



(43) International Publication Date
7 January 2016 (07.01.2016)

(10) International Publication Number
WO 2016/003681 A1

- (51) **International Patent Classification:**
B22F 1/00 (2006.01) *B22F 9/24* (2006.01)
- (21) **International Application Number:**
PCT/US2015/036874
- (22) **International Filing Date:**
22 June 2015 (22.06.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
62/020,431 3 July 2014 (03.07.2014) US
14/741,643 17 June 2015 (17.06.2015) US
- (71) **Applicant:** CARESTREAM HEALTH, INC. [US/US];
150 Verona Street, Rochester, NY 14608 (US).
- (72) **Inventor:** WHITCOMB, David, R.; c/o Carestream
Health, Inc., Patent Legal Staff, 150 Verona Street,
Rochester, NY 14608 (US).
- (81) **Designated States** (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** REDUCING AGENTS FOR SILVER MORPHOLOGY CONTROL

(57) **Abstract:** A method comprising providing at least one reducing agent comprising at least one phenol group, the at least one re-
ducing agent not also comprising a halogen atom, and reducing at least one silver ion to at least one silver nanowire in a reaction
mixture comprising the at least one reducing agent. Exemplary reducing agents are 3,4-dihydroxybenzotriazole, 2,2'-isobutylidene-
bis-(4,6-dimethyl-phenol), and tannic acid.



WO 2016/003681 A1

REDUCING AGENTS FOR SILVER MORPHOLOGY CONTROL

BACKGROUND

The general preparation of silver nanowires (10-200 aspect ratios) from silver ions is known. See, for example, Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem. Int. Ed.*, **2009**, 48, 60; J. Jiu, K. Murai, D. Kim, K. Kim, K. Suganuma, *Mat. Chem. & Phys.*, **2009**, 114, 333; U.S. patent publication no. 2013/0192423 to Yang et al.; U.S. patent no. 7,922,787 to Wang et al.; and U.S. patent no. 8,613,888 to Whitcomb et al., all of which are hereby incorporated by reference in their entirety herein. Such preparation methods typically involve the use of a reducing agent to reduce silver ions and form nanoscale silver seed particles, which may lead to the formation of silver nanowires. Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem. Int. Ed.*, **2009**, 48, 60. In some processes, silver nanowire growth may be promoted by metallic seeds from high temperature preparations, such as palladium or platinum. Y. C. Lu, K. S. Chou, *Nanotechnology*, **2010**, 215707, 6 pages, which is hereby incorporated by reference in their entirety herein.

Some relatively strong reducing agents, such as, for example, ascorbic acid, sodium borohydride, or alkylamines in toluene have been used. See, for example, Mehdi Jalali-Heravi, Hossein Robatjazi, Heshmatollah Ebrahimi-Najafabadi, *Physicochem. Eng. Aspects*, **2012**, 393, 46; M. S. Bakshi, J. Nanosci. Nanotechn. **2010**, 10, 1757; and H. Hiramatsu, F. E. Osterloh, *Chem. Mater.*, **2004**, 16, 13, 2509, all of which are hereby incorporated by reference in their entirety herein. Other less strong reducing agents, such as, for example, reducing agents thermally generated from ethylene glycol, have been used. JP Lagier, B. Blin, B. Beaudoin, M. Figlarz, *Solid State Ionics*, **1989**, 32/33, 198; S. E. Skrabalak, BJ Wiley, M. Kim, EV Formo, Y. Xia. *Nano Letters*, **2008**, 8(7), 2077-81; Silvert P-Y, et al. *J. Mater. Chem.*, **1997**, 7, 293-9; and Silvert P-Y, et al., *J. Mater. Chem.*, **1996**, 6, 573-7, all of which are hereby incorporated by reference in their entirety herein.

In some cases, large crystalline silver particles have been prepared

with a phenolic reducing compound and a polar protic solvent. See, for example, U.S. Patent No. 3,940,261 to Dannelly et al. In some cases, anisotropic metallic nanoparticles have been prepared with two different reducing agents. See, for example, U.S. Patent No. 8,030,242 to Uzio et al. and U.S. Patent No. 8,652,232 to Bisson et al. In some cases, nanoparticles have been prepared with a hydrolysable gallotannin, such as tannic acid. See, for example, U.S. Patent No. 8,361,188 to Santhanam et al.

U. S. Patent No. 8,613,888 to Whitcomb et al. and U.S. Patent Publication No. 2013/0340570 to Whitcomb et al. disclose metal ion reduction in the presence of manganese or an ion of manganese. U.S. Patent No. 8,613,888 to Whitcomb et al., U.S. Patent No. 8,551,211 to Ollmann et al., U.S. Patent Publication No. 2013/0343950 to Ollmann et al., U.S. Patent Publication No. 2013/0340570 to Whitcomb et al., and U.S. Patent Publication No. 2012/0294755 to Zhang et al. disclose metal ion reduction in the presence of tin or an ion of tin.

SUMMARY

In some embodiments, a method is disclosed as comprising producing a metal product from a reaction mixture comprising a metal compound capable of forming a reducible metal ion, a protecting agent, a halide compound capable of forming a halide ion or the halide ion produced from the halide compound, a first reducing agent, and a second reducing agent, where the second reducing agent comprises a phenol group. In some embodiments, the metal product comprises a metal seed particle. In some embodiments, the metal product comprises a metal nanowire.

In some embodiments, a first intermediate mixture comprises a first portion of the metal compound, the protecting agent, the halide compound or the halide ion produced from the halide compound, and the first reducing agent; a second intermediate mixture comprises a second portion of the metal compound and the second reducing agent; and the first intermediate mixture and the second intermediate mixture form the reaction mixture when combined.

In some embodiments, the reaction mixture comprises a reducible

metal ion produced from the metal compound. In some embodiments, the first intermediate mixture comprises a first reducible metal ion produced from the first portion of the metal compound, and the second intermediate mixture comprises a second reducible metal ion produced from the second portion of the metal
5 compound.

In some embodiments, the second reducing agent comprises 3,4-dihydroxybenzotriazole. In some embodiments, the second reducing agent comprises tannic acid. In some embodiments, the second reducing agent comprises 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol). In some embodiments,
10 the protecting agent comprises polyvinylpyrrolidone. In some embodiments, the halide compound comprises cerium(III) chloride. In some embodiments, the halide compound comprises manganese(II) chloride. In some embodiments, the first reducing agent comprises a polyol. In some embodiments, the first reducing agent comprises propylene glycol. In some embodiments, the first reducing agent
15 comprises ethylene glycol.

In some embodiments, a method is disclosed as comprising producing a metal product from a reaction mixture comprising a metal compound capable of forming a reducible metal ion, a protecting agent, a halide compound capable of forming a halide ion or the halide ion produced from the halide
20 compound, a polar aprotic solvent, and a first reducing agent, wherein the first reducing agent comprises a phenol group. In some embodiments, the metal product comprises a metal seed particle. In some embodiments, the metal product comprises a metal nanowire.

In some embodiments, the first reducing agent comprises 3,4-dihydroxybenzotriazole. In some embodiments, the first reducing agent
25 comprises tannic acid. In some embodiments, the first reducing agent comprises 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol). In some embodiments, the protecting agent comprises polyvinylpyrrolidone. In some embodiments, the halide compound comprises cerium(III) chloride. In some embodiments, the
30 halide compound comprises manganese(II) chloride. In some embodiments, the polar aprotic solvent comprises acetone. In some embodiments, the polar aprotic

solvent comprises acetonitrile.

In some embodiments, a method is disclosed as comprising producing a nanoscale metal product from a reaction mixture comprising a metal compound capable of forming a reducible metal ion, a protecting agent, a halide compound capable of forming a halide ion or the halide ion produced from the
5 halide compound, and a first reducing agent, where the first reducing agent comprises a phenol group. In some embodiments, the nanoscale metal product comprises a nanoscale metal seed particle. In some embodiments, the nanoscale metal product comprises a nanoscale metal nanowire.

10 In some embodiments, the first reducing agent comprises 3,4-dihydroxybenzotriazole. In some embodiments, the first reducing agent comprises tannic acid. In some embodiments, the first reducing agent comprises 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol). In some embodiments, the protecting agent comprises polyvinylpyrrolidone. In some embodiments, the
15 halide compound comprises cerium(III) chloride. In some embodiments, the halide compound comprises manganese(II) chloride.

DESCRIPTION OF FIGURES

FIG. 1 shows an optical micrograph of the reaction product using
20 3,4-dihydroxybenzotriazole as a reducing agent after a total of 90 minutes from when the solution AgNO_3 in PG was first added.

FIG. 2 shows an optical micrograph of the reaction product using 3,4-dihydroxybenzotriazole as a reducing agent after a total of 120 minutes from when the solution AgNO_3 in PG was first added.

25 FIG. 3 shows an optical micrograph of the reaction product using 3,4-dihydroxybenzotriazole as a reducing agent after a total of 150 minutes from when the solution AgNO_3 in PG was first added.

FIG. 4 shows an optical micrograph of the reaction product of FIG. 3 after purification.

30 FIG. 5 shows a graph of the number distribution of silver nanowire diameters, in nanometers, taken from a random sample of 75 silver nanowires

from five images of the reaction product after purification, such as that shown in FIG. 4.

FIG. 6 shows a graph of the number distribution of silver nanowire lengths, in μm , taken from a random sample of 347 silver nanowires from nine
5 images of the reaction product after purification, such as that shown in FIG. 4.

FIG. 7 shows an optical micrograph of the reaction product using 75 mg of 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol) as a reducing agent after a total of 90 minutes from when the solution AgNO_3 in PG was first added.

FIG. 8 shows an optical micrograph of the reaction product using
10 75 mg of 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol) as a reducing agent after a total of 120 minutes from when the solution AgNO_3 in PG was first added.

FIG. 9 shows an optical micrograph of the reaction product using 75 mg of 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol) as a reducing agent after a total of 150 minutes from when the solution AgNO_3 in PG was first added.

15 FIG. 10 shows an optical micrograph of the reaction product of FIG. 9 after purification.

FIG. 11 shows a graph of the number distribution of silver nanowire diameters, in nanometers, taken from a random sample of 75 silver nanowires from five images of the reaction product after purification, such as that
20 shown in FIG. 10.

FIG. 12 shows a graph of the number distribution of silver nanowire lengths, in μm , taken from a random sample of 199 silver nanowires from ten images of the reaction product after purification, such as that shown in FIG. 10.

25 FIG. 13 shows an optical micrograph of the reaction product using 101 mg of 2,2'-isobutylidene-bis(4,6-dimethyl-phenol) after a total of 90 minutes from when the solution AgNO_3 in PG was first added.

FIG. 14 shows an optical micrograph of the reaction product using 101 mg of 2,2'-isobutylidene-bis(4,6-dimethyl-phenol) after a total of
30 120 minutes from when the solution AgNO_3 in PG was first added.

FIG. 15 shows an optical micrograph of the reaction product using

101 mg of 2,2'-isobutylidene-bis(4,6-dimethyl-phenol) after a total of 150 minutes from when the solution AgNO_3 in PG was first added.

FIG. 16 shows a graph of the number distribution of silver nanowire diameters, in nanometers, taken from a random sample of 75 silver nanowires from five images of the reaction product, such as that shown in FIG. 15.

FIG. 17 shows a graph of the number distribution of silver nanowire lengths, in μm , taken from a random sample of 336 silver nanowires from eight images of the reaction product, such as that shown in FIG. 15.

FIG. 18 shows a plot of silver ion concentration in millivolts over time in minutes as measured by a silver ion specific electrode for a reaction product using 0.96 g of 2,2'-isobutylidene-bis(4,6-dimethyl-phenol).

FIG. 19 shows an optical micrograph of the purified reaction product from the reaction, which is plotted in FIG. 18.

FIG. 20 shows a graph of the number distribution of silver nanowire diameters, in nanometers, taken from image(s) of the reaction product, such as that shown in FIG. 19.

FIG. 21 shows a graph of the number distribution of silver nanowire lengths, in μm , taken from image(s) of the reaction product, such as that shown in FIG. 19.

DESCRIPTION

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. 62/020,431, filed July 3, 2014, entitled "REDUCING AGENTS FOR SILVER MORPHOLOGY CONTROL," is hereby incorporated by reference in its entirety.

Introduction

Silver nanowires (AgNW) are unique and useful silver structures

that have a wire-like shape 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. They are being used as conductors in electronic devices or as elements in optical devices, among other possible uses.

A common method of preparing nanostructures, such as, for example, nanowires, is the “polyol” process. Such a process is described in, for example, *Angew. Chem. Int. Ed.* 2009, 48, 60, Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, which is hereby incorporated by reference in its entirety. In such processes, the polyol reduces a metal cation, such as, for example, a silver cation, to the desired metal nanostructure product, such as, for example, a silver nanowire.

Applicants have discovered that phenolic reducing agents having at least one phenol group may be useful in preparing silver nanowires. A phenolic reducing agent may replace the “polyol” in the “polyol” process or used as a second reducing agent in addition to the “polyol” that is either introduced simultaneously with or subsequent to the polyol.

Preparation Methods and Materials

Silver seeds, which may lead to the formation of silver nanowires, may be produced from a reaction mixture comprising at least one reducing agent, a protecting agent, a halide compound (or a halide ion produced from the halide compound), a metal salt, and an optional solvent. In some embodiments, the reaction mixture may comprise one reducing agent, a protecting agent, a halide compound (or a halide ion produced from the halide compound), a metal salt, and no other solvents. In such cases, the reducing agent may act as a solvent by being capable of dissolving all other components of the reaction mixture into itself. In some embodiments, the reaction mixture may comprise one reducing agent, a protecting agent, a halide compound (or a halide ion produced from the halide compound), a metal salt, and at least one additional solvent, such as, for example,

a polar protic or a polar aprotic solvent. In some embodiments, the reaction mixture may comprise a first reducing agent, a second reducing agent, a protecting agent, a halide compound (or a halide ion produced from the halide compound), and a metal salt. The reaction mixture may be subjected to heating from about
5 100°C to about 200°C.

The reaction mixture may be formed from the combination of at least two intermediate mixtures, such as a first intermediate mixture and a second intermediate mixture. The first intermediate mixture may be subjected to a reaction condition (e.g. N₂ headspace positive pressure at 0.5 L/min, heating at
10 110.0°C ± 0.3°C, stirring at 200 rpm, selected residence time, selected amount at which another substance has been added, etc.) prior to the second intermediate mixture being added to the first intermediate mixture. The metal salt may be separated into a first portion and a second portion into the first intermediate mixture and the second intermediate mixture, respectively, for combination into
15 the reaction mixture.

In a first example, the metal salt and the halide compound (or the halide ion produced from the halide compound) may be added in a later step to the mixture containing the at least one reducing agent, the protecting agent, and the optional solvent. In such cases, the first intermediate mixture comprises the at
20 least one reducing agent, the protecting agent, and the optional solvent, and the second intermediate mixture comprises the metal salt and the halide compound (or the halide ion produced from the halide compound).

In a second example, a first portion of the metal salt may be added in a later step to the mixture containing the at least one reducing agent, the
25 protecting agent, and the optional solvent, and the halide compound (or the halide ion produced from the halide compound) and a second portion of the metal salt may be added after a certain amount (i.e. the first portion) of the metal salt has been added. In such cases, the first intermediate mixture comprises the at least one reducing agent, the protecting agent, and the optional solvent, the second
30 intermediate mixture comprises a first portion of the metal salt, and the third intermediate mixture comprises a second portion of the metal salt and the halide

compound (or the halide ion produced from the halide compound).

In a third example, the metal salt may be added in a later step to the mixture containing the at least one reducing agent, the protecting agent, the halide compound (or the halide ion produced from the halide compound), and the optional solvent. In such cases, the first intermediate mixture comprises the at least one reducing agent, the protecting agent, the halide compound (or the halide ion produced from the halide compound), and the optional solvent, and the second intermediate mixture may comprise the metal salt.

In a fourth example, a second portion of the metal salt may be added in a later step to the mixture containing a first portion of the metal salt, the at least one reducing agent, the protecting agent, the halide compound (or the halide ion produced from the halide compound), and the optional solvent. In such cases, the first intermediate mixture comprises the second portion of the metal salt, and the first intermediate mixture comprises the first portion of the metal salt, the at least one reducing agent, and the protecting agent, the halide compound (or the halide ion produced from the halide compound), and the optional solvent.

In a fifth example, a second portion of the metal salt and the halide compound (or the halide ion produced from the halide compound) may be added in a later step to the mixture containing a first portion of the metal salt, the at least one reducing agent, the protecting agent, and the optional solvent. In such cases, the first intermediate mixture comprises the second portion of the metal salt and the halide compound (or the halide ion produced from the halide compound), and the first intermediate mixture comprises the first portion of the metal salt, the at least one reducing agent, and the protecting agent, and the optional solvent.

In a sixth example, a second portion of the metal salt may be added in a later step to the mixture containing a first portion of the metal salt, the at least one reducing agent, the protecting agent, and the optional solvent, and the halide compound (or the halide ion produced from the halide compound) may be added after a certain amount of the second portion of the metal salt has been added. In such cases, the first intermediate mixture comprises the first portion of the metal salt, the at least one reducing agent, and the protecting agent, and the optional

solvent, the second intermediate mixture comprises the second portion of the metal salt, and the third intermediate mixture comprises a third portion of the metal salt and the halide compound (or the halide ion produced from the halide compound).

5 In cases where the reaction mixture comprises at least two reducing agents, the first reducing agent and the second reducing agent may be added during the same or different steps. In a seventh example, the reaction mixture may comprise the first reducing agent, the metal salt, the protecting agent, the halide compound (or the halide ion produced from the halide compound), and the optional solvent, and the second reducing agent. In an eighth example, the first intermediate mixture may comprise the first reducing agent, a second reducing agent, a first portion of the metal salt, the protecting agent, the halide compound (or the halide ion produced from the halide compound), and the optional solvent, and the second intermediate may comprise a second portion of the metal salt. In a ninth example, the first intermediate mixture may comprise the first reducing agent, a second reducing agent, a first portion of the metal salt, the protecting agent, and the optional solvent, and the second intermediate may comprise a second portion of the metal salt and the halide compound (or the halide ion produced from the halide compound). In a tenth example, the first intermediate mixture may comprise the first reducing agent, a first portion of the metal salt, the protecting agent, the halide compound (or the halide ion produced from the halide compound) and the optional solvent, and the second intermediate mixture may comprise the second reducing agent and a second portion of the metal salt. In an eleventh example, the first intermediate mixture may comprise the first reducing agent, a first portion of the metal salt, the protecting agent, and the optional solvent, the second intermediate mixture may comprise the second reducing agent and a second portion of the metal salt, and the third intermediate mixture may comprise the third portion of the metal salt and the halide compound (or the halide ion produced from the halide compound).

30

Reducing Agents

Reducing agents are substances that have the ability to transfer their electrons to another substance. As discussed above, silver seeds may be prepared from a reaction mixture comprising at least one reducing agent. In exemplary embodiments, at least one of the reducing agents may comprise a phenol group. In a first example, a reaction mixture may comprise a first reducing agent comprising a polyol and a second reducing agent comprising a phenol group. The polyol may be act as both a solvent to dissolve the metal salt (e.g. silver nitrate) to form the metal solution (e.g. silver solution) and as a reducing agent that is capable of reducing the metal salt (e.g. silver nitrate) to metal (e.g. silver). In such cases, the second reducing agent may enhance the reducing capacity of the first reducing agent and/or participate as an additional reducing agent. Non-limiting examples of polyols include ethylene glycol, glycerol, glucose, diethylene glycol, tri-ethylene glycol, propylene glycol, butanediol, a dipropylene glycol, and/or a polyethylene glycol. The polyol may be a single polyol or a mixture of two or more different polyols (e.g. three, four, five, or more different polyols).

In a second example, a reaction mixture may comprise one reducing agent comprising a phenol group. In this application, the term “phenolic” compound, “phenolic” reducing agent, or “phenol” group refers to a compound comprising at least one first aromatic ring, at least one first oxygen atom, and at least one first hydrogen atom bonded to the at least one first oxygen atom, where the at least one first aromatic ring comprises at least one first carbon atom bonded to the at least one first oxygen atom. Non-limiting examples of phenolic reducing agents include 3,4-dihydroxybenzotriazole, 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol), and tannic acid.

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 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 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
5 might, in some cases, 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 to. For example, silver would be the metal to which a silver cation would be capable of being reduced to.

10

Metal Compounds

Some embodiments provide reaction mixtures comprising a metal compound. The metal compound can be any silver compound that produces metal when reduced. The metal compound can be reduced by a polyol or a phenolic
15 reducing agent. The metal compound can be a metal oxide, a metal hydroxide, or a metal salt (organic or inorganic).

Metal salts may dissociate in a solution into a metal cation and an anion. The metal cation may be reduced by a reducing agent to form a metal product, such as a silver seed, silver nanoparticle, or silver nanowire. The metal
20 salt may be provided in various forms, such as, for example, in solution, solid (e.g. solid powder), or as a suspension. Non-limiting examples of metal salts include nitrates, nitrites, sulfates, halides, carbonates, phosphates, azides, borates, sulfonates, carboxylates, substituted carboxylates, and salts and acids where the metal is part of an anion, or combinations thereof. Specific non-limiting examples
25 of metal salts include silver nitrate, silver nitrate, silver oxide, silver fluoride, silver acetate, or combinations thereof.

Solvents

A solvent is a substance that dissolves a solute (a chemically
30 different liquid, solid, or gas) resulting in a solution. Solvents can be classified as polar or non-polar based on their dielectric constant (e.g. relative static

permittivity). The relative permittivity of a material under given conditions reflects the extent to which it concentrates electrostatic lines of flux. Solvents with a dielectric constant of less than 15 are generally considered non-polar. Polar solvents, which have a relative static permittivity greater than 15, can be further
5 classified as protic and aprotic. Protic solvents are those that possess dissociable protons, while aprotic solvents lack such dissociable protons. The Hansen δH parameters for protic solvents are generally greater than about 12, while those for aprotic solvents are generally less than about 12. Non-limiting examples of polar
10 protic solvents include formic acid, n-butanol, isopropanol, n-propanol, ethanol, methanol, acetic acid, nitromethane, and water. Non-limiting examples of polar aprotic solvents include dichloromethane, tetrahydrofuran, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, and propylene carbonate.

Protecting Agents

15 Some embodiments provide a reaction mixture comprising a protecting agent. Literature has suggested that the protecting agent may have different purposes, such as avoiding particle sintering, capability of absorbing onto the metal nanostructure, etc. Generally, it is thought that the protecting agent reduces or prevents direct contact between individual nanostructures.
20 Such literature has referred to “protecting agents” using other terms, such as “organic protective agent,” “protective agent,” “coordination compound,” “polymer capping agent,” “polymeric capping agent,” “capping agent,” “capping reagent,” and “soft template.” Use of the phrase “protecting agent” herein is intended to encompass all these other various phrases as well as other reactants
25 known in the art that are added to the polyol synthesis of metal nanostructures to thereby reduce and/or prevent sintering or agglomeration.

Generally, the protecting agent should have minimal, if any, reaction with other components in the reaction mixture. Nor should the protecting agent inhibit or prevent the solution mediated production of desired
30 nanostructures, such as silver nanowires. The protecting agent may be a substance capable of electronically interacting with a metal atom of a nanoparticle. For

example, the protecting agent may be capable of a dative interaction with a metal atom on the surface of a nanoparticle and/or of chelating the metal atom. The protecting agent can comprise one or more atoms with one or more free electron pairs, such as, for example, oxygen, nitrogen, and sulfur. The atoms with a free
5 electron pair can be in the form of a functional group, such as, for example, a hydroxyl group, a carbonyl group, an ether group, an amino group, or combinations thereof. Non-limiting examples of protecting agents that can be used alone or as mixtures include polyvinylpyrrolidone (PVP), polyvinyl alcohol, and surfactants, such as sodium dodecyl sulfate (SDS), larylamine and
10 hydroxypropyl cellulose. In some embodiments, the protecting agent is or comprises a substance that is capable of reducing the metal compound. In such cases, the protecting agent may qualify as a reducing agent.

Halide Compounds

15 A reaction mixture may comprise an optional halide compound that is capable of forming halide ion(s). It is thought that various reactants (e.g. first reducing agent and protecting agent) may be contaminated with one or more halide compounds that are capable of forming halide ion(s). Even with such halide contaminants occurring in the reaction mixture, the addition of optional
20 halide compounds may still be required for the reaction mixture to produce metal seeds that lead to the formation of the metal nanowires. Non-limiting examples of halide compounds include cerium(III) chloride heptahydrate, managanese(II) chloride tetrahydrate, and tin(II) chloride dihydrate.

25

Nanostructures and Nanowires

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
30 300 nm, and at least one other dimension being much larger than the nanoscale dimension, such as, for example, at least about 10 or at least about 100 or at least

about 200 or at least about 1000 times larger. Examples of such nanostructures are nanorods, nanowires, nanotubes, nanopyramids, nanoprisms, nanoplates, and the like. “One-dimensional” nanostructures have one dimension that is much larger than the other two dimensions, such as, for example, at least about 10 or at
5 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, preferably less than 100 nm, while the third dimension (the length dimension) is greater than
10 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.

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

EXEMPLARY EMBODIMENTS

U.S. Provisional Application No. 62/020,431, filed July 3, 2014,
entitled "REDUCING AGENTS FOR SILVER MORPHOLOGY CONTROL,"
which is hereby incorporated by reference in its entirety, disclosed the following

5 35 non-limiting exemplary embodiments:

A. A method comprising:

producing a metal product from a reaction mixture comprising a metal
compound capable of forming a reducible metal ion, a protecting agent, a halide
compound capable of forming a halide ion or the halide ion produced from the
10 halide compound, a first reducing agent, and a second reducing agent, wherein the
second reducing agent comprises a phenol group.

B. The method according to embodiment A, wherein the metal product comprises
a metal seed particle.

C. The method according to either of embodiments A or B, wherein the metal
15 product comprises a metal nanowire.

D. The method according to any of embodiments A-C,

wherein a first intermediate mixture comprises a first portion of the metal
compound, the protecting agent, the halide compound or the halide ion produced
from the halide compound, and the first reducing agent,

20 wherein a second intermediate mixture comprises a second portion of the
metal compound and the second reducing agent, and

wherein the first intermediate mixture and the second intermediate mixture
form the reaction mixture when combined.

E. The method according to any of embodiments of A-D, wherein the reaction
25 mixture comprises a reducible metal ion produced from the metal compound.

F. The method according to any of embodiments A-D, wherein the first
intermediate mixture comprises a first reducible metal ion produced from the first
portion of the metal compound, and the second intermediate mixture comprises a
second reducible metal ion produced from the second portion of the metal
30 compound.

G. The method according to any of embodiments A-F, wherein the second

- reducing agent comprises 3,4-dihydroxybenzotriazole.
- H. The method according to any of embodiments A-G, wherein the second reducing agent comprises tannic acid.
- J. The method according to any of embodiments A-H, wherein the second
- 5 reducing agent comprises 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol).
- K. The method according to any of embodiments A-J, wherein the protecting agent comprises polyvinylpyrrolidone.
- L. The method according to any of embodiments A-K, wherein the halide compound comprises cerium(III) chloride.
- 10 M. The method according to any of embodiments A-L, wherein the halide compound comprises manganese(II) chloride.
- N. The method according to any of embodiments A-M, wherein the first reducing agent comprises a polyol.
- P. The method according to any of embodiments A-N, wherein the first reducing
- 15 agent comprises polyethylene glycol.
- Q. The method according to any of embodiments A-P, wherein the first reducing agent comprises ethylene glycol.
- R. A method comprising
- producing a metal product from a reaction mixture comprising a metal
- 20 compound capable of forming a reducible metal ion, a protecting agent, a halide compound capable of forming a halide ion or the halide ion produced from the halide compound, a polar aprotic solvent, and a first reducing agent, wherein the first reducing agent comprises a phenol group.
- S. The method according to embodiment R, wherein the metal product comprises
- 25 a metal seed particle.
- T. The method according to either of embodiments R or S, wherein the metal product comprises a metal nanowire.
- U. The method according to any of embodiments R-T, wherein the first reducing agent comprises 3,4-dihydroxybenzotriazole.
- 30 V. The method according to any of embodiments R-U, wherein the first reducing agent comprises tannic acid.

- W. The method according to any of embodiments R-V, wherein the first reducing agent comprises 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol).
- X. The method according to any of embodiments R-W, wherein the protecting agent comprises polyvinylpyrrolidone.
- 5 Y. The method according to any of embodiments R-X, wherein the halide compound comprises cerium(III) chloride.
- Z. The method according to any of embodiments R-Y, wherein the halide compound comprises manganese(II) chloride.
- AA. The method according to any of embodiments R-Z, wherein the polar aprotic
10 solvent comprises acetone.
- AB. The method according to any of embodiments R-AA, wherein the polar aprotic solvent comprises acetonitrile.
- AC. A method comprising:
producing a nanoscale metal product from a reaction mixture comprising a
15 metal compound capable of forming a reducible metal ion, a protecting agent, a halide compound capable of forming a halide ion or the halide ion produced from the halide compound, and a first reducing agent, wherein the first reducing agent comprises a phenol group.
- AD. The method according to embodiment AC, wherein the nanoscale metal
20 product comprises a nanoscale metal seed particle.
- AE. The method according to either of embodiments AC or AD, wherein the nanoscale metal product comprises a nanoscale metal nanowire.
- AF. The method according to any of embodiments AC-AE, wherein the first reducing agent comprises 3,4-dihydroxybenzotriazole.
- 25 AG. The method according to any of embodiments AC-AF, wherein the first reducing agent comprises tannic acid.
- AH. The method according to any of embodiments AC-AG, wherein the first reducing agent comprises 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol).
- AJ. The method according to any of embodiments AC-AH, wherein the
30 protecting agent comprises polyvinylpyrrolidone.
- AK. The method according to any of embodiments AC-AJ, wherein the halide

compound comprises cerium(III) chloride.

AL. The method according to any of embodiments AC-AK, wherein the halide compound comprises manganese(II) chloride.

Further non-limiting exemplary embodiments include:

- 5 AM. A method comprising:
- providing at least one reducing agent comprising at least one phenol group, the at least one reducing agent not also comprising a halogen atom, and
 - reducing at least one silver ion to at least one silver nanowire in a reaction mixture comprising the at least one reducing agent.
- 10 AN. The method according to embodiment AM, wherein the at least one reducing agent comprises at least one of 3,4-dihydroxybenzotriazole, 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol), and tannic acid.
- AP. The method according to embodiment AM, wherein the at least one reducing agent is selected from a group consisting of 3,4-dihydroxybenzotriazole, 2,2'-
- 15 isobutylidene-bis-(4,6-dimethyl-phenol), and tannic acid.
- AQ. The method according to any of embodiments AM-AP, wherein the reaction mixture further comprises at least one polyol.
- AR. The method according to embodiment AQ, wherein the at least one polyol comprises propylene glycol.
- 20 AS. The method according to any of embodiments AM-AR, wherein the reaction mixture further comprises at least one protecting agent.
- AT. The method according to embodiment AS, wherein the at least one protecting agent comprises polyvinylpyrrolidone.
- AU. The method according to any of embodiments AM-AT, wherein the reaction
- 25 mixture further comprises at least one halide compound capable of forming a halide ion.
- AV. The method according to any of embodiments AM-AU, wherein the reaction mixture further comprises at least one halide ion.
- AW. The method according to any of embodiments AM-AV, wherein the
- 30 reaction mixture further comprises at least one polar aprotic solvent.
- AX. The method according to embodiment AW, wherein the at least one polar

aprotic solvent comprises acetone.

EXAMPLES

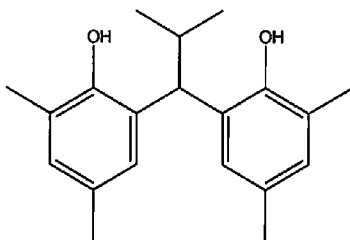
Materials

5 All materials used in the following examples are readily available from standard commercial sources, such as Sigma-Aldrich Co. LLC. (St. Louis, Missouri) unless otherwise specified. The following additional materials were used.

Propylene glycol (PG) is available from BASF.

10 Polyvinylpyrrolidone (PVP) is available from BASF under the trade name KOLLIDON®, such as KOLLIDON® 90 F.

2,2'-isobutylidene-bis-(4,6-dimethyl-phenol), which has the structure



15 , is available from Addivant (Middlebury, CT) under the trade name LOWINOX® 22IB46.

Instruments

A 0.5 L reaction flask with four necks was used to contain reaction materials. In our experiments, each of the four necks was used for inserting a stirring shaft, a condenser, a thermometer, or materials, such as reagents or nitrogen. The reaction flask is available from Chemglass Life Sciences.

A 12 gauge Teflon syringe needle was used to transfer materials from a first container (e.g. bottle) to a second container (e.g. flask).

25 A polished glass stirring shaft having dimensions of 1 cm x 40 cm with four blades angled 15° having outer diameter of 4.2 cm was used to stir materials. The stirring shaft is available from Chemglass Life Sciences.

A VS-3003 multi-gas sampling unit with a VA-3002 multi-gas

analyzer unit with a nitrogen flow rate of 1.5 L/min and selected NO range of 0-2000 ppm was used to quantitatively monitor for NO formation. The units are available from Horiba, Ltd.

5 **Example 1**

After overnight sparging, 250 mL of propylene glycol (PG), 68 mg of 3,4-dihydroxybenzotriazole, and 4.5 g of polyvinylpyrrolidone (PVP) were subjected to N₂ headspace positive pressure at 0.5 L/min, heating at 110.0 ± 0.3°C, and stirring at 200 rpm. 24.0 mL of a 1.0 M solution of silver nitrate (AgNO₃) in PG was added at a rate of 0.5 mL/min. After 2.0 mL of the 1.0 M solution of AgNO₃ in PG was added, 10 mL of 14 mM solution of cerium(III) chloride heptahydrate (CeCl₃·7H₂O) in PG was added at a rate of 0.5 mL/min. The reaction product had a small number of silver nanowires among many silver particles.

15

Example 2

The reaction product was prepared in a manner similar to that described in Example 1, except that 11.7 mg of 3,4-dihydroxybenzotriazole was used instead of 68 mg of 3,4-dihydroxybenzotriazole. Nitric oxide (NO) levels were quantitatively monitored and determined to be relatively low throughout the reaction.

Fig. 1 shows an optical micrograph of the reaction product after a total of 90 minutes from when the solution AgNO₃ in PG was first added. NO levels were at 0 ppm. Fig. 2 shows an optical micrograph of the reaction product after a total of 120 minutes from when the solution AgNO₃ in PG was first added. NO levels were at 4 ppm. Fig. 3 shows an optical micrograph of the reaction product after a total of 150 minutes from when the solution AgNO₃ in PG was first added. NO levels were at 16 ppm. Fig. 4 shows an optical micrograph of the reaction product of Fig. 3 after purification.

30

Fig. 5 shows a graph of the distribution of silver nanowire diameters taken from a random sample of 75 silver nanowires from five images of

the reaction product after purification, such as that shown in Fig. 4. For the silver nanowire diameters, the mean, median, standard deviation, minimum, and maximum were 60.24 nm, 59.55 nm, 11.21 nm, 40.01 nm, and 97.23 nm, respectively. Fig. 6 shows a graph of the distribution of silver nanowire lengths taken from a random sample of 347 silver nanowires from nine images of the reaction product after purification, such as that shown in Fig. 4. For the silver nanowire lengths, the mean, median, standard deviation, minimum, and maximum were 9.62 μm , 7.81 μm , 7.51 μm , 0.18 μm , and 37.02 μm , respectively.

10 Example 3

The reaction product was prepared in a manner similar to that described in Example 2, except that 75 mg of 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol) replaced the 11.7 mg of 3,4-dihydroxybenzotriazole.

Fig. 7 shows an optical micrograph of the reaction product after a total of 90 minutes from when the solution AgNO_3 in PG was first added. NO levels were at 0 ppm. Fig. 8 shows an optical micrograph of the reaction product after a total of 120 minutes from when the solution AgNO_3 in PG was first added. NO levels were at 16 ppm. Fig. 9 shows an optical micrograph of the reaction product after a total of 150 minutes from when the solution AgNO_3 in PG was first added. NO levels were at 20 ppm. Fig. 10 shows an optical micrograph of the reaction product of Fig. 9 after purification.

Fig. 11 shows a graph of the distribution of silver nanowire diameters taken from a random sample of 75 silver nanowires from five images of the reaction product after purification, such as that shown in Fig. 10. For the silver nanowire diameters, the mean, median, standard deviation, minimum, and maximum were 42.27 nm, 43.26 nm, 7.65 nm, 26.98 nm, and 62.8 nm, respectively. Fig. 12 shows a graph of the distribution of silver nanowire lengths taken from a random sample of 199 silver nanowires from ten images of the reaction product after purification, such as that shown in Fig. 10. For the silver nanowire lengths, the mean, median, standard deviation, minimum, and maximum were 6.85 μm , 6.89 μm , 3.24 μm , 0.27 μm , and 27.18 μm , respectively.

Example 4

The reaction product was prepared in a manner similar to that described in Example 3, except that 101 mg of 2,2'-isobutylidene-bis(4,6-dimethyl-phenol) was used and the 4.5 g of PVP was added after 2.0 mL of 1.0 M AgNO₃ in PG was added.

Fig. 13 shows an optical micrograph of the reaction product after a total of 90 minutes from when the solution AgNO₃ in PG was first added. NO levels were at 0 ppm. Fig. 14 shows an optical micrograph of the reaction product after a total of 120 minutes from when the solution AgNO₃ in PG was first added. NO levels were at 7 ppm. Fig. 15 shows an optical micrograph of the reaction product after a total of 150 minutes from when the solution AgNO₃ in PG was first added. NO levels were at 11 ppm.

Fig. 16 shows a graph of the distribution of silver nanowire diameters taken from a random sample of 75 silver nanowires from five images of the reaction product, such as that shown in Fig. 15. For the silver nanowire diameters, the mean, median, standard deviation, minimum, and maximum were 39.57 nm, 39.54 nm, 5.34 nm, 28.38 nm, and 49.73 nm, respectively. Fig. 17 shows a graph of the distribution of silver nanowire lengths taken from a random sample of 336 silver nanowires from eight images of the reaction product, such as that shown in Fig. 15. For the silver nanowire lengths, the mean, median, standard deviation, minimum, and maximum were 8.76 μm, 8.37 μm, 3.8 μm, 1.21 μm, and 24.35 μm, respectively.

Example 5

400 mL PG containing 5.55 g of PVP, 0.196 g of 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol), and 58.5 mg of MnCl₂·4H₂O was sparged with N₂ overnight and then switched to positive headspace pressure prior to AgNO₃ addition. 24.0 mL of 1.0 M AgNO₃ in PG was added to the mixture at 0.5 mL/min. The mixture was heated to 150°C ± 0.5°C and held at that temperature until the mV reading on a silver ion specific electrode stabilized at

which point the mixture was cooled. The total amount of NO produced during reaction is about 2.2 mmol.

Fig. 18 shows a plot of silver ion concentration in mV over time in minutes as measured by a silver ion specific electrode as described in U.S. Provisional Application No. 62/170,164, filed June 3, 2015, which is hereby incorporated by reference. Fig. 19 shows an optical micrograph of the purified reaction product. Fig. 20 shows a graph of the distribution of silver nanowire diameters taken from image(s) of the reaction product, such as that shown in Fig. 19. Fig. 21 shows a graph of the distribution of silver nanowire lengths taken from image(s) of the reaction product, such as that shown in Fig. 19.

Example 6

To 280 mL of ethylene glycol (EG), 5.19 g of EG containing 53.0 mg AgNO_3 and 106.5 mg of tannic acid and 2.1 g of 9.3 mM $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in EG was added. The base mixture was degassed with N_2 while being stirred at 100 rpm for two hours. A solution of 0.25 M AgNO_3 in EG and 0.84 M polyvinylpyrrolidone (PVP) was degassed and heated to 145°C for at least 60 minutes. The solution was added to the base mixture 0.8 mL/min to create the reaction mixture. When cooled to ambient temperature, the reaction mixture is diluted by an equal volume of acetone and centrifuged at 400 G for 45 minutes. The decanted solid was re-dispersed in 200 mL isopropanol (IPA), agitated for 10 minutes, centrifuged, decanted, and diluted with 15 mL of IPA. No silver nanowires were detected.

The invention has been described in detail with reference to specific embodiments, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention. The presently disclosed embodiments are therefore considered in all respects to be illustrative and not restrictive. The scope of the invention is indicated by the claims and all changes that come within the meaning and range of equivalents thereof are intended to be embraced there.

CLAIMS:

1. A method comprising:
providing at least one reducing agent comprising at least one
phenol group, the at least one reducing agent not also comprising a halogen atom,
5 and
reducing at least one silver ion to at least one silver nanowire in a
reaction mixture comprising the at least one reducing agent.
2. The method according to claim 1, wherein the at least one
10 reducing agent comprises at least one of 3,4-dihydroxybenzotriazole, 2,2'-
isobutylidene-bis-(4,6-dimethyl-phenol), and tannic acid.
3. The method according to claim 1, wherein the at least one
reducing agent is selected from a group consisting of 3,4-dihydroxybenzotriazole,
15 2,2'-isobutylidene-bis-(4,6-dimethyl-phenol), and tannic acid.
4. The method according to claim 1, wherein the reaction mixture
further comprises at least one polyol.
- 20 5. The method according to claim 4, wherein the at least one polyol
comprises propylene glycol.
6. The method according to claim 1, wherein the reaction mixture
further comprises at least one protecting agent.
25
7. The method according to claim 6, wherein the at least one
protecting agent comprises polyvinyl pyrrolidone.
8. The method according to claim 1, wherein the reaction mixture
30 further comprises at least one halide compound capable of forming a halide ion.

9. The method according to claim 1, wherein the reaction mixture further comprises at least one halide ion.

10. The method according to claim 1, wherein the reaction mixture
5 further comprises at least one polar aprotic solvent.

11. The method according to claim 10, wherein the at least one polar aprotic solvent comprises acetone.

10

1/21

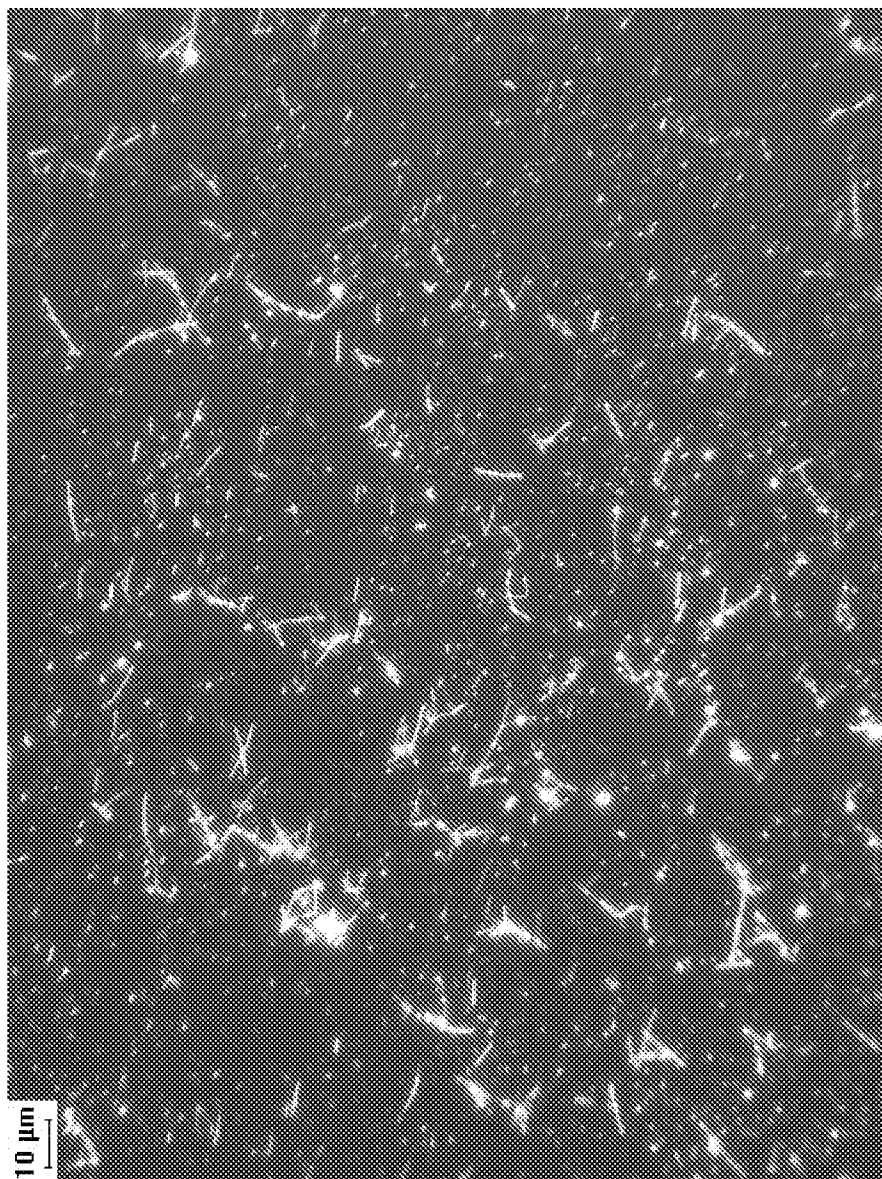


FIG. 1

2/21

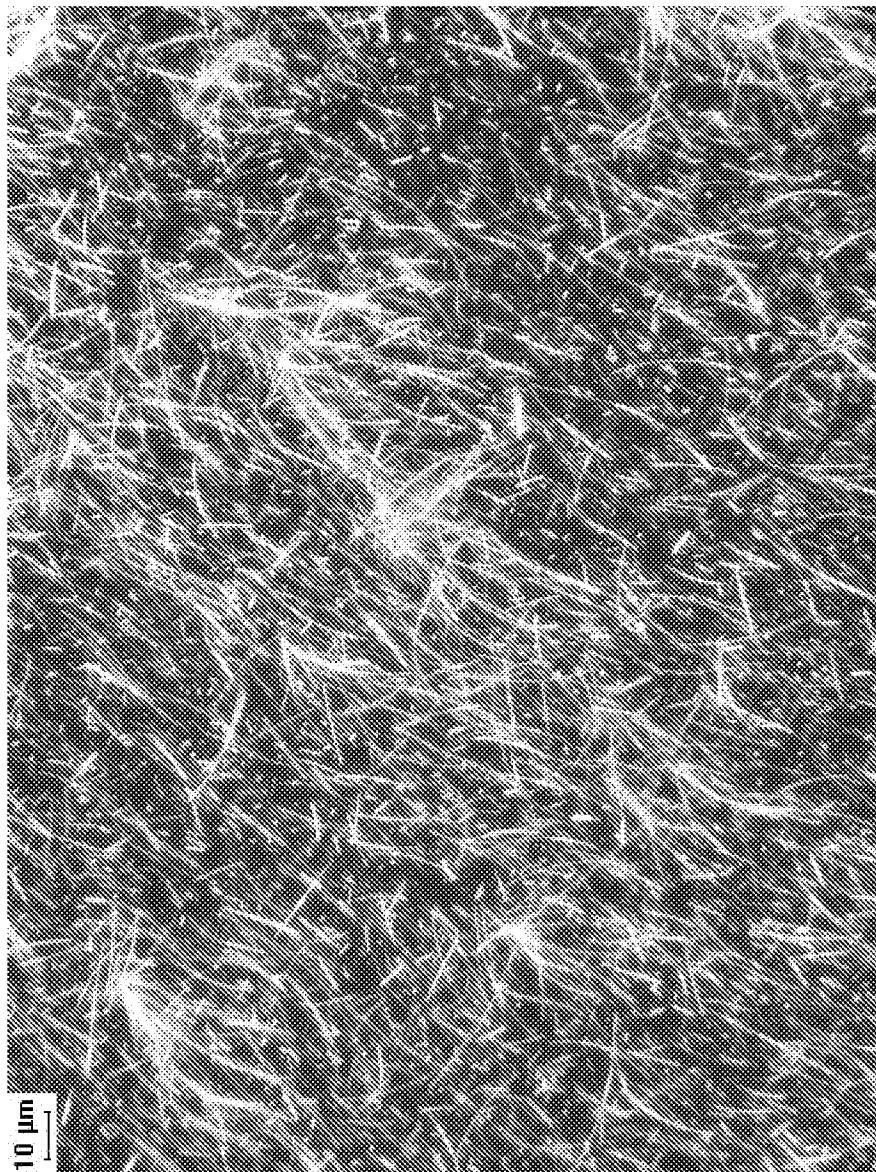


FIG. 2

3/21

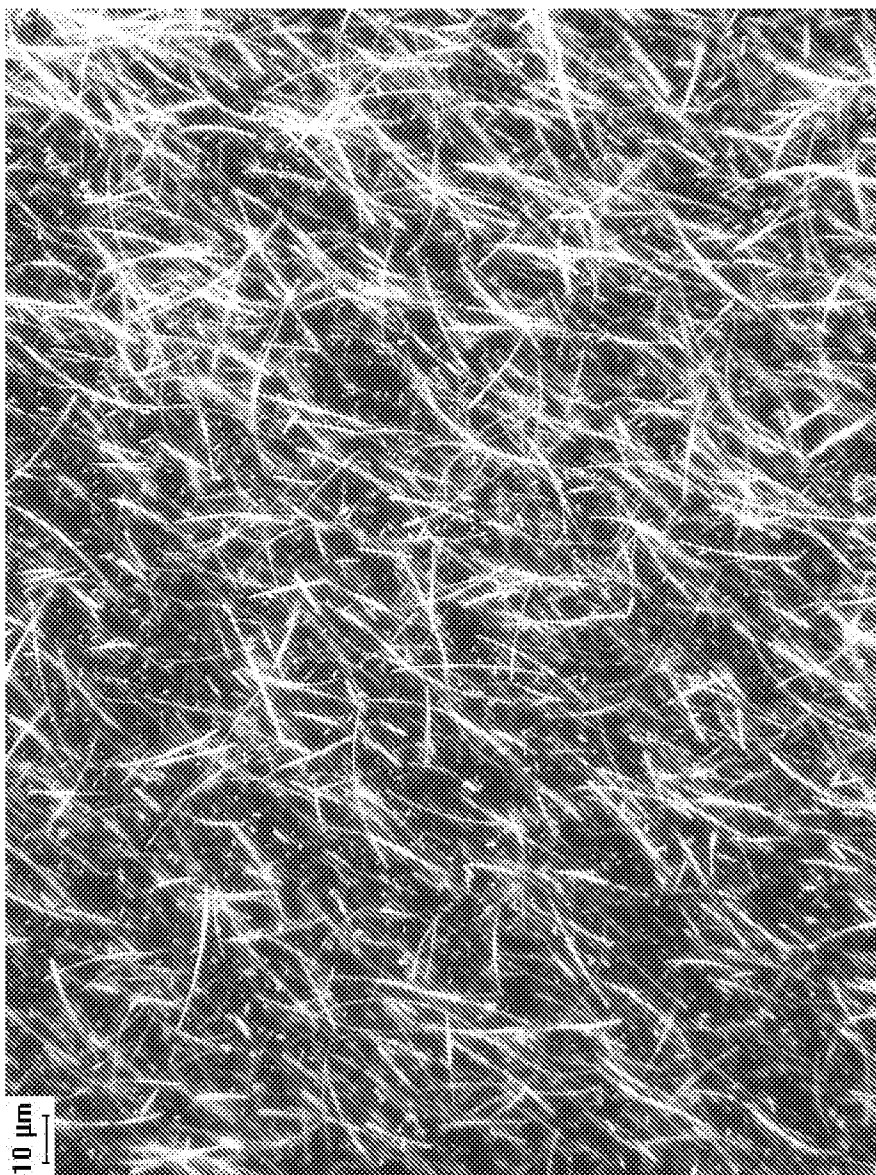


FIG. 3

4/21

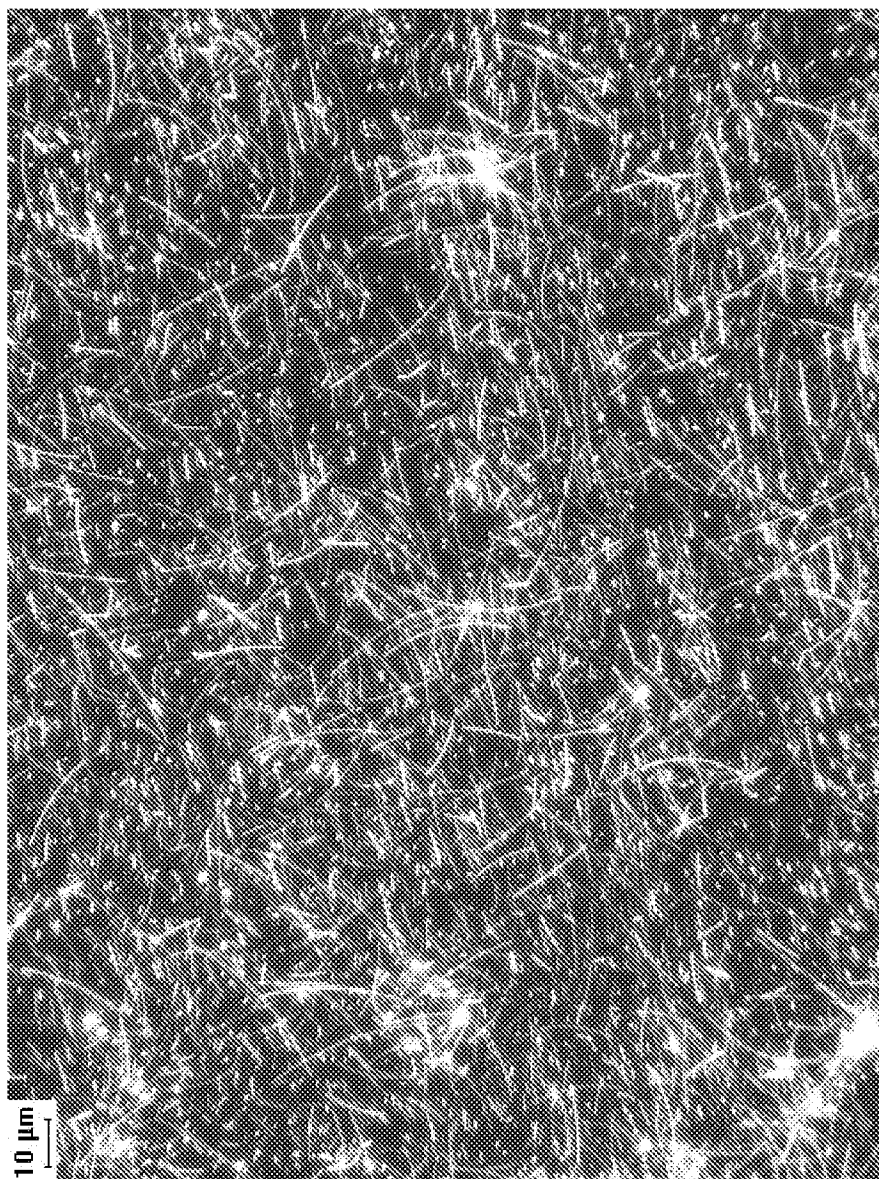


FIG. 4

5/21

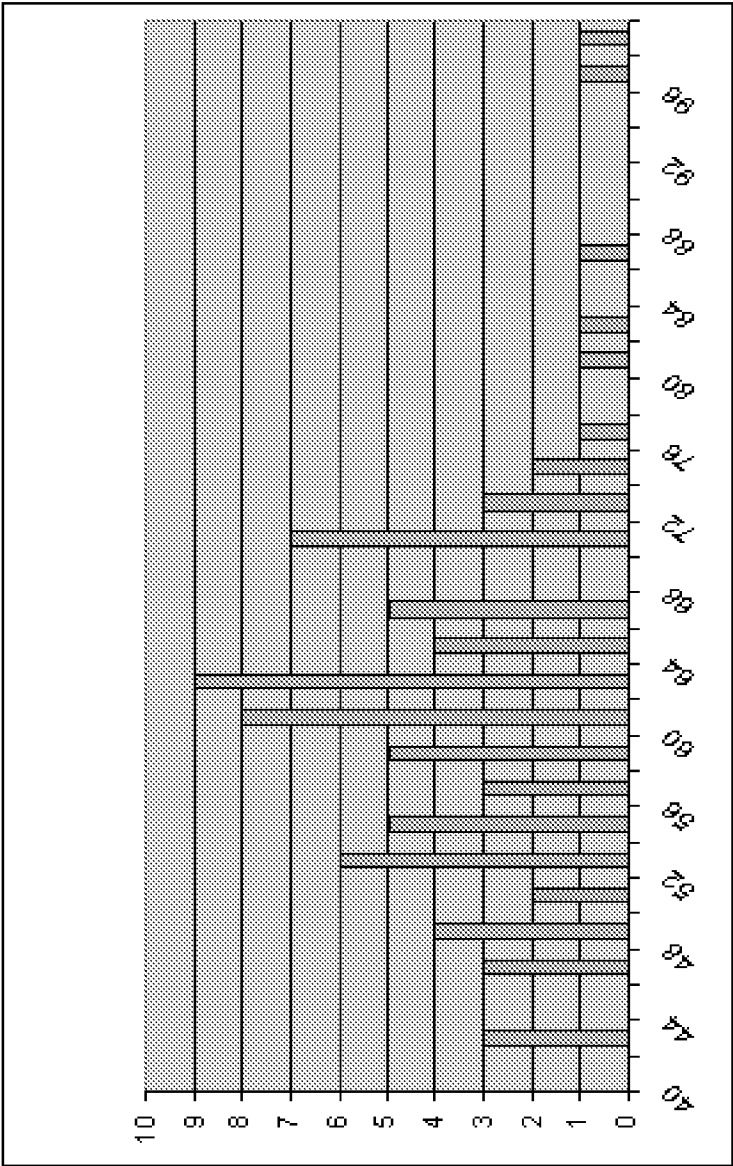


FIG. 5

6/21

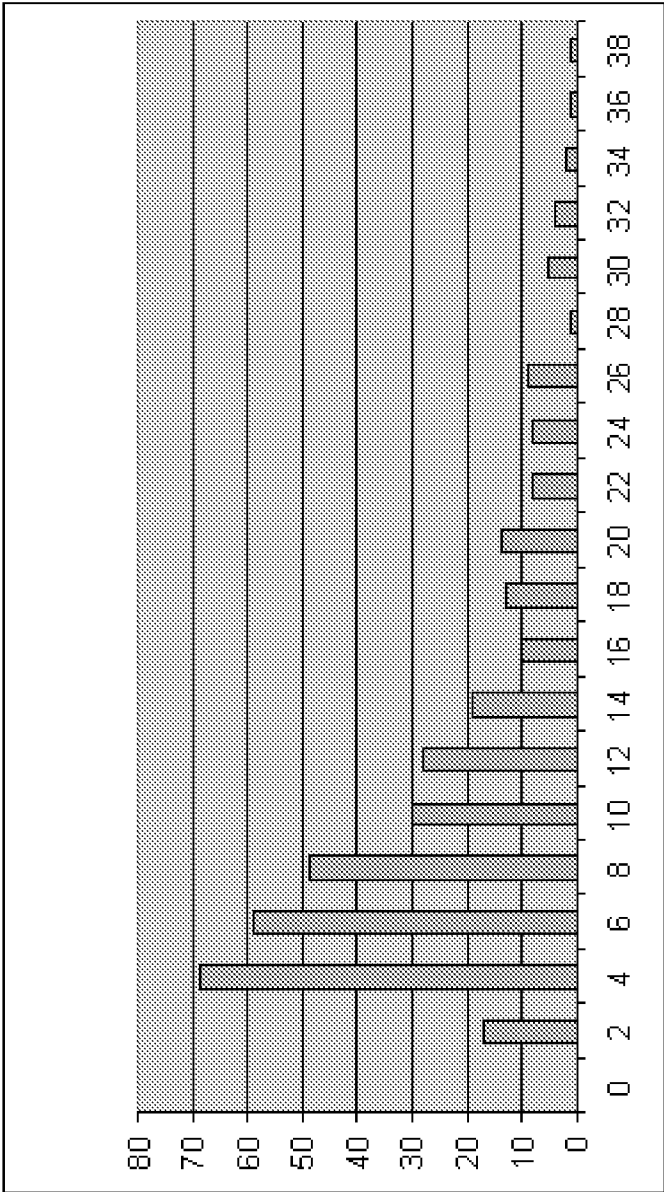


FIG. 6

7/21

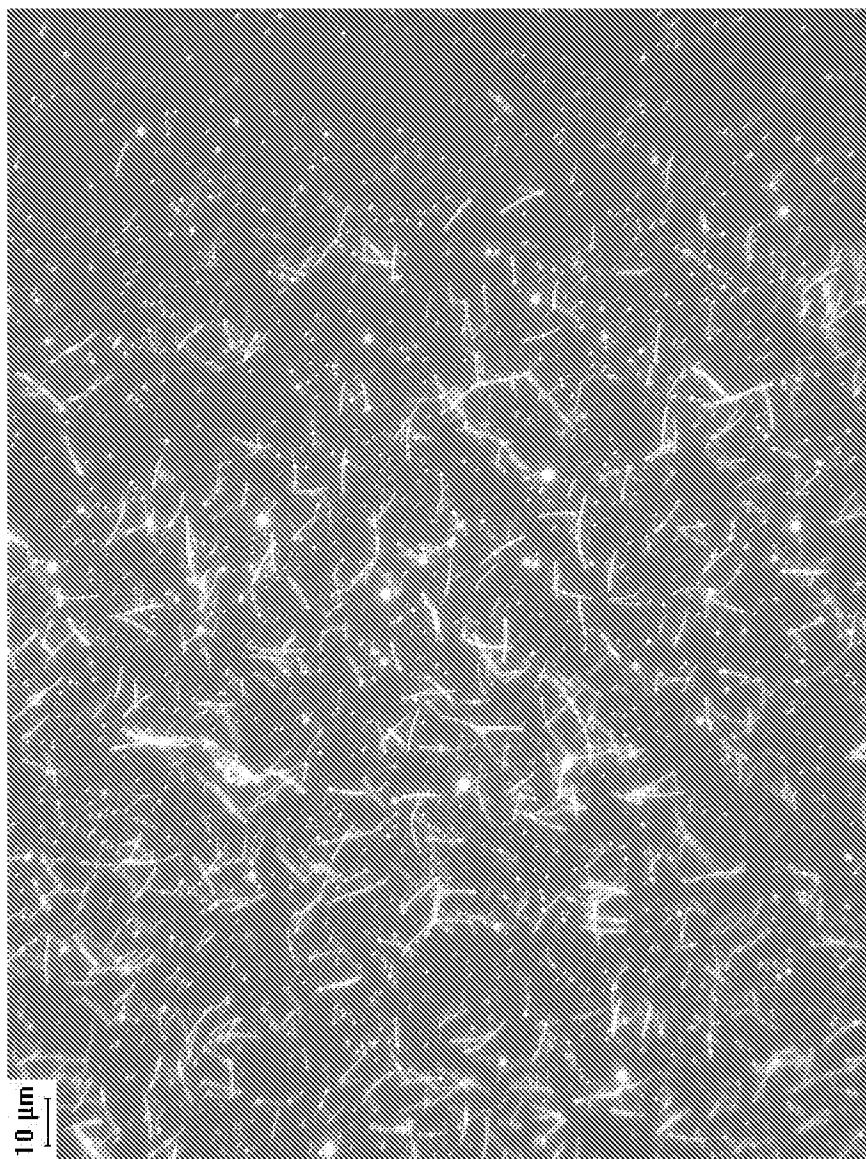


FIG. 7

8/21

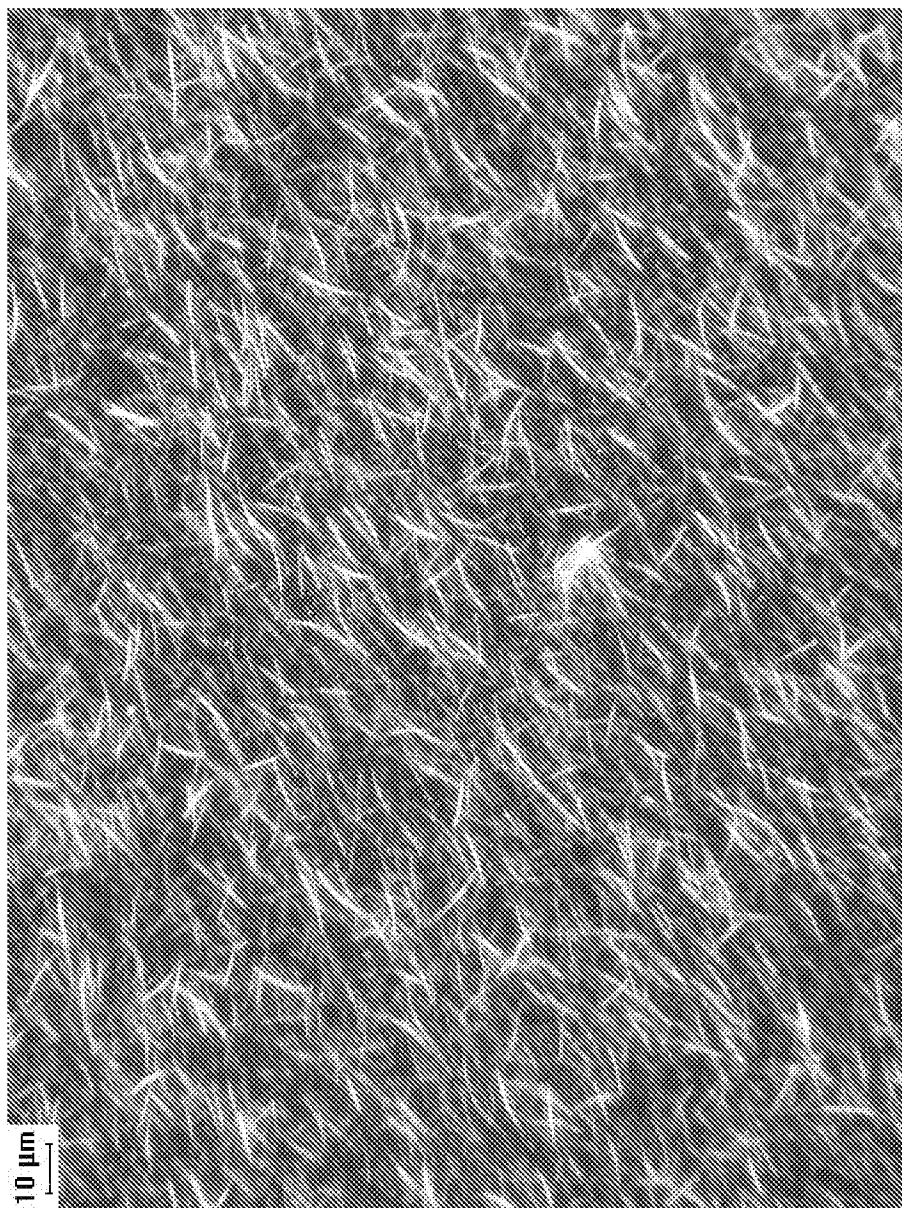


FIG. 8

9/21

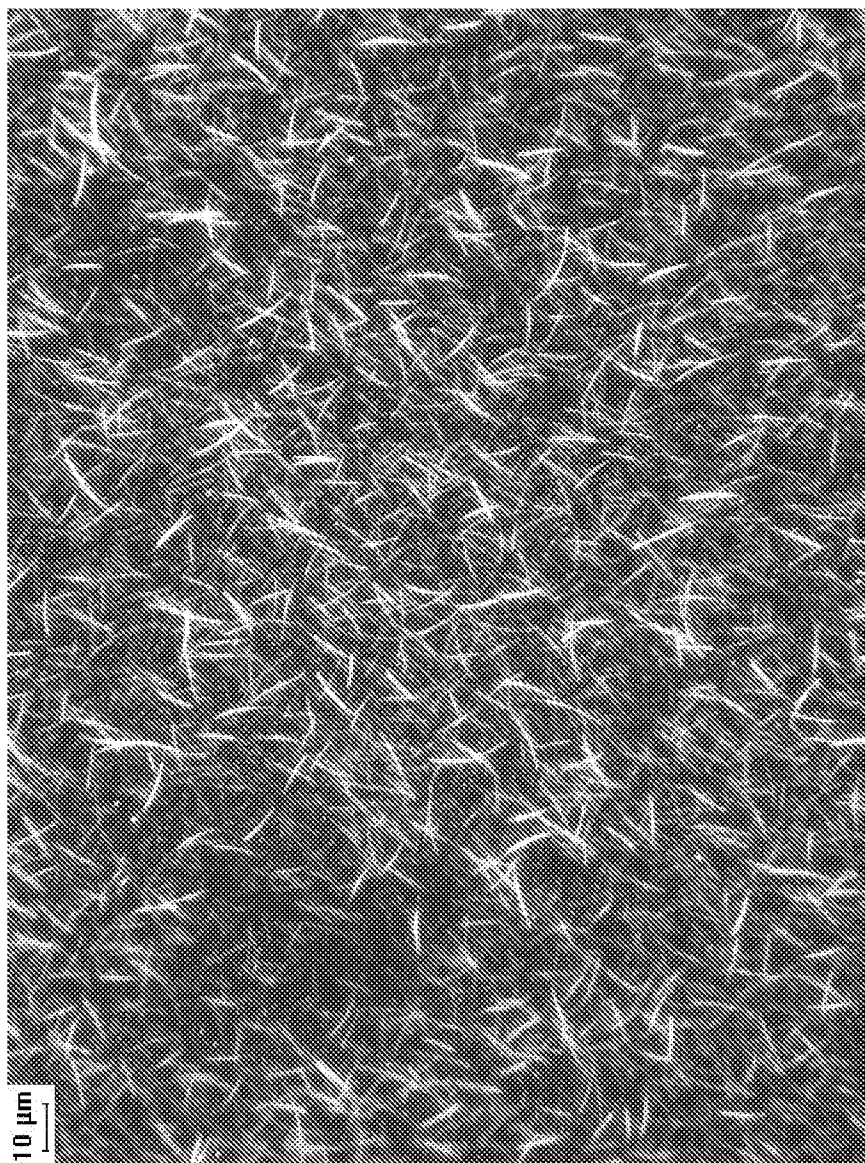


FIG. 9

10/21

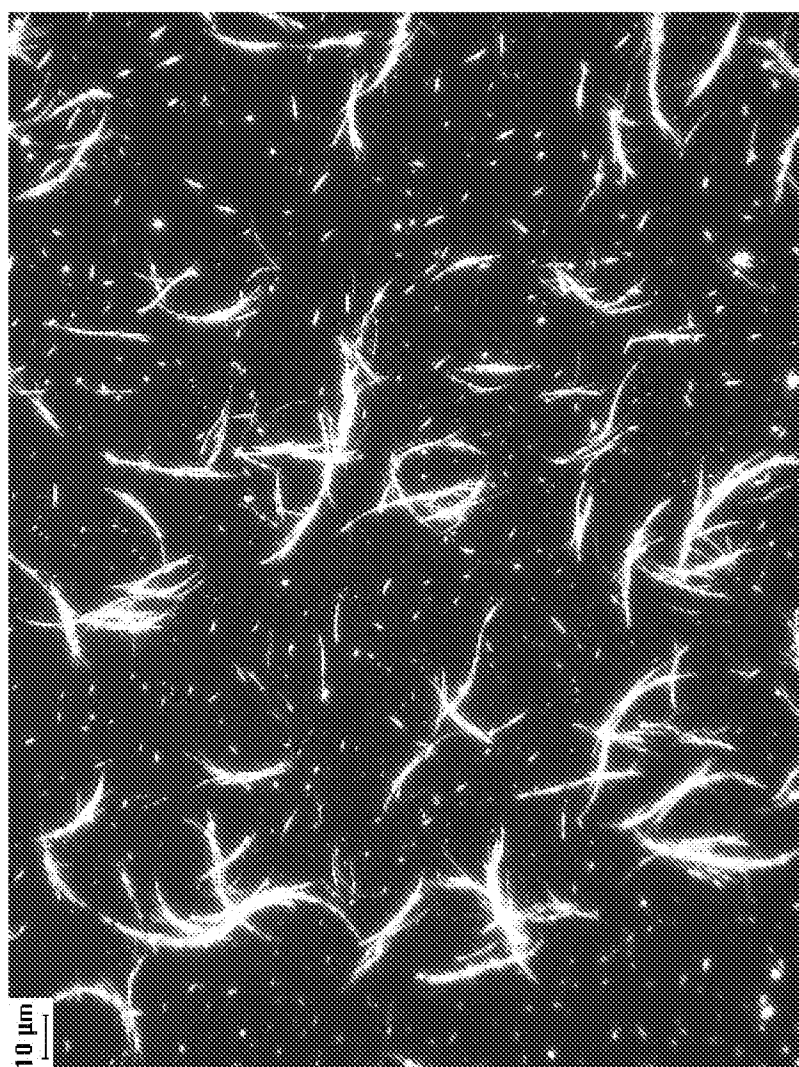


FIG. 10

11/21

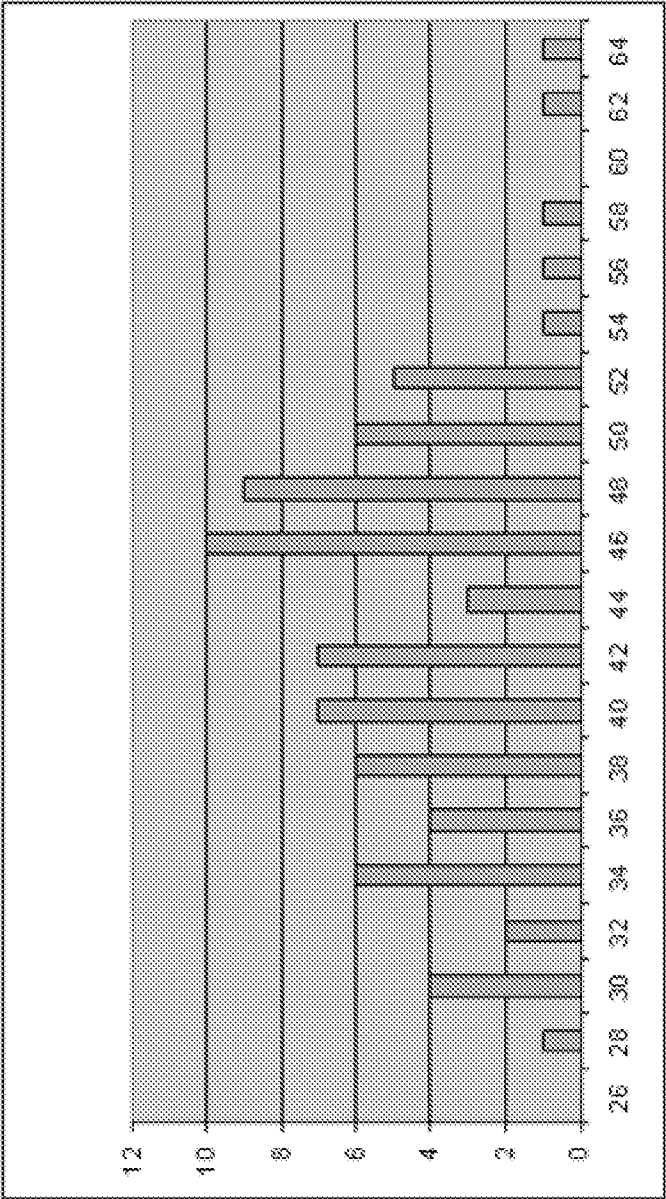


FIG. 11

12/21

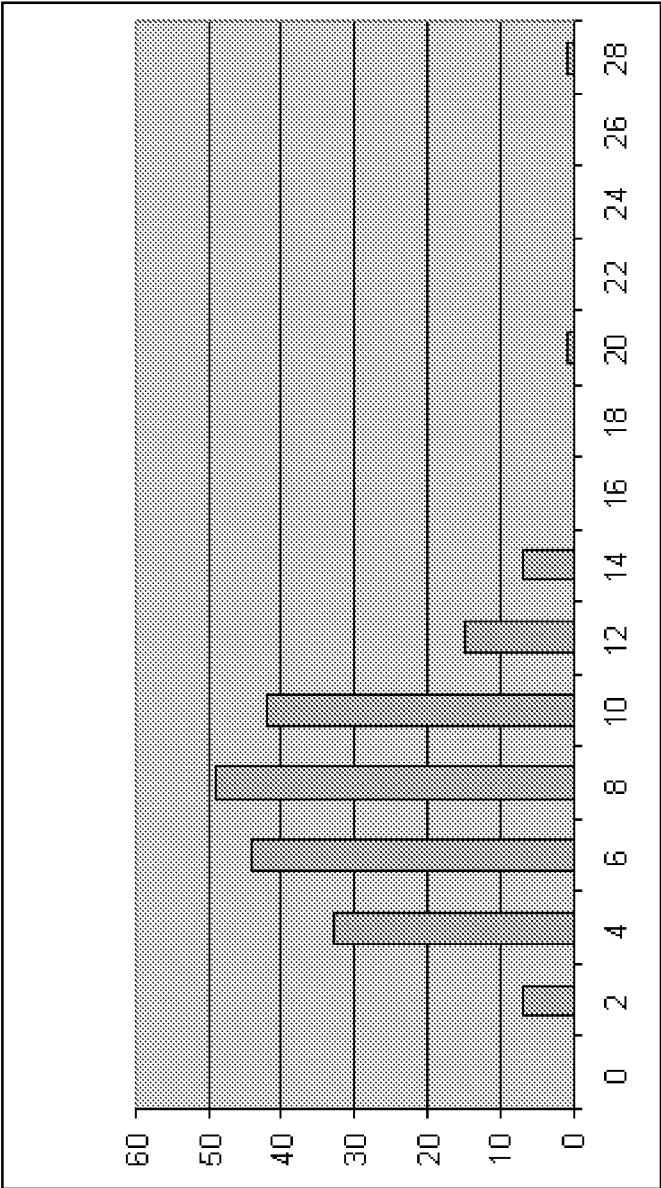


FIG. 12

13/21

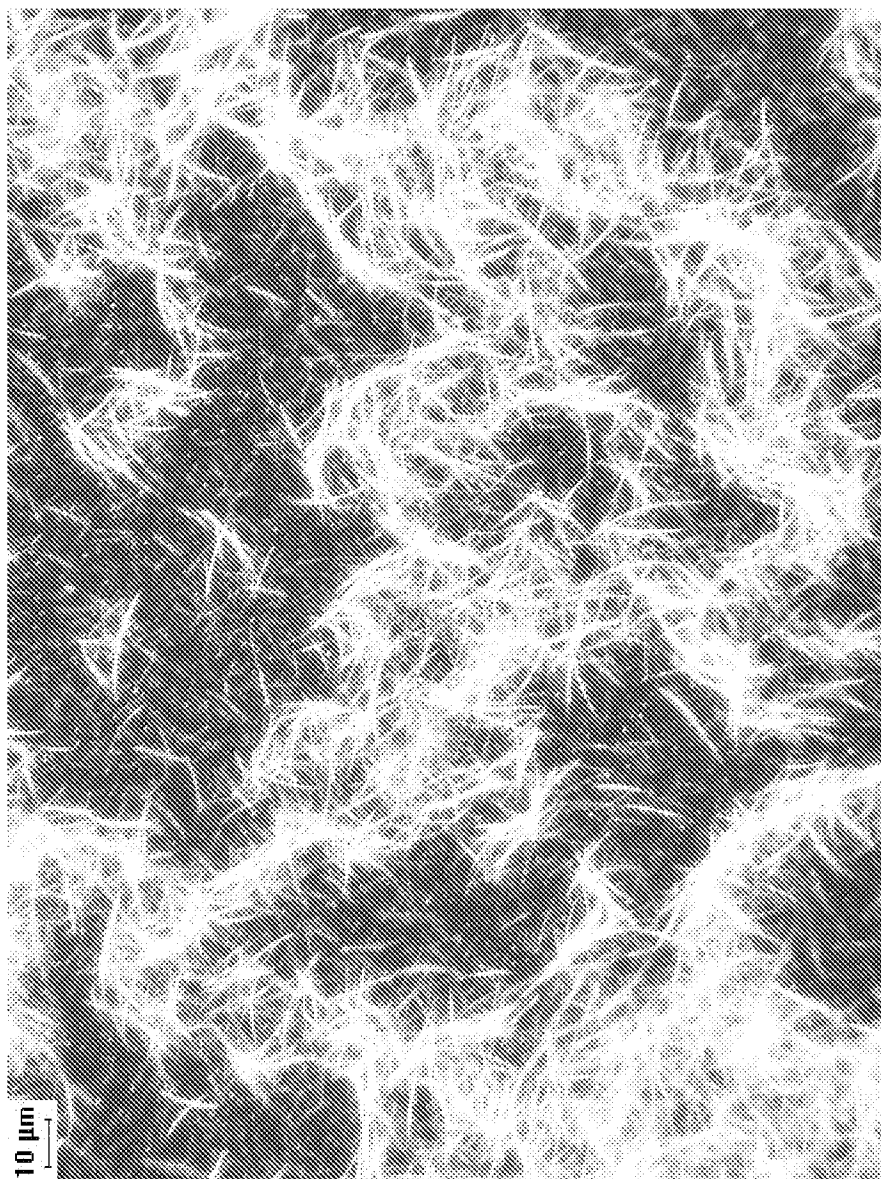


FIG. 13

14/21

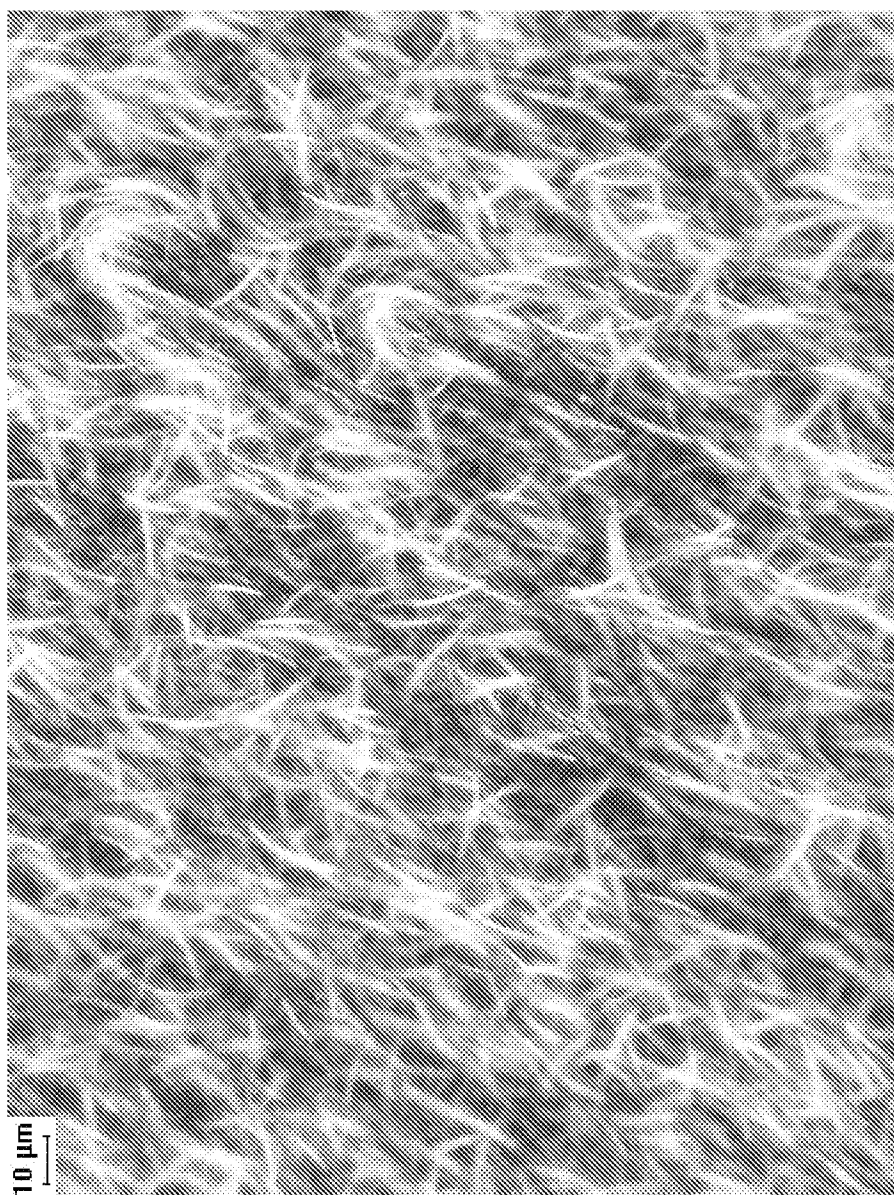


FIG. 14

15/21

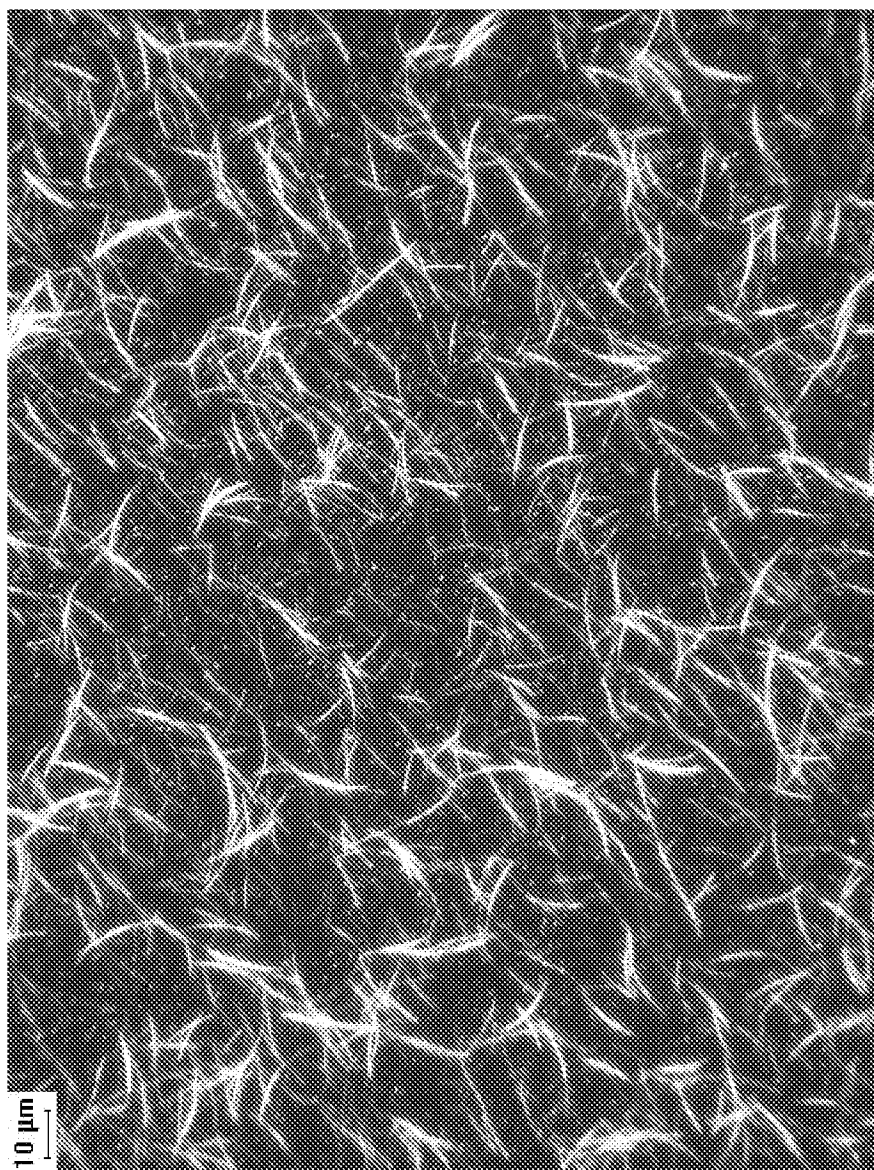


FIG. 15

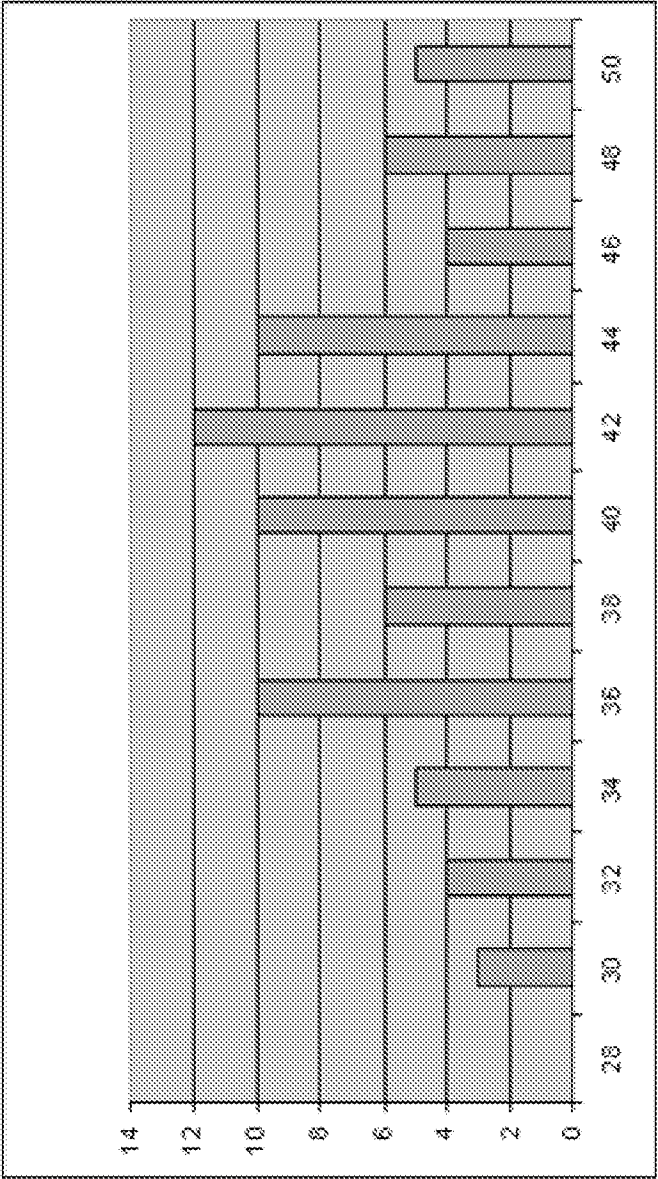


FIG. 16

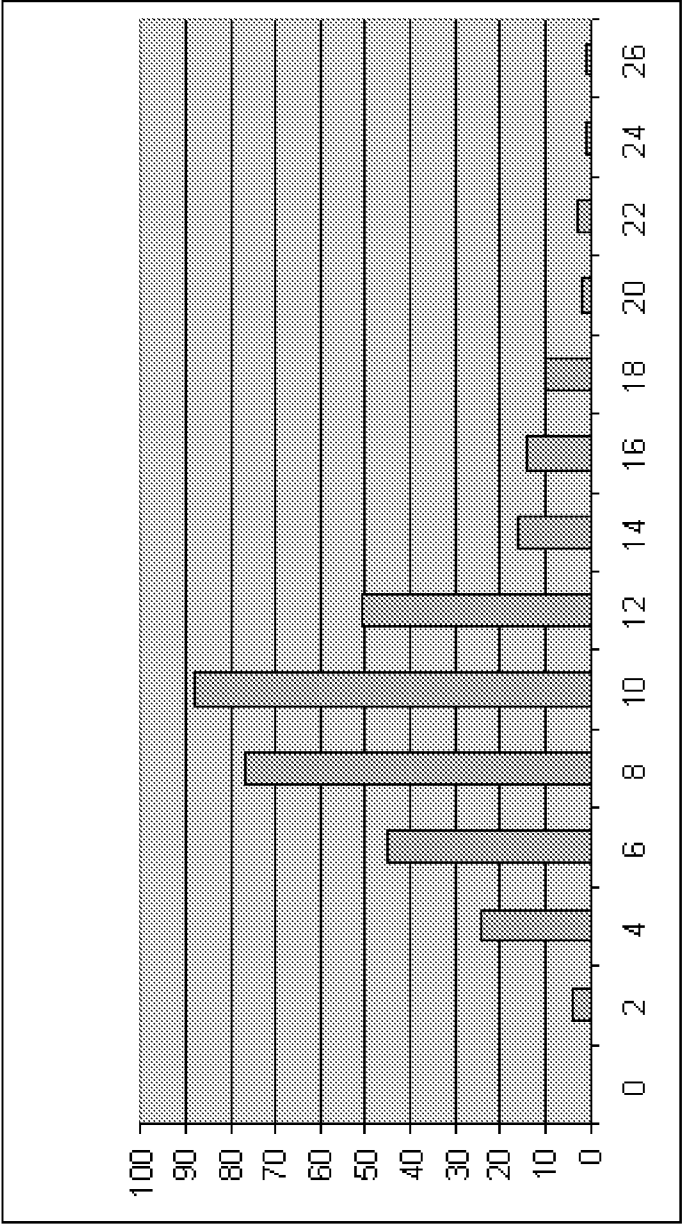


FIG. 17

18/21

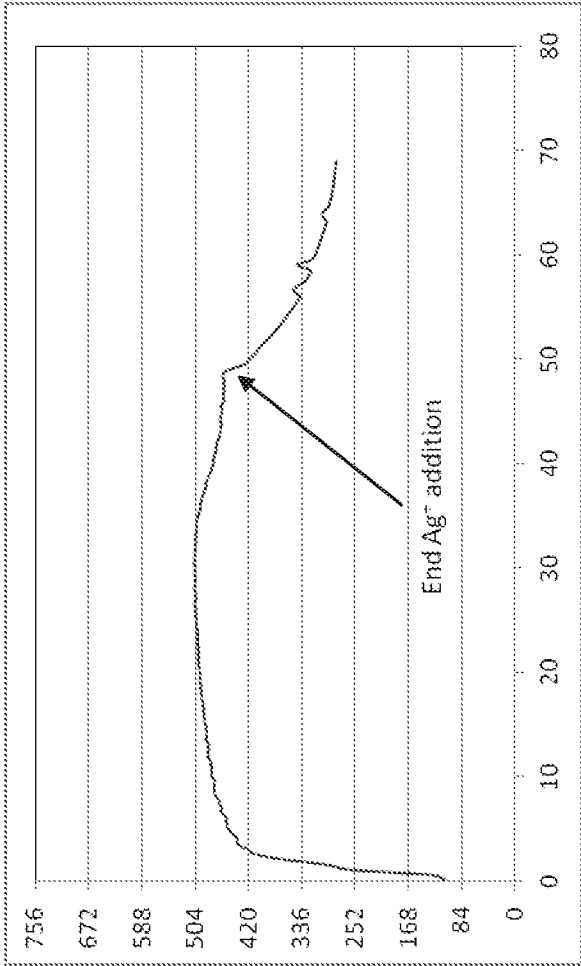


FIG. 18

19/21

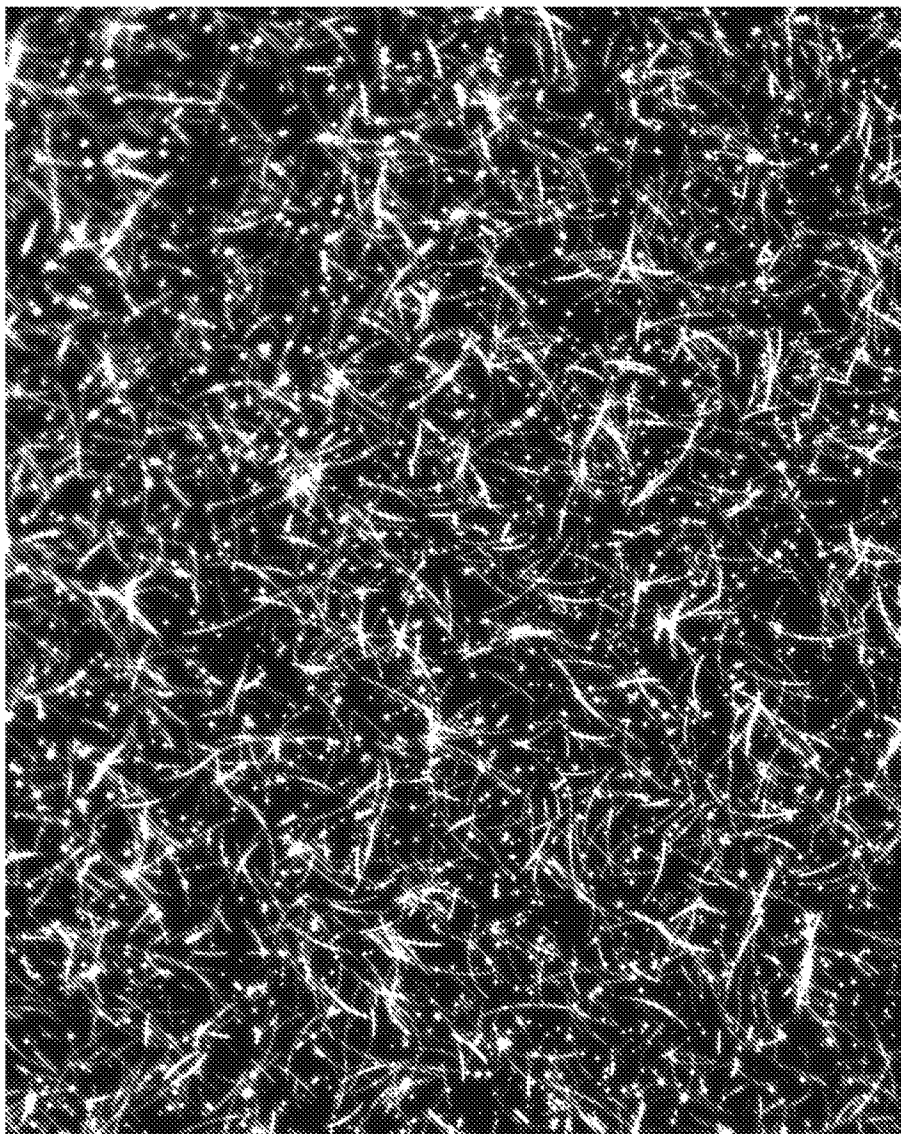


FIG. 19

20/21

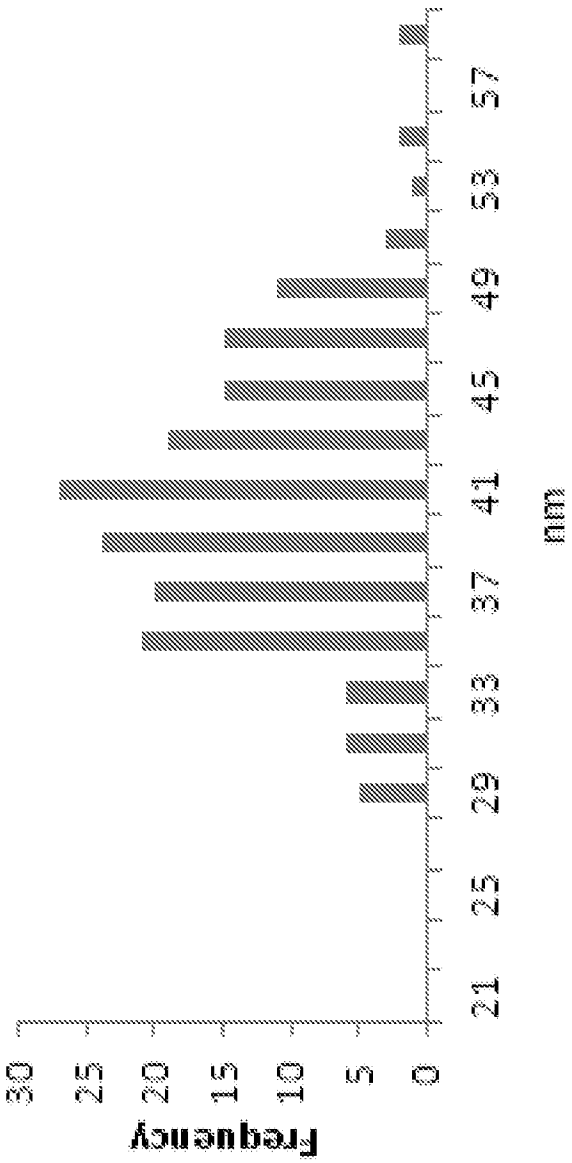
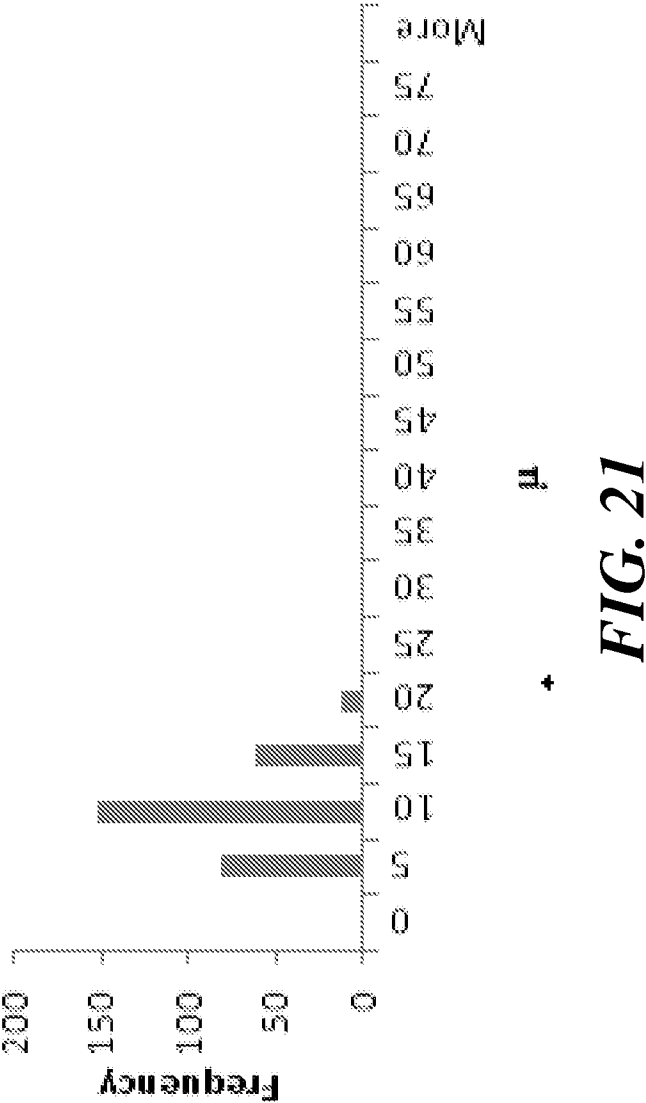


FIG. 20

21/21



INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/036874

A. CLASSIFICATION OF SUBJECT MATTER

INV. B22F1/00 B22F9/24
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	XUELIN TIAN ET AL: "Facile synthesis of single-crystal silver nanowires through a tannin-reduction process", JOURNAL OF NANOPARTICLE RESEARCH ; AN INTERDISCIPLINARY FORUM FOR NANOSCALE SCIENCE AND TECHNOLOGY, KLUWER ACADEMIC PUBLISHERS, DO, vol. 11, no. 7, 21 August 2009 (2009-08-21), pages 1839-1844, XP019752308, ISSN: 1572-896X, DOI: 10.1007/S11051-009-9700-4	1-3
A	Experimental section; page 1840	4-11
X	JP 2007 246997 A (UNIV TOKYO; MITSUBISHI CHEM CORP) 27 September 2007 (2007-09-27) pages 5-6, paragraph [0025]-[0028]	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 August 2015

Date of mailing of the international search report

07/09/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Helgadóttir, Inga

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/036874

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2007246997	A	27-09-2007	NONE
