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(71) Applicant: **Intercomet S.L.**
28860 Paracuellos del Jarama-Madrid (ES)

(72) Inventors:
- **AZANI, Mohammad-Reza**
  28860 Paracuellos del Jarama (ES)
- **HASSANPOUR, Azin**
  28860 Paracuellos del Jarama (ES)

(74) Representative: **ABG Patentes, S.L.**
Avenida de Burgos, 16D
Edificio Euromor
28036 Madrid (ES)

(54) METHOD FOR PREPARATION OF SILVER NANORINGS

(57) The present invention refers to a method for the preparation of silver nanorings as well as to the silver nanorings obtained by the method of the present invention. In addition, the present invention is directed to a conductive ink comprising the silver nanorings and to the use of silver nanorings as surface coating.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to the field of the nanotechnology, and, more in particular, relates to a method for the preparation of silver nanorings.

BACKGROUND

[0002] Nanostructures are structures having at least one dimension in the nanoscale and which their physical and chemical properties differ significantly from their analogous bulk materials since are strongly related with their size, shape and morphology. Among nanomaterials, metal nanostructures especially silver nanostructures, are very attractive for scientists because of unique performance in each structure. Silver nanostructures are classified as "conductive nanostructures" generally referring to electrically conductive nanostructures.

[0003] Until today, a great variety of shapes of silver nanostructures have been synthesized by different methods, such as cubic silver nanoparticles, silver nanorods, silver nanowires, silver nanobars, triangular (pyramid) silver nanoparticles, silver nanoprisms, flower-shaped silver nanoparticles, spherical silver nanoparticles, etc. They are widely used in different areas depending on their size, shape and morphology, such as optoelectronics, biochemical sensing, biomedical imaging, surface enhanced Raman scattering field, catalysis, electromagnetic interference shielding and antimicrobial applications.

[0004] In particular, in optoelectronic applications, silver nanowire networks have attracted great attention for the fabrication of transparent conducting films (TCFs). In fact, by using highly-conductive silver nanowires and covering only a small fraction of a surface could be achieved high conductivity and high transparency film. The resulting TCFs based on silver nanowires have been used successfully in organic solar cells and LEDs. These results highlight silver nanowires as the promising optoelectrical materials with comparable performance to indium tin oxide, along with bending and stretching stability.

[0005] Recently, Moon et al. (KR 1020140005640 A1) reported the fabrication of TCFs with improved optoelectrical properties based on silver nanorings in comparison with silver nanowires, in particular with increased transparency and decreased haze value.

[0006] The advantages of silver nanorings respect to silver nanowires are not limited to optoelectronics. It was reported that silver nanorings compared to silver nanowires have less plasmon-propagation loss and higher sensitivity. These properties highlighted silver nanorings applications as biosensors in the near-infrared region and plasmonic devices (Gong H. M. et al, Adv. Funct. Mater. 2009, 19, 298-303). Excellent morphology, purity and crystal quality are very critical parameters for these applications.

[0007] To date, there are two main approaches to prepare silver nanorings: 1) physically top-down approach including different lithography techniques; and 2) bottom-up chemical approach including template and chemical growth.

[0008] Regarding the top-down approach, it has been described silver nanorings preparation on solid substrate by using for example edge spreading lithography (McLellan J. M. et al, J. Am. Chem. Soc. 2004, 126, 10830-10831). Top-down approach required complex procedures and high cost instruments that could be limited for large-scale production of nanorings from economic or technical point of view.

[0009] Thus, the bottom-up approach based on templet and chemical growth is more convenient and many methods of this kind have been reported. Yan F. et al (Angew. Chem. Int. Ed. 2005, 44, 2084-2088) described silver nanorings preparation by using a mesoporous membrane or nanoparticle array as a primary template. Zinchenko A. A. et al (Adv. Mater., 2005, 17, 2820-2823) disclose a one-pot method to prepare well-defined silver nanorings by using deoxyribonucleic acid (DNA) condensates solution as soft nanostructured templates. Zhao S. et al (J. Am. Chem. Soc. 2006, 128, 12352-12353) reported fabrication of ordered silver nanorings arrays by using porous anodic aluminum oxide (AAO) films used as a mask. Liu H. G. et al. (Colloids Surf. A, 2008, 312, 203-208) reported silver nanorings preparation in the air/water interface via reduction of Ag^+ ions by UV-light irradiation templated by poly (9-vinylcarbazole) (PVK) thin films. Zhou et al. (CN 2012/10161858 A1) described silver nanorings with ring diameter 4-20 μm with thickness 50-200 nm via chemical growth method. Also Moon et al (KR 1020140005640 A1) reported silver nanorings via chemical growth based on polyol method. However, in all the reported bottom-up methods, it is very difficult to control the shape and size of nanorings, in addition, to the resulting low yields (less than 5%).

[0010] Therefore, there is a clear need for an efficient and low-cost method for the large-scale synthesis of pure and crystalline silver nanorings with uniform and controlled thickness and ring diameter.

BRIEF DESCRIPTION OF THE INVENTION

[0011] The author of the present invention has developed a template free, high yield and low-cost method for the preparation of silver nanorings. In particular, it has been observed that by using at least one additive salt, wherein the additive salt is at least one ammonium salt, and pressure, pure and crystalline silver nanorings are obtained with high yield via a simple solvothermal method having uniform and controlled thickness and ring diameter. In addition, since the method of the present invention is a simple procedure and it does not require complex and high cost instruments, it could be applied for large-scale production of nanorings.

[0012] Therefore, according to a first aspect, the invention is directed to a method for the preparation of silver nanorings comprising the steps of:

i) providing

a. a solution of a capping agent in a reducing agent,
b. at least one solution of an additive salt in a reducing agent, wherein at least one of said solutions contains as additive salt an ammonium salt, and
c. a solution of a silver salt in a reducing agent;

ii) adding the capping agent solution of step (ia) into a solvothermal reactor tube;
iii) adding the at least one additive salt solution of step (ib) into the solvothermal reactor tube of step (ii);
iv) adding the silver salt solution of step (ic) into the solvothermal reactor tube of step (iii);
v) heating the solvothermal reactor tube of step (iv) under pressure to form a suspension of silver nanorings; and optionally
vi) washing the suspension of silver nanorings of step (v); and
vii) filtering the suspension resulting from steps (v) or (vi) and drying the filtering solid.

[0013] The method of preparation of the present invention allows obtaining pure and crystalline silver nanorings with uniform thickness and ring diameter via a simple solvothermal method.

[0014] Therefore, in a second aspect, the present invention is directed to silver nanorings obtained by the method as defined above.

[0015] The silver nanorings obtained by the method as defined above can be easily re-dispersed in water or/and in organic solvents. The resulting suspensions of silver nanorings present high stability, thus, not being necessary the addition of surfactants or stabilizers which produce undesired residues. This allows using the resulting silver nanorings suspensions for preparing conductive ink compositions.

[0016] Therefore, another aspect of the present invention is a conductive ink comprising silver nanorings as defined above.

[0017] In addition, the good wetting or drying of the silver nanorings suspensions as defined above allows coating them on different substrates.

[0018] Therefore, another aspect of the present invention is the use of silver nanorings as defined above as surface coating.

FIGURES

[0019]

Figure 1: Absorbance of a silver nanorings suspension diluted to 10% in water of Example 1. Inset: Determination of molar absorptivity of silver nanorings suspension of Example 1 in water.

Figure 2: SEM images of silver nanorings of Example 1 by drop casting on the glass substrate in different zoom.

Figure 3: (a) TEM image of an individual silver nanoring of Example 1. (b) High resolution TEM image of PVP (about 2 nm thickness) on silver nanoring (c) Electron diffraction pattern of a randomly selected silver nanoring. (d) EDX spectrum of the silver nanoring.

Figure 4: SEM (left) and HR-TEM (right) images of a) Example 1, b) Example 5, c) Example 6 and d) Example 7.

Figure 5: SEM images of silver nanorings of Example 1 on PET substrate by spray coating method.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs.

[0021] The present invention refers to a method for the preparation of silver nanorings comprising the steps of:

i) providing

a. a solution of a capping agent in a reducing agent,
b.at least one solution of an additive salt in a reducing agent, wherein at least one of said solutions contains as additive salt an ammonium salt, and
c. a solution of a silver salt in a reducing agent;

ii) adding the capping agent solution of step (ia) into a solvothermal reactor tube;
iii) adding the at least one additive salt solution of step (ib) into the solvothermal reactor tube of step (ii);
iv) adding the silver salt solution of step (ic) into the solvothermal reactor tube of step (iii);
v) heating the solvothermal reactor tube of step (iv) under pressure to form a suspension of silver nanorings; and optionally
vi) washing the suspension of silver nanorings of step (v); and
viii) filtering the suspension resulting from steps (v) or (vi) and drying the filtering solid.

[0022] In the context of the present invention the term "silver nanoring" refers to a ring of crystalline silver metal having a diameter on the nanoscale.

[0023] The method of the present invention for the preparation of silver nanorings comprises a step (i) of providing

a. a solution of a capping agent in a reducing agent,
b.at least one solution of an additive salt in a reducing agent, wherein at least one of said solutions contains as additive salt an ammonium salt, and
c. a solution of a silver salt in a reducing agent.

[0024] The term "capping agent" refers to a strongly absorbed monolayer of usually organic molecules to the surfaces of silver nanostructures to facilitate their anisotropic growth and prevent the nanostructures from aggregation.

[0025] Examples of capping agents suitable for the method of the present invention include without limitation polymers and copolymers thereof of polyvinylpyrrolidone (PVP), polyacrylamide (PAA), polyvinyl butyral (PVB) or polyacrylic (PA), cetyltrimethylammonium bromide (CTAB), Vitamin C, Vitamin B, dodecyl benzene sulfonic acid (DBS), tetrabutyl ammonium bromide (TBAB), sodium dodecylsulfonate (SDBS) and combinations thereof.

[0026] In a preferred embodiment, the capping agent of step (ia) is polyvinylpyrrolidone (PVP).

[0027] Polyvinylpyrrolidone (PVP) is a polymer with different average molecular weight. Examples of average molecular weights of PVP suitable for the method of the present invention include, without limitation 55.000, 360.000, 1.300.000 and the like.

[0028] In a preferred embodiment, the capping agent is PVP having an average molecular weight of about 360.000 (PVP-K360).

[0029] The term "additive salt" or "ionic additive" refers to a salt containing cationic and anionic species associated by ionic interactions which can easily dissociate in polar solvents such as water, alcohol, diols and polyols (including ethylene glycol, glycerol, glucose, glycerin, 1,2 propylene glycol and 1,3-propylene glycol). The cation can be organic, including ammonium cation (NH_4^+) or proton (H^+) , or inorganic. The anions are typically inorganic. Exemplary anions include, without limitation: Halides (Cl^-, Br^-, I^-, F^-) , hydrogen sulfate (HSO_4^-) , sulfate (SO_4^{-2}) , phosphate (PO_4^{-3}), sulfonates (RSO_3^-), aryl, alkyl and the like.

[0030] The term "ammonium salt" refers to a salt formed by a quaternary ammonium cation (NH_4^+) in which each of the four hydrogens can be replaced by organic groups. Therefore, the substituted quaternary ammonium cation is typically shown by formula (NR_4^+), wherein each R is the same or different and independently an alkyl, alkenyl, alkynyl, aryl and etc. The quaternary ammonium cation can create quaternary ammonium salt by different anions.

[0031] Exemplary anions include, without limitation halides (Cl^-, Br^-, I^-, F^-) , hydrogen sulfate (HSO_4^-) , sulfate (SO_4^{-2}) , phosphate (PO_4^{-3}), sulfonates (RSO_3^-), aryl, alkyl and the like.

[0032] Exemplary quaternary ammonium salts include, without limitation tetra propyl ammonium chloride (TPA-C), tetra propyl ammonium bromide (TPA-B), 1-butyl-3-methyl imidazolium chloride (BMIM-Cl), 1-butyl-3-methyl imidazolium chloride (BMIM-Br) and combinations thereof.

[0033] In a preferred embodiment, the at least one solution of an additive salt of step (ib) is selected from a solution of KBr and a solution of an ammonium salt selected from the group of TPA-B, TPA-C and BMIM-Cl, and combinations thereof, provided that at least one solution of an additive salt is an ammonium salt solution.

[0034] Without being bound to any theory in particular, the authors of the present invention believe that a combination of ammonium salts and controlled pressure is related to a growth-induced stress causing nanostructures bending and which allows obtaining with high yield pure and crystalline silver nanorings having uniform and controlled size and thickness.

[0035] This is due to a proposed but non-limiting single-crystalline silver nanorings growth mechanism comprising three main steps. In a first step, linear structures and single-crystalline nanowires are formed. In a second step, the previous mixture gradually growths while bending into silver nanowires by increasing the length. In a third step, the free ends of bent nanowires meet to form silver nanorings. If the joining free ends exactly meet in a head-to-tail fashion (smooth joints), then circular nanorings are formed and if there is overlap between the head and the tail (intercross joints), then irregular, water-droplet shape nanorings are formed.

[0036] The authors of the present invention believe that quaternary ammonium salts may act as capping agent to kinetically control the growth rates of different crystalline faces by interacting with these faces through adsorption and desorption. More in particular, it is possible that quaternary ammonium salts have a selective adsorption ability which predominately depends on their anions and cations. They preferentially adsorbs to certain face of the primary silver nanowires. This adsorption can effect on growth direction to create non-linear structures. Also by using extra salts (organic or inorganic) along with at least one ammonium salt, the local ion concentration gradient will be changed and can affect to the adsorbability of ammonium salts on silver nanoparticles faces. Therefore, the induced stress could be originated from quaternary ammonium salts adsorbing on the silver nanowires to form non-uniform growth of silver nanowires or/and, for example, a cross-linked PVA by interfacing the ammonium salts.

[0037] As non-limitative example, when a mixture of a TPA-C solution in EG and a TPA-B solution in EG as additive salt solutions at a pressure of 150 KPa inside the reactor is used, silver nanorings having an average thickness of 120 nm and external diameter of 15 ± 5 μm are obtained with a yield of 90%. However, when a mixture of TPA-B in EG and KBr in EG as additive salt solutions at a pressure of 150 KPa inside the reactor is used, silver nanorings having an average thickness of 105 nm and external diameter of 15 ± 5 μm are obtained with a yield of 60%.

[0038] Therefore, by using at least one ammonium salt solution as additive salt solution and pressure it is not only possible to obtain silver nanorings efficiently (up to 90%) but also to control the thickness and diameter of the silver nanorings.

[0039] The term "silver salt" refers to a neutral compound having a positively charged silver ion and a negatively charged counterion. The counterion could be organic or inorganic. Exemplary silver salts include, without limitation silver nitrate ($AgNO_3$), silver chloride (AgCl), silver perchlorate ($AgClO_4$), silver acetate CH_3CO_2Ag (or $AgC_2H_3O_2$) and the like.

[0040] In a preferred embodiment, the silver salt of step (ic) is silver nitrate ($AgNO_3$).

[0041] Normally, the silver salt is soluble in the reducing solvent and dissociates into oppositely charged silver ion and counterion. Reduction of the silver salt in the reducing solvent caused to elemental silver. The elemental silver crystallizes or grows into a one-dimensional nanostructure, i.e. nanorings.

[0042] The term "reducing solvent" refers to a polar solvent with ability to solve the silver salt, the at least one additive salt and the capping agent. As mentioned above, the reducing solvent functions as well as a reducing agent to transform the silver salt to its corresponding elemental silver. Normally, the reducing solvent is a chemical reagent by having at least two hydroxyl groups such as diols, polyols, glycols, or mixtures thereof. Exemplary reducing solvent suitable for the method of the present invention include without limitation ethylene glycol, glycerol, glucose, glycerin, 1,2 propylene glycol, 1,3-propylene glycol and mixtures thereof.

[0043] In a preferred embodiment, the reducing agent of steps (ia)-(ic) is ethylene glycol (EG).

[0044] In a particular embodiment, the solution of capping agent of the step (ia) of the method the present invention is prepared by heating and afterwards cooling down.

[0045] As a non-limitative example, PVP as capping agent can be completely dissolved in ethylene glycol as reducing agent heating at 80-120°C for 2 hours.

[0046] In another particular embodiment, the solution of at least one additive salt and the solution of silver salt of the steps (ib) and (ic) of the method the present invention are prepared separately at room temperature by stirring.

[0047] As a non-limitative example, silver nitrate as silver salt and TPA-B as additive salt can be completely and separately dissolved in ethylene glycol as reducing agent at room temperature by means of vigorous stirring or/and ultrasonic vibration.

[0048] In a preferred embodiment, the solutions of capping agent, of at least one additive salt and of silver salt in a reducing agent are prepared separately and then all transferred to one solvothermal reactor tube.

[0049] Therefore, the method of the present invention for the preparation of silver nanorings comprises a further step (ii) of adding the capping agent solution of step (ia) into a solvothermal reactor tube.

[0050] The term "solvothermal reaction" refers to synthesis process wherein the temperature is above the room temperature and the pressure is higher than atmosphere pressure. Therefore, the term "solvothermal reactor tube" refers to a high temperature and pressure resistance reactor for synthesis process.

[0051] The method of the present invention for the preparation of silver nanorings comprises a further step (iii) of adding the at least one additive salt solution of step (ib) into the solvothermal reactor tube of step (ii).

[0052] As a non-limitative example, the at least one additive salt solution can be quickly added to the capping agent solution in the solvothermal reactor tube and stirring for several minutes (i.e. 10 minutes).

[0053] In a preferred embodiment, the at least one solution of an additive salt in step (iii) are two solutions of an additive salts, provided that at least one of said additive salt solutions is an ammonium salt solution, and wherein the molar concentration ratio of the ammonium salt solution to the other additive salt solution is in the range of 0.1-2.

[0054] The method of the present invention for the preparation of silver nanorings comprises a further step (iv) of adding the silver salt solution of step (ic) into the solvothermal reactor tube of step (iii).

[0055] As a non-limitative example, the silver salt can be quickly added to the solvothermal reactor tubes containing the mixture of capping agent solution and the at least one additive salt solution under vigorous stirring until the mixture appears to be homogeneous.

[0056] In a preferred embodiment, the molar concentration ratio of the capping agent solution to the silver salt solution in step (iv) is between 0.5 and 5.

[0057] The method of the present invention for the preparation of silver nanorings comprises a further step (v) of heating the solvothermal reactor tube of step (iv) under pressure to form a suspension of silver nanorings.

[0058] In a particular embodiment, the solvothermal reactor tube is heated by means of an oven.

[0059] In a preferred embodiment, the solvothermal reactor tube in step (v) is heated at a temperature between 140°C and 200°C for a period between 7 and 14 hours.

[0060] As a non-limitative example, the solvothermal reactor tube is transferred to a pre-heated oven at 185°C and kept it in for 14 hours.

[0061] In a preferred embodiment, in step (v) of the method of the present invention, the pressure inside the solvothermal reactor tube is at least 150 KPa.

[0062] As previously mentioned, without being bound to any theory in particular, the authors of the present invention believe that the growth-induced stress that allows obtaining with high yield pure and crystalline silver nanorings having uniform size and thickness is related to a combination of ammonium salts and controlled pressure. In fact, the authors of the present invention believe that the pressure inside the reactor, an more particularly, on top of the reaction solution plays a decisive role, this is, in the bulk of a liquid, each molecule is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. The molecules at the surface do not have the same molecules on all sides of them and therefore are pulled inwards. This creates some internal pressure and forces liquid surfaces to contract to the minimal area. The cohesive forces among liquid molecules are responsible for this phenomenon that is called surface tension. In this phenomenon, boundary molecules have a higher energy than internal molecules so the liquid minimize its energy state by minimizing the number of higher energy boundary molecules. The minimized quantity of boundary molecules results in a minimal surface area. On the one hand the present of pressure on surface of reaction and on the other hand internal pressure inside the solution to minimize the surface energy, push on free ends (both pressures push on ends to the bottom directions) of growth non-uniform crystalline particles that reach to the top and help to keep their bended shape.

[0063] Therefore, by using at least one ammonium salts or/and controlling the pressure in the reactor is possible to prepare with high yield silver nanorings having different thickness and diameters.

[0064] As non-limitative example, when a mixture of a solution of TPA-C in EG and a solution of TPA-B in EG as additive salt solutions at a pressure of 100 KPa inside the reactor is used, silver nanorings having an average thickness of 140 nm and external diameter of 15 ± 5 μm are obtained with a yield of 5%. However, when a mixture of a solution of TPA-B in EG and a solution of TPA-B in EG as additive salt solutions at a pressure of 150 KPa inside the reactor is used, silver nanorings having an average thickness of 120 nm and external diameter of 15 ± 5 μm are obtained with a yield of 90%.

[0065] During the heating period of step (v), the mixture of step (iv) turns turbid and more viscous, until acquires a pearlescent gray color indicating the presence of silver nanorings.

[0066] The method of the present invention for the preparation of silver nanorings optionally comprises a further step (vi) of washing the suspension of silver nanorings of step (v); and (vii) filtering the suspension resulting from steps (v) or (vi) and drying the filtering solid.

[0067] Therefore, in a particular embodiment, the obtained silver nanorings from step (v) are washed with a solvent to precipitate silver nanorings. By disregarding the supernatant, silver nanorings as a solid can be recovered. In a preferred embodiment, washing step is repeated several times to remove completely the reducing solvent, the excess of unreacted starting materials and/or other non-desirable nanostructures.

[0068] As a non-limitative example, the washing step was performed for at least 3 times by using a mixture of water and acetone as solvent.

[0069] In another particular embodiment, the resulting silver nanorings as a solid are filtered and dried under vacuum.

[0070] The silver nanorings obtained by the method of preparation of the present invention are pure and crystalline silver nanorings with uniform thickness and ring diameter via a simple solvothermal method.

[0071] Therefore, in a second aspect, the present invention is directed to silver nanorings obtained by the method as defined above.

[0072] In a particular embodiment, the silver nanorings obtained by the method of the present invention have a thickness between 75 and 120 nm and/or a ring diameter between 10 and 30 μm.

[0073] In addition, the silver nanorings obtained by the method as defined above can be easily re-dispersed, for example by mild mechanical stirring, in water or/and in organic solvents. The resulting re-dispersions of silver nanorings present high stability, thus, not being necessary the addition of surfactants or stabilizers which produce undesired residues. Non-limitative examples of re-dispersing solvents include, without limitation water and alcohols such as methanol, ethanol, isopropanol and the like.

[0074] The resulting re-dispersions in suitable solvents are stable for characterizations and storage, but also for the preparation of conductive ink compositions.

[0075] Therefore, another aspect of the present invention is a conductive ink comprising silver nanorings as defined above.

[0076] In addition, the good wetting or drying of the silver nanorings suspensions as define above allows coating them on different substrates.

[0077] Therefore, another aspect of the present invention is the use of silver nanorings as defined above in surface coating, through a variety of coating methods, such as spray coating, bar coating, Meyer rod coating and so on.

[0078] The resulting coated surfaces can be used in several applications such as optoelectronics, biochemical sensing, biomedical imaging, surface enhanced Raman scattering field, catalysis, electromagnetic interference shielding and anti-microbial applications.

EXAMPLES

Example 1: Preparation of uniform silver nanorings (Average thickness 120 nm and external diameter 15 ± 5 μm)

[0079] The following solutions were prepared separately:

4.0 mg/ml solution of TPA-C in EG (the TPA-C mother Solution)
10.0 mg/ml solution of TPA-B in EG (the TPA-B mother Solution)
8.83 mg/ml solution of PVP in EG (the PVP Solution)
10.71 mg/ml solution of $AgN0_3$ in EG (the $AgN0_3$ Solution)

[0080] Procedure: To a 50 mL round bottom flask was added the PVP powder in EG Solution. The mixture was then heated to 110°C (with the probe inserted in solution) in silicone oil bath with vigorous stirring until the temperature had stabilized for 2 hours. Then the oil bath was removed and the reaction permitted to cool to room temperature. At this time, PVP solution transferred to the 50 ml solvothermal reactor tube (6) and while the mixture was stirring, the mole ratio equal to 1.00 of TPA-B/TPA-C from their mother solution was added quickly to the PVP solution. After that, $AgN0_3$ solution was added quickly to the mixture during the stirring vigorously at room temperature and stirred for 30 min. Then we put it in the pre-heated oven (7) at 160°C for 7 h. The reaction was done under pressure of 150 KPa.

[0081] After cooling, the reaction solution was washed with the mixture of deionized water and acetone for at least 3 times to wash away the excess attached PVP and salts from the silver nanorings. After several time washing, obtained solid filtered and dried under vacuum (9). Finally, dried silver nanorings re-dispersed in deionized water or alcohols by mild stirring for characterization and storage.

Example 2: Preparation of uniform silver nanorings (Average thickness 140 nm and external diameter 20 ± 5 μm)

[0082] This example has been followed the same procedure explained in Example 1 but under pressure of 100 KPa.

Example 3: Preparation of uniform silver nanorings (Average thickness 120 nm and external diameter 20 ± 5 μm)

[0083] This example has been followed the same procedure explained in Example 1 with different salts.

[0084] The following salts were prepared:

2.0 mg/ml of KBr in EG (the KBr mother Solution)
5.6 mg/ml of BMIM-Cl in EG (the BMIM-Cl mother Solution)

[0085] The mole ratio equal to 1.52 of BMIM-Cl/KBr from their mother solution was added quickly to the PVP solution.

Example 4: Preparation of uniform silver nanorings (Average thickness 120 nm and external diameter 25 ± 5 μm)

[0086] This example has been followed the same procedure explained in Example 1 with different salts.
[0087] The following salts were prepared:

4.0 mg/ml solution of TPA-C in EG (the TPA-C mother Solution)
10.0 mg/ml solution of TPA-B in EG (the TPA-B mother Solution)

[0088] The mole ratio equal to 1.30 of TPA-B/TPA-C from their mother solution was added quickly to the PVP solution.

Example 5: Preparation of uniform silver nanorings (Average thickness 105 nm and external diameter 15 ± 5 μm)

[0089] This example has been followed the same procedure explained in Example 1 with different salts.
[0090] The following salt was prepared:

2.0 mg/ml of KBr in EG (the KBr mother Solution)
10.0 mg/ml solution of TPA-B in EG (the TPA-B mother Solution)

[0091] The mole ratio equal to 1.40 of TPA-B/KBr from their mother solution was added quickly to the PVP solution.

Example 6: Preparation of uniform silver nanorings (average thickness 90 nm and external diameter 15 ± 5 μm)

[0092] This example has been followed the same procedure explained in Example 1 with different salts.
[0093] The following salts were prepared:

4.0 mg/ml of TPA-C in EG (the TPA-C mother Solution)
2.0 mg/ml of KBr in EG (the KBr mother Solution)

[0094] The mole ratio equal to 1.61 of TPA-C/KBr from their mother solution was added quickly to the PVP solution.

Example 7: Preparation of uniform silver nanorings (average thickness 75 nm and external diameter 15 ± 5 μm)

[0095] This example has been followed the same procedure explained in Example 1 with different salts.
[0096] The following salt was prepared:

10.0 mg/ml of TPA-B in EG (the TPA-B mother Solution)

40 μmol TPA-B from the mother solution was added quickly to the PVP solution.

Example 8: Characterization of silver nanorings dispersions by Optical absorption spectroscopy

[0097] Dispersions of silver nanorings are obtained in an appropriate variety of water or some organic solvents ethanol, 1-propanol, 2-propanol and methanol by 10 min stirring.
[0098] Optical absorption spectroscopy (OAS) was measured on silver nanorings dispersions using a Perkin Elmer LAMBDA 750 UV/Vis/NIR diode array recorded over a 300-800 nm range with air as reference. 1 nm resolution is used for the OAS measurements. OAS measurements were used to estimate the concentration of silver nanorings using the Beer-Lambert law, according to the relation $A=\varepsilon bc$, where A is the absorbance, b [cm] is the light path length, c [gL^{-1}] is the concentration of the silver nanorings dispersion and ε [$L.g^{-1}.cm^{-1}$] is the absorption coefficient. The absorption coefficient ε (1.98×10^3 $L.g^{-1}.cm^{-1}$) was determined experimentally at max peak.
[0099] UV-vis absorption spectrophotometry is an important tool for investigate the Silver nanostructures in suspension and in each type of silver structure shows interesting optical properties directly related to surface plasmon resonance (SPR). As an example, in UV-Vis spectra of only silver nanowire (as precursor of nanorings) , there are 2 main peaks: The maximal peak (λ_{max}) corresponds to the transverse plasmon resonance of nanorings, and the weaker peak is attributable to the quadrupole resonance excitation of nanorings. According to UV-Vis spectra of obtained nanoring in examples (1-7), by having nanorings in the suspension, the weaker peak intensity start to decrease and in high yield nanorings percentage it disappears. **Figure 1** shows the UV-vis absorption spectra of silver nanorings (Example 1) that clearly observed the weaker peak was disappeared. It is consistent with the reported theory that the number of SPR peaks usually decreases with the increasing symmetry of nanowires (Kottmann J., P. Phys. Rev. B., 2001, 64,

235402-235410). It can imply that silver nanorings structure is changed from pentagonal (in silver nanowire as its precursor) to polygonal in final silver nanorings. Molar absorptivity determination of silver nanorings suspension in water was shown in **Figure 1(inset)**.

Example 9: Characterization of silver nanorings obtained by solvothermal method by SEM and TEM spectroscopy

[0100] The dimensions and quality of the silver nanorings in above examples were evaluated by SEM **(Figure 2)** and TEM microscopies and electron diffraction measurements **(Figure 3).**

[0101] SEM images were taken by using Hitachi Tabletop microscope model TM3030 by having magnification 15 to 30,000 X. The microscope has Pre-centered cartridge filament as electron gun and High-Sensitivity semiconductor 4-segment BSE detector as single detection system. This System operates at room temperature in ambient air conditions. The images were processed using TM3030 software. Figure 2 shows SEM images of Example 1 with uniform silver nanorings by having external ring diameter 15±5. For other examples the same result but in lower ring distribution were obtained.

[0102] TEM images were obtained in a JEOL model Transmission Electron Microscope JEM 2100 with an accelerating voltage of 200 KV. The microscope has a multi-scan CCD camera, mode composition analysis by XEDS, TEM and STEM operation modes with bright field detector. EELS analyses were carried out on electron energy loss spectroscopy (EELS), 2.5 Å point resolution and ±30° tilt goniometer. All the TEM Samples are prepared by drop casting of dispersions on carbon coated copper grids for the TEM.

[0103] **Figure 3** shows some characterizations of one nanoring obtained in example 1. **Figure 3a** present a TEM image of silver nanoring. It can be seen that the nanoring has a uniform diameter. As shown in **Figure 3b,** in higher magnification of silver nanoring, the PVP layer with about 2 nm thickness was covered on nanoring surface and the border of two panels in polygonal nanoring structure is observed. The selected-area electron diffraction patterns of randomly selected silver nanoring which are attributed to the zones (111) and (110) were shown in **Figure 3c.** The angle between these two zones was less than 30° instead of 35° in a single crystal. This indicates that the silver nanorings are singly twinned crystals (Gong J., Adv. Funct. Mater. 2009, 19, 298-303). The **Figure 3d** gives the result of EDX spectrum of the silver nanoring, which indicates that the nanorings are composed of pure silver and the possibilities of salts elements in the samples are excluded.

[0104] To comparison the thickness of nanorings, SEM and HR-TEM images of Example 1 and (3-5) were taken and shown in **Figure 4**. A circular ring with uniform thickness is clear in each example.

Table 1 shows the silver nanorings characterization obtained in different examples.

Number	Additive salts	Pressure (Kpa)	External diameter (±5 μm)	Thickness (±10 nm)	Yield (%)
Example 1	TPA-C, TPA-B	150	15	120	90
Example 2	TPA-C, TPA-B	100	15	140	5
Example 3	KBr, BMIM-Cl	150	20	120	80
Example 4	TPA-C, TPA-B	150	25	120	80
Example 5	TPA-B, KBr	150	15	105	60
Example 6	TPA-C, KBr	150	15	90	50
Example 7	TPA-B	150	15	75	30

Example 9: Coating substrates with ink composition.

(a) Spray coating:

[0105] The substrates were sprayed using a DH-115 SPARMAX airbrush with nozzle size of 0.35 mm, Side feed fluid cup size of 7 ml. It operates in pressure between 26 to 29 PSI. **Figure 5** shows SEM images of PET coated by silver nanorings (Example 1) suspension in ethanol. It clearly shows there is no deformation of ring structure during spray coating process.

(b) Bar coating:

[0106] The PTE substrates were coated by silver nanoring dispersion in Ethanol. This coating was performed by Coating machine model GN-TMB100 at 50°C by adjustable bar coater fixed on 50 μm.

(c) Meyer rod coating:

[0107] Meyer rod model BGD 211/10 was used to coat silver nanorings suspension in Ethanol to coat wet thickness of 10 μm of example 1 on PET substrate.

[0108] Same SEM images like Spray method were obtained by other methods and deformation in ring shape was not observed.

Claims

1. A method for the preparation of silver nanorings comprising the steps of:

   i) providing

      a. a solution of a capping agent in a reducing agent,
      b.at least one solution of an additive salt in a reducing agent, wherein at least one of said solutions contains as additive salt an ammonium salt, and
      c. a solution of a silver salt in a reducing agent;

   ii) adding the capping agent solution of step (ia) into a solvothermal reactor tube;
   iii) adding the at least one additive salt solution of step (ib) into the solvothermal reactor tube of step (ii);
   iv) adding the silver salt solution of step (ic) into the solvothermal reactor tube of step (iii);
   v) heating the solvothermal reactor tube of step (iv) under pressure to form a suspension of silver nanorings; and optionally
   vi) washing the suspension of silver nanorings of step (v); and
   vii) filtering the suspension resulting from steps (v) or (vi) and drying the filtering solid.

2. The method for the preparation of silver nanorings according to claim 1, wherein the capping agent of step (ia) is polyvinylpyrrolidone (PVP).

3. The method for the preparation of silver nanorings according to any of claims 1 to 2, wherein the at least one solution of an additive salt of step (ib) is selected from a solution of KBr and a solution of an ammonium salt selected from the group of tetra propyl ammonium bromide (TPA-B), tetra propyl ammonium chloride (TPA-C) and butyl-3-methyl imidazolium chloride (BMIM-Cl) and combinations thereof, provided that at least one solution of an additive salt is an ammonium salt solution.

4. The method for the preparation of silver nanorings according to any of claims 1 to 3, wherein the silver salt of step (ic) is silver nitrate.

5. The method for the preparation of silver nanorings according to any of claims 1 to 4, wherein the reducing agent of steps (ia)-(ic) is ethylene glycol (EG).

6. The method for the preparation of silver nanorings according to any of claims 1 to 5, wherein the at least one solution of an additive salt in step (iii) are two solutions of an additive salt, provided that at least one of said additive salt solutions is an ammonium salt solution, and wherein the molar concentration ratio of the ammonium salt solution to the other additive salt solution is in the range of 0.1-2.

7. The method for the preparation of silver nanorings according to any of claims 1 to 6, wherein the molar concentration ratio of the capping agent solution to the silver salt solution in step (iv) is between 0.5 and 5.

8. The method for the preparation of silver nanorings according to any of claims 1 to 7, wherein the solvothermal reactor tube in step (v) is heated at a temperature between 140°C and 200 °C for a period between 2 hours and 24 hours.

9. The method for the preparation of silver nanorings according to any of claims 1 to 8, wherein the pressure inside the solvothermal reactor tube in step (v) is at least 150 KPa.

10. The method for the preparation of silver nanorings according to any of claims 1 to 9, wherein the suspension of silver nanorings of step (vi) is washed with a mixture of water and acetone.

11. Silver nanorings obtained by the method according to any of claims 1 to 10.

12. Silver nanorings according to claim 11 having a thickness between 75 and 120 nm and/or a ring diameter between 10 and 30 μm.

13. A conductive ink comprising silver nanorings according to any of claims 11 to 12.

14. Use of the silver nanorings according to any of claims 11 to 12 as surface coating.

15. Use of the silver nanorings according to claim 14 in optoelectronics, biochemical sensing, biomedical imaging, surface enhanced Raman scattering field, catalysis, electromagnetic interference shielding and anti-microbial applications.

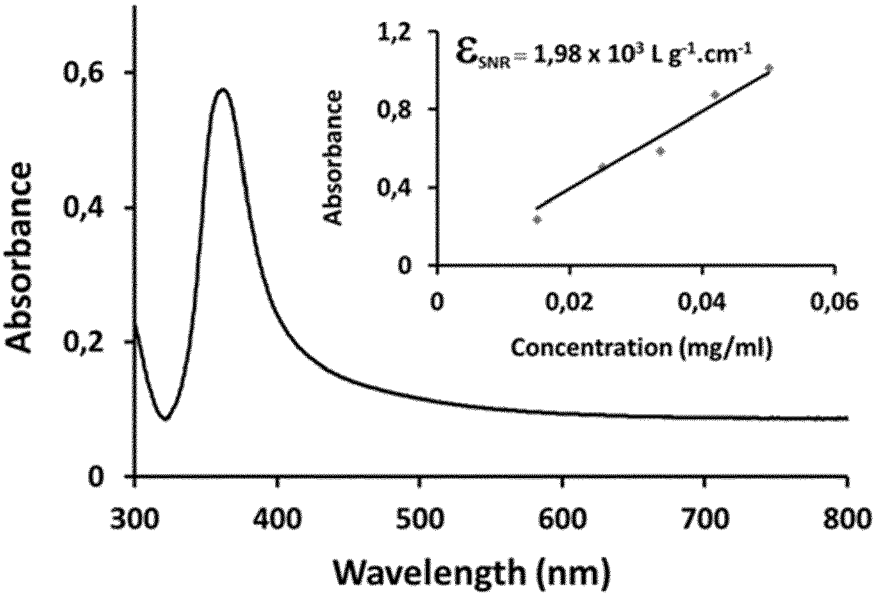
Absorbance
0,6
0,4
0,2
0
300
400
500
600
700
800
Wavelength (nm)
1,2
ε_{SNR} = 1,98 x 10^3 L g^{-1}.cm^{-1}
0,8
0,4
0
Absorbance
0
0,02
0,04
0,06
Concentration (mg/ml)

Figure 1

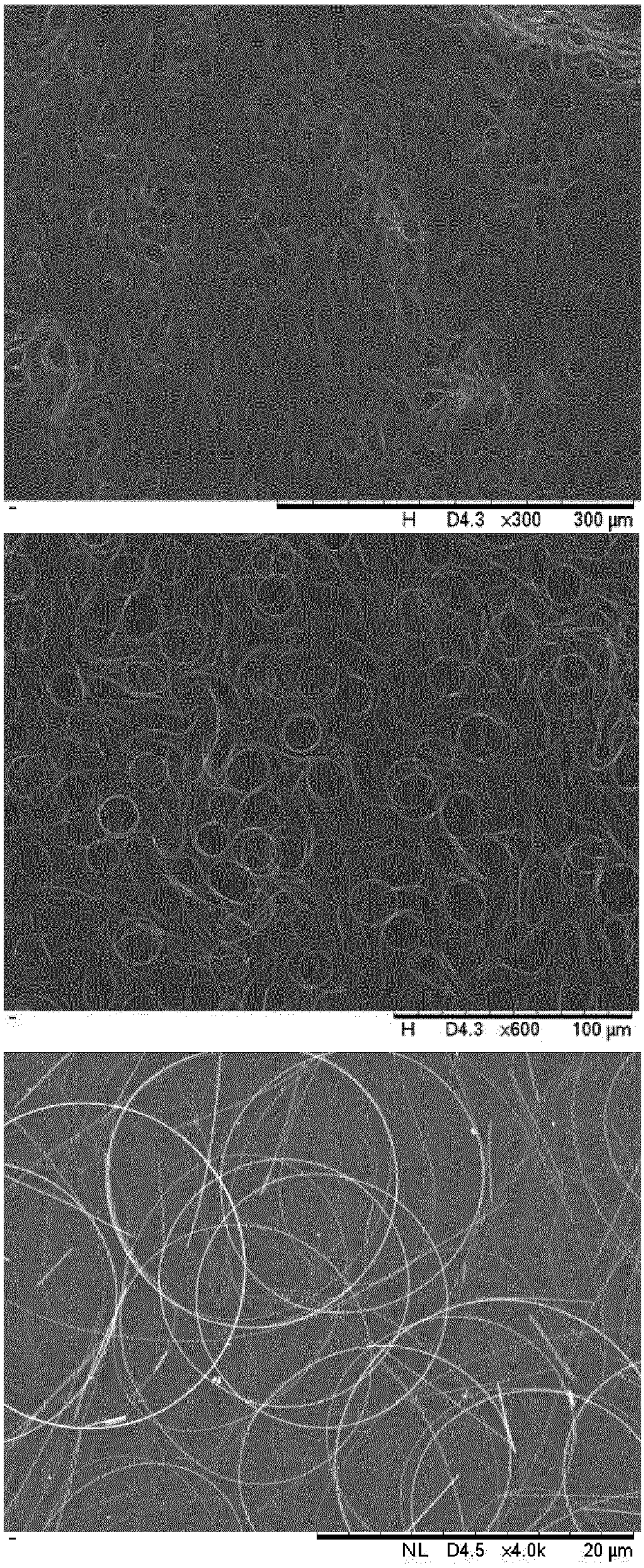

Figure 2

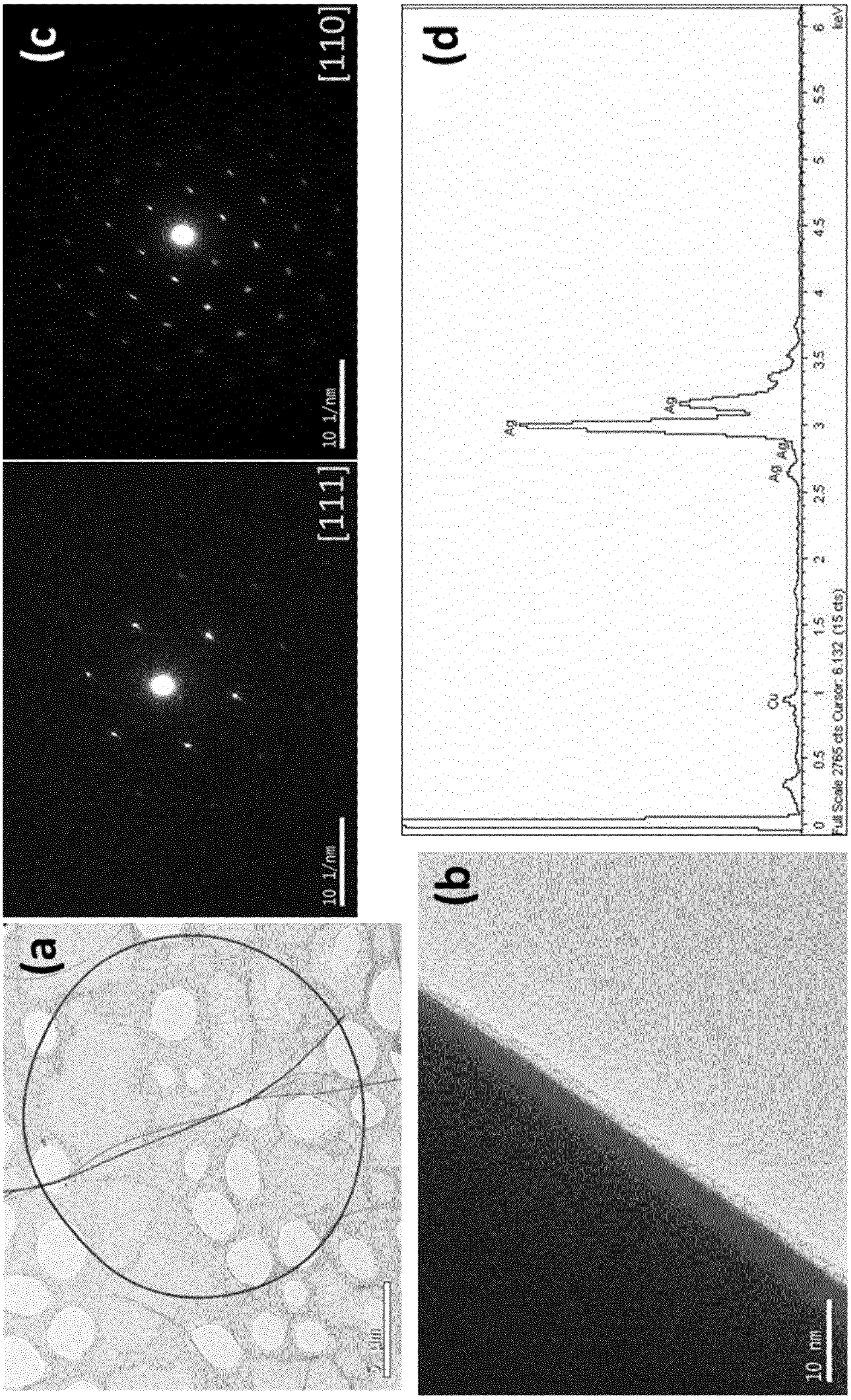
(a
5 µm
(b
10 nm
(c
[111]
[110]
10 1/nm
10 1/nm
(d
Ag
Ag
Ag
Ag
Cu
Full Scale 2765 cts Cursor: 6.132 (15 cts)
keV

Figure 3

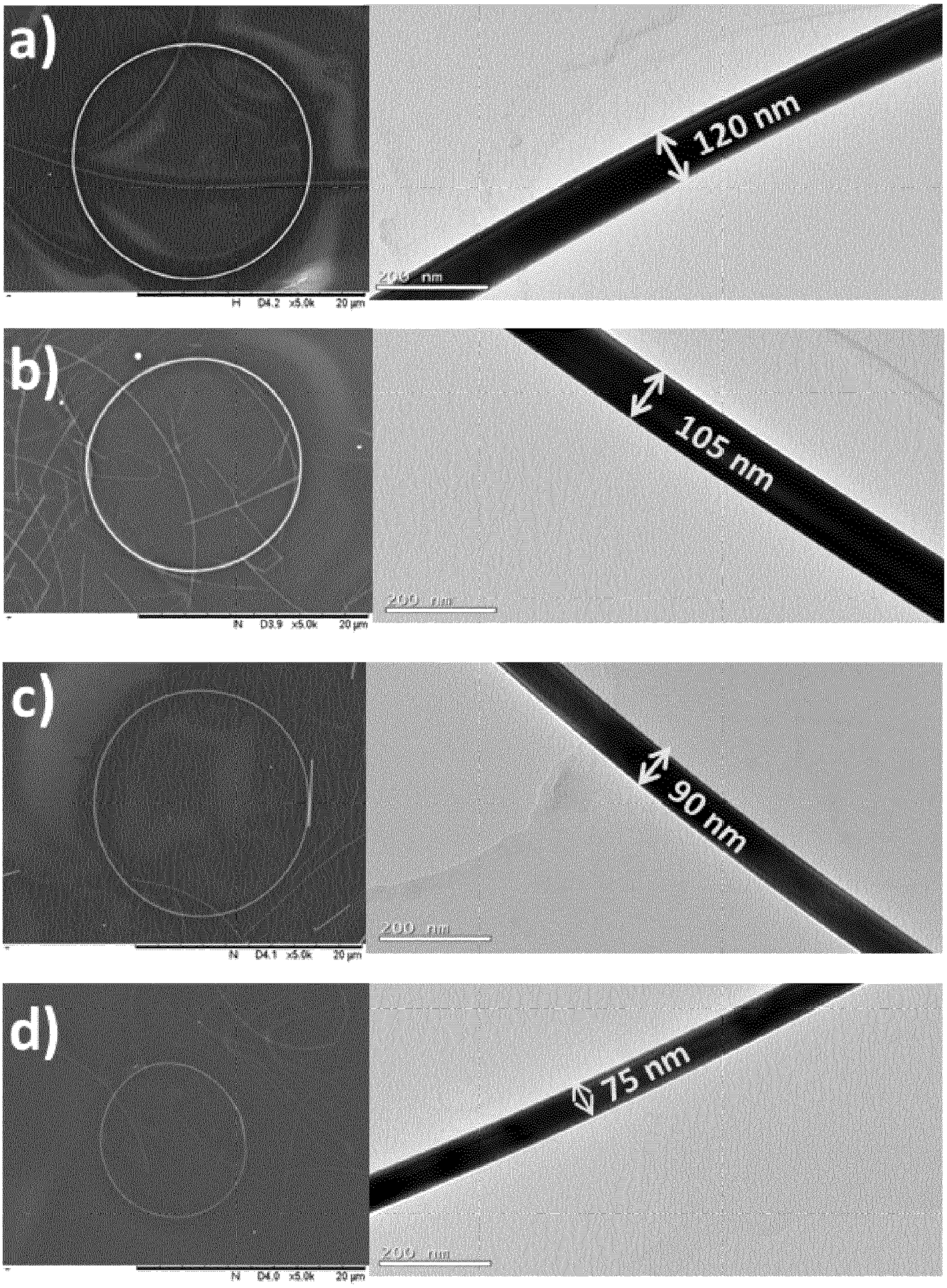
a)
120 nm
200 nm
H D4.2 x5.0k 20 µm
b)
105 nm
200 nm
N D3.9 x5.0k 20 µm
c)
90 nm
200 nm
N D4.1 x5.0k 20 µm
d)
75 nm
200 nm
N D4.0 x5.0k 20 µm

Figure 4

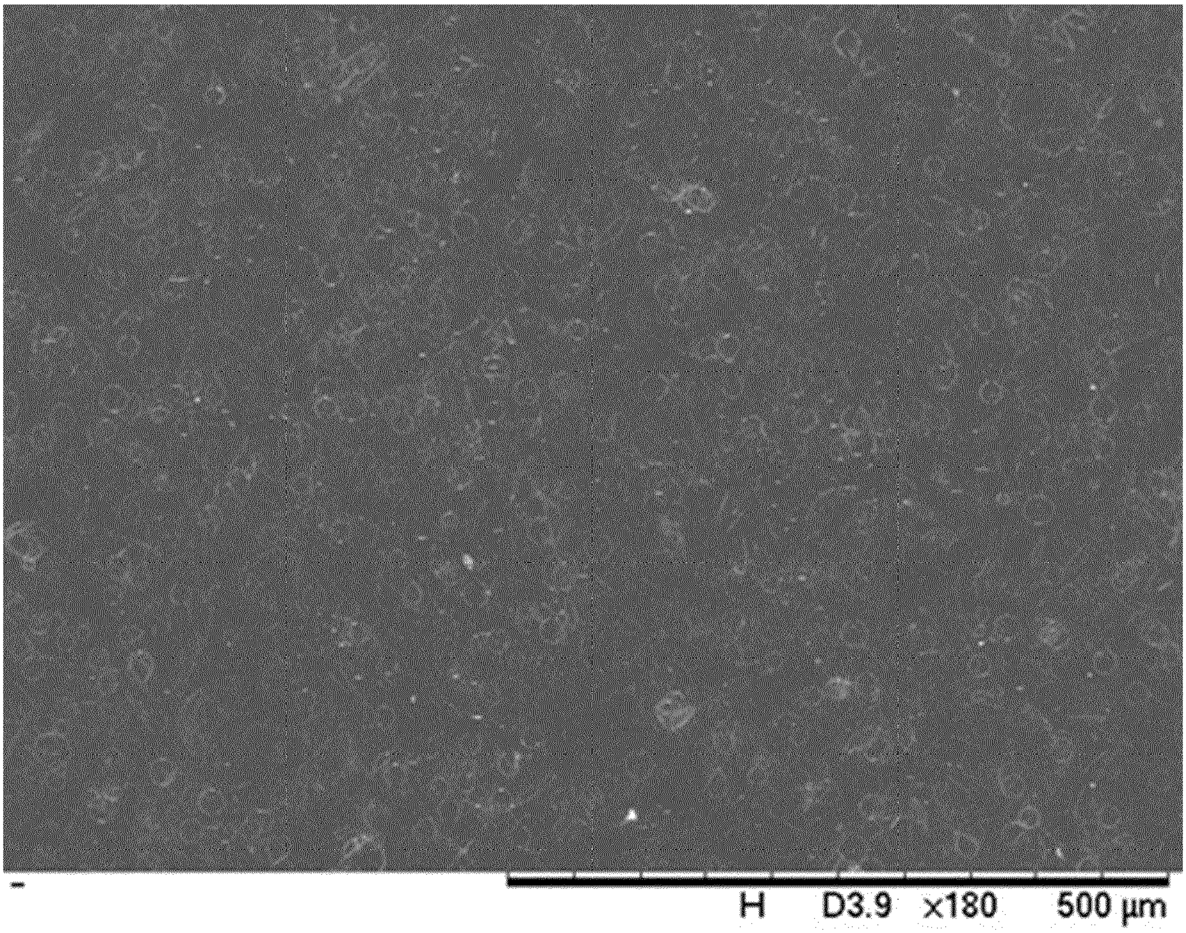

Figure 5

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EUROPEAN SEARCH REPORT

Application Number
EP 16 38 2395

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	HONG-MEI GONG ET AL: "Illuminating dark plasmons of silver nanoantenna rings to enhance exciton-plasmon interactions", ADVANCED FUNCTIONAL MATERIALS, WILEY - V C H VERLAG GMBH & CO. KGAA, DE, vol. 19, no. 2, 23 January 2009 (2009-01-23), pages 298-303, XP001520291, ISSN: 1616-301X, DOI: 10.1002/ADFM.200801151 * page 298, left-hand column, paragraph 1 * * page 298, right-hand column, paragraph 3 * * page 299, left-hand column, paragraph 1; figure 1B * -----	11-15	INV. B22F1/00 B22F9/24
X,D A	CN 102 658 373 A (UNIV WUHAN) 12 September 2012 (2012-09-12) * page 3, paragraph [0003] * * page 6, paragraph [0029] * -----	11,13-15 1-10,12	
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A	KR 101 527 522 B1 (HYOSUNG CORP [KR]) 18 June 2015 (2015-06-18) * the whole document * -----	1-15	B22F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	15 February 2017	Helgadóttir, Inga

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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15-02-2017

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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