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(54) **Title**: GREEN CHEMISTRY METHOD OF MAKING COPPER NANOWIRES

(57) **Abstract**: The present invention provides a method of making copper nanowires in a basic aqueous solution using benign or biocompatible reducing agents and capping agents. In another aspect, copper nanowires are provided that are made by the method.

GREEN CHEMISTRY METHOD OF MAKING COPPER NANOWIRES

BACKGROUND OF THE INVENTION

Field Of The Invention

[001] The present disclosure relates to the field of copper nanowires, specifically methods of making copper nanowires and suspensions of copper nanowires using green chemistry.

Description Of The Background

[002] Green chemistry, also called sustainable chemistry, involves the design of chemical products and processes that reduce or eliminate the generation of hazardous substances.

[003] Copper nanowires have been proposed as components of several components of "clean energy," including supercapacitors, flexible and transparent displays, and solar cells, What is needed is a green chemistry method of manufacturing copper nanowires, and copper nanowires produced by the method.

[004] Metallic nanowires are a promising set of materials that have found use in electronics, sensors and catalysis. Their use in electronics as thin films of transparent conductor stands out with the recent commercialization of silver nanowires in display devices. Copper being a close rival of silver in electrical conductivity, such high quality transparent conductor can, in principle, be made of copper nanowires and their alloys as well. It has been reported that good quality transparent conducting films can be made with copper nanowires.

[005] Known methods for the production of copper nanowires involve an aqueous synthesis by reduction of copper (II) salt using hydrazine, N_2H_4, as the reducing agent and ethylenediamine (EDA) as the ligand (stabilizing or capping agent) in a highly concentrated NaOH solution. Chang, Y., et al., Large-Scale Synthesis of High-Quality Ultralong Copper Nanowires,

Langmuir, 21, 3746-3748, Rathmell, A.R., et al., The Growth Mechanism of Copper Nanowires and Their Properties in Flexible, Transparent Conducting Films, *Adv. Mater.* 22: 3558-3562, 2010. However, hydrazine is highly toxic, dangerously unstable unless handled in solution, and regarded as a toxic waste for disposal purposes.

[006] The principles of green chemistry have been applied to the synthesis of nanocrystals and nanocomposites. Nadagouda, M.N., Green Synthesis of Nanocrystals and Nanocomposites, Chapter 17, pp. 395-412 in Kolesnikov, N., Modern Aspects of Bulk Crystal and Thin Film Preparation, Intech 2012. However, many of such green chemistry synthetic approaches have used poorly characterized vegetable extracts that are believed to act as both reducing agent(s) and stabilizing or capping agents. Von White II, G., et al., Green Synthesis of Robust, Biocompatible Silver Nanoparticles Using Garlic Extract, *J. Nanomaterials*, 2012, 1-12, doi:10.1155/2012/730746. The use of such poorly characterized vegetable extracts is unsuitable for scaling-up the synthesis for industrial use.

[007] We have discovered that high quality copper nanowires can be made by a green chemistry process that uses benign or biocompatible reagents, and specifically avoiding the use of hydrazine and any toxic amines. In preferred embodiments of the present chemical synthesis method, a copper (II) salt is used to make copper nanowires by reduction with a non-toxic reagent, preferably a biocompatible reducing agent, to avoid the use of compounds such as hydrazine. The method is simple, economical and scalable.

SUMMARY OF THE INVENTION

[008] The present invention provides a method of making copper nanowires in a basic aqueous solution using benign or biocompatible reducing agents and capping agents. In another aspect, copper nanowires are provided that are made by the method.

[009] In certain embodiments, the present invention provides a method of making copper nanowires comprising the steps of providing a copper (II) salt in an aqueous solution of hydroxide to form a basic aqueous reaction solution of the copper (II) salt; heating the reaction solution of the copper (II) salt to about 70 to about 90 degrees Celsius; adding an effective amount of a compound of formula I, $NH_2(CH_2)_nCOOH$, where n is an integer from 1-6, inclusive; and adding an effective amount of a biocompatible reducing agent, thereby forming copper nanowires in the reaction solution. In certain embodiments of the method, the step of providing a copper (II) salt includes the step of adding an aqueous solution of a copper (II) salt to an aqueous solution of hydroxide. In certain embodiments of the method, the step of adding an effective amount of a biocompatible reducing agent may precede the step of adding an effective amount of a compound of formula I. In other embodiments of the method, the step of adding an effective amount of a biocompatible reducing agent may follow the step of adding an effective amount of a compound of formula I.

[0010] In preferred embodiments, the method further includes the step of removing the copper nanowires from reaction solution. Preferably, the copper nanowires are washed and re-suspended in a suitable storage solution. In certain embodiments, the storage solution comprises at least one of a surfactant and an antioxidant. In preferred embodiments, the surfactant is polyvinylpyrrolidone and the antioxidant is ascorbic acid. In certain solutions, the reaction solution comprises a surfactant.

[0011] In certain embodiments, the aqueous solution of hydroxide is an aqueous solution of NaOH, KOH, RbOH or CsOH. NaOH is preferred. In certain embodiments, the aqueous solution of NaOH is about12 molar to about 15 molar. In certain embodiments, the compound of formula I is glycine or beta-alanine. In certain embodiments, the biocompatible reducing agent is a reductone. In preferred embodiments, the reductone is ascorbic acid, an ascorbic acid derivative or an acceptable salt thereof.

[0012] In another aspect, copper nanowires produced by the method of the present invention are provided.

[0013] The above described and other features are exemplified by the following figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The foregoing and other features and advantages will be apparent from the following more particular description of exemplary embodiments of the disclosure, as illustrated in the accompanying drawings, in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the disclosure.

[0015] FIG. 1A is an optical microscope image of copper nanowires made according to the method of Example 1, showing wires at about 40 μm to about 50 μm long. The maze of nanowires can be separated by sonication or surfactants. The scale bar indicates 20 μm.

[0016] FIG. 1B is a scanning electron microscope (SEM) image showing copper nanowires made according to the method of Example 1, and few, if any, particles. The scale bar indicates 2 μm.

[0017] FIG. 2 is a transmission electron micrograph of a copper nanowire made according to the method of Example 1, with diameters measured at the indicated points: a, 56.01 nm, b, 76.93 nm, and c, 81.52 nm. The scale bar indicates 100 nm.

[0018] FIG. 3 is a transmission electron micrograph of a thinner copper nanowire made according to the method of Example 1, with diameters measured at the indicated points: a, 16.49 nm, b, 27.75 nm, and c, 24.75 nm. The scale bar indicates 100 nm.

[0019] FIG. 4 is a X-ray diffractogram of copper nanowires made according to the method of Example 1, showing a cubic crystal structure and no spurious phases.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0020] As used herein, "reductone" refers to a compound containing an enediol structure stabilized by conjugation and hydrogen bonding with an adjacent carbonyl group, RC(OH)=C(OH)C(=O)R. Reductones are strong reducing agents, fairly strong acids and commonly derived from saccharides by oxidation at the carbon atom alpha to the carbonyl function. IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook. The use of reductones as antioxidants in vegetable oils is known in the field of food chemistry. Evans, CD., et al., Amino-Hexose-Reductones As Antioxidants. I. Vegetable Oils, Journal of the American Oil Chemist's Society, February 1958, 35 (2), 84-88. Reductones include hydroxyacetone, 2,3-dihydroxyacrylaldehyde (also known as triosereductone), 2-amino-2-deoxy-L-ascorbic acid, ascorbic acid, sodium ascorbate, tartronaldehyde ((E)-2,3-dihydroxyprop-2-enal), cyclopentediolone (also known as reductic acid), alpha-amino-beta-ketobutyric acid, and amino-hexose-reductones. See U.S. Patent No. 3,883,299. Further ascorbic acid derivatives are known, for example in U.S. Patent Nos. 3,883299 and 6,444,144. A preferred reductone is ascorbic acid.

[0021] As used herein, "biocompatible" means being compatible or harmonious with life; not having toxic or injurious effects on biological functions.

[0022] The following non-limiting examples further illustrate the various embodiments described herein.

Example 1

Synthesis of Copper Nanowires

[0023] Copper nanowires were synthesized in aqueous solutions under normal room atmosphere. Ascorbic acid and glycine were added in excess to

a solution of $Cu(NO_3)_2$ in 15 M (aq.) NaOH. The reagents are listed in Table 1, below.

Table 1 **Reagents**
1 ml 0.1 M (aq.) $Cu(NO_3)_2$ [1 equivalent]
0.5625 g, 7.5 mM glycine [75 equivalents]
20 mL, 15 M (aq.) NaOH
176.12 mg ascorbic acid [10 equivalents] (1.5 mL of a 1 mM (aq.) stock solution)

[0024] One milliliter of a 0.1 M (aq.) $Cu(NO_3)_2$ stock solution was added to 20 mL, 15 M (aq.) NaOH in a 100 mL three-necked round bottom flask. Glycine was added to a concentration of 7.5 mM (0.5625 g). All aqueous solutions were made using deionized water. The flask was placed on a heating mantle and heated gradually to 70°C (over about 0.5 hour) while stirring continuously. In a separate scintillation vial, ascorbic acid (176.12 mg, 1 mM, 10 equivalents) was dissolved in 1.5 mL deionized water and the solution was added rapidly by syringe to the reaction solution in the round bottom flask. The ascorbic acid stock solution was typically freshly made; solutions more than a day old were discarded. After about 10 – 60 minutes, copper nanowires were formed and floated to the surface of the reaction liquid forming a maze-like ensemble.

[0025] The reaction appears to reach completion at 10 minutes under these conditions; no appreciable increase in product is obtained by continuing to run the reaction for 60 minutes. Typically, 10-20 mg of copper nanowires were produced in 10 minutes by such reactions at the 20 mL scale. The reaction conditions and reaction product are summarized in Table 2, below, in column A.

[0026] The reaction solution was gently centrifuged to precipitate the copper nanowires, which were washed with 2X-5X of the reaction volume with

an aqueous solution of 3% ascorbic acid and 1% polyvinylpyrrolidone (PVP). The copper nanowires were re-suspended in the 3% ascorbic acid, 1% PVP wash solution for storage at room temperature for two to six weeks. In certain embodiments, N,N-diethylhydroxylamine (DEHA) was added to the storage solution to final concentration of 1-3% to reduce oxidation of the copper nanowires.

[0027] The copper nanowires made according to the method of Example 1are illustrated in FIG. 1A, which is an optical microscope image showing nanowires that are about 40 μm to about 50 μm long. The maze of nanowires can be separated by sonication or surfactants. The scale bar indicates 20 μm.

[0028] FIG. 1B is a scanning electron microscope (SEM) image showing the copper nanowires made according to the method of Example 1, and few, if any, particles. The scale bar indicates 2 μm. The copper nanowires can be straight over the span of 10-20 μm, but tend to curve and tangle. The copper nanowires can be over 100 μm in length.

[0029] FIG. 2 is a transmission electron micrograph of a copper nanowire with diameters measured at the indicated points: a, 56.01 nm, b, 76.93 nm, and c, 81.52 nm. The scale bar indicates 100 nm. The ends of the nanowires show a smooth contour at the ends, indicating that the nanowires are not faceted.The nanowires are mostly independent with very few instances showing the nanowires originating from the same seed. Under high resolution electron microscopy crystalline domains were observed with a *d* plane spacing of 1.8 Å. The surface of some nanowires showed many islands of single crystal domains, indicating twinned crystal defects at various places. However, most of the nanowires are single crystals. Electron diffraction studies of single nanowires indicated the presence of twinned crystal zones.

[0030] FIG. 3 is a transmission electron micrograph of a thinner copper nanowire with diameters measured at the indicated points: a, 16.49 nm, b, 27.75 nm, and c, 24.75 nm. The scale bar indicates 100 nm.

[0031] The reaction temperature range for the production of copper nanowires for the reagents listed in Table 1 was 70°C-90°C. When the reaction was run at temperatures above 80°C, the diameters of the nanowires that were formed were 10-20% greater than that of the nanowires formed when the reaction was run at 70°C. See Table 2, below, column B. Only copper nanoparticles and no nanowires were formed at temperatures below 70°C. See Table 2, below, column C.

[0032] The formation of copper nanowires was found to be subject to an interaction between the strength of the NaOH solution and the reaction temperature. If a 12 M (aq.) NaOH solution was used, the reaction temperature had to be raised to 80°C to obtain the formation of copper nanowires. See Table 2, below, column D. If a 10 M (aq.) NaOH solution was used, the reaction temperature had to be raised to 90°C to obtain the formation of copper nanowires. See Table 2, below, column E. As noted above, the copper nanowires that were formed at higher temperatures were thicker.

[0033] Solutions of other copper (II) salts were tried, and the anion did not appear to affect the ability to form copper nanowires. $CuCl_2$ is suitable for the formation of copper nanowires. See Table 2, below, column F. Other suitable copper salts include, but are not limited to, copper (II) salts such as copper (II) acetate, copper (II) acetate tetrahydrate, copper (II) bromide, copper (II) carbonate, copper (II) chlorate, copper (II) chloride, copper (II) cyanide, copper (II) fluoride, copper (II) hydroxide, copper (II) bromate, copper (II) iodate, copper (II) iodate tetrahydrate, copper (II) iodide, copper (II) nitrate hexahydrate, copper (II) oxalate, copper (II) orthophosphate, copper (II) pyrophosphate, copper (II) sulfate, copper (II) sulfate heptahydrate, and copper (II) sulfate hexahydrate. Preferably, the copper salt comprises copper (II) nitrate.

[0034] The aqueous solution of hydroxide is an aqueous solution of NaOH, KOH, RbOH or CsOH. NaOH is preferred.

[0035] The order in which glycine or ascorbic acid is added did not affect the production of copper nanowires. However, in the abscence of glycine, the reaction produced only copper nanoparticles and no copper nanowires. Decreasing glycine from the amount in Table 1 resulted in an increase in the production of copper nanoparticles and a decrease in the production of copper nanowires. See Table 2, below, column G.

[0036] When the reaction was run under a nitrogen or an argon atmosphere at atmospheric pressure using the reactants listed in Table 1, above, copper nanowires were produced. The reaction appeared to proceed at the same rate and yield about the same amount of product as obtained when the reaction was run under room atmosphere. While not wanting to be bound by theory, these results suggest that oxygen is not required under the reaction conditions of this Example, which are summarized in Table 2, below, column H.

[0037]

Table 2

The Effects of Variations In Reaction Conditions

	A	B	C	D
Copper (II) Salt	1 eq. $Cu(NO_3)_2$ (1 ml 0.1 M (aq.))	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$
Reducing Agent	10 eq. ascorbic acid (176.12 mg)	10 eq. ascorbic acid	10 eq. ascorbic acid	10 eq. ascorbic acid
Capping agent	75 eq. Glycine (0.5625 g, 7.5 mM)	75 eq. Glycine	75 eq. Glycine	75 eq. Glycine
Solvent	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH	**20 mL, 12 M (aq.) NaOH**
Reaction Temp.	70°C	**80°C**	**<70°C**	**80°C**

Reaction Time Typical [range] (minutes)	10 [10-60]	10 [10-60]	10 [10-60]	10 [10-60]
Atmosphere	Room Air	Room Air	Room Air	Room Air
Reaction Product	Predominantly CuNWs (10-20 mg)	**CuNWs, 10-20% thicker than @ 70°C**	**Only Cu nanoparticles, no CuNWs**	**Predominantly CuNWs 10-20% thicker than @ 70°C**

[0038]

Table 2 (continued)
The Effects of Variations In Reaction Conditions

	E	F	G	H
Copper (II) Salt	1 eq. $Cu(NO_3)_2$	**1 eq. $CuCl_2 \cdot 2H_2O$**	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$
Reducing Agent	10 eq. ascorbic acid	10 eq. ascorbic acid	10 eq. ascorbic acid	10 eq. ascorbic acid
Capping agent	75 eq. Glycine	75 eq. Glycine	**<75 eq. Glycine**	75 eq. Glycine
Solvent	**20 mL, 10 M (aq.) NaOH**	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH
Reaction Temp.	**90°C**	70°C	70°C	70°C
Reaction Time Typical [range] (minutes)	10 [10-60]	10 [10-60]	10 [10-60]	10 [10-60]
Atmosphere	Room Air	Room Air	Room Air	**N_2**
Reaction Product	**Predominantly CuNWs 10-20% thicker than @ 70°C**	Predominantly CuNWs	**Predominantly Cu nanoparticles, some CuNWs**	**Predominantly CuNWs**

[0039] FIG. 4 is a X-ray diffractogram of copper nanowires made according to the method of Example 1, showing a cubic crystal structure and no spurious phases. The x-ray diffraction shows that copper nanowires are formed in the expected cubic lattice structure, consistent with a lattice constant of 3.610 Å. All of the peaks could be indexed in agreement with the formula

$$d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}.$$

[0040] . The major peaks correspond to <111>, <200>,< 220> and <222> Miller indices. The peaks are narrow, with the full width at half maximum (FWHM) suggesting a crystallite size of ~60 nm.

Example 2

Replacement of Ascorbic Acid With Sodium Borohydride

[0041] The reaction was prepared and run as described in Example 1, except the 10 molar equivalents of ascorbic acid were replaced by10 molar equivalents of $NaBH_4$. Copper nanoparticles were formed, but copper nanowires were not produced under the reaction conditions of this Example, although sodium borohydride is generally recognized as an effective reducing agent. The reaction conditions and reaction product are summarized in Table 3, below.

Example 3

Replacement of Ascorbic Acid With Citric Acid

[0042] The reaction was prepared and run as described in Example 1, except the 10 molar equivalents of ascorbic acid were replaced by 10 molar equivalents of citric acid. Copper nanoparticles were formed, but copper nanowires were not produced under the reaction conditions of this Example, although citric acid is a commonly used as a green chemistry reducing agent. See Table 3, below.

Example 4

Replacement of Ascorbic Acid With Glutamic Acid

[0043] The reaction was prepared and run as described in Example 1, except the 10 molar equivalents of ascorbic acid was replaced by 10 molar equivalents of glutamic acid. Copper nanoparticles were formed, but copper nanowires were not produced under the reaction conditions of this Example. See Table 3, below.

Example 5

Replacement of Ascorbic Acid With Acetaldehyde

[0044] The reaction was prepared and run as described in Example 1, except the 10 molar equivalents of ascorbic acid were replaced by 10 molar equivalents of acetaldehyde. Copper nanoparticles were formed, but copper nanowires were not produced under the reaction conditions of this Example. See Table 3, below.

Table 3
The Effects Of Substitution Of Reactants

	Example 2	Example 3	Example 4	Example 5
Copper (II) Salt	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$
Reducing Agent	**1-10 eq. $NaBH_4$**	**10 eq. citric acid**	**10 eq. glutamic acid**	**10 eq. acetaldehyde**
Capping agent	75 eq. Glycine	75 eq. Glycine	75 eq. Glycine	75 eq. Glycine
Solvent	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH
Reaction Temp.	70°C	70°C	70°C	70°C
Reaction Time Typical [range] (minutes)	10 [10-60]	10 [10-60]	10 [10-60]	10 [10-60]
Atmosphere	Room Air	Room Air	Room Air	Room Air
Reaction Product	**Copper nanoparticles, no CuNWs**	**Copper nanoparticles, no CuNWs**	**Copper nanoparticles, no CuNWs**	**Copper nanoparticles, no CuNWs**

Table 3 (continued)
The Effects Of Substitution Of Reactants

	Example 6	Example 7	Example 8	Example 9
Copper (II) Salt	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$	1 eq. $Cu(NO_3)_2$
Reducing Agent	**10 eq. formaldehyde**	10 eq. ascorbic acid	10 eq. ascorbic acid	10 eq. ascorbic acid
Capping agent	75 eq. Glycine	**75 eq. beta-alanine**	**75 eq. cysteine**	**75 eq. asparagine**
Solvent	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH	20 mL, 15 M (aq.) NaOH
Reaction Temp.	70°C	70°C	70°C	70°C
Reaction Time Typical [range] (minutes)	10 [10-60]	10 [10-60]	10 [10-60]	10 [10-60]
Atmosphere	Room Air	Room Air	Room Air	Room Air
Reaction Product	**Copper nanoparticles, no CuNWs**	**Copper CuNWs**	**Copper nanoparticles, no CuNWs**	**Copper nanoparticles, no CuNWs**

Example 6

Replacement of Ascorbic Acid With Formaldehyde

[0045] The reaction was prepared and run as described in Example 1, except the 10 molar equivalents of ascorbic acid were replaced by 10 molar equivalents of formaldehyde. Copper nanoparticles were formed, but copper nanowires were not produced under the reaction conditions of this Example. See Table 3, above.

Example 7

Replacement of Glycine With Beta-alanine

[0046] The reaction was prepared and run as described in Example 1, except the 75 molar equivalents of glycine were replaced by 75 molar equivalents of beta-alanine. Copper nanowires were formed under the reaction conditions of this Example. See Table 3, above.

Example 8

Replacement of Glycine With Cysteine

[0047] The reaction was prepared and run as described in Example 1, except the 75 molar equivalents of glycine were replaced by 75 molar equivalents of cysteine. Copper nanoparticles were formed, but copper nanowires were not produced under the reaction conditions of this Example. See Table 3, above.

Example 9

Replacement of Glycine With Asparagine

[0048] The reaction was prepared and run as described in Example 1, except the 75 molar equivalents of glycine were replaced by 75 molar equivalents of asparagine. Copper nanoparticles were formed, but copper nanowires were not produced under the reaction conditions of this Example. See Table 3, above.

[0049] Two capping agents, glycine and beta-alanine were successful in forming copper nanowires in the present method, but the amino acids cysteine and asparagine did not produce copper nanowires.

[0050] Glycine (2-aminoacetic acid) and beta-alanine (3-aminopropionic acid) are aminocarboxylic acids described by formula I

$NH_2(CH_2)_nCOOH$, (I)

where ***n*** is an integer from 1-6 inclusive, as illustrated in Table 4, below.

Table 4 Compounds of Formula I		
n	**Compound**	**IUPAC Name**
1	glycine	2-aminoacetic acid
2	beta-alanine	3-aminopropionic acid
3	gamma-aminobutyric acid (GABA)	4-aminobutanoic acid
4	delta-aminovaleric acid	5-aminopentanoic acid
5	ε-aminocaproic acid	6-aminohexanoic acid
6	ω-aminooenanthic acid	7-aminoheptanoic acid

Example 10

Scaling Up Production of Copper Nanowires

[0051] The reaction was prepared and run as described in Example 1 in larger reaction volumes. As noted above, about 10-20 mg of copper nanowires were produced from a 20 mL reaction volume. The same reaction has been scaled up proportionally and run at 2 L-3 L volumes. A reaction scaled up to 2 L produced 1.2 g of copper nanowires.

[0052] While the disclosure has been described with reference to an exemplary embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the disclosure. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the disclosure without departing from the essential scope thereof. Therefore, it is intended that the disclosure not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this disclosure, but that the disclosure will include all embodiments falling within the scope of the appended claims.

Patent claims

1. A method of forming copper nanowires comprising the steps of:

providing a copper (II) salt in an aqueous solution of hydroxide to form a basic aqueous reaction solution of the copper (II) salt;

heating the reaction solution of the copper (II) salt;

adding an effective amount of a compound of formula I

$$NH_2(CH_2)_nCOOH, \qquad (I)$$

where ***n*** is an integer from 1-6, inclusive; and

adding an effective amount of a biocompatible reducing agent,

thereby forming copper nanowires in the reaction solution.

2. The method of claim 1 wherein the step of providing a copper (II) salt includes the step of adding an aqueous solution of a copper (II) salt to an aqueous solution of hydroxide.

3. The method of claim 1 or 2 wherein the step of adding an effective amount of a biocompatible reducing agent precedes the step of adding an effective amount of a compound of formula I.

4. The method according to any of claims 1 to 3 wherein the step of adding an effective amount of a biocompatible reducing agent follows the step of adding an effective amount of a compound of formula I.

5. The method according to any of claims 1 to 4 wherein heating the reaction solution oft he copper (II) salt involves heating to about 70 to about 90 degrees Celsius.

6. The method according to any of claims 1 to 5 wherein the reaction solution further comprises a surfactant.

7. The method of claim 6 wherein the surfactant is polyvinylpyrrolidone.

8. The method according to any of claims 1 to 7 further comprising the step of removing the copper nanowires from the reaction solution.

9. The method of claim 8 further comprising the step of washing the copper nanowires and re-suspending the copper nanowires in a storage solution suitable for the copper nanowires.

10. The method of claim 9 wherein the storage solution comprises at least one of a surfactant and an antioxidant.

11. The method of claim 10 wherein the surfactant is polyvinylpyrrolidone and the antioxidant is ascorbic acid.

12. The method according to any of claims 1 to 11 wherein the aqueous solution of hydroxide is an aqueous solution of NaOH, KOH, RbOH or CsOH.

13. The method according to any of claims 1 to 12 wherein the aqueous solution of hydroxide is about 12 molar to about 15 molar NaOH.

14. The method according to any of claims 1 to 13 wherein n =1 and the compound is glycine.

15. The method according to any of claims 1 to 13 wherein n =2 and the compound is beta-alanine.

16. The method according to any of claims 1 to 15 wherein the biocompatible reducing agent is a reductone.

17. The method of claim 16 wherein the reductone is ascorbic acid, an ascorbic acid derivative or an acceptable salt thereof.

18. A copper nanowire produced by the method of any one of claims 1 to 17.

Drawings

Fig. 1A

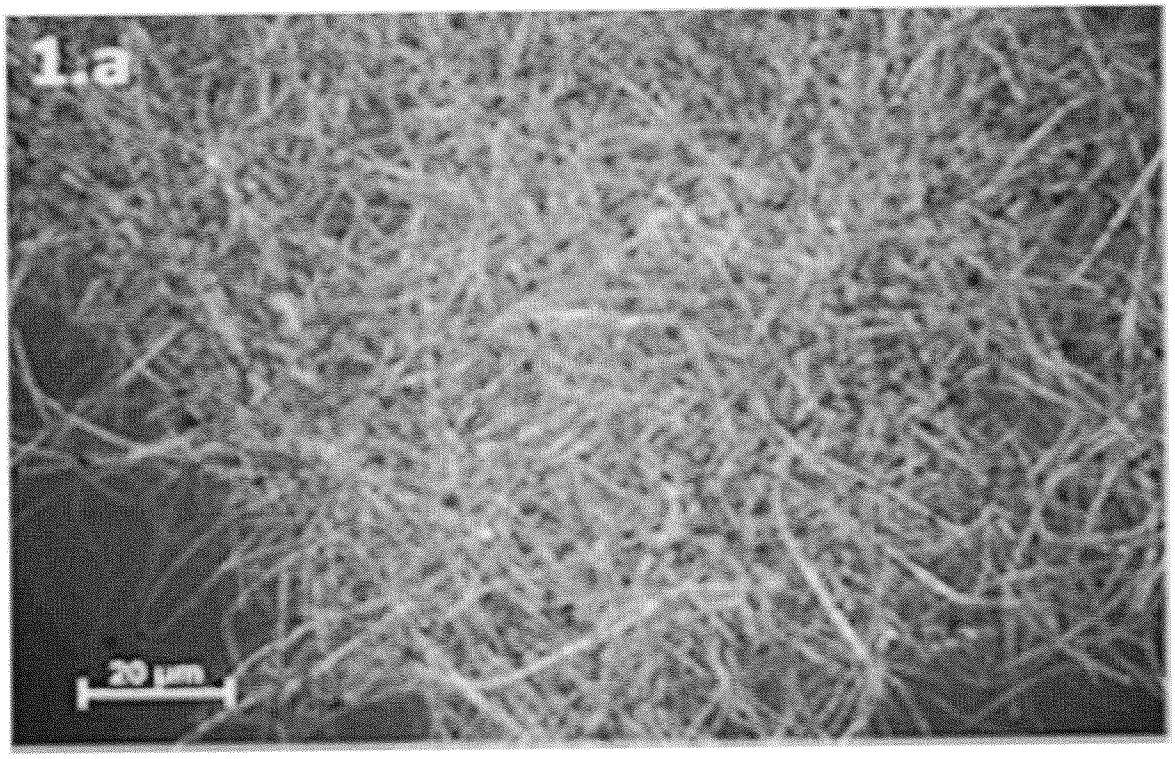


Fig. 1B

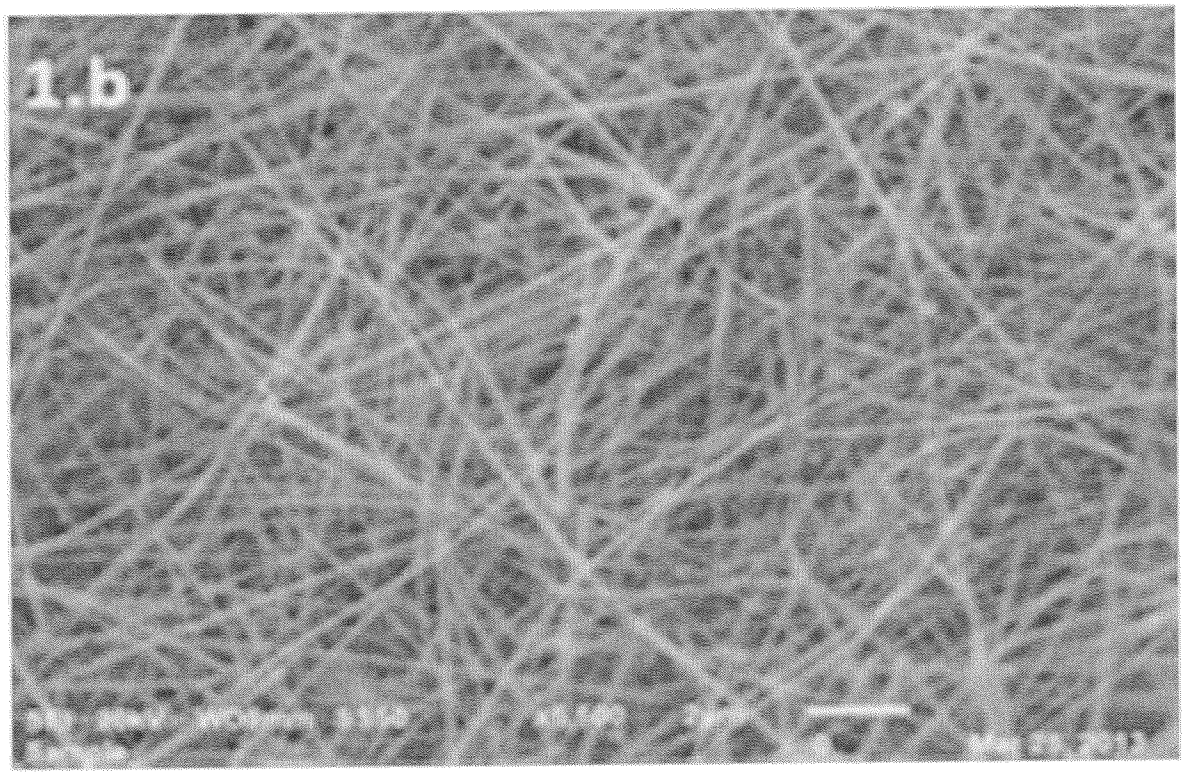


Fig. 2

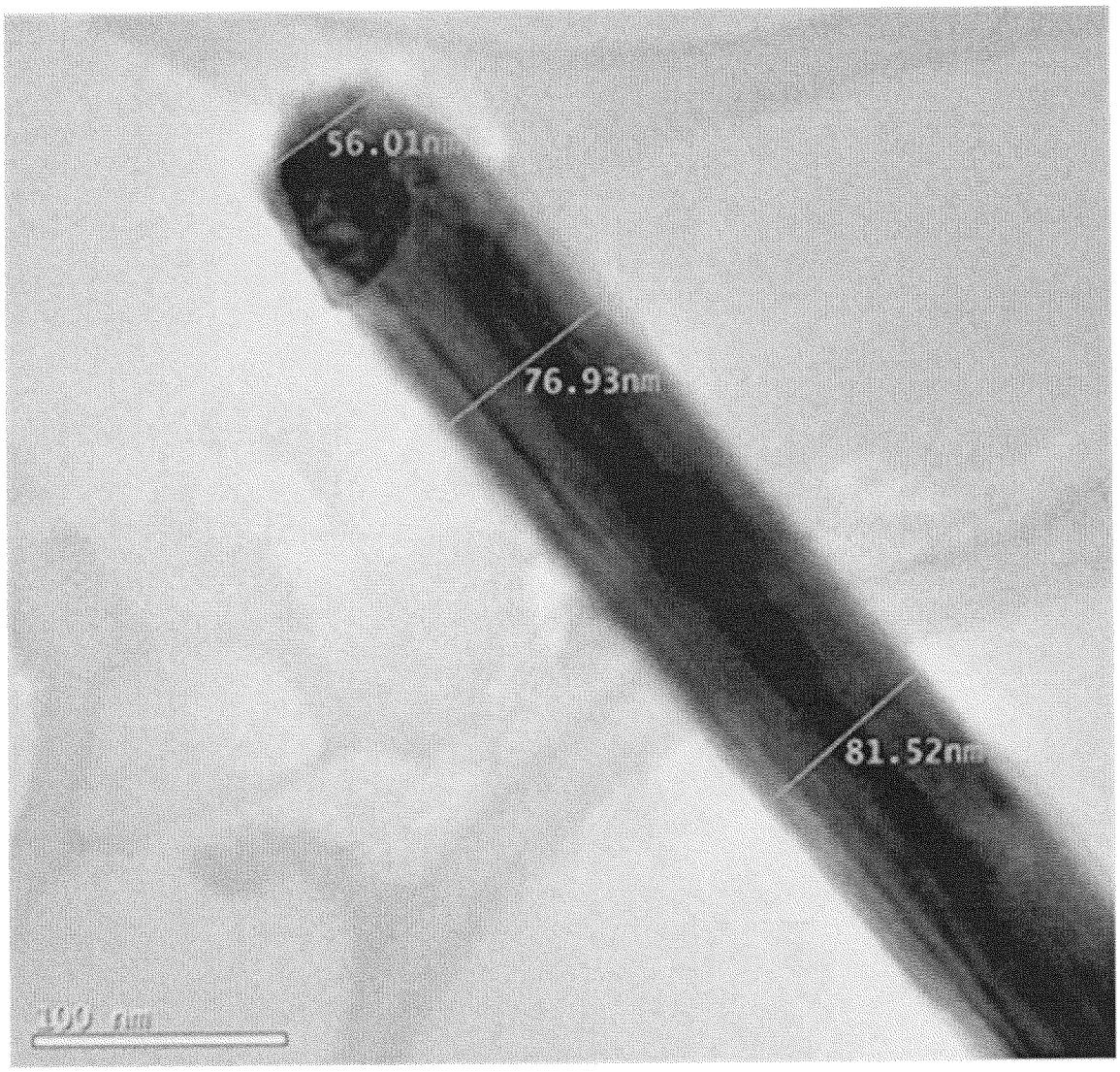


Fig. 3

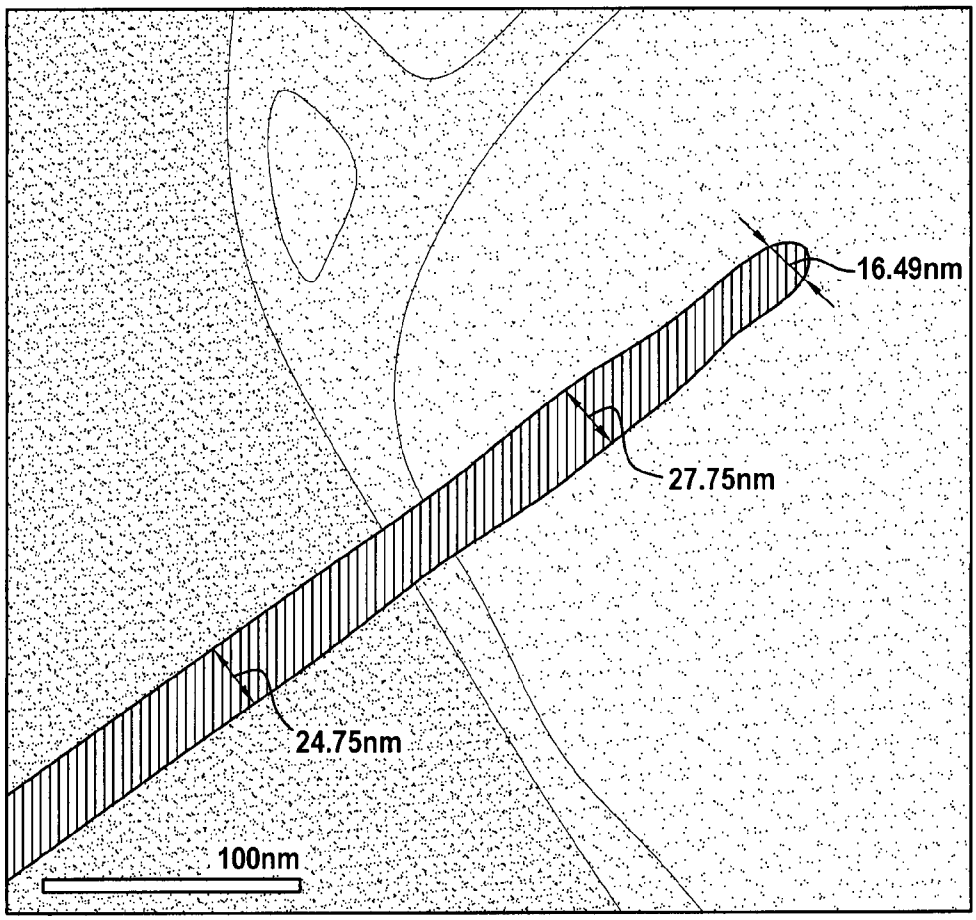
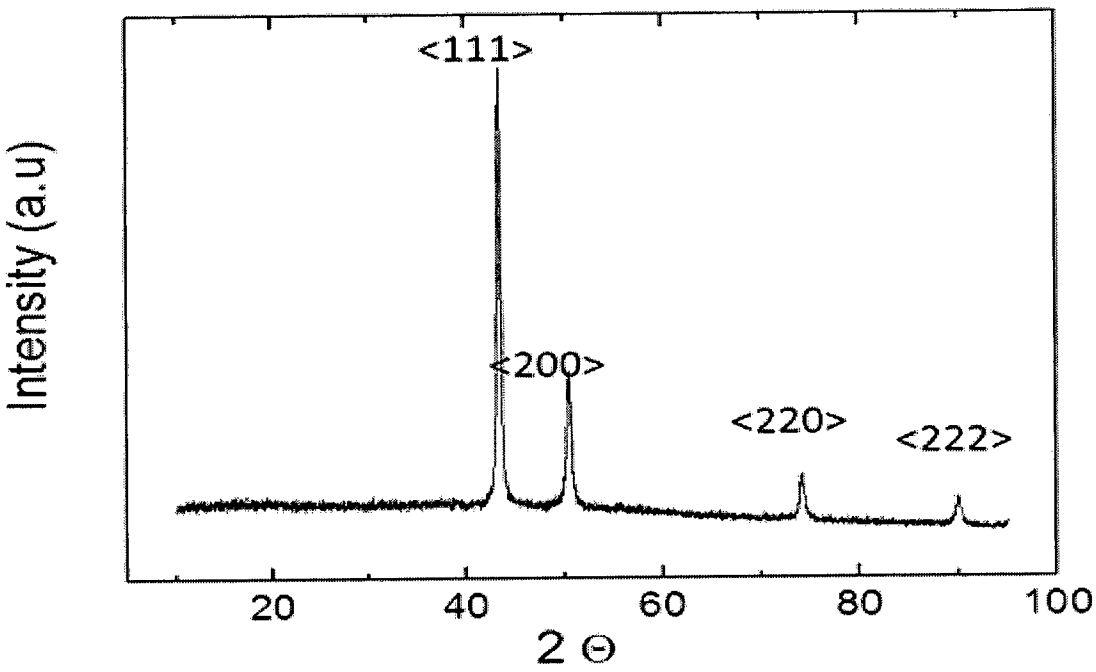


Fig. 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/000179

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, COMPENDEX, INSPEC, EMBASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/071885 A2 (UNIV DUKE [US]; WILEY BENJAMIN [US]; RATHMELL AARON [US]) 16 June 2011 (2011-06-16)	18
A	pages 5-6, paragraph [0038] page 7, paragraph [0042] - page 8, paragraph [0046]	1-17

X	US 2013/230717 A1 (XIA YOUNAN [US] ET AL) 5 September 2013 (2013-09-05)	18
A	page 1, paragraph [0007]	1-17

X	WO 2013/146509 A1 (FUJIFILM CORP [JP]) 3 October 2013 (2013-10-03)	18
A	pages 5-6, paragraph [0027]	1-17

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

☒ See patent family annex.

* Special categories of cited documents :

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 May 2015	01/06/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Helgadóttir, Inga

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/000179

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011071885 A2	16-06-2011	AU 2010328361 A1	26-07-2012
		CN 102792385 A	21-11-2012
		EP 2510524 A2	17-10-2012
		JP 2013513220 A	18-04-2013
		KR 20120115298 A	17-10-2012
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		WO 2011071885 A2	16-06-2011
US 2013230717 A1	05-09-2013	NONE	
WO 2013146509 A1	03-10-2013	JP 2013199690 A	03-10-2013
		WO 2013146509 A1	03-10-2013