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(54) **PROCESS FOR PRODUCING ANTIMONY NANOWIRES**

(57) The present invention relates to a process for producing antimony nanowires comprising at least the process step of electrochemically depositing antimony directly onto at least one surface of an electrode from a solution comprising at least one antimony compound (A), at least one gallium compound (B) and at least one ionic liquid (C).

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Description

[0001] The present invention relates to a process for producing antimony nanowires comprising at least the process step of electrochemically depositing antimony directly onto at least one surface of an electrode from a solution comprising at least one antimony compound (A), at least one gallium compound (B) and at least one ionic liquid (C).

[0002] High quality Sb nanostructures are normally synthesized by vacuum techniques like CVD [Gopal Sapkota and U Philipose, Semicond. Sci. Technol., 29 (2014) 035001] or by focused ion beam induced synthesis [Ch. Schoendorfer, A. Lugstein, Y.-J. Hyun, E. Bertagnolli, L. Bischoff, P. M. Nellen, V. Callegari and P. Pongratz, J. Appl. Phys., 102 (2007) 044308]. However, these methods are considered to be high-cost techniques.

[0003] The preparation of Sb nanowires by electrochemical methods are well known, but only the template-assisted electrodeposition was successfully carried out as described by D. Bouchet et al. in Eur. Phys. J. Appl. Phys., 30 (2005) 193 and by Y. Chen et al. in Mater. Chem. Phys., 126 (2011) 386 (pulsed electrochemical deposition). This method includes extra steps, namely pre-sputtering of the nonconductive membrane with a conductive layer and post-dissolution of it to get the free nanowires. These pre- and post-treatments might affect/harm the nanostructures and would be disadvantageous for a technological process.

[0004] WO 2012/170311 discloses a method of making metal nanoneedles on the surface of a substrate material via electrodeposition. The SEM images of the nanoneedles show needles with an uneven surface and also needles being tapered along the axis.

[0005] WO 2013/052456 describes a method for producing nanostructured materials such as silicon nanowires and their application as anode component for lithium ion batteries. The preparation of antimony nanowires is experimentally not disclosed.

[0006] A. Lahiri et al., Angew. Chem. Int. Ed. 2015, 54, 11870 describes the electroless depositon of GaSb semiconductor nanostructures from ionic liquids at room temperature. Formation of antimony nanowires is not disclosed.

[0007] WO 2015/071189 discloses a process for producing tin nanowires by electrochemically depositing tin directly onto at least one surface of an electrode from a solution comprising at least one tin compound (A) such as $SnCl_4$, at least one silicon compound (B) such as $SiCl_4$ and at least one ionic liquid (C). Conditions for the preparation of antimony nanowires are not disclosed.

[0008] Proceeding from this prior art, the object was to find a flexible and more efficient synthesis route to antimony nanowires which are useful in different applications as anode material in lithium ion batteries. In particular the object was to avoid the use of any template which has to be removed after formation of the antimony nanowires.

[0009] This object is achieved by a process for producing antimony nanowires having a thickness in the range from 10 nm to 300 nm comprising at least the process step of

(a) electrochemically depositing antimony directly onto at least one surface of an electrode from a solution comprising

(A) at least one antimony compound,

(B) at least one gallium compound selected from the group consisting of gallium(III) halides and organo gallium halides, and

(C) at least one ionic liquid,

wherein the concentration of the antimony compound in the solution is in the range from 0.1 M to 1.0 M and the concentration of the gallium compound in the solution is in the range from 0.05 M to 1 M.

[0010] The antimony nanowires obtainable or obtained by the inventive process are preferably crystalline. The thickness of antimony nanowires obtainable or obtained by the inventive process is in the range from 10 nm to 300 nm, preferably in the range from 20 nm to 150 nm, in particular in the range from 30 nm to 60 nm.

[0011] In a preferred embodiment of the present invention the antimony nanowires consist essentially of antimony, that means that the antimony-content of the antimony nanowires is preferably at least 90 %, more preferably in the range of from 95 % to 100 %, in particular from 97 % to 100 % by weight based on the total weight of the antimony nanowires.

[0012] The length of the antimony nanowires can be varied depending on the reaction conditions. Antimony is electrochemically deposited onto at least one surface of an electrode. In particular the length of the antimony nanowires depends on e.g. the time antimony is electrochemically deposited onto the at least one surface of an electrode.

[0013] In a preferred embodiment of the invention the antimony nanowires show an aspect ratio of at least 50, more preferably an aspect ratio in the range from 75 to 1000, in particular in the range from 100 to 200.

[0014] The definition of the aspect ratio as used herein is for example given in WO 2013/052456, page 8, paragraph [0050].

[0015] The length, the thickness, the aspect ratio or the morphological arrangement of the antimony nanowires obtained by the inventive process can be determined from the SEM images of the corresponding samples.

[0016] In process step (a) of the inventive process antimony nanowires are directly electrochemically deposited onto at least one surface of an electrode from a solution comprising at least one antimony compound (A), at least one gallium compound (B) selected from the

group consisting of gallium(III) halides and organo gallium halides and at least one ionic liquid (C).

[0017] The method of electrochemical deposition is well known as mentioned in WO 2013/052456, page 17, paragraph [0074] and referring the literature cited therein.

[0018] The solution from which antimony nanowires are electrochemically deposited comprises at least one antimony compound (A), also referred to hereinafter as component (A) for short. The antimony of component (A) is usually in the oxidation state +3 or +5, preferably in the oxidation state +3. Component (A) is preferably at least partly, preferably completely soluble in the formed solution.

[0019] Examples of antimony compounds (A) in the oxidation state +3 are antimony (III) halides like, $SbCl_3$ and $SbBr_3$.

[0020] Examples of antimony compounds (A) in the oxidation state +5 are antimony (V) halides like SbF_5 or $SbCl_5$

[0021] Instead of using a single antimony compound (A) it is also possible to use two or more different antimony compounds (A) in the solution including mixtures of at least two antimony compounds (A) in the oxidation state +3, mixtures of at least two antimony compounds (A) in the oxidation state +5 or mixtures of at least one antimony compounds (A) in the oxidation state +3 and at least one antimony compounds (A) in the oxidation state +5.

[0022] Preferred antimony compounds (A) are antimony (III), in particular antimony trichloride.

[0023] In one embodiment of the present invention, the inventive process is characterized in that the antimony compound (A) is antimony trichloride

[0024] The concentration of component (A) in the solution can be varied in a wide range depending on the solubility of component (A) in the solution. Usually the concentration of component (A) in the solution is in the range from 0.1 M to 1.0 M, more preferably in the range from 0.2 M to 0.8 M, in particular in the range from 0.3 M to 0.6 M.

[0025] The solution from which antimony nanowires are electrochemically deposited comprises further at least one gallium compound selected from the group consisting of gallium(III) halides and organo gallium halides, also referred to hereinafter as component (B) for short. The gallium of component (B) is usually in the oxidation state +3. Component (B) is preferably at least partly, more preferably completely soluble in the formed solution.

[0026] Examples of gallium compounds (B) selected from the group consisting of gallium(III) halides and organo gallium(III) halides are GaF_3, $GaCl_3$, $GaBr_3$, GaI_3, $GaCl_2Me$, $GaClMe_2$, $GaBr_2Me$, $GaBrMe_2$, $GaBr_2Ph$ or $GaBrPh_2$.

[0027] Instead of using a single gallium compound (B) it is also possible to use two or more different gallium compounds (B) in the solution.

[0028] Preferred gallium compounds (B) are gallium(III) halides, in particular gallium trichloride.

[0029] In one embodiment of the present invention, the inventive process is characterized in that the gallium compound (B) is gallium trichloride.

[0030] In one embodiment of the present invention, the inventive process is characterized in that either the antimony compound (A) or the gallium compound (B) is a trihalide, in particular a trichloride.

[0031] The electrochemical deposition of antimony from a solution comprising only one antimony compound (A) and an ionic liquid (C) and no gallium compound (B) results in dendritic growth of metallic antimony with granular morphology, while antimony nanowires are formed by the electrochemical deposition of antimony from a solution comprising component (A), component (B) and at least one ionic liquid (C), wherein the concentration of the gallium compound (B) in the solution is in the range from 0.05 M to 1 M, preferably in the range from 0.075 M to 0.2 M, more preferably in the range from 0.09 M to 0.15 M.

[0032] In one embodiment of the present invention, the inventive process is characterized in that the concentration of the gallium compound (B) in the solution is in the range from 0.09 M to 0.15 M.

[0033] The molar ratio of antimony to gallium in the solution can be varied in a wide range. Preferably the molar ratio of antimony to gallium in the solution is in the range from 20 to 0.1, preferably in range from 15 to 0.5, more preferably in the range from 10 to 1, in particular in the range from 7 to 2.

[0034] In one embodiment of the present invention, the inventive process is characterized in that the molar ratio of antimony to gallium in the solution is in the range from 7 to 2.

[0035] In addition to the at least one component (A) and to the at least one component (B) the solution, from which antimony nanowires are electrochemically deposited, comprises further at least one ionic liquid (C), also referred to hereinafter as component (C) for short. Ionic liquids (C) are known to the person skilled in the art. Several ionic liquids, which are liquid salts with a melting point below 100 °C, in particular below room temperature, are commercially available or can be prepared according to known protocols. The ionic liquid (C) can be varied in a wide range as long as component (C) is liquid at the temperature of the deposition and dissolves the components (A) and (B) sufficiently and does not chemically react with them. In addition the ions of the ionic liquid (C) preferably do not react under the conditions of the electrochemical deposition.

[0036] Examples of suitable ionic liquids (C) are salts comprising a cation selected from the group of cations consisting of substituted imidazolium, substituted pyrrolidinium, substituted piperidinium, substituted pyridinium, substituted phosphonium and substituted ammonium, preferably consisting of substituted imidazolium and substituted pyrrolidinium, wherein substituted means the presence of at least on organic radical, and an anion selected from the group of anions consisting of

$(CF_3SO_2)_2N$- (TFSI-), CF_3SO_3- (TFO-), $ROSO_3^-$, RSO_3^- (R = Me or Et), tosylate, acetate, dialkylphospates and hydrogensulfate, preferably consisting of of $(CF_3SO_2)_2N^-$, $CF_3SO_3^-$, RO-SO_3^- and RSO_3^- with R = Me or Et.

[0037] Preferred examples of ionic liquids (C) are 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (BMP-TFSI), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EM-Im-TFSI) and 1-butyl-1-methylpyrrolidinium triflate (BMP-TFO).

[0038] Instead of using only one ionic liquid (C) it is also possible to use two or more different ionic liquids (C) in the solution.

[0039] In one embodiment of the present invention, the inventive process is characterized in that the ionic liquid (C) is selected from the group consisting of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (BMP-TFSI), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIm-TFSI) and 1-butyl-1-methylpyrrolidinium triflate (BMP-TFO), preferably BMP-TFSI.

[0040] In addition to the at least one component (A), to the at least one component (B) and to the at least one ionic liquid the solution might comprise further components, which are inert under the conditions of the electrochemical deposition reaction like polar aprotic solvents which are usually used in electrolytes of electrochemical cell. Preferably the solution is essentially free of water, i.e. the water content in the solution is below 0.1 % by weight, preferably below 500 ppm, in particular in the range from 0.1 ppm to 10 ppm.

[0041] If component C, for example as technical grade, comprises more water than desired, the water can be removed by known methods, like stripping the water from component A by heating it under reduced pressure, or by adding drying reagents like molecular sieves or by adding scavengers like aluminum alkyls, magnesium alkyls or lithium alkyls. It is also possible to remove excess water by adding additional amount of antimony trichloride or gallium trichloride, which form insoluble compounds by reacting with water.

[0042] Preferably the sum of the weight of all components (A), (B) and (C) is at least 90% by weight, preferably in the range from 95% to 100% by weight, in particular in the range from 98% to 100% by weight based on the total weight of the solution.

[0043] The electrochemical deposition of antimony nanowires from a solution comprising at least one antimony compound (A), at least one gallium compound (B), wherein the concentration of the antimony compound in the solution is in the range from 0.1 M to 1.0 M, more preferably in the range from 0.2 M to 0.8 M, in particular in the range from 0.3 M to 0.6 M and the concentration of the gallium compound in the solution is in the range from 0.05 M to 1 M, preferably in the range from 0.075 M to 0.2 M, more preferably in the range from 0.09 M to 0.15 M, and at least one ionic liquid (C) is also possible in the presence of at least one organic solvent (D). Preferably the organic solvent (D) is a polar aprotic solvent, more preferably a polar aprotic solvent selected from the group consisting of cyclic carbonates, in particular propylene carbonate, ethylene carbonate and fluoroethylene carbonate, acetonitrile, dimethylformamide, tetrahydrofurane, acetone and dimethyl sulfoxide.

[0044] In one embodiment of the present invention, the inventive process is characterized in that the solution comprises at least one organic solvent (D), preferably at least one polar aprotic solvent (D), more preferably a polar aprotic solvent selected from the group consisting of cyclic carbonates, in particular propylene carbonate, ethylene carbonate and fluoroethylene carbonate, acetonitrile, dimethylformamide, tetrahydrofurane, acetone and dimethyl sulfoxide.

[0045] The concentration of component (C) in the solution, which comprises beside component (A) and component (B) also component (D), can be varied in a wide range. Preferably the concentration of all ionic liquids (C) in the solution is at least 0.05 M, more preferably at least 0.1 M, in particular at least 0.2 M up to the maximal concentration of the sum of all ionic liquids (C) in a solution comprising no organic solvent (D).

[0046] In one embodiment of the present invention, the inventive process is characterized in that the concentration of all ionic liquids (C) in the solution is at least 0.05 M, more preferably at least 0.1 M, in particular at least 0.2 M up to the maximal concentration of the sum of all ionic liquids (C) in a solution comprising no organic solvent (D).

[0047] For economic reasons the amount of ionic liquids, which are usually more expensive than suitable organic solvents, is reduced in the solution, which is the electrolyte, as far as possible.

[0048] In one embodiment of the present invention, the inventive process is characterized in that the solution comprises at least one organic solvent (D), preferably at least one polar aprotic solvent (D), more preferably a polar aprotic solvent selected from the group consisting of cyclic carbonates, in particular propylene carbonate, ethylene carbonate and fluoroethylene carbonate, acetonitrile, dimethylformamide, tetrahydrofurane, acetone and dimethyl sulfoxide, and wherein the concentration of all ionic liquids (C) in the solution is at least 0.05 M, more preferably at least 0.1 M, in particular at least 0.2 M up to the maximal concentration of the sum of all ionic liquids (C) in a solution comprising no organic solvent (D).

[0049] The solution used in process step a) is usually prepared by simply mixing the components (A), (B) and (C) preferably under inert and dry, i.e. water-free, conditions, using Schlenk technique or working in a glove-box.

[0050] The electrochemical deposition can be take place in a wide temperature range. Preferably process step (a) takes place at a temperature in the range from 0 °C to 100 °C, more preferably in the range from 15 °C to 50 °C, in particular in the range from 20 °C to 35 °C.

[0051] In one embodiment of the present invention, the inventive process is characterized in that process step (a) takes place at a temperature in the range from 15 °C

to 50 °C, in particular in the range from 20 °C to 35 °C.

[0052] The time of electrochemically depositing antimony can be varied in a broad range and is preferably adjusted to the desired length of the antimony nanowires deposited.

[0053] The electrochemical deposition can be take place in a wide range of deposit potentials which are given by reference to a Pt quasi-reference electrode. Preferably process step (a) takes place at a deposit potential in the range from -1.9 V to - 2.5 V vs. Pt quasi-reference electrode.

[0054] In one embodiment of the present invention, the inventive process is characterized in that process step (a) takes place at a deposit potential in the range from -1.9 V to - 2.5 V vs. Pt quasi-reference electrode.

[0055] During the electrochemical deposition the surface of the electrode and the solution can be static to each other or the solution is in motion relative to the surface of the electrode, e.g. by simply stirring the solution or by continuously supplying the surface of the electrode with new solution using a pump around system.

[0056] The surface of the electrode, where the antimony nanowires are deposited during the electrochemical deposition, can be selected from a large number of electrically conductive materials like metals and conductive carbons. Preferably the electrochemical deposition of the antimony nanowire takes place on the surface of an electrode, wherein the surface is composed of glassy carbon.

[0057] In one embodiment of the present invention, the inventive process is characterized in that the surface of the electrode, where the antimony nanowires are deposited, is composed of glassy carbon.

[0058] Antimony nanowires with an aspect ratio in the range from 100 to 200 and a high number of nanowires per electrode area are preferably obtained in process step a) of the inventive process under conditions wherein the antimony compound (A) is antimony trichloride, wherein the concentration of antimony trichloride in the solution is in the range from 0.2 M to 0.7 M, in particular in the range from 0.3 to 0.6 M, and the gallium compound (B) is gallium trichloride, wherein the concentration of gallium trichloride in the solution is in the range from 0.075 M to 0.2 M, in particular in the range from 0.09 M to 0.15 M, and wherein process step (a) takes place at a temperature in the range from 15 °C to 50 °C, preferably 25 °C to 35 °C, and at a deposit potential in the range from -1.9 V to - 2.5 V vs. Pt quasi-reference electrode.

[0059] In one embodiment of the present invention, the inventive process is characterized in that the antimony compound (A) is antimony trichloride, wherein the concentration of antimony trichloride in the solution is in the range from 0.2 to 0.7 M, and the gallium compound (B) is gallium trichloride, wherein the concentration of gallium trichloride in the solution is in the range from 0.075 M to 0.2 M, and wherein process step (a) takes place at a temperature in the range from 15 °C to 50 °C and at a deposition potential in the range from -1.9 V to - 2.5 V vs. Pt quasi-reference electrode.

[0060] The inventive process is characterized in that for the first time no templates are needed during the electrochemical synthesis and pulsed electrochemical deposition can be avoided and the deposition can be performed at room temperature in one-step process.

[0061] The antimony nanowires obtained in process step a) of the inventive process are usually isolated by separation them mechanically from the surface of the electrode, for example by cutting.

[0062] The isolated antimony nanowires can be used in different applications e.g. in electronics and gas sensor applications.

[0063] The present invention further also provides antimony nanowires having a thickness in the range from 10 nm to 300 nm, preferably in the range from 20 nm to 150 nm, in particular in the range from 30 nm to 60 nm, and preferably having an aspect ratio of at least 50, more preferably an aspect ratio in the range from 75 to 1000, in particular in the range from 100 to 200 obtainable by a process for producing antimony nanowires as described above. This process comprises the above-described process step (a) especially also with regard to preferred embodiments thereof.

[0064] The present invention likewise also provides antimony nanowires having a thickness in the range from 10 nm to 300 nm, preferably in the range from 20 nm to 150 nm, in particular in the range from 30 nm to 60 nm, and preferably having an aspect ratio of least 50, more preferably an aspect ratio in the range from 75 to 1000, in particular in the range from 100 to 200, wherein the antimony nanowires are prepared by a process comprising at least the process steps of

(a) electrochemically depositing antimony directly onto at least one surface of an electrode from a solution comprising

(A) at least one antimony compound,

(B) at least one gallium compound selected from the group consisting of gallium(III) halides and organo gallium halides, and

(C) at least one ionic liquid,

wherein the concentration of the antimony compound in the solution is in the range from 0.1 M to 1.0 M and the concentration of the gallium compound in the solution is in the range from 0.05 M to 1 M.

[0065] The process step a) has been described above. In particular, preferred embodiments of the process step have been described above.

[0066] The antimony nanowires having a thickness in the range from 10 nm to 300 nm, preferably in the range from 20 nm to 150 nm, in particular in the range from 30 nm to 60 nm, and preferably having an aspect ratio of least 50, more preferably an aspect ratio in the range from 75 to 1000, in particular in the range from 100 to

200, which are obtainable or obtained by the inventive process, are preferably crystalline.

[0067] In a preferred embodiment of the present invention the antimony nanowires consist essentially of antimony, that means that the antimony-content of the antimony nanowires is preferably at least 90 %, more preferably in the range of from 95 % to 100 %, in particular from 97 % to 100 % by weight based on the total weight of the antimony nanowires.

[0068] The invention is illustrated by the examples, which follow, but these do not restrict the invention.

[0069] Figures in percent are each based on % by weight, unless explicitly stated otherwise.

I. Electrochemical deposition of antimony

Used Chemicals:

[0070] The ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (BMP-TFSI, Io-Li-Tec) is used after drying under vacuum at 100 °C for several hours to water content below 3 ppm. $SbCl_3$ (99.99%, Sigma-Aldrich), $SiCl_4$ (99.998%, Alfa Aesar) and $GaCl_3$ (99.999%, Sigma-Aldrich) were used for the electrodeposition experiments as received.

General Electrochemical Setup:

[0071] Cu foil (> 99.9%, GOULD Electronics) and glassy carbon plate (Alfa Aesar) are used as substrates for the electrodeposition of Sb nanowires. Pt wires (99.997%, Alfa Aesar) were used as quasi-reference and counter electrodes. The electrochemical cell was made of Teflon and clamped over a Teflon-covered O-ring yielding a geometric surface area of 0.5 cm^2 of the used substrate. A Pt wire was coiled into three rings with a diameter of ~ 1.5 cm and was embedded into the Teflon cavity (0.6 cm deep and 0.5 cm thick) which surrounds the reaction area of the working electrode. In other words, the Teflon cell looks like a small cylinder (8 mm in diameter, where the working electrode is underneath) surrounded by a bigger cylinder (18 mm in diameter, where the coiled Pt wire is placed on its Teflon ground). This coiled wire was serving as a counter electrode. A Pt wire was immersed into the reaction solution near from the working electrode (about 2 mm away from it) to serve as a quasi-reference electrode.

General Performance of Electrochemical Experiments:

[0072] Due to the hygroscopic nature of the deposit-precursors, all of solutions were prepared inside an argon-filled glove-box (MBRAUN) with oxygen and water content below 1 ppm. All of the electrochemical measurements were performed inside the glove-box as well. These measurements were performed by using BioLogic potentiostat/galvanostat controlled by EC-Lab software.

I.1 Comparative and inventive examples for the electrochemical deposition of antimony Example 1 (comparative)

[0073] The above described Teflon cell was filled with about 2 ml solution of 0.5 M $SbCl_3$ in BMP-TFSI IL. The Sb deposition on Cu foil was then performed by applying a constant potential of -1.9 V vs. Pt quasi-reference electrode for ~ 1 hour at room temperature (~25 °C). Figure 1 shows SEM images of the obtained deposit. No nanowires were obtained in the absence of $GaCl_3$.

Example 2 (comparative)

[0074] The Teflon cell was filled with about 2 ml solution of 0.5 M $SbCl_3$ + 0.1 M $SiCl_4$ in BMP-TFSI IL. The Sb deposition on Cu foil was then performed by applying a constant potential of -2.4 V vs. Pt quasi-reference electrode for ~ 1 hour at room temperature (~25 °C). Figure 2 shows SEM images of the obtained deposit. No Sb nanowires were obtained in the presence of $SiCl_4$.

Example 3 (inventive)

[0075] The Teflon cell was filled with about 2 ml of a solution of 0.5 M $SbCl_3$ + 0.1 M $GaCl_3$ in BMP-TFSI ionic liquid and the substrate was a Cu foil with a geometric surface area of 0.5 cm^2. The deposition was performed by applying a constant potential of - 1.9 V vs. Pt quasi-reference electrode for 1 hour at 25 °C. The obtained deposit (Sb nanowires) was then removed from the reaction solution and was carefully rinsed with dried acetone for several times inside the glove box to remove the traces of the ionic liquid solution. Figure 3 shows SEM images of the obtained Sb nanowires.

Example 4 (inventive)

[0076] The Teflon cell was filled with about 2 ml of a solution of 0.5 M $SbCl_3$ + 0.1 M $GaCl_3$ + 0.2 M BMP-TFSI ionic liquid in propylene carbonate (PC) solvent and the substrate was a Cu foil with a geometric surface area of 0.5 cm^2. The deposition was performed by applying a constant potential of - 1.9 V vs. Pt quasi-reference electrode for 1 hour at 25 °C. The obtained deposit (Sb with1-dimensional growth) was then removed from the reaction solution and was carefully rinsed with dried acetone for several times inside the glove box to remove the traces of the solution. Figure 4 shows SEM images of the obtained Sb deposit.

Example 5 (inventive)

[0077] The Teflon cell was filled with about 2 ml of a solution of 0.5 M $SbCl_3$ + 0.1 M $GaCl_3$ in BMP-TFSI ionic liquid and the substrate was a glassy carbon plate with a geometric surface area of 0.5 cm^2. The deposition was performed by applying a constant potential of - 1.9 V vs.

Pt quasi-reference electrode for 1 hour at 25 °C. The obtained deposit (Sb nanowires) was then removed from the reaction solution and was carefully rinsed with dried acetone for several times inside the glove box to remove the traces of the ionic liquid solution. Figure 5 shows a SEM image of the obtained Sb nanowires.

Figure 1.: SEM images of Sb deposit obtained from a solution of 0.5 M $SbCl_3$ in BMP-TFSI IL. Deposition potential: -1.9 V, deposition time: 1 hour. Temperature: 25 °C.

Figure 2.: SEM images of Sb deposit obtained from a solution of 0.5 M $SbCl_3$ + 0.1 M $SiCl_4$ in BMP-TFSI IL. Deposition potential: -2.4 V, deposition time: 1 hour. Temperature: 25 °C.

Figure 3.: SEM images of Sb nanowires obtained from a solution of (0.5 M $SbCl_3$ + 0.1 M $GaCl_3$) in BMP-TFSI IL. Deposition potential: -1.9 V, deposition time: 1 hour. Temperature: 25 °C.

Figure 4.: SEM images of Sb nanostructures obtained from a solution of (0.5 M $SbCl_3$ + 0.1 M $GaCl_3$ + 0.2 M BMP-TFSI) in PC solvent. Deposition potential: -1.9 V, deposition time: 1 hour. Temperature: 25 °C.

Figure 5.: SEM image of Sb nanowires obtained from a solution of (0.5 M $SbCl_3$ + 0.1 M $GaCl_3$) in BMP-TFSI IL on glassy carbon. Deposition potential: -1.9 V, deposition time: 1 hour. Temperature: 25 °C.

Claims

1. A process for producing antimony nanowires having a thickness in the range from 10 nm to 300 nm comprising at least the process step of

(a) electrochemically depositing antimony directly onto at least one surface of an electrode from a solution comprising

(A) at least one antimony compound,
(B) at least one gallium compound selected from the group consisting of gallium(III) halides and organo gallium halides, and
(C) at least one ionic liquid,

wherein the concentration of the antimony compound in the solution is in the range from 0.1 M to 1.0 M and the concentration of the gallium compound in the solution is in the range from 0.05 M to 1 M.

2. The process according to claim 1, wherein the antimony compound (A) is antimony trichloride.

3. The process according to claim 1 or 2, wherein the gallium compound (B) is gallium trichloride.

4. The process according to any of claims 1 to 3, wherein the molar ratio of antimony to gallium in the solution is in the range from 7 to 2.

5. The process according to any of claims 1 to 4, wherein the solution comprises at least one organic solvent (D).

6. The process according to any of claims 1 to 5, wherein the concentration of all ionic liquids (C) in the solution is at least 0.05 M.

7. The process according to any of claims 1 to 4, wherein the solution comprises at least one organic solvent (D) and wherein the concentration of all ionic liquids (C) in the solution is at least 0.05 M.

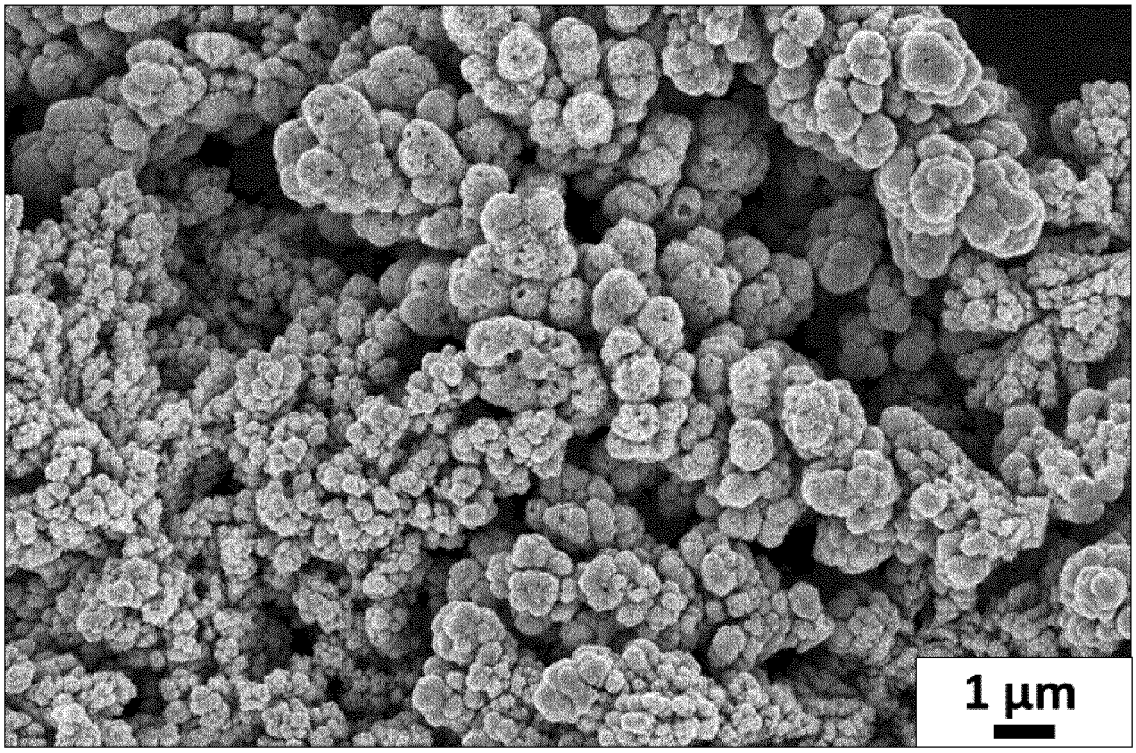
8. The process according to any of claims 1 to 7, wherein process step (a) takes place at a temperature in the range from 15 °C to 50 °C.

9. The process according to any of claims 1 to 8, wherein process step (a) takes place at a deposition potential in the range from -1.9 V to - 2.5 V vs. Pt quasi-reference electrode.

10. The process according to any of claims 1 to 9, wherein the surface of the electrode, where the antimony nanowires are deposited, is composed of glassy carbon.

11. The process according to claim 1, wherein the antimony compound (A) is antimony trichloride, wherein the concentration of antimony trichloride in the solution is in the range from 0.2 to 0.7 M, and the gallium compound (B) is gallium trichloride, wherein the concentration of gallium trichloride in the solution is in the range from 0.075 M to 0.2 M, and wherein process step (a) takes place at a temperature in the range from 15 °C to 50 °C and at a deposition potential in the range from -1.9 V to - 2.5 V vs. Pt quasi-reference electrode.

Fig 1



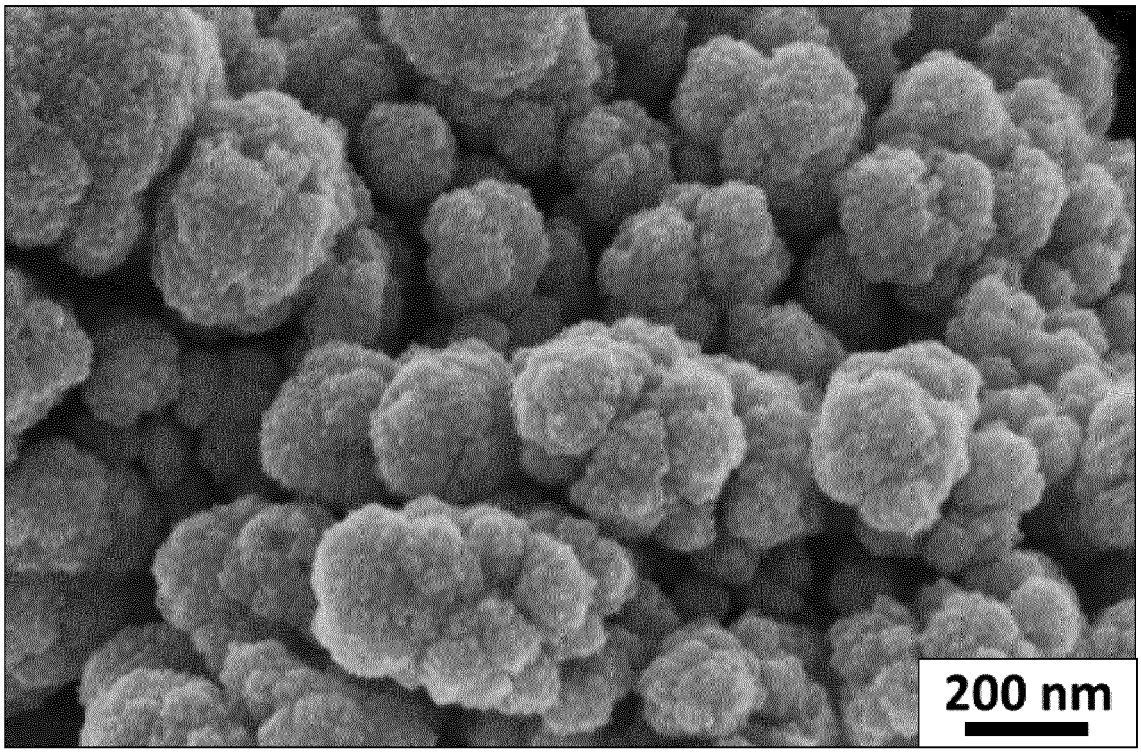


Fig 2

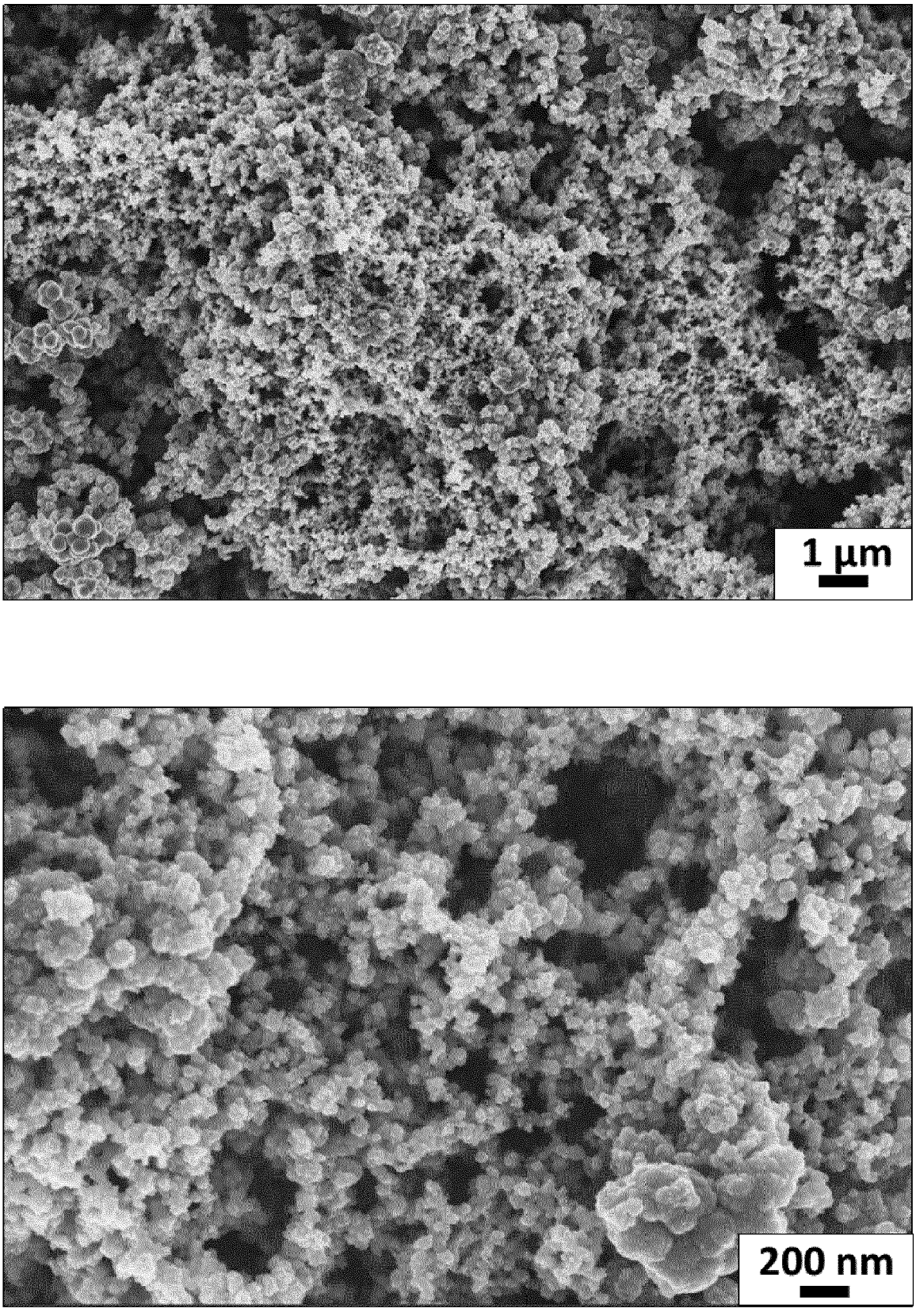
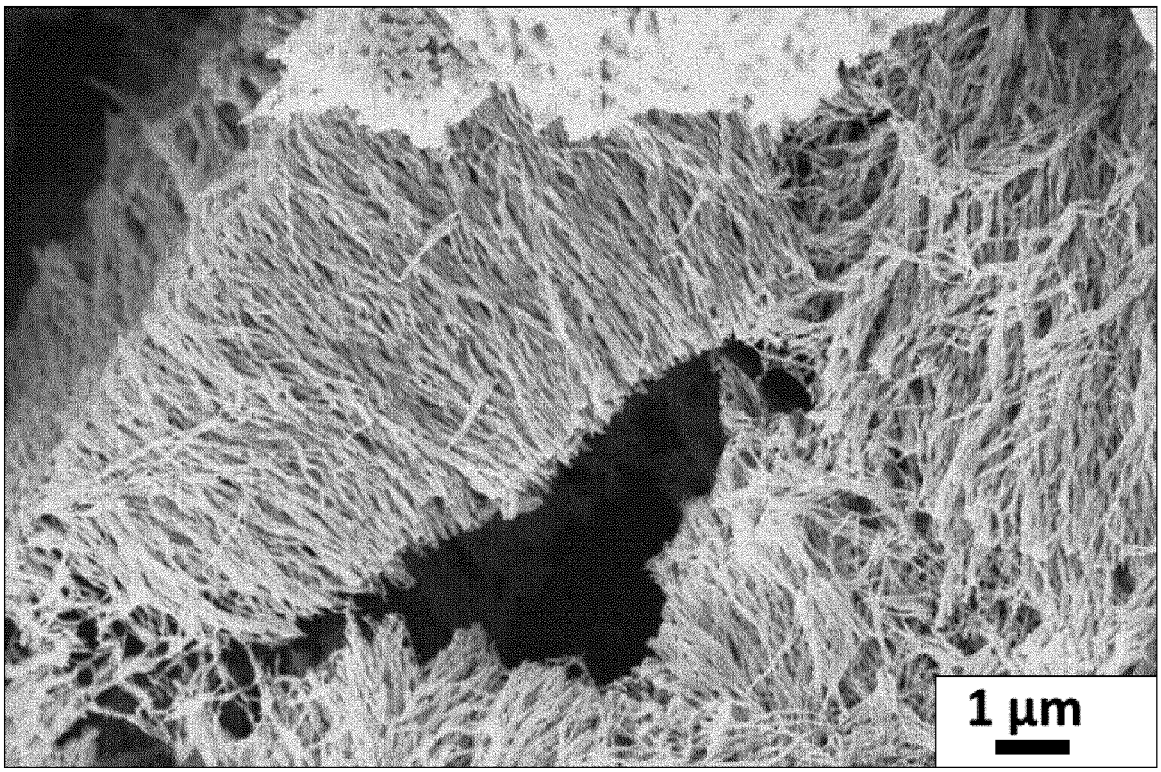


Fig 3



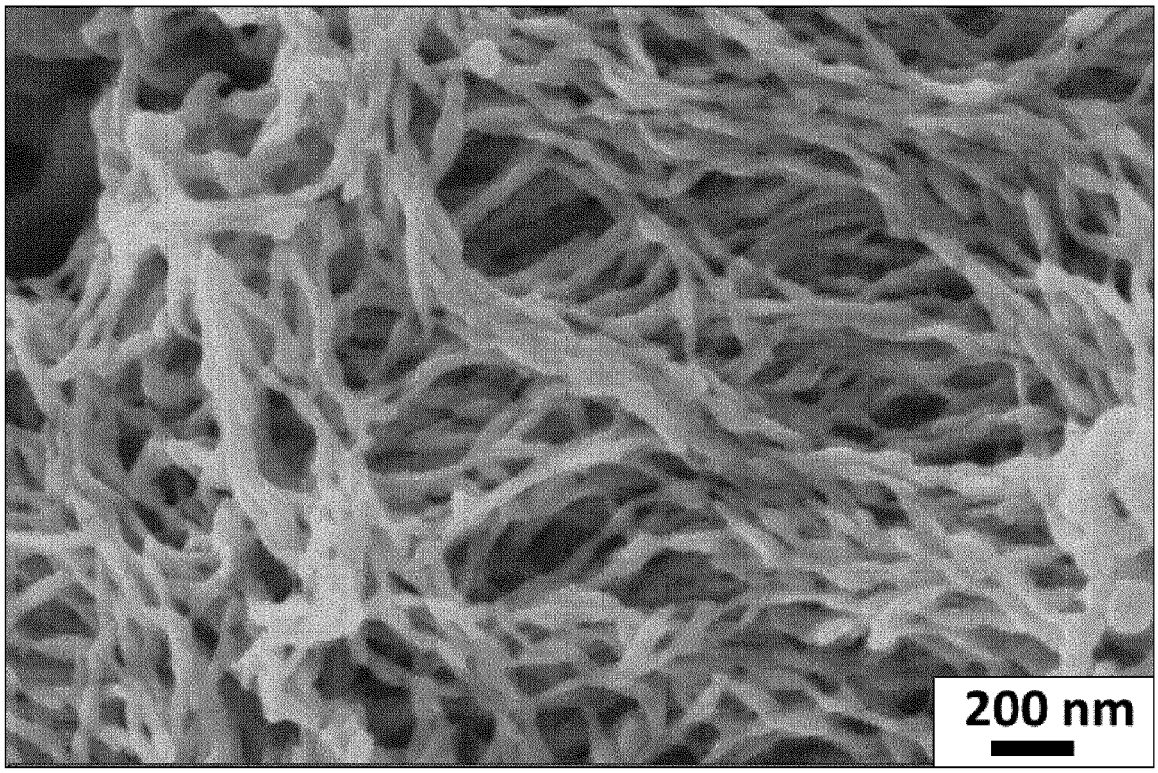
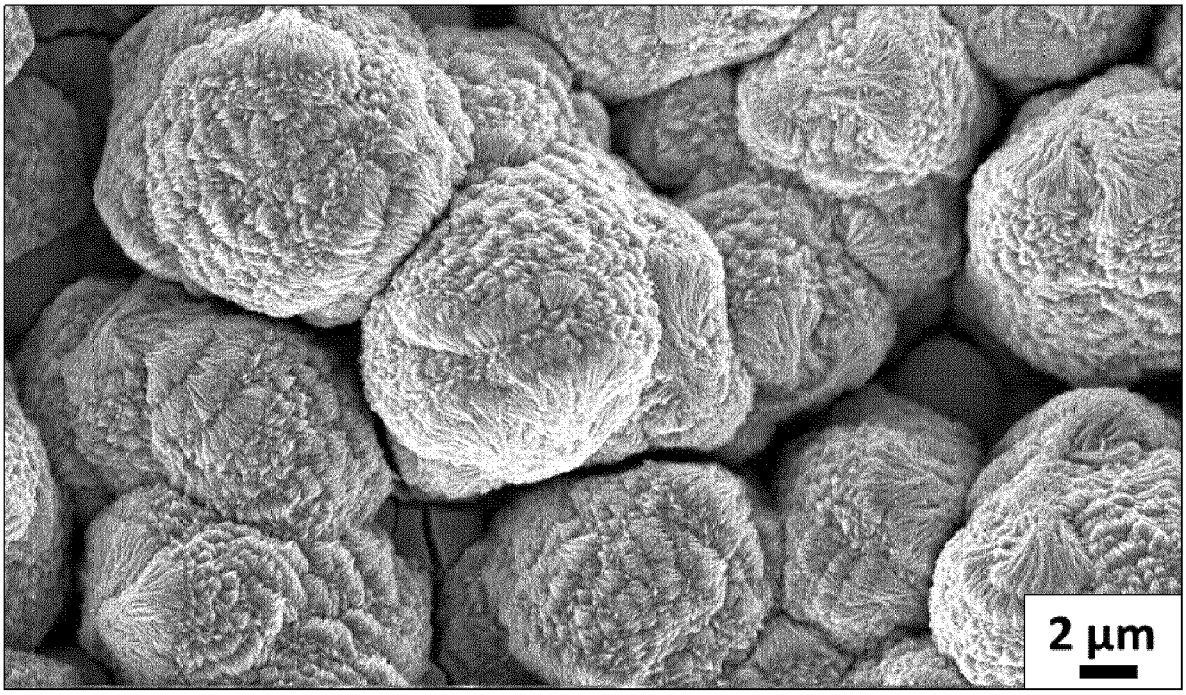


Fig 4



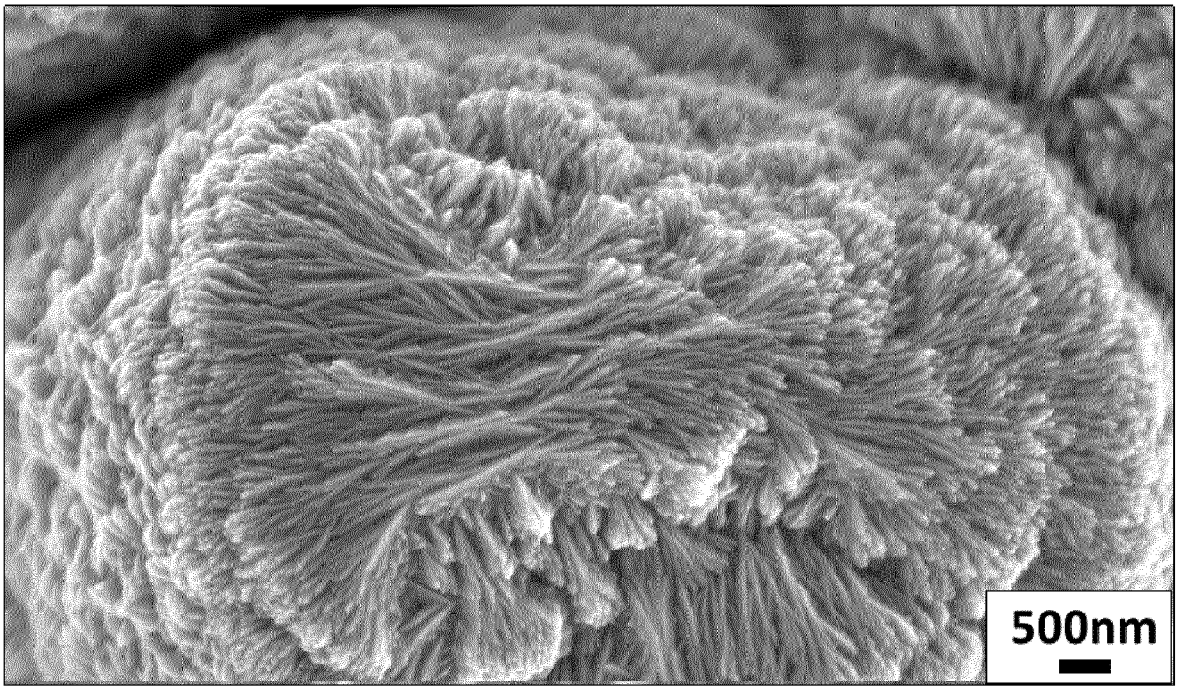
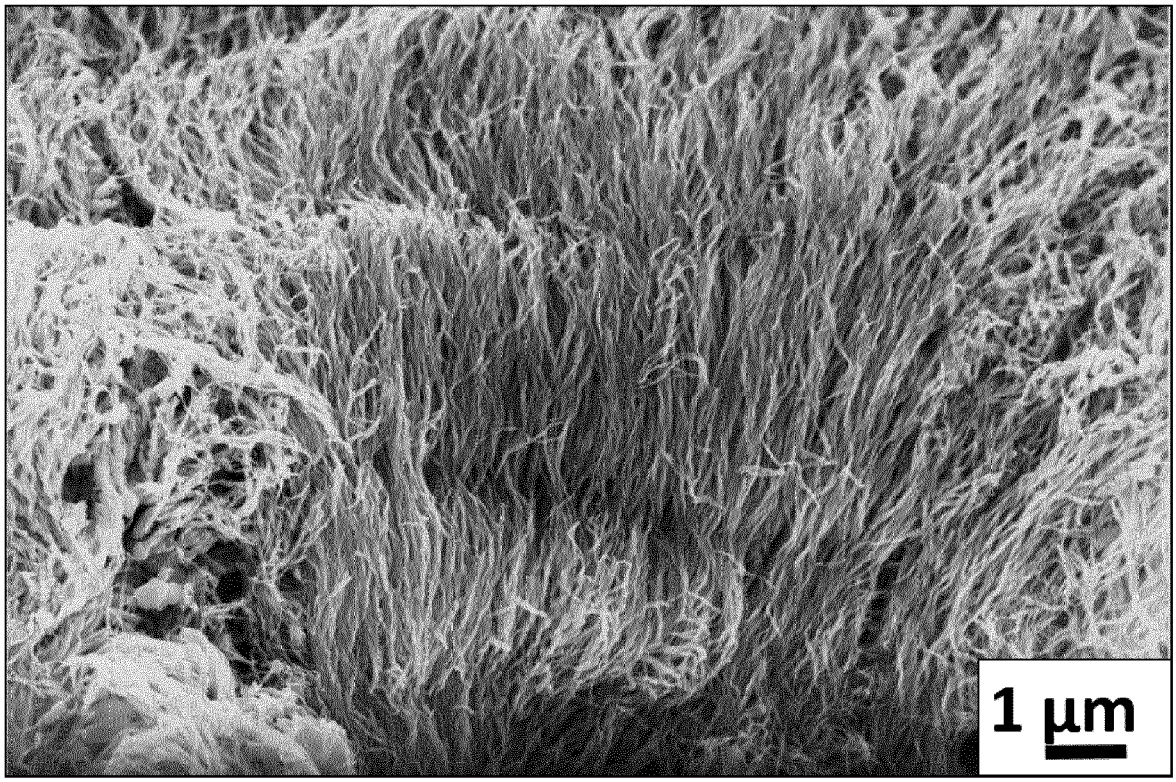


Fig 5



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EUROPEAN SEARCH REPORT

Application Number
EP 16 15 7979

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	YANG M-H ET AL: "ELECTRODEPOSITION OF ANTIMONY IN A WATER-STABLE 1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE TETRAFLUOROBORATE ROOM TEMPERATURE IONIC LIQUID", JOURNAL OF APPLIED ELECTROCHEMISTRY, SPRINGER, DORDRECHT, NL, vol. 33, no. 11, 1 November 2003 (2003-11-01), pages 1077-1084, XP001225266, ISSN: 0021-891X, DOI: 10.1023/A:1026223314259 * abstract * * figure 1 * * paragraphs 2.2, 3.1 * -----	1-11	INV. C25D3/66 C25D3/54
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The Hague	3 August 2016	Lange, Ronny

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A	ABHISHEK LAHIRI ET AL: "Stromlose Abscheidung von III-V-Halbleiternanostrukturen aus ionischen Flüssigkeiten bei Raumtemperatur", ANGEWANDTE CHEMIE, vol. 127, no. 40, 28 September 2015 (2015-09-28), pages 12038-12042, XP055292754, DE ISSN: 0044-8249, DOI: 10.1002/ange.201504764 * abstract * * figure 1 * -----	1-8	TECHNICAL FIELDS SEARCHED (IPC)

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