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(54) **ELECTROGRAFTING METHOD FOR FORMING AND REGULATING A STRONG ADHERENT NANOSTRUCTURED POLYMER COATING**

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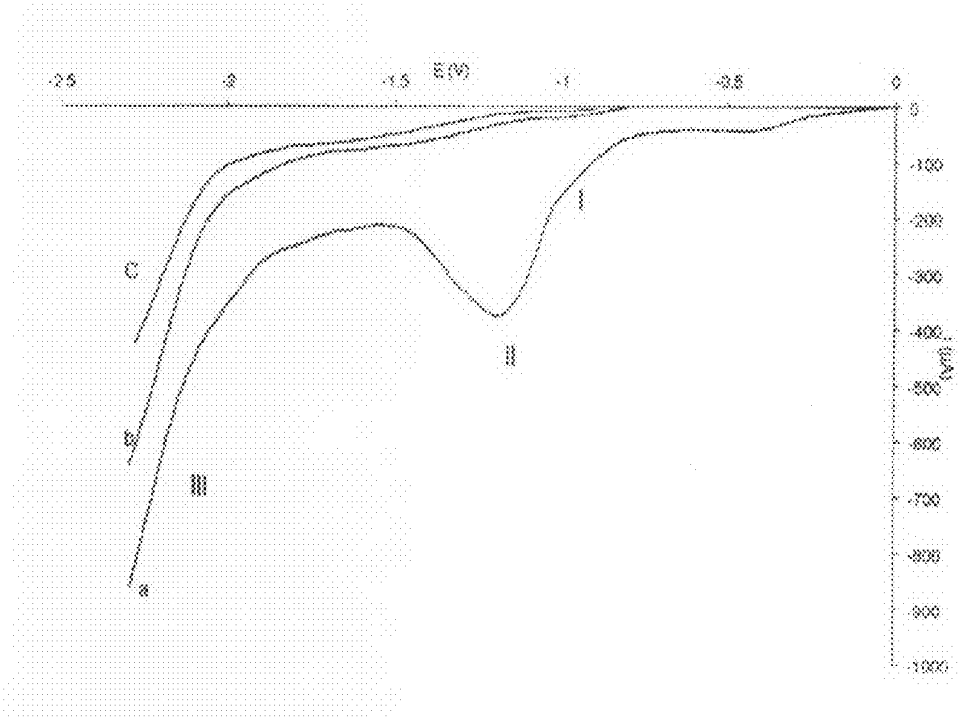
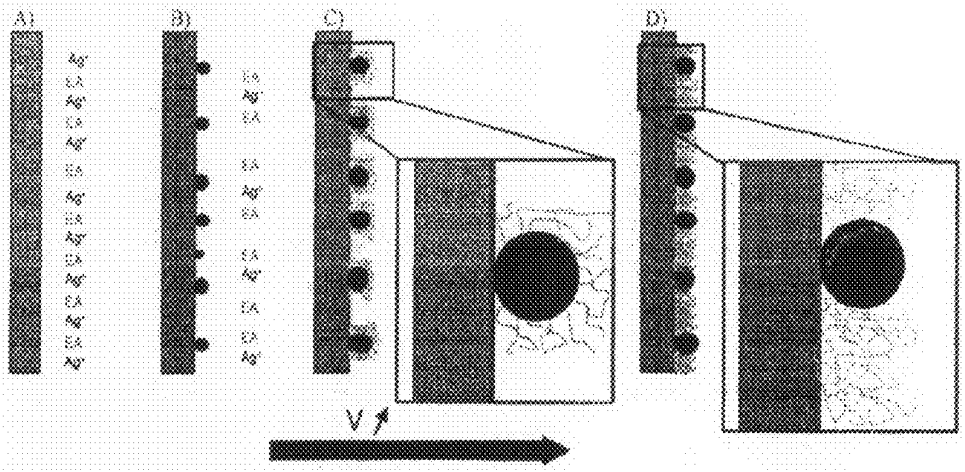
(57) **ABSTRACT**

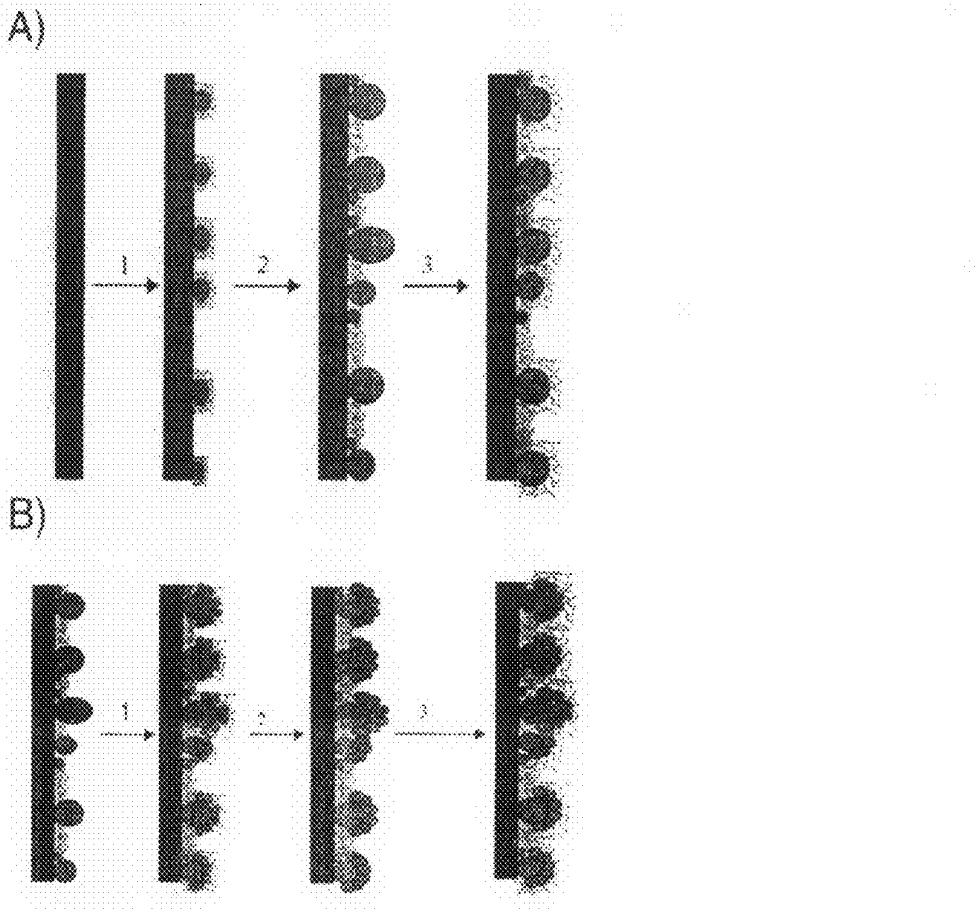
Electrografting method for forming and regulating a strongly adherent nanostructured polymer coating onto an electro-conductive surface profile characterized in that the surface profile is regulated by electrodeposition of nanometre- and/or micrometre-scale nuclei onto the surface profile prior to or simultaneously to the formation of the polymer coating.



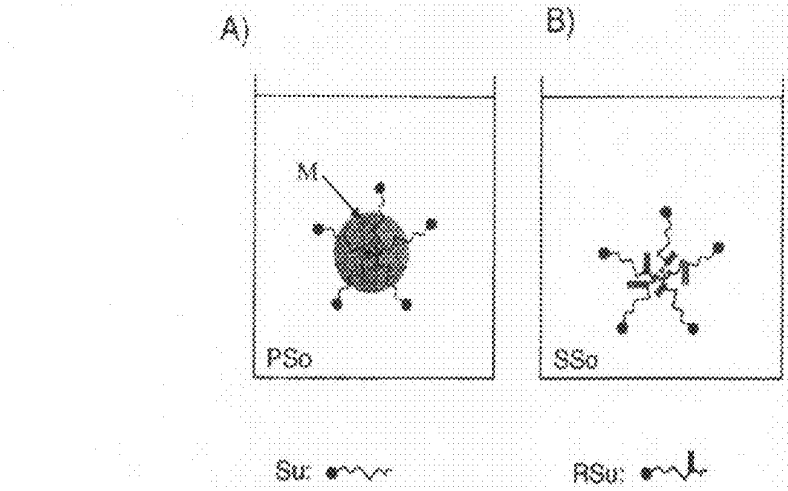
Scheme. 1



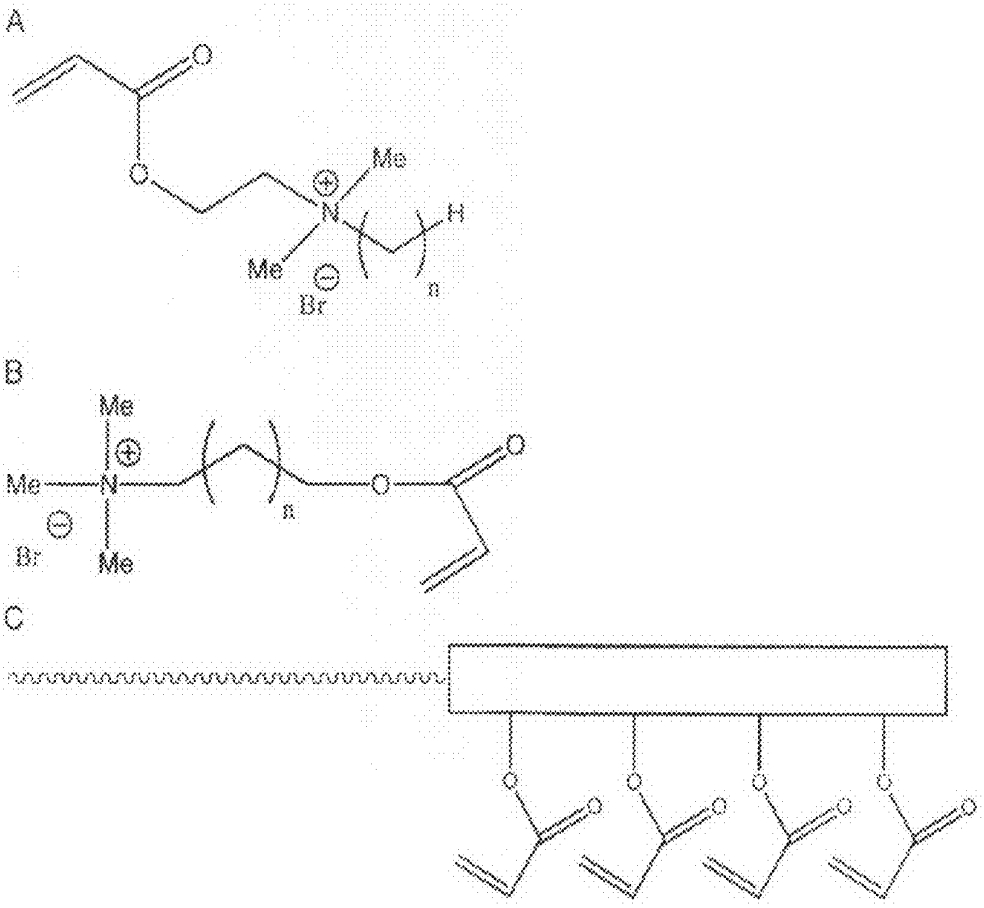
scheme 2



scheme 3



scheme 4



Scheme 5

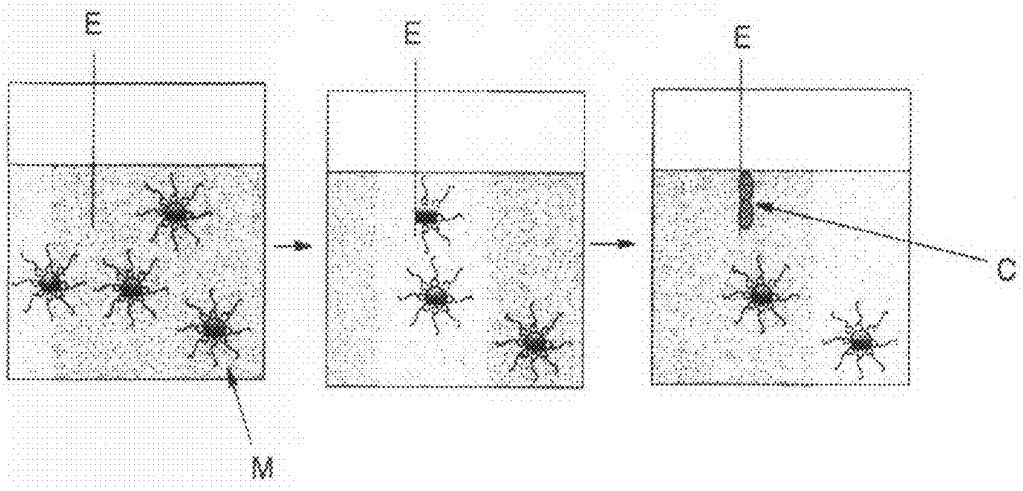


Figure 1

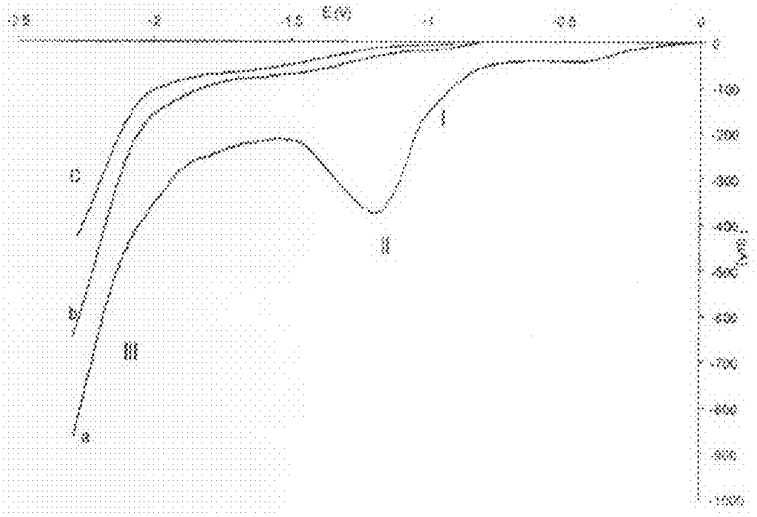


Figure 2

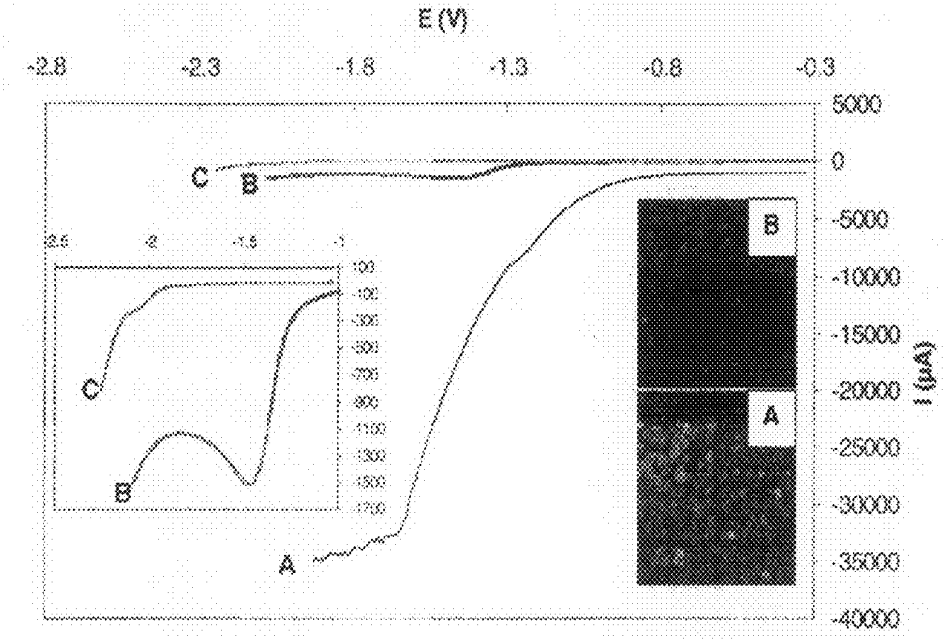


Figure. 3

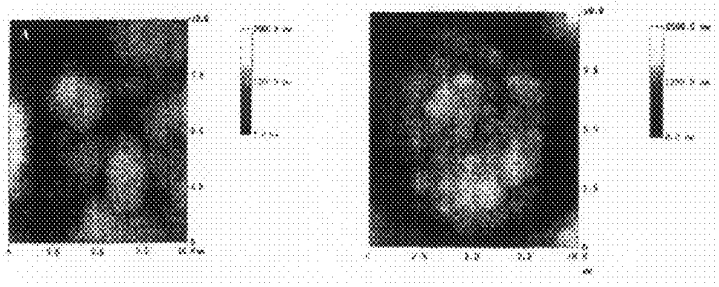


Figure. 4

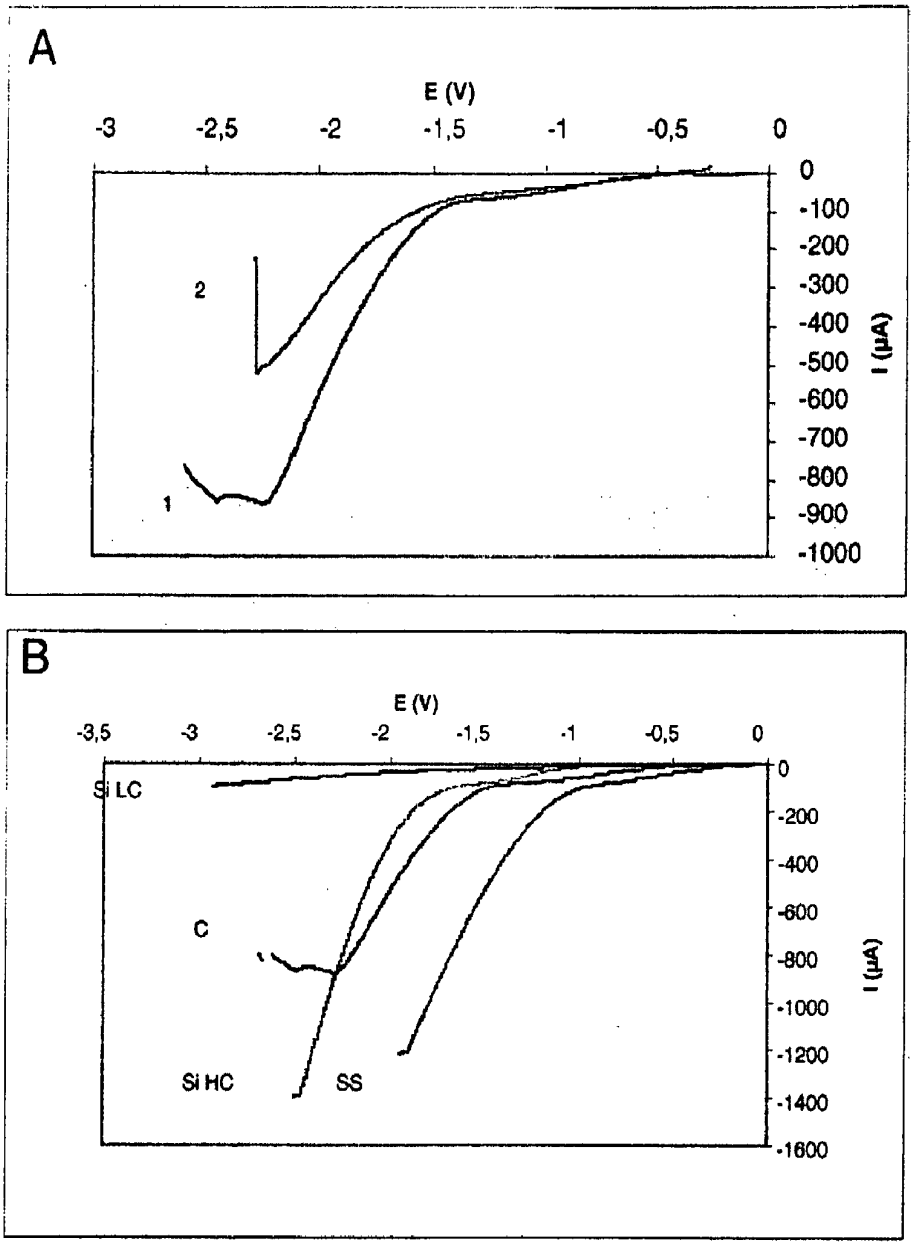

A
E (V)
-3
-2,5
-2
-1,5
-1
-0,5
0
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
I (µA)
2
1
B
E (V)
-3,5
-3
-2,5
-2
-1,5
-1
-0,5
0
0
-200
-400
-600
-800
-1000
-1200
-1400
-1600
I (µA)
Si LC
C
Si HC
SS

Figure 5

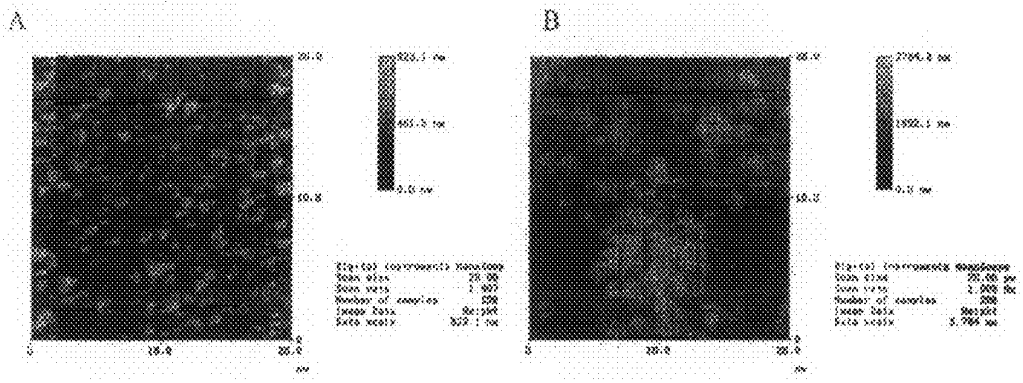
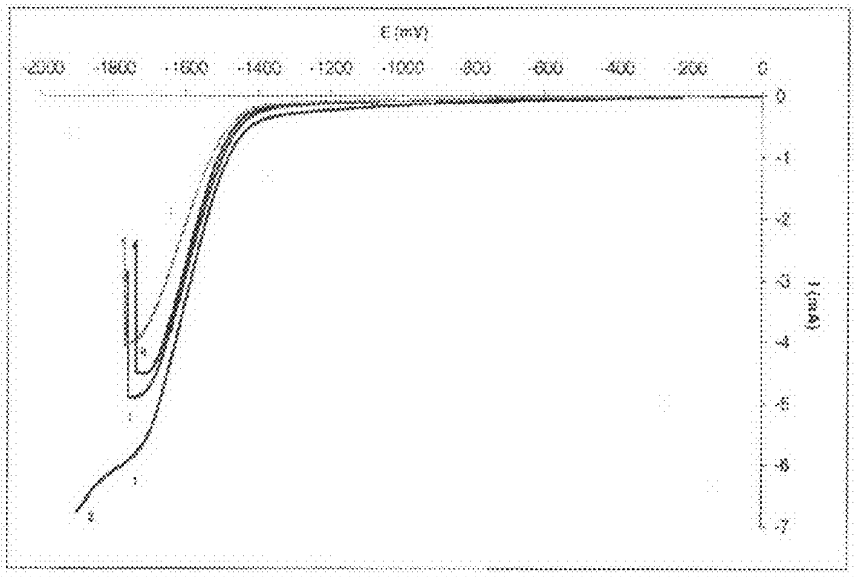


Figure 6



ELECTROGRAFTING METHOD FOR FORMING AND REGULATING A STRONG ADHERENT NANOSTRUCTURED POLYMER COATING

[0001] The present invention relates to a new method for forming and regulating by electrografting a strongly adherent nanostructured polymer coating onto an electro-conductive surface by controlling its surface profile. The present invention also relates to the strongly adherent nanostructured polymer coating obtained thereof and its uses.

[0002] Electrografting methods for forming a polymer coating are known in the art. WO 02/098926 and WO 2005/033378 describe a polymer film forming at the surface of an electroconductive surface. Nevertheless, the polymer coatings obtained by such methods known in the art require aprotic or nearly aprotic conditions to be formed. Organic solvents are therefore required which are costly and toxic for the environment.

[0003] WO 2005/033378 describes that protic substances like Brönsted acids hinder anionic polymerisation during preparation of a polymer coating by electrografting. Cathodic polarisation induces an anionic polymerisation which is stopped in the presence of protic compounds because propagating anions react irreversibly with the said protic compounds. The formation of a strongly adherent polymer coating is thus impossible in the presence of such protic compounds and only very low molecular weight polymer chains may be formed at the cathode.

[0004] Moreover, if some regulation of such polymer-coated surfaces is possible in the electrografting methods described in WO 02/098926, it is limited to a rough thickness control of the polymeric coating onto the surface. No other specific properties of the conductive surface profile (such as for example, roughness) are regulated during the electrocoating preparation.

[0005] One interesting characteristic of the surface profile is its surface roughness which influences many properties of the surface such as its wetting, adhesion, compatibility and reactivity with one or more polymeric coating. "Surface roughness" in the context of the present invention can be defined as small-scale (i.e., nanometer- and/or micrometer-scale) variations in the height of a solid surface as would be caused by a plurality of nodular formations present on a surface.

[0006] The surface roughness has an influence on many properties of the said surface and cannot be easily tuned while preparing a strongly adherent coating. On the other hand, because a modification of the surface roughness can enhance existing properties or impart new properties to a surface, the control of surface roughness is desired for many applications. Varying the surface roughness may for example modify the wetting, adhesion and reactivity properties of the surface. It can also enhance or reduce the contact between two surfaces, the friction at the surface, the specific area of a surface, the refractive index and so on.

[0007] Beside the good adhesion of the coatings, all these properties are of the utmost importance if the coating has to be used for example as self-cleaning surfaces, as anti-adhesive surfaces, in anti-corrosion, for the design of biosensors, as a primer to promote adhesion of a second coating or as molecular Velcro to form composites of different materials. For example, biosensors may be more sensitive if the surface area of the functional coating used to detect an analyte is increased. Furthermore, it can be desirable to optimize the wetting properties of these functional coatings used in biosensors and this can also be easily done by tuning the surface profile, particularly the surface roughness.

[0008] We have now found a new electrografting method comprising a step of nuclei deposition at a conductive surface regulating its surface profile and the polymeric coating properties before, during or resulting from electrografting. The surface profile is therefore controlled by a controlled nucleation step at the conductive surface inducing nanostructuration of the coating.

[0009] Accordingly, the present invention provides an electrografting method for forming and regulating a strongly adherent nanostructured polymer coating onto an electroconductive surface profile characterized in that the surface profile is regulated by electrodeposition of nanometre- and/or micrometre-scale nuclei onto the surface profile prior to or simultaneously to the formation of the polymer coating.

[0010] In the context of the present invention, the term "nuclei" refers to a nodule of an electrodeposited material with a nanometre- and/or micrometer-scale diameter, wherein the diameter is considered to be the greatest diameter of the nodule.

[0011] The electrografting method according to the present invention may be carried out with conventional electrochemical techniques, as for example, a three-electrode cell connected to a potentiostat. A working electrode, i.e., the electroconductive surface to be electrocoated, is a conductive or semi-conductive surface made for example from noble metals such as gold or platinum, transition metals such as chromium, titanium, iron, copper or nickel, or semi-conductors, such as doped silicon or carbon.

[0012] In a first embodiment, the present invention provides an electrografting method wherein the nuclei are made of an inorganic material provided by electrodeposition from a precursor salt.

[0013] The inorganic material is preferably a transition metal such as iron, copper, cobalt, nickel, titanium, silver or an alloy thereof.

[0014] The precursor salt according to the invention is generally an inorganic salt such as for example chloride, chlorate, triflate, perchlorate of iron, cupper, cobalt, nickel, titanium, silver, and the like or a mixture thereof.

[0015] Preferably, the electrografting method comprises a step of regulating the surface profile by inorganic (metallic) nuclei deposition onto the conductive surface upon application of a potential x to said surface immersed in a solution comprising a monomer and the inorganic (metallic) precursor-salt, prior to or in alternation with the electropolymerization step of the monomer resulting in a nanostructured surface profile.

[0016] In such embodiment, one selected potential x may be applied constantly or repeatedly to the electrically conductive or semi-conductive surface (also called hereafter (semi)-conductive surface), so that an inorganic salt is electrolyzed forming inorganic nuclei on the surface consequently modifying the surface profile. At another selected potential y, a strongly adherent polymer coating can be formed from a selected monomer. The strongly adherent polymer coating totally or partly covers the surface profile depending on the nature, size and shape of the inorganic nuclei deposited on the surface.

[0017] As illustrated in scheme 1, the surface profile is therefore regulated by the consecutive (step A to D) or simultaneous formation (step C) of such inorganic nuclei electrodeposited on the (semi)-conductive surface and electrografting of the monomer. The resulting nanostructured polymer coating is therefore also regulated by such nucleation step. Size and shape of the nuclei deposited on the surface are regulated

by the selected potentials and the surrounding polymer formation at the surface (particularly in step B and C of scheme 1).

[0018] The strongly adherent polymer coating according to the present invention may be at least partially covalently bonded to the surface and/or to the metal nuclei formed on the surface upon electrolysis of the salt, so that even if the polymer is not cross-linked, it cannot be completely removed by a continuous washing with a good solvent of the polymer or by a so-called peel test.

[0019] The selected potential x applied to the electrically conductive surface may be, for example, in the potential range between 10 V and −10 V, being especially preferred between 0 V and −4.5 V. In some preferred embodiments of the present invention, the potential applied to the electrically-conductive or semi-conductive surface may be constant or vary during electrolysis, for example, at a speed between 0.1 mV/s and 5 V/s, preferably between 1 mV/s and 250 mV/s. Furthermore, a constant potential (or current) may be applied to the electrically conductive or semi-conductive surface, for example, during between 0.001 seconds and 15 minutes, preferably between 0.1 seconds and 1 minute. Two or more different selected potentials may also be applied to the surface. A sequence of different potentials can be applied one time or repeated several times (up to 100 times for example) to the electrically conductive or semi-conductive surface.

[0020] It is also preferred in the first embodiment to select two (or more) different potentials to form the nanostructured coating on the electrically (semi)-conductive surface. For example, nucleation and electrografting may be not simultaneous but may also occur at different polarisation conditions. By polarization is meant application of a selected potential or current to an electrode.

[0021] It is preferred in the first embodiment to repeat the steps of the selected potential x applied to the electro-conductive surface in order to tailor the nanostructuration of the surface profile and reach efficient electrografting of polymer chains.

[0022] The profile and particularly the surface roughness of the nanostructured coating may be modified by applying the same selected potential x a second time or even several times. For example, the surface roughness may be controlled by repeating in alternation, the electro-nucleation and the electrografting steps as illustrated in step 1 to 3 of scheme 2A. The dimension of the nuclei formed during the first electro-nucleation step 1 increases with an increasing number of cycles. The alternating polymer electrografting step regulates the growth of these nuclei. Above a maximum of cycles, the size of the nuclei may decrease again (step 3). The control of the size of the nuclei thus allows the precise tailoring of the surface roughness.

[0023] By tuning the applied potential during these cycles, different levels of nanostructuration of the surface may be achieved for example by creating raspberry-shaped nuclei (as illustrated in scheme 2B).

[0024] Surfaces with a two-scale roughness, for example a roughness at the micrometer scale provided by the nuclei and a roughness at the nanometer scale provided by the nanostructuration of these nuclei may be created also by variation of the polarisation time as illustrated in scheme 2B.

[0025] The monomer according to the first embodiment are acrylic or methacrylic derivatives, such as alkyl(meth)acrylate, fluorinated (meth)acrylate, succinimidyl (meth)acrylate, (meth)acrylonitrile, pyrrole (meth)acrylate, thiophene (meth) acrylate, and the like, and polymers bearing one or more acrylic or methacrylic functions, such as poly(ethylene oxide), polysiloxanes, polyesters, polyurethanes, poly(methylvinyl ether), polystyrene, and the monomers and polymers described in WO 02/098926, which are incorporated herein by reference.

[0026] The solution according to the first embodiment of the invention comprising a monomer and an inorganic precursor salt may further comprise an organic solvent.

[0027] The organic solvent may be selected, for example, from ethyl acetate, dichloromethane, chloroform, dimethylformamide, acetonitrile, diethylcarbonate, dimethylsulfoxide, hexamethylenephosphoramide, ionic liquids (for example, immidazolium salts), supercritical solvents (for example, supercritical CO_2) and a combination of these solvents.

[0028] In such embodiments, the electrografting method has to take place in a mainly oxygen-free atmosphere which may, for example, be a nitrogen or argon atmosphere. A mainly oxygen-free atmosphere according to the invention means an atmosphere which contains between 0 ppm and 499000 ppm of oxygen, most preferrably between 0 ppm and 300 ppm of oxygen.

[0029] A preferred method allows formation of a composite metal-polymer coating by a combination of electrodeposition of a metallic salt and electrografting of at least one (macro)monomer. The strongly adherent polymer coating is nanostructured by the metal nuclei that are electrodeposited before and during the electropolymerization as illustrated in schemes 1 and 2.

[0030] Moreover, the electrografting method according to the present invention may be successfully applied to a surface of any size and shape. For example, surfaces of medical devices, such as coronary stents, dentistry tools or surfaces of analytical devices, such as atomic force microscopy (AFM) tips, microelectronic circuitry, microfluidic devices and also conducting (metallic) surfaces used in packaging, householding, the automobile sector, or design goods.

[0031] The advantages of such embodiments for the nanostructured strongly adhering polymer coatings are a precise tailoring of both chemistry and topography of the (semi)-conducting surface. When controlling both parameters, new properties can be afford to the coated material, such as superhydrophobicity, superhydrophilicity and anti-fouling properties. Other surface properties can also be deeply enhanced such as anti-bacterial activity, reactivity, catalytic reaction selectivity, friction, and reflectivity.

[0032] Applications of such nanostructured and strong adhering polymer coatings are found when corrosion-resistant coatings and self-cleaning coatings are required for biocompatibilization or the building-up of bioactive medical implants, for the elaboration of (bio)sensors particularly electrochemical biocaptors, for functionalization of channels of microfluidic devices, for tuning the visual aspect of goods (for example, decorative handles and watches), for imparting anti-bacterial properties to surfaces (such as air filters and medical tools).

[0033] In a second embodiment, the present invention provides an electrografting method wherein the nuclei are made of an organic material provided by electrodeposition from monomer droplets.

[0034] By monomer droplet is meant a droplet comprising a monomer (M). A monomer droplet is for example an emulsion droplet as illustrated in scheme 3A and comprising a monomer (M), a surfactant (Su) and a protic solvent (PSo) or a droplet as illustrated in scheme 3B comprising a reactive amphiphile (R) in a selective (protic) solvent (SSo).

[0035] Reactive amphiphile is defined as a molecule comprising a hydrophilic part and a hydrophobic part, and bearing

at least one polymerizable moiety such as a (meth)acrylic function as illustrated in scheme 4.

[0036] The protic solvent according to the present embodiment means a solvent having one dissociable proton such as water, but also methanol, ethanol, formamide and the like and combinations thereof.

[0037] The surfactant according to the present embodiment may be any molecule comprising a hydrophilic part and a hydrophobic part. The surfactant may be an anionic (such as sodium dodecyl sulfate), a cationic (such as alkyl quaternary ammonium), a zwiterionic (such as betaines), or a neutral (non-ionic) (such as pluronics) surfactant.

[0038] The amount of surfactant which is added in the emulsion, preferably exceeds the critical micellar concentration (CMC) of the surfactant in the protic solvent. It is, for example, 10^{-7} M to 10 M, preferably between 10^{-5} M to 10^{-1} M.

[0039] The electrografting method using such monomer containing droplets allows regulating both topography and chemistry of the (semi)-conducting surface by electrochemical formation of organic (polymer) nuclei onto the conductive surface upon application of a potential z to said surface.

[0040] In such second embodiment the electro conductive surface is preferably immersed in a monomer droplets suspension comprising a protic solvent

[0041] By the application of at least one selected potential z to the electricallyconductive or semiconductive surface of electrode (E), the droplets of the monomer which are formed in a protic solvent such as water may form a nanostructured strongly adherent polymer coating (C) on the electrically conductive or semiconductive surface as illustrated in scheme 5.

[0042] The monomer droplets upon applying a potential to the electrically conductive surface may be attracted to the electrically conductive surface (scheme 5 step 1). The droplets of the monomer which are formed in the protic solvent may be projected onto the electrically conductive surface, forming nuclei at the surface, and therefore modifying the profile of the conductive surface. While upon reaching said surface, the formation of a strongly adherent polymer coating begins at the edge of the droplets which first contacts with the electrically conductive surface. Each said droplet may therefore form a strongly adherent polymer protuberance, especially a hemispheric or ellipsoidal polymer protuberance, on the electrically conductive surface (scheme 5). Depending on the potential which is used to project the droplets against the electrode, the crash of the droplets may be strong enough to spread the monomer on the electrode so that a smoother coating may be obtained.

[0043] The diameter of the polymer protuberances of the strongly adherent polymer coating which are formed on the electrically (semi)conductive surface may depend on the diameter of the droplets which are formed in the protic solvent.

[0044] It is therefore possible to tune the conductive surface profile particularly the surface roughness of the at least partially polymer coated surface by modifying the diameter of the droplets of the monomer which may be formed in the protic solvent and/or by tuning the selected potential(s) which may be applied to the electrically conductive or semiconductive surface, going progressively from a nearly smooth polymer coated surface, which can for example be obtained using small droplets, especially, for example, droplets with a mean diameter <100 nm, and/or high potential(s), to a rough polymer coated surface, which can for example be obtained using large droplets, especially, for example, droplets and/or aggregates with a diameter >100 nm, and/or low potential(s).

[0045] The selected potential y applied to the electrically conductive surface may be, for example, in the potential range between 10 V and −10 V, preferably between 0 V and −4.5 V. In some preferred embodiments of the present invention, the potential applied to the electrically conductive or semiconductive surface may vary during application, for example, at a speed between 0.1 mV/s and 5 V/s, preferred between 1 mV/s and 250 mV/s. Furthermore, a constant potential may be applied to the electrically conductive or semiconductive surface, for example, during between 0.001 seconds and 15 minutes, preferably 0.1 seconds and 1 minute.

[0046] The monomer involved in the monomer droplets in the second embodiment of the invention is any kind of acrylic or methacrylic derivatives, such as alkyl(meth)acrylate, fluorinated (meth)acrylate, succinimidyl (meth)acrylate, pyrrole (meth)acrylate, thiophene (meth)acrylate, and so on, and polymers bearing one or more acrylic or methacrylic functions, such as polysiloxanes, polyesters, polyurethanes, poly (methylvinyl ether), polystyrene, polyethers, and the monomers and polymers described in WO 02/098926 incorporated herein by reference.

[0047] In the second embodiment of the invention, the electroconductive surface is also preferably immersed in a micellar composition comprising a reactive amphiphile in a selective (protic)solvent (Sso).

[0048] The reactive amphiphile (also called a reactive surfactant) involved in the monomer droplets in case of micelles are amphiphilic monomers that self-assemble in a selective solvent (eg, water). For example, alkyl quaternary ammonium bearing a (meth)acrylate, amphiphilic block copolymers bearing one or several (meth)acrylic functions on one block, or a combination thereof.

[0049] Emulsions in water require hydrophobic monomers and consequently lead to polymer coatings with a hydrophobic character (if prepared in one step). Whenever hydrophilic coatings have to be prepared in one step in water, the emulsion has to be replaced by a micellar composition as illustrated in scheme 3B. For that purpose, reactive surfactants have to be prepared that meet several requirements. Such reactive surfactants have to be able to form micelles in water, to repulse water from the electrical double layer upon polarization and to electrochemically react to form the strongly adhering nanostructured coating. Examples of suitable monomers for this strategy are described in scheme 4. Indeed in schemes 4A and 4B, there is illustrated amphiphilic and reactive (acrylic derivative) molecules that are able to self-associate in water to form micelles thanks to their hydrophilic (charged) and hydrophobic (long alkyl chain) character, whereas because of the (meth)acrylic group they can also electropolymerize. In such systems, the polymer coating is built by the polymerized surfactant and thus includes some charged groups that increases the hydrophilicity of the coating.

[0050] In scheme 4C, a similar use of a polymeric reactive surfactant is illustrated.

[0051] In such cases, the hydrophilic part and the hydrophobic part are constituted by two polymer sequences, one made of a hydrophilic polymer, such as poly(ethylene oxide) or quaternized poly(vinylpyridine), and one made of a hydrophobic chain bearing at least one (meth)acrylic group, for example a copolymer of ϵ-caprolactone and γ-acryloyl-ϵ-caprolactone.

[0052] Advantages of the second embodiment of the invention with monomer droplets are that nuclei formation for the nanostructured polymer coating is in general similar to that described for the first embodiment of the invention. Furthermore, the applications for a nanostructured polymer coating

obtained from the method of the second embodiment are also in the same fields as those cited in respect of the first embodiment.

[0053] Most advantageous of the second embodiment of the invention compared to the first embodiment is the use of protic solvents, and particularly the cheap, non-toxic solvent water, a solvent being particularly opportune for the industrial development of the method of the invention.

[0054] The present invention also refers to a strong adherent nanostructured polymer coating obtained by the electrografting method according to the invention. The nanostructuration is made of nuclei that can be provided by inorganic material such as metal or by organic (monomer) droplet that may be further polymerized to form a polymer aggregate and formation of a nanostructured polymer coating.

[0055] The invention is now illustrated with reference to the following Schemes and Figures of the accompanying drawings:

Scheme 1:

[0056] Schematic representation of the first embodiment of the electrografting method according to the present invention as performed in the example 1 in which upon applying an increasing cathodic potential (from left to right on the scheme) to the electrically (semi)conductive surface immersed in a solution comprising Ag(I) ions and ethyl acrylate (EA) (represented under A), Ag(0) metal nuclei may be formed in a first step (represented under B), before a strongly adherent polymer coating is formed on the Ag nuclei (represented under C). Finally, if the selected potential further increases the strongly adherent polymer coating is removed from the Ag(0) nuclei and a strongly adherent coating surrounding the metal nuclei is formed on the electrically (semi) conductive surface (represented under D).

Scheme 2:

[0057] Schematic representation of the first embodiment of the electrografting method according to the present invention as performed in example 2 comprising the application of three different selected potential in three steps. A) Repeating 15 times, the cycling of the three steps below. B) Repeating the cycling of the steps more than 15 times.

[0058] In a first step, a selected potential is applied to the electrically conductive surface to form Cu(0) nuclei which are coated by a strongly adherent polymer coating from a Cu(I) and ethyl acrylate (EA) solution (step 1 part A). In a second step, another selected potential is applied one or more than one time to further reduce the Cu(I) ions and to remove the strongly adherent polymer coating from the Cu(0) nuclei while forming an adherent polymer coating on the electrically conductive surface. By further reducing the Cu(I) ions the diameter of the Cu(0) nuclei increases (step 2 part A). Finally, a third selected potential is applied in a third step to form a strongly adherent polymer coating on the Cu(0) nuclei (step 3 part A). By repeating the second step it may be possible to get metal nuclei which are at least partially covered by smaller metal nuclei (not shown).

[0059] By repeating the sequence of the first and second steps up to 40 times (steps 1 and 2 part B) before performing the third step, the roughness of the polymer coated nanostructured surface may be increased. Beyond 40 cycles, the metal nuclei merge together and the surface roughness decreases again. For a number of cycles comprised between 15 and 40 metal nuclei at least partially covered by smaller metal nuclei may be formed so that the at least partially polymer-coated nanostructured surfaces may comprise a roughness on two different scales (step 3 part B) (for example, a roughness at the micrometre scale and a roughness at the nanometre scale).

Scheme 3

[0060] Schematic description of the monomer droplets of the second embodiment of the invention showing an emulsion system (diagram A) and a micellar system (diagram B), wherein M represents a hydrophobic monomer, Su a surfactant, RSu a reactive surfactant, PSo a protic solvent, and SSo a selective solvent.

Scheme 4:

[0061] Possible structures for the reactive surfactants able to give micelles as monomer droplets. Diagram C shows a polymeric surfactant with one hydrophilic (left-side part) and one hydrophobic and reactive (right-side part) segments.

[0062] Scheme 5: Schematic description of the nanostructuration of the surface by using the monomer droplets systems. Firstly, the monomer droplets (M) are in suspension in the solvent (e.g. water) (left-side image). Then, upon polarization (middle image), some droplets go to the electrode (E) surface forming there nuclei from which the electropolymerization starts. The polymer grown from these droplets nuclei forms a nanostructured coating (C) (right-side image), the nanostructuration originating from the original monomer compartmentation within the droplets.

[0063] FIG. **1**: Typical voltammogram recorded on a stainless steel surface for the electrografting method according to the present invention as performed in example 1 using a 8-quinolinyl acrylate (0.5 M) as monomer in dimethylformamide (DMF) solution saturated by silver acetate and added with 0.05 M tetraethylammonium perchlorate (TEAP) (selected potential variation speed=20 mV/s). The first increase of the measured current intensity (I), is due to the formation of silver nuclei, the second increase of the measured current intensity (II), is due to the formation of a strongly adherent poly(8-quinolinyl acrylate) coating on the silver nuclei, the third increase of the measured current intensity (III), due to the electrografting of 8-quinolinyl acrylate onto the steel surface. First, second and third scans are represented by traces (a), (b) and (c), respectively. The measured current intensity decreases with each potential scanning because of the formation of the insulating properties of the strongly adherent polymer coating.

[0064] FIG. **2**: Voltammogram recorded on stainless steel surface in a DMF solution of (A) Cu(II) ions, (B) Cu(II) ions with added ethyl acrylate (EA), and (C) for ethyl acrylate (EA) without Cu(II) ions as in example 2. ESEM micrographs of the accordingly obtained surfaces (5 μm×5 μm) after the electrograftingmethod in case of A and B, respectively. The left-side insert is a zoom of the voltammogram.

[0065] FIG. **3**: Atomic force microscopy (AFM) height micrographs for the samples of nanostructured surfaces of example 2 corresponding to (A) sample entry 1 in Table 1 and (B) for the "raspberry-shaped" surface of the sample entry 3 in Table 2. These AFM height micrographs clearly evidence the possibility of a double-level of structuration of the surface with a raspberry-shaped surface comprising a roughness at the micrometer scale and a roughness at the nanometre scale.

[0066] FIG. **4**: Voltammogram illustrating the second embodiment of the invention for the reduction of an emulsion of heptadecafluorodecyl acrylate (2M) with cetyltrimethylammonium bromide as surfactant recorded on carbon surface (A), with two reduction cycles (1 and 2) on the same electrode, and (B) different substrates (i.e., SS: stainless steel,

SiHC: highly-doped silicon, SiLC: slightly-doped silicon, C: carbon) as performed in example 3.

[0067] FIG. **5**: AFM micrographs showing the nanostructuration of steel (micrograph A) and carbon (micrograph B) surfaces after electrografting step as described in example 3 for the second embodiment of the invention.

[0068] FIG. **6**: Voltammogram illustrating the second embodiment for the reduction of a micellar solution of reactive monomer on carbon surface as performed in example 4.

[0069] The invention will now be illustrated with reference to the following examples which are not intended to limit the scope of the claimed invention.

EXAMPLES OF THE FIRST EMBODIMENT ACCORDING TO THE INVENTION

Example 1

[0070] Preparation of Nanostructured Polymer Coated Surfaces with Antibacterial Properties

General Conditions.

[0071] Cyclic voltammetry and chronoamperometry were carried out in a one-compartment cell with a platinum counter electrode and a platinum pseudo-reference in a glove box under an inert and dry nitrogen atmosphere (5 ppm of oxygen and <10 ppm of water) at room temperature using an EG&G potentiostat/galvanostat (M273). The working electrode (2 cm^2 square-like plate of stainless steel) was washed with heptane and acetone, and dried overnight at 150° C. under vacuum. For the preparation of the polymer coatings, dry DMF solutions of the monomer (ethyl acrylate (EA), 8-quinolinyl acrylate (8QA) or an acrylate with nitroxide-mediated polymerization (NMP) initiator (i.e. 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethylacrylate (PTEA) are used) [for the structure of the last monomer see *Chem. Mater.*, 2003, 15, 923] in the concentration range 0.3 to 1 M saturated with $AgOOCCH_3$ and added with tetraethyl ammonium perchlorate (TEAP) (5×10^{-2} M) as an additional conducting salt were used. The potential of the conductive substrate was varied at 20 mV/s during voltammetry (FIG. **1**). After polarization, the nanostructured polymer surfaces were extensively rinsed with dried DMF and acetonitrile before characterization. Different nanostructured coatings made of metal nuclei and different polyacrylate have been obtained and are illustrated below.

Coatings Comprising Silver and Polyethyl Acrylate (PEA)

[0072] When a reduction ramp is applied to ethyl acrylate (concentration 1 M) and Ag acetate mixture in dimethylformamide (DMF), with deposition of Ag(0) nuclei at −0.7 V, then a strongly adherent poly(ethylacrylate) film is formed at a lower cathodic potential (~−1.5 V). At a more cathodic potential (~−2 V), the formation of a strongly adherent polyacrylate coating can occur on the stainless steel surface in between the silver nuclei. At the same time, the increased potential on the metal nuclei removes the PEA coating which was formed at −1.5 V because of the local overpotential occurring at the top of the nuclei that induces local polymer degrafting. This was confirmed by the AFM analysis of samples prepared by scanning a solution containing ethyl acrylate, silver (I) acetate and a conducting salt (TEAP) until −1.5 V and −2.1 V, respectively. This potential dependence of the polyacrylate grafting/degrafting process permits the underlying silver to be apparent again for the external medium, which is of prime importance for controlling the growth of these Ag nuclei. The samples were prepared by increasing the selected potential from 0 V up to −2.1V and applying a selected potential of −2.1 V for 30 seconds, so that the silver nuclei are not coated, but surrounded by the electrografted polyacrylate. The coatings were characterized by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Energy Dispersive X-ray spectroscopy (EDX) surface analysis which confirmed the presence of both of PEA and Ag on the surface. By ATR-FTIR absorptions characteristic of PEA are observed at 2960 cm^{-1}-2860 cm^{-1} (alkyl C—H), 1735 cm^{-1} (ester C═O) and 1180 cm^{-1} (ester C—O). The contact angle is reported in Table 1.

Coatings Comprising Silver and poly(8-quinolinyl)acrylate (P8QA)

[0073] The procedure is repeated with 8-quinolinyl acrylate (8QA) as the monomer rather than EA. The 8QA bears a complexing function that can act as a ligand for the Ag(I), the resulting coatings will thus contain both Ag(I) ions and Ag (0) nuclei that are expected to exhibit powerful antibacterial properties. As for the EA/Ag(I) system, three reduction reactions are observed by a raise in the measured current intensity when the potential varies between 0 V and −2.5 V using 8QA instead of EA. By analogy with the EA/Ag(I) model, Ag(I) is reduced to Ag(0) at between −1 V and −1.5 V and a strongly adherent polymer coating of P8QA chains is formed on the Ag(0) nuclei. At −2 V the P8QA chains are released from the surface and new ones are formed on stainless steel.

[0074] The samples were prepared by decreasing the selected potential from 0 V down to −2.1 V and applying a selected potential of −2.1 V for 30 seconds. At this potential the silver nuclei are not coated, but surrounded by the polyacrylate (P8QA) as evidenced by AFM phase contrast measurements. The water contact angle measurements (Table 1) show that the coatings so obtained are quiet hydrophilic, which is expected as compared to PEA coatings. ATR-FTIR and EDX surface analysis confirmed the presence of both P8QA and Ag on the electrically conducting or semiconducting surface. By ATR-FTIR absorptions characteristic of P8QA are observed at 2960 cm^{-1}-2860 cm^{-1} (alkyl C—H), 1735 cm^{-1} (ester C═O) and 1180 cm^{-1} (ester C—O).

Coatings Comprising Silver and poly(2-Phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethylacrylate) (PPTEA)

[0075] As for the other two acrylic monomers/Ag(I) systems cited here before, three reduction reactions are observed when the PPTEA is used instead of other acrylates. By analogy with the EA/Ag(I) model, Ag(I) is reduced to Ag(0) at between −1V and −1.5V, and a strongly adherent polymer coating of PPTEA chains is formed on the Ag(0) nuclei. At −2 V these chains are released from the surface and new ones are formed on stainless steel.

[0076] The samples were prepared increasing the selected potential from 0 V up to −2.1 V and applying a selected potential of −2.1 V for 30 seconds. Again, the coatings were characterized by contact angle (Table 1), showing that the coatings are hydrophobic, ATR-FTIR and EDX surface analysis confirmed the presence of both PTEA and Ag on the surface. By ATR-FTIR absorptions characteristic of PPTEA are observed at 2960 cm^{-1}-2860 cm^{-1} (alkyl C—H), 1735 cm^{-1} (ester C═O) and 1180 cm^{-1} (ester C—O).

Nitroxide-Mediated Random Copolymerization of butyl acrylate (BuA) and 2-(dimethylamino ethyl)acrylate (DAEA) from Coatings Comprising Silver and PPTEA

[0077] Advantages of the PPTEA-based coatings are the possible chemical initiation of a second and controlled polymerization from the surface. Random copolymers of BuA and DAEA were prepared from the PPTEA/silver coating. These random copolymers have already been prepared from PPTEA electrografted on stainless steel. It was shown that making

polyBuA more hydrophilic by copolymerization with DAEA increases the anti-adhesive properties towards proteins (fibrinogen). On the other hand, the presence of silver in the coating imparts antibacterial properties to the coating, as it will be shown in the following.

[0078] To a reaction tube containing a stainless steel surface modified by PTEA containing Ag, was added a mixture of BuA (2.3 ml, 15.8 mmol), DAEA (2.4 ml, 15.8 mmol), 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (0.086 g, 0.263 mmol), 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (0.0033 g, 0.0132 mmol) and 0.6 ml dry toluene. The reaction mixture was degassed by three freeze/throw cycles, closed by a three-way stopcock under nitrogen, and heated at 125° C. for 24 h. After extensive washing with dry toluene, the coated plates were dried in vacuum, and analyzed by ATR-FTIR, AFM and Environmental Scanning Electron Microspcope (ESEM).

[0079] The coatings were characterized by contact angle (Table 1), showing that they are hydrophilic. The presence of the copolymer was assessed by ATR-FTIR. Absorptions characteristic of the copolymer are observed at 2952 cm^{-1} and 2923 cm^{-1} (aliphatic C—H stretching vibration), 1727 cm^{-1} (C═O stretching vibration), 1444 cm^{-1}, 1383 cm^{-1} (aliphatic C—H bending vibration) and 1157 cm^{-1} (C—O stretching vibration).

Antibacterial Activity of Coated Stainless Steel Surfaces

[0080] The antibacterial activity of modified stainless steel with nanostructured silver/polymer coatings against the Gram-negative bacteria *Escherichia coli* and Gram-positive *Staphyloccocus aureus* were measured by classical analytical techniques clearly described in *Langmuir,* 2003, 19, 8971, 2004, 20, 10718, and 2006, 22, 255.

Adhesion of *E. coli* to Nanostructured Silver/Polymer Coated Stainless Steel.

[0081] Uncoated stainless steel surfaces do not inhibit the growth of *E. coli*. In all cases, the coated plates containing silver particles are active against *E. coli*. The highest inhibition zone of 30 mm is observed in the case of stainless steel containing silver particles modified with P8QA. This effect was probably due to remarkable antibacterial properties of silver particles and 8-hydroxyquinoline derivatives. An inhibition zone of 20 mm is observed in the case of plates modified with PEA containing silver particles and 5 mm for the modified PPTEA/Ag plates. The differences in the hydrophobicity of these two polymer films that surround the silver particles probably influence antibacterial activity of these coatings.

Adhesion of *S. aureus* to Nanostructured Silver/Polymer Coated Stainless Steel

[0082] Clinical studies show that among the species that dominate biomaterial-centred infections, *S. aureus* is one of the most common pathogens which causes implant-associated infection. That is why we also evaluated the adhesion of Gram-positive bacteria *S. aureus* onto modified stainless steel plates containing silver particles by using a test that determined the number of viable bacteria that adhered to the support.

[0083] The test showed that most effective in preventing bacterial adhesion were the nanostructured surfaces comprising P8QA and Ag, the nanostructured surface comprising PEA and Ag, the nanostructured surface comprising P(BuA-co-DAEA) and PPTEA and Ag which reduce completely (100%) the adhesion of *S. aureus*. A reduction of two orders of magnitude over uncoated stainless steel is observed for Ag and PPTEA coatings in agreement with the antibacterial activity observed against the Gram-negative bacteria *E. coli*. In comparison, the number of bacteria adhered for 1 h contact onto uncoated stainless steel surfaces is ~6.4×10^4 colony-forming units (cfu)/ml. The lower effect of bacteria reduction observed for coatings comprising PPTEA and Ag compared to the other silver nanostructured coatings was probably due to higher hydrophobicity of the coating.

[0084] The incorporation of groups with intrinsic antibacterial properties 8QA or hydrophilic groups, which are biocompatible (copolymer brushes of BuA and DAEA or PEA) in combination with the silver nuclei leads to particularly efficient, i.e. complete, reduction of the number of adhered bacteria compared to uncoated stainless steel plates.

Example 2

[0085] Preparation of Nanostructured Surfaces with Hydrophobic or Superhydrophobic Properties

[0086] For this example, acetonitrile (Aldrich), ethyl acrylate (EA, Aldrich) and heptadecafluorodecyl acrylate (HDFDA) (from ABCR) were dried over calcium hydride and distilled under reduced pressure. Dimethylformamide (DMF, Aldrich) was dried over P_2O_5 and distilled under reduced pressure. Tetraethylammonium perchlorate (TEAP, Fluka) and copper (II) acetate (Aldrich) were heated in vacuum at 80° C. for 12 h prior to use.

[0087] Cyclic voltammetry and chronoamperometry were carried out in a one-compartment cell equipped with a platinum counter-electrode and a platinum pseudo-reference by using an EG&G potentiostat/galvanostat (M273) in a glove box, under an inert and dry atmosphere nitrogen atmosphere (±5 ppm of oxygen and <10 ppm of water) at room temperature. The working electrode (2 cm^2-stainless steel plates) was washed with heptane and acetone, and dried overnight at 150° C. in vacuum. The electrode was immersed in dry DMF containing the acrylate (EA (1M) or HDFDA (2.5 M)), the conducting salt (TEAP, 5×10^{-2} M) and $Cu(OOCCH_3)_2$ (at saturation) and at least one selected potential was applied. The potential scanning rate was 20 mV/s during voltammetry. The nanostructured surfaces were washed extensively with dry DMF followed by acetonitrile in case of electrografting of polyEA and by trifluorotoluene when fluorinated polyacrylate was used. It was dried in vacuum before characterization.

Coatings Comprising Copper and poly(ethylacrylate)

[0088] A nanostructured surface comprising Cu(0) nuclei and strongly adherent poly(ethylacrylate) (PEA) was formed using a stainless steel surface and a 1 M EA solution of DMF containing TEAP (5×10^{-2}M). The reduction peak of very low intensity observed at −2.1V is the signature of the cathode passivation as a consequence of the formation of an insulating PEA coating. Indeed, even after extensive washing of the surface with a good solvent for PEA, a polyacrylate coating is detected on the surface by ATR-FTIR spectroscopy. At −2.3 V, the PEA coating is removed from the electrically conductive or semiconductive surface and the polymerization of EA may continue in solution.

[0089] Before investigating the behavior of a EA/Cu salt mixture in a TEAP/DMF solution, the electrodeposition of Cu has been first studied, in a saturated solution of Cu acetate in DMF added with TEAP (0.05 M). Under these conditions, Cu starts to be electrodeposited on stainless steel by voltammetry (FIG. **2**, curve A) at −0.8 V and the intensity reaches a maximum at −1.6 V, as a result of the limited diffusion of Cu(II) to the cathode. When ethyl acrylate is added to the solution of Cu acetate (concentration 1 M), FIG. **2**, curve B shows that the current intensity decreases dramatically because of the formation of an insulating polyethylacrylate coating on the electrically conductive surface and/or on the metal nuclei. Formation of Cu(0) nuclei on stainless steel has

been attested by EDX analysis and directly observed by ESEM (FIG. **2** insert). The nuclei which are formed are smaller in the presence of ethylacrylate when all other conditions are identical. The presence of both EA and Cu(0) has been confirmed by the surface analysis by ATR-FTIR (detection of PEA) and EDX (detection of Cu). A typical ATR-FTIR spectrum for the coating formed by varying the selected potential from 0 V to −1.6 V is in agreement with the spectrum for PEA which is formed in absence of Cu(II). The absorptions characteristic of PEA are observed at 2960 cm^{-1}-2860 cm^{-1} (alkyl C—H), 1735 cm^{-1} (ester C═O) and 1180 cm^{-1} (ester C—O). Moreover, if the selected potential varies scanned until higher values (i.e., −2.1 V), the ATR-FTIR and EDX spectra confirmed the persistence of polyethyl acrylate and Cu on the electrode. From these experiments, it may be concluded that the acrylic monomer (EA) forms a strongly adherent polymer coating while the Cu(II) is simultaneously reduced at −1.5 V. Although the use of a pseudo-reference does not allow the experimental potential to be directly compared, the potential at which the formation of a strongly adherent polymer coating of EA is observed to change from −2.1 V to −1.5 V upon the addition of Cu acetate to the solution, all the other conditions being the same. This qualitative shift is important enough to assign it, at least partly, to the modification of the cathode surface by the deposition of Cu(0). The growing Cu(0) nuclei contribute to the roughness of the surface and to the local increase of the potential at the Cu(0) nuclei as compared to the selected potential which is applied to the underlying nearly planar stainless steel surface because of the "tip effect" or "rod effect". The formation of the PEA coating occurs on the Cu(0) nuclei. The formation of a strongly adherent PEA coating occurs therefore on the Cu(0) nuclei at a lower cathodic potential (−1.5 V). At a more cathodic potential (−2.1 V), the formation of a PEA coating can occur on the stainless steel surface in between the Cu(0) nuclei. At the same time, the increase of the potential at the Cu(0) nuclei removes the PEA chains of the polymer coating which were formed at −1.5 V from the Cu(0) nuclei. This is confirmed by the AFM analysis of the samples prepared by varying the selected potential from 0 V to −1.6 V and from 0 V to −2.1 V, respectively. AFM shows that the surface is homogeneously covered by Cu(0) nuclei with a diameter of 30-80 nm for the at least partially polymer-coated nanostructured surface by varying the selected potential from 0 V to −1.6 V, and the phase contrast measurement while scanning the surface shows only a little differences of the phase delay. When the selected potential is varied from 0 V to −2.1 V, the surface is smoother, because of the insertion of the PEA polymer coating in between the Cu(0) nuclei and exhibits by AFM phase contrast measurements different phase delays for the neat metallic Cu(0) nuclei and the surrounding strongly adherent polymer coating which is partially covalently bonded to the stainless steel surface.

[0090] The potential dependence of the formation and the removing of the strongly adherent PEA coating is thus important to regulate the growth of Cu(0) nuclei and thus to tune the surface roughness and the surface coverage of the polymer coating.

Superhydrophobic Surfaces: Nanostructured Coatings Comprising Copper and poly(heptadecafluorodecyl acrylate)

[0091] The formation of nanostructured coating comprising Cu(0) nuclei and a strongly adherent poly(heptadecafluorodecyl acrylate) has been shown to be effective at a concentration of 2.5 M in DMF solution containing TEAP (5×10^{-2} M). $Cu(OAc)_2$ remains soluble in this medium. As for the EA/Cu(II) system, two reduction reactions are observed when the fluorinated acrylate is used instead of EA. By analogy with what we have observed using a solution comprising EA and Cu(II), Cu(II) is reduced to Cu(0) at −1.2 V, while the poly(heptadecafluorodecyl acrylate) forms a strongly adherent polymer coating on the Cu(0) nuclei simultaneously. At −2 V this coating is removed from the Cu(0) nuclei and strongly adherent polymer coating is formed on stainless steel surface. According to analysis of the surface by ATR-FTIR and EDX, the fluorinated polyacrylate and Cu(0) coexist on nanostructured surface even when the selected potentials varies only from 0 V to −1.6 V.

[0092] When a selected potential of −1.6 V is applied to the electrically conducting stainless steel surface for 20 seconds, the contact angle of water is approximately 118°, which is nearly the same value, as the one measured in case of electrografting of fluorinated polyacrylate on polished stainless steel in the absence of Cu salt (contact angle of water of approximately 120°). A similar result is reported whenever a selected potential of −2 V is applied for 20 seconds (contact angle of water of approximately 117°). The surface coating is thus hydrophobic in these cases mainly because of the presence of the fluorinated polymer. The AFM analysis of the two samples shows respectively a nanostructured surface that comprises of a limited number of protuberances with a diameter comprised between 80-150 nm when a selected potential of −1.6 V is applied for 20 seconds or many smaller protuberances when a potential of −2 V is applied for 20 seconds. However, in these two cases the surface is essentially smooth.

[0093] The size of the Cu(0) nuclei can then be increased at the benefit of the surface area of the coating and the expense of the intimate contact of water droplets with the underlying surface via a mechanism of air occlusion.

[0094] For this purpose, the electrografting conditions have been changed as follows. A first selected potential of −1.2 V has been applied to the stainless steel surface to form Cu(0) nuclei coated by fluorinated polyacrylate. In a second step, a second selected potential of −2.2 V has been applied to the stainless steel surface, so that the stainless steel left available in between the Cu(0) nuclei is coated by a strongly adherent fluorinated polyacrylate, while the fluorinated polyacrylate is removed from the Cu(0) nuclei, allowing the Cu(0) nuclei to grow further. In a third step, a selected potential which varies from 0 V to −1.6 V is applied to the stainless steel surface to form a strongly adherent fluorinated polyacrylate coating on the copper nuclei, so that the whole nanostructured surface (Cu(0) nuclei and stainless steel) may be coated by the fluorinated polyacrylate.

[0095] The first two steps have been conducted by chronoamperometry (CA), that means that a selected potential is applied during a certain time, recording the measured current intensity as a function of the application time of the selected potential, and the third one by cyclic voltammetry (CV), that means that the selected potential which may be applied varies in a selected potential range with a selected variation speed during a selected application time.

[0096] In addition, the selected potential of −2.2 V has been applied for increasing period of time to increase the size of the Cu(0) nuclei. Each time in the third step, after the third selected potential which varies from 0 V to −1.6 V, a selected potential of −1.6 V has been applied until the current intensity dropped, due to the formation of a strongly adherent insulating fluorinated polyacrylate coating even on the copper nuclei. The experimental observations are reported in Table 1, together with the experimental contact angle of water. The roughness of nanostructured surface and the surface coverage by the polymer coating may be estimated by AFM. In all the cases, coexistence of Cu(0) and fluorinated polymer has been confirmed by ATR-FTIR and EDX.

[0097] Atomic force microscopy shows that large protuberances with a micrometric size coexist with nanosized entities, the roughness being determined using 100 μm×100 μm AFM pictures (Table 2). However, the contact angle of water is close to 140°, independently of the duration of the second step, which ranges from 30 seconds to 120 seconds. A possible explanation is that the fluorinated polyacrylate chains that are released at −2.2 V from the copper surface are poorly soluble in DMF and remains accumulated in the close vicinity of this surface, which dramatically slows down the growth of the Cu(0) nuclei.

[0098] The three steps previously used have therefore been implemented differently. Indeed, the duration of the two first steps has been fixed at 3 seconds and 15 seconds, respectively. The first step was followed by the second step and then the first step followed by the second step again. This was repeated several times to repeat the first step followed by the second step sequence from 10 to 40 times (Table 3). At the end of each first step followed by the second step sequence the solution has been stirred vigorously in order to prevent the fluorinated polyacrylate removed from the Cu(0) from accumulating at the Cu(0) nuclei surface. The third step has been carried out as before, i.e. varying a selected potential by CV from 0 V to −1.6 V and applying a selected potential of −1.6 V until the measured current intensity dropped.

[0099] Entries 1 to 3 in Table 3 shows that the surface roughness related to the average diameter of the Cu(0) nuclei, increase with the number of times the first step followed by the second step sequence is repeated. In parallel, the contact angle of water increases from 120° to 157, which is the desired transition from a hydrophobic and superhydrophobic surface. There is however an ideal number of cycles because too many cycles (40 cycles, Entry 4 Table 3) results in the merging of the Cu(0) nuclei and thus in a decreased roughness and hydrophobicity.

[0100] It is worth nothing that the superhydrophobic surfaces reported in entries 2 and 3 of Table 3 exhibit a hierarchical roughness which comprises both a roughness at the micrometer and the nanometer scale, due to Cu(0) nuclei with a diameter between ~5-10 μm that comprise other small Cu(0) nuclei with a diameter between ~500-999 nm. The large Cu(0) nuclei which are at least partially covered by small Cu(0) nuclei confer a raspberry-shaped structure to the surface as shown in FIG. **3**. In contrast, none of the surface prepared in Table 1 shows a two-scale roughness. As a rule, the number of nuclei is determined by the first step of the process. These nuclei are allowed to grow during the second step. Provided that the sequence of the two first steps is not repeated too many time (for example 10 to 15 times), formation of additional nuclei is not observed, being hampered by the passivation of the stainless steel by the fluorinated chains. However, when the Cu(0) nuclei are large enough (thus for example beyond 10-15 cycles), Cu nucleation at the surface of the Cu(0) nuclei providing them with a raspberry-shaped aspect as seen in FIG. **5**B. A contact angle of water of 157° confirms the superhydrophobicity.

[0101] The contact angle values and the roughness measured for the samples of the coating comprising copper and poly(HDFDA) prepared in example 2 by varying the surface and the polarization method show that both the surface, this underlying roughness and the polarization method have an influence on the contact angle values and the roughness measured for the strongly adherent polymer coatings.

EXAMPLES OF THE SECOND EMBODIMENT ACCORDING TO THE INVENTION

Example 3

[0102] Preparation of Nanostructured Surfaces from Monomer Droplets Consisting of an Emulsion in Protic Solvents

[0103] Emulsions are used to create droplets of an organic hydrophobic compound, the monomer, in protic hydrophilic medium, e.g. water. The emulsion of hydrophobic acrylates in water has been performed in the presence of a cationic surfactant (long alkyl chain bearing quaternary ammonium groups). Moreover the conductivity of the solution is thus ensured by the cationic surfactant, so there is no need to add other salt to the medium.

[0104] Acetonitrile (Aldrich), tert-butyl methacrylate (TBMA, Aldrich), isooctyl acrylate (iOA, Aldrich) and heptadecafluorodecyl acrylate (HDFDA, ABCR) were dried over calcium hydride and distilled under reduced pressure. Dimethylformamide (DMF, Aldrich) was dried over P_2O_5 and distilled under reduced pressure. Tetraethylammonium perchlorate (TEAP, Fluka) and copper(II) acetate (Aldrich) were heated in vacuum at 80° C. for 12 h prior to use.

[0105] Voltammetry and chronoamperometry were carried out in a one-compartment cell equipped with a platinum counter-electrode and a platinum pseudo-reference by using an EG&G potentiostat/galvanostat (M273) under the ambient atmosphere. The working electrode (2 cm^2 stainless steel, silicon or carbon plates) was washed with heptane and acetone (the silicon plates were washed with HF), and dried overnight at 150° C. in a vacuum. The working electrode was immersed in dry DMF containing the acrylate (tBMA) (1.5 M) or HDFDA (2 M), the surfactant cetyltrimethylammonium bromide (12.5 mg) and a selected potential was applied. The potential varies at 20 mV/s during voltammetry. The nanostructured surfaces were washed extensively with dry DMF followed by acetonitrile in the case of PtBMA and by trifluorotoluene when fluorinated polyacrylate was used. The nanostructured surface was dried in vacuum before characterization.

Preparation of Nanostructured Poly(Heptadecafluorodecyl) Acrylate Coatings in Water: Formation of Superhydrophobic Surfaces

[0106] If a surfactant, cetyltrimethylammonium bromide, is added to water until saturation, the surfactant self-associates and may be characterized by dynamic light scattering (DLS). The diameter of the observed aggregates is large, about 3 to 10 μm, with a mean diameter of about 5 μm these aggregates are formed of micellar rods.

[0107] After addition of the acrylate (HDFDA) and a subsequent sonication, an emulsion comprising droplets of HDFDA at least partially surrounded by the surfactant molecules is formed in the protic solvent. The diameter of the droplets of HDFDA of the emulsion may also be measured by DLS. The diameter of the droplets is about 600 nm to 800 nm, with a mean diameter of about 700 nm.

[0108] The formation of the strongly adherent polymer coating is performed in an electrochemical cell containing 5 ml of a 2M HDFDA solution comprising 12.5 mg of cetyltrimethylammonium bromide in water at about −2 V on doped-silicon, steel and carbon. The cationic surfactant insures the conductivity of the aqueous solution. After each application of a selected potential the electrically conductive or semiconductive surface is washed with water and trifluorotoluene.

[0109] Cetyltrimethylammonium bromide surfactant comprises an alkyl chain containing 16 carbon atoms and is only poorly soluble in the aqueous solution (saturation for about 30 mg of surfactant added to 10 ml water 2M in HDFDA).

[0110] However, a decrease of the current intensity is measured after each scan (FIG. **4**). The current intensity corresponding to the hydrolysis of H_2O decreases after each potential scanning, because hydrophocicity of the electrically conductive or semiconductive surface increases due to the formation of a strongly adherent hydrophobic polymer coating which reduces the access of water to the working electrode.

[0111] The formation of a strongly adherent fluorinated polyacrylate coating on steel, stainless steel, carbon and silicon (of different resistivity values from 0.001 Ω*cm heavily p- and n-doped Si, to 50 Ω*cm lightly n-doped Si: LC=low conductivity and HC=high conductivity) surfaces evidenced by voltammetry (FIG. **4**) is confirmed by ATR-FTIR. Absorptions characteristic of the polymer are observed at 1727 cm^{-1} (C═O stretching vibration) and 1157 cm^{-1} (C—O stretching vibration). The contact angle values measured for the different nanostructured surfaces confirm the presence of a strongly adherent hydrophobic poly(HDFDA) on the different electrically conductive or semiconductive surfaces. Depending on the method which is used, chronoamperometry or voltammetry, the contact angle of water may vary. However all the contact angles measured for nanostructured coatings prepared using a surfactant and a protic solvent are higher then the contact angle which can be measured for a strongly adherent poly(HDFDA) coating prepared using a 2 M HDFDA DMF based solution on the same surfaces (average contact angle 118°±4°). Moreover, nanostructured coatings, which may be called superhydrophobic because they exhibit a contact angle of more then 130°, may be obtained for all the different electrically conductive or semiconductive surfaces, due to the roughness of the strongly adherent polymer coating (FIG. **5**). Although the roughness seems to be correlated to the diameter of the droplets which are formed in the emulsion, the formation of hydrogen bubbles at the working electrode during the formation of the strongly adherent polymer coating, may induce an additional porosity of the polymer coating because hydrogen bubbles may be trapped in the strongly adherent polymer coatings, so that this porosity may also contribute to increase the overall roughness of the obtained strongly adherent polymer coatings.

[0112] Furthermore, the roughness depends on how the selected potential(s) is/are applied to the electrically conductive or semiconductive surfaces. When using chronoamperometry, i.e. applying a constant potential with time, rather than cyclic voltammetry, the coatings are more hydrophobic (Table 4) because the number of strongly adherent protuberances which are formed and subsequently the roughness of the strongly adherent polymer coating is higher. AFM measurements have confirmed that roughness of the nanostructured coating is increased when the coating is prepared by chronoamperometry whatever the used surface (carbon, steel or stainless steel). This explains the increase of the contact angle of water for these nanostructured surfaces prepared by chronoamperometry.

Preparation of Nanostructured Coatings Comprising Poly (Tert-Butyl methacrylate) or poly(isooctyl acrylate) using a Protic Solvent

[0113] After addition of tert-butyl methacrylate (tBMA) or isooctyl acrylate (iOA) to water, an emulsion is formed upon sonication. The diameter of the droplets of tBMA and iOA of the emulsion may be measured by DLS. The diameter of the droplets is about 1 μm to 3 μm for tBMA and about 0.8 to 2 μm for iOA. The emulsion prepared using 1.5 ml of tBMA is not stable and 600 μl of decaline (decahydronaphtalene) have been added to the emulsion to decrease the diameter of the tBMA droplets and to increase the stability of the emulsion.

[0114] The formation of the strongly adherent polymer coating is performed in a electrochemical cell containing 5 ml of a 1.5 M tBMA or iOA solution comprising 15 mg of cetyltrimethylammonium bromide in water at about −2.2 V for both monomers on carbon and stainless steel. The cationic surfactant also increases the conductivity of the aqueous solution. After each application of a selected potential the electrically conductive surface is washed with water and good solvents for the polymer (toluene or THF).

[0115] The nanostructured coatings prepared using tBMA or iOA, a surfactant and water are smoother as compared to coatings obtained with HDFDA. However, the presence of the strongly adherent polymer coating was assessed by ATR-FTIR. Absorptions characteristic of the polymer are observed at 1727 cm^{-1} (C═O stretching vibration) and 1157 cm^{-1} (C—O stretching vibration).

Preparation of Strongly Adherent Nanostructured Coatings of ZONYL™ Fluoromonomer Using a Protic Solvent

[0116] After addition of ZONYL™ fluoromonomer (2-(perfluoroalkyl)ethyl methacrylate) to the surfactant/water mixture, an emulsion is formed upon sonication. The size of the droplets measured by DLS is about 0.5 μm to 2 μm.

[0117] The formation of the strongly adherent polymer coating is performed in a electrochemical cell containing 5 ml of 0.05 M to 1 M ZONYL™ fluoromonomer (average Mn~534) solutions comprising 15 mg of cetyltrimethylammonium bromide in water at potentials between −0.8 V and −2 V depending on the concentration on stainless steel. After each application of a selected potential the electrically conductive or semiconductive surface is washed with water and trifluorotoluene.

[0118] The presence of the strongly adherent polymer coating was assessed by ATR-FTIR. Absorptions characteristic of the polymer are observed at 1727 cm^{-1} (C═O stretching vibration) and 1157 cm^{-1} (C—O stretching vibration). Comparable contact angle as with poly(HDFDA) were reached on these surfaces.

Example 4

[0119] Preparation of Nanostructured Surfaces from Monomer Droplets Consisting of Micelles of a Reactive Surfactant in a Selective Solvent

[0120] The monomer dimethyldecylaminoethylacrylate quaternary ammonium bromide (DMDAEABr) (scheme 4 structure A with n=10) has been synthesized by quaternization of dimethylamino-ethylacrylate (DMAEA) with decylbromide following a general synthesis pathway described in *Polymer Preprints,* 2003, 44(2), 264-265 and references therein.

[0121] The formation of the nanostructured and strongly adherent polymer coating is performed in an electrochemical cell containing 5 ml of a 0.1 M of DMDAEABr solution in water at about −2.2 V on carbon. The ionic reactive surfactant ensures the conductivity of the aqueous solution. Voltammetry (FIG. **6**) shows four successive scans of the potential on the same carbon electrode and clearly evidence the at least

partial passivation of the surface due to the formation of the strongly adherent polymer coating. In such coating, quaternary ammonium salt is part of the nanostructured coating so that the contact angle decreases drastically below 40°. Nanostructuration of the coating is still present due to the micellar monomer droplets spontaneously formed when the monomer is put in water. Interestingly, it must be noted that surfaces coated with quaternary ammonium of this type have efficiency in bacterial lyses. In a one step and in an aqueous micellar medium, such coatings have thus been achieved.

TABLE 1

Contact angle values measured for the samples prepared in example 1.

Sample type	Contact Angle of water (°)
Coatings comprising silver and PEA	90° ± 2°
Coatings comprising silver and P8QA	66° ± 3°
Coatings comprising silver and PPTEA	109° ± 3°
Coatings comprising silver and PPTEA + random copolymer of BuA and DAEA	32° ± 5°

TABLE 2

Contact angle values measured for the samples of the coating comprising copper and poly(HDFDA) prepared in example 2 by varying the duration of the second step.

Entry	Polarization procedure	Contact angle of water (°)	Roughness (nm) 100 μm × 100 μm surface
1	CA: −1.2 V 60 s, CA −2.2 V 30 s, CV with hold at −1.6 V	140 ± 4	260
2	CA: −1.2 V 60 s, CA −2.2 V 60 s, CV with hold at −1.6 V	135 ± 2	270
3	CA: −1.2 V 60 s, CA −2.2 V 120 s, CV with hold at −1.6 V	144 ± 2	300

TABLE 3

Contact angle values measured for the samples of the coating comprising copper and poly(HDFDA) prepared in example 2 by varying the number of times the cycle formed by the sequence step one followed by step two is repeated.

Entry	Polarization procedure	Contact angle of water (°)	Roughness (nm) 100 μm × 100 μm surface
1	10 cycles: CA: −1.2 V 3 s + CA −2.2 V 15 s, CV with hold at 1.6 V	120 ± 2	130
2	20 cycles: CA: −1.2 V 3 s + CA −2.2 V 15 s, CV with hold at 1.6 V	141 ± 1	190
3	30 cycles: CA: −1.2 V 3 s + CA −2.2 V 15 s, CV with hold at 1.6 V	157 ± 2	290
4	40 cycles: CA: −1.2 V 3 s + CA −2.2 V 15 s, CV → −1.6 V	148 ± 2	210

TABLE 4

Contact angle values measured and roughness for the samples of the coating comprising copper and poly(HDFDA) prepared in example 2 by varying the surface and the polarization method.

Surface	Polarization method	Contact angle of water (°)	Roughness (AFM)
Carbon	chronoamperometry	152° ± 2°	208 nm
Carbon	cyclic voltammetry	135° ± 2°	33 nm
Steel	chronoamperometry	157° ± 2°	91 nm
Steel	cyclic voltammetry	128° ± 3°	25 nm
Stainless steel	chronoamperometry	140° ± 3°	52 nm
Stainless steel	cyclic voltammetry	125° ± 4°	12 nm

1. An electrografting method for forming and regulating a strongly adherent nanostructured polymer coating onto an electro-conductive surface profile characterized in that the surface profile is regulated by electrodeposition of nanometre- and/or micrometre-scale nuclei onto the surface profile prior to or simultaneously to the formation of the polymer coating.

2. The electrografting method according to claim **1** wherein the electro-conductive surface is made of conductive and semi-conductive material.

3. The electrografting method according to claim **1** characterised in that the nuclei are inorganic nuclei provided by electrodeposition of a precursor salt.

4. The electrografting method according to claim **1** comprising the steps of:

a) regulating the surface profile by inorganic, preferably metallic, nuclei deposition onto the conductive surface upon application of a potential x to said surface immersed in a solution comprising a monomer and a precursor salt prior to or alternate with

b) forming a nanostructured polymer by application of a potential y onto the resulting surface profile.

5. The electrografting method according to claim **4** characterised in that the potential y equals the potential x.

6. The electrografting method according to claim **4** characterised in that the potential x is applied repeatedly during the formation of the nanostructured polymer onto the resulting surface profile.

7. The electrografting method according to claim **4** characterised in that the potentials x and y are applied repeatedly with different values.

8. The electrografting method according to claim **1** characterised in that the nuclei are made of metallic nuclei selected from the group consisting of a transition metal or a combination of transition metals.

9. The electrografting method according to claim **1** characterised in that the nuclei are made of an organic material provided by electrodeposition from a monomer droplet.

10. The electrografting method according to claim **9** characterised in that the nuclei further comprise a polymer provided by polymerisation of the monomer droplet at the conductive surface upon application of a potential z.

11. The electrografting method according to claim **9** characterised in that the monomer droplet is provided by an emulsion comprising the monomer in a protic solvent.

12. The electrografting method according to claim **11** characterised in that the emulsion further comprises a surfactant.

13. The electrografting method according to claim **11** characterised in that the protic solvent is water.

14. The electrografting method according to claim **10** characterised in that the potential z is applied repeatedly with different values.

15. The electrografting method according to claim **1** comprising a nucleation step at the electroconductive surface inducing nanostructuration of the coating.

16. The nanostructured polymer coating obtained by the electrografting method according to claim **1**.

17. Use of the nanostructured polymer coating according to claim **16** for a medical device application.

18. Use of the nanostructured polymer coating according to claim **16** for a biosensor application.

19. Use of the nanostructured polymer coating according to claim **16** for a microfluidic application.

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