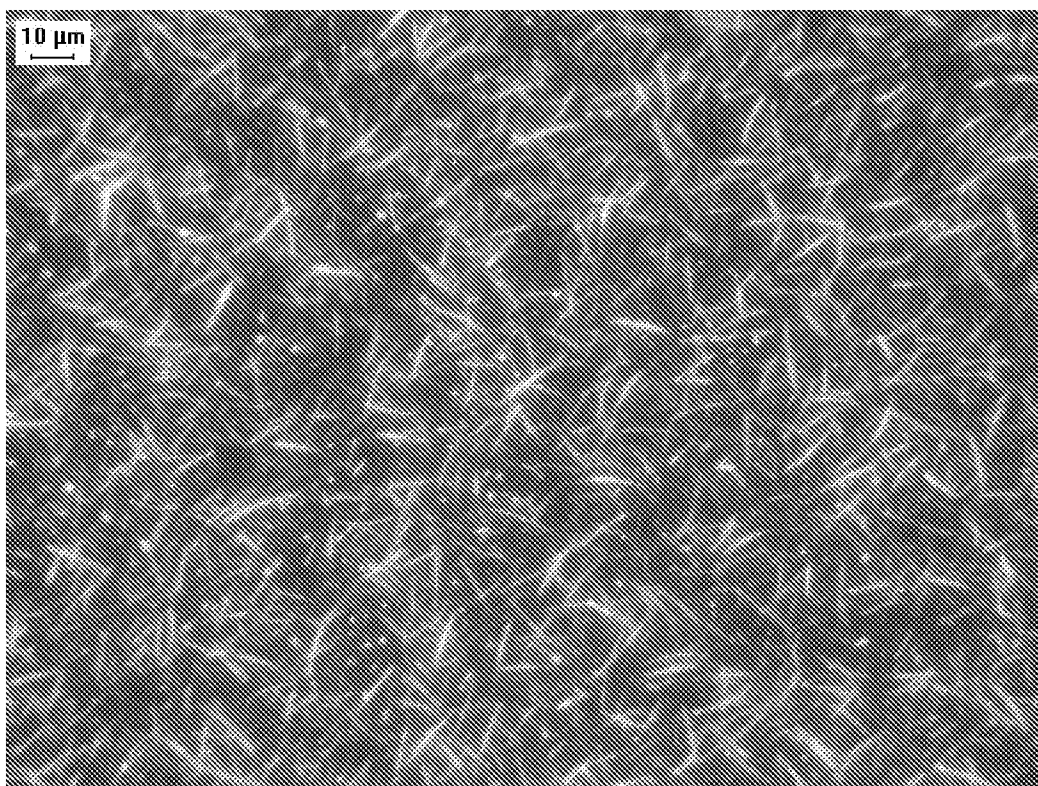


FIG. 3

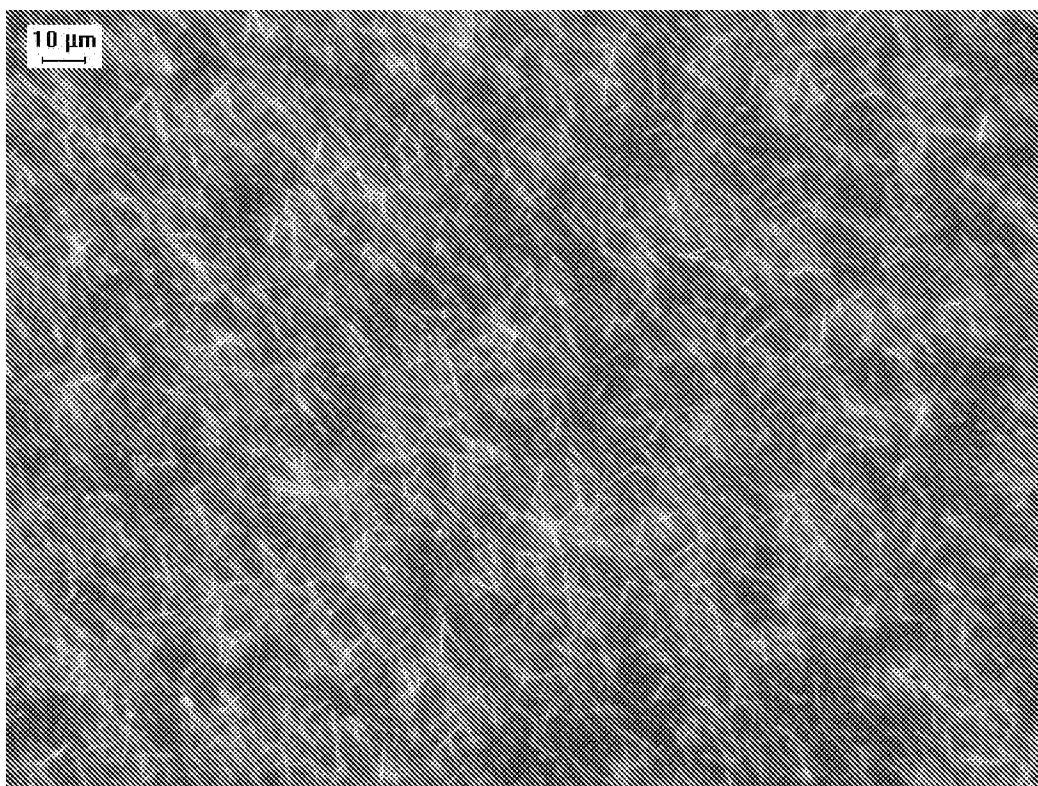


FIG. 4

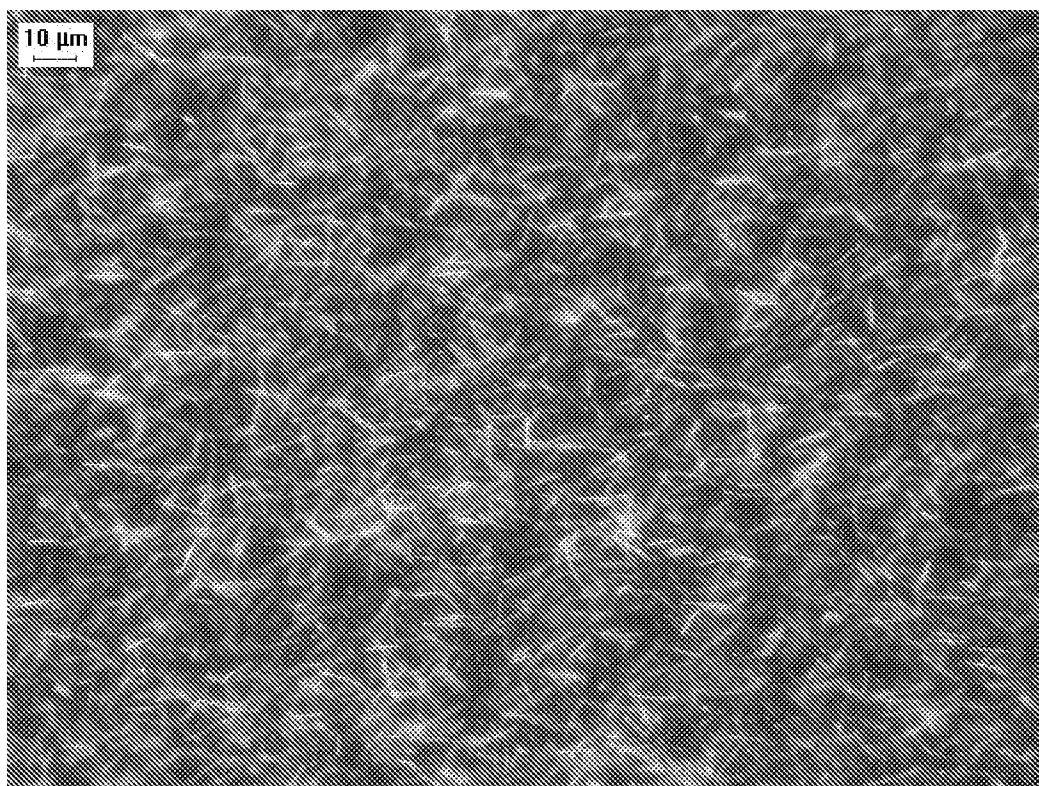


FIG. 5

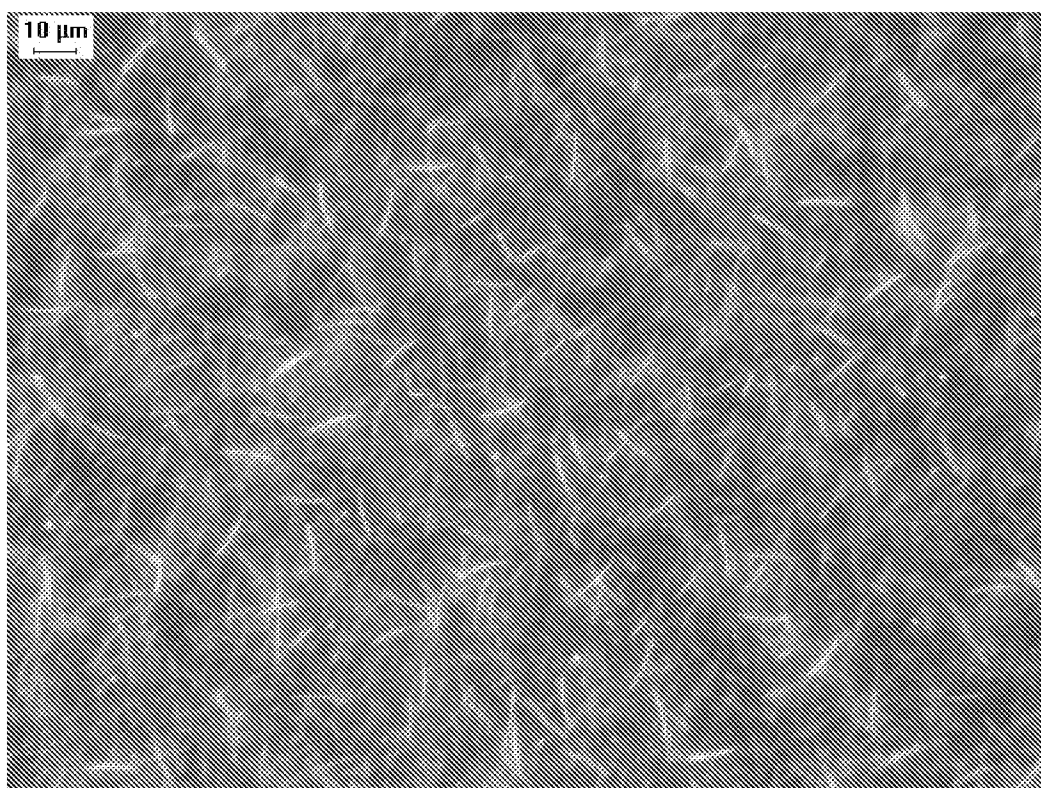


FIG. 6

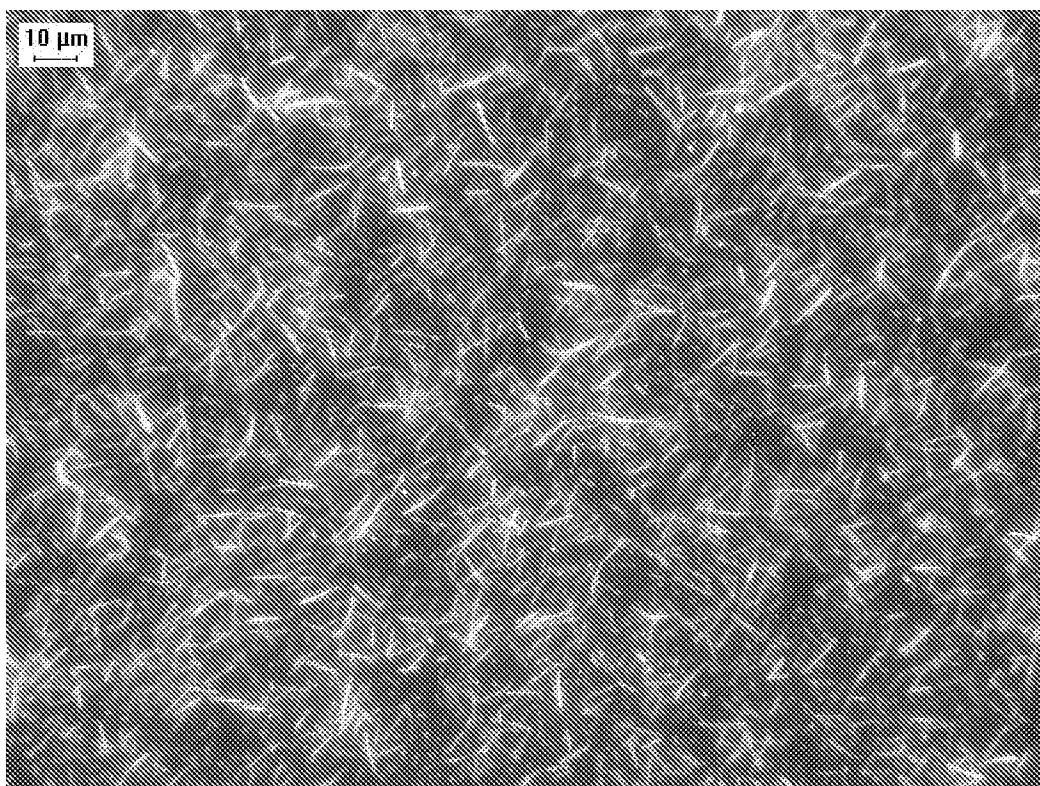


FIG. 7

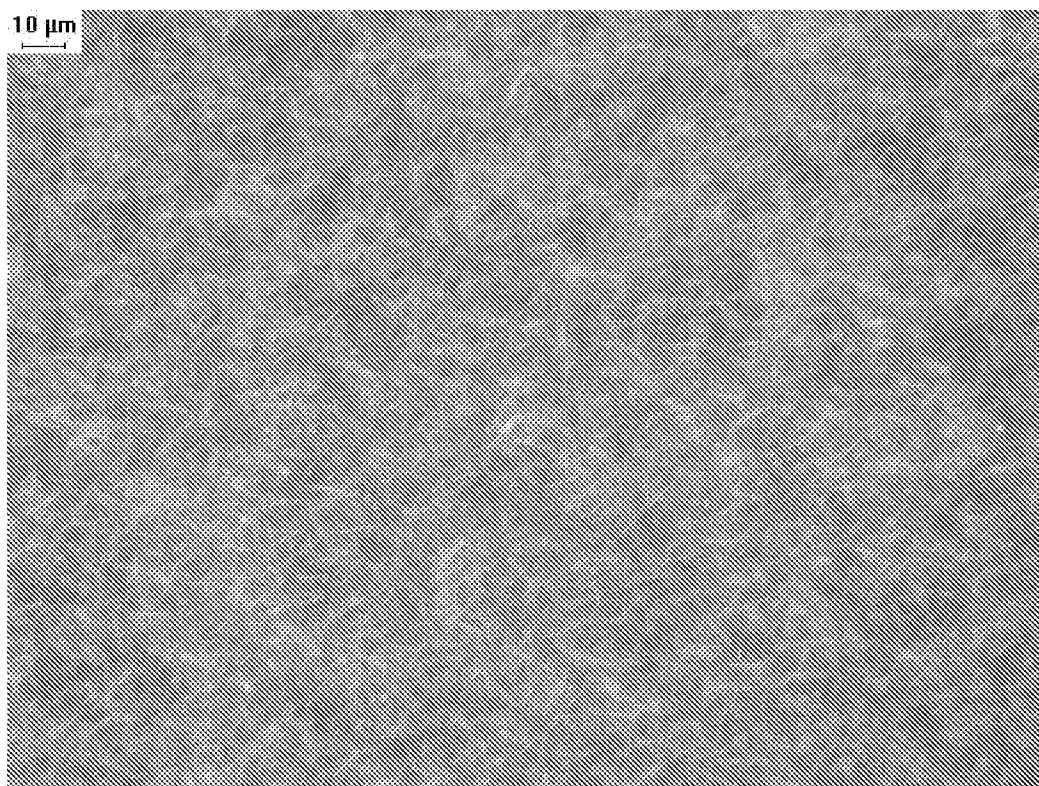


FIG. 8

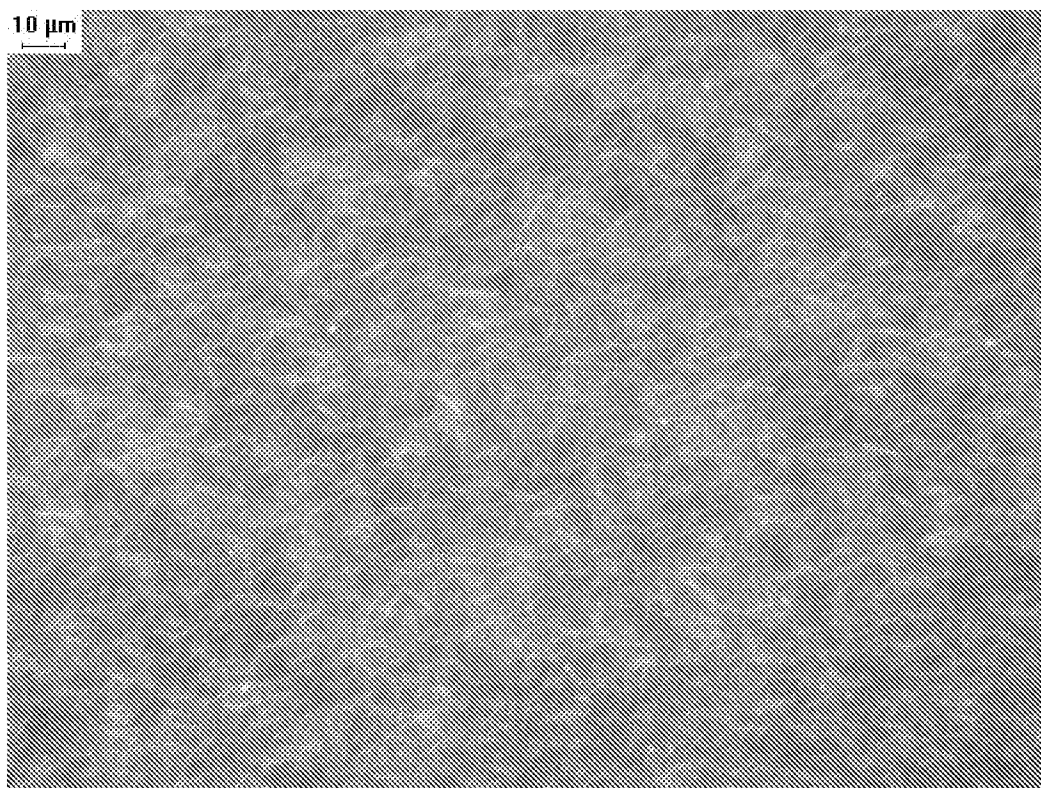


FIG. 9

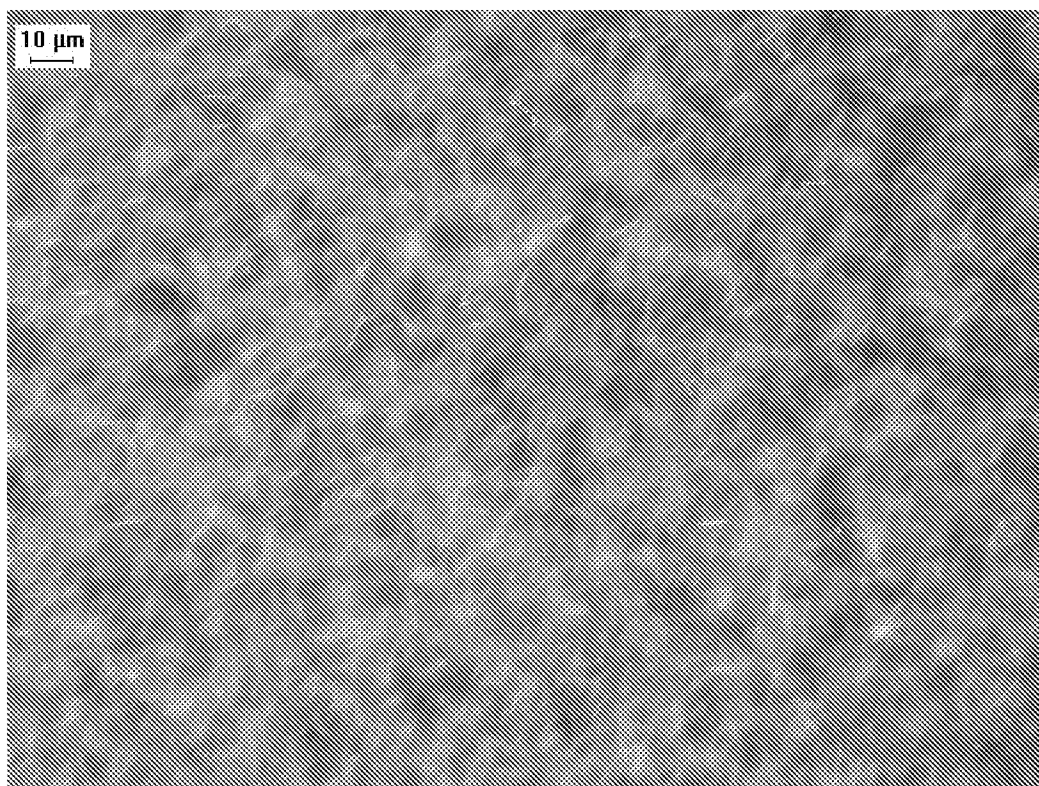
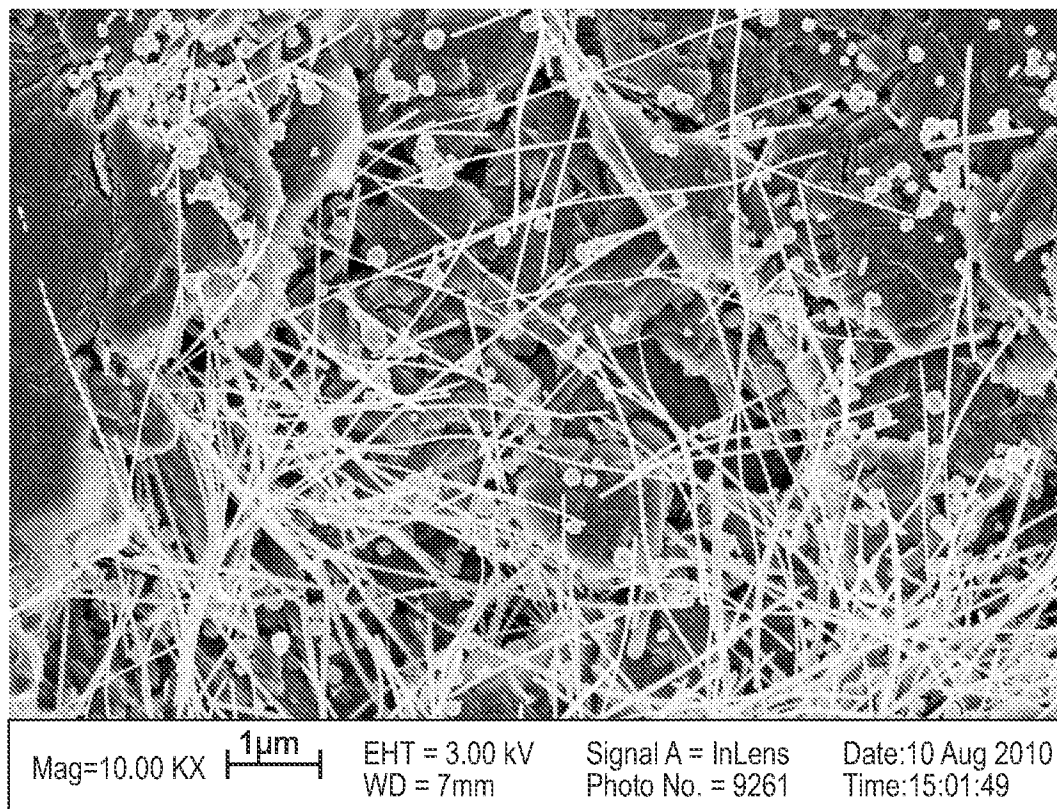


FIG. 10

11/21

**FIG. 11**

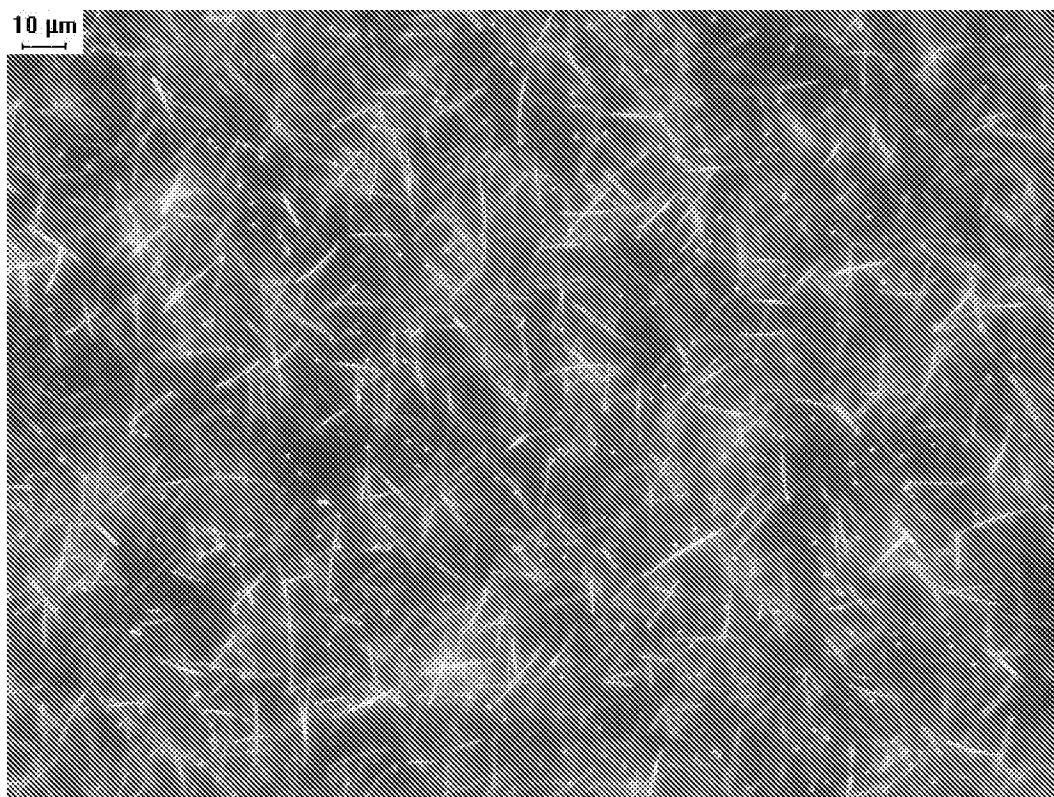


FIG. 12



FIG. 13

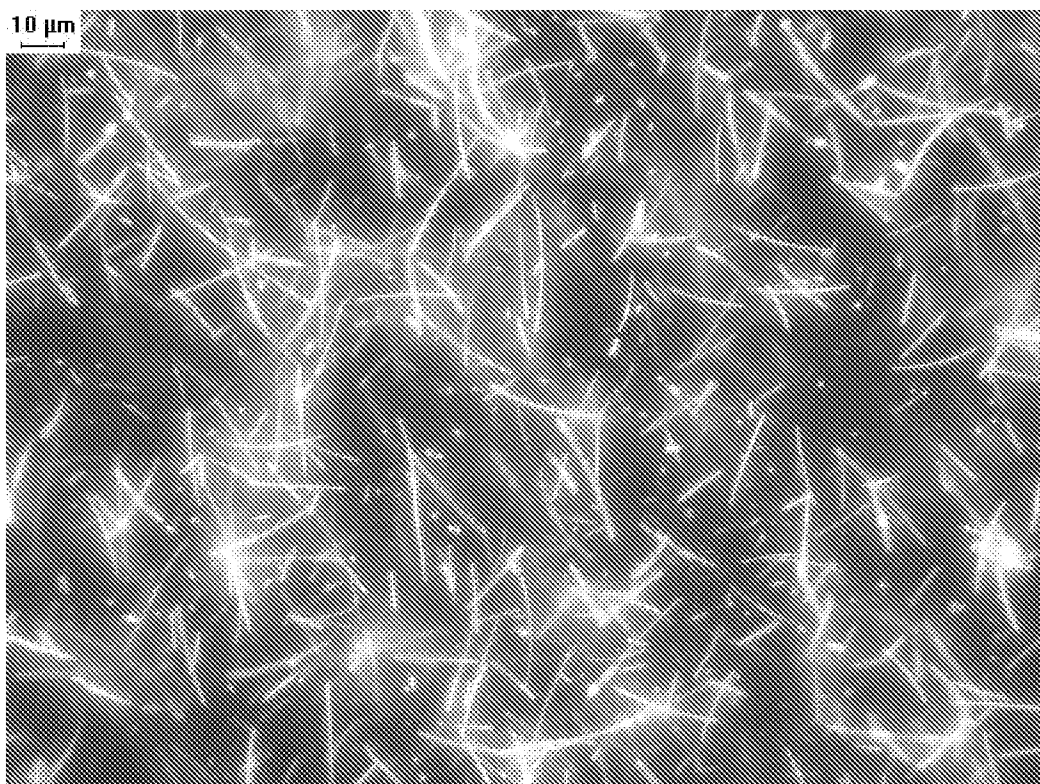


FIG. 14

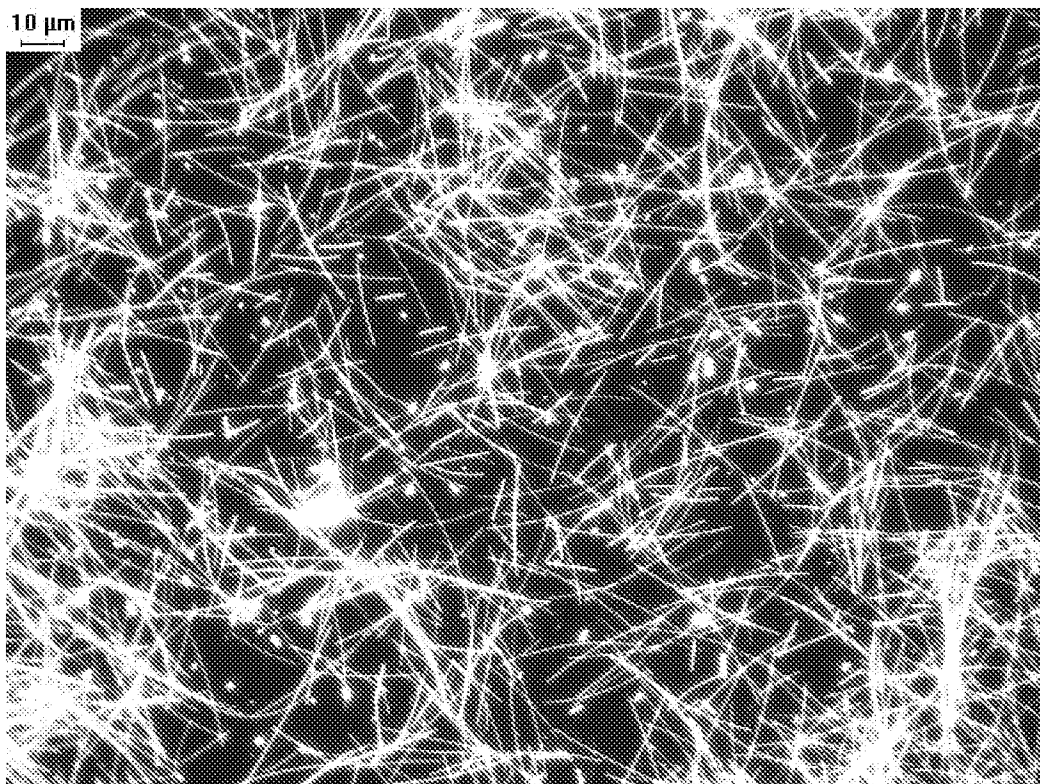


FIG. 15

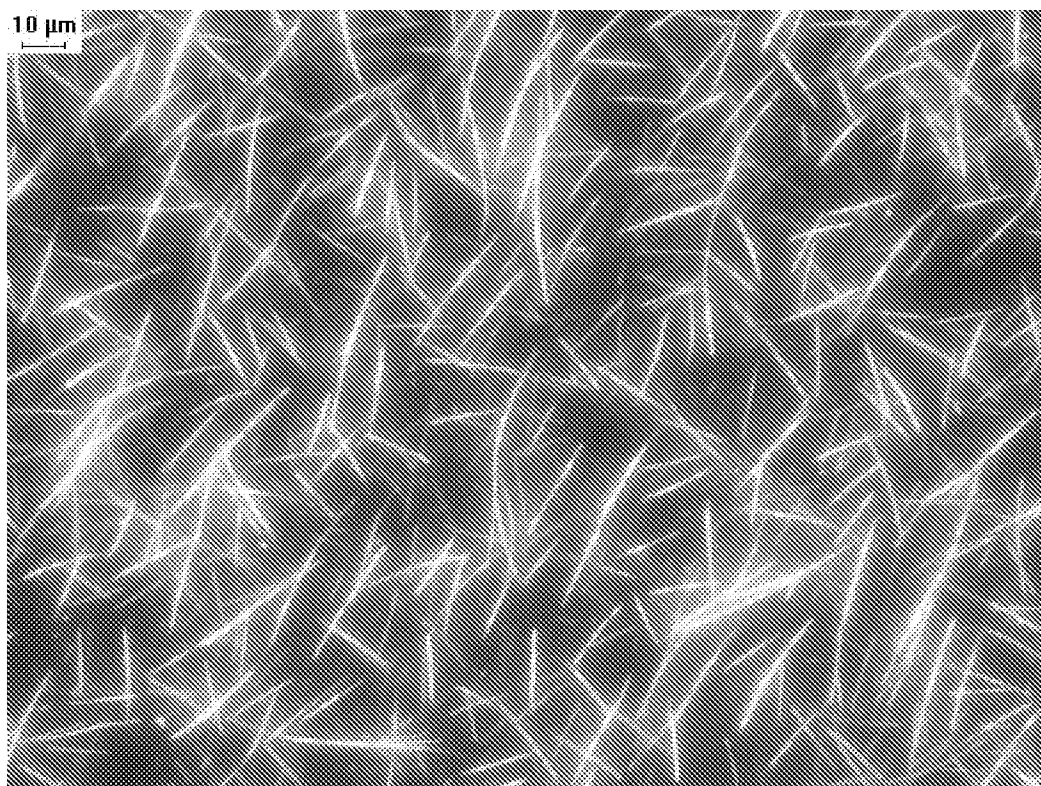


FIG. 16

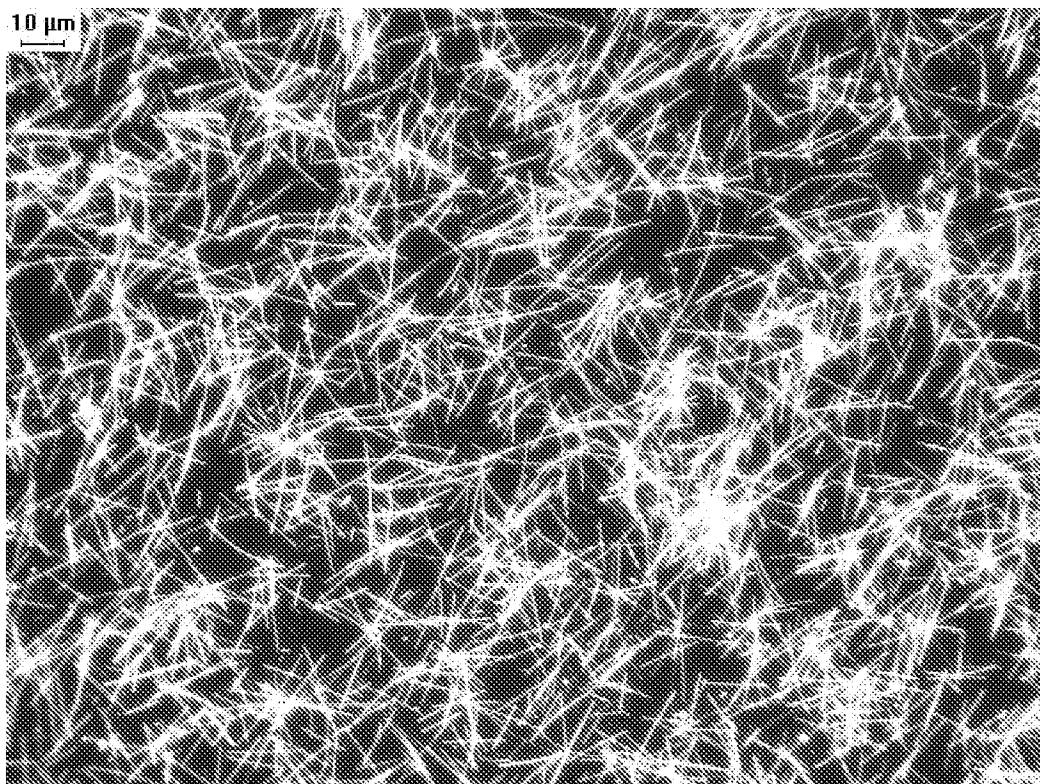


FIG. 17

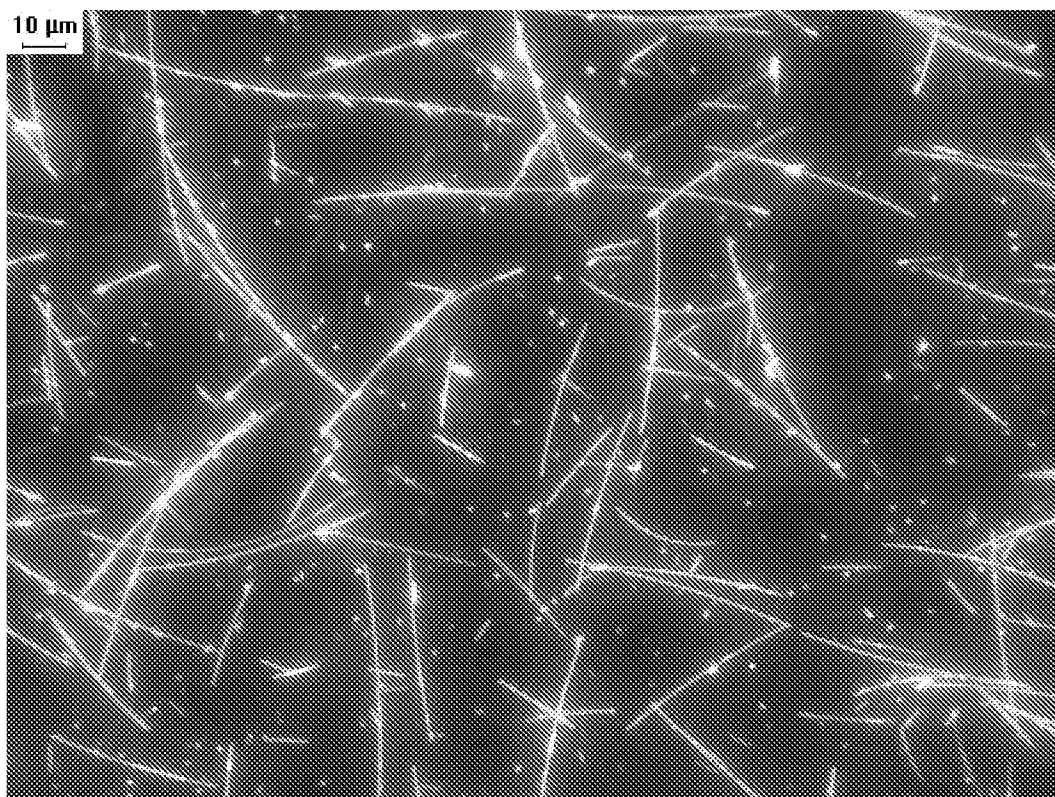


FIG. 18

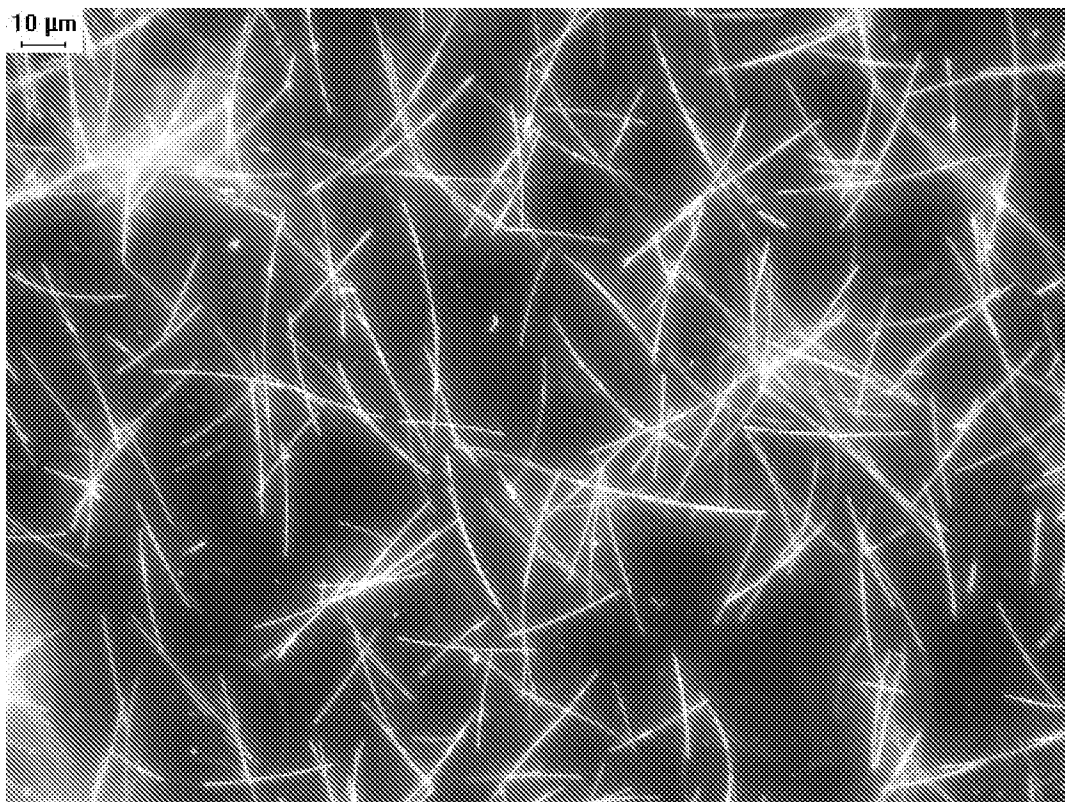


FIG. 19

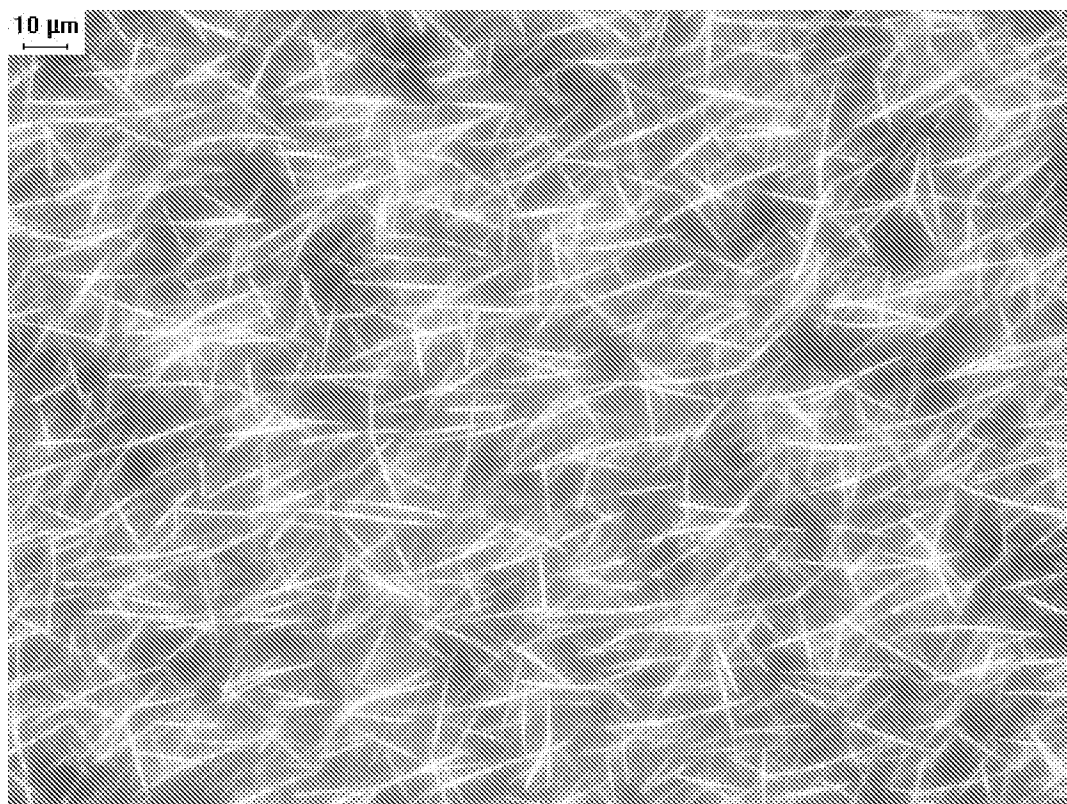


FIG. 20

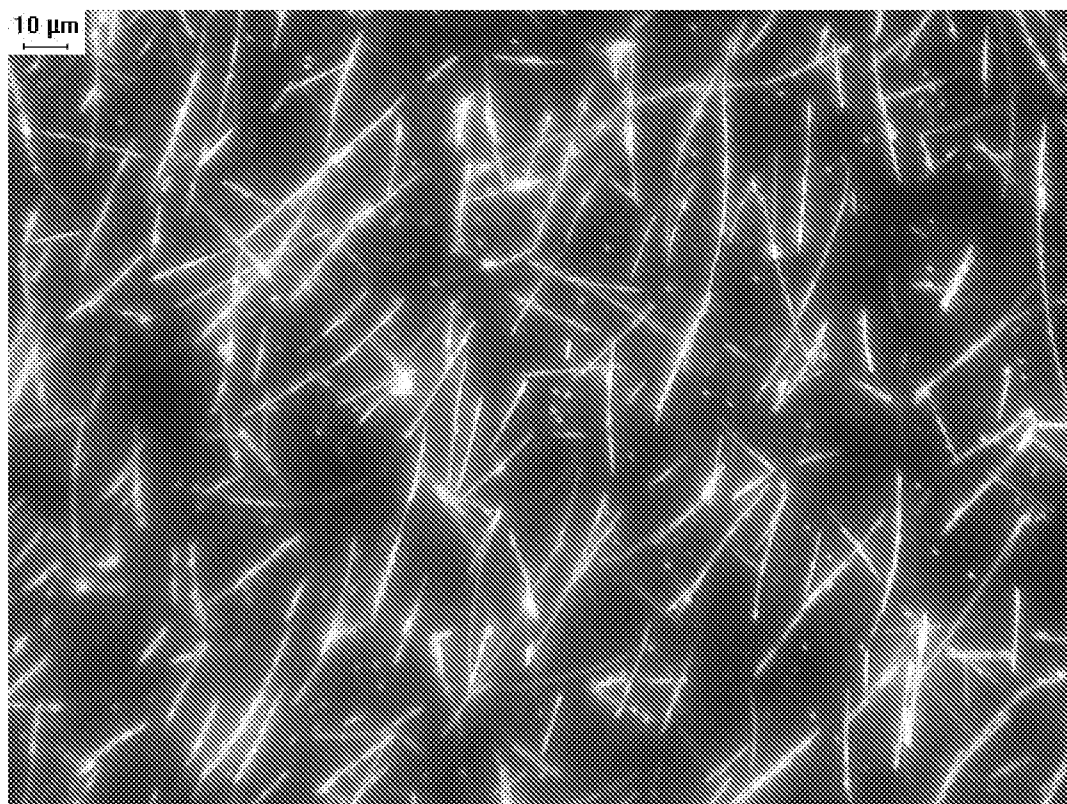


FIG. 21