(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 934 793 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
01.06.2022 Bulletin 2022/22

(21) Application number: **13819044.2**

(22) Date of filing: **23.12.2013**

(51) International Patent Classification (IPC):
B22F 9/24 *(2006.01)* ***C25C 5/02*** *(2006.01)*
C25C 1/14 *(2006.01)* ***C25C 1/20*** *(2006.01)*
B22F 1/00 *(2022.01)*

(52) Cooperative Patent Classification (CPC):
(C-Sets available)
B22F 9/24; C25C 1/14; C25C 1/20; C25C 5/02;
B22F 1/054; B22F 2999/00 (Cont.)

(86) International application number:
PCT/FI2013/051201

(87) International publication number:
WO 2014/096556 (26.06.2014 Gazette 2014/26)

(54) **MANUFACTURE OF NOBLE METAL NANOPARTICLES**

HERSTELLUNG VON EDELMETALL-NANOPARTIKELN

FABRICATION DE NANOPARTICULES DE MÉTAL NOBLE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **21.12.2012 FI 20126373**
21.12.2012 US 201261740532 P

(43) Date of publication of application:
28.10.2015 Bulletin 2015/44

(73) Proprietors:
- **Inkron Ltd.**
  Hong Kong (CN)
- **Rantala, Juha**
  Hong Kong (CN)

(72) Inventor: **RANTALA, Juha**
Hong Kong (CN)

(74) Representative: **Laine IP Oy**
Porkkalankatu 24
00180 Helsinki (FI)

(56) References cited:
JP-A- 2007 327 117
US-A1- 2009 178 933
US-A1- 2012 093 680

- **UEDA M ET AL: "Double-pulse technique as an electrochemical tool for controlling the preparation of metallic nanoparticles", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 48, no. 4, 20 December 2002 (2002-12-20), pages 377-386, XP004397091, ISSN: 0013-4686, DOI: 10.1016/S0013-4686(02)00683-7 cited in the application**
- **KOMSIYSKA L ET AL: "Electrocrystallization of Au nanoparticles on glassy carbon from HClO4 solution containing [AuCl4]<->", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 54, no. 2, 30 December 2008 (2008-12-30), pages 168-172, XP025536091, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2008.08.013 [retrieved on 2008-08-19]**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Processed by Luminess, 75001 PARIS (FR)

(Cont. next page)

(52) Cooperative Patent Classification (CPC): (Cont.)

C-Sets
B22F 2999/00

Description

FIELD OF THE INVENTION

[0001] The present invention relates to the manufacture of noble metal nanoparticles. In particular the present invention concerns a method of producing nanoparticles by electrodeposition.

BACKGROUND ART

[0002] Electrodeposition provides a cost effective (G. Staikov, Electrocrystallisation in Nanotechnology, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, 2007) and non-equipment intensive method for the preparation of nanocrystalline and nanophase metallic materials (metals, alloys, compositionally modulated alloys and composites) as free standing objects even in complex shapes. Electrodeposition can be used with conventional or modified electroplating baths and conditions to produce grain sizes in the range from essentially amorphous to micrometric. The production of nanostructured materials/nanoparticles by electrochemical procedures is very advantageous because of the crucial steps in nanocrystal formation, nuclei formation and nuclei growth, can be controlled by physical parameters i.e. current density, current characteristics and chemical parameters (grain refiners, complex formation) (Hatter et al., J. Phy. Chem. 100 (1996) 19525; Alfantazi et al., J. Mater. Sci. Letter, 15 (1996) 1361). Several groups have electrodeposited metallic nanoparticles on various substrates, such as glassy carbon (GC) (Isse et al., Electrochem. Commun. 8 (2006)), highly oriented pyrolitic graphite (HOPG) (Liu et al., Electrochim. Acta 47 (2001) 671-677), and indium doped tin Oxide (ITO) (Ueda et al., Electrochim. Acta 48 (2002) 377-386).

[0003] The choice of electrodes is also an important aspect of the electrodeposition process. The reproducibility of results from electrodeposition experiments is quite poor when solid metal electrodes are used. Ultramicroelectrodes (UME) are the best tools to study concentrated electrolytes (R. M. Wightman, D. O. Wipf, "Voltammetry at Ultramicro-electrodes" in: A. J. Bard (Ed), Electroanalytical Chemistry, Vol. 15, Marcel Dekker, NY, 1988.). Ultramicroelectrodes arrays can be easily used in a commercial process and can be manufactured at low cost using well established methods. The usage of ultramicroelectrodes makes the electrodeposition process very efficient mostly due to the increase of mass transport of electroactive species. The application of ultrasound irradiation to electrochemistry process dates back to the early thirties (Moriguchi, J. Chem. Soc. Jpn, 55 (1934) 749-750). The fundamental basis of the pulsed sonoelectrochemical technique for the production of nanopowders is massive nucleation (Aqil et al., Ultrason Sonochem. 15 (2008) 1055-1061). The variety of induced effects on electrochemistry processes by ultrasound waves is attributed to the generation, growth and collapse of microbubbles in the electrolyte.

[0004] The pulsed electrodeposition technique is a versatile method for the preparation of nanostructured metals and alloys because this technique (Puippe and Leaman (Ed.), Theory and Practice of Pulse Plating, American Electroplaters and Surface Finishers Society, Orlando, Florida, 1986) allows for the preparation of large bulk samples with high purity, low porosity and enhanced thermal stability. This electrochemical process enables the adjustment of the nanostructure (grain-size, grain size distribution, microstress) which is responsible for physical and chemical properties. In this technique, metal nuclei are formed during a short nucleation pulse with a high overpotential. The nucleation pulse is followed by the growth pulse, where the nuclei slowly grow at low overpotential to their final size. Recently, gold nanoparticles have been prepared by electrochemical deposition on highly oriented pyrolytic graphite (HOPG) and boron doped epitaxial 100-oriented diamond layers using a potentiostatic double pulse technique with a particle size in the range of 5 to 30 nm in case of HOPG. Also well-dispersed metallic nanoparticles in the mesoscopic range with average particle diameters of 50 nm and above and very narrow particle size distributions on HOPG (Penner et al., J. Phys. Chem. B 106 (2002) 3339-3353; Liu et al., J. Phys.Chem. B 104 (2000) 9131-9139; Ueda et al., Electrochim. Acta 48 (2002) 377-386; Sandmann et al., J. Electroanal. Chem. 491 (2000) 78-86) and indium tin oxide (ITO) could be obtained by a deposition method consisting of two potentiostatic pulses. It is possible to independently control the particle density and particle size using this technique. Recently, copper powders and nanopowders have been produced from industrial electrolytes by using potentiostatic pulse electrolysis method (See US Published Patent Application No. 2012/0093680).

[0005] Thus, a method of extracting metal nanoparticles from electrolytic solutions containing metal ions through an electrochemical process on an electrode, wherein the electrolytic solution undergoes potentiostatic pulse electrolysis in the presence of a first electrode and a second electrode, and the electrochemical nucleation takes a place at the first electrode and the metal particles are extracted from the electrolytic solution is disclosed in the art, for example by patent publication US 2012/093680 A1 and publications Ueda et al., Electrochim. Acta 48 (2002) 377-386 and Komsiyska L et al., Electrochim. Acta 54 (2008) 168-172.

[0006] Patent publication JP 2007327117 A presents utilization of pulse electrolysis and ultrasonic oscillation to provide nano-sized partciles.

[0007] Besides the pulse electrodeposition technique, other synthesis techniques are of large industrial interest for the synthesis of metal nanoparticles. Recently, sol-flame synthesis has been used as a general strategy to decorate nanowires with metal oxide/ noble metal nanoparticles. The nanoparticle-decorated nanowires serve as a desirable structure for applications including batter-

ies, dye-sensitized solar cells, photoelectrochemical water splitting and catalysis (Feng et al. 2012). Silver nanoparticles obtained by chemical reduction technique display appealing properties such as catalytic and antibacterial activity (Mukherjee et al., Nonoletters, 10 (2001) 515; Soudi et al. J. Colloid. Interface Sci. 275 (2004) 177) which open perspectives in medical applications (Chen, et al., Toxicol Letter 176 (2008) 1). Collodial PT NPS synthesized by reduction of H_2PtCl_2 in the presence of a citrate capping agent acts as a novel hydrogen storage medium (Yamauchi et al. Chem. Phys. Chem. 2009, 10:2566). Furthermore, Au NPS exhibit excellent optical properties (Hostetler et al. Langmuir, 14 (1998) 17). And also known for their high chemical stability, catalytic use and size dependent properties (Sardar et al., Langmuir, 25 (2009) 13840). Further applications of metal nanoparticles are inkjet printing with the use of inks. Most of the conductive inks at present are based on Ag NPS since Ag possesses the highest electrical conductivity among metals. Cu- NP based inkjet sets are of commercial interest due to its long term stability under ambient conditions (Magdass et al. NIP 25 and Digital Fabrication, Tech Program 2009 611-613, Grouchko et al. J. Mater. Chem. 19 (2009) 3057-3062).

[0008] Noble metal nanoparticles exhibit increased photochemical activity because of their high surface/volume ratio and unusual electronic properties. Noble metal nanoclusters in the nanometer scale display numerous interesting optical, electronic and chemical properties that depend on size enabling them for manifold applications in the development of biological nanosensors and optoelectronic devices. Also, inorganic nanoparticles especially bimetallic nanoparticles have attracted much interest among the broad scientific community since the catalytic properties and electronic structures of such nanomaterials can be tuned by varying their compositions and structures (Schmid et al., Angew Chem. Int. Ed. 30 (1991) 874; Joshima et al. Langmuir 1994, 104574. 1994; Sinfelt, J. Catal. 29 (1973) 308).

[0009] Currently, noble metal nanoparticles are produced by a series of different processes depending on the necessary product size and parts. Much attention has been devoted in recent years to methods, many anions, such as Cl^-, NO_3^- and SO_4^{2-}, often remain in the prepared solution and removal of these anions adds to the cost. Therefore, the development of low cost, low environmental load and high yield process is important for the synthesis of metal nanoparticles. Methods such as microemeulsion method yield narrow particle size distributions, but the variation of particle sizes is difficult. Sputtering followed by thermal treatment is a convenient deposition method allowing adjustment of different coverage, however the distribution of particle sizes is rather broad.

[0010] It is therefore of great industrial interest to have a production method which best combines cost efficiency and versatility.

Brief Summary of the invention

[0011] As is apparent from the above, there are considerable problems associated with the known technology. In order to address these issues, there is need for improved control of nanoparticle growth controlled by the composition of the deposition solution, deposition overpotential, actual overpotential at the electrode/electrolyte interface, current density and temperature.

[0012] Thus, it is an aim and to provide a novel method of producing of metal nanoparticles by electrodeposition.

[0013] The present invention is based on the idea of extracting metal nanoparticles from electrolytic solutions containing ions of the corresponding metals through an electrochemical process on an electrode, wherein the electrolytic solution is subjected to potentiostatic pulse electrolysis in the presence of a first electrode and a second electrode such that electrochemical nucleaction takes a place at the first electrode. Metal particles are extracted from the electrolytic solution.

[0014] In an embodiment, metal particles having a maximum dimension of 1 micron or less, are produced from a first and a second salt in aqueous solution, the first salt comprising transition metal or semi-metal and the second salt comprising alkali metal or alkaline earth metals, and both of the salts further comprising NO_3^-, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}, ClO_4^-, $(COO)_2^{2-}$ or halo. The aqueous is subjected to a voltage between electrodes such that transition metal or semi-metal particles are formed and dispersed within the aqueous solution, said particles having an average maximum dimension of less than 1 micron; and said particles are separated from the solution, e.g. by filtering.

[0015] The present invention is defined by the appended claims.

[0016] Considerable advantages are obtained by the present invention. Thus, the present invention provides for efficient production of metal particles, in particular of particles in one embodiment, nanoparticles, consisting at least to 95% or more of a desired element, are extracted from electrolytic solutions containing two or more metals or metal ions. In a further embodiment, nanoparticles of other elements, consisting at least to 95% or more of a desired element, are sequentially extracted from electrolytic solutions containing two or more metals or metal ions.

[0017] This allows for selective removal of the desired metal. In such an embodiment, it is possible to continue the process when the first metal has been removed by removing a second (and third etc.) metal. Thus, for example, it is possible first to remove Ag and then to continue by removing Cu in order to produce particles or either or both of said metal.

Brief Description of the Drawings

[0018]

Figures 1A and 1B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 1;

Figures 2A and 2B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 2;

[0019] This allows for selective removal of the desired metal. In such an embodiment, it is possible to continue the process when the first metal has been removed by removing a second (and third etc.) metal. Thus, for example, it is possible first to remove Ag and then to continue by removing Cu in order to produce particles or either or both of said metal.

Brief Description of the Drawings

[0020]

Figures 1A and 1B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 1;

Figures 2A and 2B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 2;

Figures 3A and 3B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 3;

Figures 4A and 4B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 4;

Figures 5A and 5B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 5;

Figures 6A and 6B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 6;

Figures 7A and 7B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 7;

Figure 8 shows an SEM image of the Cu particles formed in Example 8;

Figures 9A and 9B show an SEM image of Cu particles formed and the rate of electrodeposition of particles as a function of energy (in keV) for Example 9;

Figure 10A and 10B show an SEM image of Ag particles formed and the rate of electrodeposition of said particles as a function of energy (in keV) for Example 10; and

Figure 11 shows an SEM image of Ag particles formed in Example 11.

Description of Embodiments

[0021] The present invention relates to the manufacture of metal or metalloy nanoparticles from multimetal electrolytes/complex matrix industrial electrolytes by using potentiostatic pulse electrodeposition process. In particular the process is suitable for noble metals and transition metals. Examples include Ag, Sn, Cu, Au, and Ni; preferred are noble metals, such as Ag, Au and Pt, as well as transition metals, such as Sn and Ni.

[0022] As discussed above, the present technology comprises the steps of extracting metal nanoparticles from electrolytic solutions through an electrochemical process on an electrode, comprising that the metal ions containing electrolytic solution undergoes potentiostatic pulse electrolysis in the presence of a first electrode, which for example is an array electrode containing plurality of micrometer or sub-micrometer sized electrodes, and a second electrode. The electrochemical nucleaction takes a place at the first electrode and the metal particles are or extracted, preferably continuously, from the electrolytic solution.

[0023] In one embodiment, nanoparticles, consisting at least to 95% or more of a desired element, are extracted from electrolytic solutions containing two or more metals or metal ions. The desired metal nanoparticles are formed through an electrochemical process on an electrode, wherein the electrolytic solution is subjected to potentiostatic pulse electrolysis in the presence of a first electrode and a second electrode such that electrochemical nucleaction takes a place at the first electrode. Metal particles, containing 95% or more of desired metal, can be extracted from the electrolytic solution leaving undesired metals in the electrolyte.

[0024] In a further embodiment, nanoparticles of other elements, consisting at least to 95% or more of a desired element, are sequentially extracted from electrolytic solutions containing two or more metals or metal ions. The desired metal nanoparticles are formed through an electrochemical process on an electrode, wherein the electrolytic solution is subjected to potentiostatic pulse electrolysis in the presence of a first electrode and a second electrode such that electrochemical nucleaction takes a place at the first electrode. Metal particles, containing 95% or more of desired metal, can be extracted from the electrolytic solution leaving undesired metals in the electrolyte. Once the first desired metal has been extracted, process parameters are adjusted to permit removal of a second or further elements.

[0025] In a preferred embodiment, metal particle extraction is achieved by combining potentiostatic pulse electrodeposition technique using ultramicroelectrodes (UME) and synchronized ultrasound in the presence of a megasonic transducer.

[0026] In one embodiment, the electrolyte is formed by

metal ions and corresponding anions of a soluble metal salt in an aqueous medium. The electrolyte preferably additionally comprises an acid. It is particularly preferred to employ salts and corresponding acids. In advantageous embodiments, mineral acids and corresponding metal salts are employed such as hydrochloric acid and chlorides, or suitably nitric acid and nitrates of sulphuric acid and sulphates.

[0027] In one preferred embodiment, the electrolytic solution has a pH of less than 7. The pH lies in particular in the range from 1 to 6.

[0028] One embodiment of the invention relates to the formation of Ag nanoparticles on the stainless steel (SS) substrate. Metal in the form of nanopowders are deposited on the SS surface by potentiostatic pulse electrodeposition from a solution comprising metal nitrate and nitric acid. One of the pulse electrodeposition processes includes applying a number of electrical pulses having a pulse width. The number of electrical pulse cycles may be up to 400 and the pulse duration may be from 0-0.1s.

[0029] In another embodiment, the number of nanoparticles formed per unit area of the stainless steel surface may be affected by controlling the duration of electrical pulses used for deposition. The composition of the nanoparticles placed on the surface of SS substrate may be affected by controlling the chemical composition of the precursor solution.

[0030] The invention comprises producing nanoparticles of a D_{100} of less than 100 nm.

[0031] In one embodiment, only one type of the metals is extracted from the electrolytic solution.

[0032] In another embodiment, only one type of the metals is extracted from the polymetallic electrolytic solution selectively.

[0033] In a preferred embodiment, several types of metals are sequentially and selectively extracted from the polymetallic electrolytic solution. The polymetallic solution may contain impurities as such or other metal salts may have been added in the solution to alter the electrolyte conductivity.

[0034] The number of electrical pulses or pulse cycles is, preferably, less than 450.

[0035] The electrolytic process comprises an ultrasonic or megasonic transducer.

[0036] In one preferred embodiment, the first electrode is a diode. For example, the diode is a photo diode. Further, one the first electrode is a diode, the first electrode passes the current once the diode is activated by a light.

[0037] In one embodiment, the potentiostatic pulse changes current direction. Generally, the anodic potential E_a can be about 2.5 V. The cathodic potential E_c can be about -1.0 V. In one embodiment, the pulse in the anodic potential is for a period (t_a) of about 0.1 s. The pulse in the cathodic potential is for a period (t_c) of about 0.1 s

[0038] In another embodiment, the potentiostatic pulse changes current direction. Generally, the anodic potential E_a is regulated to permit selective production of metal nanoparticles with elemental purity of 95% or more. The cathodic potential E_c can similarly be regulated. In one embodiment, the pulse in the anodic potential is for a period (t_a) of about 0.1 s. The pulse in the cathodic potential is for a period (t_c) of about 0.1 s

[0039] In one particular embodiment, the extracted metal nucleates does not adhere on the cathode and returns back to the plating solution as free particles or nanoparticles.

[0040] The present method makes it possible to regulate the size of the particles by simply adjusting the distance between the electrodes. Thus, in the invention the electrodes are spaced apart at a first distance in order to produce particles having a first size and then the electrodes are shifted so as to be spaced apart at a second distance in order to produce particles having a second size, second size being greater than the first size when the second distance is smaller than the first distance.

[0041] In a particularly preferred method, the method is carried out in an apparatus for obtaining Ag or Sn nanopowders from industrial electrolytes through electrochemical deposition of Ag or Sn on the cathode. In the case of Ag, the electrolytic solution comprises Ag ions, for example at a concentration of about 5 g/L to 80 g/L. In the case of Sn, the electrolytic solution comprises Sn ions for example at a concentration of about 1.19 g/L to 45 g/L.

[0042] The apparatus comprises an electrolytic chamber (such as an ultrasonic bath as mentioned below) for the electrolyte; means for providing a potentiostatic pulse electrolysis; an ultramicroelectrode cathode, such as a microelectrode comprising of stainless steel; an anode for example comprising Pt coated titanium mesh plates; and means for regulating the processing temperature of the electrolytic chamber. Typically, the process is carried out at a temperature of about 5 to 90 °C, for example about 10 to 70 °C, in particular about 15 to 50 °C, for example 20 to 30°C, or about 25 °C.

[0043] Another embodiment, outside the scope of the present invention relates to a method of making Ag nanoparticles including performing pulse electrodeposition in a solution comprising of a nanoparticle precursor placed in an ultrasonic bath to form a metal powder/precipitate at the bottom of the electrochemical cell during the potentiostatic cycles and annealing the filtered precipitate to form the nanoparticles wherein the average diameter of Ag nanoparticles is capable of being arbitrarily controlled during processing from about 200 nm-325 nm.

[0044] Another aspect of the disclosure, outside the scope of the present invention, is to produce Sn nanoparticles with particle sizes of up to 200 nm.

[0045] Formed or precipitate metal particles are separated from the electrodes. In order to avoid or mitigate entanglement of such particles to the electrodes for example ultrasound can be directed to the electrolyte or electrodes or both.

[0046] Based on the above, one embodiment for mak-

ing metal particles, comprises the steps of

- mixing with water, together or separately,

  a) a transition metal salt, and
  b) a soluble conductivity enhancing compound,
  so as to form an electrolyte solution;

- providing the electrolyte solution between electrodes;
- performing potentiostatic pulse electrolysis so as to cause the formation of metal oxide particle at the first or second electrode;
  wherein the metal oxide particles become separated from the first or second electrode back into the electrolytic solution; and
- separating the metal oxide particles from the electrolytic solution.

[0047] The electrolytic solution has a pH of less than 7, preferably a pH of from 1 to 6.

[0048] The potentiostatic electrolysis comprises a series of voltage pulses having a pulse width of less than 1 second, for example the pulse width is less than 0.5 second, in particular less than 0.1 second.

[0049] The transition metal salt comprises a transition metal selected from Ni, W, Pb, Ti, Zn, V, Fe, Co, Cr, Mo, Mn and Ru. The transition metal salt is a nitrate, sulphate, carbonate, phosphate or halogen salt.

[0050] The soluble conductivity enhancing compound is an acid, in particular the conductivity enhancing compound is, for example, a water soluble acid, such as sulphuric acid, nitric acid, a chlorine containing acid, phosphoric acid or carbonic acid.

[0051] Alternatively, the soluble, conductivity enhancing compound is a halogen containing salt or acid. The soluble conductivity enhancing compound is a salt, for example .a transition metal salt comprises a late transition metal.

[0052] Both the transition metal salt and the soluble conductivity enhancing compound may comprise the same nitrate, sulphate, carbonate, phosphate or halogen group element or ion derived therof.

[0053] In another embodiment, outside the scope of the present invention, a method for forming metal particles having a maximum dimension of less than 1 micron, comprises the steps of:

- adding into water a first salt comprising a metal or semi-metal;
- adding to water a second salt comprising an alkali metal or alkaline earth metal, wherein the first and second salts are added to water together or separately to form at least one aqueous electrolyte solution;
- providing the at least one aqueous electrolyte solution between an anode and cathode;
- providing an anode and cathode, and providing the at least one aqueous electrolyte solution there between;
- providing electrical pulses through the electrolyte solution so as to form metal particles in the solution having a maximum dimension of less than 1 micron.

[0054] In still a further embodiment, a method of forming metal particles having a maximum dimension of 1 micron or less, comprises:

- providing to water a first salt having a) a transition metal or semi-metal, and b) a NO_3^-, $SO4^2$, PO_4^{3-}, BO_3^{3-}, ClO_4^-, $(COO)_2^{2-}$ or a halogen group, and providing to water a second salt having a) an alkali metal or alkaline earth metal, and b) a NO3, SO4, PO4, BO3, CLO4, (COOH)2 or a halogen group, so as to form an at least one aqueous solution;
  disposing the aqueous solution between electrodes;
- providing a voltage across the electrodes such that transition metal or semi-metal particles are formed and dispersed within the aqueous solution having an average maximum dimension of less than 1 micron; and
- filtering out the transition or semi-metal particles from the solution.

[0055] The first salt may comprise a noble metal and Y may be NO_3^- or $(COOH)_2$.

[0056] The first salt may comprise Sn, or the first salt may comprise a metal selected from group 10 or group 11 of the periodic table.

[0057] The voltage provided across the electrodes is provided as alternating positive and negative potentials between the electrodes.

[0058] Further ultrasound may be directed to the electrolyte solution.

[0059] The transition metal or semi-metal is Ag, Sn, Cu, Au, Cu or Ni. The alkali metal is Na or K.

[0060] The voltage is provided across the electrodes as a series of voltage pulses. Preferably the voltage pulses are provided as a series of alternating positive and negative pulses.

[0061] The particles formed are crystalline particles.

[0062] The following examples are given for illustrative purposes only.

Reference Example 1

[0063] A stainless steel plate serving as a cathode and a Pt-coated titanium mesh plate serving as a reference electrode (anode) were placed in an electrochemical cell. The width of the electrodes was: anode 1 mm, cathode 1 mm). The cathode and the anode were immersed at equivalent depth into the electrolyte yielding an area ratio of 1:1. The electrolyte consisted of 80 g/L of $AgNO_3$ and 120 g/L of HNO_3. The distance between the anode and cathode was adjusted to 2 cm. The pulse cycle was as follows: E_a= 2.5V, t_a= 0.1 s, E_c= -1.0V, t_c = 0.1 s. A total

of 400 cycles were run.

[0064] A precipitate formed during the electrodeposition on the cathode. The precipitate continuously settled toward the bottom of the electrochemical cell during the potentiostatic cycles. The precipitate was removed from the solution by filtration, dried and analyzed using SEM-EDS. The analysis confirmed that the precipitate was 100 % Ag and the smallest Ag- particles exhibited a size of ca. 300 nm, determined by SEM. The particle size was determined to be 1400 nm with a polydispersity index of 0.81 by DLS after re-dispersion and dilution.

Reference Example 2

[0065] The procedure in Reference Example was repeated with an altered configuration. Into an electrochemical cell was placed a stainless steel plate serving as a cathode and a Pt-coated titanium mesh as a reference electrode (anode). The width of the electrodes was the same as in Reference Example 1. The cathode and the anode were immersed to equivalent depth into the electrolyte yielding an area ratio of 1:2 resulting from the holes in the anode structure. The distance between the anode and cathode was adjusted to 3.5 cm. The electrolyte consisted of 80 g/L of $AgNO_3$ and 120 g/L of HNO_3. The electrolyte and the pulse sequence was held as in Example 1. The precipitate was removed from the solution by filtration, dried and analyzed using SEM-EDS. The analysis confirmed that the precipitate was 100% Ag and the smallest ag particles size determined by SEM-measurement was ca 200 nm. The particle size was determined to be 750 nm with a polydispersity index of 0.90 by DLS after re-dispersion and dilution. The distance between anode and cathode has an influence on the particle size nucleation.

Reference Example 3

[0066] The procedure in Reference Example 2 was repeated. The electrochemical cell was placed in an ultrasonic bath during the nanoparticle synthesis. SEM-EDS analysis confirmed that the collected precipitate was 100 % Ag and the size of the smallest Ag-particles determined by SEM-measurement was ca. 200 nm. The particle size was determined to be 325 nm with a polydispersity index of 0.91 by DLS after re-dispersion and dilution. The ultrasound has an influence on the particles size and morphology

Reference Example 4

[0067] The procedure in Reference Example 3 was repeated. The electrolyte was diluted to 5 g/L of $AgNO_3$ and 15 g/L of HNO_3. The electrochemical cell was placed in an ultrasonic bath during the nanoparticle synthesis. The cathode and the anode were immersed to equivalent depth into the electrolyte yielding an area ratio of 1:2 SEM-EDS analysis confirmed that the collected precipitate was 100 % Ag and the smallest Ag-particles size determined by SEM-measurement was ca 200 nm. The particle size was determined to be 325 nm with a polydispersity index of 0.91 by DLS after re-dispersion and dilution.

Reference Example 5

[0068] The procedure in Reference Example 4 was repeated. The electrolyte was diluted to 5 g/L of $AgNO_3$ and 15 g/L of HNO_3. The electrochemical cell was placed without ultrasonic bath during the nanoparticle synthesis. SEM-EDS analysis confirmed that the collected precipitate was 100 % Ag and the smallest Ag-particles size determined by SEM-measurement was ca. 200 nm. The particle size was determined to be 164 nm with a polydispersity index of 0.81 by DLS after re-dispersion and dilution.

Reference Example 6

[0069] Into an electrochemical cell was placed a stainless steel plate serving as a cathode and a Pt-coated titanium mesh plate as a reference electrode (anode). The width of the electrodes was (anode 1 mm, cathode 1 mm). The cathode and the anode were immersed to equivalent depth into the electrolyte yielding an area ratio of 1:2. The electrolyte consisted of = 45g/l Sn 120g/l H_2SO_4. The distance between the anode and cathode was adjusted to 3.5cm. The pulse cycle was as follows: E_a= 2.5 V, t_a= 0.1 s, E_c= -1.0 V, t_c= 0.1 s. A total of 400 cycles were run. A precipitate formed during the electrodeposition at the cathode. The precipitate continuously settled toward the bottom of the electrochemical cell during the potentiostatic cycles. The precipitate was removed from the solution by filtration, dried and analyzed using SEM-EDS. The analysis confirmed that the precipitate was 97 % Sn and its smallest particle had a size, determined by SEM, to be ca. 200 nm. The particle size was determined to be 740 nm with a polydispersity index of 0.81 by DLS after re-dispersion and dilution.

Reference Example 7

[0070] The procedure of Reference Example 6 was repeated. The electrolyte was diluted to Sn 1.1 g/l + 2.9 g/l H_2SO_4. The electrochemical cell was placed with ultrasonic bath during the nanoparticle synthesis. SEM-EDS analysis confirmed that the collected precipitate was 40 % Sn (ca. 50 % impurities due to the dissolution of anode and cathode material during the electrodeposition, see EDS-curves) and the size of the smallest Sn-particles was determined, by SEM-measurement, to be ca. 100 nm. After re-dispersion and dilution, the particle size was determined to be 1240 nm with a polydispersity index of 0.81 by DLS.

Example 1

[0071] An electrolyte solution of $CuSO_4$ in aqueous H_2SO_4 was prepared by weighing 200g of $CuSO_4 \cdot 5H_2O$ and 240g of concentrated H_2SO_4 into de-ionized water and the total volume was diluted to 3L. A stainless steel plate serving as a cathode and a Pt-coated titanium mesh plate serving as a reference electrode (anode) were placed in an electrochemical cell. The width of the electrodes was: anode 1 mm, cathode 1 mm). The cathode and the anode were immersed at equivalent depth into the electrolyte yielding an area ratio of 1:1. The distance between the anode and cathode was adjusted to 5 cm. The pulse cycle was as follows: E_a= 2.5V, t_a= 3 ms, E_c= -1.0V, t_c = 1ms.

[0072] A precipitate formed during the electrodeposition on the cathode. After 2min, the precipite was collected, washed with water, dried and analyzed using SEM-EDS. The analysis confirmed that the precipitate was 100 % Cu and the diameter of smallest Cu-particles were less than 100 nm, determined by SEM.

Reference Example 8

[0073] An electrolyte solution containing $CuSO_4$ was prepared by weighing 100g of a enriched ore and allowing the components to dissolve in 300g of 8% aqueous aqueous H_2SO_4. Main elements in this ore were Cu (673 mg/g), Al (7 mg/g), Fe (31 mg/g), Mg (2 mg/g) and Zn (1 mg/g). The process in example 1 was repeated for 3h. A precipitate formed during the electrodeposition on the cathode. After 2min, the precipitate was collected, washed with water, dried and analyzed using SEM-EDS. The EDS analysis confirmed that the precipitate was pure Cu.

Reference Example 9

[0074] The procedure in Reference Example 2 was repeated. The electrolyte consisted of 20 g/L of $AgNO_3$ and 30 g/L of HNO_3. $CuSO_4$ was added into the electrolyte as an impurity to obtain a 20% metal ion impurity level. The electrolyte and the pulse sequence was held as in Reference Example 1 and the experiment was carried out for 3h. The precipitate was removed from the solution by filtration, dried and analyzed using SEM-EDS. The EDS-analysis confirmed that the precipitate was pure Ag.

Reference Example 10

[0075] An aqueous electrolyte solution containing 20g/L Ag (as nitrate) and 40g/L of KNO3 was prepared. The pulse cycle was as follows: E_a= 2.5V, t_a= 3 ms, E_c= -1.0V, t_c = 1ms. The precipitate formed was removed from the solution by filtration, dried and analyzed using SEM-EDS. The EDS-analysis confirmed that the precipitate was pure Ag.

[0076] References:

Patent Literature:

[0077] US Published Patent Application No. 2012/0093680).

Non Patent Literature:

[0078]

G. Staikov, Electrocrystallisation in Nanotechnology, Wiley-VCH, Verlag GMBH & Co KGaA, Weinheim, 2007.

Hatter et al., J. Phy. Chem. 100 (1996) 19525.

Alfantazi et al., J. Mater. Sci. Letter, 15 (1996) 1361.

Isse et al., Electrochem. Commun. 8 (2006).

Liu et al., Electrochim. Acta 47 (2001) 671-677).

Ueda et al., Electrochim. Acta 48 (2002) 377-386.

R. M. Wightman, D. O. Wipf, "Voltammetry at Ultramicro-electrodes" in: A. J. Bard (Ed), Electroanalytical Chemistry, Vol. 15, Marcel Dekker, NY, 1988.

Moriguchi, J. Chem. Soc. Jpn., 55 (1934) 749-750.

Aqil et al., Ultrason Sonochem. 15 (2008) 1055-1061.

Puippe and Leaman (Ed.), Theory and Practice of Pulse Plating, American Electroplaters and Surface Finishers Society, Orlando, Florida, 1986.

Penner et al., J. Phys. Chem. B 106 (2002) 3339-3353.

Liu et al., J. Phys.Chem. B 104 (2000) 9131-9139.

Ueda et al., Electrochim. Acta 48 (2002) 377-386.

Sandmann et al., J. Electroanal. Chem. 491 (2000) 78-86

Komsiyska et al., Electrochim. Acta 54 (2008) 168-172.

Feng et al. 2012.

Mukherjee et al., Nanoletters 10 (2001) 515.

Soudi et al., J. Colloid. Interface Sci. 275 (2004) 177.

Chen, et al., Toxicol Letter 176 (2008) 1

Yamauchi et al., Chem. Phys. Chem. 10 (2009) 2566.

Hostetler et al., Langmuir 14 (1998) 17.

Sardar et al., Langmuir 25 (2009) 13840.

Magdass et al., NIP 25 and Digital Fabrication, Tech Program 2009 611-613.

Grouchko et al., J. Mater. Chem. 19 (2009) 3057-3062.

Schmid et al., Angew Chem. Int. Ed. 30 (1991) 874.

Joshima et al., Langmuir 1994, 104574.

Sinfelt, J. Catal. 29 (1973) 308).

Rioux et al., Topics in Catalysis 39 (2006) 167-174.

Chen et al., Chemical Reviews, 110 (2010), No. 6, 3767-3804.

Seo et al., J. Am Chem. Soc. 128 (2006), No. 46, 14863-14870.

Tao et al., Angewandte Chemie Int. Edn., 45 (2006), No. 28, 4597-4601.

Hoefelmeyer et al., Nanoletters 5 (2005), No. 3, 435-438.

Park et al., Proceedings of the Combustion Institute 31 (2007) 2643-2652.
Zettsu et al., Angewandte Chemie International Edition 118 (2006), No. 46, 7988-7992.

Claims

1. A method of extracting transition metal or semi-metal nanoparticles from electrolytic solutions containing metal ions through an electrochemical process on an electrode, wherein the electrolytic solution undergoes potentiostatic pulse electrolysis in the presence of a first electrode and a second electrode, and the electrochemical nucleation takes a place at the first electrode, wherein the electrodes are spaced apart at a first distance in order to produce particles having a first size and then the electrodes are shifted so as to be spaced apart at a second distance in order to produce particles having a second size, second size being greater than the first size when the second distance is smaller than the first distance and the metal particles are extracted from the electrolytic solution, the method further comprises performing pulse electrodeposition in a solution comprising of a nanoparticle precursor placed in an ultrasonic bath to form a metal powder or precipitate at the bottom of the electrochemical cell during the potentiostatic cycles, wherein the method further comprises annealing the filtered precipitate to form the nanoparticles, wherein the nanoparticles are less than D_{100} 100nm, determined by SEM.

2. The method of claim 1, wherein the metals are extracted from the electrolytic solution as a powder or nanopowder, said nanopowder comprises at least one of the metals silver, gold and tin.

3. The method of claim 1 or 2, wherein the first electrode is an array and contains a plurality of micrometer or sub-micrometer sized electrodes.

4. The method of any of the preceding claims, wherein only one type of the metals is extracted from the electrolytic solution selectively, or the extracted metal is an alloy.

5. The method of any of the preceding claims, wherein the number of electrical pulses or pulse cycles is less than 450.

6. The method of any of the preceding claims, wherein the electrolytic process comprises an ultrasonic or megasonic transducer.

7. The method of any of the preceding claims, wherein the first electrode is a cathode and the second is an anode.

8. The method of any of the preceding claims, wherein the first electrode is a diodeand is configured to pass the current once activated by a light.

9. The method of any of the preceding claims, wherein the potentiostatic pulse changes current direction.

10. The method of any of the preceding claims, wherein the pulse in the anodic potential is for a period (t_a) of 0- 0.1 s, and the pulse in the cathodic potential is for a period (t_c) of 0-0.1 s

11. The method according to any of the preceding claims, wherein the extracted metal nucleates does not adhere on the cathode and returns back to the plating solution as free particles or nanoparticles.

12. The method according to any of the preceding claims, comprising producing Ag or Sn nanopowders from industrial electrolytes through electrochemical deposition of Ag on the cathode, comprising an electrolytic solution of Ag ions of a concentration of 5 g/L - 80 g/L, based on the weight of the corresponding Ag salt, or an electrolytic solution of Sn ions of a concentration of 1.19 g/L - 45 g/L based on the weight of the corresponding Sn salt.

13. The method according to claims 1-12 , wherein the electrolytic solution comprisies a first salt having a) a cation selected from transition metal and semi-metal ions, and b) an anion selected from NO_3^-, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}, ClO_4^-, $(COO)_2^{2-}$ and ions of a halogen group element, and a second salt having a) a cation selected from alkali metal, such as Na or K and alkaline earth metal ions, and b) an anion selected from NO_3^-, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}, ClO_4^-, $(COO)_2^{2-}$ or a halogen group.

14. The method according to claim 13, wherein the first salt comprises Sn, or the first salt comprises a metal selected from group 10 or group 11 of the periodic table.

Patentansprüche

1. Verfahren zum Extrahieren von Übergangsmetall- oder Halbmetall-Nanopartikeln aus elektrolytischen Lösungen, die Metallionen enthalten, durch ein elektrochemisches Verfahren an einer Elektrode, wobei die elektrolytische Lösung in Anwesenheit einer ersten Elektrode und einer zweiten Elektrode einer potentiostatischen Impulselektrolyse unterzogen wird, und die elektrochemische Keimbildung an der ersten Elektrode stattfindet, wobei die Elektroden in einem ersten Abstand voneinander beabstandet sind, um Partikel mit einer ersten Größe zu erzeugen, und dann die Elektroden so verschoben werden, dass

sie in einem zweiten Abstand voneinander beabstandet sind, um Partikel mit einer zweiten Größe zu erzeugen, wobei die zweite Größe größer als die erste Größe ist, wenn der zweite Abstand kleiner als der erste Abstand ist, und die Metallpartikel aus der elektrolytischen Lösung extrahiert werden, wobei das Verfahren weiter die Durchführung einer Pulselektroabscheidung in einer Lösung umfasst, die einen Nanopartikel-Vorläufer umfasst, der in ein Ultraschallbad gegeben wird, um ein Metallpulver oder einen Niederschlag am Boden der elektrochemischen Zelle während der potentiostatischen Zyklen zu bilden, wobei das Verfahren weiter das Tempern des gefilterten Niederschlags umfasst, um die Nanopartikel zu bilden, wobei die Nanopartikel kleiner als D_{100} 100nm sind, bestimmt durch SEM.

2. Verfahren nach Anspruch 1, wobei die Metalle aus der elektrolytischen Lösung als Pulver oder Nanopulver extrahiert werden, wobei das Nanopulver mindestens eines der Metalle Silber, Gold und Zinn umfasst.

3. Verfahren nach Anspruch 1 oder 2, wobei die erste Elektrode ein Array ist und eine Vielzahl von Elektroden in Mikrometer- oder Submikrometergröße enthält.

4. Verfahren nach einem der vorstehenden Ansprüche, wobei nur eine Art der Metalle selektiv aus der elektrolytischen Lösung extrahiert wird oder das extrahierte Metall eine Legierung ist.

5. Verfahren nach einem der vorstehenden Ansprüche, wobei die Anzahl der elektrischen Impulse oder Impulszyklen weniger als 450 beträgt.

6. Verfahren nach einem der vorstehenden Ansprüche, wobei der elektrolytische Prozess einen Ultraschall- oder Megaschall-Wandler umfasst.

7. Verfahren nach einem der vorstehenden Ansprüche, wobei die erste Elektrode eine Kathode und die zweite eine Anode ist.

8. Verfahren nach einem der vorstehenden Ansprüche, wobei die erste Elektrode eine Diode ist und so konfiguriert ist, dass sie den Strom durchlässt, sobald sie durch ein Licht aktiviert wird.

9. Verfahren nach einem der vorstehenden Ansprüche, wobei der potentiostatische Impuls die Stromrichtung ändert.

10. Verfahren nach einem der vorstehenden Ansprüche, wobei der Impuls im anodischen Potential für eine Periode (t_a) von 0-0,1 s und der Impuls im kathodischen Potential für eine Periode (t_c) von 0-0,1 s erfolgt.

11. Verfahren nach einem der vorstehenden Ansprüche, wobei die extrahierten Metallkeime nicht an der Kathode haften und als freie Partikel oder Nanopartikel in die Plattierungslösung zurückkehren.

12. Verfahren nach einem der vorstehenden Ansprüche, umfassend die Herstellung von Ag- oder Sn-Nanopulvern aus industriellen Elektrolyten durch elektrochemische Abscheidung von Ag auf der Kathode, umfassend eine elektrolytische Lösung von Ag-Ionen mit einer Konzentration von 5 g/L - 80 g/L, basierend auf dem Gewicht des entsprechenden Ag-Salzes, oder eine elektrolytische Lösung von Sn-Ionen mit einer Konzentration von 1,19 g/L - 45 g/L, basierend auf dem Gewicht des entsprechenden Sn-Salzes.

13. Verfahren nach Anspruch 1-12, wobei die elektrolytische Lösung ein erstes Salz umfasst mit a) einem Kation, ausgewählt aus Übergangsmetall- und Halbmetallionen, und b) einem Anion, ausgewählt aus NO_3^-, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}, ClO_4^-, $(COO)_2^{2-}$ und Ionen eines Elements der Halogengruppe, und ein zweites Salz mit a) einem Kation, ausgewählt aus Alkalimetall-, wie Na- oder K- und Erdalkalimetallionen, und b) einem Anion, ausgewählt aus NO_3^-, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}, ClO_4^-, $(COO)_2^{2-}$ oder einer Halogengruppe.

14. Verfahren nach Anspruch 13, wobei das erste Salz Sn umfasst oder das erste Salz ein Metall umfasst, das aus der Gruppe 10 oder der Gruppe 11 des Periodensystems ausgewählt ist.

Revendications

1. Procédé d'extraction de nanoparticules métalliques ou semi-métalliques de transition à partir de solutions électrolytiques contenant des ions métalliques par l'intermédiaire d'un processus électrochimique sur une électrode, dans lequel la solution électrolytique subit une électrolyse potentiostatique pulsée en présence d'une première électrode et d'une seconde électrode, et la nucléation électrochimique intervient à la première électrode, dans lequel les électrodes sont espacées d'une première distance afin de produire des particules présentant une première taille puis les électrodes sont déplacées de manière à être espacées d'une seconde distance afin de produire des particules présentant une seconde taille, la seconde taille étant supérieure à la première taille lorsque la seconde distance est inférieure à la première distance et les particules métalliques sont extraites de la solution électrolytique, le procédé comprenant en outre la réalisation d'un dépôt électroly-

tique pulsé dans une solution comprenant un précurseur de nanoparticules placé dans un bain ultrasonique pour former une poudre métallique ou un précipité métallique au fond de la cellule électrochimique au cours des cycles potentiostatiques, dans lequel le procédé comprend en outre le recuit du précipité filtré pour former les nanoparticules, dans lequel les nanoparticules sont moins que D_{100} 100 nm, comme déterminé par SEM.

2. Procédé selon la revendication 1, dans lequel les métaux sont extraits de la solution électrolytique sous forme d'une poudre ou d'une nanopoudre, ladite nanopoudre comprenant au moins l'un parmi les métaux argent, or et étain.

3. Procédé selon la revendication 1 ou 2, dans lequel la première électrode est un réseau et contient une pluralité d'électrodes micrométriques ou sub-micrométriques.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel un seul type de métaux est extrait sélectivement de la solution électrolytique, ou le métal extrait est un alliage.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le nombre d'impulsions électriques ou de cycles d'impulsions est inférieur à 450.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le processus électrolytique comprend un transducteur ultrasonique ou mégasonique.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la première électrode est une cathode et la seconde électrode est une anode.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel la première électrode est une diode et est configurée pour laisser passer le courant une fois qu'elle est activée par une lumière.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'impulsion potentiostatique change une direction de courant.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'impulsion dans le potentiel anodique est pendant une période (t_a) de 0-0,1 s, et l'impulsion dans le potentiel cathodique est pendant une période (t_c) de 0-0,1 s

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le métal extrait nucléé n'adhère pas à la cathode et retourne dans la solution de placage sous forme de particules libres ou de nanoparticules.

12. Procédé selon l'une quelconque des revendications précédentes, comprenant la production de nanopoudres Ag ou Sn à partir d'électrolytes industriels par l'intermédiaire d'un dépôt électrochimique d'Ag sur la cathode, comprenant une solution électrolytique d'ions Ag d'une concentration de 5 g/l - 80 g/l, sur la base du poids du sel Ag correspondant, ou une solution électrolytique d'ions Sn d'une concentration de 1,19 g/l - 45 g/l sur la base du poids du sel Sn correspondant.

13. Procédé selon les revendications 1-12, dans lequel la solution électrolytique comprend un premier sel ayant a) un cation sélectionné parmi des ions métalliques et semi-métalliques de transition, et b) un anion sélectionné parmi NO_3^-, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}, ClO_4^-, $(COO)_2^{2-}$ et des ions d'un élément de groupe halogène, et un second sel ayant a) un cation sélectionné parmi des ions métalliques alcalins, comme Na ou K, et des ions métalliques alcalino-terreux, et b) un anion sélectionné parmi NO_3^-, SO_4^{2-}, PO_4^{3-}, BO_3^{3-}, ClO_4^-, $(COO)_2^{2-}$ ou un groupe halogène.

14. Procédé selon la revendication 13, dans lequel le premier sel comprend Sn, ou le premier sel comprend un métal sélectionné parmi le groupe 10 ou le groupe 11 de la table périodique.

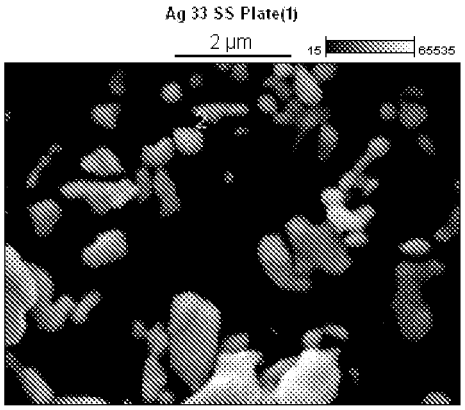


Fig. 1A

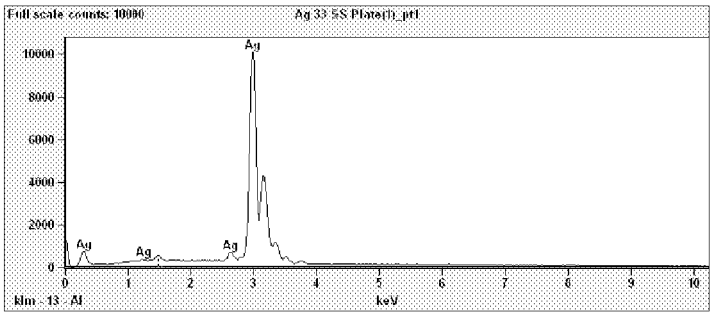


Fig. 1B

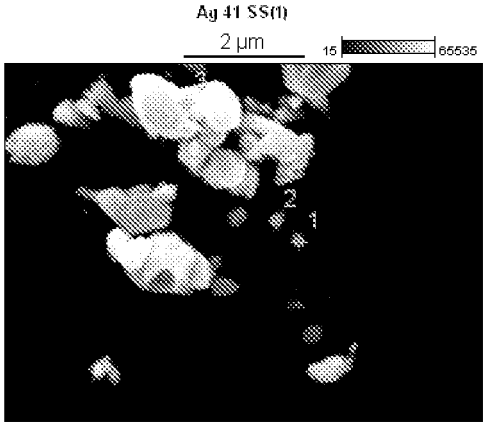


Fig. 2A

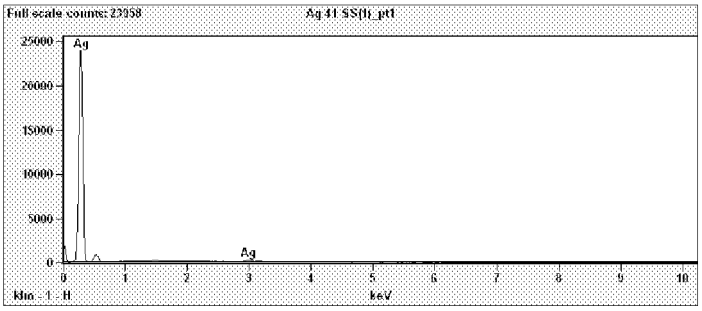


Fig. 2B

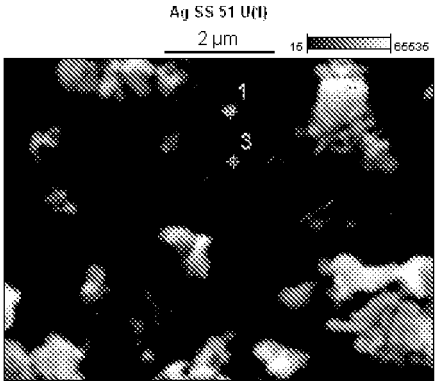


Fig. 3A

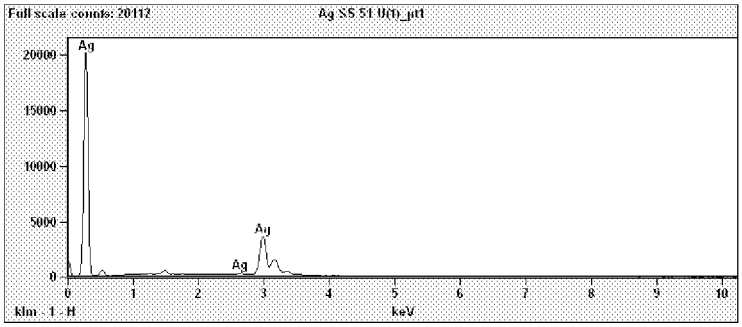
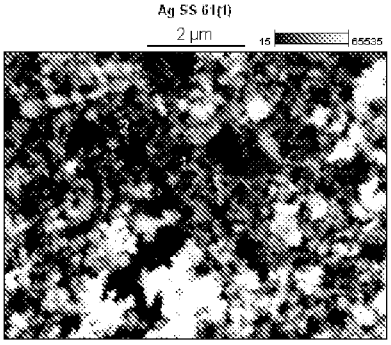


Fig. 3B



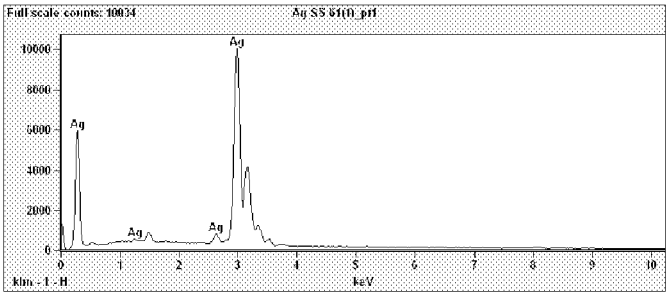
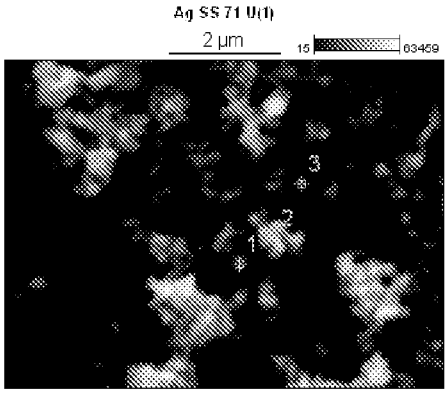


Fig. 4A Fig. 4B



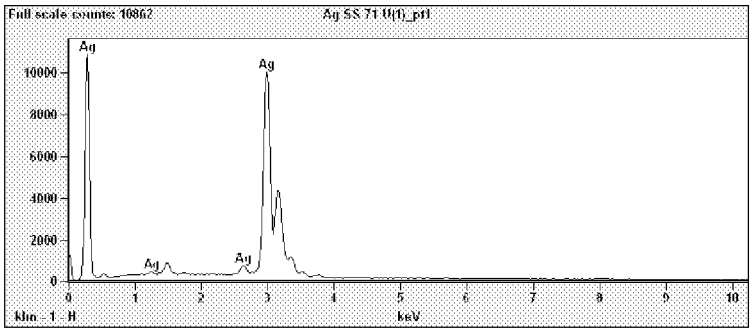
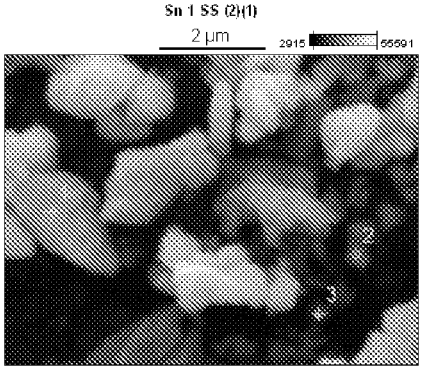


Fig. 5A Fig. 5B



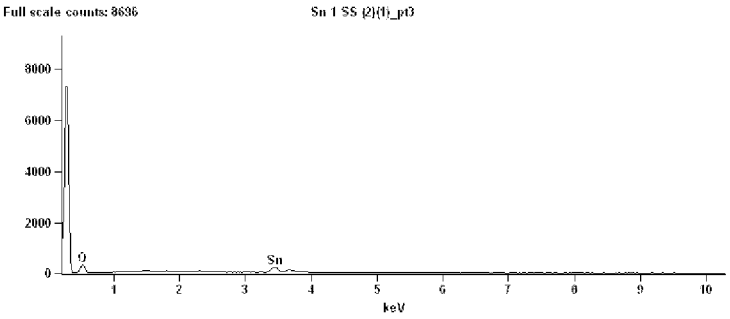


Fig. 6A Fig. 6B

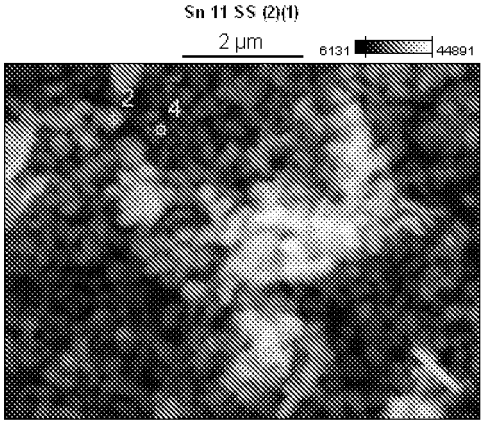


Fig. 7A

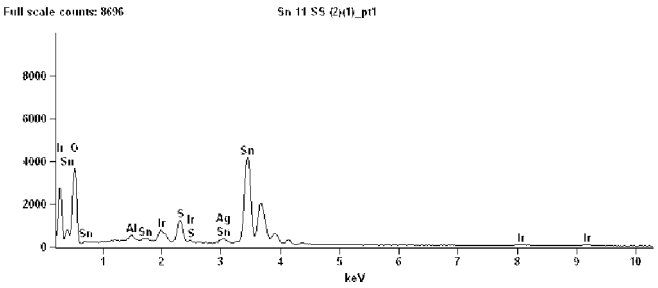


Fig. 7B

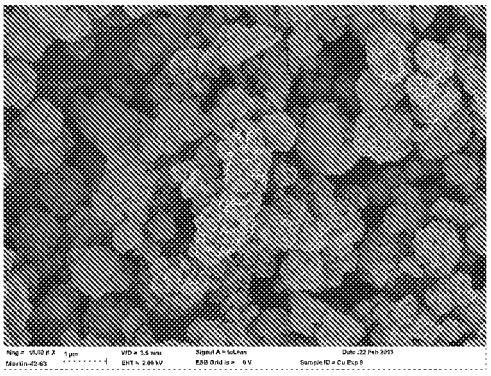


Fig. 8

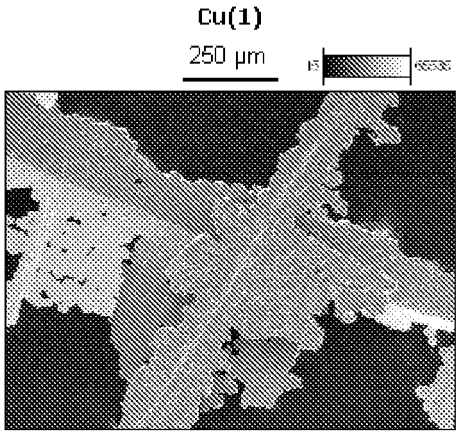


Fig. 9A

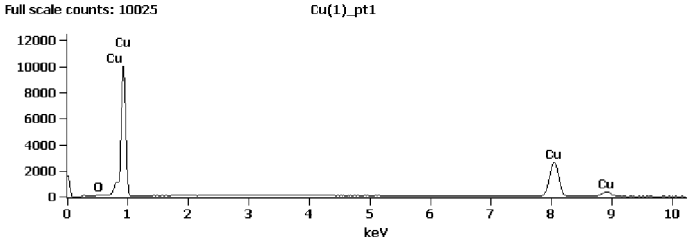


Fig. 9B

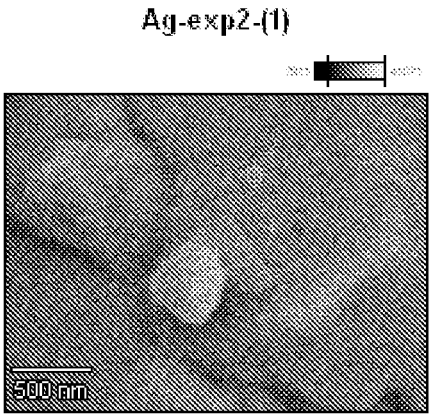


Fig. 10A

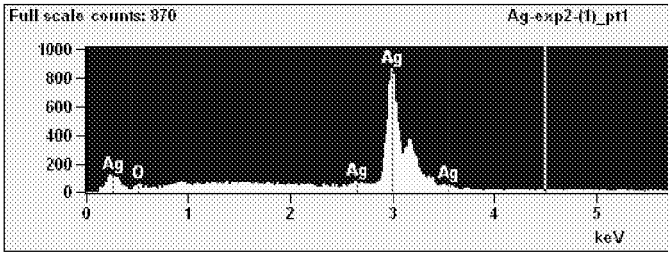


Fig. 10B

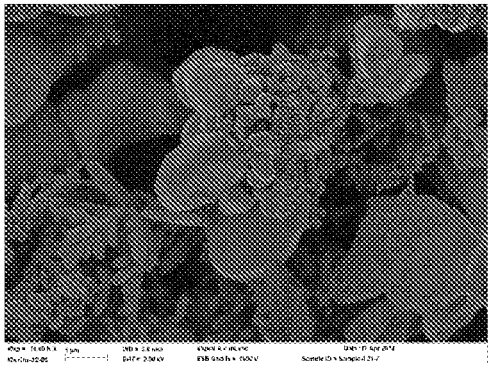


Fig. 11

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 20120093680 A **[0004] [0077]**
- US 2012093680 A1 **[0005]**
- JP 2007327117 A **[0006]**

Non-patent literature cited in the description

- **G. STAIKOV.** Electrocrystallisation in Nanotechnology. Wiley-VCH Verlag GmbH & Co KGaA, 2007 **[0002]**
- **HATTER et al.** *J. Phy. Chem.,* 1996, vol. 100, 19525 **[0002] [0078]**
- **ALFANTAZI et al.** *J. Mater. Sci. Letter,* 1996, vol. 15, 1361 **[0002] [0078]**
- **ISSE et al.** *Electrochem. Commun.,* 2006, vol. 8 **[0002] [0078]**
- **LIU et al.** *Electrochim. Acta,* 2001, vol. 47, 671-677 **[0002] [0078]**
- **UEDA et al.** *Electrochim. Acta,* 2002, vol. 48, 377-386 **[0002] [0004] [0005] [0078]**
- Voltammetry at Ultramicro-electrodes. **R. M. WIGHTMAN ; D. O. WIPF.** Electroanalytical Chemistry. Marcel Dekker, 1988, vol. 15 **[0003]**
- **MORIGUCHI, J.** *Chem. Soc. Jpn,* 1934, vol. 55, 749-750 **[0003]**
- **AQIL et al.** *Ultrason Sonochem,* 2008, vol. 15, 1055-1061 **[0003] [0078]**
- Theory and Practice of Pulse Plating. American Electroplaters and Surface Finishers Society, 1986 **[0004] [0078]**
- **PENNER et al.** *J. Phys. Chem. B,* 2002, vol. 106, 3339-3353 **[0004] [0078]**
- **LIU et al.** *J. Phys.Chem. B,* 2000, vol. 104, 9131-9139 **[0004] [0078]**
- **SANDMANN et al.** *J. Electroanal. Chem.,* 2000, vol. 491, 78-86 **[0004] [0078]**
- **KOMSIYSKA L et al.** *Electrochim. Acta,* 2008, vol. 54, 168-172 **[0005]**
- **MUKHERJEE et al.** *Nonoletters,* 2001, vol. 10, 515 **[0007]**
- **SOUDI et al.** *J. Colloid. Interface Sci.,* 2004, vol. 275, 177 **[0007] [0078]**
- **CHEN et al.** *Toxicol Letter,* 2008, vol. 176, 1 **[0007] [0078]**
- **YAMAUCHI et al.** *Chem. Phys. Chem.,* 2009, vol. 10, 2566 **[0007] [0078]**
- **HOSTETLER et al.** *Langmuir,* 1998, vol. 14, 17 **[0007] [0078]**
- **SARDAR et al.** *Langmuir,* 2009, vol. 25, 13840 **[0007] [0078]**
- **MAGDASS et al.** *NIP 25 and Digital Fabrication, Tech Program,* 2009, 611-613 **[0007] [0078]**
- **GROUCHKO et al.** *J. Mater. Chem.,* 2009, vol. 19, 3057-3062 **[0007] [0078]**
- **SCHMID et al.** *Angew Chem. Int. Ed.,* 1991, vol. 30, 874 **[0008] [0078]**
- **JOSHIMA et al.** *Langmuir,* 1994, 104574 **[0008] [0078]**
- **SINFELT.** *J. Catal.,* 1973, vol. 29, 308 **[0008] [0078]**
- **G. STAIKOV.** Electrocrystallisation in Nanotechnology. Wiley-VCH, Verlag GMBH & Co KGaA, 2007 **[0078]**
- oltammetry at Ultramicro-electrodes. **R. M. WIGHTMAN ; D. O. WIPF.** Electroanalytical Chemistry. Marcel Dekker, 1988, vol. 15 **[0078]**
- **MORIGUCHI.** *J. Chem. Soc. Jpn.,* 1934, vol. 55, 749-750 **[0078]**
- **KOMSIYSKA et al.** *Electrochim. Acta,* 2008, vol. 54, 168-172 **[0078]**
- **MUKHERJEE et al.** *Nanoletters,* 2001, vol. 10, 515 **[0078]**
- **RIOUX et al.** *Topics in Catalysis,* 2006, vol. 39, 167-174 **[0078]**
- **CHEN et al.** *Chemical Reviews,* 2010, vol. 110 (6), 3767-3804 **[0078]**
- **SEO et al.** *J. Am Chem. Soc.,* 2006, vol. 128 (46), 14863-14870 **[0078]**
- **TAO et al.** *Angewandte Chemie Int. Edn.,* 2006, vol. 45 (28), 4597-4601 **[0078]**
- **HOEFELMEYER et al.** *Nanoletters,* 2005, vol. 5 (3), 435-438 **[0078]**
- **PARK et al.** *Proceedings of the Combustion Institute,* 2007, vol. 31, 2643-2652 **[0078]**
- **ZETTSU et al.** *Angewandte Chemie International Edition,* 2006, vol. 118 (46), 7988-7992 **[0078]**