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(54) METHOD FOR PLASMA POWDER TREATMENT AND COATING

(57) A method (100) for changing at least one surface property of particles, the method comprising the steps of: providing (110) an electrical discharge assembly; providing (120) a liquid, and providing (120) the particles mixed in the liquid, in the electrical discharge assembly, wherein the liquid is provided in the electrical charge assembly such that when an electrical gas discharge is generated in a gas between two electrodes of the electrical discharge assembly, the electrical gas discharge is in contact with the liquid; modifying (130) at least one surface property of the particles by generating the electrical gas discharge using the two electrodes.

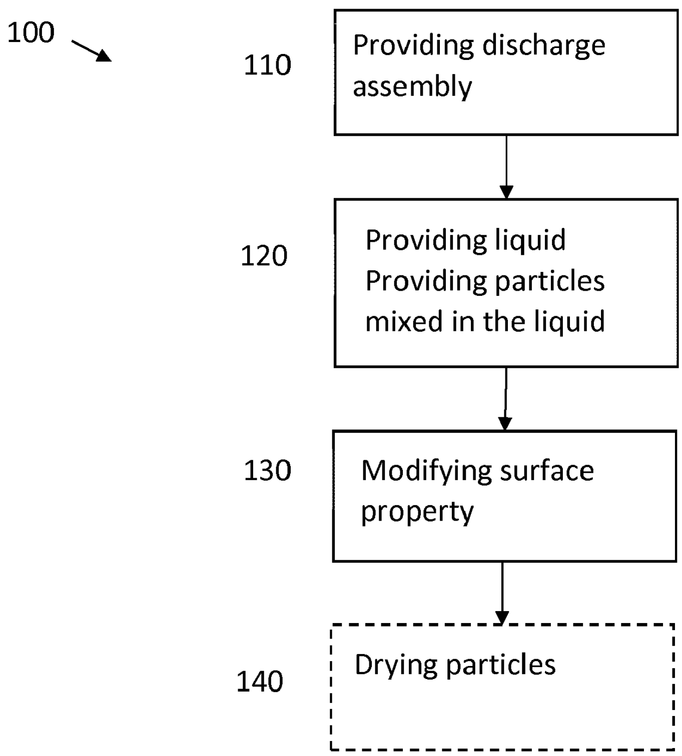

FIG. 1

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Description

Field of the invention

[0001] The present invention relates to methods for changing the surface properties of particles. More specifically it relates to methods for changing the surface properties of particles by electrical gas discharge.

Background of the invention

[0002] Small particles, for example with a size between 0.1 nm up to a few millimeters, have unique physical properties that are directly related to their small size and high specific surface area. Such particles exhibit an inherent propensity to agglomerate, resulting in an increase of their apparent particle size. Agglomeration has a direct impact on the functional properties of the particles such as their optical and magnetic characteristics as well as the catalytic and conductive properties. In addition, many of these small particles are made of heat sensitive materials and have a hydrophobic surface that prevents use of them in different applications where uniform dispersion of the particles without agglomeration in liquid phase is desirable.

[0003] Electrical discharge surface treatment has been previously used as a surface modification technique to enhance the hydrophobicity, hydrophilicity, adhesion, and corrosion resistance of many substrates, including polymeric materials. It has also found widespread use in cleaning and etching applications. However, the method of plasma surface modification is not free of important drawbacks including high energy costs of treatment process, long treatment time, considerable thermal damage of the particles during plasma treatment and aging effect resulting in rapid decrease of the plasma effect on the particles surface during post treatment time.

[0004] US2011006039 recognizes the problem of heat removal in plasma systems, particularly for those using metal plate type electrodes. For solving this problem, it discloses a plasma discharge generating assembly wherein at least one of the electrodes comprises a housing inside which an at least substantially non-metallic electrically conductive material selected from the group of liquid and/or conductive polymer paste is present. The aim thereof is to obtain a homogenous electrically charged dielectric surface and thermal management of heat generated by the plasma. In this plasma discharge the plasma is generated in a gap from 3 to 50 mm for example 5 to 25 mm. It is typically used for coating films, fibers and powders.

[0005] Besides existing technologies for manufacturing of small particles it is important to provide a method to modify the surface of particles without altering their structure and bulk chemical/mechanical properties. There is therefore room for improvements in methods and apparatus for changing the surface of small particles with a size ranging between 0.1 nanometer and a few millimeters.

Summary of the invention

[0006] It is an object of embodiments of the present invention to provide a good method for altering at least one surface property of particles.

[0007] The above objective is accomplished by a method and device according to the present invention.

[0008] Embodiments of the present invention relate to a method for changing at least one surface property of particles. The method comprises:

- providing an electrical discharge assembly,
- providing a liquid, and providing the particles mixed in the liquid, in the electrical discharge assembly,
- wherein the liquid is provided in the electrical charge assembly such that when an electrical gas discharge is generated in a gas between two electrodes of the electrical discharge assembly, the electrical gas discharge is in contact with the liquid,
- modifying at least one surface property of the particles by generating the electrical gas discharge using the two electrodes.

[0009] It is an advantage of embodiments of the present invention that the surface properties of particles can be changed without causing thermal damage to the particles structure. This is achieved by providing the particles such that they are mixed in a liquid. This is especially important for heat sensitive particles which would get damaged when applying a gas phase plasma treatment. The treatment temperature may for example be preferably below 60°C or even below 40 °C.

[0010] It is an advantage of embodiments of the present invention that the surface of the particles can be uniformly modified. This is achieved by modifying the surface of the particles by generating an electrical gas discharge in contact with the fluid wherein the particles are mixed. This allows to obtain desirable properties of the surface of the particles.

[0011] It is an advantage of embodiments of the present invention that the modification effect of changing the surface properties of the particles (e.g. the increase of particles hydrophilicity) has a long-lasting time (e.g. a decrease of the treatment effect below 10 % after 1 month of storage). No substantial aging effect is detected in contrast to prior art solutions where the treatment effect is reduced significantly within 1-10 days after the treatment. Prior art solutions are for example solutions wherein particles in gas phase are subjected to plasma treatment.

[0012] In embodiments of the present invention the liquid is provided such that one of the electrodes comprises the liquid.

[0013] It is an advantage of embodiments of the present invention that the use of liquid electrode with admixing small particles directly in the liquid prevents overheating of the particles and allows applying considerable high plasma power for treatment that results in short and effective particles surface treatment.

[0014] It is an advantage of embodiments of the present invention that the risk of damage of the particle structure is reduced by applying an electrical discharge during a limited period.

[0015] In embodiments of the present invention the electrical discharge assembly is operated at atmospheric pressure or sub-atmospheric pressure.

[0016] It is an advantage of embodiments of the present invention that expensive vacuum installations are not required because the gas in the electrical discharge assembly is at atmospheric or sub-atmospheric pressure.

[0017] In embodiments of the present invention the method comprises providing a gas flow between both electrodes.

[0018] In embodiments of the present invention the gas in between the electrodes may be provided in a static way, meaning that it is not flowing during operation of the electrical discharge assembly.

[0019] In alternative embodiments it may be flowing. It is an advantage of embodiments of the present invention that the gas between the electrodes, on which an electrical gas discharge is generated, is a flowing gas. By providing the gas flow, the generated plasma can be extended in the directions of the flow.

[0020] In embodiments of the present invention modifying the surface properties of the particles comprises reacting the surface of the particles with the electrical gas discharge.

[0021] In embodiments of the present invention modifying the surface properties of the particles comprises admixing a coating material precursor into the liquid and depositing said coating material on the surface of the particles producing a coating on the particles by generating the electrical gas discharge.

[0022] It is an advantage of embodiments of the present invention that a coating can be achieved on the particles which allows to control the surface properties of the particles.

[0023] It is an advantage of embodiments of the present invention that the coating can be applied in one step. This is particularly advantageous compared to wet chemistry methods wherein a multistep approach is used.

[0024] In embodiments of the present invention the coating material precursor is selected such that the coating is from the following groups: polymeric, organic, inorganic, metallic or oxide materials.

[0025] In embodiments of the present invention the material precursor is selected from the following materials group: polymeric, organic, inorganic, metallic or oxide materials.

[0026] In embodiments of the present invention said coating material precursor comprises a chemical undergoing plasma polymerization reaction or plasma oxidation/reduction reaction.

[0027] In embodiments of the present invention the particles are selected from the group consisting of micro-particles, nano- particles and mixtures thereof.

[0028] In embodiments of the present invention the powder particles are selected from the group consisting of polymer particles, metallic particles, oxides of metallic particles and mixtures thereof.

[0029] In embodiments of the present invention the method comprises mixing the liquid which comprises the particles before and/or while generating the electrical gas discharge.

[0030] It is an advantage of embodiments of the present invention that a uniform treatment of the particles can be achieved by mixing the particles with the liquid.

[0031] In embodiments of the present invention the method comprises drying the particles after modifying their surface properties.

[0032] In embodiments of the present invention the method comprises providing the particles by means of an aerosol generator thus obtaining liquid drops which are comprising one or more particles.

[0033] Particular and preferred aspects of the invention are set out in the accompanying independent and dependent claims. Features from the dependent claims may be combined with features of the independent claims and with features of other dependent claims as appropriate and not merely as explicitly set out in the claims.

[0034] These and other aspects of the invention will be apparent from and elucidated with reference to the embodiment(s) described hereinafter.

Brief description of the drawings

[0035]

FIG. 1 shows a sequence of typical method steps of a method in accordance with embodiments of the present invention.

FIG. 2 shows a cross-section of an electrical discharge assembly for treating powder using a method in accordance with embodiments of the present invention wherein the electrodes have a coplanar geometry.

FIG. 3 shows a cross-section of an electrical discharge assembly for treating powder using a method in accordance with embodiments of the present invention wherein the plasma is generated in a perforation hole in the center of the electrodes.

FIG. 4 shows a cross-section of an electrical discharge assembly for treating powder using a method in accordance with embodiments of the present invention wherein one of the electrodes is placed around a dielectric tube and a counter electrode is placed inside the dielectric tube.

FIG. 5 shows a cross-section of an electrical discharge assembly for treating powder using a method in accordance with embodiments of the present invention wherein one of the electrodes is placed around a dielectric tube and a counter cylindrical electrode is placed inside the dielectric tube and wherein the fluid which comprises the particles circulates at the inside and the outside of the counter cylindrical electrode.

FIG. 6 shows a cross-section of an electrical discharge assembly for treating powder using a method in accordance with embodiments of the present invention wherein first electrodes and second electrodes are alternatingly stacked with a spacing in between them through which the particles can flow.

FIG. 7 shows a scanning electron microscopy (SEM) image of untreated particles.

FIG. 8 shows a SEM image of particles treated for 10 minutes at an input power of 20 W using a method in accordance with embodiments of the present invention.

FIG. 9 shows an FTIR spectrum of particles treated for 1, 2.5, 5, 10 min in plasma of 20 W input power using a method in accordance with embodiments of the present invention.

FIG. 10 shows a SEM image of particles coated with MnO_2 during 240 s at an input power of 20 W using a method in accordance with embodiments of the present invention.

[0036] Any reference signs in the claims shall not be construed as limiting the scope. In the different drawings, the same reference signs refer to the same or analogous elements.

Detailed description of illustrative embodiments

[0037] The present invention will be described with respect to particular embodiments and with reference to certain drawings but the invention is not limited thereto but only by the claims. The drawings described are only schematic and are non-limiting. In the drawings, the size of some of the elements may be exaggerated and not drawn on scale for illustrative purposes. The dimensions and the relative dimensions do not correspond to actual reductions to practice of the invention.

[0038] The terms first, second and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequence, either temporally, spatially, in ranking or in any other manner. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

[0039] Moreover, the terms top, under and the like in the description and the claims are used for descriptive purposes and not necessarily for describing relative positions. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other orientations than described or illustrated herein.

[0040] It is to be noticed that the term "comprising", used in the claims, should not be interpreted as being restricted to the means listed thereafter; it does not exclude other elements or steps. It is thus to be interpreted as specifying the presence of the stated features, integers, steps or components as referred to, but does not preclude the presence or addition of one or more other features, integers, steps or components, or groups thereof. Thus, the scope of the expression "a device comprising means A and B" should not be limited to devices consisting only of components A and B. It means that with respect to the present invention, the only relevant components of the device are A and B.

[0041] Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, the particular features, structures or characteristics may be combined in any suitable manner, as would be apparent to one of ordinary skill in the art from this disclosure, in one or more embodiments.

[0042] Similarly it should be appreciated that in the description of exemplary embodiments of the invention, various features of the invention are sometimes grouped together in a single embodiment, figure, or description thereof for the purpose of streamlining the disclosure and aiding in the understanding of one or more of the various inventive aspects. This method of disclosure, however, is not to be interpreted as reflecting an intention that the claimed invention requires more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment. Thus, the claims following the detailed description are hereby expressly incorporated into this detailed description, with each claim standing on its own as a separate embodiment of this invention.

[0043] Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art. For example, in the following claims, any of the claimed embodiments can be used in any combination.

[0044] In the description provided herein, numerous specific details are set forth. However, it is understood that embodiments of the invention may be practiced without these specific details. In other instances, well-known methods, structures and techniques have not been shown in detail in order not to obscure an understanding of this description.

[0045] Embodiments of the present invention relate to a method 100 for changing the surface properties of particles. The particles being treated are typically small particles. Where in embodiments of the present invention reference is made to small particles, reference is made to particles with a geometric mean size between 0.1 nanometer and 5 millimeter or even between 0.1 nanometer and 1 millimeter or even between 0.1 nanometer and 0.5 millimeter. These particles are also referred to as micro- or nano-particles.

[0046] The method comprises providing 110 an electrical discharge assembly.

[0047] The method moreover comprises providing 120 a liquid and providing particles mixed in the liquid, in the electrical discharge assembly.

[0048] The electrical discharge assembly comprises two electrodes. Although at least two electrodes are required the electrical discharge assembly may consist of more than two electrodes. The provided liquid itself may serve as one of the electrodes. The liquid is provided in such a position in the electrical discharge assembly that when an electrical gas discharge is generated in a gas between the two electrodes, the electrical gas discharge is in contact with the liquid.

[0049] The method furthermore comprises modifying 130 the surface properties of the particles by generating the electrical gas discharge using the two electrodes. In embodiments of the present invention a plasma is generated by the electrical gas discharge.

[0050] An example of such a method is illustrated in FIG. 1. The method illustrated in this figure comprises an optional step 140, drying the particles after changing their surface properties.

[0051] The electrical gas discharge is generated by applying a voltage over the electrodes. This voltage may be a DC/AC/pulsed voltage. In case of a pulse, the pulse width of the voltage over the electrodes or of the current through the electrodes may for example be in the ms or s range, or it may be in the μs or ns range.

[0052] Using this method, the surface of micro- and/or nanoparticles can be treated. This is achieved by applying an electrical discharge which is in contact with a liquid phase containing the particles. The electrical discharge may be applied at atmospheric pressures or sub-atmospheric pressure conditions. The electrodes of the electrical discharge assembly may for example be placed in coplanar or axial configuration. In embodiments of the present invention at least one of the electrodes is covered with dielectric material.

[0053] In embodiments of the present invention the liquid is in contact with plasma formed in between the electrodes. The direct contact between the plasma and the liquid may be achieved by providing a recipient in the electrical discharge assembly which is positioned such that when the liquid is in the recipient and a voltage is applied over the electrodes, this results in an electrical field over the liquid. The recipient may be positioned between two electrodes.

[0054] The liquid may be provided such that one of the electrodes of the electrical discharge assembly comprises the liquid. The liquid may even serve as one of the electrodes.

[0055] In a typical embodiment of surface treatment, the present disclosure relates to a process in which the surface chemistry of the particles (e.g. micro- and/or nanoparticles) is modified by means of reaction with the plasma discharge. In a further typical embodiment of surface treatment, the present disclosure relates to a process in which the surface chemistry of the micro- and/or nanoparticles is modified by means of deposition of a coating material. In an embodiment, the present disclosure relates to a process for the preparation of coated micro- and nanoparticles in which the thickness of the applied coating and its chemical composition may be advantageously controlled. The thickness of the coating typically ranges from less than one nanometer to hundreds of nanometers. The coating process is realized through admixing appropriate organic or inorganic chemicals or mixtures thereof into the liquid media where treated particles are dispersed. The admixed chemicals undergo transformation under plasma action that leads to formation of the appropriate coating on the surface of the treated particles.

[0056] In embodiments of the present invention the liquid may be a conducting or dielectric liquid. The conductivity is preferably below 400 μSiemens/cm or even below 300 μSiemens/cm. The reason therefore is that a higher conductivity may result in an increased temperature which can damage the particles. A higher conductivity may lead to microdischarges and/or filamentary paths through the liquid. High current filaments may be formed which are characterized by a high gas temperature inside the filaments. This should be avoided to prevent heating of the particles especially when the particles are polymer based.

[0057] In embodiments of the present invention the electrical discharge assembly comprises a discharge chamber between the electrodes (e.g. between a first and second electrode). A gas is present in the discharge chamber. In embodiments of the present invention the discharge chamber comprises an inlet and outlet for the gas and a flow of gas is applied through the discharge chamber. The electrical discharge assembly comprises means for generating a plasma between the first and second electrode.

[0058] The electrical discharge assembly may moreover comprise a feed unit to mix the particles with liquid; a power supply to generate an electrical discharge; and a mixing unit to uniformly disperse treated particles in the liquid.

[0059] In embodiments of the present invention the particles are mixed in the liquid before providing the mixture to the electrical discharge assembly. In some embodiments the electrical discharge assembly may comprise an inlet for feeding the powder particles to the liquid in the electrical discharge assembly. The electrical discharge assembly may comprise a mixing component for mixing the powder particles with the liquid.

[0060] A cross section of such an electrical discharge assembly is schematically drawn in FIG. 2. In this example the electrodes have a coplanar geometry. In this example the top electrode 1 consists of conducting material and is covered with dielectric material 2 and the bottom electrode 1 is made of conducting material and is covered by dielectric material 2. The distance between both electrodes may for example be between 0.01 mm and 10 cm, for example between 0.05 mm and 10 cm. In this example the walls 3 and the electrodes 1 covered with the dielectric material 2 are forming a chamber. The electrical discharge assembly of the example moreover comprises optional inlet/outlet ports 4 for liquid circulation. The liquid 7 containing particles 10 to be treated is placed in the chamber on the surface of bottom electrode. The liquid 7 may be mixed using a mixer 8 to achieve uniform treatment of the particles 10. The surface properties of the particles are modified by generating an electrical gas discharge using the electrodes wherein the electrical gas discharge is in contact with the liquid. In the example of FIG. 2 a plasma discharge is created in the gas filled zone 5 between both electrodes by passing a plasma forming gas through the discharge chamber and by applying a unipolar or bipolar voltage in the range of hundreds of volts to tens of kilovolts at a frequency range from below 50 Hz to 2 MHz from the power supply 6 to the bottom and top electrode assembly through high voltage connectors 9. The plasma discharge in the gas filled zone 5 causes modification of the surface properties of the particles 10. The same apparatus can be used also for coating of the particles 10 by admixing an appropriate soluble precursor in the liquid 7.

[0061] FIG. 3 shows a cross section of an alternative electrical discharge assembly which can be used for treatment of powder which is mixed in a liquid according to embodiments of the present invention. The apparatus presented in FIG. 3 can be used to treat particles dispersed in any liquid including dielectric and conduction liquids.

[0062] In this example the plasma is generated in between two metal electrodes 1 on the bottom of device separated by dielectric material 2. Each of the electrodes and dielectrics has a perforation hole 5 in the center. The diameter of the hole may for example be in the mm to cm range (e.g. between 0.5 mm and 2 cm). In embodiments of the present invention a plurality of holes may be provided to increase the number of particles that can be treated in a certain time period. The electrical gas discharge may be achieved by applying a high voltage (e.g. with an amplitude of hundreds volts to tens of kilovolts) to the electrode using an alternating or direct current power supply 6 through electro conducting connectors 9. The applied voltage may be a pulsed voltage. Alternating positive and negative voltage pulses may be applied. The liquid 7 mixed with the particles 10 to be treated is filled in a recipient of the electrical discharge assembly through inlet/outlet connections 4. The recipient is formed by the walls 3 and an electrode 1. Optionally a mixer 8 may mix the liquid 8 to achieve uniform distribution of the particles. Methods according to embodiments of the present invention may comprise applying a flow of gas through an inlet port 11 of the electrical discharge assembly to create a gas atmosphere in a zone 5 in between the electrodes. By applying a voltage over the electrodes, a plasma is created in this gas filled zone.

[0063] FIG. 4 shows a cross section of yet another electrical discharge assembly which can be used for treatment of powder which is mixed in a liquid in accordance with embodiments of the present invention. The apparatus provides a way to treat any conducting or dielectric liquid containing particles by a plasma generated remotely above the liquid or having a contact with liquid when generating the plasma. According to embodiments of the present invention, the liquid 7 containing particles 10 is placed in the assembly 3. The electrical discharge is generated above the liquid in the electrical discharge assembly by a jet which comprises a conducting electrode 14 placed around a dielectric tube 13 having a typical diameter between 0.1 and 100 mm, or even between 1 and 6 mm and a counter electrode 15 having a size such that it fits in the dielectric tube 13. The spacing between the counter electrode 15 and the dielectric tube 13 may range from the order of μm up to the diameter of the opening of the dielectric tube. The spacing may for example range between 1 and 5 mm. The electrical discharge is created in the gap formed by the axial electrode 15 and the dielectric material of the tube 13 by applying a unipolar or bipolar high voltage between the electrodes. The applied voltage has a typical value of some kilovolts (e.g. between 1 and 10 kilovolts or even higher depending on the dimensions of the electrical discharge assembly) with frequency in the range of Hz up to some GHz (e.g. between 1 Hz and 10 GHz). The voltage is applied from the power supply 6 through contacts 9 to the electrode assembly. The applied voltage is depending on the dimensions of the assembly. The required voltage is thereby increasing with increasing dimensions of the assembly (the breakdown in air is for example 30 kV/cm). A gas flow 12 may be applied between the electrode assembly. The electrical gas discharge is then produced on the gas which flows inside the dielectric tube. The gas flow is applied such that it flows in the direction of the liquid thereby further extending the plasma towards the fluid such that it is in contact with the fluid which contains the particles to the treated. In order to increase the number of particles that can be treated several jets can be positioned in parallel with each other.

[0064] The electrical discharge assembly presented in FIG. 2 and FIG. 3 can be made in a coaxial geometry as shown in a cross section of the electrical discharge assembly illustrated in FIG. 5. The apparatus presented in FIG. 5 allows to treat powder mixed with conducting or dielectric liquid and can be applied for continuous powder treatment.

[0065] The electrical discharge assembly of FIG. 5

comprises a first conducting electrode 16 placed around a dielectric tube 17. The diameter of the dielectric tube 17 may for example be between 1 and 100 cm, or even between 2 and 60 cm and has a wall thickness of for example between 0.1 and 10 mm. The electrical discharge assembly moreover comprises a second electrode 18 comprising a tube with open top end placed coaxially with the dielectric tube 17. In operation the liquid 7 containing the particles 10 is pumped through an inlet port 20 and forms a film 19 which is covering the outside of the second electrode. The plasma is formed in a gap 5 of typical size of some mm (e.g. between 1 and 5 mm) between the liquid film surface and the dielectric tube 17. The electrical discharge is created in the gap formed by the electrodes by applying unipolar or bipolar high voltage of typical value of some kilovolts (e.g. between 5 and 50 kV) with frequency in the range of Hz up to some GHz (e.g. between 1 Hz and 10 GHz or for example between 1000 and 50000 Hz) from power supply 6 through contacts 9 to the electrode assembly. In the set-up illustrated in FIG. 5 the size of the particles is limited by the thickness of the liquid film which is covering the outside of the second electrode. This film may for example have a thickness below 1 mm. Films with such a thickness allow for example to treat particles with a size up to 100 μm.

[0066] FIG. 6 shows a cross section of yet another electrical discharge assembly which can be used for treatment of powder which is mixed in a liquid in accordance with embodiments of the present invention.

[0067] In methods according to embodiments of the present invention the particles can be dried, and the solvent may be removed after modifying the surface properties of the particles. This may for example be done using a set-up as illustrated in FIG. 6.

[0068] In an electrical discharge assembly as illustrated in FIG. 6 the electrical discharge is generated in a system of parallel electrodes 22, 23 wherein a first conducting electrode assembly 22 is placed inside of a dielectric material assembly 21 and a counter electrode assembly 23 is placed inside of a dielectric assembly 24. In this example the first and second electrodes are alternating.

[0069] Both electrode assemblies are positioned in a way that a small gap with a typical size of some mm (e.g. between 1 and 3 mm) is created in between the electrodes. The plasma can be created in gas filled regions 5 between the electrode assemblies by applying a high alternating voltage of some kilo volts up to hundreds of kilovolts (e.g. between 5 and 50 kV) to the conducting electrodes through contacts 9. A unipolar, bipolar or pulsed voltage with a frequency of for example in the Hz to MHz range can be applied to generate the discharge.

[0070] The liquid, containing particles to be treated, is supplied from above the electrode assembly in a direction 27 towards the assembly by means of an aerosol generator 25 which creates small drops of a solution 26 to be treated by plasma. The size of the drops is thereby preferably smaller than the size of the gaps in between the electrodes. The size of the gaps can for example be between 1 mm and 3 mm, and the size of the drops between 50 and 250 micro-meters.

[0071] In this example the treated particles are collected after passing the drops through the electrical discharge region 5 on the bottom of the reaction chamber by separation methods.

[0072] In embodiments of the present invention a coating material precursor is admixed into the liquid for depositing said coating material on the surface of the particles. The particles and the coating precursor in the liquid are exposed to the reactive species produced in the plasma. This results in activation (e.g. dissociation, excitation...) of the precursor using electrons, ions, radicals or components which are generated in the plasma and which are in excited states in the plasma. In embodiments of the present invention reactive species may be produced coming from one precursor that can activate another precursor molecule.

[0073] Thus, a thin film layer can be achieved on the particles surface. A thin layer with a thickness between 0.1 nm and 2 mm, or between 0.1 nm and 1 mm, or between 0.1 nm and 100 nm can be achieved which allows to control surface properties of nano- or mirco-particles without alternation of their bulk chemical and mechanical properties. Such a coating may for example be applied for manufacturing new generation catalytically active polymeric particles where an organic or inorganic layer (e.g. Si_xO_y, Fe_xO_y, TiO_2, C_xH_y, or Mn_xO with x for example between 1 and 3 and with y for example between 1 and 4 to obtain for example MnO, Mn_2O_4, Mn_2O_3, MnO_3, Mn_2O_2) is deposited on the surface of polymeric particles that results in engineering of new materials with catalytic activity. It is an advantage of embodiments of the present invention that such a coating can be achieved in a single step coating process at a good speed. In embodiments of the present invention microspheres up to 1 mm or even more are created starting from a particle that is coated. This particle is the nucleation particle.

[0074] In embodiments of the present invention the treated particles can be covered with organic or inorganic layers mixing suitable precursors with the solution in which the particles are dispersed. The coating of the particles can be performed in a single step combining both particles treatment and coating deposition that makes the process cost effective and allow high yield of final product with unique properties.

[0075] The coating material precursor may be selected such that the coating is from the group consisting of polymeric, organic, inorganic, metallic or oxide materials. The following precursors may for example be used:

- to obtain an organic coating: alcohols (ethanol, propanol, etc.), acids (acrylic acid), amides (acrylamide);
- to obtain an organosilicon coating: hexamethyldisiloxane (HMDSO), tetramethyldisiloxane (TMDS), hexamethyldisilazane (HMDSN);

- to obtain an inorganic coating (metal oxides): $KMnO_4$; $C_{12}H_{28}O_4Ti$; titanium isopropoxide; $Fe(NO_3)_3$;
- to obtain a metal coating: $HAuCl_4$; $AgNO_3$.

[0076] In embodiments of the present invention the liquid is selected such that the particles are insoluble or only partially soluble in the liquid used as an electrode or as a substrate.

[0077] An exemplary method according to embodiments of the present invention is applied on polystyrene particles (PS) for changing the surface properties of these particles. Initially these particles have a spherical shape and an average size of 400 nm. The untreated particles are hydrophobic with averaged water contact angle (WCA) of 120 degrees.

[0078] In this example the electrical discharge assembly is a barrier discharge reactor wherein water is used as second electrode. The gas between the two electrodes is Helium. One gram of particles per treatment is mixed with the water. The plasma treatment time is varied between 30 and 600 seconds and the applied discharge power is between 2 and 20 W.

[0079] It has been found that the particles WCA substantially changes after 120 second of treatment and that the particles become hydrophilic. After plasma modification, no damage of the particles morphology is detected with SEM. The effect of treatment is stable even after 1 month of particles storage in solution.

[0080] In another exemplary method according to embodiments of the present invention a coating is applied on the surface of PS particles by deposition of a Mn_xO_y (with x and y between 1 and 2) coating. This coating is applied in one step. The method comprises plasma treatment of the PS particles dispersed in a liquid phase which serves as second electrode in the barrier discharge reactor. The precursor used in this example was $KMnO_4$ and has been added to the liquid phase in a concentration of up to 5 g/l in order to produce desirable coating on the PS particles. The plasma generated in the reactor leads to reduction of $KMnO_4$ into Mn_xO_y (with x and y between 1 and 2) and simultaneous treatment of PS particles. It has been found that a uniform coating of the PS particles with inorganic layer of MnO_2 can be achieved with only 240 s of treatment. Moreover, no damage of the nanoparticles of PS is detected. All particles are well dispersed in the solution after the treatment with no agglomeration.

[0081] The method of nano-/micro- particles modification has been tested on PS particles. Initial particles have spherical shape and average size of about 400 nm as indicated in FIG. 7. The image is obtained with SEM acceleration voltage of 7 kV. Treatment of the particles has been carried out in the barrier discharge reactor as one presented in FIG. 2. The inter-electrodes distance was fixed at 5 mm. Liquid with mixed particles has been placed in the chamber on the top surface of second metal electrode and was used as an interface for the plasma. In a first set of experiments a solution with four different conductivities (150, 350, 750, 1000 μS/cm) was used for particles mixing and 4 different treatment times (30, 60, 150, 300 and 600 second) were set for every conductivity value. Higher conductivities of the solution (e.g. 1000 μS/cm is allowable for low power discharge. When increasing the power, it may lead to unstable discharge and damage of the particles. NaH_2POH_4 was the salt used to obtain the different values of starting conductivity and for every treatment 35 ml of solution was used. He atmosphere with flow of 300 standard cubic centimeters per minute (sccm) was used to ignite the discharge between electrode and surface of liquid where particles are mixed.

[0082] Plasma discharge has been ignited by application of high voltage in the range of 2-6 kV peak to peak with fixed frequency of 67 kHz. Plasma treatment has been performed with the discharge power variable in between 2 and 20 W. Particles to be treated, as presented in FIG. 7, were loaded in the chamber with constant weight of the load for all experiments of 1 g per treatment. Analysis of the particles treatment has been evaluated by SEM images of the particles morphology, FTIR spectroscopy was used to evaluate surface chemistry of the particles after the treatment and water contact angle (WCA) was used to characterize the particles wettability.

[0083] In first tests the treatment of the particles has been performed in liquid phase with only admixing of NaH_2POH_4 salt used to control the solution conductivity. It has been found that particles after treatment even at longest exposure time of 600 second do not show any indication of the damage. Typical SEM image of the treated particles is presented in FIG. 8. It shows the SEM image of particles treated for 10 minutes at input power of 20 W. The initial solution conductivity is 350 μS/cm. The particles shape is not affected by plasma treatment. Without being bound by theory it is assumed that visible assemblies of the particles which are present in this figure are caused by charge accumulation on the surface of the particles during the treatment. For practical application of the treated particles it is important to ensure that volumetric properties of the particles are not changed during the treatment and only surface chemical composition is affected. To this end FTIR spectroscopy of the particles has been performed and results are shown in FIG. 9. It shows the FTIR spectrum of particles treated for 1, 2.5, 5 and 10 minutes in plasma of 20 W input power. Without being bound by theory it is assumed that the band around 2400 cm^{-1} is from traces of CO_2 in the FTIR unit and not to the effect of plasma treatment. It is revealed that despite variation of the absorption peaks intensity detected in the range of 2700-3100 cm^{-1} no new bands or peaks appear even at longest treatment time of 10 min. This clearly indicated that no chemical changes are induced by the plasma treatment inside of the particles. The visible effect observed during plasma sustaining is the transfer of the particles from the liquid surface into the volume during the treatment. As indicated above the untreated particles are hydrophobic with WCA of 134.6 degrees.

After the treatment at the applied voltage of 4.5 kV for 1 minute the WCA decreases to 115 degrees and it decreases to 110 degrees for longer treatment time of 10 minutes. The WCA below 115 degrees corresponds to hydrophilic surface of the particles and results in well mixing of the particles with liquid phase that clearly indicates an effect of plasma treatment on the surface chemistry of the particles.

[0084] It is important to emphasize that after plasma modification, no damage of the particles morphology has been detected with SEM as seen in FIG. 8. The effect of treatment was stable even after 1 month of particles storage in solution.

[0085] In another exemplary embodiment of the present invention a Mn_xO_y (with x and y between 1 and 2) was deposited on PS particles. It is advantageous that the coating on the PS particles can be applied in one step. The method comprises plasma treatment of PS particles dispersed in a liquid phase which serves as second electrode in the barrier discharge reactor presented in FIG. 2. $KMnO_4$ is used as additive to the liquid phase in concentration up to 5 g/l in order to produce desirable coating on PS particles. Plasma generated in the reactor leads to reduction of $KMnO_4$ into Mn_xO_y and simultaneous treatment of PS particles. Initially spherical particles as presented by SEM image on FIG. 7 are coated during the plasma treatment process with Mn_xO_y coating. It has been found that uniform coating of the PS particles with an inorganic layer of Mn_xO_y can be achieved even after 240 s of treatment. An example of particles coated with Mn_xO_y in single step process is shown on FIG. 10. The used input power for this example is 20 W. The initial solution conductivity is 350 μS/cm and the concentration of $KMnO_4$ is 0.1 g/l.

[0086] No damage of the nanoparticles of PS has been detected. All the particles have changed the color to brown due to presence of Mn_xO_y coating and were well dispersed in solution after the treatment with no agglomeration.

[0087] The volume of the electrical discharge assembly can be increased thereby increasing the volume of liquid which can be inserted and hence also the number of particles which can be treated in one batch. A volume of liquid above 100 ml or even above 1l is possible.

Claims

1. A method (100) for changing at least one surface property of particles, the method comprising the steps of:

   - providing (110) an electrical discharge assembly,
   - providing (120) a liquid, and providing (120) the particles mixed in the liquid, in the electrical discharge assembly,
   - wherein the liquid is provided in the electrical discharge assembly such that when an electrical gas discharge is generated in a gas between two electrodes of the electrical discharge assembly, the electrical gas discharge is in contact with the liquid,
   - modifying (130) at least one surface property of the particles by generating the electrical gas discharge using the two electrodes.

2. A method (100) according to claim 1 wherein the liquid is provided such that one of the electrodes comprises the liquid.

3. A method (100) according to any of the previous claims, the method comprising operating the electrical discharge assembly at atmospheric pressure or sub-atmospheric pressure.

4. A method (100) according to any of the previous claims, the method comprising providing a gas flow between both electrodes.

5. A method (100) according to any of the previous claims wherein modifying the surface properties of the particles comprises reacting the surface of the particles with the electrical gas discharge.

6. A method (100) according to any of the previous claims, wherein modifying (130) the surface properties of the particles comprises admixing a coating material precursor into the liquid and depositing said coating material on the surface of the particles producing a coating on the particles by generating the electrical gas discharge.

7. A method (100) according to claim 6, wherein the coating material precursor is selected such that the coating is from the group consisting of polymeric, organic, inorganic, metallic or oxide materials.

8. A method according to claim 6, wherein said coating material precursor comprises a chemical undergoing plasma polymerization reaction or plasma oxidation/reduction reaction.

9. A method according to any of the previous claims, wherein the particles are selected from the group consisting of micro-particles, nano- particles and mixtures thereof.

10. A method according to any of the previous claims wherein the powder particles are selected from the group consisting of polymer particles, metallic particles, oxides of metallic particles and mixtures thereof.

11. A method according to any of the previous claims, the method comprising mixing the liquid which com-

prises the particles before and/or while generating the electrical gas discharge.

12. A method according to any of the previous claims the method comprising drying (140) the particles after modifying their surface properties.

13. A method according to any of the previous claims the method comprising providing the particles by means of an aerosol generator thus obtaining liquid drops which are comprising one or more particles.

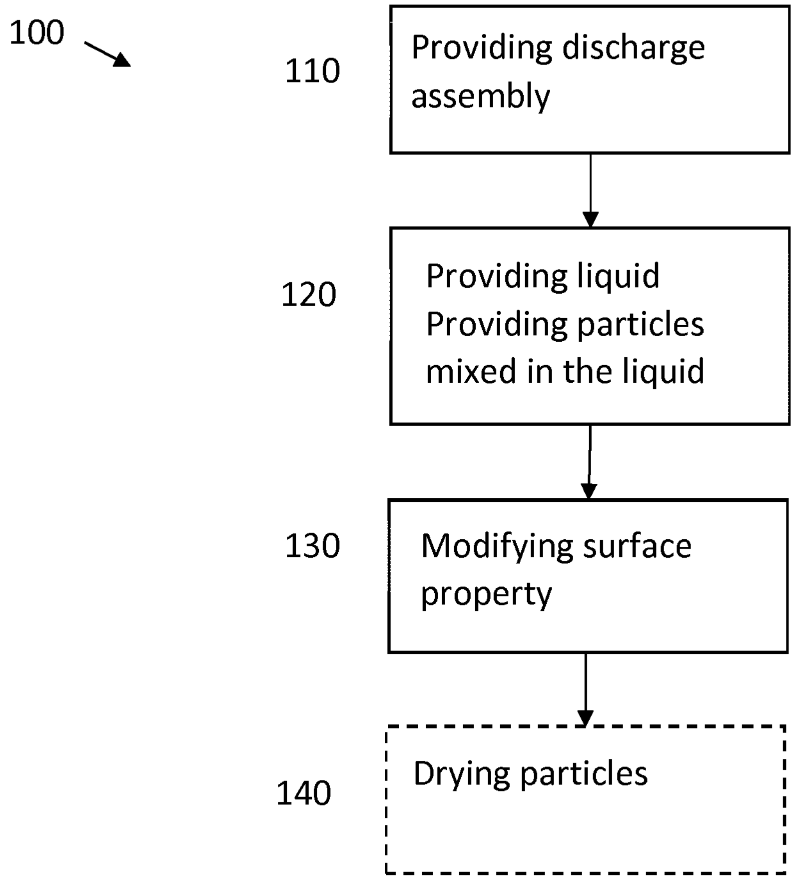
100
110
Providing discharge assembly
120
Providing liquid
Providing particles mixed in the liquid
130
Modifying surface property
140
Drying particles

FIG. 1

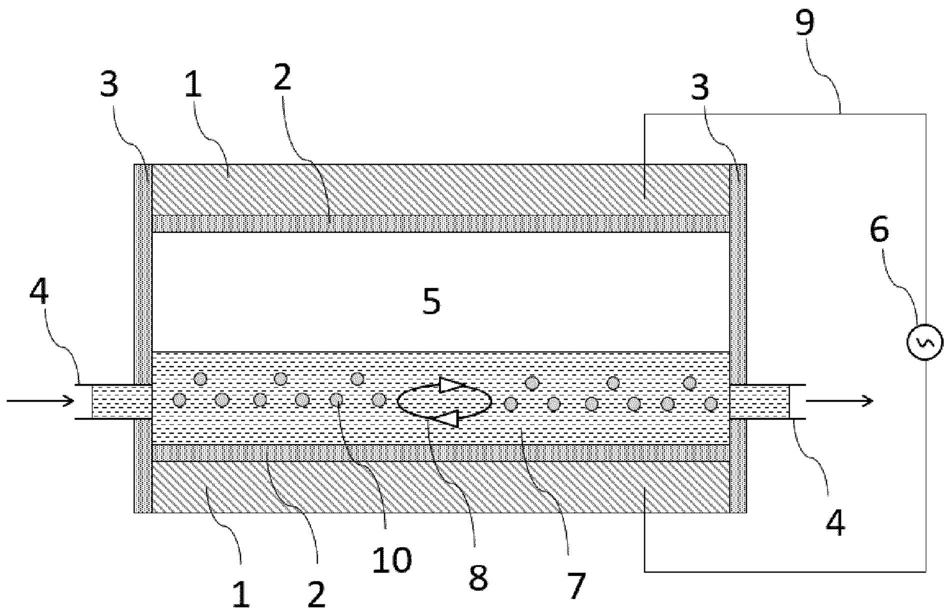
9
3
1
2
3
6
4
5
4
10
8
7
1
2

FIG. 2

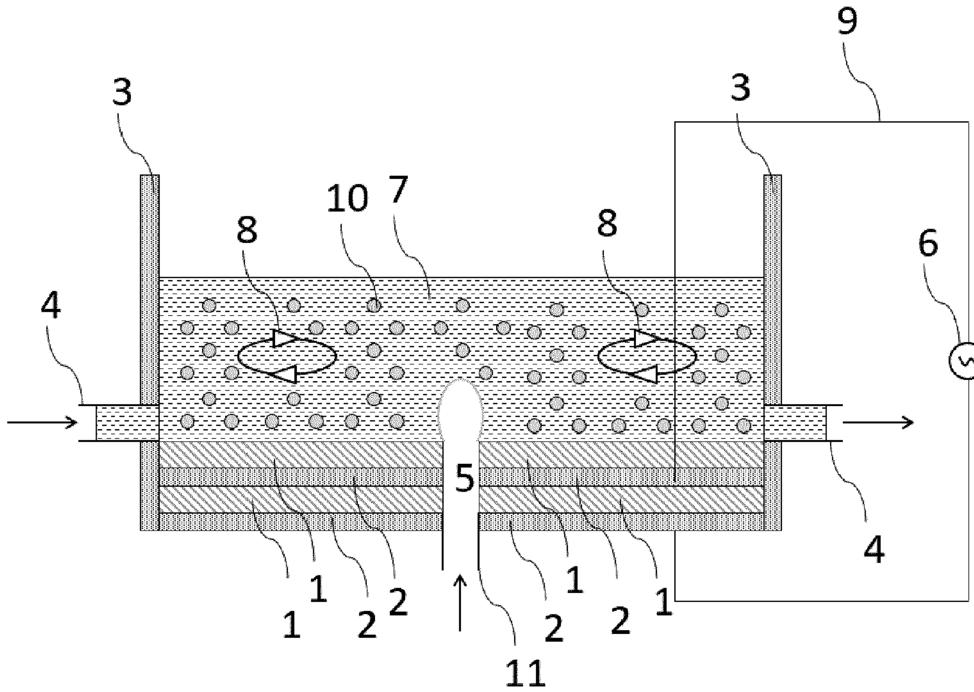

FIG. 3

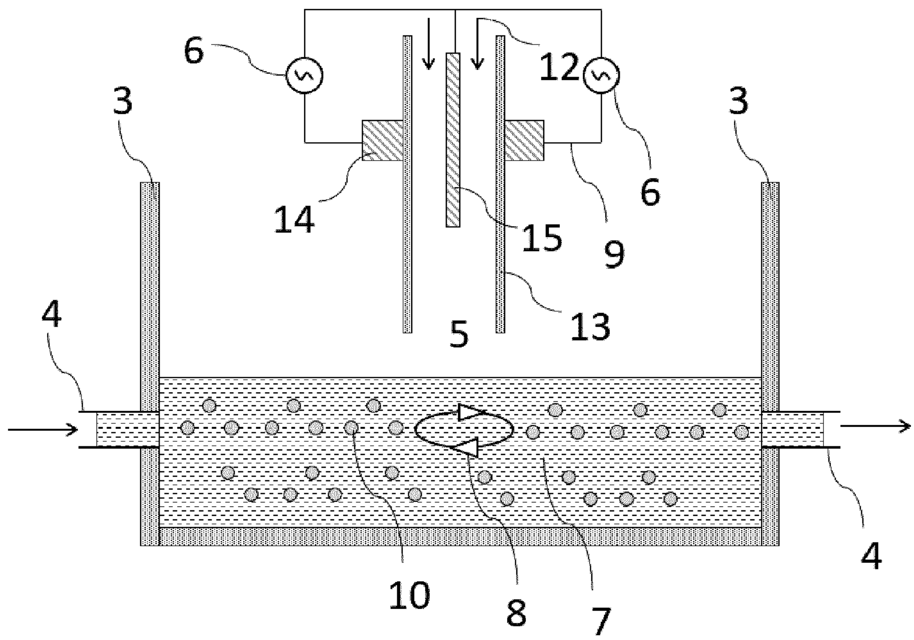

FIG. 4

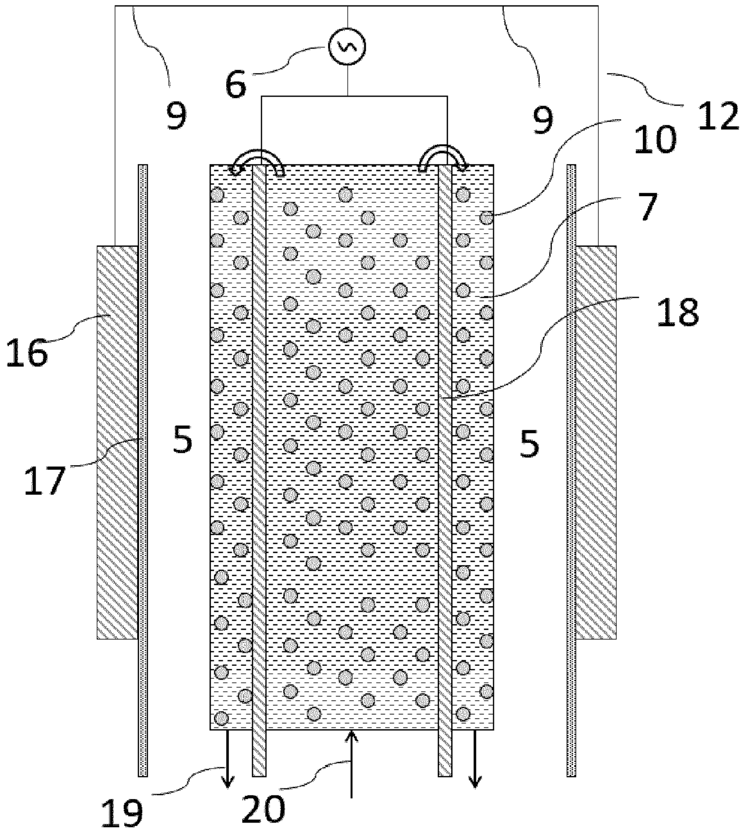

FIG. 5

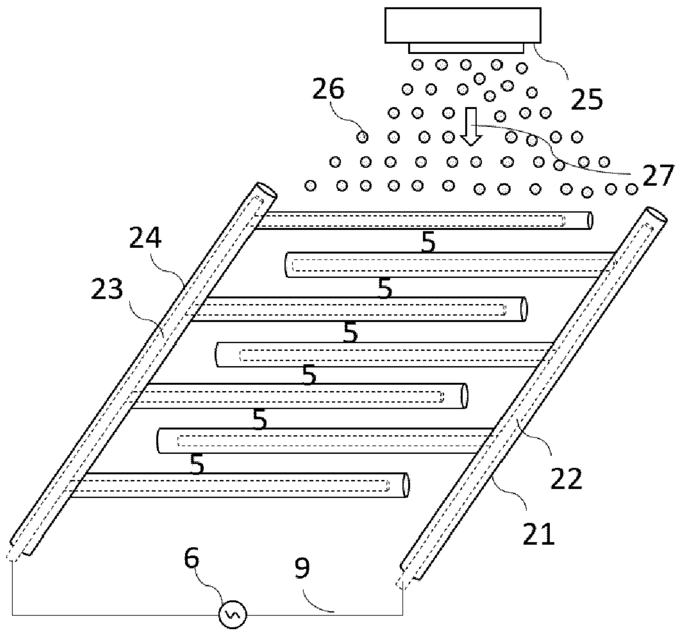

FIG. 6

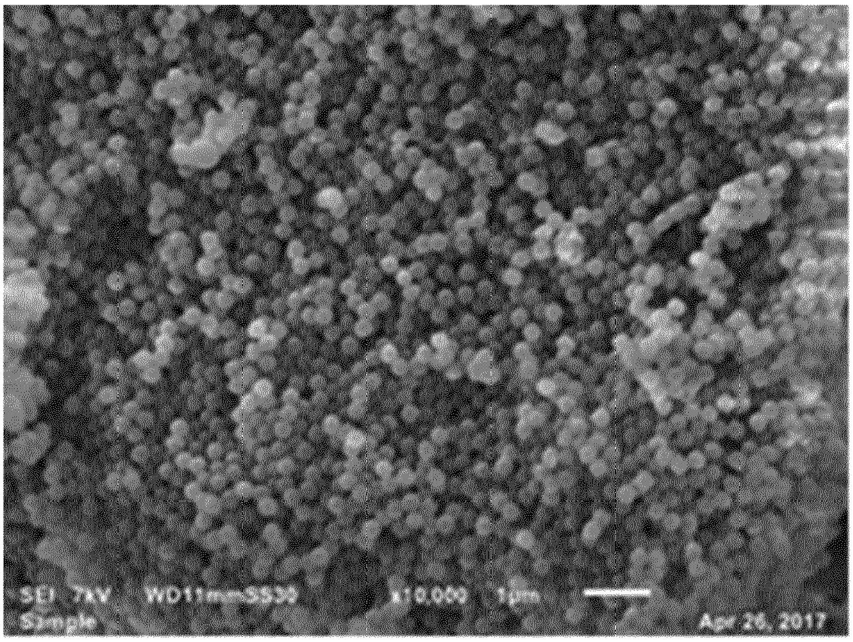

FIG.7

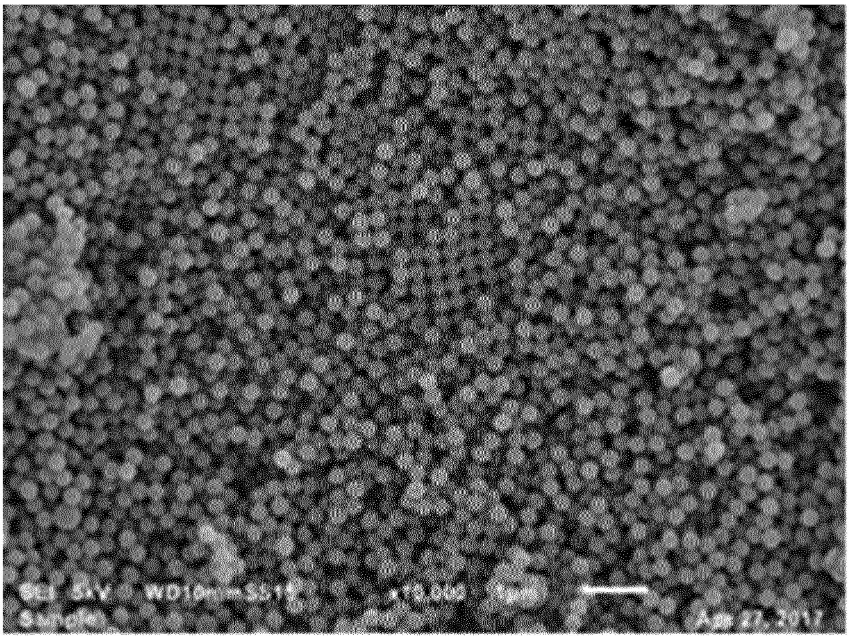

FIG. 8

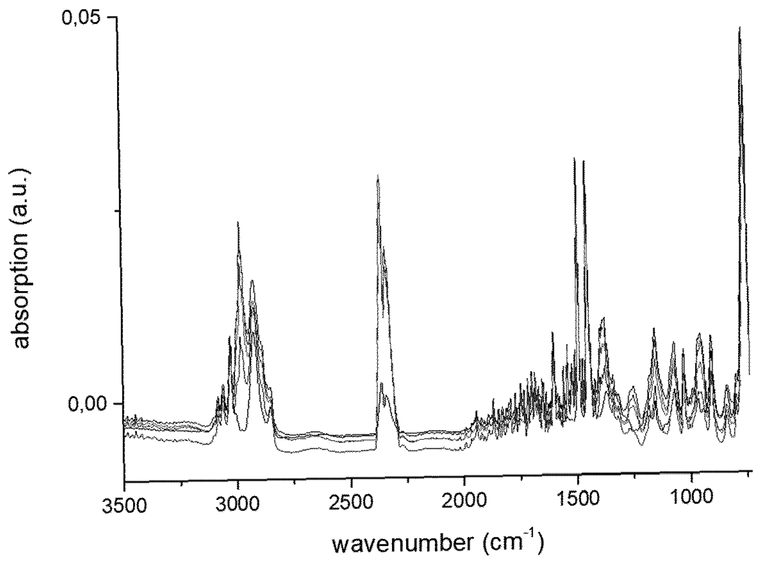
0,05
0,00
absorption (a.u.)
3500
3000
2500
2000
1500
1000
wavenumber (cm^{-1})

FIG. 9

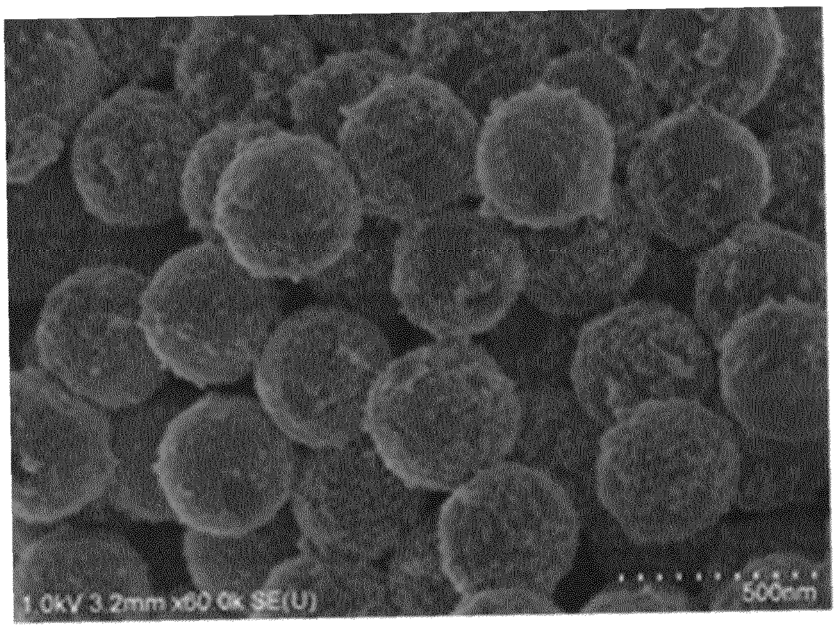
1.0kV 3.2mm x60.0k SE(U)
500nm

FIG. 10

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EUROPEAN SEARCH REPORT

Application Number
EP 18 17 0221

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X Y	WO 2016/095035 A1 (UNIVERSITÉ LAVAL [CA]) 23 June 2016 (2016-06-23) * abstract; figure 10 * * paragraphs [0084] - [0088] *	1-5,9-12 6-8,13	INV. H05H1/48 C25C5/00
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H05H
C25C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	25 October 2018	Crescenti, Massimo

2

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25-10-2018

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

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