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(54) **METHOD AND APPARATUS FOR PREPARING COATED PARTICLES**

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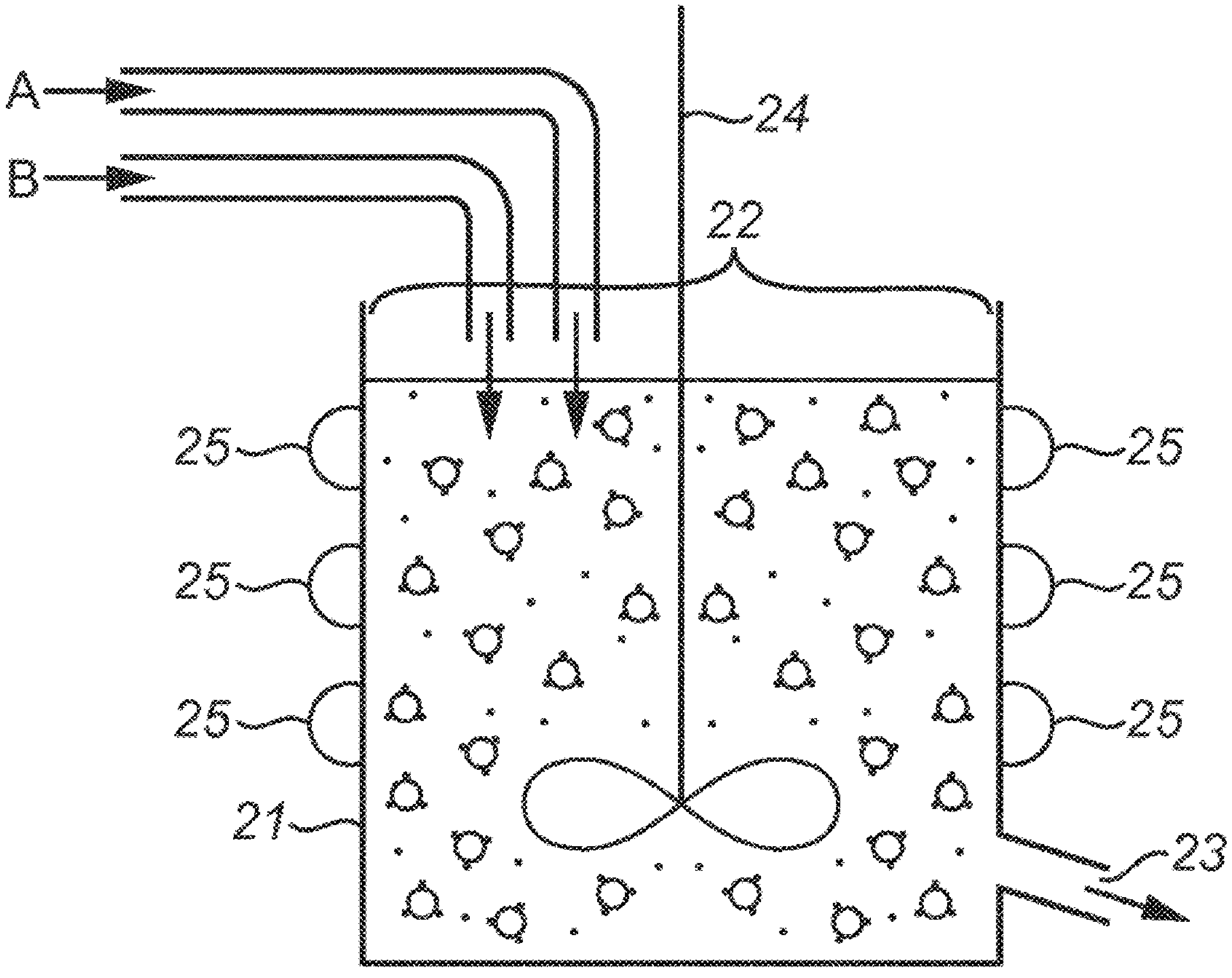
(57) **ABSTRACT**

The present invention relates to a method of forming a metal coated particle, to metal coated particles prepared according to the method and the use of these metal coated particles. The method comprising the steps of:

providing a source of base particles to be coated;

providing a source of a metal-comprising coating particles; and

feeding the base particles specified in step (a) and the source of metal comprising coating particles specified in step (b) into a continuous reactor including heat exchange means to cause contact of the base particles with the source of coating particles thereby to form the metal coated particles. The coated particles include a homogeneous coating and can be used in a variety of applications.



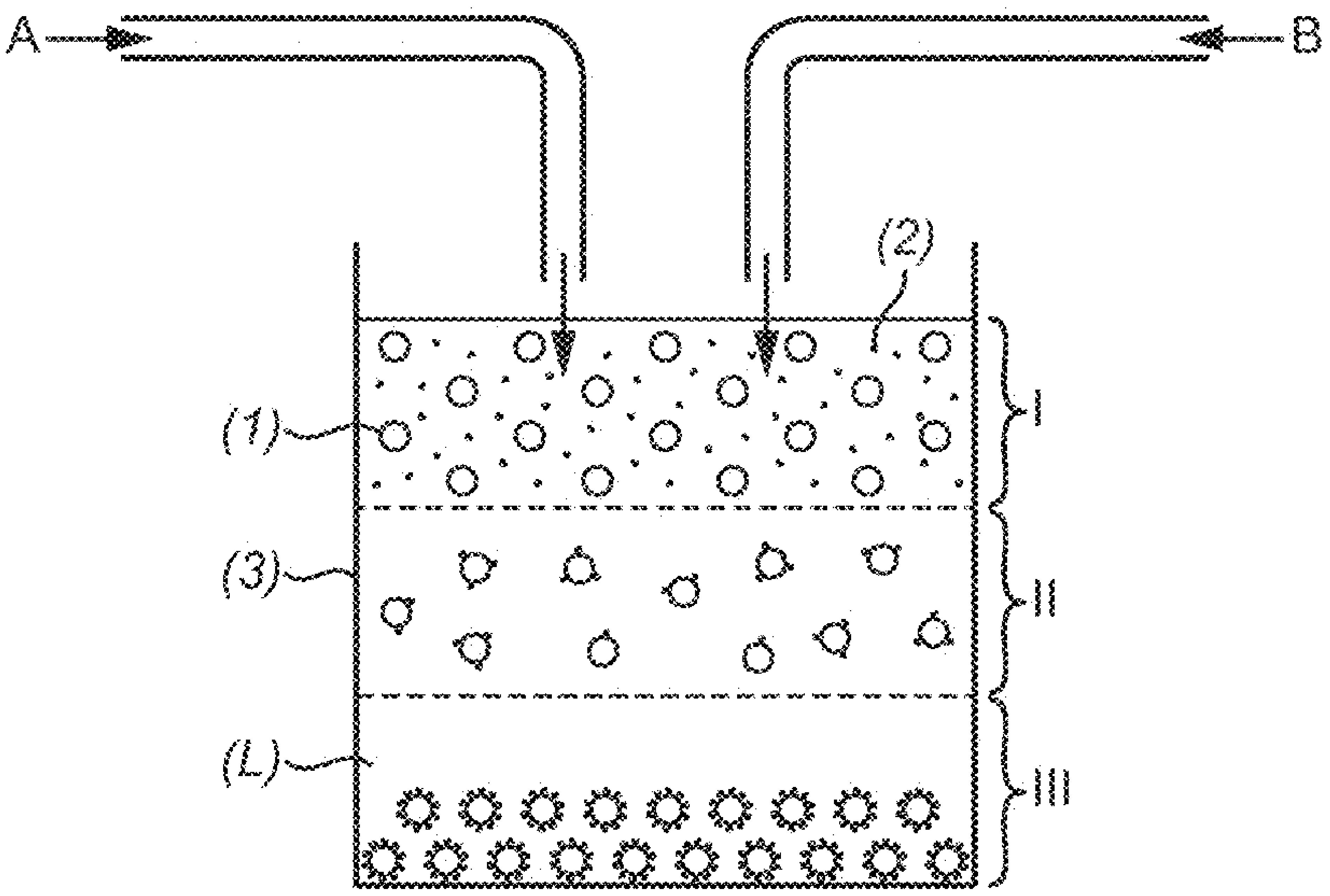


FIG. 1

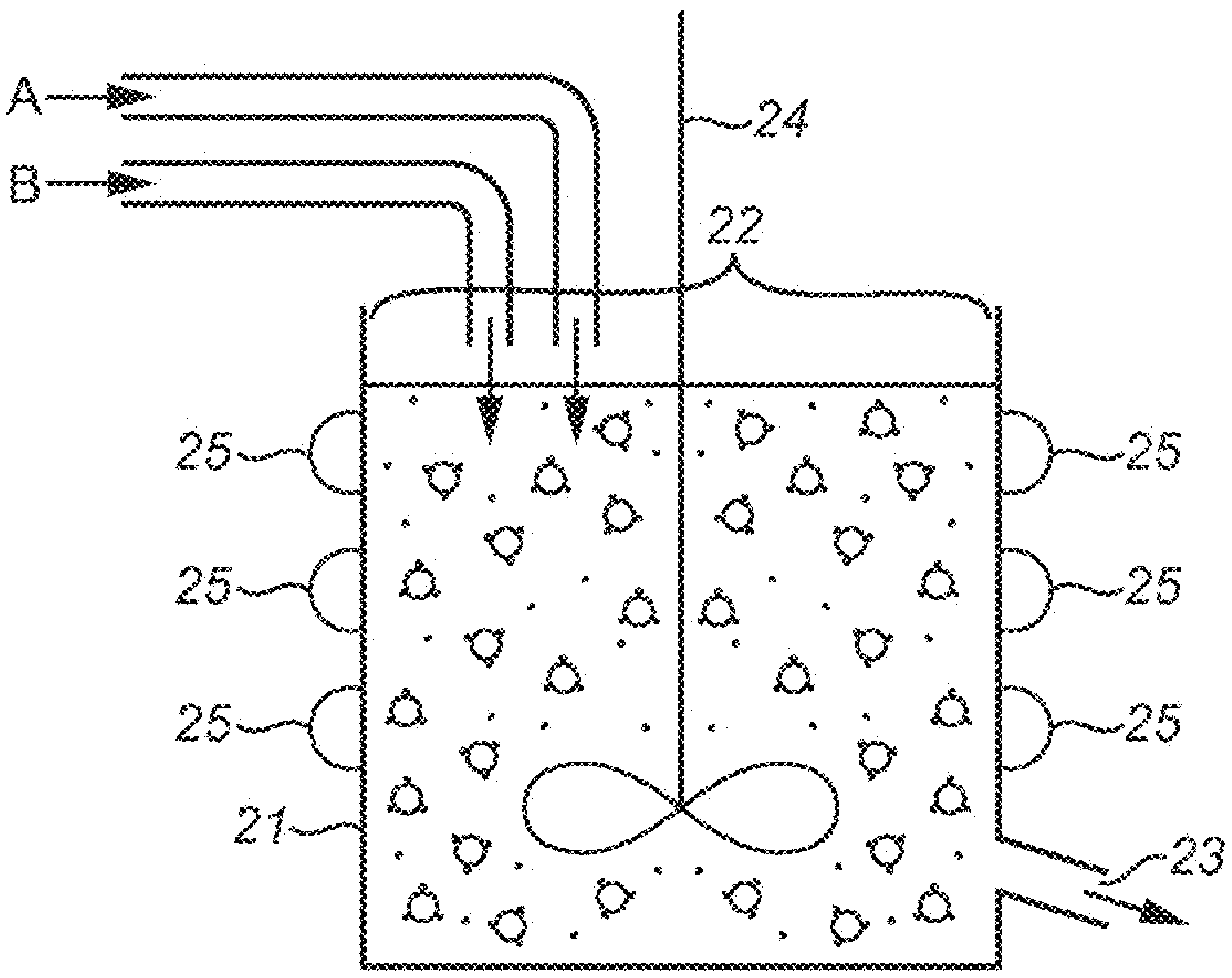


FIG. 2

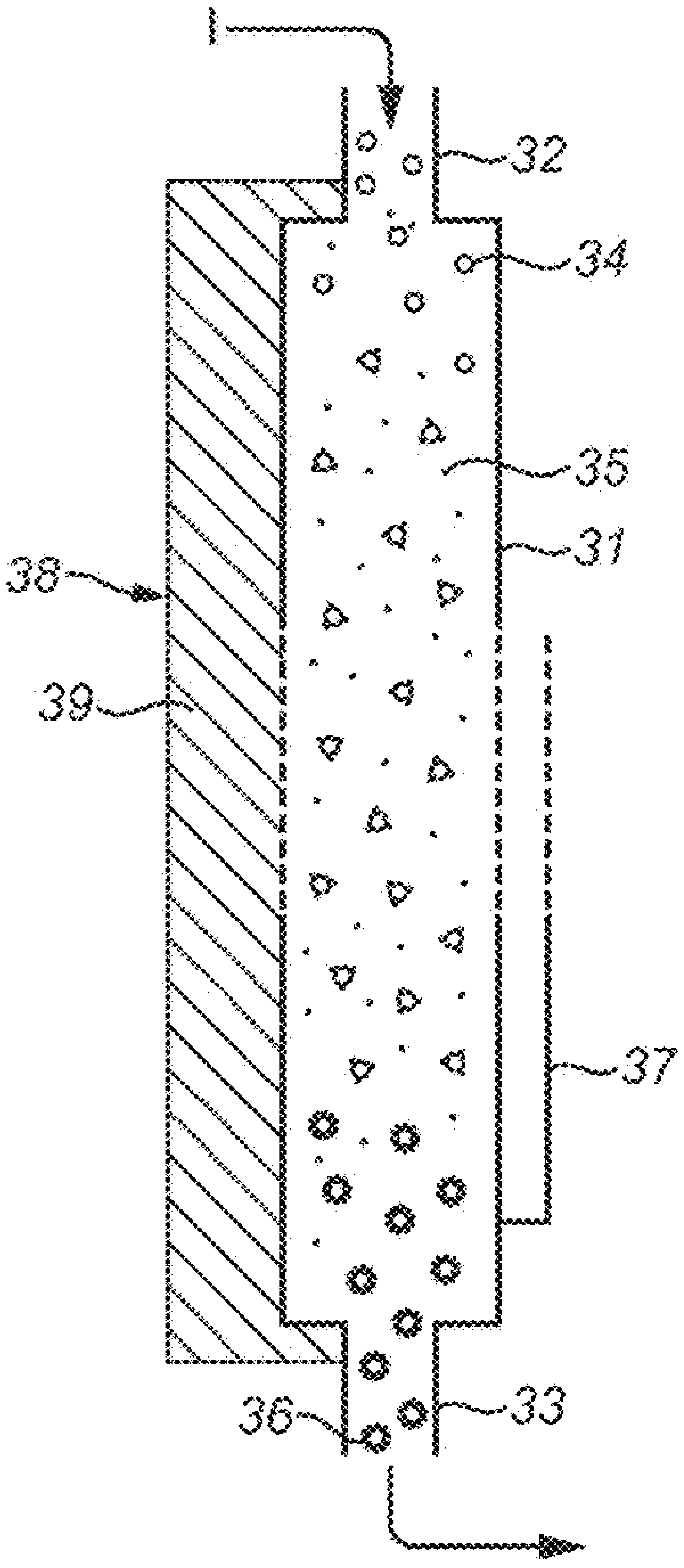


FIG. 3

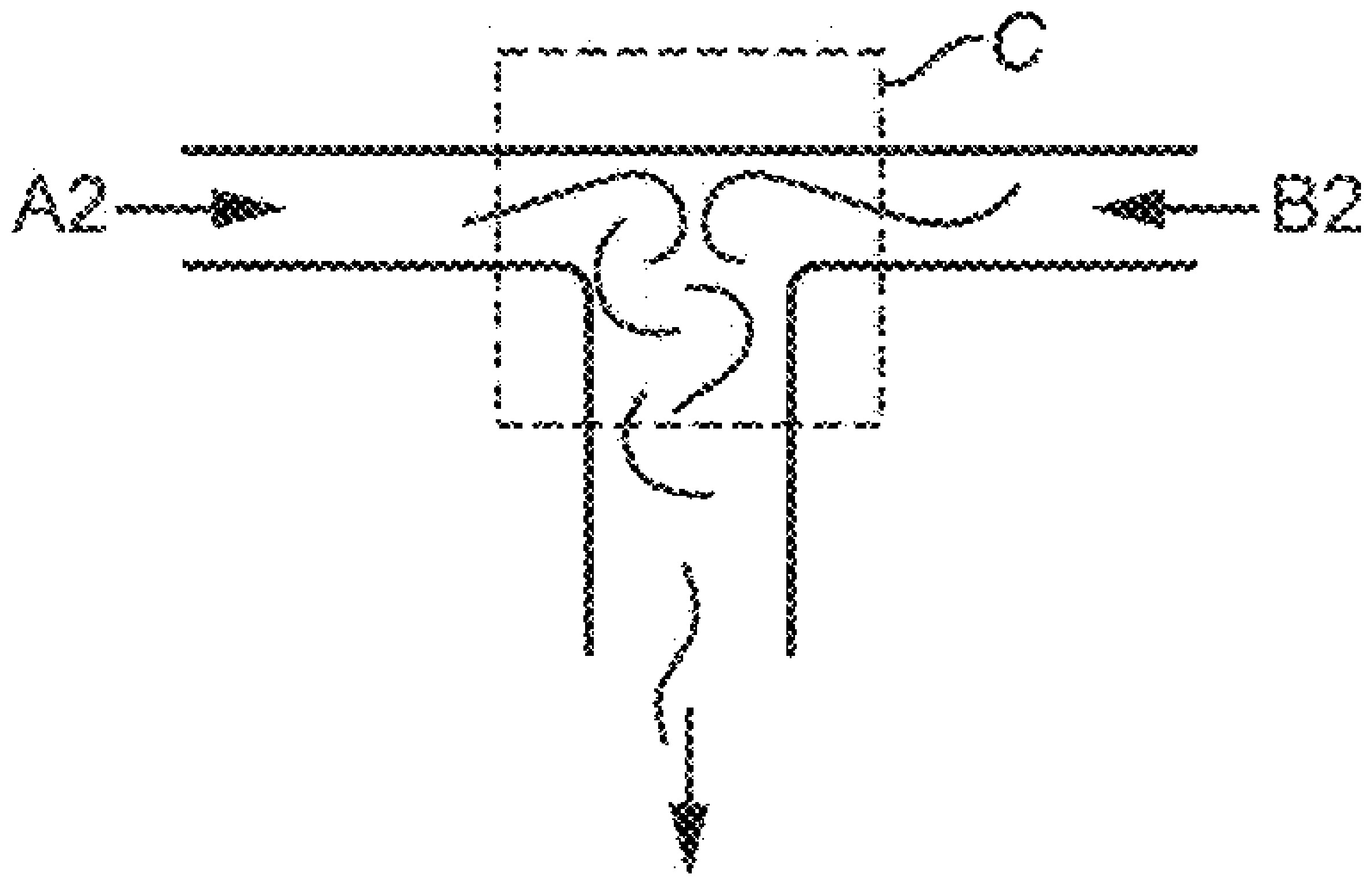


FIG. 4a

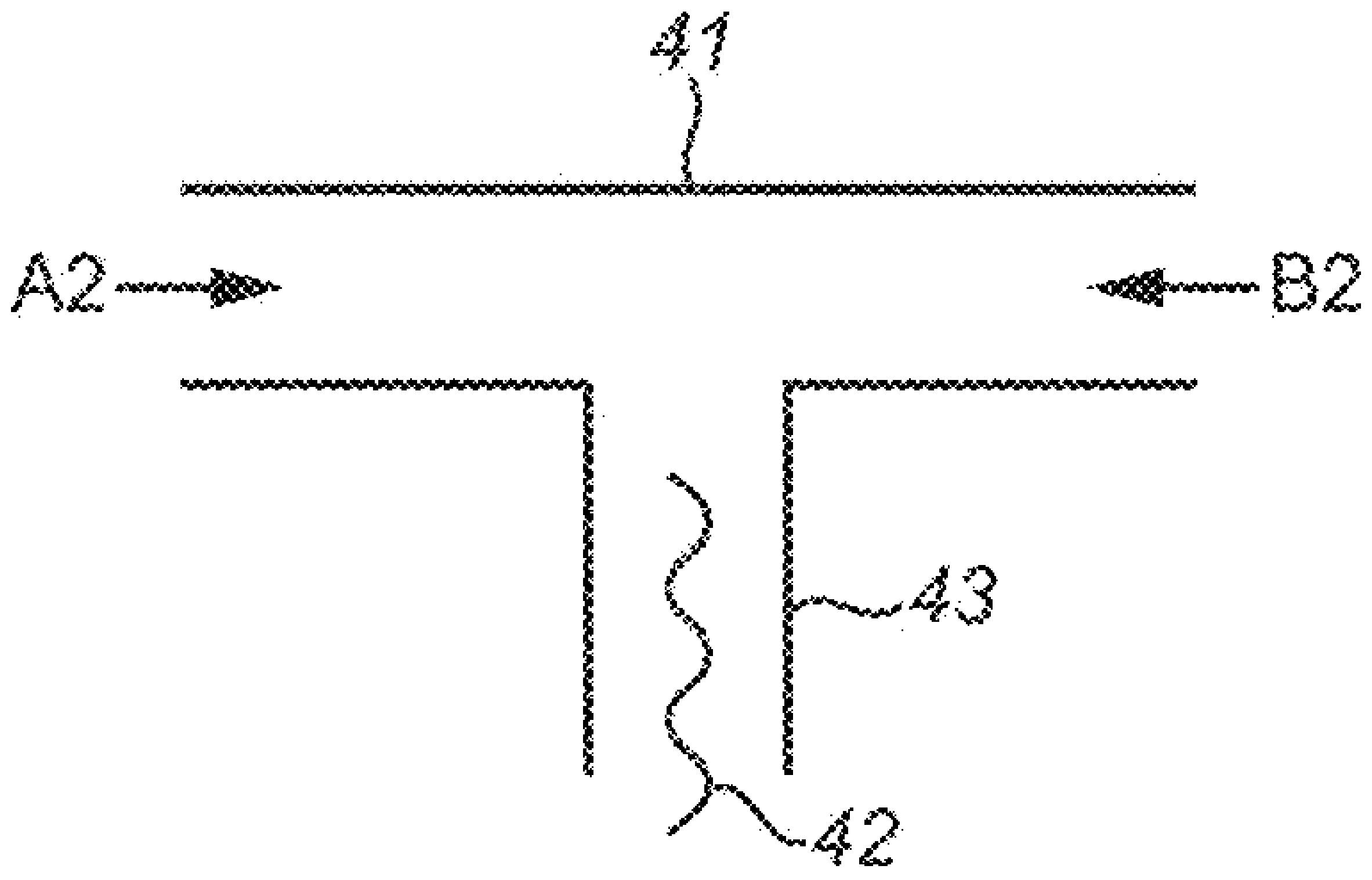


FIG. 4b

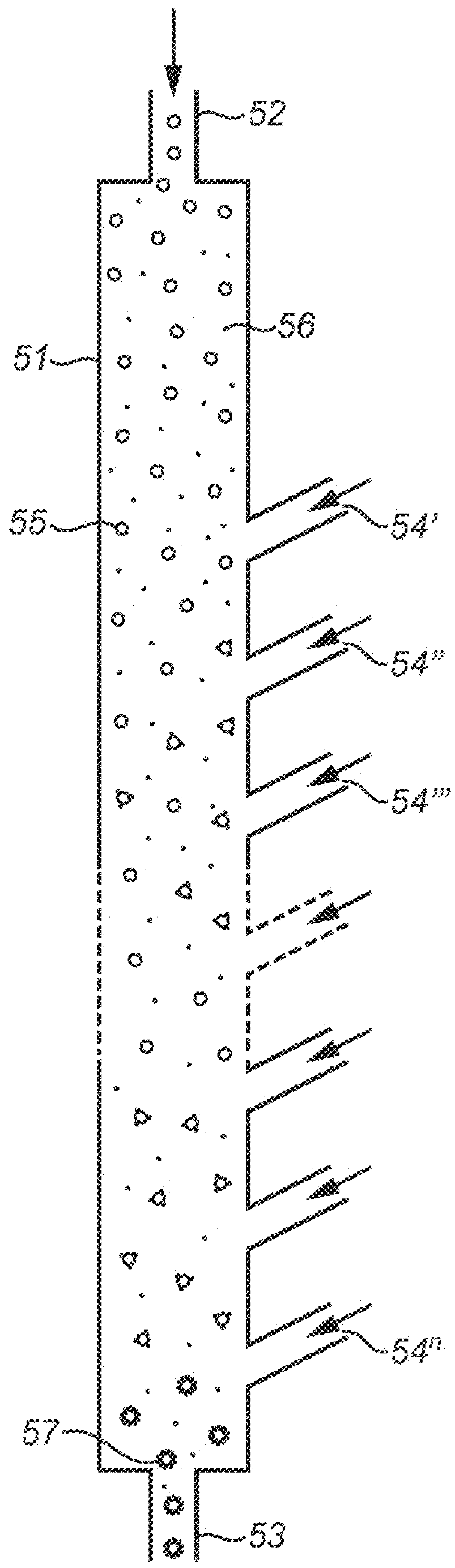


FIG. 5

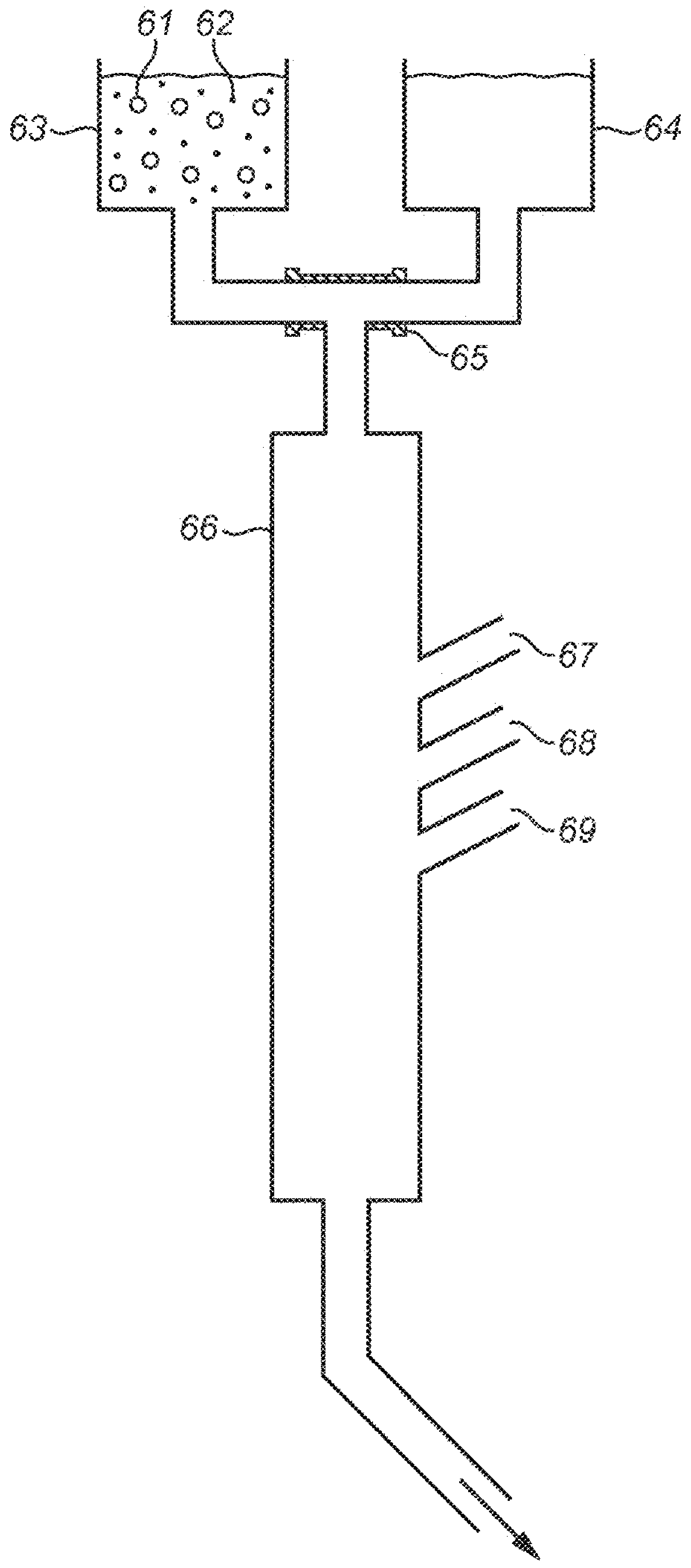


FIG. 6

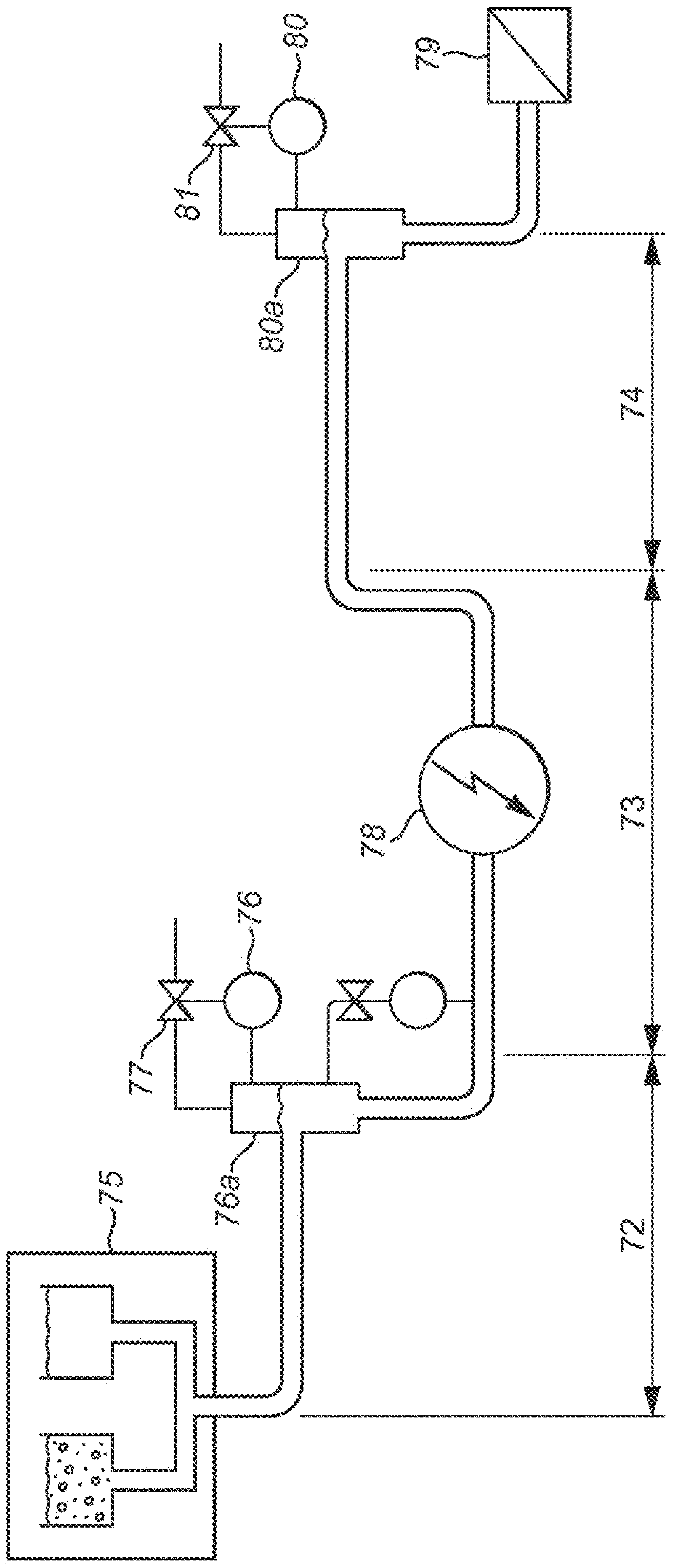


FIG. 7

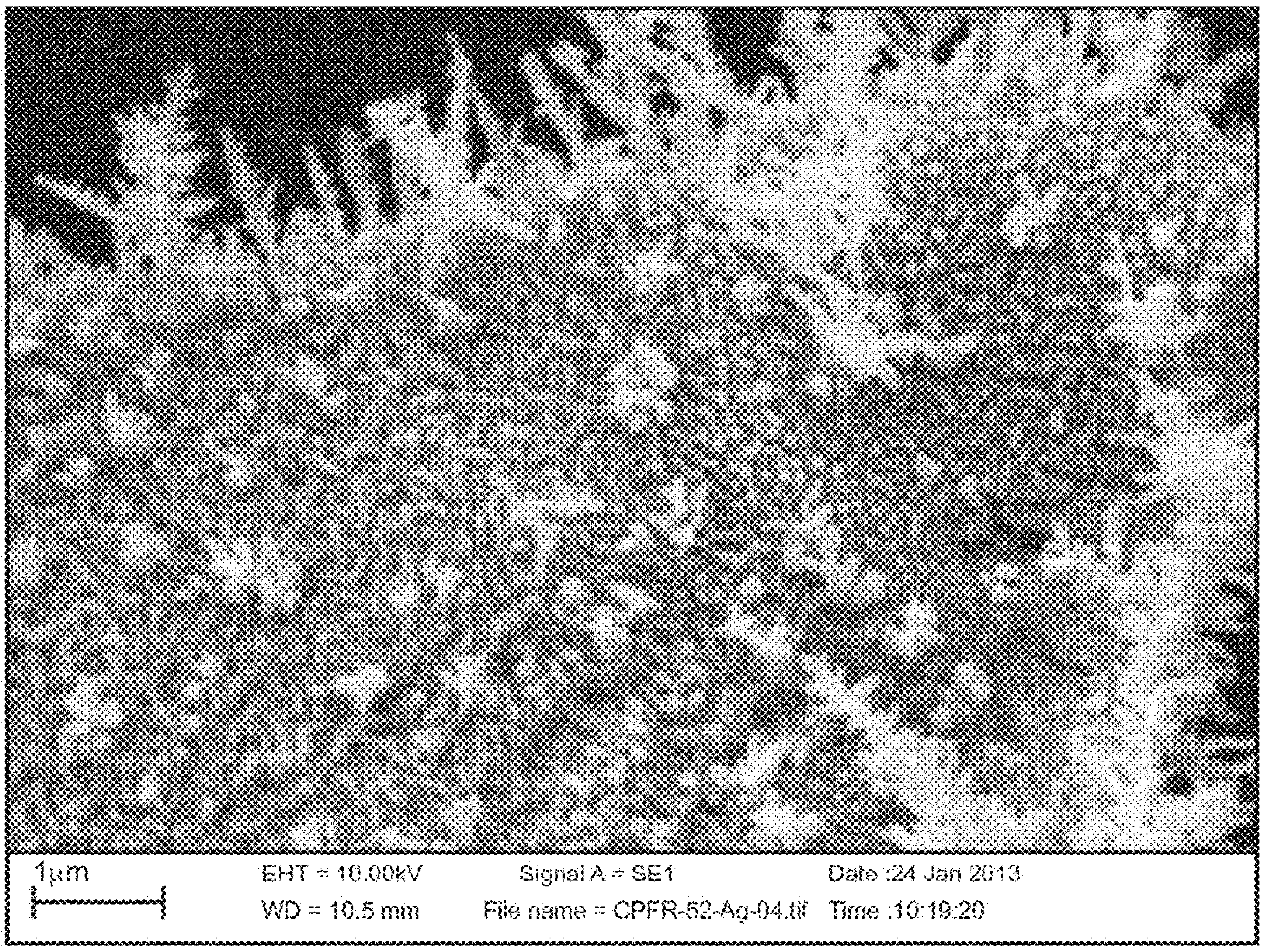
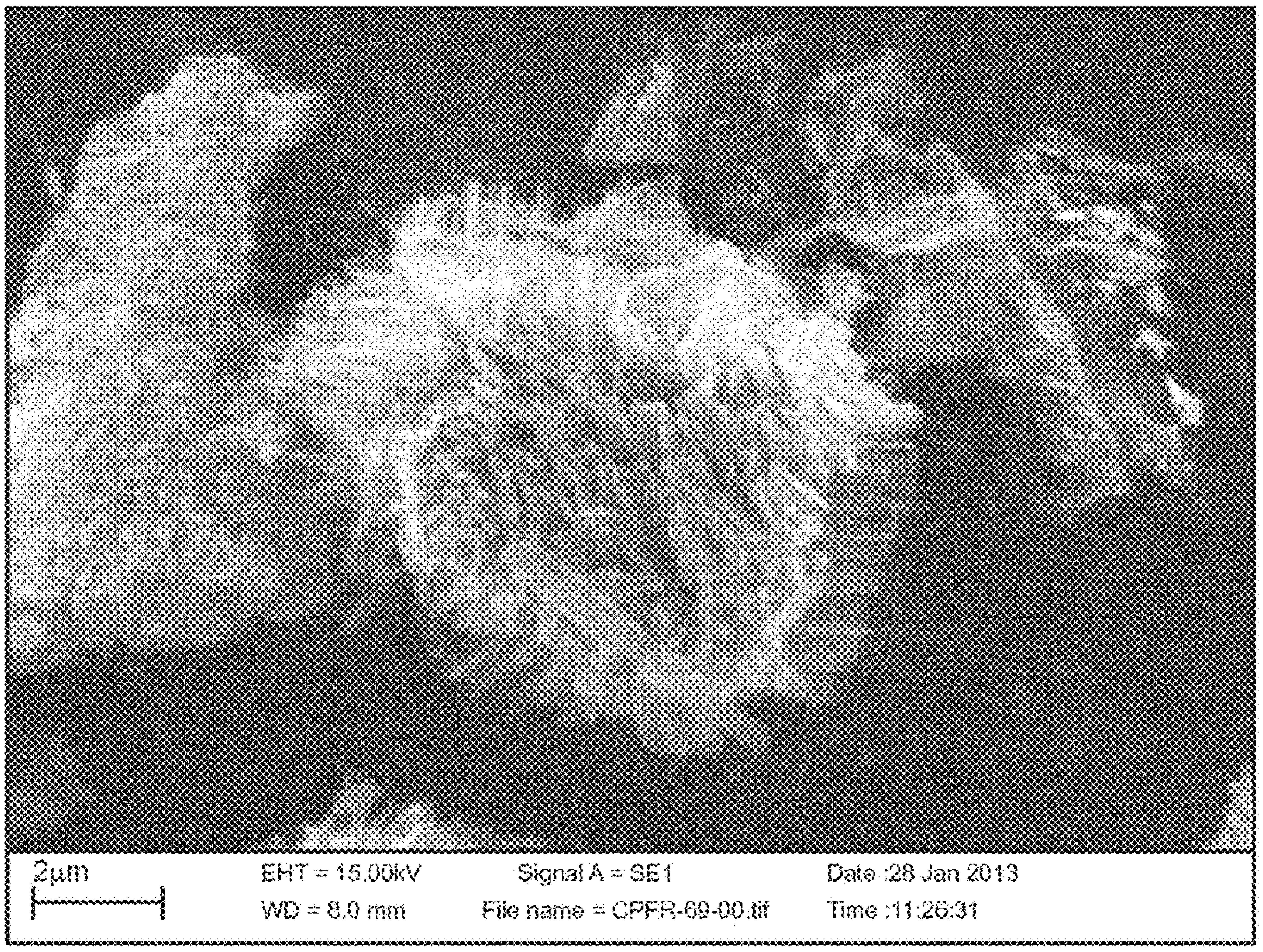

1μm
EHT = 10.00kV
WD = 10.5 mm
Signal A = SE1
File name = CPFR-52-Ag-04.tif
Date :24 Jan 2013
Time :10:19:20

FIG. 8


2µm
EHT = 15.00kV
WD = 8.0 mm
Signal A = SE1
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Date :28 Jan 2013
Time :11:26:31

FIG. 9

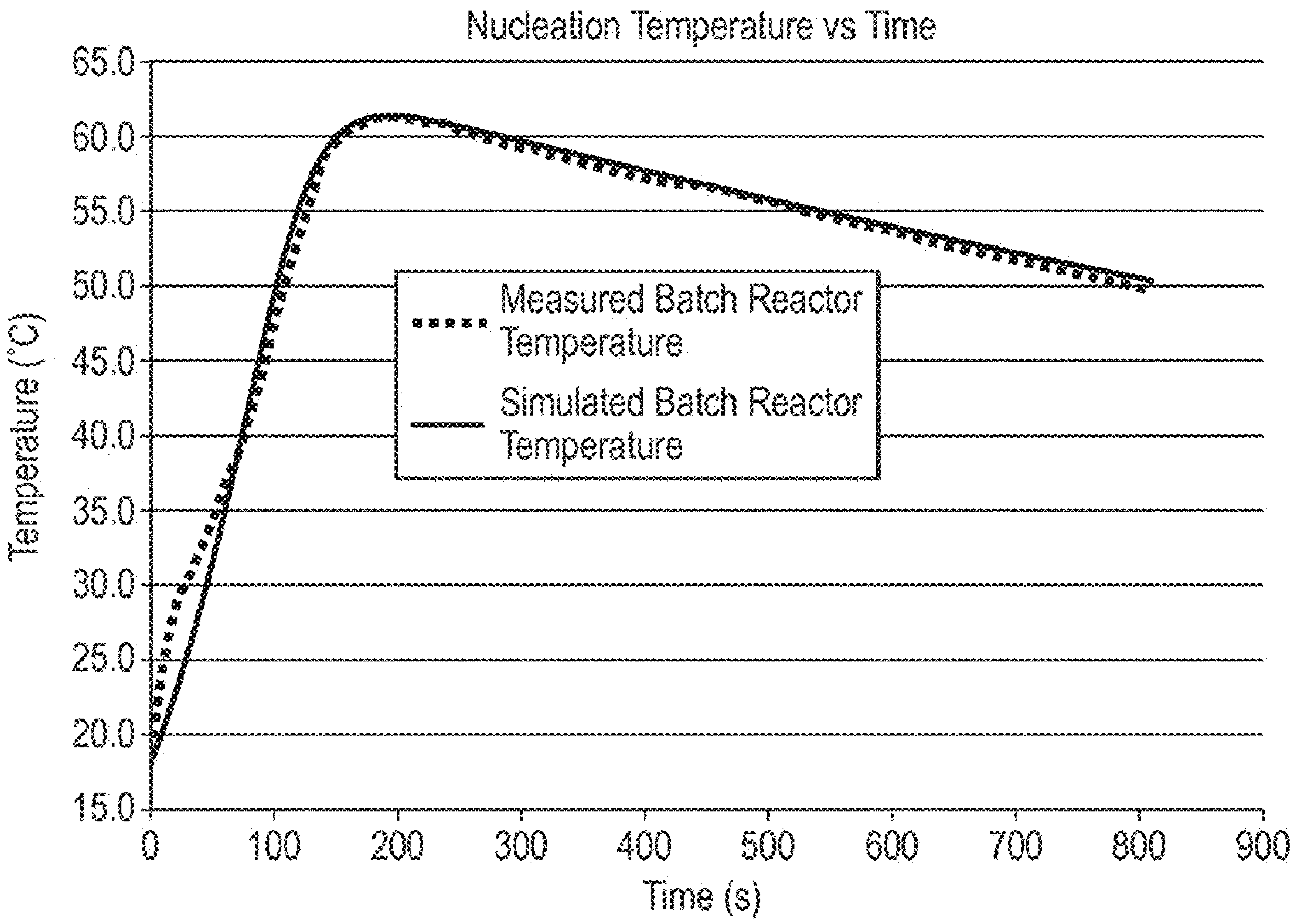
Nucleation Temperature vs Time
65.0
60.0
55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
Temperature (°C)
0
100
200
300
400
500
600
700
800
900
Time (s)
Measured Batch Reactor Temperature
Simulated Batch Reactor Temperature

FIG. 10

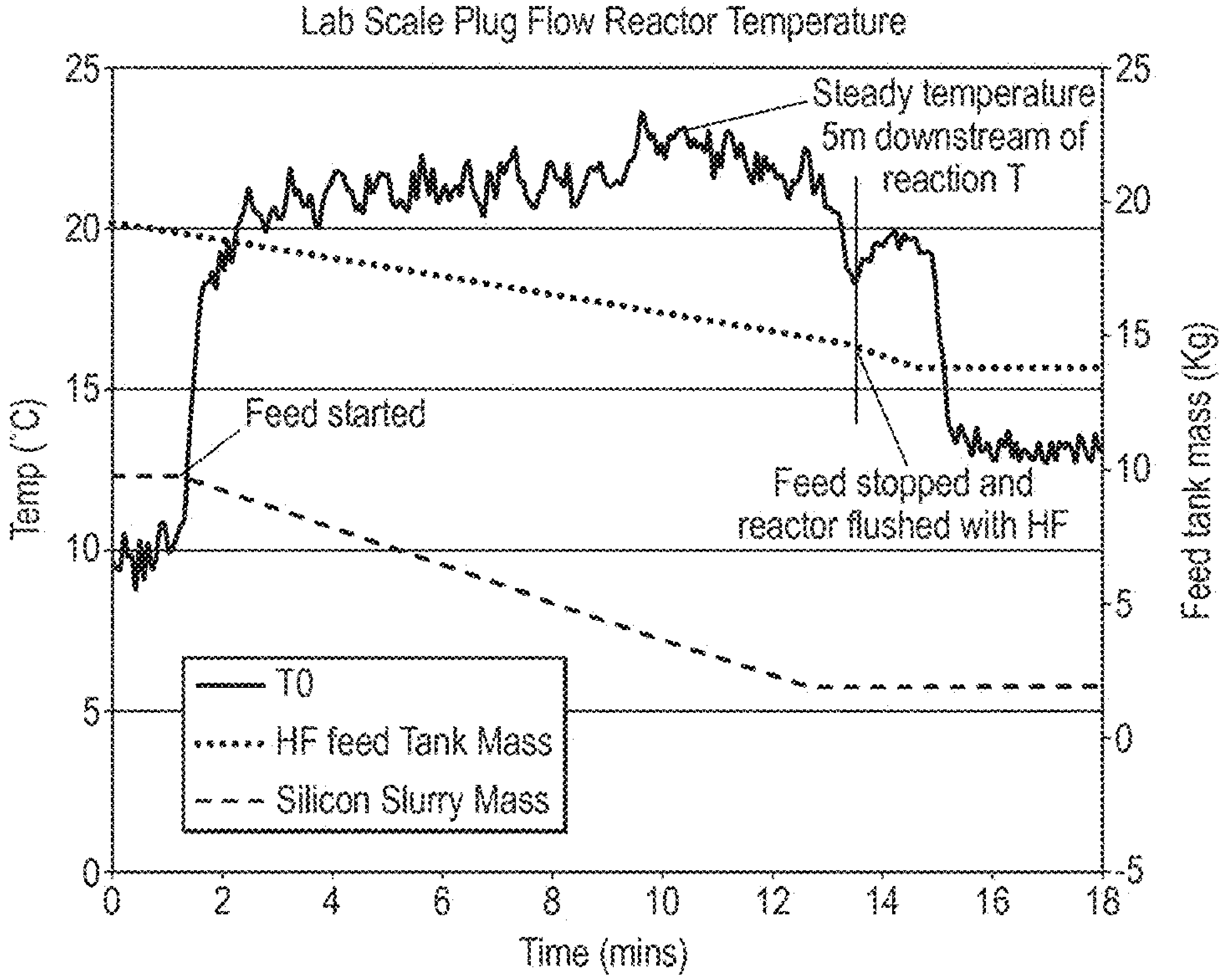
Lab Scale Plug Flow Reactor Temperature
25
20
15
10
5
0
Temp (°C)
25
20
15
10
5
0
-5
Feed tank mass (Kg)
0
2
4
6
8
10
12
14
16
18
Time (mins)
Steady temperature 5m downstream of reaction T
Feed started
Feed stopped and reactor flushed with HF
T0
HF feed Tank Mass
Silicon Slurry Mass

FIG. 11

METHOD AND APPARATUS FOR PREPARING COATED PARTICLES

FIELD OF THE INVENTION

[0001] The present invention relates to a method of forming a metal coated particle, to metal coated particles prepared according to the method and the use of these metal coated particles.

BACKGROUND OF THE INVENTION

[0002] Metal coated materials, including metal coated particles are well known to a person skilled in the art and have been used in applications such as corrosion protection, medical implants and anti-fouling systems. Metal coatings have also been used in the repair and protection of and for modifying the thermal and electrical conductivity of underlying substrates. Materials comprising either a silver or a copper coating are commonly used for anti-bacterial applications. Carbon or carbon-coated silicon nano-wires comprising a disperse coating of metal nano-particles such as platinum (Pt), ruthenium (Ru), iron (Fe), cobalt (Co), gold (Au), chromium (Cr), molybdenum (Mo), tungsten (W), manganese (Mn), technetium (Tc), rhenium (Re), osmium (Os), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd), copper (Cu), silver (Ag), zinc (Zn), tin (Sn) and aluminium (Al) have been used as electrodes in fuel cell applications (EP2378597). Coatings of silver nano-particles are known to catalyse acid etching of a metal or semi-metal surface (such as a silicon surface) to which they are applied to give an etched silicon product including pillars on its surface. Etched metal or semi-metal particles (such as silicon) are known for use in applications such as electrochemical cells, metal-ion batteries such as secondary battery applications, lithium air batteries, flow cell batteries, fuel cells, solar cells, filters, sensors, electrical and thermal capacitors, micro-fluidic devices, gas or vapour sensors, thermal or dielectric insulating devices, devices for controlling or modifying the transmission, absorption or reflectance of light or other forms of electromagnetic radiation, chromatography or wound dressings.

[0003] The metal coated materials described above can be prepared using a variety of methods that are known to a person skilled in the art and include mechanical plating, thermal spraying, electrolysis, lithographic and electroless deposition methods. Mechanical plating methods involve tumbling work-pieces with a mixture of water, a coating metal powder, media, and additives. Common coating materials are zinc, cadmium, tin, copper, and aluminium. The mechanical action alloys the coating material to the work-piece surface. The method works well if the work-piece comprises a resilient, non-frangible material. However, less resilient materials tend to fragment.

[0004] Thermal spraying techniques are used to form relatively thick coatings of up to 12 mm and involve spraying a melted or heated coating material onto a substrate (or target) surface. The coating material may be heated using electrical or thermal energy. Examples of coating materials that can be thermally sprayed include metals, alloys, ceramics, plastics and composites. High surface area forms of the coating materials are heated to a molten or semi-molten state and accelerated towards target substrates in the form of micrometre or sub-micrometre-size particles. Coatings are formed through the accumulation of particles on the surface of the target substrate. The degree of coverage and thickness of the coating can be controlled by altering the rate at which the coating substance is introduced into the spray chamber as well as the residence time of the target substrate in the chamber.

[0005] Chemical and physical vapour deposition techniques can be used to form thin layers (micron and sub-micron thickness) on a substrate. Chemical vapour deposition (CVD) can be used to deposit a volatile source of the coating material onto a target surface. CVD can be used to form transition metal coatings on a target surface using a source material comprising a volatile transition metal compound. Physical vapour deposition (PVD) can be used to deposit a coating onto a target surface from a physically generated source of that coating material. Examples of physical vapour deposition techniques include cathodic arc deposition, electron beam deposition, evaporative deposition, pulsed laser deposition and sputter deposition. CVD and PVD procedures are typically carried out batch-wise in reaction chambers evacuated to low pressure.

[0006] US2009/0311532 discloses an apparatus and method for forming surface modified silica-titania mixed oxide particles. In a first stage SiCl4 and TiCl4 vapours are burnt at a temperature of between 700 to 1000 C in an atmosphere of hydrogen and oxygen to form the mixed oxide particles. In a second stage surface modifying metal particles are deposited from a vapour phase onto the mixed oxide particles downstream of and at a temperature below that used in the region in which the mixed oxide particles are formed. A heat exchanger is used to reduce the temperature of the mixed oxide particles prior to the second stage in which the surface modifying metal particle are deposited thereon.

[0007] WO 97/30797 discloses a method and apparatus for depositing a coating of a metal, binder or sintering aid onto a Geldhart class C substrate powder. The substrate powder is suspended in a fluidized bed and the coating materials are contacted with the substrate using a CVD (Chemical Vapour Deposition) technique.

[0008] Ink-jet spraying and spin coating techniques can also be used to deposit colloidal metal particles onto a substrate surface.

[0009] Electrochemical cells can be used to plate or coat a metal onto a work-piece or substrate. A cathode comprising the substrate or work-piece is immersed in an electrolyte comprising a solution of the coating metal ions. Applying a voltage between the cathode and the anode causes ions of the coating metal to form on the surface of the cathodic work-piece or substrate. The work-piece may be provided in the form of a foil or as a fluidised bed of cathodic particles (U.S. Pat. No. 4,824,541). Foil cathodes can only be coated using a batch process. Electroplating using a fluidised bed can be either a batch or a continuous process; continuous processes tend to be less efficient as the residence time of the cathodic particle in the fluidised bed may not be long enough to adequately coat the particle and it may be necessary to feed the cathodic particles through the fluidised bed several times before a coating of adequate thickness is formed, which increases both the plating time and the expense of the technique. Although batch electrolytic processes are more efficient they tend to be more suited to smaller scale processing.

[0010] Electroless deposition is a solution-based coating method, without the need for an externally applied electric potential, which involves the reduction of a metal ion at the surface of a substrate to form a metal coated substrate. Electroless deposition of metals is s described in Lin et al, "Aqueously Dispersed Silver Nanoparticle-Decorated Boron Nitride Nanosheets for Reusable, Thermal Oxidation-Resistant Surface Enhanced Raman Spectroscopy (SERS) Devices", Applied Materials and Interfaces, 2012, 4, 1110-1117; Lv et al, "Long-Term Antimicrobial Effect of Silicon Nanowires Decorated with Silver Nanoparticles", Adv. Mater. 2010, 22, 5463-5467; Shi et al, "Easy decoration of carbon nanotubes with well dispersed gold nanoparticles and the use of the material as an electrocatalyst" Carbon 47 (2009) 1146-1151; Ma et al, Silver nanoparticles decorated, flexible SiO_2 nanofibers with long-term antibacterial effect as reusable wound cover" Colloids and Surfaces A: Physicochem. Eng. Aspects 387 (2011) 57-64 Djokic et al, Electrodeposition and Electroless Deposition of Metallic Powders: A Comparison, ECS Transactions, 33 (18) 7-31 (2011); and Yae et al, New Surface-Activation-Process for Electroless Deposition of Adhesive Metal (Ni, Cu) Films on Si Substrates, ECS Transactions, 33 (18) 33-37 (2011). The metal coating may be continuous or discontinuous or may be in the form of nucleated particles distributed over the surface of the substrate particle. Depending on the coating metal, the nucleated particle may be in the form of clusters or agglomerates of metal particles on the substrate surface. These nucleates may have dendrites formed from the same coating metal species attached to them and a plurality of such dendrites may be joined together in a network by dendritic bridges also formed by the coating metal species. The formation of dendritic bridges between agglomerates of metal particles particularly occurs when silver is used as the coating metal. For some coating metals such as copper, dendrites are not usually formed and instead the tendency is to initially form a monolayer coating of the nucleates on the base particle.

[0011] The metal coated substrates can be used to catalyse the growth of nanowires or other structures from the particle core. The nanowires or other structures may be grown from a vapour source, for example using the known vapour-liquid-solid (VLS) process. In this case the material of the grown structures will depend on the vapour source. The catalysed growth of structures such as nanowires may also be done using known solid-liquid-solid (SLS) and vapour induced SLS techniques (VI-SLS). In the VI-SLS process, nanowire growth consumes the base particle material and the grown structures comprise material from the base particle and a vapour source. The VI-SLS growth of silicon-based nanowires out of silicon particles coated with a nickel catalyst layer is described in Zhang et al. "Vapor-induced solid-liquid-solid process for silicon-based nanowire growth", J. Power Sources, 195, 2010, 1691-1697. US2011/0309306 describes the VLS growth of silicon nanowires from gold catalyst nucleates supported on alumina particles using a batch method.

[0012] The metal coated particles may also be used as a particulate biocide in coatings, adhesives, surface treatment and impregnation of other materials, textiles, shoes, medical disposables, water and air purification and in crop protection. US2012/0301553 discloses a batch method for forming a colloidal dispersion of silica particles with a silver coating for use in biocidal applications.

[0013] Alternatively the electroless deposition of silver metal onto a silicon wafer or a particulate silicon substrate to form silver coated wafers or particles is an important step in a process for etching silicon wafers or particles. The silver coating catalyses the etching reaction, which leads to the formation of wafers or particles having either a porous surface or a surface having silicon pillars extending there from. WO 2007/083152 discloses an etching method including an electroless deposition step described above. Electroless deposition is a two step process defined by equations (1) and (2) below in which silicon is exposed to a source of fluoride ions, for example HF, in a first step to generate electrons (Equation 1) that in a second step reduce silver ions to solid silver on the silicon surface (Equation 2). Other electron generating species can be used instead of fluoride ions, for example citrate and hydroxide ions.

$$\mathrm{Si}+6\mathrm{F}^{-}\rightarrow\mathrm{SiF}_6^{2}-+4e^{-} \qquad \text{(Equation 1)}$$

$$\mathrm{Ag}^{+}+e^{-}\rightarrow\mathrm{Ag(s)} \qquad \text{(Equation 2)}$$

[0014] Thereafter, the deposited silver catalyses the etching of the silicon particle.

[0015] It will be appreciated from equation 1 above that electroless deposition of silver onto a silicon substrate is accompanied by dissolution of $SiFe^{2-}$ species from the silicon oxide surface. The rate of the deposition reaction is generally high; it generally reaches a maximum by around 100 seconds and is complete within 5 minutes. Further the deposition reaction is characterised by a significant release of heat and a large increase in temperature, typically an increase of 40° C. or more. Maximum temperatures reached using batch processing methods are typically greater than 50° C., for example greater than 80° C.

[0016] Where the silver is provided in the form of AgNO3, the overall deposition reaction is defined by equation 3 below:

$$2\mathrm{Si}+2\mathrm{AgNO}_3\rightarrow 12\mathrm{HF}\rightarrow\mathrm{H}_2\mathrm{SiFe}_6+2\mathrm{Ag}+\mathrm{NO}+\mathrm{NO}_2+\mathrm{H}_2+3\mathrm{H}_2\mathrm{O} \qquad \text{(Equation 3)}$$

[0017] Hydrogen gas formation is also observed due to dissolution by HF of the oxide layer at the silicon surface. Nitrogen oxide and nitrous oxide formation may also be observed. Although this combination of energy and gas release can be readily managed on an experimental scale, as reaction volumes are scaled up it becomes increasingly difficult to efficiently remove heat generated within the reaction chamber as a result of the energy released on deposition of the metal on the silicon surface.

[0018] It is believed that a known coating process used to deposit metal particles onto a base particle surface in a liquid media involves a three stage process as illustrated by FIG. **1**. In a first stage (I) base particles (**1**) from a source (A) and a source of metal coating particles (**2**) from a source (B) are introduced into reaction chamber (**3**). The particles (**1**) of source (A) may be in the form of a slurry suspended in a carrier liquid (L). Alternatively the base particles (**1**) at source A may be in the form of a powder. The base particles may be in the form of substantially spherical or cuboidal particles or elongate elements. The metal coating particles (**2**) from source (B) may be in the form of a slurry suspended in a carrier liquid or may be a solution containing ions of the coating metal species in a solvent. Where the source A comprises a powder of base particles, a carrier liquid L may be provided separately.

[0019] As illustrated in FIG. **1**, on introduction to the reaction chamber, the base particles (**1**) and source of metal coating particles (**2**) start to diffuse through the volume of liquid in the reaction chamber in a first stage (I) thereby bringing particles (**1**) into close proximity with particles (**2**). In a second stage (II), the base particles (**1**) and source of metal coating particles (**2**) contact each other such that particles (**2**) begin to form on the surface of the base particle (**1**) to form a part coated base particle. During stage (III) a plurality of metal coating particles (**2**) form a coating over the surface of the base particle (**1**) to form a coated base particle as illustrated in FIG. **1**. Where the coating metal is silver, above a certain nucleate density, the coating is characterised by a plurality of particulate clusters or aggregates joined into a network via dendritic bridges extending there between. The particles formed in stage (III) tend to be more dense than the carrier liquid and sink to the bottom of the reaction chamber; the batch process according to the prior art is therefore stopped when all the particles (**1**) have precipitated at the bottom of the chamber. Prior art coating methods are generally carried out using a batch processing technique since these provide a quick and simple way to isolate and recover the metal coated particulate product.

[0020] The time taken for formation of coated metal particles is relatively short, generally less than five minutes. Formation of the metal coat according to solution based prior art methods requires a large excess of the source of coating metal particles (**2**) due to differences in the mass transport properties between the base particles and the source of coating particles as well as the relatively fast rate at which the coating metal species precipitates on the surface of the base particle. The relatively large base particles tend to diffuse through the bulk liquid of the reaction mixture more slowly than the metal nano-particles or metal ions used as a source of coating metal particles; an excess of the source of metal coating particles is therefore needed to ensure a relatively uniform coverage of all the base particles. Further, the precipitation from the liquid of metal on the surface of the base particles may be accompanied by the release of a large amount of heat; although this may be easy to manage on an experimental scale, this might pose a significant problem when the process is scaled up.

[0021] As indicated above, metal coated substrate particles can be used in a variety of applications as disclosed herein above. Silver or copper coated particles of metalloids such as silicon, tin, germanium, gallium and lead can be etched using known metal-assisted metal etching (MACE) processes in liquid media to give structured particles comprising pores or pillars extending from a particle core; the particulate silver coating catalyses the etching of the underlying metalloid region on which it sits. The particulate metal coatings can also be used to catalyse the growth of metal, semi-metal and non-metallic nano-wires, including carbon fibres and nanotubes, from the surface on the particle surface. Structured particles of the type described herein can be used in the manufacture of lithium ion batteries. The metal coated particles may also be used as biocides, for example as disinfectants or as anti-fouling agents in paints and other industrial coatings. The metal coatings can also be used as catalysts in fuel cells and other energy applications or for the chemical conversion of feedstock materials or by-products in the industrial manufacture of chemicals. When the metal coatings are used as a catalyst for the growth of nanowires from the base particles, then the grown nanowires may themselves be used as catalysts or biocides for the applications described herein.

[0022] The formation and use of silver coated silicon materials is disclosed in U.S. Pat. No. 7,402,829, Geng et al, J. Electronic Materials (40), 12, 2011; PCT/GB2012/052483; PCT/GB2012/053241 and PCT/GB2013/050742.

[0023] U.S. Pat. No. 7,402,829 discloses the fabrication in liquid media of structured silicon materials for use in lithium ion batteries by etching silicon substrate including an electrolessly deposited silver coating; the etched structures include pillars extending there from. WO 2009/010758 discloses how silicon particles including an electrolessly deposited silver coat can be etched to make silicon material for use in lithium ion batteries. The resulting etched particles contain pillars on their surface.

[0024] The electroless deposition techniques disclosed in U.S. Pat. No. 7,402,829 and WO 2009/010758 require a large excess of silver in solution to form a silver coated silicon substrate including sufficient nucleation sites to catalyse etching of the silicon. The silver coat is characterised by a network of silver nucleates having silver dendrite bridges between the nucleation sites. The nucleates may be dusters or agglomerates of particles joined together by dendritic bridges.

[0025] Alternative solution based electroless deposition approaches that can be used for forming metal-coated silicon particles include the use of the silver mirror reaction as outlined by Geng et al, "Metal-Assisted Chemical Etching Using Tollen's Reagent to Deposit Silver Nano-particle Catalysts for Fabrication of Quasi-ordered Silicon Micro/nanostructures" Journal of Electronic Materials, Vol. 40, No. 12, 2011.

[0026] The formation of copper coated silicon particles is disclosed in PCT/GB2012/052483.

[0027] PCT/GB 2012/053241 discloses how the principles of negative template etching can be used in combination with electroless deposition techniques to form silicon particles including a layered metal coating.

[0028] PCT/GB2013/050742 discloses a method of depositing particulate metal onto the surface of a silicon particle using a solution of a coating metal ion substantially free of HF.

[0029] The methods disclosed in many of the prior art documents referred to above involve a relatively large number of steps, which make the process both time consuming and inefficient. Control of the reaction is also a problem due to the large amount of heat released as a result of electroless deposition of metal onto the surface of the base particle. There is therefore a need for an efficient system and a method for forming metal-coated particles, which can address the problems specified herein above. The present invention addresses these problems.

SUMMARY OF THE INVENTION

[0030] A first aspect of the invention provides a method for fabricating a plurality of metal coated particles in a liquid medium, the method comprising the steps of:

- **[0031]** (a) providing in a carrier liquid a first reagent comprising a source of base particles to be coated;
- **[0032]** (b) providing a second reagent comprising a source of metal-comprising coating particles;
- **[0033]** (c) providing a continuous reactor including a reaction chamber and a heat exchange means; and
- **[0034]** (d) forming a liquid reaction mixture by feeding the base particles specified in step (a) and the source of metal comprising coating particles specified in step (b)

into a continuous reactor including heat exchange means thereby to contact the base particles with the source of coating-metal particles thereby to form the metal coated particles.

[0035] By the use of the term "carrier liquid" it should be understood to mean that the base particles are provided in the form of a slurry, a dispersion or a suspension and that the formation of metal-coated structures takes place in a liquid medium.

[0036] The term "source of metal-comprising particles" should be understood to include a material source from which coating metal particles can be formed. In this respect the source of metal-comprising coating particles can be selected from the group comprising a dispersion of metal particles, preferably metal nano-particles in a dispersion medium (also referred to as a carrier liquid) and a solution of a soluble salt of a coating-metal ion in a solvent. Complex metal ion salts such as those disclosed in PCT/GB2013/050742 may be used. Where the source of metal-comprising particles is a metal ion salt, the metal ion is suitably reduced to a zero oxidation state in the reaction mixture to form metal particles, either at the surface of the base particle or in solution.

[0037] The terms "continuous reactor", "reaction mixture" and "reagent" are defined herein below with reference to the third aspect of the invention. For the avoidance of doubt it should be understood that the continuous reactor comprises as an essential element a reaction chamber.

[0038] The term "heat exchange means" should be understood to include means via which the temperature of the reaction mixture in the continuous reaction chamber is maintained within a pre-determined temperature range. Depending upon the desired temperature range, heat exchange means can be used to either heat or cool the reaction mixture until the desired temperature range is achieved. Temperature maintenance can either be via a transfer of energy into or away from the reaction mixture via conduction, convection or radiation. Examples of heat transfer means include fins, which essentially comprises a sheet-like conductive material, which is typically positioned on the exterior of the reaction chamber and transfers heat away from the reaction chamber via a mixture of conduction, convection and radiation. Another example of heat transfer means includes heat transfer coils, which typically comprise hollow, heat conductive coils, which can be located either on the exterior or the interior of the reaction chamber. The coils are filled with a heat transfer medium, which maintains the temperature of the coils at a different temperature to that of the reaction chamber; this temperature difference can be used to transfer heat away from or into the reaction chamber. Further, a reaction chamber having a high surface area to volume ratio can be formed from a thermally conductive material that is inert to the reaction mixture; heat generated during the coating process can be quickly and readily conducted away from the reaction centre; the reaction chamber may also comprise fins formed integrally with the body of the chamber. Finally a heat exchange bath comprising a heat exchange media can be located around the reaction chamber to transfer heat away from or into the reaction chamber, the heat exchange media is maintained at a different temperature to the reaction chamber to facilitate this transfer.

[0039] Optionally the metal-coated particles comprise base particles completely coated with metal-comprising coating particles.

[0040] Optionally the metal-coated particles comprise base particles that are partially coated with metal-comprising coating particles.

[0041] Optionally the coating comprises a network of agglomerated particles connected by dendritic bridges.

[0042] Optionally, the base particles are selected from the group comprising but not limited to flakes, discs, ribbons, wires, threads, cuboidal, substantially spherical or spheroidal particles.

[0043] Optionally, the source of base particles comprises a dispersion of base particles in a solvent.

[0044] Optionally the source of base particles comprises a material selected from the group comprising silicon, tin, germanium, gallium, lead, zinc, aluminium and carbon and additionally oxides (including silica and alumina), alloys, compounds and mixtures including such materials.

[0045] Optionally the base particles are suspended in a liquid medium (or carrier liquid) prior to their introduction into the reaction chamber.

[0046] Optionally, the source of metal-comprising coating particles comprise a metal selected from the group comprising silver, copper, platinum, palladium, iron, cobalt, rhodium, nickel, vanadium, ruthenium, iridium and gold.

[0047] Optionally, the source of metal comprising coating particles is an elemental metal, an alloy or a compound including the metal.

[0048] Optionally, the source of metal comprises a dispersion of metal nano-particles in a carrier liquid.

[0049] Optionally, the source of metal comprising coating particles comprises a solution comprising the ions of the coating-metal in a solvent, preferably a soluble salt of the coating metal.

[0050] Optionally, the salt of the coating metal ion is selected from the group comprising a water-soluble salt of silver, copper, nickel, platinum, rhodium, vanadium, palladium and gold.

[0051] Optionally, the source of metal comprising coating particles comprises a surfactant to prevent agglomeration of metal-coated base particles. Optionally the surfactant is selected from a group comprising an alcohol and cetyltrimethylammonium bromide.

[0052] Optionally an initiating agent is provided to initiate a reaction between the base particles specified in step (a) and the metal comprising coating particles specified in step (b). The initiating agent may be added to the source of metal coating particles or may be separately introduced into the reaction chamber.

[0053] Optionally, the initiating species is a reducing agent.

[0054] Optionally, the reducing agent is selected from the group comprising an alkaline solution of a C_{1-4} aldehyde, glucose, an alkali metal salt of citric acid, ascorbic acid, sodium hypophosphite, glucose and hydrazine.

[0055] Optionally, the initiating species is hydrogen fluoride (HF).

[0056] Optionally, the initiating solution is combined with the dispersion of base particles prior to introduction into the reaction chamber.

[0057] Optionally, HF is mixed with the source of metal comprising coating particles prior to mixing with the base particles specified in step (a).

[0058] Optionally, the base particles specified in step (a) and the metal comprising coating particles specified in step (b) are mixed together prior to the introduction of the initiating agent.

[0059] Optionally, the reagent comprising a source of base particles to be coated is introduced into the continuous reactor stepwise.

[0060] Optionally, the reagent comprising a source of metal-comprising coating particles is introduced to the continuous reactor stepwise.

[0061] Optionally, the reagent comprising an initiating agent is introduced into the continuous reactor stepwise.

[0062] Optionally the continuous reactor is elongate and one or more reagents of the reaction mixture are introduced into the reactor at two or more positions along its length.

[0063] Optionally, the reaction mixture is mixed at a temperature of at least −5° C.

[0064] Optionally, the reaction mixture is mixed at a maximum temperature of no more than 120° C., preferably no more than 80° C.

[0065] Optionally the reaction mixture is mixed at a temperature of at least 10° C.

[0066] Optionally the reaction mixture is mixed at a maximum temperature of no more than 65° C., preferably no more than 50° C.

[0067] Optionally the reaction mixture is mixed at a temperature of at least 20° C.

[0068] Optionally the reaction mixture is mixed at a temperature of no more than 30° C.

[0069] Optionally the maximum temperature rise in the reaction mixture is less than 30° C., preferably less that 20° C., especially less than 15° C.

[0070] Optionally, the metal-coated particles are separated from the reaction mixture. Optionally the metal coated particles are separated from the reaction mixture by filtration.

[0071] Optionally the pressure in the reaction chamber is no more than 20 bar (2000 KNm^2).

[0072] Optionally, the source of base particles comprises silicon particles and the source of metal comprising coating particles is a metal ion salt selected from silver nitrate and ammoniacal silver nitrate or a mixture thereof. Optionally the initiating agent is HF.

[0073] Optionally, the metal coated particles are contacted with an etching solution thereby to etch the particles.

[0074] Optionally the metal coating is removed from the etched particle.

[0075] Optionally the continuous reactor including heat exchange means is a stirred tank reactor.

[0076] Optionally the elongate reactor is tubular.

[0077] Optionally the elongate reactor comprises a tube having an internal surface area to volume ratio of at least 5:1. Optionally the tubular reactor has an internal surface area to volume ratio of no greater than 600:1, preferably no greater than 500:1. Optionally the tubular reactor has an internal surface area to volume ratio of at least 40:1, preferably at least 60:1, especially at least 200:1. Optionally the tubular reactor has an internal surface area in the range 50:1 to 300:1, especially 60:1 to 200:1 and particularly 66:1 to 200:1.

[0078] Optionally the diameter of the tubular reactor is greater than 3 mm. Preferably the diameter of the elongate reactor is greater than 5 mm.

[0079] Optionally the diameter of the tubular reactor is less than 14 mm, preferably less than 12 mm.

[0080] Optionally the diameter of the tubular reactor is between 6 mm and 10 mm.

[0081] Optionally the diameter of the tubular reactor varies along the length of the reaction chamber.

[0082] Optionally the diameter of the tubular reactor increases along the length of the reaction chamber.

[0083] Optionally the tubular reactor has a length of at least 20 m, preferably at least 50 m, more preferably at least 80 m, especially at least 100 m.

[0084] Optionally the base particles have a surface area (using the BET method) of at least 0.005 m^2/g.

[0085] Optionally, the base particles have a surface area (using the BET method) of no greater than 15 m^2/g.

[0086] A second aspect of the invention provides a metal-coated particle prepared by a method according to the first aspect of the invention.

[0087] Optionally the metal-coated particles are characterised by a surface area (using the BET method) of at least 0.005 m^2/g.

[0088] Optionally the metal-coated particles are characterised by a surface area (using the BET method) of no greater than 15 m^2/g.

[0089] A third aspect of the invention provides an apparatus for continually coating base particles, the apparatus comprising a continuous reactor including heat exchange means, the reactor comprising:

[0090] a. a reaction chamber having a first inlet for receiving one or more reagents of a reaction mixture comprising base structures and a source of metal-comprising coating particles into the reaction chamber;

[0091] b. an outlet for releasing products and/or spent reagents from the reaction chamber;

[0092] c. means for continually causing reagents and coated products to flow from the inlet to the outlet; and

[0093] d. heat exchange means to maintain the temperature of the reaction mixture within a defined temperature range

[0094] wherein the reaction chamber is adapted to support a liquid reaction mixture.

[0095] By the term "reaction mixture" it should be understood to mean a mixture of at least the essential components needed to form the coated particles according to the second aspect of the invention, namely the base particles and the source of coating-metal. Each component may be provided in the form of a solution or a slurry in a supporting solvent or carrier liquid prior to their introduction into the reaction chamber. Alternatively, each reagent may be combined with a solvent or carrier liquid in the body of the reaction chamber; in this case the reaction chamber includes an additional inlet for the introduction of a carrier liquid or solvent so that the reaction can take place in liquid media. Additional components may be included in the mixture, either to facilitate the path of the reaction or improve the nature of the product. Examples of additional components include, but are not limited to, an initiating agent and a surfactant. Each of the components of the reaction mixture may also be referred to as a "reagent" and the term "reagent" should be interpreted accordingly.

[0096] The apparatus of the present invention supports the coating of base particles with a source of metal particles in a liquid medium. The base particles are suitably provided in the form of a slurry or dispersion in a liquid medium herein after referred to as a carrier liquid. The particles of the slurry or dispersion have a very low solubility in the carrier liquid but are suspended in the carrier liquid under the conditions established in the reaction mixture.

[0097] Where the source of metal particles comprises a slurry or dispersion in a liquid medium, the liquid medium in which they are provided is also referred to as a carrier liquid. Such particles have a very low solubility in their carrier liquid.

[0098] Where the source of metal particles comprises a metal ion compound (which is then reduced in the reaction mixture to form coating particles), the liquid media in which these metal ion are suspended is referred to as a solvent since the metal ions typically have noticeable solubility in the liquid media.

[0099] It should be understood that the term "slurry" as used herein refers to a dispersion or suspension of particles in a solvent or carrier liquid.

[0100] Optionally the inlet is adapted to receive the base particles. Preferably the base particles are provided in the form of a slurry in a carrier liquid. Optionally the reaction chamber is cylindrical.

[0101] Optionally the reaction chamber has an elongate cylindrical form having an outlet distal to the first inlet. Optionally the reaction chamber is tubular.

[0102] Optionally the reaction chamber is further provided with one or more inlet means. The additional inlet means can be used to introduce a source of metal-comprising coating particles into the reaction chamber at specified time intervals after the start of the reaction.

[0103] Optionally, where the reaction chamber is elongate, the one or more further inlet means are disposed between the first inlet and the outlet and can be used for maintaining the concentration of one or more of the initiating agent, the base structures and optionally a surfactant in the reaction chamber. Introducing the source of metal-comprising coating particles into the reaction chamber.

[0104] Optionally the inlet means are selected from a transfer pipe, a spray nozzle, a T-mixer and a static mixer.

[0105] Optionally the apparatus includes means for controlling the speed of flow of the particles between the inlet and the outlet.

[0106] Optionally the apparatus includes a means for breaking up any agglomerates that form from the agglomeration of individual particles.

[0107] Optionally the apparatus includes means for isolating the metal coated particles.

[0108] Optionally the means for isolating the metal coated particles comprises a filter.

[0109] Optionally the apparatus includes means for separating the metal coated particles from the reaction mixture. Optionally the means for separating the metal coated particles comprises a filter.

[0110] Optionally the apparatus includes means for monitoring the pressure of the reaction mixture. Optionally the means for monitoring pressure is a pressure gauge. Optionally the apparatus includes means for controlling the pressure of the reaction mixture. An example of means for controlling the pressure of the reaction mixture is a pressure valve.

[0111] Optionally the apparatus includes means for monitoring the temperature of the reaction mixture. Optionally means for controlling the temperature of the reaction mixture are provided and comprise heat exchange means selected from the group comprising fins, heat exchange coils, a heat exchange bath and heat exchange media.

[0112] Optionally the heat exchange means comprise cooling means provided in the body of the reactor. Optionally the cooling means are cooling fins. Optionally the cooling means are provided on an external wall of the reaction chamber.

[0113] Optionally the temperature of the reaction mixture can be controlled by providing a reaction chamber having a surface area to volume ratio in excess of 5:1. Optionally the reaction chamber has an internal surface area to volume ratio of no greater than 600:1, preferably no greater than 500:1. Optionally the reaction chamber has an internal surface area to volume ratio of at least 40:1, preferably at least 60:1, especially at least 200:1.

[0114] Optionally the reaction chamber has an internal surface area in the range 50:1 to 300:1, especially 60:1 to 200:1 and particularly 66:1 to 200:1. The high surface area to volume ratio ensures that heat generated by the reaction mixture is efficiently removed through a combination of conduction and convection.

[0115] Optionally the reaction chamber comprises a heat conductive material that is inert to the components of the reaction mixture. Optionally the heat conductive material is selected from silicon carbide, copper, copper-tungsten alloys, aluminium-silicon-carbon alloys and beryllium oxide in beryllium.

[0116] Optionally the continuous reaction chamber including heat exchange means is tubular.

[0117] Optionally the continuous reaction chamber comprises a tube extending from the input to the output.

[0118] Optionally the continuous reaction chamber comprises a tube having diameter of greater than 3 mm. Preferably the diameter of the tube is greater than 5 mm.

[0119] Optionally the continuous reaction chamber comprises a tube having diameter of less than 14 mm, preferably less than 12 mm.

[0120] Optionally the continuous reaction chamber comprises a tube having diameter of between 6 mm and 10 mm.

[0121] Optionally the diameter of the tube of the continuous reaction chamber varies along the length of the reaction chamber.

[0122] Optionally the diameter of the tube increases along the length of the reaction chamber.

[0123] Optionally the continuous reaction chamber comprises three stages of tubing. Optionally the first stage comprises tubing having a diameter of 5 to 7 mm, preferably 6 mm. Optionally the second stage comprises tubing having a diameter of 7 to 9 mm, preferably 8 mm.

[0124] Optionally the third stage comprises tubing having a diameter of 9 to 11 mm, preferably 10 mm.

[0125] Optionally the apparatus includes means for separating the gaseous by-products from the liquid reaction mixture.

[0126] Optionally the apparatus is a plug flow reactor.

[0127] The method, product and apparatus of the present invention facilitate the efficient and effective control of a method for coating substrate particles in a liquid medium to give a uniform product with reduced wastage of reagents. To this end the method and apparatus of the present invention allow a skilled person to better control the temperature range over which the coating reaction takes place in a liquid medium; a temperature increase of the order of 10 to 15° C., for example 12° C. has been observed using the apparatus of the present invention. Prior art apparatus are typically associated with a temperature increase of the order of 40° C. or greater. The invention advantageously consumes reagents more efficiently than prior art methods and apparatus. The amount of coating material used is significantly reduced compared to prior art methods. Further the evolution of gases such as H_2 and NO_x can be controlled.

[0128] In particular the maximum temperature that the reaction mixture of the present invention is suitably less than 80° C., preferably less than 50° and especially less than 30° C. The maximum observed increase in the temperature for the reaction mixture of the present invention is suitably less than 30° C., preferably less than 20° C. and especially less than 15° C.

DESCRIPTION OF THE DRAWINGS

[0129] FIG. **1** illustrates the established basics of the coating process.

[0130] FIG. **2** illustrates apparatus used in one embodiment of the present invention.

[0131] FIG. **3** illustrates apparatus used in a further embodiment of the present invention.

[0132] FIG. **4** illustrates inlets that may be used for introducing reagents into the reaction chamber described herein.

[0133] FIG. **5** illustrates a further embodiment of the present invention, the apparatus including further inlet means for introducing reagents into the reaction chamber as the reaction progresses.

[0134] FIG. **6** illustrates a further embodiment of the present invention.

[0135] FIG. **7** illustrates a further embodiment of the present invention.

[0136] FIG. **8** illustrates a nucleated particle prepared using the apparatus of the present invention.

[0137] FIG. **9** illustrates an etched particle prepared by etching the nucleated particles illustrated in FIG. **8**.

[0138] FIG. **10** is a graph illustrating how the temperature of the reaction mixture varies with time in the batch methods of the prior art.

[0139] FIG. **11** is a graph illustrating how the temperature of the reaction mixture varies with time using the apparatus of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0140] The present inventors have surprisingly found that it is possible to produce high quality, uniformly coated particles in a safe and efficient manner by carrying out the reaction in a continuous flow reactor including a heat exchange means. The use of a continuous flow reactor including a heat exchanger minimises any fluctuations in the temperature of the reaction mixture immediately after mixing. Control of the coating process is significantly improved and more thorough mixing of the reagents generally leads to the formation of more uniformly coated particles at a controlled rate of reaction. Further and as a result of the efficient mixing of reagents that occurs in a continuous reactor, the amount of the source of the coating metal needed to coat the base particles can be reduced, which reduces the cost of the process and increases the production rate of the product, without compromising yield as the need to recover unused coating metal can be readily controlled. Further, evolution of gaseous by-products within the reaction chamber can be controlled or inhibited. Improved mixing efficiency and temperature control are inherent features of the present invention; for this reason the method and apparatus of the present invention can be easily scaled up to produce large quantities of good quality metal-coated particles.

[0141] The method of the present invention facilitates the production of coated particles in an ongoing quick and efficient manner. Exemplary coatings include nano-particles of materials such as silver, gold, copper, nickel, platinum, vanadium and palladium. The source of coating metal particles may be provided as a dispersion of nano-particles in a solvent. Alternatively, the coating metal may be provided in the form of a metal ion salt. Exemplary metal ion salts include salts of copper, silver, platinum, vanadium, palladium and gold.

[0142] It should be understood that the term "continuous reactor" when used herein with reference to the present invention means a continuous reactor, which includes means for maintaining the temperature of reaction mixture within a predetermined temperature range within the reaction chamber. These means are referred to herein as "heat exchange means" and where not explicitly stated the term "continuous reactor" should be interpreted to include a "continuous reactor including heat exchange means". The heat exchange means included with the continuous reactor either transfers heat away from or into the reaction chamber depending upon whether the temperature of the reaction mixture immediately after mixing exceeds or falls below a predetermined temperature range as a result of the coating reaction and can be used to control the rate at which the reagents react with each other in the reaction mixture. Where the coating reaction generates energy in the form of heat (an exotherm), the heat exchange means may function to transfer energy away from the reaction mixture so that the temperature of the reaction mixture is maintained at a pre-determined temperature range and overheating of the reaction mixture is prevented. Where the coating reaction absorbs energy (an endotherm), the heat exchange means transfers energy from the surroundings to the reaction mixture.

[0143] Examples of heat exchange means include fins that can transfer heat from the reaction chamber to the surroundings, cooling coils and a heat exchange bath. The cooling coils or fins may be hollow. Cooling coils can be provided on the interior or exterior of the reaction chamber. Where the coils or fins are provided on the exterior of the reaction chamber, a coolant may be circulated in or around the fins to promote heat exchange and temperature control. The heat exchange means preferably comprise a thermally conductive material that is inert to the reagents of the reaction mixture. Examples of suitable materials include silicon carbide, copper, copper alloys, aluminium-silicon-carbon alloys and beryllium oxide in beryllium. Silicon carbide is preferred.

[0144] Alternatively, the reactor may be designed and proportioned so that any heat generated within the reaction chamber is inherently transferred away therefrom via the walls of the chamber. In particular, where a reaction chamber has a surface area to volume ratio of at least 5:1, energy generated within the reaction mixture as a result of an exothermic reaction may be quickly and efficiently transferred away from the reaction chamber via the walls; in this way the temperature of the reaction mixture can be readily controlled. The term "coating concentration" as used herein with reference to the coating material means the concentration or weight of coating material that is required to form a coating over a unit surface area of the base particles in solution. The coating concentration is expressed in millimoles (mM) (of coating material)/m^2 of base particles to be coated (mM/m^2). The coating may be continuous or discontinuous. Preferably the coating is discontinuous. A discontinuous coating comprises a plurality of metal particles separated by pores or voids within its structure. The morphology of the coating can be controlled by controlling the concentration of the source of the coating metal species; in this way the number and size of pores in the coating can be varied as desired.

[0145] The inlet of the continuous reactor is designed to facilitate efficient and intimate mixing of the reagents on or prior to introduction to the reaction chamber. Under certain circumstances this can result in a reduction in the consumption of a source of metal-coating particles, particularly where the base particles have a smooth surface or a regular shape. Examples of suitable inlet means include transfer pipe, a spray nozzle, a T-mixer and a static mixer.

[0146] The continuous reactor may also include means to control the pressure at which the coating reaction is carried out. Preferably the pressure inside the reactor does not exceed 2000 KNm^2. Carrying the reaction out at a pressure of up to 2000 $KNm\text{-}^{2}$ has the effect of reducing the amount of hydrogen or nitrogen oxide gases that are released as by-products of the coating process.

[0147] The continuous reactor may be provided with a pressure value to facilitate the release of excess pressure from the reaction chamber. One or more pressure valves may be provided along the length of the continuous reactor to facilitate the control of pressue along its entire length.

[0148] The continuous reactors according to the third aspect of the present invention include a reaction chamber having an inlet and an outlet. The reaction chamber may be cylindrical as illustrated in FIG. **2** or may be provided in the form of an elongate cylinder or tube as illustrated in FIG. **3**.

[0149] The reaction chamber illustrated in FIG. **2** comprises a cylindrical reaction chamber (**21**) having an inlet (**22**) for the introduction of reagents. Inlet 22 is suitably provided with inlet means A and B for selectively introducing reagents into the chamber. An outlet (**23**) is provided to remove metal coated base particles and a stirrer is provided to cause intimate mixing of the reagents. Base particles are suitably formed into a slurry using a carrier liquid such as water and are fed into the chamber via inlet A. A source of the coating-metal particles, suitably provided in the form of a water soluble salt, is introduced into the chamber via inlet B. An initiating agent may be added to initiate the reduction of the metal salt at the surface of the base particle. A surfactant may also be added to the reaction mixture to prevent agglomeration of the metal coated base particles. Heat exchange means (**25**) can be provided in the form of either a heat exchange coil or a heat transfer fin to maintain the temperature of the reagents within a pre-determined temperature range within the reaction chamber (**21**).

[0150] Alternatively, a mixture of the base particles and source of metal-coating particles may be introduced together via inlet A and an initiating agent, such as HF, can be introduced via inlet B. Mixing of the base particles and source of metal-coating particles prior to introduction into the reaction chamber improves the efficiency of the coating process and minimises wastage of the source of the coating-metal particles in particular.

[0151] An alternative embodiment of the third aspect of the invention is illustrated in FIG. **3**. FIG. **3** illustrates a continuous reactor including an elongate cylindrical or tubular reaction chamber (**31**) having an inlet (**32**) and an outlet (**33**). Base particles, such as silicon particles (**34**) and a source of coating-metal particles (**35**) are fed into the inlet (**32**) and a pumped through the reaction chamber (**31**), where they combine to form a metal coated base particle (**36**). The base particles and source of coating-metal particles may be pre-mixed prior to being fed into the reaction chamber via inlet (**32**). An initiating agent may be added to the reaction chamber via inlet (**32**) to initiate the formation of metal particles on the surface of the base particles. A surfactant may also be added to prevent agglomeration of the metal-coated base particles, where this has a tendency to occur. Fins (**37**) may be provided to help maintain the temperature of the reaction mixture within a pre-determined temperature range. Alternatively, the temperature of the reaction mixture immediately after mixing may be controlled through the use of a heat exchange bath (**38**) including heat exchange media (**39**) via which heat can be introduced or removed from the reaction chamber to maintain the temperature of the reaction mixture within a pre-determined temperature range.

[0152] The inlets (A), (B) and (**32**) can be provided with means for intimately mixing the reagents prior to their introduction into the reaction chamber of the continuous reactor. Examples of typical mixers are illustrated in FIGS. **4**(*a*) and **4**(*b*). FIG. **4**(*a*) illustrates a T-mixer. Reagents to be mixed are fed into the T-mixer from opposite directions (A**1**) and (B**1**) at a speed sufficient to ensure that intimate mixing of the reagents occurs at region C. FIG. **4**(*b*) illustrates a static mixer. Reagents (A**2**) and (B**2**) are fed into pipe (**41**) from opposite directions. As they pass into pipe (**43**) they encounter a baffle (**42**) which causes turbulence in the flow of the liquid and causes intimate mixing of the reagents to occur.

[0153] A further embodiment of the third aspect of the invention is illustrated in FIG. **5**. A reactor of FIG. **5** includes a reaction chamber (**51**) having an inlet (**52**) and an oulet **53**. Base particles (**55**) and a source of coating-metal particles (**56**) are fed into the chamber via the inlet (**52**), are intimately mixed with the source of coating-metal particles and pass out of the chamber via outlet (**53**). Further reagents may be introduced into the reaction chamber (**51**) during the course of the reaction via inlets **54'**, **54"**, **54'"** . . . $\mathbf{54}^{n}$. Inlets **54'**, **54"**, **54'"** . . . $\mathbf{54}^{n}$ may be used to facilitate the step-wise introduction the source of coating-metal particles or may be used to add or maintain the concentration of initiating agent and/or surfactant in the reaction mixture. The temperature of the reaction mixture in the reaction chamber (**51**) may be controlled by placing it in a heat exchange medium. Alternatively the temperature of the reaction mixture in reaction chamber (**51**) can be controlled by constructing the reaction chamber from a thermally conductive material such as silicon carbide.

[0154] In a preferred embodiment of the third aspect of the invention as illustrated in FIG. **6**, base particles (**61**) and a solution of a soluble salt of the coating metal ion (**62**) are intimately mixed and stored in feed tank (**63**). A solution of HF (50 wt %) was stored in feed tank (**64**). Reagents from feedtank (**63**) and feedtank (**64**) were through a T-mixer (**65**) and into a reaction chamber (**66**). The HF initiates the reaction leading to the reduction of the metal ion salt and the formation of nucleated metal particles on the surface of the base particle. Further inlets (**67**), (**68**) and (**69**) may be provided to facilitate the introduction of further HF, metal ion salt or surfactant during the passage of the reagents through the reaction chamber and/or to ensure that the concentration of these species remains constant throughout the reaction.

[0155] In FIG. **7** a further embodiment of the third aspect of the invention is illustrated. The reaction chamber (**71**) comprises three sections, (**72**), (**73**) and (**74**). The first section (**72**) comprises inlet means (**75**) for introducing the base particles and source of coating particles into the reaction chamber. Section (**72**) suitably comprises a PFA tube having a diameter of approximately 6 mm and a length of the order of 30 m. Section (**72**) optionally further includes a pressure gauge (**76**) and valve (**77**) for controlling monitoring and controlling the pressure of the reaction mixture within the reaction chamber. Reagents entering the reaction chamber at (**75**) suitably flow under gravity through section (**72**) and into section (**73**). During their passage through section (**72**), the reagents are thoroughly mixed and the temperature of the reaction mixture rises. The reaction mixture then enters the second section of the reaction chamber (**73**). Section (**73**) comprises a heat conductive material such as silicon carbide and acts as a heat exchanger to control the temperature of the reaction mixture. The heat exchanger suitably comprises a tubular silicon carbide body having a diameter of approximately 8 mm and a length of 50 m. The high surface area to volume ratio of the second section of reaction chamber efficiently transfers heat away from the reaction mixture thereby to control the temperature and rate of reaction within the reaction mixture. The reaction mixture then passes from section (**73**) into section (**74**). Section (**74**) suitably comprises PFA tubing having a diameter of 10 mm and a length of 20 m. Section (**74**) may also be provided with a pressure gauge (**80**) and valve (**81**) to monitor and control the pressure of the reaction mixture within section (**74**) of the reaction chamber (**71**). Coated particles such as the one illustrated in FIG. **8** are collected in a filter (**79**) and can be etched to produce etched particles as illustrated in FIG. **9**.

[0156] The term "initiating agent" as used herein means an agent that helps to drive the coating reaction to completion.

[0157] In investigating the method of the present invention, the present inventors have surprisingly found that the yield and quality of the coated product can be affected by the following factors:

[0158] a. the size of the base particle;

[0159] b. the loading of the base particle in the reaction mixture (g of base particle/Kg of reaction mixturer);

[0160] c. the surface area per unit weight of the base particle (m^2/g);

[0161] d. the concentration of the source of metal coating particles relative to the surface area of base particles in the reaction mixture (mM/m^2);

[0162] e. the flow speed of the reaction mixture through the reaction chamber;

[0163] f. the presence of an initiating reagent or a surfactant as discussed herein; and

[0164] g. the efficiency of mixing the reagents

[0165] The present inventors have found that it is possible to produce high quality coated particles having different coat morphologies by controlling one or more of the concentration of the source of metal coating particles relative to the surface area of the particles to be coated and the temperature of the reaction mixture.

[0166] The total surface area of the base particles in the reaction mixture depends on the size of the particles, their surface roughness and their loading in the reaction mixture. Smaller and rougher particles tend to have a larger surface area compared to larger particles and smoother particles.

[0167] As indicated above, both efficient and effective coating of the base particles depends on maintaining these particles in suspension during their passage through the reaction chamber. Any precipitation can lead to the production of poor quality products and result in potentially dangerous blockages in the continuous reactor system.

[0168] It is important to establish the surface area of the base particles prior to mixing with the source of coating metal. The specific surface area (m^2/g) of the base particles can be measured using the Brunauer Emmett Teller (BET) method or any other alternative method such as laser diffractometry prior to their introduction into the continuous reaction chamber. The specific surface area measured using the BET technique may be at least 0.005 m^2/g, preferably at least 1, 2 or 3 m^2/g. The specific surface area using the BET technique may be no greater than 1000 m^2/g, suitably no greater than 500 m^2/g, for example no greater than 200 m^2/g and preferably no greater than 15 m^2/g.

[0169] The base particles are preferably introduced into the reaction chamber of the continuous reactor in the form of a slurry in which the base particles are suspended or dispersed in a carrier liquid or solvent. The choice of carrier liquids will depend on the base particles used. Suitable carrier liquids include aprotic solvents such as water and ethanol. The loading of the base particles will depend upon the size of the suspended particles.

[0170] The base particles may be substantially spherical, disc-shaped, flake-like, cuboidal or elongate structure. The base particles may have a size with a largest dimension up to about 100 μm, preferably less than 50 μm, more preferably less than 30 μm. The base particles may be defined in terms of their aspect ratio, which is the ratio of the longest dimension to the shortest dimension of the base particle. Suitably the base particles have an aspect ratio of at least 1:1. Preferably the aspect ratio does not exceed 100:1. Preferably the base particles have an aspect ratio in the range 1:1 to 100:1. Elongate particles suitably have an aspect ratio of at least 2:1, preferably no greater than 100:1. Examples of elongate particles include ribbons, wires, pillars and threads. The base particles may have a smallest dimension of greater than 10 nm, suitably greater than 20 nm. Preferably the smallest dimension is at least 0.5 microns. Preferably the base particles have at least one dimension of at least 5 μm. The base particles preferably have a largest dimension of no greater than 1000 μm, suitably no greater than 500 μm and preferably no greater than 200 μm as measured using laser diffraction techniques as defined below.

[0171] Base particle sizes may be measured using optical methods, for example scanning electron microscopy or laser diffraction techniques as described herein below.

[0172] In a composition containing a plurality of base particles, for example a powder, preferably at least 20%, more preferably at least 50% of the particles have smallest dimensions in the ranges described above. Base particle size distribution may be measured using laser diffraction methods or optical digital imaging methods.

[0173] A distribution of the base particle sizes within a powder may be measured by laser diffraction, in which the base particles being measured are typically assumed to be spherical, and in which particle size is expressed as a spherical equivalent volume diameter, for example using the Mastersizer™ particle size analyzer available from Malvern Instruments Ltd. A spherical equivalent volume diameter is the diameter of a sphere with the same volume as that of the particle being measured. If all particles in the powder being measured have the same density then the spherical equivalent volume diameter is equal to the spherical equivalent mass diameter which is the diameter of a sphere that has the same mass as the mass of the particle being measured. For measurement the powder is typically dispersed in a medium with a refractive index that is different to the refractive index of the powder material. A suitable dispersant for powders of the present invention is water. For a powder with different size dimensions such a particle size analyser provides a spherical equivalent volume diameter distribution curve.

[0174] Size distribution of particles in a powder measured in this way may be expressed as a diameter value Dn in which at least n % of the volume of the powder is formed from particles have a measured spherical equivalent volume diameter equal to or less than D.

[0175] Preferred size distributions for a powder of base particles include $D50 \leq 25$ μm, optionally ≤15 μm, optionally ≤10 μm. Base particles having a D50 in the range 4-15 μm are preferred.

[0176] Preferably the base particles are provided in the form of a slurry at a loading of at least 0.001 Kg/Kg, preferably at least 0.003 kg/kg, more preferably at least 0.005 kg/kg. The loading of base particles in the slurry is preferably not more than 0.030 kg/kg, preferably not more than 0.020 kg/kg. Preferably the base particles are provided in the form of a slurry at a loading of between 0.001 kg/kg and 0.030 kg/kg, for example 0.007 kg/kg or 0.015 kg/kg.

[0177] The concentration of the source of metal coating particles is selected to ensure the formation of a coating having a thickness of at least 30 nm, preferably at least 40 nm and especially at least 50 nm. Preferably the metal coating does not exceed a thickness of 90 nm, preferably 80 nm and especially 70 nm. The source of the coating metal may be provided as a soluble salt of a coating metal ion in a suitable aprotic solvent such as water. Alternatively, the source of the coating metal ion may be provided as a slurry of coating metal particles in a suitable carrier liquid. Exemplary coatings include coatings of silver, gold, platinum, nickel and copper.

[0178] Microscopy techniques such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) can be used to measure the thickness of the coatings. The techniques require the preparation of a cross-section of the coated particles for analysis.

[0179] The concentration of the coating metal ion salt in solution or particle loading of the coating metal source in a carrier liquid is calculated with reference to the total surface area of the base particles used in the reaction mixture. The concentration of a coating metal ion salt in solution is therefore expressed in terms of the unit area of the base particle surfaces being coated (mM/m^2). Where the source of coating metal is provided as a slurry the particle loading of the coating material in the slurry is expressed in terms of the weight of the source of the coating metal per unit weight of reaction mixture (Kg/Kg).

[0180] Where the source of the coating metal is provided as a salt of a coating metal ion in an aprotic solvent, the concentration of the metal ion in the solution is at least 2 mM/m^2 of exposed base particle surfaces, preferably at least 3 mM/m^2. The concentration of the coating metal ion salt solution is suitably not more than 10 mM/m^2, preferably not more than 7 mM/m^2 and especially not more than 6 mM/m^2.

[0181] Where the source of the coating metal is a slurry in a carrier solvent, the concentration of the source of the coating metal in the slurry is at least 0.003 Kg/kg, preferably at least 0.005 Kg/kg. The concentration of the source of the coating metal in the slurry is suitably not more than 0.030 Kg/Kg, preferably not more than 0.020 Kg/Kg.

[0182] In one embodiment of the method according to the first aspect of the invention, base particles are formed into a slurry, either before or after introduction into the continuous reaction chamber and are mixed with a source of coating metal in the reaction chamber. The source of coating metal may be added to the reaction chamber simultaneously with the introduction of the base particles. Alternatively the source of the coating metal may be added at fixed time intervals during the progression of the reaction mixture through the continuous reaction chamber. This has the advantage of maintaining the concentration of coating metal species at a fixed level throughout the course of the reaction which makes control of the reaction easier and improves the quality of the coated product.

[0183] In a second preferred embodiment of the method according to the first aspect of the invention the source of coating-metal is provided as a soluble metal ion salt in solution. The base particles are provided as a slurry in a suitable carrier liquid, such as water. The reagents (solution of metal ion salt and the base particles) are intimately mixed to give metal coated base particles. An initiating agent may be required to cause the source of coating-metal to deposit on the surface of the base particles; this may be added to the reagents before or after introduction into the reaction chamber. A surfactant may also be used to reduce or prevent agglomeration of coated base particles. The reagents may be mixed prior to their introduction into the reaction chamber of the continuous reactor. To this end the continuous reactor is provided with means for mixing the reagents prior to their introduction into the reaction chamber. The means for mixing the reagents may be in the form of a spray nozzle, a T-mixer or a static mixer. T-mixers and static mixers are preferred.

[0184] Deposition of the coating metal onto the base particle surfaces may occur simultaneously on contact of the two species. Alternatively, the presence of an initiating agent or a catalyst may be required for the deposition to take place. The catalyst or initiating agent may be added to the reaction chamber together with either the base particles or the source of the coating metal or separately. Where the initiator or catalyst causes the coating metal to precipitate out of solution or slurry in the absence of the base particles, the initiator is either added together with the base particles or separately.

[0185] The initiating species may be a reducing agent. Examples of educing agents that may be used include an alkaline solution of a C_{1-4} aldehyde, glucose, an alkali metal salt of citric acid, ascorbic acid, sodium hypophosphite, glucose and hydrazine. Alternatively the initiating agent may be a strong oxidant such as HF. Where the initiating agent is a reducing agent this may be combined with the base particles prior to introduction into the reaction chamber.

Where the initiating agent is HF, this may be combined with the coating metal ions prior to introduction into the reaction chamber. In a further embodiment, the base particles and the source of metal coating may be mixed together before introduction to an initiating agent.

[0186] The base particles may be used as received or they may be subject to a pre-treatment prior to their introduction into the reaction chamber. Suitable pre-treatments include washing the base particles with water, a dilute solution of an acid such as HF, ammonium hydroxide and hydrogen peroxide. The base particles may be pre-treated to change the surface charge of the particles to promote adhesion of the metal coating particles during the reaction.

[0187] The method is carried out at a temperature of at least −5° C., preferably at least 10° C., more preferably at least 20° C. The method is preferably carried out at a temperature of no more than 120° C., preferably no more than 65° C.

[0188] The reaction is carried out at a pressure of no more than 20 bar (2000 Nm^{-2})

[0189] The coated particles may be isolated and separated from the reaction mixture. The coated base particles may be etched to form a structured silicon particle having pillars and/or pores over the surface thereof. Alternatively, the metal coating can be used to catalyse the growth of nano-wires, such as carbon, silicon or tin nano-wires from the surface of the metal-coated base particle. The metal coating can also be used as a catalyst for numerous other known applications where it is used to increase the rate of a chemical reaction without being consumed in the process. By providing a metal catalyst coating on the surface of a particulate powder, the surface area available to catalyse the chemical reaction is greatly increased. Coated particles with a metal catalyst coating can, for example, be used in fuel cell electrodes, hydrogenation of fats, the manufacture of fine chemicals, producing hydrogen from water and in the refining of petroleum products and conversion of hydrocarbons or carbon dioxide. The coated particles may also be used in biocidal applications where the base particles act as a carrier for a biocidal metal coating. Exemplary biocide coatings comprise silver or copper and an exemplary base particle material to carry a biocide coating is silica. A biocidal metal coating may be a pesticide or antimicrobial. Such coated particles could for example act as anti-fouling agents or disinfectants.

[0190] Suitable apparatus for carrying out the method according to the first aspect of the invention are illustrated in FIGS. **2** to **7**. The apparatus must be able to transport (i) the base particles through the reaction chamber at a speed sufficient to maintain the base particles in suspension and (ii) maintain the temperature of the reaction mixture within a pre-determined temperature range. This speed is also known as the superficial fluid velocity. Preferably the particles are transported through the continuous reaction chamber at a speed just above the speed at which particles precipitate from suspension. Preferably the superficial fluid velocity is greater than 0.05 m/s, for example 0.5 m/s. Preferably the heat exchange means transports heat into or away from the reaction chamber, thereby to maintain the temperature of the reaction mixture at within a pre-determined temperature range.

[0191] Where a continuous stirred tank reactor is used (as illustrated in FIG. **2**), the base particles and the source of coating metal particles are introduced via separate inlet means, either in the form of a liquid stream or in the form of a spray. The speed of stirring in a continuous stirred tank reactor is sufficient to allow the coated particles to precipitate from the reaction mixture whilst maintaining the uncoated and incompletely coated base particles in solution. Precipitated coated particles may be removed using a gravity feed, centrifugation or a rotating filter system or both. Heat exchange means may be provided in the form of fins, heat exchange coils or temperature controlled path. The heat exchange means functions to transfer heat into or away from the reaction chamber of the continuous reactor in order to maintain the temperature of the reaction mixture within a pre-determined temperature range. Fins or heat exchange coils may be hollow to accommodate heat exchange media.

[0192] Alternatively, the continuous reactor may have a shape and structure, which inherently facilitates heat transfer into and away from the reaction chamber via the walls of the reaction chamber. Inherent heat transfer is suitably achieved through the use of a continuous reactor comprising a tubular reaction chamber (as illustrated in FIGS. **3** to **7**), wherein the ratio of its surface area to volume is large. Optionally the tubular reaction chamber has an internal surface area to volume ratio of no greater than 600:1, preferably no greater than 500:1. Optionally the tubular reaction chamber has an internal surface area to volume ratio of at least 40:1, preferably at least 60:1, especially at least 200:1. Optionally the tubular reaction chamber has an internal surface area in the range 50:1 to 300:1, especially 60:1 to 200:1 and particularly 66:1 to 200:1. In a preferred embodiment the tubular reaction chamber has an internal diameter in the range 5 mm to 14 mm, preferably 6 mm to 12 mm, more preferably 6 mm to 10 mm. Preferably the tubular reaction chamber has a length of at least 20 m, preferably at least 30 m, for example 50 or 100 m. The reaction mixture may be transported through the reactor using gravity; alternatively a pump may be employed to maintain the velocity of reactants through the reactor. The velocity of particles through the plug flow reactor is just sufficient to prevent precipitation of the particles within the reactor. Preferably, the speed of flow is greater than 0.05 m/s, more preferably greater than 0.5 m/s

Methods for Coating Base Particles

[0193] A variety of solution based coating methods can be carried out using the continuous reactor including heat exchange means as described herein.

[0194] Solution based coating methods are well known to a person skilled in the art and include methods similar to those employed for ink jet printing and electroless deposition methods such as those used to electrolessly deposit a metal onto the surface of a silicon particle; the metal coating may be capable of catalysing subsequent etching of the underlying silicon structure to give a structured silicon particle including pillars and/or voids on its surface, which can be used as an anode material in a lithium ion battery, for example.

[0195] Alternatively, the metal coating may be used to catalyse the growth of nano-particles on the surface of the base particle. Examples of nano-wire types that can be grown on the surface of the base particle include silicon, carbon and tin. Alternatively the metal coating could be used as a catalyst for chemical conversion in energy applications or industrial processing, or the metal coating could be used as a biocide.

[0196] Electroless deposition of metals is described in Lin et al, "Aqueously Dispersed Silver Nanoparticle-Decorated Boron Nitride Nanosheets for Reusable, Thermal Oxidation-Resistant Surface Enhanced Raman Spectroscopy (SERS) Devices", Applied Materials and Interfaces, 2012, 4, 1110-1117; Lv et al, "Long-Term Antimicrobial Effect of Silicon Nanowires Decorated with Silver Nanoparticles", Adv. Mater. 2010, 22, 5463-5467; Shi et al, "Easy decoration of carbon nanotubes with well dispersed gold nanoparticles and the use of the material as an electrocatalyst" Carbon 47 (2009) 1146-1151; Ma et al, Silver nanoparticles decorated, flexible SiO_2 nanofibers with long-term antibacterial effect as reusable wound cover" Colloids and Surfaces A: Physicochem. Eng. Aspects 387 (2011) 57-64 Djokic et al, Electrodeposition and Electroless Deposition of Metallic Powders: A Comparison, ECS Transactions, 33 (18) 7-31 (2011); and Yae et al, New Surface-Activation-Process for Electroless Deposition of Adhesive Metal (Ni, Cu) Films on Si Substrates, ECS Transactions, 33 (18) 33-37 (2011), the contents of each of which are incorporated herein by reference.

[0197] Suitable techniques that can be used for coating base particles using the continuous flow reactor in accordance with the method of the present invention are exemplified in PCT/GB2012/052483, PCT/GB2012/053241, PCT/GB2013/050742, US2011/0269019, US2011/0250498, EP2183804 and EP2556551.

[0198] The base particles may be cleaned prior to electroless deposition of the metal. Exemplary cleaning materials include acids, for example nitric acid, hydroxides, for example ammonium hydroxide, and peroxides, for example hydrogen peroxide. A preferred cleaning composition is a mixture hydrogen peroxide and ammonium hydroxide. The cleaning composition may be heated during cleaning. Heating may be up to 100° C., optionally up to 90° C.

PREFERRED EMBODIMENTS

[0199] Preferably the base particles used in the method of the first aspect of the invention comprise metal or semimetal materials such as graphite, hard carbon, silicon, tin, gallium, germanium, lead, zinc and aluminium and oxides (such as silica, SiO_x, Alumina) or alloys thereof.

[0200] Preferably the base particles comprise silicon. The silicon may be undoped, n-doped, p-doped or a mixture thereof. Preferably, the silicon is n- or p-doped. Examples of p-type dopants for silicon include B, Al, In, Mg, Zn, Cd and Hg. Examples of n-type dopants for silicon include P, As, Sb and C. Dopants such as germanium and silver can also be used.

[0201] The silicon to be coated may be supported on a surface of another material.

[0202] The silicon may be pure silicon or may be an alloy or other mixture of silicon and one or more other materials. The silicon may have a purity of at least 90.00 wt %, optionally at least 99 wt %. Optionally the silicon purity may be less than 99.9999 wt %. The silicon may be metallurgical grade silicon.

[0203] The silicon may have a resistivity of between 0.0001-100 Ω·cm, preferably less than 1 Ω·cm, preferably less than 0.1 Ω·cm.

[0204] The silicon may be crystalline or amorphous. The base particles may be derived from fragmented silicon wafers or from grinding or jetmilling metallurgical grade bulk silicon to a desired size. Suitable example silicon powders include "Silgrain™" sold by Elkem of Norway.

[0205] The base particles may be in the form of flakes, discs, ribbons or wires, or in the form of cuboid, substantially spherical or spheroidal particles. They may be multifaceted or may have substantially continuous curved surfaces. Non-spherical particles may have an aspect ratio of at least 1.5:1, optionally at least 2:1.

[0206] The particles may have a size with a largest dimension up to about 100 μm, preferably less than 50 μm, more preferably less than 30 μm.

[0207] The particles may have at least one smallest dimension less than one micron. Preferably the smallest dimension is at least 0.5 microns, preferably at least 5 microns

[0208] Particle sizes may be measured using optical methods, for example scanning electron microscopy or laser diffraction techniques as described herein above.

[0209] Preferred size distributions for silicon base particles according to the first aspect of the invention include $D50 \leq 25$ μm, optionally ≤15 μm, optionally ≤10 μm. Silicon base particles having a D50 dimension in the range 4 to 15 μm are preferred, for example a D50 dimension of 4.5 μm, 9.89 μm or 13.4 μm.

[0210] The surface area per unit mass of a sample of silicon base particles may be measured by various techniques including BET (Brunauer, Emmett and Teller) and laser diffractometry. The specific surface area measured using the BET technique may be at least 0.5 m^2/g, preferably at least 1, 2 or 3 m^2/g, for example 0.72 m^2/g, 0.97 m^2/g, 2 m^2/g or 2.5 m^2/g.

[0211] The silicon base particle may consist essentially of silicon as described above, for example silicon having a purity of at least 90% such as metallurgical grade silicon as described above, or it may contain one or more further materials. The silicon base-particle may have a non-silicon core, for example a core of graphite, and a silicon shell onto which the metal coating particles may be deposited. Preferably silicon particles have a purity of at least 98%, preferably at least 98.8%. Preferably the silicon particles used have a purity of no greater than 99.999%.

[0212] Where the base particle has a silicon shell, the shell thickness may be greater than 0.5 microns, optionally in the range of 1-10 microns or 1-5 microns. The material having a non-silicon core may be a powder, and the non-silicon core of this material may have a diameter greater than 5 microns.

[0213] The silicon base particles may have a surface layer of a silicon compound, for example a silicon oxide layer. Silicon may have a native silicon oxide surface layer which may have a thickness of about 1-2 nm. This may be increased by heating to a thickness of no more than 20 nm.

[0214] Preferably the silicon base particles are coated with a layer of silver nano-particles via electroless deposition of silver from a solution of silver nitrate in the presence of HF.

[0215] Preferably the silicon base particles are coated with silver nano-particles in a liquid medium in a continuous plug flow reactor. Preferably the continuous plug flow reactor is provided with separate inlet means for introducing the silver nitrate solution and the silicon base particles into the continuous plug flow reactor. Further inlet means may be provided along the length of the continuous plug flow reactor for introducing further silver nitrate or a second source of a coating metal. The provision of these further inlet means that the coating reaction can be carefully controlled and the coated product comprises a good quality homogeneous coating.

[0216] Preferably the silicon base particles are provided in the form of a slurry at a loading of at least 0.001 Kg/Kg, preferably at least 0.003 kg/kg, more preferably at least 0.005 kg/kg. The loading of silicon base particles in the slurry is preferably not more than 0.030 kg/kg, preferably not more than 0.020 kg/kg. Preferably the silicon base particles are provided in the form of a slurry at a loading of between 0.001 kg/kg and 0.030 kg/kg, for example 0.007 kg/kg or 0.015 kg/kg.

[0217] Preferably, the concentration of silver nitrate is sufficient to provide a coating of silver nano-particles having a thickness of at least 30 nm. Preferably the coating comprises a network of agglomerated silver particles connected by a plurality of silver endrites. Preferably, the coating of silver nano-particles is less than 90 nm. The silver nitrate is suitably provided in a monolayer concentration to provide a coating of the desired morphology and thickness on the base particle. It will be appreciated from the foregoing that the concentration of silver nitrate used will depend on the total surface area of base particles to be coated, is calculated with reference to the surface area and loading of the base particles in solution and is expressed in terms of the unit area of the base particles being coated (nM/m^2). Preferably silver nitrate solutions having a concentration of at least 2 mM/m^2 of silicon particles are used, more preferably at least 3 mM/m^2. Preferably the silver nitrate coating solutions do not have a concentration of greater than 10 mM/m^2, preferably not more than 7 mM/m^2 and especially not more than 6 mM/m^2. Solutions of silver nitrate having a concentration of between 3.2 and 6.3 mM/m^2 of silicon are most preferred.

[0218] Where the electroless deposition takes place in the presence of HF, this is suitably present at a concentration of at least 0.002M to 10M, preferably 0.01 to 5M, more preferably 0.01 to 2M. Preferably the carrier liquid for the silicon base particles comprises HF at the concentration specified above. Alternatively, HF may be introduced to the system together with the silver nitrate species.

[0219] The silicon particles and silver nitrate solution are mixed together and fed through the reactor at a speed, which is just sufficient to maintain the silicon particles in suspension and, as indicated above, will depend on the size and loading of the particles in the slurry. Preferably the mixture of the silicon base particles and the silver nitrate solution is transported through the reactor at a speed (flow rate) of at least 0.05 kg/minute, more preferably at least 0.10 kg/minute. Preferably the speed of transport of the reaction mixture through the reactor does not exceed 2 kg/minute, preferably it does not exceed 1 kg/minute. Flow speeds in the range 0.05 kg/minute to 0.08 kg/minute, preferably 0.07 kg/minute are preferred.

[0220] As indicated above, the metal coated silicon particles can be etched to give structured silicon particles, such as silicon pillared particles and the like, using etching solutions that are well known to a person skilled in the art. The etching solution can be added to the continuous reactor together with the base particles and the silver nitrate solution. Alternatively, the etching solution can be added to the continuous reactor via a further inlet spaced from the base particle and silver nitrate inlet or inlets. The coated particles may be removed from the continuous flow reactor and etched using a separate etching solution. The invention will be described with reference to the following non-limiting examples. Variations on these examples falling within the scope of the present invention will be apparent to a person skilled in the art.

Example 1

[0221] In a first holding tank silicon particles (Elkem Silgrain HQ) having a D50 value of 9.89 μm and a specific surface area of 0.977 m^2/g at a loading of 0.0072 kg silicon/kg in a carrier liquid comprising a solution of silver nitrate in deionised water having a silver concentration of 6.3 mmol/m^2 silicon. HF (50 wt %) was placed in a second holding tank and deionised water placed in a third tank. Metering pumps were used to pump the deionised water and HF though a mixing T and into a PFA tube of 6 mm diameter and length 30 meters. The 6 mm tube stepped up in diameter to 8 mm for a further 50 m before stepping up to 10 mm for a further 20 m. The tubular reactor was immersed in a bath of water that was cooled via a refrigerated chilling circuit. The solution comprising silicon and silver nitrate was pumped into the reaction tube 2 m downstream of the HF/Water addition point. The flow rates of the deinonised water, HF and silicon slurry and cooling bath temperature were adjusted to achieve the following parameters. 1) Minimum superficial fluid velocity of 0.5 m/s, 2) an HF concentration in the combined stream of 5.4M and 3) a temperature of between 20 and 30 C in the reactor. The coated particles were collected in a filter having a mesh dimension in the range 10 to 15 μm.

Example 2

[0222] The procedure of Example 1 was followed with the exception that a solution of silver nitrate having a silver concentration of 5.4 mmol/m^2 silicon was used instead of a silver nitrate solution having a silver concentration of 6.3 mmol/m^2.

Example 3

[0223] The procedure of Example 1 was followed with the exception that a solution of silver nitrate having a silver concentration of 4.1 mmol/m^2 silicon was used instead of a silver nitrate solution having a silver concentration of 6.3 mmol/m^2.

Example 4

[0224] The procedure of Example 1 was followed with the exception that a solution of silver nitrate having a silver concentration of 3.2 mmol/m^2 silicon was used instead of a silver nitrate solution having a silver concentration of 6.3 mmol/m^2.

Example 5

[0225] The procedure of example 1 was followed with the exception that silicon particles (Elkem Silgrain HQ) having a D50 value of 4.6 μm and a specific surface area of 0.725 m^2/g were used instead of the silicon particles of Example 1 and were suspended at a loading of 0.015 kg silicon/kg in a carrier liquid comprising solution of silver nitrate in deionised water having a silver concentration of 6 mmol/m^2 silicon. The fluid velocity of the reaction mixture was 0.68 kg/minute. The coated particles were collected in a filter having a mesh dimension in the range 6 to 10 μm.

Example 6

[0226] The procedure of example 1 was followed with the exception that silicon particles having a D50 value of 13.4 μm and a specific surface area of 2.48 m^2/g were used instead of the silicon particles of Example 1 and were suspended at a loading of 0.01 kg silicon/kg in a carrier liquid comprising a solution of silver nitrate in deionised water having a silver concentration of 4.3 $mmol/m^2$ silicon. The fluid velocity of the reaction mixture was 0.68 kg/minute. The coated particles were collected in a filter having a mesh dimension in the range 15 to 20 μm.

Example 7

[0227] Silver coated silicon particles were prepared in accordance with the procedure set out in Example 1. The particles were transferred from a continuous reactor in which coating occurred to a continuous reactor provided with an etching solution comprising a mixture of silver nitrate and HF.

Example 8

[0228] Silver coated silicon particles were prepared using the reagents at concentrations specified in Example 1 with the exception that the coating reaction was carried out in a batch processing apparatus having a surface area to volume ratio of less than 5:1. The temperature of the reaction mixture was recorded periodically over the first 500 seconds of the reaction and a graph of temperature vs time for this reaction is illustrated by FIG. **10**. From this figure it can be seen that the temperature reaches a maximum at 200 seconds. The temperature rise is of the order of 40° C.

[0229] The temperature of the reaction mixture was recorded as a function of time for the reaction carried out in the apparatus of Example 1 above. This is illustrated in FIG. **11** from which it can be seen that the overall temperature rise was less than 12° C. It can therefore be seen that continuous reactor including heat exchange means is effectively able to control the temperature of the reaction mixture.

[0230] The observed rate of reaction in the apparatus of Example 1 was also observed to be less than that observed in the batch processing apparatus associated with the prior art. It will therefore be appreciated that better control of the final product can be achieved through the use of the apparatus of the present invention.

1. A method for fabricating a plurality of metal coated particles in a liquid medium, the method comprising the steps of:

- a. providing in a liquid carrier a source of base particles to be coated,
  - the source of base particles being selected from the group consisting of silicon, tin, germanium, gallium, lead, zinc, aluminium, graphite, oxides thereof, compounds thereof, and mixtures thereof,
  - the source of base particles being provided at a loading of at least 0.001 Kg/Kg;
- b. providing a source of metal-comprising coating particles;
- c. providing a continuous reactor including a tubular reaction chamber having an internal diameter of greater than 5 mm and comprising a heat conductive material thereby to provide heat exchange between the continuous reactor and surroundings; and
- d. forming a reaction mixture by feeding the source of base particles and the source of the metal-comprising coating particles into the continuous reactor at a velocity of at least 0.05 m/s thereby to contact the source of base particles with the source of metal-comprising coating particles thereby to form a metal coating on base particle having a diameter of greater than 0.5 μm.

2-6. (canceled)

7. The method according to claim **1**, wherein the source of metal-comprising coating particles is selected from the group consisting of silver, copper, platinum, palladium, iron, cobalt, rhodium, vanadium, nickel, ruthenium, iridium, and gold.

8. (canceled)

9. The method according to claim **1**, wherein the source of metal-comprising coating particles comprises a dispersion of metal nano-particles in a carrier liquid.

10. The method according to claim **1**, wherein the source of metal-comprising coating particles comprises a solution comprising ions of the metal coating.

11-18. (canceled)

19. The method according to claim **1**, wherein the reaction mixture is mixed at a temperature of no more than 120° C.

20-34. (canceled)

35. The method according to claim **1**, which further comprises the step of separating the base particles comprising the metal coating from the reaction mixture.

36. The method according to claim **1**, wherein the continuous reactor is at a pressure less than or equal to 2000 KNm^{-2}.

37. The method according to claim **1**, wherein the source of base particles comprises silicon and the source of metal-comprising coating particles is a metal ion salt selected from group consisting of silver nitrate, ammoniacal silver nitrate, and a mixture thereof.

38. The method according to claim **1**, which further comprises the step of contacting the metal base particles comprising the metal coating with an etching solution thereby to etch the base particles comprising the metal coating.

39-40. (canceled)

41. The method according to claim **1**, wherein the continuous reactor is a tubular reactor having an internal surface area to volume ratio of greater than 5:1 m^{-1}.

42. The method according to claim **1**, wherein the continuous reactor has an internal diameter of less than 14 mm.

43-45. (canceled)

46. The method according to claim **1**, wherein the base particles have a BET Specific Surface Area of at least 1 m^2/g.

47-48. (canceled)

49. An apparatus for continually coating base particles in a liquid carrier, the apparatus comprising a continuous reactor including heat exchange means, the reactor comprising:

- a. a tubular reaction chamber having an internal diameter of at least 5 mm and a first inlet for receiving one or more reagents of a reaction mixture comprising a source of base particles to be coated in a liquid carrier at a loading of at least 0.001 Kg/Kg and a source of metal coating particles;
- b. an outlet for releasing products and/or spent reagents from the tubular reaction chamber;

c. means for continually causing reagents and coated products to flow from the inlet to the outlet at a fluid velocity of at least 0.05 m/s thereby to contact the source of base particles with the source of metal-comprising coating particles thereby to form a metal coating on base particles having a diameter of greater than 0.5 μm; and

d. heat exchange means to maintain temperature of the reaction mixture within a defined temperature range.

50-57. (canceled)

58. The apparatus according to claim **49**, which is provided with one or more inlet means for introducing reagents into the chamber, the inlets being disposed between the first inlet and the outlet.

59-60. (canceled)

61. The apparatus according to claim **49**, which further includes means for controlling the velocity of the particles between the first inlet and the outlet.

62-73. (canceled)

74. The method according to claim **9**, wherein the concentration of metal nano-particles in the carrier liquid is at least 0.003 kg/kg.

75. The method according to claim **10**, wherein the metal ion is provided at a concentration of at least 2 mM/m^2 of exposed base particle surface.

76. The method according to claim **1**, wherein the source of base particles is provided in the form of a slurry comprising a dispersion of particles in a carrier liquid.

77. The method according to claim **1**, wherein the source of base particles is provided at a loading of no greater than 0.03 kg/kg.

78. The method according to claim **1**, wherein the velocity of feeding the source of base particles and the source of metal-comprising coating particles into the continuous reactor is greater than 0.5 m/s.

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