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(54) Title: METHOD OF COATING A HEARING AID COMPONENT AND A HEARING AID

(57) Abstract: A method for coating a hearing aid component, which comprises providing a hearing aid component; providing organic nanoparticles, such as polymeric particles or carbon nanotubes; optionally functionalising the organic nanoparticles with perfluoro moieties; suspending the optionally functionalised nanoparticles in a volatile solvent; applying the suspension of the optionally functionalised nanoparticles to the hearing aid component; and evaporating the volatile solvent to form a coating. The invention also relates to a coating for a hearing aid component produced in the method of the invention, and a hearing aid component provided with the coating. The invention also relates to a hearing aid comprising the component.



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## METHOD OF COATING A HEARING AID COMPONENT AND A HEARING AID

### **Field of the invention**

The present invention relates to a method for coating a hearing aid component. The method comprises providing a hearing aid component; providing organic nanoparticles; suspending the nanoparticles in a volatile solvent; applying the suspension of the nanoparticles to the hearing aid component; evaporating the volatile solvent to form a coating. The method may also comprise a step of functionalising the organic nanoparticles with perfluoro moieties. The nanoparticles may be prepared by polymerising organic precursor molecules, or they may be carbon nanotubes, which may be functionalised, e.g. with perfluoro moieties. The invention also relates to a coating for a hearing aid component produced in the method of the invention, and a hearing aid component provided with the coating. The invention also relates to a hearing aid comprising the component.

### **Background of the invention**

Hearing aids generally include a range of components such as housing, internal electronic circuitry, transducers, sound conduits, ear pieces, switches, buttons, connectors and various accessories such as earwax guards, mechanical adaptors and FM units. More specifically the housing may be made out of shells and further comprise battery lid, battery compartment and protective microphone grids. The internal electronic circuitry and the transducers may be at least partly covered by sleeve-like gaskets providing sealing connection as well as resilient suspension and the transducers may further include additional protective screens in the acoustical path.

In-the-Ear (ITE) and completely-in-canal (CIC) hearing aids generally comprise a shell, which anatomically fits the relevant part of the user's ear canal. A receiver is placed in the shell in communication with an acoustic outlet port arranged at the proximal end, i.e. the end of

the shell adapted for being situated in the ear canal close to the tympanic membrane. The distal end of the shell, i.e. the opposite end, intended to be oriented towards the surroundings, is closed by a faceplate subassembly, connected to the receiver by leads. In one design, the  
5 faceplate subassembly incorporates a microphone, electronics, a battery compartment and a hinged lid. The microphone communicates with the exterior through a port, which may be covered by a grid.

Whereas an ITE hearing aid may be regarded as an earpiece integrating all parts of a hearing aid, a Behind-The-Ear (BTE) hearing aid  
10 comprises a housing adapted for resting over the pinna of the user and an ear piece adapted for insertion into the ear canal of the user and serving to convey the desired acoustic output into the ear canal. The earpiece is connected to the BTE housing by a sound conduit or, in case it houses the receiver, by electric leads. In either case it has an output  
15 port for conveying the sound output.

During normal use, a hearing aid is exposed to environmental factors such as wear, moisture, sweat, earwax, fungi, bacteria, dirt and water. Some of those factors may have a corroding influence; others may cause development of an undesired biofilm or of an otherwise irregular surface patina. Corrosion may be controlled by the selection of  
20 durable materials. However the environmental factors may over time create an unsightly appearance.

It is often desirable to apply a coating onto a hearing aid surface. This may be a hydrophobic coating in order to improve moisture  
25 resistance and hereby protect the hearing aid electronics. It could also be a scratch resistant coating in order to maintain the hearing aid appearance or it could be some other form of coating.

WO2008/025355 describes a filter for a hearing aid serving as an earwax guard. Such filters may be treated in a coating process involving an initial plasma treatment to activate the surface of the filter  
30 element by introducing superficial hydroxyl groups before coating in a vapour deposition method utilising silane chemistry. In order to make the exterior surface hydrophobic, perfluoroalkylsilanes or alkylsilanes may be used. The plasma treatment is particularly important for non-

metallic, polymeric substrates, which require that an adhesion layer is applied prior to the silane coating. The substrate may further be microstructured by physical etching or chemical etching prior to any coating so that the final, coated filter will be provided with a superhydrophobic surface.

PCT/DK2007/000002 discloses components for hearing aids the surfaces of which are made hydrophobic or superhydrophobic in a process involving plasma treatment followed by attachment of a self-assembled monolayer of a perfluoroalkylsilane or an alkylsilane from a vapour phase deposition. The surfaces may be microstructured prior to the silane coating, and in order to provide superhydrophobicity a microstructuring step will be necessary before the coating.

EP 1432285 relates to a hydrophobic coating for a component for a hearing aid. The object of EP 1432285 is to seal the hearing aid components from penetration of humidity into the component while maintaining capillary openings available for penetration of gas. This object is achieved by providing a hydrophobic coating to the surface of the hearing aid component. The coating may be provided by applying hydrophobic nanoparticles to the component surface. Such particles may be prepared in a sol-gel process. The particles produced in the sol-gel process of EP 1432285 comprise organic and inorganic components, and the particles may be sprayed on the substrate material and the coating subsequently hardened in a sintering process at high temperature.

The coatings of EP 1432285 do not, however, appear to provide any microstructure to the coated surface, and as such no superhydrophobic properties are mentioned in EP 1432285.

US2006/0286305 relates to hydrophobic coatings comprising reactive nanoparticles. The nanoparticles may be inorganic oxide particles, such as aluminium oxide, silicon oxide, zirconium oxide, titanium oxide, antimony oxide, zinc oxide, tin oxide, indium oxide, and cerium oxide. The nanoparticles of US2006/0286305 have reactive groups, such as acrylates, and apolar groups, such as perfluoroalkyl chains, on their surfaces. The reactive groups can make the particles part of a cross-linked network after coating by allowing reactive groups on different par-

ticles to react with each other to form the network. Coating compositions with the particles of US2006/0286305 may comprise a polymerisation initiator to enable the cross-linking of the particles, or the cross-linking may be induced physically, such as with UV-light or application of heat.

5           While the coatings of US2006/0286305 appear to constitute an improvement over the coatings of EP 1432285, the coatings rely on the cross-linking to provide the coating. It is suspected that this cross-linking may be detrimental to the microstructure of the coated surface so that the contact angle between a water droplet and the coated surface  
10       may be lower than desired. US2006/0286305 also suggests the use of organic nanoparticles, such as carbon nanotubes, although no specific disclosure is given as to how to employ such particles.

          DE 10051182 describes nanoparticles with substituents consisting of hydrocarbon chains or chains of perfluorinated hydrocarbon  
15       chains; the hydrocarbon chains may also comprise functional groups, such as epoxies or methacrylates. The nanoparticles disclosed are based on a matrix prepared from polymerisation of silane molecules and as such should be described as inorganic. The nanoparticles may be applied to a substrate to form a coating, and for this purpose the particles are  
20       dispersed in a solvent before applying to the substrate and drying. The drying may be performed at temperatures from room temperature up to 350°C and the heating or other physical means, such as UV, IR, electron or microwave irradiation may induce a cross-linking of the particles and/or link the particles with the substrate surface. While the coated  
25       surfaces are described as dirt rejecting, DE 10051182 contains no indication that superhydrophobic properties are provided with the coating.

          As described above there is a need to provide hydrophobic coatings, especially superhydrophobic coatings, to electronic devices such as hearing aids. The present invention aims to provide a superhydrophobic  
30       coating to a hearing aid or a hearing aid component, which coating may be produced in a process that does not require conditions which may jeopardise the hearing aid component, such as high temperatures or irradiation with ultraviolet light, and which process furthermore may be applied to a hearing aid component that does not have a microstructured

surface.

### **Brief description of the invention**

- The present invention relates to a method for coating a hearing aid component comprising the steps of:
- providing a hearing aid component;
  - providing organic nanoparticles;
  - suspending the nanoparticles in a volatile solvent;
  - applying the suspension of the nanoparticles to the hearing aid component;
  - evaporating the volatile solvent to form a coating.

In one embodiment the method further comprises a step of functionalising the organic nanoparticles with perfluoro moieties. It is preferred to functionalise the nanoparticles before suspending them in the volatile solvent, although the functionalisation may also be performed at another step in the method.

The hearing aid component may be any component used in the construction of a hearing aid, or it may be an assembly of several such components, e.g. on a substrate; the hearing aid component may also be a fully assembled hearing aid. The method for coating of the hearing aid component aims to provide superhydrophobicity to the surface of the hearing aid component to prevent accumulation of water, sweat, dirt, grease, earwax and the like. The nanoparticles employed in the coating method may be any kind of organic nanoparticles. Nanoparticles are considered to be particles within the size range of 1 to 1000 nm; for example, the particles may be approximately round with a size of 1 to 50 nm, such as about 20 nm, or the particles may be rod-shaped or tube-like with a diameter of 1 to 20 nm, such as about 10 nm and a length of 50 to 500 nm, such as about 200 nm. The nanoparticles are preferably organic, meaning that they comprise a base structure of covalently linked carbon atoms. The nanoparticles preferably do not comprise any metallic or ceramic portions. The organic nanoparticles may have perfluoro moieties, in particular the perfluoro moieties may be covalently

bound to the material of the core structure, and these moieties may be located on the surface of the nanoparticles. In one embodiment, nanoparticles prefunctionalised with perfluoro moieties are employed in the method of the invention; in another embodiment the organic  
5 nanoparticles are functionalised with perfluoro moieties before suspending them in the volatile solvent.

The, preferably perfluoro functionalised, organic nanoparticles are suspended in a volatile solvent, and this suspension is applied to the hearing aid component. Any volatile solvent may be used, although the  
10 solvent should preferably not be reactive towards either the nanoparticles or the surface of the hearing aid component, nor towards any substrate to which the hearing aid component may be attached. Suitable solvents for the method of the invention are ketones, ethers, alkanes, halogenated alkanes or mixtures of these. Ketones and cyclic ethers are  
15 preferred. The solvent is preferably liquid at ambient or moderately increased temperature, e.g. between about 0 to 100°C, such as up to 70°C or up to 60°C, and has a high vapour pressure. Acetone is a preferred volatile solvent.

The invention is not limited regarding how the nanoparticles are  
20 suspended in the volatile solvent, and any suited technique for suspending particles in a liquid may be used. The suspension of nanoparticles is preferably homogenous before applying to the hearing aid component, and therefore the method may comprise bringing the suspension to homogeneity. Suited methods for bringing a suspension of particles to ho-  
25 mogeneity are well-known to a skilled person, and comprise treating the suspension with sonication, e.g. exposing the suspension to ultrasound; high-shear, e.g. in a blender; or by impingement, e.g. in a French press or a high-pressure homogeniser. The concentration of particles in the suspension for application to the hearing aid component will depend on  
30 the nature of the particles employed, but it will generally be within the range of 0.1 to 5 g/L, for example from 0.1 to 1 g/L, such as 0.5 g/L, or from 0.5 to 1.5 g/L, such as 1 g/L.

Application of the suspension of organic nanoparticles to a hearing aid component, e.g. to a substrate comprising a hearing aid compo-

ment may be achieved using any suited technique; several techniques are known within the art and comprise spraying the suspension on the substrate, immersing or dipping the substrate in the suspension, applying the suspension with a paintbrush, roller or the like. It is preferred to spray the suspension onto the substrate. It is suspected that the spray process (e.g. atomisation of the solvent) can accelerate solvent evaporation and therefore reduce any potential risks towards damaging the surface of hearing aid. It is further preferred that a controlled amount of suspension is applied to the substrate; for example, the amount to be applied may be expressed as a volume of suspension applied per total surface area of components or substrate and components. The amount to be applied may also be calculated as a mass of particles to be applied per total surface area of components or substrate and component. The total surface area may be correlated with the mass or volume of the hearing aid components so that these parameters may be used to replace the total surface area in the calculation of the mass of nanoparticles to be applied. The amount to be applied may also be expressed relative to the number of hearing aid components to be coated. A preferred range of nanoparticles to be applied may depend on the type of nanoparticles, but will typically be within the range of 0.03 mg to 0.07 mg per square centimetre, although for certain substrates larger amounts may also be appropriate. Likewise, some substrates may be coated with a smaller amount.

After application of the suspension of organic nanoparticles in the volatile solvent, the volatile solvent is evaporated to form the coating. The volatility of the solvent allows that the solvent is evaporated without application of heat. It is preferred that the volatile solvent is evaporated at ambient temperature without application of heat. However, the solvent may also be evaporated with application of heat to moderate temperatures. With moderate temperatures is to be understood that the temperature is not sufficiently high to alter, e.g. melt or cause sintering, of the nanoparticles, nor to alter the hearing aid component. Moderate heating may be applied using e.g. a heating lamp, an oven, infrared light emitting diodes etc. It is also within the scope of the

invention to promote evaporation of the solvent by circulation of or removing and replacing the ambient atmosphere above the substrate with the applied suspension. For example, the coated substrate may be placed in a chamber with an air inlet and an air outlet allowing replacement of the ambient atmosphere so that evaporated solvent may be removed via the outlet thereby decreasing the partial pressure of the solvent in the ambient atmosphere above the substrate. The evaporation may also be promoted by decreasing the total pressure of the ambient atmosphere above the substrate. The above means to promote evaporation of the solvent may also be combined.

The method for coating a hearing aid component according to the invention may also comprise preparing the organic nanoparticles. Thus, in one embodiment the step of providing the nanoparticles comprises forming an aqueous emulsion of a first organic precursor molecule and a surfactant; and initiating a reaction involving the first organic precursor molecule to form polymer particles. In another embodiment the step of providing the nanoparticles comprises forming an aqueous emulsion of a first organic precursor molecule, a second organic precursor molecule and a surfactant; and initiating a reaction involving the first and the second organic precursor molecules to form polymer particles.

Thus, the organic nanoparticles may be formed by polymerising one or more appropriately reactive monomers, i.e. the organic precursor molecules. When only one type of organic precursor molecule is employed it will have one or more reactive groups, which groups may react with each other to form the polymer, i.e. polymerise. The reactive groups may be of the same reactivity, or the reactive groups may be of complementary reactivity allowing two groups of complementary reactivity to react with each other. The organic precursor molecule may also comprise two or more non-complementary groups which may be reacted with identical groups on another precursor molecule. When a first and a second precursor molecule are employed in the same reaction, they will have reactive groups allowing first and second precursor molecules to react with each other to form a polymer containing a base structure made from both the first and the second precursor molecule.

Any kind of surfactant, i.e. cationic, anionic, zwitter-ionic or non-ionic, may be used in the method of the invention. However, the surfactant will generally be selected based on its properties, such as the critical micelle concentration (CMC), the hydrophilic-lipophilic-balance (HLB), the size of micelles formed in aqueous solution, etc., as well as the nature of the precursor molecule(s). In one embodiment sodium dodecyl sulfate (SDS) is used as the surfactant.

The polymerisation reaction may take place spontaneously, e.g. by adding the first, or the first and the second precursor molecules to the surfactant solution or emulsion. The polymerisation may also be initiated by addition of an initiator to the aqueous emulsion of the surfactant and the precursor(s). The polymerisation reaction between the precursor molecule(s) may be controlled by controlling the temperature of the reaction mixture. For example, the reaction mixture may be heated to a temperature up to the boiling point of the reaction mixture, e.g. to a temperature within the range of 20 to 100°C, or 40 to 80°C, such as about 60°C. However, if an initiator, such as a free-radical initiator, is employed the reaction temperature may be selected with consideration of the decomposition temperature of the initiator.

The reaction time allowed for the polymerisation is preferably controlled, e.g. to a reaction time of up to 24 hours, for example up to 16 hours, up to 8 hours, or up to 4 hours, such as about 1 hour. The reaction of the first and the optional second precursor molecule may be terminated by separating the formed nanoparticles from unreacted precursor molecules in the emulsion. For example, the polymerisation may be terminated by precipitating the nanoparticles, e.g. by addition of an appropriate solvent, such as methanol, to the reaction mixture. The solvent will cause the nanoparticles to aggregate so that the nanoparticles may be removed from the reaction mixture by filtration or centrifugation. It is also possible to remove the nanoparticles directly by filtration, such as ultrafiltration, or centrifugation without the solvent mediated precipitation, thus separating the formed particles from the other reactants and terminating the polymerisation. Alternatively, the soluble components of the emulsion may be removed from the formed nanoparticles

by dialysing the emulsion, e.g. against water.

Many appropriate reactive groups for a precursor molecule are known within the art, and these comprise vinyls, acrylates, epoxies, etc. In a preferred embodiment the method employs divinyl benzene (DVB) as a first organic precursor molecule, while the second organic precursor molecule is glycidyl methacrylate (GMA) or perfluoro acrylate (PFA), e.g. 1H,1H,2H,2H-heptadecafluorodecyl acrylate. In these embodiments it is preferred to include a free-radical initiator, e.g. 2,2'-azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044), to the reaction mixture. The initiator may be chosen based on its solubility and decomposition temperature. For example, the size, morphology and size distribution of the formed polymer nanoparticles may depend on the reaction temperature. In general terms it may be said that a higher reaction temperature tends to favour formation of larger, or even aggregated, particles whereas a lower reaction temperature favours smaller particles with narrow size distribution. Thus, an initiator having a decomposition temperature below the desired reaction temperature may be chosen in order to allow polymerisation at this temperature.

In one embodiment of the method of the invention, the nanoparticles are functionalised with a perfluoro moiety. In general, moieties on the surface of the nanoparticles may be reacted with a compound containing the perfluoro moiety and a moiety of complementary reactivity to the moieties on the surface of the nanoparticles. It may also be necessary to employ a linker molecule or a molecule to promote linkage between the moieties on the surface of the nanoparticles and the compound containing the perfluoro moiety. Appropriate pairs of complementary reactivities include, e.g. nucleophile-epoxy, carboxylate-amine (via a carbodiimide compound), aldehyde-amine (optionally via a reducing agent), carbonyldiimidazole-amine etc.; many more are known within the art as described in e.g. Scopes, R.K., Protein purification. Principles and practice. Third edition, Springer-Verlag, New York 1993, or Atherton, E.; Sheppard, R.C. Solid phase peptide synthesis: A practical approach. Oxford, England: IRL press (1989), which are hereby incorporated by reference. In a preferred embodiment the nanoparticles

comprise epoxy groups, e.g. in the form of glycidyl moieties, which may be reacted with a compound with a perfluoro group and a nucleophilic group, such as heptadecafluoroundecylamine (HTFA).

In another embodiment, the organic nanoparticles comprise  
5 carbon nanotubes (CNTs). The CNTs may be single-walled (SW) or multi-walled (MW), or the CNTs may be molecules known as fullerenes. When CNTs are employed in the method of the invention these preferably comprise functional groups, such as perfluoro moieties, in order to obtain a homogeneous suspension of the CNTs in the volatile solvent. In  
10 a preferred embodiment, the CNTs used in the method of the invention the CNTs are functionalised with perfluoro moieties prior to suspending them in the volatile solvent in a process comprising the steps of subjecting the CNTs to oxidising conditions to form carboxylate groups on the CNTs followed by coupling perfluoro moieties to the CNTs via the formed  
15 carboxylate groups. The oxidising conditions may be provided using any sufficiently strong oxidising agent, e.g. a solution of concentrated  $\text{H}_2\text{SO}_4$  and aqueous  $\text{H}_2\text{O}_2$ , which is also known as "Piranha solution". The formed carboxylate groups may be functionalised with perfluoro moieties using any appropriate method; coupling of functional groups via carboxylate groups is well-known from the preparation of e.g. chromatog-  
20 raphy supports as outlined above and as detailed in Scopes, 1993, or other textbooks on methods within organic chemistry, e.g. solid phase synthesis. A preferred method for coupling involves coupling a perfluoro molecule with an amine group via a carbodiimide compound, such as  
25 N,N'-dicyclohexylcarbodiimide (DCC), N,N'-diisopropylcarbodiimide (DIC), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) or the like. A preferred perfluoro molecule with an amine group is HTFA.

The oxidising conditions used to oxidise the CNTs may introduce  
30 carboxylate groups at the ends (i.e. the two terminals) of the CNTs, or the carboxylate groups may also be introduced along the sides of the CNTs.

In another aspect the invention relates to a coating produced in a method of the invention. In a preferred embodiment the coating is su-

perhydrophobic.

In a further aspect the invention relates to a hearing aid component which is provided with a coating produced according to the method of the invention. The component to be provided with the coating may comprise an outer surface of a polymeric material. The outer surface of the component is not limited to a specific polymeric material, and any polymeric material is within the scope of the invention. However, preferred polymeric materials are polyoxymethylene (POM), acrylonitrile butadiene styrene (ABS), and a blend of ABS and polycarbonate (PC) known as ABS/PC. POM is also known as Acetal plastic. Further relevant types of polymeric materials are cellulose acetate-propionate/cellulosepropionate (CAP/CP), methyl methacrylate acrylonitrile butadiene styrene (MABS), polyamide (PA), thermoplastic polyester (PBT) and polymethyl methacrylate (PMMA). A component with a metallic outer surface is also appropriate for the invention. Any type of metal may be coated, but metals such as steel, stainless steel, gold, silver, platinum or titanium are preferred.

The invention also relates to a hearing aid comprising a hearing aid component coated with a coating according to the invention.

20

### **Brief description of the figures**

The invention will be readily understood from the following detailed description in conjunction with the accompanying figures. As will be realised, the invention is capable of other different embodiments, and its several details are capable of modification in various, obvious aspects all without departing from the invention. Accordingly, the figures and descriptions will be regarded as illustrative in nature and not as restrictive.

Fig. 1 Effect of PFA content in the nanoparticles on contact angle,

30 Fig. 2 XPS spectrum of the CNTs,

Fig. 3a Water droplet on F-GMA-DVB-coated silicon wafer,

Fig. 3b Water droplet on PFA-DVB-coated silicon wafer,

Fig. 3c SEM image of F-GMA-DVB-coated silicon wafer,

- Fig. 3d SEM image of PFA-DVB-coated silicon wafer,  
 Fig. 4a Water droplet on CNT-coated silicon wafer,  
 Fig. 4b Water droplet on CNT-coated PMMA,  
 Fig. 4c Water droplet on CNT-coated PC,  
 5 Fig. 4d Water droplet on CNT-coated CAP/CP,  
 Fig. 4e Water droplet on CNT-coated metal foil,  
 Fig. 4f Water droplet on uncoated metal foil,  
 Fig. 5 SEM image of CNT-coated silicon wafer,  
 Fig. 6a PFA-DVB-based coatings of hearing aid components,  
 10 Fig. 6b Water droplet on PFA-DVB-coated hearing aid component,  
 Fig. 6c PFA-DVB-based coatings of hearing aid components,  
 Fig. 6d Water droplet on PFA-DVB-coated hearing aid component,  
 15 Fig. 7a CNT-based coatings of hearing aid components,  
 Fig. 7b Water droplet on CNT-coated hearing aid component,  
 Fig. 7c CNT-based coatings of hearing aid components,  
 Fig. 7d Water droplet on CNT-coated hearing aid component.

## 20 Detailed description of the invention

In order to more fully detail the present invention the terms used in the definition of the invention are explained in the following.

- A "component for a hearing aid" may be any individual component used in manufacturing a hearing aid, such as housings, casings,  
 25 shells, internal electronic circuitry, transducers, faceplates, grids, barriers, hooks, lids, battery compartments, buttons, switches, manipulators, connectors, sound conduits, electrical wires, ear pieces, earwax guards, FM units etc., or the component may also be an assembly of several such components, or even an essentially fully assembled hearing aid. A  
 30 component may range in complexity from an individual element created from a single material, such as a polymer, a metal, or another appropriate material, to elements comprising several different such materials as well as including mechanical and/or electronic functionalities. Materials

comprising several different materials may also be known as composites. The surface of a component for a hearing may also be referred to as a "hearing aid surface". Such a hearing aid surface may be a metallic, plastic, metallised, painted or otherwise coated surface.

5           The term "precursor molecule" as used throughout this document generally refers to molecules or compounds taking part in chemical reactions. The precursor molecules may be organic molecules which may be polymerised to form a polymer particle. Thus, the precursor molecules may also be described as "monomers". Precursor molecules for po-  
10           lymerisation may have more than one reactive group or moiety, and when the molecule carries two groups of identical reactivity it may be described as "homobifunctional"; likewise, when a molecule carries two groups of different reactivity it may be described as "heterobifunctional". Precursor molecules may also comprise an additional reactive group not  
15           involved in the polymerisation, such as a glycidyl moiety, or a functional group, such as a perfluoro moiety, also not involved in the polymerisation. Such additional reactive groups may be further employed to attach a functional group to a polymer formed in the polymerisation reaction, and when the precursor molecule has a functional group this functional-  
20           ity will be transferred to a polymer formed in the polymerisation reaction. The precursor molecule is preferably organic. It is further preferred that the precursor molecule does not contain any reactive inorganic moieties.

          The organic precursor molecules are polymerised to form or-  
25           ganic nanoparticles. With "organic nanoparticles" is meant that the particles are of an organic, i.e. carbon-based, nature. The organic nanoparticles comprise a base structure of covalently linked carbon atoms, optionally also comprising other covalently linked atoms. The organic nanoparticles preferably do not comprise any metallic or semimetallic  
30           elements as part of the base structure although metal ions, such as ions of alkaline metals, alkaline earth metals or other metals may be bound to the particles via electrostatic interactions. In particular, the organic nanoparticles do not contain any metallic or ceramic parts. The organic nanoparticles may comprise polymer particles or particles based on car-

bon nanotubes (CNTs); in the context of the invention "carbon nanotubes" should be construed broadly to include single walled CNTs, multi-walled CNTs, fullerenes, such as C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, and C<sub>84</sub>, etc.

In the present application the term "nanoparticle" is a particle  
5 within the size range of about 1 nm up to 1000 nm, such as from 1 to 100 nm, or from 10 to 30 nm, e.g. about 20 nm. The size may also be described as the "particle diameter". However, the particles of the present invention need not be round or spherical. In some embodiments the particles may be oblong (meaning that one dimension is larger than the  
10 other two) or shaped as discs or flakes (meaning that two dimensions are larger than the third dimension). In one embodiment it is, however, preferred that the three dimensions of a given particle are approximately equal. It is also preferred that a preparation of particles made according to this embodiment are relatively monodisperse meaning that the particles in the preparation are of approximately the same size. A "particle"  
15 may also appear as a cluster of several smaller particles. In another embodiment the nanoparticles are based on CNTs, and in this case one particle dimension is larger than the other two, e.g. CNT-based nanoparticles may have an approximate average length of 200 nm with a diameter of the tube of about 8 to 10 nm.  
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In the context of this invention "perfluoro moieties" or "perfluoro groups" refer to hydrocarbon chains where at least a fraction of the chain consists of only fluorine and carbon atoms. Typically, the perfluoro moiety will be part of a bigger portion which also has other functional groups, such as an amine group, an acrylate group etc., so that  
25 the perfluoro moiety may be covalently coupled via the other functional group to a group with complementary functionality. For example, an amine group may serve as a nucleophile to react with glycidyl group, or an acrylate group may take part in a polymerisation involving the vinyl  
30 groups of divinyl benzene.

A "volatile solvent" for use in the present invention is a solvent that is liquid at ambient to moderate temperatures and pressure, e.g. such as at about 25°C while retaining a high vapour pressure. The high vapour pressure will allow the volatile solvent to be evaporated quickly

without application of heat. Thus, for example a substrate may be coated with particles suspended in a volatile solvent by applying the suspension to the substrate and allowing the solvent to evaporate at the ambient temperature, i.e. without applying any heat to the substrate. The volatility of the solvent will result in a coating substantially free of residual solvent after evaporation. The solvent is preferably of low reactivity, in particular the solvent is of low reactivity towards chemical moieties in or on the organic nanoparticles, the hearing aid component and the substrate with the hearing aid component. Suited volatile solvents for use in the present invention are low molecular weight ketones, such as acetone, low molecular weight ethers, such as diethyl ether, low molecular weight cyclic ethers, such as tetrahydrofuran, 1,4-dioxan, short chain halogenated alkanes, such as di-, tri- or tetrachloromethane, alkanes, or mixtures of these solvents. Low molecular weight ketones, such as acetone, and low molecular weight cyclic ethers, such as tetrahydrofuran, 1,4-dioxan, or mixtures of these solvents are preferred.

A suspension of nanoparticles for use in the method of the invention may be prepared by mixing the particles with a solvent and exposing the mixture to sonication. In this context "sonication" refers to exposing the mixture of solvent and particles to sound, in particular ultrasound, i.e. sound of a frequency higher than 20,000 Hz. Sonication with ultrasound is expected to disrupt weak physical bonds between particles and between particles and other surfaces thus providing a suspension of the particles with fewer aggregated particles, i.e. the suspension is preferably homogeneous following sonication. Sonication, in particular with ultrasound, may be provided using an ultrasonic bath or by immersing an ultrasonic probe in the suspension. Sonication with ultrasound and appropriate devices are well-known within the art.

The organic nanoparticles may be produced in a micro- or nanoemulsion polymerisation. In its broadest sense this type of polymerisation may be viewed as a polymerisation process performed within the hydrophobic cores of surfactant micelles in an oil-in-water emulsion. In a microemulsion polymerisation an aqueous solution or suspension of a surfactant is prepared and one or more organic precursor molecules

added to the emulsion. While any type of surfactant, such as cationic, anionic, zwitter-ionic or non-ionic, may be used to form the emulsion the concentration of the surfactant must be above its critical micelle concentration (CMC) so that the surfactant will form micelles. When the surfactant is dissolved in water above its CMC the individual surfactant molecules will group together so that the hydrophobic portions will be 'shielded' from the water molecules by the hydrophilic portions. The micelle may be described as having a hydrophobic core surrounded by a hydrophilic outer surface. When an apolar molecule, such as an organic precursor molecule, is present in the aqueous solution of the surfactant the apolar molecule will generally be present inside the micelles. Thereby the size, and other properties, of the micelle can be said to influence on the particles formed in the process.

A preferred surfactant is sodium dodecyl sulfate (SDS). However, in certain embodiments non-ionic surfactants are used. Multiple types of non-ionic surfactants exist and are readily available and known to a skilled person [e.g. Nonionic surfactant: Physical chemistry. Edited by Martin J. Schick, Marcel Dekker, New York (1987)]. These surfactants typically comprise compounds with one or more hydrophilic portions covalently linked to one or more hydrophobic portions; the hydrophilic and hydrophobic portions will normally be linked covalently via ether or ester links, or thioether or thioester links. Different portions may also be indirectly linked to each other via a linker molecule, such as a glycerol molecule where the ether or ester bonds may be formed with the hydroxyls of the glycerol. The different portions may be derived from natural sources, such as from sugar moieties and fatty acids for the hydrophilic and hydrophobic portions, respectively, or the different portions may be prepared artificially. Artificially made portions of surfactants may be constructed from monomers, such as ethylene oxide or propylene oxide, of appropriate characteristics; these monomers may be joined in polymeric blocks of the same type, and hydrophobic and hydrophilic blocks may then be joined together to form a block copolymer. Block copolymers may have two or more blocks, for example in a tri block copolymer the blocks may be linked in the following pattern 'hydrophilic-

hydrophobic-hydrophilic'. The size of a surfactant may range from a few hundred Daltons to several thousands Daltons for polymeric types of surfactants.

"Superhydrophobicity" is used to describe a material property, i.e. wettability, where a drop of water will slide or roll off a "superhydrophobic" surface. This property may be more precisely characterised by the contact angle between the water droplet and the surface. Thus, one quantitative measure of the wetting of a solid by a liquid is the contact angle, which is defined geometrically as the internal angle formed by a liquid at the three-phase boundary where the liquid, gas and solid intersect. Contact angle values below 90° indicate that the liquid spreads out over the solid surface in which case the liquid is said to wet the solid (this may be termed "hydrophilic"). If the contact angle is greater than 90° the liquid instead tends to form droplets on the solid surface and is said to exhibit a non-wetting (or "hydrophobic") behaviour.

In this terminology it follows that the larger the contact angle, the better the ability of a surface to repel a respective substance. For untreated surfaces the contact angle is normally less than 90°. It is well known in the art to coat a solid with a hydrophobic layer in order to increase the contact angle and thereby obtain a moisture repellent surface. Such a surface coating may typically increase the contact angle of water to around 115-120°. A structural modification, such as microstructuring, of the surface of certain materials will improve the ability of the material to repel aqueous and oily substances. Several methods have been employed in the prior art to provide a microstructure to a surface, such as physical etching or chemical etching. When the surface is modified by a combination of such structuring and a hydrophobic coating, e.g. with a chemical compound with low surface energy, such as a perfluorocompound, the contact angle of water exceeds 145° for a variety of materials, and this characteristic is termed superhydrophobic in the context of this invention. In addition to the superhydrophobic surface characteristics, the modified materials may also obtain superoleophobic surface characteristics.

With the method of the present invention it is possible to pro-

vide a superhydrophobic coating to a substrate material, such as a hearing aid component, without a need for microstructuring the surface.

A preferred embodiment of the invention relates to a method for coating a hearing aid component, the method comprising the steps of:

- 5 - providing a hearing aid component;
- providing organic nanoparticles by forming an aqueous emulsion of a first organic precursor molecule, a second organic precursor molecule and a surfactant; and initiating a reaction involving the first organic precursor molecule to form polymer particles;
- 10 - suspending the nanoparticles in a volatile solvent;
- applying the suspension of the nanoparticles to the hearing aid component;
- evaporating the volatile solvent to form a coating.

In this embodiment, the first organic precursor molecule is divinyl benzene (DVB) and the second organic precursor molecule may be glycidyl methacrylate (GMA) or a perfluoro acrylate (PFA), such as 1H,1H,2H,2H-heptafluorodecyl acrylate.

More specifically, in the step of providing the nanoparticles an aqueous solution of a surfactant is initially prepared. Although sodium dodecyl sulfate (SDS) is preferred, the method is not limited to this surfactant. It has been found by the present inventors that the size of the nanoparticles prepared in the method are influenced by the concentration of SDS; the concentration of the surfactant must be above the CMC, and for SDS it should be lower than 30%(w/w), for example within the range of 1 to 20%(w/w), e.g. 10 to 15%(w/w), such as about 12%(w/w). An SDS concentration of 12%(w/w) has been found to enable manufacture of nanoparticles of approximately 20 nm size. It is preferred that the particles are within 10 to 30 nm, such as about 20 nm.

It is speculated by the inventors that other types of surfactants may be employed in other concentrations, and that such other surfactants may thus be used to produce nanoparticles of other sizes and shapes. For example, it is expected that the size and dispersity of the nanoparticles may be controlled by considering the CMC, the HLB, and the size of micelles typical for a given surfactant.

The first and the second precursor molecules are now added to the surfactant solution. For example, the first precursor molecule, e.g. DVB is added to the solution of the surfactant, e.g. SDS, at a concentration of about 1 to 10 g/L, such as about 5 g/L, followed by the second precursor molecule. When GMA or PFA are used as the second precursor molecule these are added to the mixture in a molar ratio of GMA or PFA of at least 50% GMA or PFA, as appropriate, compared to the total of GMA or PFA and DVB. The molar ratio of PFA should be within in the range of 50 to 80%, preferably about 55%. The molar ratio of GMA is preferably in the range of 70 to 90%. This ratio of GMA is used in order to provide enough active epoxy groups in the nanoparticles for a further coupling reaction.

After addition of the precursor molecules to the surfactant solution, an emulsion may be allowed to form by exposing the mixture to shear forces, such as by stirring, for an appropriate amount of time, for example up to 2 hours, such as up to 1 hour, such as about 30 minutes.

If required by the nature of the precursor molecules an initiator molecule, e.g. a free-radical initiator molecule, may now be added to the emulsion. For example, when DVB is reacted with acrylate containing second precursors, such as GMA or PFA, the water soluble free-radical initiator 2,2'-azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (also known as VA-044) is preferred. The amount of initiator for use in a polymerisation reaction is well-known to the skilled person. The reaction may be initiated by increasing the temperature of the emulsion. The reaction temperature may be up to the boiling point of the emulsion, for example in the range of 20 to 100°C, or 40 to 80°C. A temperature about 60°C is preferred for reacting DVB with PFA or GMA. When a free-radical initiator, such as VA-044, is used the reaction is initiated by increasing the temperature to above the decomposition temperature of the initiator. The reason for using VA-044 as the initiator is that it has a relatively low decomposition temperature of 44°C. It has been found that a high polymerisation temperature will result in aggregation of nanoparticles and wide size distribution of the nanoparticles. Thus, by using VA-044 the polymerisation may be performed at temperatures above 44°C,

such as about 60°C, at which temperature the precursor molecules polymerise to form nanoparticles of an advantageous size, e.g. about 20 nm, size distribution and morphology.

The reaction of the first and the optional second precursor molecule may be terminated after an appropriate reaction time has passed, for example after up to 24 hours, up to 16 hours, up to 8 hours, or up to 4 hours, such as about 1 hour. The termination may be obtained by separating the formed nanoparticles from unreacted precursor molecules in the emulsion. It is preferred to aggregate the nanoparticles and subsequently separate the nanoparticles from the liquid using filtration. The nanoparticles may be aggregated by adding a solvent, such as methanol, to the reaction mixture, or by adding the reaction mixture to the solvent. Aggregation conditions may also be selected from well-known techniques for the precipitation of proteins. Thus, relevant parameters for consideration are the expected hydrophobicity of the formed nanoparticles, their isoelectric point, i.e. the pH at which the nanoparticles have zero charge, the pH of the emulsion, e.g. at the isoelectric points the nanoparticles may aggregate more easily than at a higher or a lower pH, ionic strength of the emulsion, polarity of the solvent added to the emulsion, etc.

When GMA is employed as the second organic precursor molecule the method includes a step of functionalising the organic nanoparticles with perfluoro moieties. In this step the epoxy groups of the glycidyl moieties are reacted with a molecule containing a perfluoro group and a nucleophilic group, such as heptadecafluoroundecylamine (HTFA). The reaction will generally be performed under conditions promoting a nucleophilic substitution reaction, for example in a solvent such as dimethylformamide (DMF). Appropriate reaction conditions are well-known within the art, but the reaction will generally be performed in a large molar excess of the molecule containing a perfluoro group and a nucleophilic group to the nanoparticles.

In another preferred embodiment the organic nanoparticles comprise CNTs. CNTs may be functionalised with perfluoro moieties in a process comprising the steps of subjecting the carbon nanotubes to oxi-

dising conditions to form carboxylate groups on the carbon nanotubes; and coupling perfluoro moieties to the carbon nanotubes via the formed carboxylate groups. Any types of CNTs are appropriate for use in the method and these may be prepared using methods that are well-known  
5 within the art, for example by arc discharge, laser ablation, high pressure carbon monoxide, chemical vapour deposition etc. The CNTs are oxidised to introduce carboxylate groups on the surface of the CNTs. Without being bound by any particular theory it is suspected that the oxidising conditions will introduce the carboxylate groups at sites with  
10 defects in the structure. With "defects" is to be understood that the structure deviates from the ideal hypothetical structure of the carbon skeleton. Such defects occur at the end of the CNTs but may also occur along the sides. The oxidising conditions preferably comprise treating the CNTs with the so-called Piranha solution, i.e. a mixture of concentrated  
15 sulphuric acid with aqueous hydrogen peroxide (e.g. 9:1 of concentrated  $H_2SO_4$  to 30% aqueous  $H_2O_2$ ); the reaction will typically be stirred and may be performed for a reaction time up to 24 hours, for example up to 16 hours, such as about 12 hours.

The formed carboxylate groups may be functionalised using any  
20 appropriate coupling chemistry for functionalising carboxylate groups as discussed above. It is preferred to react the oxidised CNTs with a perfluoro molecule with an amine group via a carbodiimide compound, such as N,N'-dicyclohexylcarbodiimide (DCC). A preferred perfluoro molecule with an amine group is HTFA. The reaction to perfluoro functionalise the  
25 CNTs is preferably done at a large molar excess of HTFA to CNTs. The reaction may be performed for a reaction time up to 24 hours, for example up to 16 hours, such as about 12 hours. The functionalised CNTs may be separated from the reactants, e.g. carbodiimide compounds, HTFA and other added substances, by filtration and subsequent washing  
30 with an appropriate solvent, such as ethanol.

Non-modified CNTs cannot immediately be homogeneously suspended into most kinds of solvents because of the strong molecular interactions between CNTs and it has been found by the present inventors that it is advantageous to functionalise the CNTs in order to suspend

the CNTs in a volatile solvent for coating a hearing aid component. Unfunctionalised CNTs were found not to disperse sufficiently homogeneously to provide a suspension suited for coating because of the strong interactions between CNTs.

5           Either type of nanoparticles discussed above may be suspended in a volatile solvent, preferably acetone, to prepare a coating suspension. It is preferred to spray coat the coating suspension onto a substrate comprising a hearing aid component and it has been found by the inventors that the properties of the resulting coating depends on the  
10           concentration of nanoparticles in the coating suspension. The concentration of nanoparticles can thus be regarded as an important parameter for obtaining a desired hydrophobicity, for example superhydrophobicity. The nanoparticle concentration is preferably within the range of 0.1 to 5 g/L. When the nanoparticles are produced by polymerising DVB and ei-  
15           ther GMA or PFA, it is preferred that the concentration of nanoparticles in the coating suspension is in the range of 0.5 to 1.5 g/L, such as 1 g/L. When functionalised CNTs are employed a preferred concentration range is from 0.1 to 1 g/L, such as 0.5 g/L. Application of suspensions of nanoparticles outside the indicated ranges was found to produce sur-  
20           faces not having superhydrophobic properties.

          The suspension of nanoparticles in the volatile solvent is preferably homogenised by subjecting it to sonication. Sonication, e.g. using an ultrasound probe, a "sonicator", will disrupt weak interactions between the nanoparticles to suspend the particles and provide a homoge-  
25           neous suspension. Thus, the nanoparticle suspension is sonicated until a homogeneous suspension is obtained. Sonication may be performed for approximately 5 to 15 minutes, for example at least 10 minutes although longer sonication times are also contemplated.

          Following application of the coating suspension with the  
30           nanoparticles the solvent is allowed to evaporate. The evaporation is preferably performed at ambient, i.e. room, temperature. It is believed that the volatility of the solvent leads to formation of a tightly packed layer of nanoparticles with features and structures of sizes comparable to the size of the nanoparticles employed, i.e. the features and struc-

tures have sizes ranging from the size of the smallest nanoparticles up to a few hundred nanometers. An illustration of a superhydrophobic coating of the invention is illustrated by scanning electron microscopy (SEM) of a coated substrate in Fig. 3c, 3d and 5. It is further believed that the features and structures in combination with the hydrophobic properties of the nanoparticles lead to a superhydrophobic coating of the coated substrate. It is suspected that by increasing or decreasing the evaporation rate of the volatile solvent, e.g. by increasing or decreasing the temperature during evaporation or decreasing or increasing the ambient pressure, the exact shape of the features and structures may be controlled.

The superhydrophobicity of a coated substrate may be analysed by measuring the contact angle between a droplet of water and the coated surface. Different substrates were coated according to the method of the invention and the results, expressed as the water-substrate contact angles, are given in Table 1.

Table 1, water-substrate contact angles after coating of various substrates with perfluoro polymeric nanoparticles or carbon nanotubes

| <b>Substrate</b> | <b>Particle types for coating</b> |                              |
|------------------|-----------------------------------|------------------------------|
|                  | <b>Carbon nanotubes</b>           | <b>Polymer nanoparticles</b> |
| Silicon wafer    | 157°                              | 161°                         |
| PMMA             | 152°                              | 153°                         |
| PC               | 151°                              | -                            |
| CAP/CP           | 122°                              | -                            |
| Metal            | 158°                              | 159°                         |
| Hearing aid      | 153°                              | 163°                         |
| Uncoated metal   | 88°                               |                              |

20

The invention will now be illustrated in the following non-limiting examples.

## Examples

### 25 Example 1, F-GMA-DVB-particles

A batch of polymer nanoparticles of the present invention were prepared by emulsifying glycidyl methacrylate (GMA) and divinyl benzene (DVB) in

a 12%w/w solution of sodium dodecyl sulfate (SDS) under nitrogen. Initially, the solution of the SDS-surfactant was prepared by dissolving 2.4 g of SDS in 20 mL of degassed milliQ water. Subsequently, 0.4 g of GMA and 0.1 g of DVB were added to the surfactant solution and the mixture was subjected to vigorous stirring for 30 min under a nitrogen atmosphere. Then 12 mg of a water soluble initiator, 2,2'-Azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044), was added. The microemulsion was purged with nitrogen for further 30 min, and then heated to 60°C to initiate polymerisation. The polymerisation was carried out for 1 hour under nitrogen atmosphere, and a turbid milky solution was obtained. The resulting suspension was immediately poured into 200 ml methanol to precipitate the polymer nanoparticles and filtered through a polycarbonate (PC) membrane filter (of 0.2 µm poresize). The filtered nanoparticle cake was washed with methanol and then dried in a vacuum desiccator for further modification.

The particles were subsequently perfluoro functionalised by reacting the particles as follows. From the prepared particles, 50 mg dry GMA-DVB nanoparticles were added to 5 mL dimethylformamide (DMF) and the mixture was subjected to sonication until a milky suspension was obtained. Then, 0.5 g heptadecafluoroundecylamine (HTFA) was added into the suspension. The mixture was heated to 70°C for 2 days. The resulting suspension was quickly poured into 50 mL methanol to quench the reaction and precipitate the polymer nanoparticles (i.e. the "F-GMA-DVB-particles"), which were then filtered through a PC membrane filter (0.2 µm). The filter nanoparticle cake was washed with methanol and then suspended in a polar, volatile solvent for coating.

During the experiment, it was found that the particle size and distribution were sensitive to the surfactant concentration. In our experiment, the surfactant concentration was kept at 12%w/w since this concentration was found to yield particles of an optimal particle size, particle morphology and size distribution (e.g. particles of approximately 20 nm diameter). The concentration of the SDS was above the critical micelle concentration (CMC), and the inventors suspect that the size of the micelles formed gave an indication of the final nanoparticles pre-

pared in the process. Thus, the surfactant and its concentration appeared to be an important parameter for the final particles produced and thereby also for a coating produced with these particles. The skilled person has a wide selection of surfactants available, e.g. anionic, cationic, non-ionic and zwitterionic, and in general a surfactant and the concentration in which to use it may be selected to give micelles in solution of a desired size and morphology. Other parameters affecting the size of the micelles are the temperature, the ionic strength of the solution, the presence of other solvents, pH, shear forces etc. These parameters may therefore also be modified in order to control the size of the micelles and thereby the particles produced in the process.

#### Example 2, PFA-DVB-particles

In an alternative approach, perfluoro functionalised nanoparticles were prepared by reacting a first organic precursor molecule, i.e. DVB, with a second organic precursor molecule carrying perfluoro groups, i.e. perfluoro acrylate (PFA). In this process, 4.8 g of SDS was dissolved in 40 mL degassed milliQ water to make a 12%w/w solution. To this solution was then added 0.1 g DVB and varying amounts of perfluoroacrylate (PFA) (1H,1H,2H,2H-heptafluorodecyl acrylate) together with 3.0 ml 1-pentanol. The amount of PFA was selected so as to give molar ratios of PFA to DVB of from 10% PFA:90% DVB to 80% PFA:20% DVB; for example, in order to provide a molar ratio of 55% PFA:45% DVB, 0.4 g of PFA was added to the mixture. Several different ratios were examined as illustrated in Fig. 1 showing the contact angles obtained from coatings with the nanoparticles prepared using different PFA:DVB ratios. Since the polymerisation was initiated by free radicals, it is important to get rid of oxygen, an inhibitor of free radical. Therefore, the reaction mixture was kept under nitrogen. The mixtures were emulsified under nitrogen for 30 min and while subjected to vigorous stirring. To each reaction mixture was then added 24 mg of the water soluble initiator 2,2'-azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044). The microemulsions were purged with nitrogen for further 30 min, and then heated to 60°C to initiate polymerisation. The polymerisation

was carried out for 2 hours under nitrogen atmosphere, and a turbid milky suspension was obtained. The resulting suspensions were each quickly poured into 400 mL methanol to precipitate the polymer nanoparticles (i.e. the "FMA-DVB-particles"), and the particles were filtered, washed and resuspended in a polar, volatile solvent as described above.

The same observations as seen above for the glycidyl-reactive particles regarding the concentration of the surfactant applied when particles were prepared directly with perfluoro groups. Thus, the concentration of SDS was an important parameter for controlling the size of the particles, and 12%w/w was found to yield optimal results.

The purity of the DVB employed was about 80% (Sigma-Aldrich). This purity was used to calculate the molar ratio between DVB and PFA employed in the reaction. It was found that the value should be higher than 40% in order to provide a superhydrophobic coating, i.e. a contact angle between water and a coated surface  $>150^\circ$  (Fig. 1), since lower values resulted in inferior results with non-superhydrophobic coatings. The molar ratio of 55% PFA to 45% DVB was found to give the best results. Further increasing molar ratio of PFA to DVB might result in solubility problem of nanoparticles in the coating solvent (acetone).

#### Example 3, Preparation of perfluoro-functionalised carbon nanotubes

Single-walled carbon nanotubes (CNTs) were obtained from a commercial source (e.g. Sigma-Aldrich Co.) and functionalised as outlined below. The CNTs were supplied in a dry form and an acetone solution of CNTs of the present invention was prepared by initial introduction of carboxylic groups and subsequent coupling of perfluorocarbon onto the CNTs.

To introduce carboxylic acid groups on the surface of the CNTs, 14 mg of CNTs were added into 5 mL of 9:1 concentrated  $\text{H}_2\text{SO}_4$  / 30%  $\text{H}_2\text{O}_2$  aqueous solution. This solution is also known as "Piranha solution" or "Piranha acid" and is known within the field as a powerful oxidising agent for e.g. removal of organic contaminations from various substrates. The mixture was subjected to stirring for 30 min. An additional amount of 15 mL of Piranha solution was then added and the mixture

was left overnight. The solution was diluted 250 times using distilled water and filtered through a 0.2  $\mu\text{m}$  Millipore polycarbonate filter membrane. The resulting solid product was washed with distilled water until the filtrates reached pH 7. The resulting carboxylated CNTs were further  
5 washed thoroughly with acetone and dried under vacuum.

The carboxylic acid groups resulting from the above treatment were further functionalised by coupling perfluoro moieties via amide links. An activation solution was prepared from N,N'-dichlorohexylcarbodiimide (DCC, 94 mg, 0.45 mmol), 4-(dimethylamino)  
10 pyridine (DMAP, 34 mg, 0.28 mmol) and 1-hydroxybenzotriazole anhydrous (HOBT, 61 mg, 0.45 mmol) by dissolving in 20 mL dimethyl sulfoxide (DMSO). In a routine experiment, 30 mg of the carboxylated CNTs were added to the activation solution and the solution was subjected to sonication for 2 hours. Subsequently, 0.5 mL heptadecafluoroundecylamine was added and the coupling reaction carried out  
15 overnight. The suspension was diluted with ethanol and filtered through a 0.2  $\mu\text{m}$  Millipore polycarbonate filter membrane. The resulting perfluorocarbon modified CNTs were washed thoroughly with ethanol and then dried under vacuum. The modification process was monitored by  
20 XPS analysis (X-ray Photoelectron Spectroscopy) (Fig. 2). Analysis of fluorine region showed a new peak at 688.08 eV from F1s for the perfluoro-functionalised CNTs ("CNTs-F" in Fig. 2), which was not detectable in unfunctionalised CNTs ("CNTs" in Fig. 2) or carboxylated CNTs ("CNTs-COOH" in Fig. 2). This binding energy is typical from fluorine in  
25 an organic C-F bond suggesting that perfluoro compound was covalently bonded to CNTs. A new visible peak at 400.08 eV from N1s also confirmed that carboxylic acid groups were successfully activated by DCC and a new amide bond was formed in CNTs.

#### 30 Example 4, Coating of substrates with nanoparticles

The two types of perfluorofunctional particles and the perfluoro functionalised CNTs were employed to coat various substrates with the nanoparticles. To prepare a suspension, 0.1 to 2 g/L particles were suspended in a solvent by sonicating the particles for at least 10 min. The following

polar, volatile solvents were tested: acetone, tetrahydrofuran, 1,4-dioxan. In a typical experiment, 4 mL prepared suspension was sprayed onto a substrate using an airbrush tool with pressured air flow (3 bar). For the F-GMA-DVB particles and the PFA-DVB particles, the coatings  
5 were applied to substrates of a silicon wafer, polymethyl methacrylate (PMMA), metal surfaces and a substrate with hearing aid components. The CNT-based nanoparticles were applied to polymeric substrates (e.g. polycarbonate (PC), PMMA or cellulose acetate propionate/cellulose propionate (CAP/CP)), a metal foil and a surface with hearing aid com-  
10 ponents. After application of a suspension with the airbrush tool, the solvent was allowed to evaporate at ambient temperature, e.g. about 25°C with no applied heating, to provide the final coating. The coatings were analysed by measuring the contact angle between a droplet of water and the substrate. Contact angles were measured using a Kruss Drop Shape  
15 Analysis System (DSA10-Mk2, Kruss GmbH, Germany). The apparatus applied a water droplet of a volume of 2.5 µl to the substrate and the droplets were recorded photographically. Contact angles were measured in the recorded image and the average value of three measurement made at different positions of the same sample was adopted as the con-  
20 tact angle.

Exemplary results for acetone suspensions of particles produced in Example 1 and 2 are given in Fig. 3, showing droplets of water placed on silicon wafers coated with the two coatings (panels a and b) and SEM images (panels c and d) of the coatings. The effect of the molar compo-  
25 sition of the polymerisation mixture of Example 2 is illustrated in Fig. 1, where the contact angle between water and a silicon wafer substrate coated with the particles is shown vs. the molar ratio of PFA in the reaction mixture.

Contact angles obtained from coatings based on CNTs (Example  
30 3) are illustrated and summarised in Fig. 4, showing water droplets on a silicon wafer (panel a), PMMA (panel b), PC (panel c), CAP/CP (panel d), a metal foil (panel e); a water droplet is also shown placed on an uncoated metal substrate (panel f).

Table 1 summarises contact angles obtained between the differ-

ent substrates coated with particles produced in Example 2 and 3; the results presented in the Table are from 1 g/L suspensions of the particles of Example 2 and 0.5 g/L of particles of Example 3.

5 The quality of the coating, such as the uniformity and the appearance of the nanoparticles, e.g. the size of the particles, was controlled by scanning electron microscopy (SEM) of silicon wafers coated with acetone suspensions of particles of Example 1, 2 and 3, as shown in Fig. 3c, 3d and 5, respectively.

10 Of the tested solvents it was found that acetone gave better overall results than the other solvents. Especially it was found that acetone provided easier handling and fast evaporation with the airbrush tool. Different particle concentrations were tested and the indicated contact angles were produced with a concentration of 1 g/L for particles of Example 2, and 0.5 g/L for those of Example 3. The inventors suspect  
15 that at these respective concentrations for the two types of particles there is a balance between the amount of particles and evaporation of the solvent to provide a sufficiently thick layer of particles while still retaining a nanostructure on the coated surface to provide a stable, superhydrophobic coating.

20 Inspection of the SEM images in Fig 2 indicates that both types of polymer-based particles (i.e. of Example 1 and 2, respectively) containing the DVB-polymer provided coatings with particles of approximately 20 nm size arranged in a random, tightly packed structure with micro- and nanoscaled features. It is believed that quick evaporation of  
25 the volatile solvent causes the formation of the micro- and nanoscaled features due to the strong driving force of the solvent to evaporate from the liquid state. It is in turn further believed that this same effect also results in a tight packing of the particles on the surface. When the particle concentration deviated from the optimal concentration of 1 g/L it was  
30 found that both higher and lower concentrations resulted in fewer micro- and nanoscaled features, which seems to be the cause for lower contact angles between water and a coated substrate observed in these cases. The thickness of the coatings appears to be about 100 to 1000 nm.

The CNT-based particles have a different shape, i.e. fibrous with

long, narrow strands, where the length of each strand is about 200 nm and the diameter of about 8 to 10 nm. The CNT-based particles also yielded superhydrophobic coatings on several chemically different substrates. As for the particles of Example 1 or 2, the coatings showed a tightly packed structure with micro- and nanoscaled features when observed by SEM (See Fig. 5). However, in this case the optimal concentration for use during the coating step was lower than for the particles of Example 1 and 2. From Fig. 3 to 7, and as summarised in Table 1, it is evident that the nanoparticle coatings generally provided contact angles  $>150^\circ$  for the substrates so that the coatings can be said to be superhydrophobic.

Fig. 6 shows hearing aid components coated with a suspension of particles according to Example 2, and hearing aid components coated with particles of Example 3 are shown in Fig. 7. In both figures, panels a) show the substrates before ('-') and after ('+') coating, and panels b) show the corresponding substrates with a droplet of water applied to the substrates. Panels c) and d), respectively, illustrate different substrates with coated or uncoated hearing aid components and a water droplet placed on the coated substrates.

A particle concentration of 1 g/L of the particles of Example 2 was applied as described above to obtain contact angles of  $150^\circ$  and  $163^\circ$  for panels b) and d), respectively, of Fig. 6. The hearing aid substrates coated with particles of Example 3 likewise showed contact angles indicating superhydrophobicity as seen from Fig. 7. It is noted that the simple coating method employing direct spray coating of hearing aid components in a partly assembled hearing aid provided a superhydrophobic coating to the substrate materials. As is evident from panel a) of Fig. 6, the coating (indicated with a '+') was barely visible on the substrate when compared to the uncoated substrate (indicated with a '-'). Furthermore, neither type of coating appeared to have an effect on the electric properties of the components so that the coated, partly assembled hearing aids could be employed to assemble fully functional hearing aids when coated with either particles of Example 2 or Example 3. This coating method is therefore advantageous since no microstructuring of

the substrate is necessary prior to the coating, it does not involve any heating step or exposure to UV-radiation or the like to cross-link reactive groups and the coating process does not jeopardise the microelectronic components.

## P A T E N T   C L A I M S

1. A method for coating a hearing aid component, the method comprising the steps of:
  - providing a hearing aid component;
  - 5        - providing organic nanoparticles;
  - suspending the nanoparticles in a volatile solvent;
  - applying the suspension of the nanoparticles to the hearing aid component;
  - evaporating the volatile solvent to form a coating.
- 10        2. A method for coating a hearing aid component according to claim 1 further comprising a step of functionalising the organic nanoparticles with perfluoro moieties.
3. A method for coating a hearing aid component according to claim 1 or 2, wherein the step of providing organic nanoparticles comprises forming an aqueous emulsion of a first organic precursor molecule and a surfactant; and initiating a reaction involving the first organic precursor molecule to form polymer particles.
- 15        4. A method for coating a hearing aid component according to claim 1 or 2, wherein the step of providing organic nanoparticles comprises forming an aqueous emulsion of a first organic precursor molecule, a second organic precursor molecule and a surfactant; and initiating a reaction involving the first and the second organic precursor molecules to form polymer particles.
- 20        5. A method for coating a hearing aid component according to claim 4, wherein the first organic precursor molecule is divinyl benzene (DVB) and the second organic precursor molecule is glycidyl methacrylate (GMA) or perfluoro acrylate (PFA).
- 25        6. A method for coating a hearing aid component according to claim 1 or 2, wherein the organic nanoparticles comprise carbon nanotubes (CNTs).
- 30        7. A method for coating a hearing aid component according to claim 6, wherein the carbon nanotubes are functionalised with perfluoro moieties in a process comprising the steps of subjecting the carbon nanotubes to oxidising conditions to form carboxylate groups on the car-

bon nanotubes; and coupling perfluoro moieties to the carbon nanotubes via the formed carboxylate groups.

8. A method for coating a hearing aid component according to any of the preceding claims, wherein the volatile solvent is acetone.

5           9. A method for coating a hearing aid component according to any of the preceding claims, wherein the nanoparticles are subjected to sonication in order to suspend the nanoparticles in the volatile solvent.

10           10. A method for coating a hearing aid component according to any of the preceding claims, wherein the nanoparticles are suspended at a concentration of 0.1 to 5 g/L in the volatile solvent.

11. A coating for a hearing aid component, wherein the coating is produced in a method according to any one of claims 1 to 10.

12. A coating for a hearing aid component according to claim 11, wherein the coating is superhydrophobic.

15           13. A hearing aid component provided with a coating according to any of claims 11 to 13.

14. A hearing aid component according to claim 13, wherein the component provided with the coating comprises an outer surface of a polymeric material.

20           15. A hearing aid component according to claim 14, wherein the polymeric material is polyoxymethylene (POM).

16. A hearing aid component according to claim 14, wherein the polymeric material is acrylonitrile butadiene styrene (ABS).

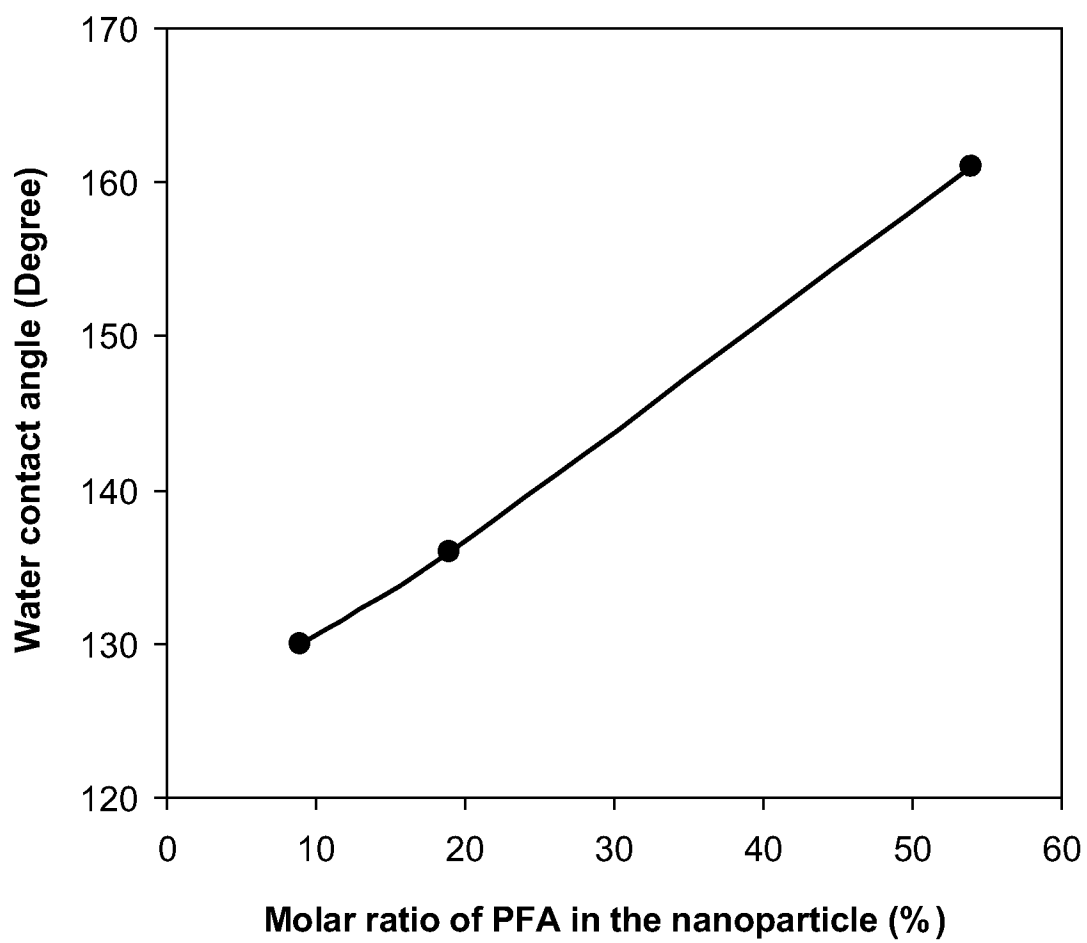
25           17. A hearing aid component according to claim 14, wherein the polymeric material is acrylonitrile butadiene styrene/polycarbonate (ABS/PC).

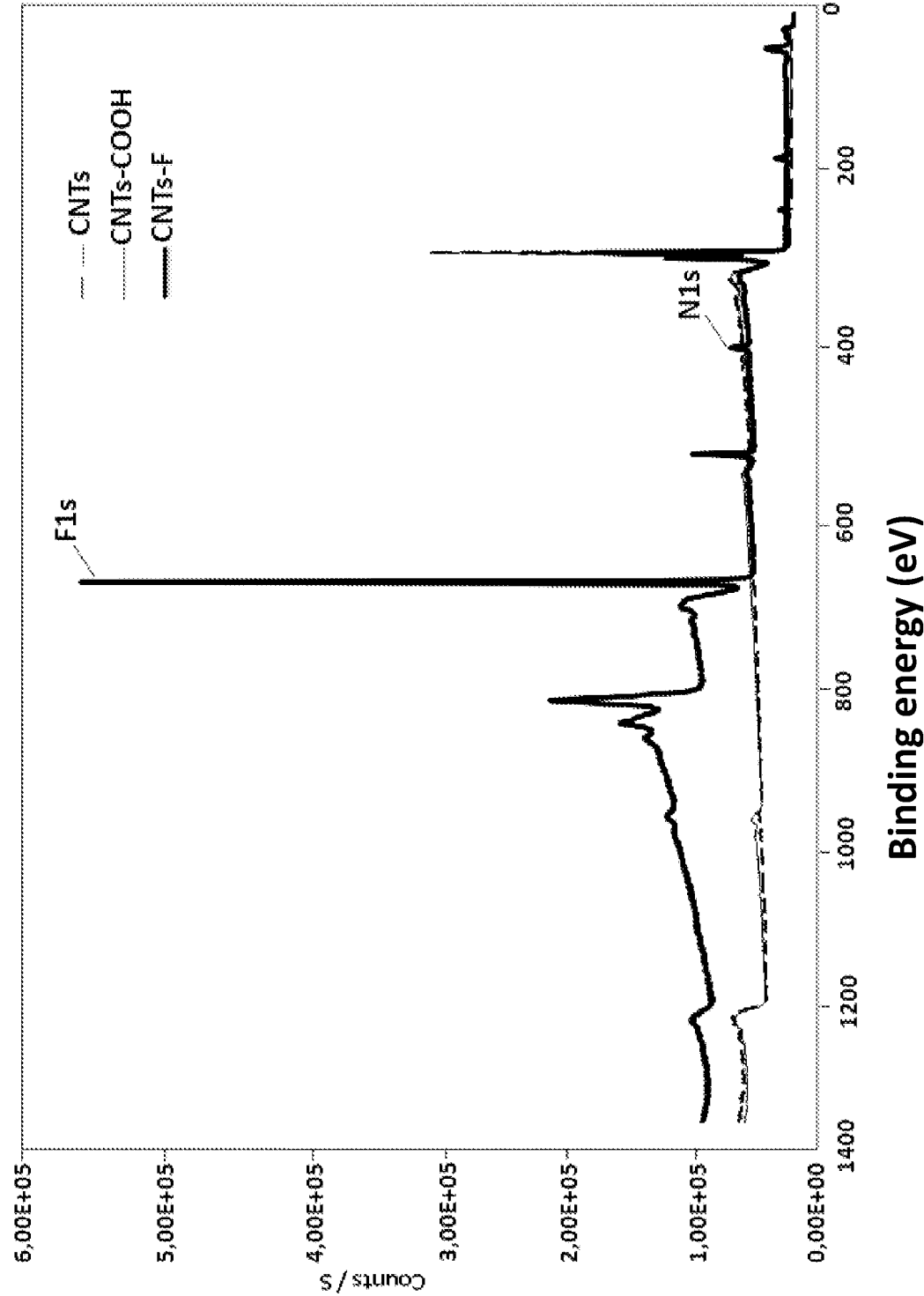
18. A hearing aid component according to claim 13, wherein the component provided with the coating comprises an outer surface of a metallic material.

30           19. A hearing aid component according to claim 18, where the metallic material is steel.

20. A hearing aid comprising a component according to any one of claims 13 to 19.

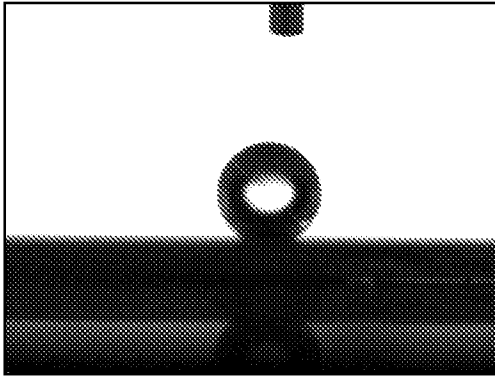
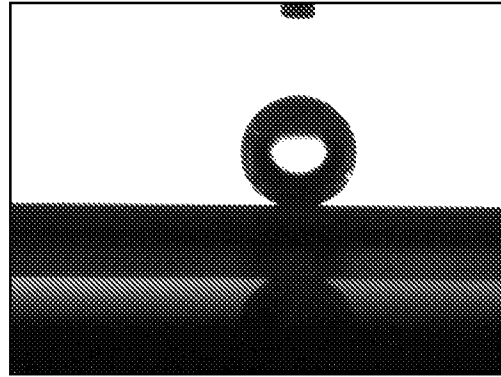
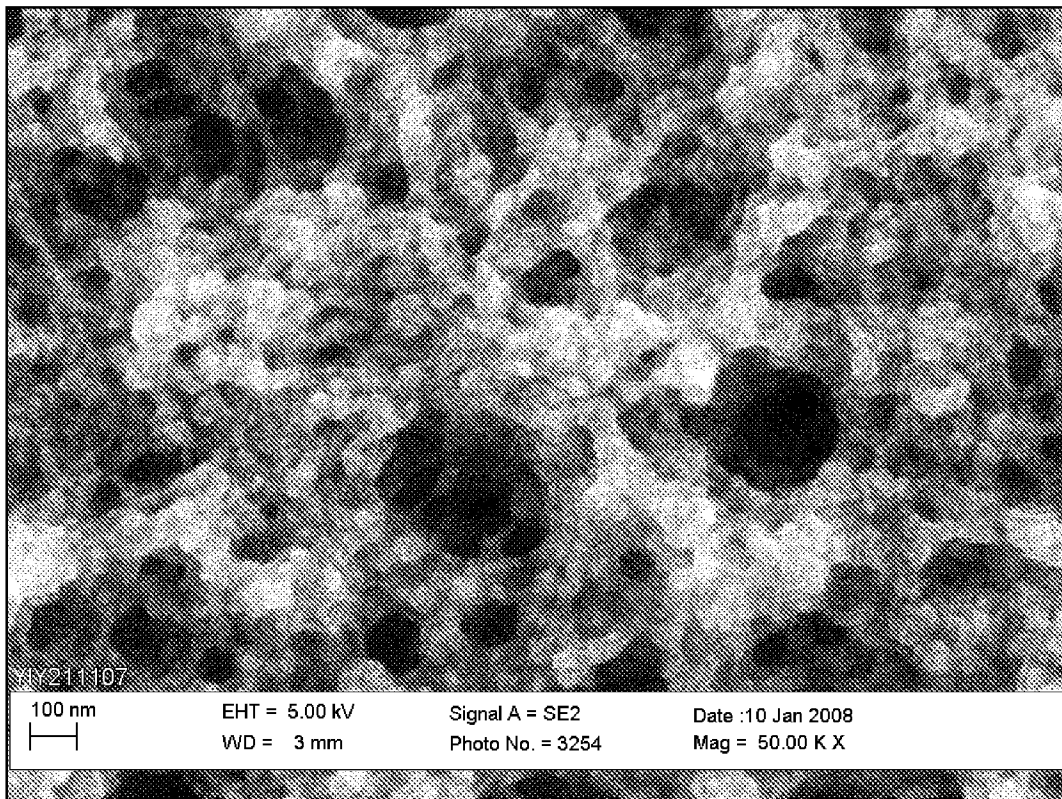
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**Fig. 1**

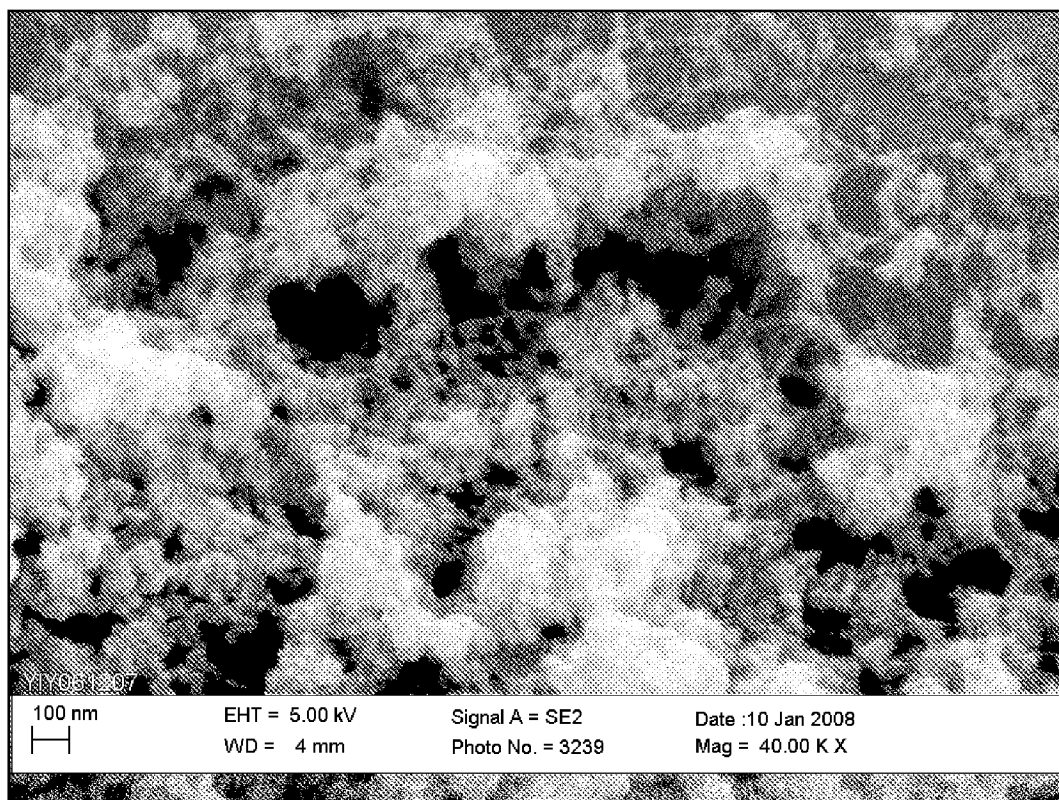
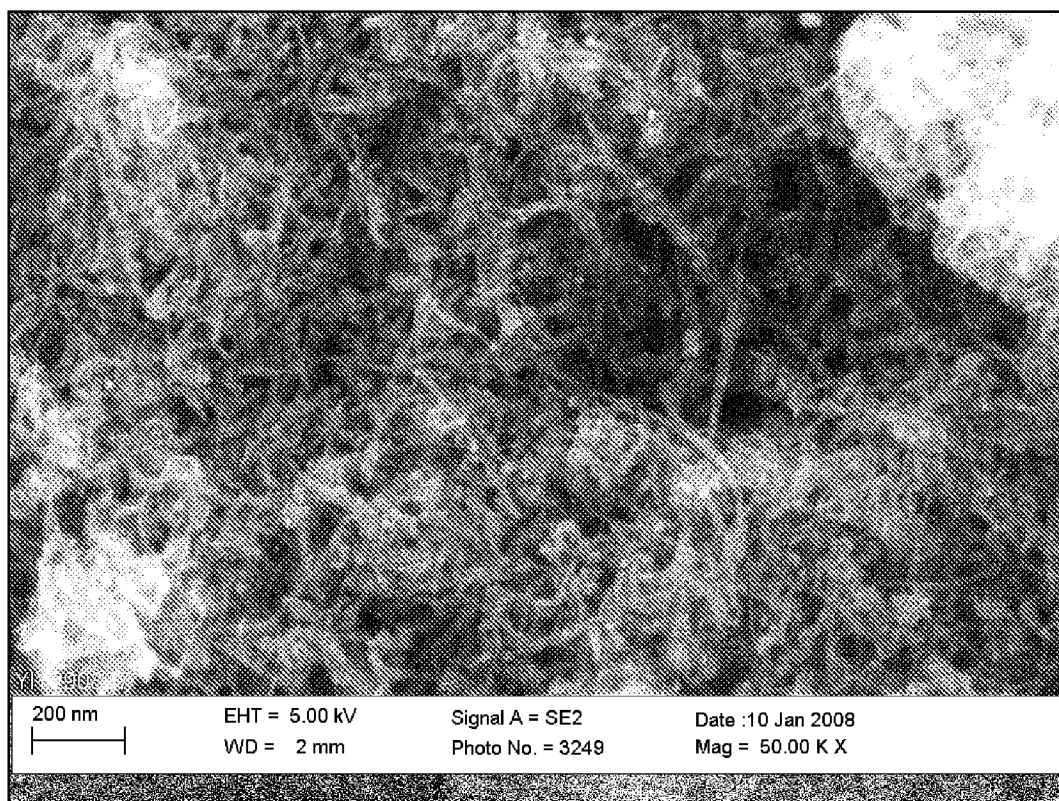


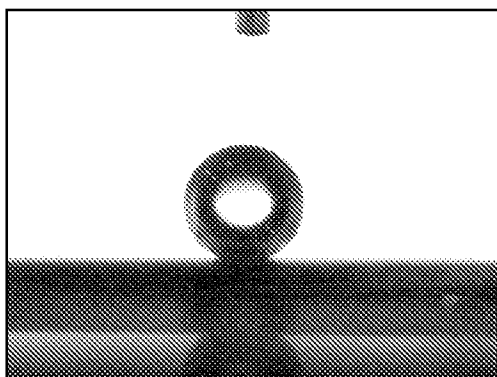
**Fig. 2**

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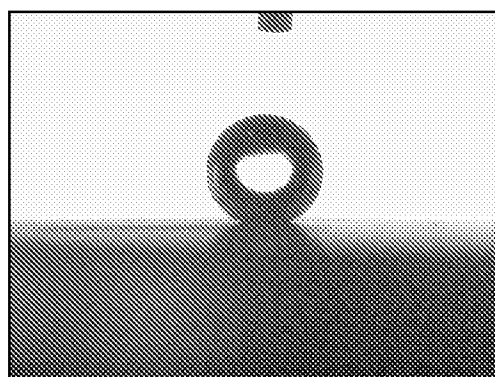
**Fig. 3a****Fig. 3b****Fig. 3c**

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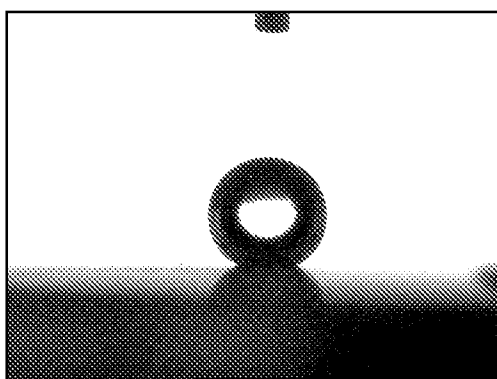
**Fig. 3d****Fig. 5**



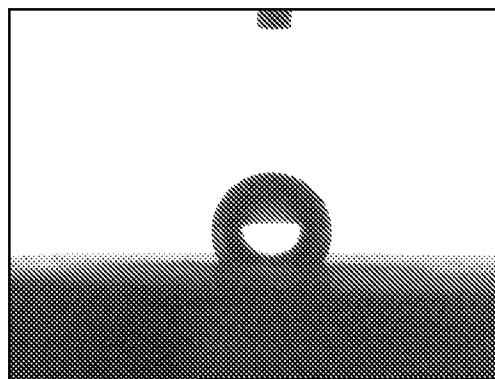
**Fig. 4a**



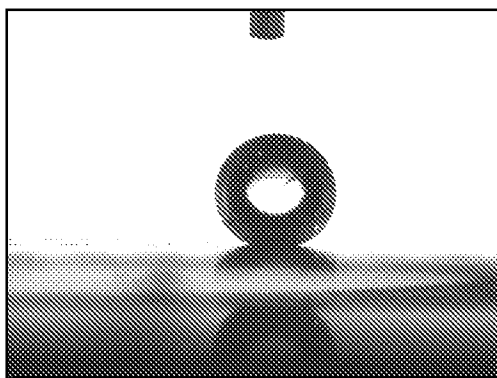
**Fig. 4b**



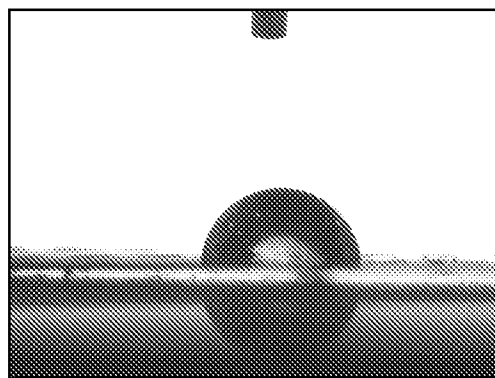
**Fig. 4c**



**Fig. 4d**

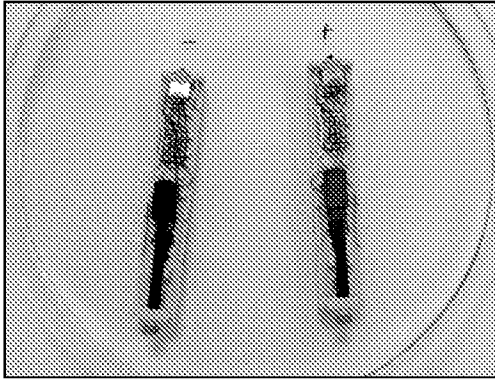


**Fig. 4e**

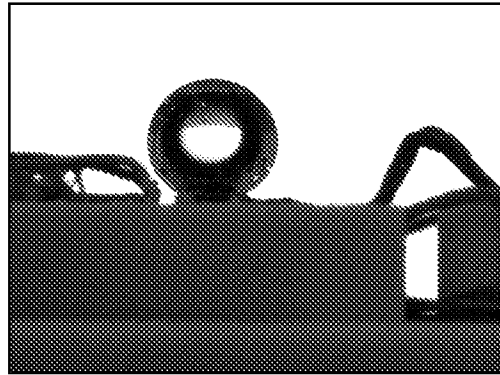


**Fig. 4f**

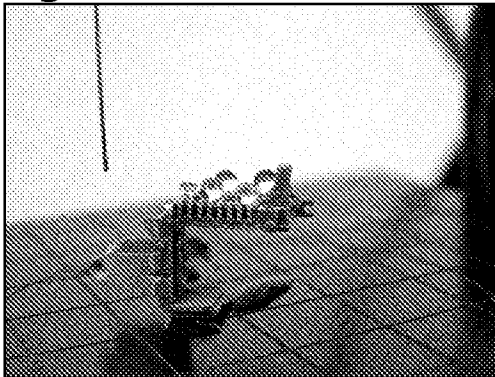
6/6



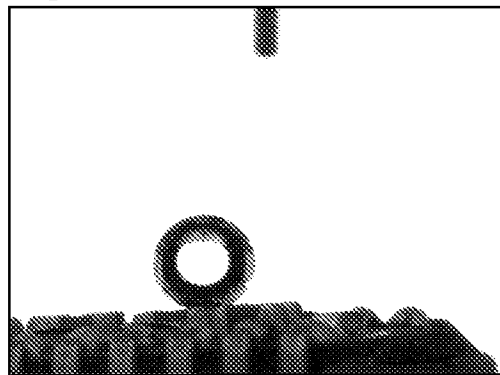
**Fig. 6a**



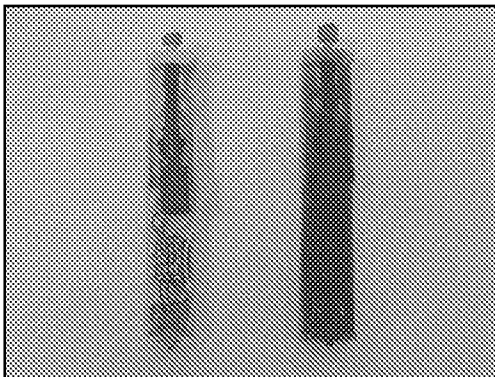
**Fig. 6b**



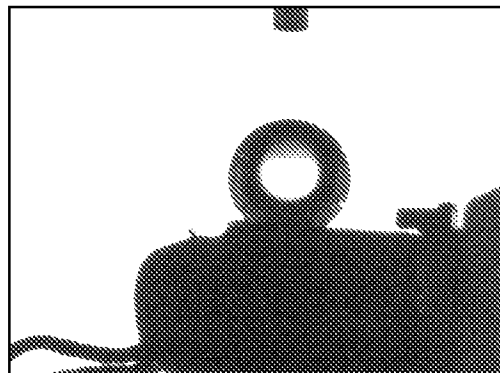
**Fig. 6c**



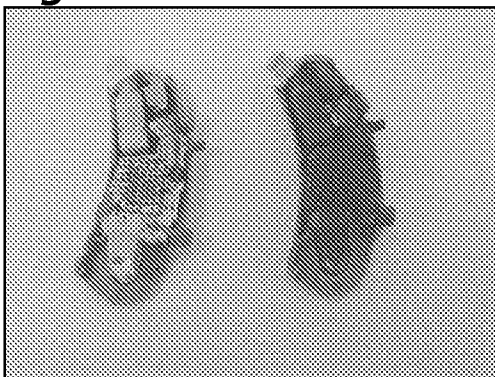
**Fig. 6d**



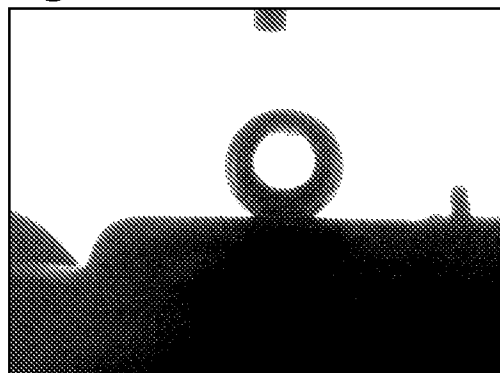
**Fig. 7a**



**Fig. 7b**



**Fig. 7c**



**Fig. 7d**

## INTERNATIONAL SEARCH REPORT

International application No

PCT/DK2008/050311

## A. CLASSIFICATION OF SUBJECT MATTER

INV. H04R25/00

C09D5/00

C09D7/12

C09D133/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H04R C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

2 September 2009

Date of mailing of the international search report

15/09/2009

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                      | Relevant to claim No. |
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Information on patent family members

International application No

PCT/DK2008/050311

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