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(54) Title: METHOD FOR PRODUCING SELF-HEALING ORGANIC-INORGANIC MATERIALS

(57) **Abstract:** The present invention refers to a self-healing organic-inorganic material, a process for the preparation of self-healing organic-inorganic materials, a self-healing organic-inorganic material obtainable by said process and to the uses of the self-healing organic-inorganic hybrid.

METHOD FOR PRODUCING SELF-HEALING ORGANIC-INORGANIC MATERIALS

FIELD OF THE INVENTION

The present invention relates to the area of vapor phase processing for producing self-healing organic-inorganic materials. More specifically, the present invention relates to a self-healing organic-inorganic material, a method for the preparation of self-healing organic-inorganic materials, to a self-healing organic-inorganic material obtainable by said method, and to the uses of said organic-inorganic material.

BACKGROUND

Self-healing materials are artificial or synthetically-created substances that have the built-in ability to automatically repair damages to themselves without any external diagnosis of the problem or human intervention. Materials degrade over time due to fatigue, environmental conditions, or damage incurred during operation. Cracks and other types of damage on a microscopic level have been shown to change the properties of materials, and the propagation of cracks can lead to eventual failure of the material. Self-healing covers all classes of materials, including polymers, metals, ceramics, and cementitious materials.

Commonly, metallic conductor self-healing materials are formed with bottom-up approaches. For example, healing electrode materials can be formed by embedding a liquid metal into a polymer. This was demonstrated for an eutectic Ga-In alloy (EGaIn) droplets dispersed in a silicone elastomer by Markvicka et al. (E. J. Markvicka, M. D. Bartlett, X. Huang, and C. Majidi, Nat. Mater., vol. 17, no. 7, pp. 618–624, Jul. 2018). In addition, Tee et al. (B. C. K. Tee, C. Wang, R. Allen, and Z. Bao, Nat. Nanotechnol., vol. 7, no. 12, pp. 825–832, Nov. 2012) dispersed chemically modified micro-nickel particles into an organic polymer. Besides, healing of an inorganic metal oxide surface can be achieved for oxide coatings deposited on substrates of the same metal. For example, Yang et al describes aluminum oxide films healed in Al/Al_2O_3 systems (Y. Yang, A. Kushima, W. Han, H. Xin, and J. Li, *Nano Lett.*, vol. 18, no. 4, pp. 2492–2497, 2018). However, these routes significantly limit the choice of the substrates and also offer a poor control of the material at the microstructure level. Furthermore, when using synthesis methods comprising a solvent; the solvent molecules can seriously damage the properties of the resulting materials through shielding of reactions or simply by creating cavities in the material that negatively affect the mechanical, electronic or optical properties of those materials.

In summary, prior art methods for the preparation of self-healing organic-inorganic materials do not allow to selectively modify the nano/microstructure of the material. Additionally, there is a need for new versatile processes that produce self-healing organic-inorganic materials. In addition, new self-healing organic-inorganic materials with enhanced stability, mechanical properties and durability are required.

BRIEF DESCRIPTION OF THE INVENTION

The inventors of the present invention have found a method that allows the preparation of self-healing organic-inorganic materials. The method is able to selectively modify the nano/microstructure of the self-healing organic-inorganic materials in a controlled way. Moreover, the self-healing organic-inorganic materials of the invention have an enhanced stability, mechanical properties (such as good flexibility and bending properties) and durability. In addition, the authors of the present invention have observed that the self-healing organic-inorganic materials of the invention are able to correct damage caused by normal usage of those materials (such as cracks) therefore, preventing costs incurred by material failure and reducing material inefficiency caused by material degradation over time.

Thus, in a first aspect, the invention is directed to a self-healing organic-inorganic material comprising:

- a polymeric substrate,
- a coating layer directly on the surface of the polymeric substrate, and
- an infiltrated layer within the polymeric substrate;

wherein the coating layer and the infiltrated layer comprise at least a metal, semimetal or semiconductor element;

wherein said at least a metal, semimetal or semiconductor element is the same in the coating and infiltrated layers; and

wherein the polymeric substrate or the infiltrated layer within the polymeric substrate, comprises a halogen.

A second aspect of the invention is directed to a process for the preparation of self-healing organic-inorganic materials, comprising the steps of:

i) providing a polymeric substrate in a reaction chamber;
ii) if the polymeric substrate does not comprises a halogen, pulsing a precursor comprising an halogen into the reaction chamber followed by an exposure time and then, purging of the reaction chamber,
   to obtain the polymeric substrate of step (i) infiltrated and optionally coated;
iii) pulsing a precursor comprising a metal, semimetal or semiconductor element into the reaction chamber followed by an exposure time and then, purging of the reaction chamber; and
   pulsing a co-reactant into the reaction chamber followed by an exposure time and

then purging of the reaction chamber, wherein the co-reactant reacts with at least part of the precursor comprising a metal, semimetal or semiconductor element, to obtain the polymeric substrate of step (i) or of step (ii) coated and infiltrated;

wherein the exposure time between the pulsing and the purging of step (ii) and/or of step (iii) is at least 5 seconds.

In a third aspect, the present invention is directed to a self-healing organic-inorganic material obtainable by the process of the invention in any of its particular embodiments.

A further aspect of the invention is directed to a device comprising

- at least a layer of the self-healing organic-inorganic material of the invention in any of its particular embodiments; and
- an organic light-emitting device (OLED) comprising at least one electrode;

wherein the layer of the self-healing organic-inorganic material is coating the at least one electrode.

In a further aspect, the present invention is directed to the use of the self-healing organic-inorganic material of the invention according to any of its particular embodiments, in the fabrication of electronic materials, optoelectronic materials, absorbent materials, personal safety equipment, sport equipment, construction and building materials, textiles, packaging, automotive and aircraft materials.

FIGURES

Figure 1: Transmission electron microscope (TEM) micrograph of a ParyleneC sample infiltrated with In_2O_3.

Figure 2: EDX (a) elemental composition depth profile and (b) Atomic concentrations after different etching times calculated from XPS data of a ParyleneC sample infiltrated with In_2O_3.

Figure 3: SEM images of ParyleneC/In_2O_3 cross-sections before and after exposure to air.

Figure 4: SEM images of a cut done by a focus ion beam (FIB) on the surface of a ParyleneC/In_2O_3 sample before (a) and after exposure to air (b).

Figure 5: SEM image of a FIB cut on the surface of PVC infiltrated with DEZ/water (a) before exposure to ambient air; (b) after exposure to ambient air and room temperature.

Figure 6: SEM image of a FIB cross-section of a PDMS polymer infiltrated with 15 cycles of thionyl chlorine/DEZ/water (a) before exposure to ambient air; (b) after exposure to ambient air and room temperature; and (c) enlarged image of the image B.

Figure 7: SEM image of focus ion beam (FIB) cross-section of a Nylon polymer infiltrated with 15 cycles of thionyl chlorine/DEZ/water: (a) before exposure to ambient air and (b) after exposure to ambient air and room temperature.

DETAILED DESCRIPTION OF THE INVENTION

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. As used herein, the singular forms “a” “an” and “the” include plural reference unless the context clearly dictates otherwise.

Self-healing organic-inorganic material

In the context of the present invention the term “self-healing organic-inorganic material” refers to what is commonly understood in the art and includes materials that can repair damages to themselves, for example, some self-healing materials may counter degradation through the initiation of a repair mechanism that responds to micro-damage such as cracks, in particular, said repair mechanism comprises chemical reparation of the damage.

In the context of the present invention the term “organic-inorganic” refers to materials that comprise organic and inorganic compounds or mixtures of compounds as commonly understood in the art.

In a first aspect, the invention is directed to a self-healing organic-inorganic material comprising:

- a polymeric substrate,
- a coating layer directly on the surface of the polymeric substrate, and
- an infiltrated layer within the polymeric substrate;

wherein the coating layer and the infiltrated layer comprise at least a metal, semimetal or semiconductor element;

wherein said at least a metal, semimetal or semiconductor element is the same in the coating and infiltrated layers; and

wherein the polymeric substrate or the infiltrated layer within the polymeric substrate, comprises a halogen.

In an embodiment, the self-healing organic-inorganic material consists of

- a polymeric substrate,
- a coating layer directly on the surface of the polymeric substrate, and
- an infiltrated layer within the polymeric substrate;

wherein the coating layer and the infiltrated layer comprise at least a metal, semimetal or semiconductor element;

wherein said at least a metal, semimetal or semiconductor element is the same in the coating and infiltrated layers; and

wherein the polymeric substrate or the infiltrated layer within the polymeric substrate, comprises a halogen.

Polymeric substrate

In the context of the invention the term “polymeric substrate” refers to an organic based polymeric material that may be coated and infiltrated such as polymers, biopolymers, polymeric hybrid materials, polymeric layered structures, and combinations thereof; preferably a polymer, a polymer derivative or a combination thereof. In an embodiment, the biopolymers are selected from polypeptides, nucleic acids and polysaccharides, such as starch, pectin, chitosan, alginate, carrageenan, cellulose and cellulose (e.g. methylcellulose, hydroxymethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose).

In an embodiment, the polymeric substrate is an organic based polymer, preferably selected from homopolymers, copolymers, multicomponent polymers or combinations thereof.

In an embodiment of the invention, the polymeric substrate of the present invention comprises an organic polymer having one or more functional groups selected from hydroxyl, ether, amino, ketone, halogen, carboxylic acid, ester, amide, acid halide, imide, imine, acrylate, terephthalate, alkenyl, and aryl.

In an embodiment, the polymeric substrate is selected from organosilicon polymers, polyurethanes, polyamides, polyxylylenes, parylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polymethacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, halopolymers, polypyrroles, polythiophenes, polystyrenes, polyaromatic hydrocarbons, polysaccharides, polypeptides, polysiloxanes, polysilazanes, polyketones and mixtures thereof. In a particular embodiment, the polymeric substrate of the present invention comprises a polymer selected from organosilicon polymers, polyurethane, polyamides, polyxylylenes, parylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polymethacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, halopolymers, polypyrroles, polythiophenes, polystyrenes, polyketones, and mixtures thereof; preferably from organosilicon polymers, polyurethane, polyamides, polyxylylenes, parylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, polypyrroles, polythiophenes, polystyrenes, polyketones, and mixtures thereof; more preferably from organosilicon polymers such as silanols, siloxides, silenes, siloles or siloxanes for example polydimethylsiloxane (PDMS), polyamides such as aliphatic polyamides for example polycaprolactam, polyphthalamides or aromatic polyamides, polyxylylenes such as poly(2,5 dichloro xylylene); parylenes such as poly(chloro-p-xylylene), poly(iodine-p-xylylene), poly(fluoro-p-xylene), poly(difluoro-p-xylene), poly (tetrafluoro-p-xylene), poly(dichloro-p-xylylene), poly(tetrachloro-p-xylylene), poly(bromo-p-xylene), poly(dibromo-p-xylene) or poly(tetrabromo-p-xylene); polyvinyls such as polyvinyl chloride, chlorinated polyvinyl chloride, polyvinyl iodine, iodate polyvinyl iodine, polyvinyl bromide, or polyvinyl fluoride, polyvinylidenes such as polyvinylidene chloride, polyvinylidene iodine, polyvinylidene bromide or polyvinylidene fluoride, and mixtures thereof.

In a particular embodiment, the polymeric substrate consists of a polymer selected from organosilicon polymers, polyurethanes, polyamides, polyxylylenes, parylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polymethacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, halopolymers, polypyrroles, polythiophenes, polystyrenes, polyaromatic hydrocarbons, polysaccharides, polypeptides, polysiloxanes, polysilazanes, polyketones and mixtures thereof. In a particular embodiment, the polymeric substrate of the present invention consist of a polymer selected from organosilicon polymers, polyurethane, polyamides, polyxylylenes, parylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polymethacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, halopolymers, polypyrroles, polythiophenes, polystyrenes and polyketones, and mixtures thereof; preferably from organosilicon polymers, polyurethane, polyamides, polyvinyls, polyamines, polyimides, polyalkylenes, polyacrylates, polyalcohols, polyethers, polyesters, polypyrroles, polythiophenes, polystyrenes, polyketones, and mixtures thereof; more preferably from organosilicon polymers, polyamides, polyxylylenes, parylenes, polyvinyls, polyvinylidenes and mixtures thereof.

In a particular embodiment, the polymeric substrate comprises a halogen; wherein the halogen is selected from a chlorine, fluorine, iodine, bromine or a mixture thereof; preferably the halogen is chlorine. In a more particular embodiment, the polymer substrate comprises a halogen as a functional group such as a halogen covalently bonded to a carbon atom of the polymeric substrate.

In a particular embodiment, the polymeric substrate of the present invention comprises a halogen-containing polymer; preferably selected from the group consisting of halogen-containing polyxylylenes, parylenes, polyvinyls, polyvinylidenes and mixtures thereof; more preferably selected from the group consisting of poly(chloro-p-xylylene), poly(dichloro-p-xylylene), poly(tetrachloro-p-xylylene), polyvinyl chloride, chlorinated polyvinyl chloride, polyvinylidene chloride, poly(Iodine-p-xylylene), polyvinyl Iodine, iodate polyvinyl iodine, polyvinylidene Iodine, polyvinyl bromide, polyvinylidene bromide, polyvinyl fluoride, polyvinylidene fluoride, poly(fluoro-p-xylene), poly(difluoro-p-xylene), poly (tetrafluoro-p-xylene), poly(bromo-p-xylylene), poly(dibromo-p-xylylene), poly(tetrabromo-p-xylylene), and combinations thereof.

In a particular embodiment, the polymeric substrate of the present invention consists of a halogen-containing polymer; preferably selected from the group consisting of halogen-containing polyxylylenes, parylenes, polyvinyls, polyvinylidenes and mixtures thereof; more preferably selected from the group consisting of poly(chloro-p-xylylene), poly(dichloro-p-xylylene), poly(tetrachloro-p-xylylene), polyvinyl chloride, chlorinated polyvinyl chloride, polyvinylidene chloride, poly(Iodine-p-xylylene), polyvinyl Iodine, iodate polyvinyl iodine, polyvinylidene Iodine, polyvinyl bromide, polyvinylidene bromide, polyvinyl fluoride, polyvinylidene fluoride, poly(fluoro-p-xylene), poly(difluoro-p-xylene), poly (tetrafluoro-p-xylene), poly(bromo-p-xylylene), poly(dibromo-p-xylylene), poly(tetrabromo-p-xylylene), and combinations thereof.

In another particular embodiment, the polymeric substrate can be selected from homopolymers and copolymers, including alternating copolymers, block copolymers and random copolymers.

In another embodiment, the polymeric substrate can alternatively be an inorganic-organic hybrid polymer or a blend of organic polymer and inorganic-organic hybrid material. Inorganic-organic hybrid polymers can be prepared by conventional methods from the prior art.

In a particular embodiment, the polymeric substrate of the present invention comprises one or more layers, such as one or more layers of different polymers. In a particular embodiment, the expression “one or more layers” refers to 1, 2, 3, 4, 5 or more polymeric layers; preferably refers to between 1 and 5 polymeric layers; more preferably refers to 1 or 2 polymeric layers. In an embodiment, each layer of the polymeric substrate has a thickness of at least 0.5 microns; preferably of at least 1 micron; preferably of between 1 and 250 µm, more preferably between 2 and 100 µm, even more preferably between 10 and 70 µm; even much more preferably of about 50 µm. In another embodiment, the polymeric substrate of the present invention is porous; preferably having macro porosity or microporosity as known in the art.

In a particular embodiment, the polymeric substrate of the present invention is in the form of spheres, cylinders, lamellae, films, fibers and bicontinuous structures; preferably it is a polymeric fiber.

In an embodiment, the polymeric substrate has a thickness of at least 1 micron; preferably of between 1 and 250 µm, more preferably between 1 and 100 µm, even more preferably between 1 and 50 µm. In another embodiment, the polymeric substrate has a length between 0.5 and 40 cm, preferably between 0.5 and 20 cm, more preferably between 1 and 10 cm, even more preferably between 1 and 8 cm.

In an embodiment, the polymeric substrate is a polymeric fiber with a diameter of between 1 and 100 µm, preferably between 1 and 50 µm, more preferably between 2 and 30 µm, even more preferably between 5 and 20 µm. In another embodiment, the polymeric substrate is a polymeric fiber with a diameter of between 1 and 100 µm, preferably between 2 and 20 µm, and a length between 0.5 and 40 cm, preferably between 0.5 and 10 cm.

Halogen

The polymeric substrate and/or the infiltrated layer within the polymeric substrate, comprises a halogen. In an embodiment, the halogen of the self-healing organic-inorganic material of the invention is selected from a chlorine, fluorine, Iodine, bromine or a mixture thereof; preferably is chlorine.

The halogen comprised in the infiltrated layer may be:(a) part of an organic compound such as a precursor comprising an halogen, for example thionyl chloride, malonyl chloride, terephthaloyl chloride or diacyl chloride; and/or (b) an halogen-containing compound of the metal, semimetal or semiconductor element such as an halide, oxyhalide or an hydroxyhalide of said metal, semimetal or semiconductor element and/or (c) part of a functional group in the polymer substrate such as Cl- group in polyvinyl chloride (PVC) or in Parylene C.

The halogen comprised in the polymeric substrate, may be (a) part of a halogen-containing compound of the metal, semimetal or semiconductor element such as an halide, oxyhalide or an hydroxyhalide of said metal, semimetal or semiconductor element and/or may be (b) a functional group in the polymer substrate such as Cl- group in polyvinyl chloride (PVC) or in Parylene C.

Coating layer.

The self-healing organic-inorganic material of the invention comprises a coating layer directly on the surface of the polymeric substrate (i.e. the coating layer is in direct contact with the surface of the polymeric substrate).

In a particular embodiment the coating layer covers partially or totally the surface of the polymeric substrate. In a more particular embodiment, the coating layer covers at least a 20% of the surface of the polymeric substrate; preferably at least a 50% of the surface of the polymeric substrate; more preferably at least a 90%; even much more preferably at least a 99%. In a more particular embodiment, the coating layer covers between a 20 and a 99% of the surface of the polymeric substrate.

In a particular embodiment the coating layer has a thickness of at least 1 nm, 5 nm, 10 nm, 15 nm, 20 nm, 25 nm, 30 nm or 50 nm; preferably at least 100 nm; more preferably at least 200 nm.

In a particular embodiment, the coating layer of the present invention has a thickness of between 1 and 500 nm; preferably between 5 and 200 nm; more preferably between 10 and 150 nm.

In a particular embodiment, the coating layer comprises a halogen.

In another embodiment, the coating layer comprises one or more coating layers on top of it (on the surface of the coating layer); preferably comprises one layer directly on its surface.

In a particular embodiment, the coating layer is chemically functionalized. In a particular embodiment, the coating layer is not continuous. In a particular embodiment, the coating layer is continuous. In a particular embodiment, the coating layer is porous.

In a more particular embodiment the coating layer comprises an oxide of the at least a metal, semimetal or semiconductor element. In an even more particular embodiment the coating layer consist of an oxide of the at least a metal, semimetal or semiconductor element.

Infiltrated layer

The self-healing organic-inorganic material of the invention comprises an infiltrated layer within the polymeric substrate. In the context of the present invention the term “infiltrated layer” is similar to “infiltration layer”. As explained in detail in the description of the process for the preparation of the self-healing organic-inorganic material of the invention, the infiltrated layer corresponds to the polymeric substrate wherein the metal, semimetal or semiconductor element has penetrated into said polymeric substrate. Also the halogen, if not originally present in the polymeric substrate, is infiltrated into said polymeric substrate forming an infiltrated layer. This means that the infiltration layer is a polymeric material as defined above comprising the metal, semimetal or semiconductor element and the halogen physically or chemically binding to at least part of the available functional groups in the subsurface of said polymeric material, i.e. infiltrating said polymeric substrate. In an embodiment, the infiltration layer of the self-healing organic-inorganic material is situated directly below the surface of the polymeric substrate, in contact with that surface and preferably extends to the interior of said polymeric substrate; in particular, the thickness of the infiltration layer is measured from the surface of the polymeric substrate.

In a particular embodiment the infiltration layer has a thickness of at least 1 nm, 5 nm, 10 nm, 15 nm, 20 nm, 25 nm, 30 nm or 50 nm; preferably at least 100 nm; more preferably at least 200 nm.

In a particular embodiment, the infiltrated layer of the present invention has a thickness of between 1 and 500 nm; preferably between 5 and 200 nm; more preferably between 10 and 150 nm.

In a particular embodiment, the infiltrated layer within the polymeric substrate comprises a halogen. In a more particular embodiment, only the infiltrated layer comprises a halogen within the polymeric substrate (i.e. the rest of the polymeric substrate does not comprise a halogen).

A metal, semimetal or semiconductor element

The coating layer and the infiltrated layer of the self-healing organic-inorganic material of the invention comprise at least a metal, semimetal or semiconductor element.

The coating layer and the infiltrated layer of the self-healing organic-inorganic material of the invention comprise the same at least one metal, semimetal or semiconductor element.

In the context of the present invention the term “metal” refers to what is commonly understood in the art, and includes earth metals, alkaline earths, transition metals, lanthanides, actinides and other metals such as B, Al, Ga, In, Tl, Nh, Sn, Pb, Fl, Mc and Lv. In the context of the present invention, the term “semimetal” or metalloid refers to what is commonly understood in the art and includes As, Sb, Te, Se and Bi. In the context of the present invention, the term “semiconductor” refers to what is commonly understood in the art and includes Ge and Si.

In a particular embodiment, the metal, semimetal or semiconductor element is selected from Al, Zn, Si, Ti, W, Sb, As, Ba, Bi, B, Cd, Ca, Ce, Cr, Co, Cu, Er, Eu, Gd, Ga, Ge, Hf, Fe, La, Mg, Mn, Mo, Ni, Nb, Os, Pt, Pr, Re, Rh, Ru, Sm, Se, Si, Sr, Ta, Te, Tb, Tm, Sn, Ti, W, V, Yb, Y, Zr, Pd, In, Ir, Li, and mixtures thereof; preferably selected from In, Zn, Al, As, Bi, B, Ca, Cr, C

o, Cu, Ga, Ge, Hf, Fe, La, Mg, Mn, Mo, Ni, Pt, Re, Sb, Si, Se, Ti, Ta, Te, Tm, Sn, W, V, Y, Zr, Li and mixtures thereof; more preferably selected from In, Zn, Al, Si, Ti and mixtures thereof; more preferably is Zn or In.

In an embodiment, the coating and/or infiltrated layer comprises an oxides, nitrides, halides, sulfides, phosphides, phosphates, salts, halogen-containing organic compounds or mixtures thereof of the metal, semimetal or semiconductor element; preferably oxides, nitrides, halogen-containing organic compounds or mixtures thereof of the metal, semimetal or semiconductor element.

Non-limiting examples of compounds that might be at the coating and/or infiltrated layer are Li_2O, Li_2S, Li_3N, LiF, BeO, B_2O_3, BN, MgF_2, MgO, Al_2O_3, Al_2S_3, AlF_3, AlN, AlP, SiO_2, CuCl, CaF_2, CaO, CaS, TiN, TiO_2, TiS_2, V_2O_3, VN, VO_2, VS_x, CrO_x, Mn_5O_8, MnF_2, MnO_x, MnS, FeN_x, FeO_x, FeS_2, Co_3O_4, CoO, CoN_x, Ni_3N, NiO, NiS, Cu_2O, Cu_3N, CuCl, CuO, CuS_x, Zn_3N_2, ZnF_2, ZnO, ZnS, Ga_2O_3, GaN, GaP, GaS_x, GeO_2, GeS_x, SrF_2, SrO, SrS, Y_2O_3, YF_3, ZrF_4, ZrN_x, ZrO_2, ZrS_2, Nb_2O_5, NbN, MoN_x, MoO_3, RuO_2, Rh_2O_3, PdO, AgO_2, CdO, CdS, In_2O_3, In_2S_3, InN, SnN_x, SnO, SnO_2, SnS_2, Sb_2O_5, Sb_2S_3, BaO, BaS, $Ba(OH)_2$, La_2O_3, La_2S_3, LaF_3, CeO_2, PrO_x, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, TbF_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, HfF_4, HfN_x, HfO_2, HfS_2, Ta_2O_5, TaN_x, TaO_x, WN_x, WO_3, WS_2, IrO_2, PtO_x, PbO_2, PbS, Bi_2O_3, Bi_2S_3, BiOCl and combinations thereof; wherein X and Y are integers between 0.1 and 6.

In a particular embodiment, the coating and/or infiltrated layer comprises an oxide, nitride, halide, sulfide, halogen-containing organic compound of the metal, semimetal or semiconductor element or mixtures thereof; preferably oxide, halogen-containing organic compound of the metal, semimetal or semiconductor element or mixtures thereof. Non-limiting examples of oxides that may be present at the coating and/or infiltrated layer are In_2O_3, ZnO, Al_2O_3, SiO_2, TiO_2 and mixtures thereof. Non-limiting examples of halides that may be present at the coating and/or infiltrated layer are indium chloride, zinc chloride, aluminium chloride, silicon chloride, titanium chloride and mixtures thereof.

In a more particular embodiment, the coating layer consist of an oxide, nitride, halide, sulfide or mixtures thereof of the metal, semimetal or semiconductor element or mixtures thereof; preferably an oxide of the metal, semimetal or semiconductor element.

In another embodiment, the coating layer and the infiltrated layer comprise an oxide of the metal, semimetal or semiconductor element.

In a more particular embodiment, the infiltrated layer comprises a halogen-containing compound of the metal, semimetal or semiconductor element. The halogen-containing compound of the metal, semimetal or semiconductor element may be an halide, oxyhalide, an hydroxyhalide, an halogen-containing organic compound of said metal, semimetal or semiconductor element or a mixture thereof.

In a particular embodiment, the halogen-containing compound of the metal, semimetal or semiconductor element of the infiltration layer is an halide, oxyhalide or hydroxyhalide of the metal, semimetal or semiconductor element; preferably is a chloride, oxychloride or hydroxychloride of the metal, semimetal or semiconductor element; more preferably wherein the metal, semimetal or semiconductor element is selected from In, Zn, Al, Si, Ti and mixtures thereof.

In a particular embodiment, the halogen-containing compound of the metal, semimetal or semiconductor element form inclusions in the infiltration layer.

In a particular embodiment, the halogen-containing compound of the metal, semimetal or semiconductor element is homogeneously distributed through all the thickness of the infiltration layer.

In an embodiment, the infiltrated layer comprises a mixture of:

- an oxide of the metal, semimetal or semiconductor element, and
- an halogen-containing compound of the metal, semimetal or semiconductor element.

In a more particular embodiment, the coating layer and/or the infiltrated layer comprise an oxide of the metal, semimetal or semiconductor element; wherein the metal, semimetal or semiconductor element is selected from In, Zn, Al, Si, Ti and mixtures thereof.

In an embodiment, the amount of the at least a metal, semimetal or semiconductor element of the infiltrated layer is not constant in all the thickness of the infiltrated layer; particularly, said amount is reduced from the top to the bottom of the infiltrated layer, being the top of the infiltrated layer in contact with the coating layer.

In a more particular embodiment, the infiltrated layer comprise an oxide of the metal, semimetal or semiconductor element; particularly, the amount of the at least a metal, semimetal or semiconductor oxide of the infiltrated layer is not constant in all the thickness of the infiltrated layer; more particularly said amount is reduced from top to the bottom of the infiltrated layer, being the top of the infiltrated layer in contact with the coated layer.

In a more particular embodiment, the infiltrated layer comprises an halogen-containing compound of the metal, semimetal or semiconductor element; particularly the amount of the halogen-containing compound of the metal, semimetal or semiconductor element of the infiltrated layer is not constant in all the thickness of the infiltrated layer; more particularly said amount increases from top to the bottom of the infiltrated layer, being the top of the infiltrated layer in contact with the coated layer.

In a particular embodiment, the self-healing organic-inorganic material comprises:

- a polymeric substrate selected from organosilicon polymers, polyurethane, polyamides, polyxylylenes, parlylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polymethacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, halopolymers, polypyrroles, polythiophenes, polystyrenes and polyketones and mixtures thereof,
- a coating layer directly on the surface of the polymeric substrate, and
- an infiltrated layer within the polymeric substrate;

wherein the coating layer and the infiltrated layer comprise at least a metal, semimetal or semiconductor element selected from In, Zn, Al, Si, and/or Ti;

wherein said at least a metal, semimetal or semiconductor element is the same in the coating and in the infiltrated layer; and

wherein the polymeric substrate and/or the infiltrated layer within the polymeric substrate, comprises a halogen;

preferably wherein the infiltrated layer comprises a halogen-containing compound of the metal, semimetal or semiconductor element selected from an halide, oxyhalide, an hydroxyhalide, an halogen-containing organic compound of said metal, semimetal or semiconductor element or a mixture thereof.

In a particular embodiment, the self-healing organic-inorganic material comprises:

- a polymeric substrate selected from organosilicon polymers, polyurethane, polyamides, polyxylylenes, parlylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polymethacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, halopolymers, polypyrroles, polythiophenes, polystyrenes and polyketones and mixtures thereof,
- a coating layer directly on the surface of the polymeric substrate, and
- an infiltrated layer within the polymeric substrate;

wherein the coating layer and the infiltrated layer comprise at least a metal, semimetal or semiconductor element selected from In, Zn, Al, Si, and/or Ti;

wherein said at least a metal, semimetal or semiconductor element is the same in the coating and in the infiltrated layer; and

wherein the polymeric substrate and/or the infiltrated layer within the polymeric substrate, comprises a halogen;

wherein the infiltrated layer comprises a halogen-containing compound of the metal, semimetal or semiconductor element selected from an halide, oxyhalide, an hydroxyhalide, an halogen-containing organic compound of said metal, semimetal or semiconductor element or a mixture thereof; and

wherein the coating and the infiltrated layer comprise oxides, nitrides, halides, sulfides, phosphides, phosphates, salts, halogen-containing organic compounds or mixtures thereof of the metal, semimetal or semiconductor element.

In a more particular embodiment, the self-healing organic-inorganic material comprises:

- a polymeric substrate selected from organosilicon polymers, polyurethane, polyamides, polyxylylenes, parlylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polymethacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, halopolymers, polypyrroles, polythiophenes, polystyrenes and polyketones and mixtures thereof,

- a coating layer directly on the surface of the polymeric substrate, and
- an infiltrated layer within the polymeric substrate;

wherein the coating layer and the infiltrated layer comprise at least a metal, semimetal or semiconductor element selected from In, Zn, Al, Si, and/or Ti;

wherein said at least a metal, semimetal or semiconductor element is the same in the coating and in the infiltrated layer; and

wherein the polymeric substrate and/or the infiltrated layer within the polymeric substrate, comprises a halogen;

wherein the infiltrated layer comprises a halogen-containing compound of the metal, semimetal or semiconductor element selected from an halide, oxyhalide, an hydroxyhalide, an halogen-containing organic compound of said metal, semimetal or semiconductor element or a mixture thereof; and

wherein the coating and the infiltrated layer comprise an oxide of the metal, semimetal or semiconductor element.

Process for the preparation of self-healing organic-inorganic materials

A second aspect of the invention is directed to a process for the preparation of self-healing organic-inorganic materials, comprising the steps of:

i) providing a polymeric substrate in a reaction chamber;

ii) if the polymeric substrate does not comprises a halogen, pulsing a precursor comprising an halogen into the reaction chamber followed by an exposure time and then, purging of the reaction chamber,

to obtain the polymeric substrate of step (i) infiltrated and optionally coated;

iii) pulsing a precursor comprising a metal, semimetal or semiconductor element into the reaction chamber followed by an exposure time and then, purging of the reaction chamber; and

pulsing a co-reactant into the reaction chamber followed by an exposure time and then purging of the reaction chamber, wherein the co-reactant reacts with at least part of precursor comprising a metal, semimetal or semiconductor element, to obtain the polymeric substrate of step (i) or of step (ii) coated and infiltrated;

wherein the exposure time between the pulsing and the purging of step (ii) and/or of step (iii) is at least 5 seconds.

In an embodiment, the process for the preparation of self-healing organic-inorganic materials, consist of the steps of:

i) providing a polymeric substrate in a reaction chamber;

ii) if the polymeric substrate does not comprise a halogen, pulsing a precursor comprising an halogen into the reaction chamber followed by an exposure time and then, purging of the reaction chamber,

to obtain the polymeric substrate of step (i) infiltrated and optionally coated;

iii) pulsing a precursor comprising a metal, semimetal or semiconductor element into the reaction chamber followed by an exposure time and then, purging of the reaction chamber; and

pulsing a co-reactant into the reaction chamber followed by an exposure time and then purging of the reaction chamber, wherein the co-reactant reacts with at least part of precursor comprising a metal, semimetal or semiconductor element, to obtain the polymeric substrate of step (i) or of step (ii) coated and infiltrated;

wherein the exposure time between the pulsing and the purging of step (ii) and/or of step (iii) is at least 5 seconds; and

(iv) optionally, repeating steps (ii) and/or (iii).

Each step of the process can be independently repeated a desired number of times, for example until the desired thickness (of the coating and/or infiltration layers) is achieved; in particular at least 10 times; more particularly at least 100 times. The number of repetitions of each step may be the same or different.

Step (i)

In a particular embodiment, the reaction chamber of the present invention is arranged for gas-to-surface reactions. Preferably, the expression “reaction chamber” refers to the chamber of a chemical vapor processing apparatus as known in the art such as a chemical vapor deposition (CVD), vapor phase infiltration (VPI) or atomic layer deposition (ALD) apparatus. Preferably the reaction chamber of the present invention is an atomic layer deposition reaction chamber such as those available from Cambridge Nanotech Inc. of Cambridge, Mass. In an embodiment, the reaction chamber is an atomic layer deposition chamber.

The polymeric substrate of step (i) of the process of the present invention may have all the characteristics as described above for the polymeric substrate of the self-healing organic-inorganic material of the invention in any of its particular embodiments.

Step (ii)

Step (ii) of the process of the present invention comprises pulsing a precursor comprising a halogen into the reaction chamber followed by an exposure time and then, purging of the reaction chamber, to obtain the polymeric substrate of step (i) infiltrated and optionally coated, when the polymeric substrate does not comprise a halogen element in its composition.

In the context of the present invention, the term “precursor” refers to a compound from which another compound is optionally formed.

The precursor comprising a halogen penetrates the surface of the polymeric substrate and may bind to at least part of the available functional groups in the subsurface of said polymeric substrate, thus infiltrating said polymeric substrate. Said precursor may also bind to the surface of said polymeric substrate, coating at least partially said polymeric substrate.

All the reagents used in the process of the invention (for example, the precursor comprising an halogen, the precursor comprising a metal, semimetal or semiconductor element, the co-reactant and the purge gas) may be injected or pulsed in the reaction chamber in the form of vapor or gas.

In the context of the present invention the term “pulse” is related to the period of time wherein a compound such as a metal, semimetal or semiconductor precursor, a precursor comprising an halogen, an organic molecule, water or any other reactant or co-reactant is dosed into the reaction chamber. In this sense, the term “pulsing” refers to dosing a compound into the reaction chamber of the present invention during a (short) period of time. The pulsing time may be adapted by the expert in the art lasting from a few hundredths of a second to several seconds, depending on the precursor, type of reactor, volume of the chamber, etc.

In a particular embodiment, pulsing times are independently between 0.01 and 20 seconds; preferably between 0.01 and 10 seconds, more preferably between 0.01 and 5 seconds, even more preferably between 0.01 and 2 seconds. In a further embodiment, pulsing times are independently between 0.01 and 1 second, preferably between 0.02 and 0.80 seconds, more preferably between 0.02 and 0.6 seconds; even more preferably between 0.05 and 0.5 seconds.

In the context of the present invention the term “exposure time” is related to the period of time or “hold” time wherein a static atmosphere or a non-flowing atmosphere inside the chamber is created and a compound or a mixture of compounds previously introduced in the chamber (by one or more pulses) are able to diffuse into the sub-surface of the polymeric substrate. Exposure time may be adapted by the expert in the art depending on the polymeric substrate characteristics, precursor, density of the polymeric substrate, desired infiltration depth, etc. It may last from a few seconds to a few minutes. In special cases it may last for hours. As used in the art, exposure time generally refers to the time between the end of pulsing and the start of purging.

In a particular embodiment, exposure times are at least 5 seconds; preferably at least 10 seconds; even more preferably at least 20 seconds.

In a particular embodiment, exposure times are between 5 and 300 seconds; more preferably between 1 and 200 seconds, even more preferably between 5 and 200 seconds. In a further embodiment, exposure times are between 5 and 150 second, preferably between 5 and 90 seconds, more preferably between 10 and 60 seconds; even more preferably between 20 and 40 seconds.

In the context of the present invention the term “purge” is related to the period of time wherein any non-reacted compound in the reaction chamber is removed. The purging time may be adapted by the expert in the art depending on the precursor, reaction chamber characteristics, pulsing time, etc. and may last from a few seconds to several minutes per cycle. In a particular embodiment, the purging of the present invention is performed by flowing a purge gas through the said reaction chamber or by evacuating said reaction chamber by means of vacuum; preferably by flowing an inert purge gas. In an embodiment, the inert purge gas is selected from nitrogen, argon, helium, neon, and mixtures thereof; preferably it is nitrogen.

In a particular embodiment, purging times are at least 5 seconds; preferably at least 10 seconds; even more preferably at least 20 seconds; even much more preferably at least 40 s.

In a particular embodiment, purging times are between 5 and 300 seconds; more preferably between 1 and 200 seconds, even more preferably between 5 and 200 seconds. In a further embodiment, exposure times are between 5 and 150 second, preferably between 5 and 90 seconds, more preferably between 10 and 80 seconds; even more preferably between 15 and 70 seconds.

In a particular embodiment, the precursor comprising an halogen is an organic or inorganic compound comprising an halogen selected from chlorine, fluorine, Iodine, bromine or a mixture thereof; preferably chlorine, fluorine, or bromine; more preferably chlorine.

In a particular embodiment, the precursor comprising a halogen is an organic or inorganic compound comprising a halogen. In a more particular embodiment, the inorganic compound comprising a halogen is a hydrogen halide such as hydrogen chloride, a phosphoryl halide such as phosphoryl chloride, a metal halide or mixtures thereof. Metal halide suitable as precursor comprising an halogen can be selected from those having a metal element selected from Al, Si, P, Ti, V, Cr, Mn, Cu, Zn, Ga, Ge, Zr, Nb, Mo, Cd, In, Sn, Sb, Hf, Ta, W, Pb and mixtures thereof.

In a more particular embodiment the organic compound comprising a halogen is an acyl halide. Non-limiting examples of acyl halides suitable as a precursors comprising a halogen are malonyl chloride, diacyl chloride, terephthaloyl chloride or mixtures thereof.

In a more particular embodiment, the precursor comprising a halogen comprises a sulfoxide group; preferably a thionyl group; more preferably thionyl chloride.

In a more particular embodiment, the precursor comprising a halogen is selected from hydrogen halides, phosphoryl halides, acyl halides, thionyl halides or mixtures thereof.

In a particular embodiment, the polymeric substrate of step (i) is infiltrated and optionally coated in step (ii) by the precursor comprising an halogen.

Step (iii)

Step (iii) of the process of the present invention comprises:

- pulsing a precursor comprising a metal, semimetal or semiconductor element into the reaction chamber followed by an exposure time and then, purging of the reaction chamber; and
- pulsing a co-reactant into the reaction chamber followed by an exposure time and then purging of the reaction chamber, wherein the co-reactant reacts with at least part of precursor comprising a metal, semimetal or semiconductor element,

to obtain the polymeric substrate of step (i) or of step (ii) coated and infiltrated.

In an embodiment, the precursor comprising a metal, semimetal or semiconductor element penetrates the surface of the polymeric substrate and binds to at least part of the available functional groups in the subsurface of said polymeric substrate, thus infiltrating said polymeric substrate. In addition, the precursor comprising a metal, semimetal or semiconductor element penetrates the surface of the polymeric substrate and binds to at least part of the precursor comprising an halogen Said precursor comprising a metal, semimetal or semiconductor element may also bind the surface of said polymeric substrate, coating said polymeric substrate.

The pulsed co-reactant (s) may react with at least part of the metal, semimetal or semiconductor containing precursors creating infiltrated metal, semimetal or semiconductor compounds. Said co-reactant may also react with at least part of the metal, semimetal or semiconductor containing precursors on the surface of said polymeric substrate, coating said polymeric substrate with metal, semimetal or semiconductor compounds.

In a particular embodiment, the precursor comprising a metal, semimetal or semiconductor element of the present invention is selected from metal halides, metal alkoxides, metal alkyls, metal diketonates, metal alkylamides, metal amidinates, metal aryls and cyclopentadienyl metals; preferably are independently selected from metal halides and metal alkoxides; more preferably from metal alkoxides.

The metal, semimetal or semiconductor element of the precursor of step (iii) may have all the characteristics as described above for metal, semimetal or semiconductor element of the self-healing organic-inorganic material of the invention in any of its particular embodiments.

Non-limiting examples of the precursor comprising a metal, semimetal or semiconductor element suitable for the present invention are trimethylaluminum, triisobutylaluminum, aluminum tris(2,2,6,6-tetramethyl-3,5-heptanedionate), tris(dimethylamido)aluminum, aluminum trichloride, triphenylantimony, tris(dimethylamido)antimony, antimony pentachloride, triphenylarsine, triphenylarsine oxide, barium bis(2,2,6,6-tetramethyl-3,5-heptanedionate), barium nitrate, bis(pentamethylcyclopentadienyl)barium, bis(triisopropylcyclopentadienyl)barium, bis(aceto-O)triphenylbismuth, tris(2-methoxyphenyl)bismuthine, triisopropyl borate, triphenylborane, tris(pentafluorophenyl)borane, cadmium acetylacetonate, dimethyl cadmium, calcium bis(2,2,6,6-tetramethyl-3,5-heptanedionate), tris(tetramethylcyclopentadienyl) cerium (III), bis(cyclopentadienyl)chromium (II), bis(pentamethylcyclopentadienyl)chromium (II), chromium (III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate), bis(cyclopentadienyl)cobalt (II), bis(pentamethylcyclopentadienyl)cobalt (II), bis(ethylcyclopentadienyl)cobalt (II), cobalt tris(2,2,6,6-tetramethyl-3,5-heptanedionate), copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate), copper bis(6,6,7,7,8,8,8,-heptafluoro-2,2-dimethyl-3,5-octanedioate), copper hexafluoroacetylacetonate, bis(N,N’-diisopropylacetamidinato)copper(I), erbium tris(2,2,6,6-tetramethyl-3,5-heptanedionate), tris(N,N-bis(trimethylsilyl)amide)europium (III), tris(tetramethylcyclopentadienyl)europium (III), tris(N,N-bis(trimethylsilyl)amide)gadolinium (III), tris(tetramethylcyclopentadienyl)gadolinium (III), tris(cyclopentadienyl)gadolinium (III), triethylgallium, trimethylgallium, tris(dimethylamido)gallium (III), hexamethyldigermanium (IV), tetramethylgermanium, tributylgermanium hydrige, triethylgermanium hydride, triphenylgermanium hydride, bis(methyl-η^5−cyclopentadienyl)methoxymethylhafnium, bis(trimethylsilyl)amidohafnium(IV) chloride, d imethylbis(cyclopentadienyl)hafnium(IV), hafnium(IV) *tert*-butoxide, hafnium isopropoxide, etrakis(diethylamido)hafnium, etrakis(dimethylamido)hafnium, tetrakis(ethylmethylamido)hafnium(IV), [1,1′-bis(diphenylphosphino)ferrocene]tetracarbonylmolybdenum(0), bis(pentamethylcyclopentadienyl)iron(II), 1,1′-diethylferrocene, iron(0) pentacarbonyl, iron(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate), cyclohexadiene iron tricarbonyl, ferrocene, lanthanum(III) isopropoxide, tris (N,N-bis(trimethylsilyl)amide)lanthanum(III), tris(cyclopentadienyl)lanthanum (III), tris(tetramethylcyclopentadienyl)lanthanum (III), tris(isopropylcyclopentadienyl)lanthanum(III), bis(cyclopentadienyl)magnesium (II), bis(pentamethylcyclopentadienyl)magnesium, bis(pentamethylcyclopentadienyl)manganese (II), bis(tetramethylcyclopentadienyl)manganese (II), bromopentacarbonylmanganese(I), cyclopentadienylmanganese(I) tricarbonyl, manganese(0) carbonyl, (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylmolybdenum(0), bis(cyclopentadienyl)molybdenum(IV) dichloride, cyclopentadienylmolybdenum(II) tricarbonyl, molybdenumhexacarbonyl, (propylcyclopentadienyl)molybdenum(I) tricarbonyl dimer, molybdenum hexafluoride, allyl(cyclopentadienyl)nickel(II), bis(cyclopentadienyl)nickel(II), bis(ethylcyclopentadienyl)nickel(II), bis(triphenylphosphine)nickel(II) dichloride, nickel(II) bis(2,2,6,6-tetramethyl-3,5-heptanedionate), nickel(II) acetylacetonate, bis(cyclopentadienyl)niobium(IV) dichloride, niobium pentafluoride, niobium pentachloride, niobium pentethoxide, niobium(V) iodide, triosmium dodecacarbonyl, trimethyl(methylcyclopentadienyl)platinum(IV), praseodymium(III) hexafluoroacetylacetonate, dirhenium decacarbonyl, (acetylacetonato)(1,5-cyclooctadiene)rhodium(I), bis(cyclopentadienyl)ruthenium(II), bis(ethylcyclopentadienyl)ruthenium(II), triruthenium dodecacarbonyl, tris(tetramethylcyclopentadienyl)samarium(III), dimethyl selenide, (3-aminopropyl)triethoxysilane, *N*-*sec*-butyl(trimethylsilyl)amine, chloropentamethyldisilane, 1,2-dichlorotetramethyldisilane, 1,3-diethyl-1,1,3,3-tetramethyldisilazane, dodecamethylcyclohexasilane, hexamethyldisilane, hexamethyldisilazane, 2,4,6,8,10-pentamethylcyclopentasiloxane, pentamethyldisilane, silicon tetrabromide, silicon tetrachloride, tetraethylsilane, 2,4,6,8-tetramethylcyclotetrasiloxane, 1,1,2,2-tetramethyldisilane, *N*,*N'*,*N''*-tri-*tert*-butylsilanetriamine, tris(*tert*-butoxy)silanol, tris(*tert*-pentoxy)silanol, disilane, strontium tetramethylheptanedionate, bis(pentamethylcyclopentadienyl) strontium, pentakis(dimethylamino)tantalum(V), tantalum(V) ethoxide, tris(diethylamido)(tert-butylimido)tantalum(V), tris(ethylmethylamido)(tert-butylimido)tantalum(V), tellurium tetrachloride, terbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate), tris(cyclopentadienyl)terbium(III), tris(tetramethylcyclopentadienyl)terbium(III), tris(N,N-bis(trimethylsilyl)amide)thulium(III), tris(cyclopentadienyl)thulium(III), bis[bis(trimethylsilyl)amino]tin(II), hexaphenylditin(IV), tetraallyltin, tetrakis(diethylamido)tin, tetrakis(dimethylamido)tin, tin(IV) iodide, tetramethyltin, tetravinyltin, tin(II) acetylacetonate, trimethyl(phenylethynyl)tin, trimethyl(phenyl)tin, tetrakis(diethylamido)titanium(IV), tetrakis(dimethylamido)titanium(IV), tetrakis(ethylmethylamido)titanium(IV), titanium(IV) diisopropoxide bis(2,2,6,6-tetramethyl-

3,5-heptanedionate), titanium(IV) isopropoxide, titanium tetrachloride, bis(*tert*-butylimino)bis(*tert*-butylamino)tungsten, bis(*tert*-butylimino)bis(dimethylamino)tungsten(VI), bis(cyclopentadienyl)tungsten(IV) dichloride, bis(cyclopentadienyl)tungsten(IV), tungsten hexafluoride, bis(isopropylcyclopentadienyl)tungsten(IV), tetracarbonyl(1,5-cyclooctadiene)tungsten(0), triamminetungsten(IV) tricarbonyl, tungsten hexacarbonyl, bis(cyclopentadienyl)vanadium(II), bis(ethylcyclopentadienyl)vanadium(II), vanadium(V) oxytriisopropoxide, tris(N,N-bis(trimethylsilyl)amide)ytterbium(III), tris(cyclopentadienyl)ytterbium(III), tris(N,N-bis(trimethylsilyl)amide)yttrium, tris(butylcyclopentadienyl)yttrium(III), tris(cyclopentadienyl)yttrium(III), yttrium 2-methoxyethoxide, yttrium(III) tris(isopropoxide), yttrium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate), bis(pentafluorophenyl)zinc, bis(2,2,6,6-tetramethyl-3,5-heptanedionate)zinc(II), diethylzinc (DEZ), dimethylzinc, diphenylzinc, bis(cyclopentadienyl)zirconium(IV), bis(cyclopentadienyl)dimethylzirconium, bis(methyl-η^5−cyclopentadienyl)methoxymethylzirconium, dimethylbis(pentamethylcyclopentadienyl)zirconium(IV), tetrakis(diethylamido)zirconium(IV), tetrakis(dimethylamido)zirconium(IV), tetrakis(ethylmethylamido)zirconium(IV), zirconium(IV) dibutoxide(bis-2,4-pentanedionate), zirconium(IV) 2-ethylhexanoate, zirconium tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionate), palladium (II) hexafluoroacetylacetonate, cyclopentadienyl indium, trimethyl indium (TMIn), iridium (III) acetylacetonate, lithium tert-butoxide and mixtures thereof.

In a preferred embodiment, the precursor comprising a metal, semimetal or semiconductor element of the present invention is selected from cyclopentadienyl indium, trimethyl indium(TMIn), bis(pentafluorophenyl)zinc, bis(2,2,6,6-tetramethyl-3,5-heptanedionate)zinc(II), diethylzinc, diphenylzinc, trimethylaluminum, triisobutylaluminum, aluminum tris(2,2,6,6-tetramethyl-3,5-heptanedionate), tris(dimethylamido)aluminum, aluminum trichloride, (3-aminopropyl)triethoxysilane, *N*-*sec*-butyl(trimethylsilyl)amine, chloropentamethyldisilane, 1,2-dichlorotetramethyldisilane, 1,3-diethyl-1,1,3,3-tetramethyldisilazane, dodecamethylcyclohexasilane, hexamethyldisilane, hexamethyldisilazane, 2,4,6,8,10-pentamethylcyclopentasiloxane, pentamethyldisilane, silicon tetrabromide, silicon tetrachloride, tetraethylsilane, 2,4,6,8-tetramethylcyclotetrasiloxane, 1,1,2,2-tetramethyldisilane, *N*,*N'*,*N''*-tri-*tert*-butylsilanetriamine, tris(*tert*-butoxy)silanol, tris(*tert*-pentoxy)silanol, disilane,tetrakis(diethylamido)titanium(IV), tetrakis(dimethylamido)titanium(IV), tetrakis(ethylmethylamido)titanium(IV), titanium(IV) diisopropoxide bis(2,2,6,6-tetramethyl-3,5-heptanedionate), titanium(IV) isopropoxide, titanium tetrachloride and mixtures thereof.

In a more preferred embodiment, the precursor comprising a metal, semimetal or semiconductor element of the present invention is selected from cyclopentadienyl indium, trimethyl indium (TMIn), bis(pentafluorophenyl)zinc, bis(2,2,6,6-tetramethyl-3,5-heptanedionate)zinc(II), diethylzinc, dimethylzinc, diphenylzinc and mixtures thereof.

The term “co-reactant” refers to a compound that activates the precursor comprising a metal, semimetal or semiconductor element, modifies the precursor, or catalyzes a reaction of the metal, semimetal or semiconductor element of the precursor, to convert it into the desired metal, semimetal or semiconductor compound or element that incorporates into the polymeric substrate to form either a coating layer or an infiltration layer. Suitable co-reactants are well-known in the art.

In a particular embodiment the co-reactant is selected from an oxygen source, a hydrogen source, a sulfur source and a nitrogen source; preferably an oxygen source. In a more particular embodiment the co-reactant of step (iv) or step (v) is selected from H_2O, O_2, O_3, hydrogen, BH_3, B_2H_6, H_2S, a metal hydride, NH_3 and a hydrazine; preferably is H_2O, O_2 or O_3; more preferably is H_2O.

In a particular embodiment, the co-reactant of step (iii) reacts with the at least part of precursor comprising a metal, semimetal or semiconductor element to provide a metal, semimetal or semiconductor compound or element independently selected from a metal oxide, a metal nitride, metal sulfide and a zero valent metal; preferably a metal oxide.

In a more particular embodiment, the co-reactant of step (iii) reacts with at least a 10 wt% of the total amount of the precursor comprising a metal, semimetal or semiconductor element; preferably with at least a 20 wt%.

In a particular embodiment, the process or some of the steps of the process of the present invention is performed at a temperature of between 25 and 350ºC; preferably at between 75 and 300ºC, more preferably of between 90 and 250ºC. In an embodiment, the process or some of the steps of the process of the present invention is performed at a pressure of between 1 mbar and 1034 mbar; preferably between 100 mbar and 800 mbar; more preferably between 500 mbar and 700 mbar. In a more particular embodiment, the process or some of the steps of the process of the present invention is performed under a constant nitrogen gas flow of between 10 and 500 standard cubic centimeters per minute (sccm); preferably between 15 and 50 standard cubic centimeters per minute (sccm); more preferably at 20 standard cubic centimeters per minute (sccm).

In a particular embodiment, steps (ii) and (iii) of the process of the present invention are repeated; preferably wherein steps (ii) and (iii) are repeated a different number of times; more preferably wherein the process comprises at least a cycle that consist of

- repeating step (ii) a number of times “n”; and
- repeating step (iii) a number of times larger than “n”;

even more preferably wherein step (iii) is repeated between 2n and 20n number of times; preferably between 5n and 15n times.

In a more particular embodiment, the process of the present invention further comprises:

the pulsing time of step (ii) and/or step (iii) being between 0.1 and 100 seconds;

steps (ii) and (iii) being performed at a temperature of between 25 and 350ºC;

the precursor of the metal, semimetal or semiconductor compound comprising the metal, semimetal or semiconductor element selected from In, Zn, Al, As, Bi, B, Ca, Cr, Co, Cu, Ga, Ge, Hf, Fe, La, Mg, Mn, Mo, Ni, Pt, Re, Sb, Si, Se, Ti, Ta, Te, Tm, Sn, W, V, Y, Zr and/or Li; preferably is selected from In, Zn, Al, Si, and/or Ti; more preferably is Zn or In; and

wherein the halogen is selected from a chlorine, fluorine, Iodine, bromine or a mixture thereof; preferably is chlorine.

Product by process.

Another aspect of the present invention is directed to a self-healing organic-inorganic material obtainable by the process of the invention as described above in any of its particular embodiments. All the characteristics described above for the self-healing organic-inorganic material of the invention also apply to the self-healing organic-inorganic material obtainable by the process of the invention.

Device

A further aspect of the invention is directed to a device comprising

- at least a layer of the self-healing organic-inorganic material of the invention in any of its particular embodiments;
- and an organic light-emitting device (OLED) comprising at least one electrode;

wherein the layer of the self-healing organic-inorganic material is coating the at least one electrode; preferably wherein the layer of the self-healing organic-inorganic material is in contact with the at least one electrode; more preferably wherein the electrode is a cathode.

In the context of the present invention the OLED may be any OLED known in the art such as an active-matrix organic light-emitting diode (AMOLED). In a particular embodiment, an OLED comprises an emissive layer sandwiched between two electrodes such as a cathode and an anode; preferably the emissive layer is organic.

In an embodiment, the device comprises at least two layers of the self-healing organic-inorganic material of the invention in any of its particular embodiments, wherein both of the layers are in contact with the OLED.

In a more particular embodiment, the OLED is completely encapsulated in the self-healing organic-inorganic material of the invention.

Uses

Another aspect of the present invention is directed to the use of the self-healing organic-inorganic material of the invention, in the fabrication of electronic materials, optoelectronic materials, absorbent materials, personal safety equipment, sport equipment, construction and building materials, textiles, packaging, automotive and aircraft materials; preferably in the fabrication of polymeric transistors, capacitors, optoelectronic devices, barriers, absorbers, personal safety equipment, sport equipment, protective laminate, building materials, textiles, packaging, automotive and aircraft materials.

EXAMPLES

The invention is illustrated by means of the following examples which in no case limit the scope of the invention.

Example 1: Self-healing organic-inorganic material preparation

In the present example a Parylene C substrate was infiltrated by a VPI process with trimethylindium (TMIn) to obtain a self-healing organic-inorganic material.

Parylene C (ParC) is the generic name for poly(chloro-p-xylylene) polymer a thermoplastic, semi-crystalline polymer. ParyleneC substrates were purchased from Plasma Parylene Systems GmbH. The thickness of the polymer substrate was about 50 µm.

Indium oxide infiltration was performed by vapor phase infiltration (VPI) of trimethylindium (TMIn) and 30 % (in H_2O) of hydrogen peroxide in an atomic layer deposition (ALD) reactor (Savannah S100; Cambridge Nanotech Inc.). Water or ozone have also been successfully used as alternatives of hydrogen peroxide. Infiltration was carried out under a constant nitrogen gas flow of 20 standard cubic centimeters per minute (sccm). The reactor temperature was between 135 and 210°C.

A typical atomic layer deposition (ALD) process comprises at least a cycle consisting of Pulse/Purge/Pulse/Purge. On the contrary, in a VPI process, the substrate was exposed to the precursors for defined periods of time before purging, thereby allowing diffusion of the precursors into the substrate, for example using the following cycle:

Pulse/Exposure/Purge/Pulse/Exposure/Purge. Thus, the technical difference of VPI over ALD is an additional exposure time after the precursor pulse, so that precursor has a longer residence time in the reactor. Said additional exposure time is achieved by closing the stop-valve before the vacuum pump of the ALD reactor.

An VPI cycle for infiltrating a ParyleneC substrate with trimethylindium (TMIn) was as follows: first, TMIn was pulsed for 0.4 s to the ALD reactor and left inside the chamber for additional 30 seconds to let the precursor infiltrate the polymeric substrate. This was followed by 60 seconds of purging time to evacuate unreacted precursor and by-products. The same steps were performed for H_2O_2 thus finishing one cycle. Thus, an VPI cycle for infiltrating a ParyleneC substrate with trimethylindium (TMIn) and H_2O_2 consisted of Pulse(TMIn, 0.4s)/ Exposure(30s)/ Purge(N_2, 60s)/ Pulse(H_2O_2, 0.4s)/ Exposure(30s)/ Purge(N_2, 60s). The total number of cycles was 150.

Different samples were obtained by performing the previous infiltrating process at different temperatures: 135ºC, 140ºC, 150ºC, 170ºC, 180ºC and 210ºC.

Then, polymeric samples with infiltrated In_2O_3 , indium chloride, and indium oxychloride inclusions were obtained. The samples also showed a thin layer of In_2O_3 on the surface (see Figure 1).

Self-healing Infiltrated polymeric sample characterization

The infiltrated polymeric samples obtained above were characterized as follows.

The bonding and the element composition of the samples have been studied with X-ray photoelectron spectroscopy (XPS) using a SPECS instrument, equipped with a hemispherical electron analyzer and a monochromatized source of Al Kα X-rays. Binding energies were calibrated by the C 1s peak at 284.5 eV for all samples. Depth profiling was performed by etching the samples with an argon ion gun with an accelerating voltage of 2 keV and a current of 10 μA. To compensate a possible charge accumulation, an electron gun was used.

Attenuated Total Reflectance−Fourier Transform Infrared Spectroscopy (ATR-FTIR) measurements were performed with a PerkinElmer Frontier spectrometer with the ATR sampling stage. Typical acquisition parameters averaged 20 scans from 510 to 4000 cm^{-1} with the resolution of 4 cm^{-1}.

Scanning electron microscopy (SEM) images were taken with the FEI Helios 450S microscope with an accelerating voltage of 5 keV and a current of 50 pA. To investigate the nature and composition of the samples below the surface, cuts have been made with a focused ion beam (FIB) at 30 kV of accelerating voltage. EDX mapping in SEM was done with an EDAX Octane pro detector. FIB was also utilized for lamella preparation to study the samples in a transmission electron microscope (TEM). TEM characterization and EDX measurements were performed with an FEI Titan microscope at 300 keV acceleration voltage in STEM mode and an EDAX SDD detector.

Figure 1 shows a transmission electron microscope (TEM) micrograph of a ParyleneC sample infiltrated with In_2O_3 at 210 °C. Figure 1 shows an upper dark layer related to a thin indium oxide film, followed by a region where intermixing of organic and inorganic phases was observed. Clusters of indium oxide appear darker in TEM due to the higher atomic mass of indium than that of carbon or chlorine in ParyleneC. The density of indium inside the polymer descended promptly after about 150 nm depth.

Figure 2 (a) shows an EDX elemental composition depth profile and (b) Atomic concentrations after different etching times calculated from XPS data of a ParyleneC sample infiltrated with In_2O_3 at 210°C. Results from EDX spectra from the same area reaffirmed the sharp decline of indium oxide at that depth. However, a weak indium signal of 2-3 atomic percent reached down to 300 nm. Interestingly, the chlorine signal from the polymer was present already near the surface of the structure (Fig. 3B). It steadily grew through the whole indium oxide infiltrated area and reached its maximum of 13 at. % at 150 – 200 nm depth which was the interface between ParyleneC and layer. Beyond this point, the concentration of chlorine dropped down to 6 at. % which corresponds to the level of chlorine in the pristine polymer. Atomic percent (or at. %), gives the percentage of one kind of atom relative to the total number of atoms.

Self-healing infiltrated polymeric sample tests

FIB was used to introduce defects into the infiltrated ParyleneC polymeric samples. After etching away the metal oxide In_2O_3 thin film on the surface of the infiltrated polymeric samples by FIB, the material was exposed to ambient air and room temperature. Afterwards, the sample was extracted from the vacuum chamber to ambient atmosphere (atmospheric pressure, room temperature and air). After 5 minutes exposure to air, the samples were placed back into the microscope and examined for changes.

Figure 3 shows SEM images of ParyleneC/In_2O_3 cross-sections before and after exposure to air. Figure 3 shows swelling mostly in the indium infiltrated area. The amount of grown material increased for the samples infiltrated at higher temperatures, as these samples possessed a higher loading of the infiltrate. Moreover, for the sample infiltrated at 210°C, the formation of polycrystalline structures was observed.

Figure 4 shows SEM images of a cut done by FIB on the surface of a ParyleneC infiltrated sample before (on the left) and after exposure to air (on the right). The defect was produced by FIB by etching away sections of the thin film on the surface and exposing the infiltrated

ParyleneC to ambience. After 5 minutes of exposure to air, the structure was examined again by electron microscopy. Figure 4 (b) shows that the defect healed with a spherical deposit of an amorphous material. EDX analysis (not shown) of the cut before exposure to air showed the deficiency of oxygen and indium. In contrast, the healed structure contained oxygen and indium and had a lack of carbon and chlorine signals.

Thus, results showed that the infiltrated polymeric organic-inorganic samples obtained in the present example were able to “self-heal” defects. In particular, the authors observed that when a rupture of defect was created in the sample , the infiltrations moved to the defect site, reacted with air forming indium oxide and healing the rupture or defect with indium oxide.

Thus, the author of the invention have developed self-healing flexible transparent conductive materials, comprising polymeric substrates infiltrated with transparent conductive oxides.

Example 2: Self-healing organic-inorganic material preparation

Following the same method as in Example 1, a Parylene C substrate was infiltrated by VPI with diethylzinc (DEZ) and water as precursors at process temperatures between 100 and 210 ºC to obtain a self-healing organic-inorganic material. The number of infiltration cycles was between 50 and 100. Each VPI cycle for infiltrating a ParyleneC substrate consisted of Pulse (DEZ, 0.4s)/ Exposure(30s)/ Purge(N_2, 60s)/ Pulse(H_2O, 0.4s)/ Exposure(30s)/ Purge(N_2, 60s).

In addition, polyvinyl chloride (PVC) substrates were also infiltrated using DEZ or TMIn and water or hydrogen peroxide precursors obtaining self-healing organic-inorganic materials.

Figure 5 shows a SEM image of focus ion beam (FIB) cut on the surface of PVC infiltrated with DEZ/water A) before exposure to ambient air; B) after exposure to ambient air and room temperature.

Example 3: Self-healing organic-inorganic material preparation

In the present example a polydimethylsiloxane (PDMS) polymer substrate was infiltrated by a VPI process with thionyl chloride, diethylzinc (DEZ) and water to obtain a self-healing organic-inorganic material.

The number of infiltration cycles was about 15.

Each VPI cycle consisted of:

[Pulse (Thionyl chloride, 0.4s)/ Exposure- (30s)/ Purge (N_2, 20s)] x1 time and

[Pulse (DEZ 0.4s)/ Exposure (30s)/ Purge (N_2, 60s)/ Pulse (H_2O, 0.4s)/ Exposure (30s)/ Purge (N_2, 60s)] x7 times.

Figure 6 shows an SEM image of a focused ion beam (FIB) cross-section of a PDMS polymer infiltrated with 15 cycles of thionyl chlorine/DEZ/water A) before exposure to ambient air; B) after exposure to ambient air and room temperature; and C) magnification of a part of image B.

The results shows that the PDMS substrate was infiltrated with zinc compounds, such as zinc oxide clusters, zinc chloride and zinc oxychloride inclusions down to more than 10 µm depth as seen on the scanning electron microscopy (SEM) image (fig. 6A), obtained after sectioning the self-healing organic-inorganic material with a focused ion beam (FIB).

After exposure of the cross-section to ambient air at room temperature, the growth of zinc oxide structures (see fig. 6B and 6C) as consequence of the partial conversion of metal chlorines to metal oxides.

In addition, results showed that the higher part of the cross-section has more amount of zinc oxide. In addition, surprisingly, a Zn depletion layer was observed in Figure 6C, indicating mobility of the inorganic clusters towards the growth sites located below.

Example 4: Self-healing organic-inorganic material preparation

In the present example a PA-6 or Nylon-6 polymer substrate was infiltrated by the VPI process described above in Example 3 using thionyl chloride, diethylzinc (DEZ) and water to obtain a self-healing organic-inorganic material.

Figure 7 shows a SEM image of a focused ion beam (FIB) cross-section of a Nylon polymer infiltrated with 15 cycles of thionyl chloride/DEZ/water A) before exposure to ambient air; B) after exposure to ambient air and room temperature.

Results showed that the substrates were infiltrated with zinc compounds, such as zinc oxide clusters and zinc chlorines and, after exposure of the cross-section to ambient air at room temperature, the growth of zinc oxide structures was observed.

Example 5: Permeation barriers for OLEDs

The self-healing organic-inorganic materials fabricated in examples 1-4 are used as permeation barriers for organic light-emitting devices (OLEDs) by thin film encapsulation of said OLEDs with the self-healing organic-inorganic materials.

In particular, the cathode of an active-matrix organic light-emitting diode (AMOLED) is coated with a polymer substrate as described in examples 1-4 by any technique known in the art. Then, said polymer substrate is infiltrated as described in examples 1-4 to obtain a self-healing organic-inorganic material.

The lifetime of encapsulated OLEDs was extended over non encapsulated OLEDs.

Example 6: Electronic devices

The self-healing organic-inorganic materials fabricated in examples 1-4 are used as part of electronic devices such as parts of polymeric transistors or capacitors. For example, the electrodes of a capacitor are coated with the self-healing organic-inorganic materials fabricated in examples 1-4 .

Example 7: Textile

The self-healing organic-inorganic materials fabricated in examples 1-4 are applied to fibers or yarns and used in textile materials in personal safety equipment, sport equipment,. Applications of such woven or non-woven materials include also protective laminate, construction/building materials, packaging, reinforcing or functional materials in automotive, aircraft and aerospace applications.

Example 8: Packaging

The self-healing organic-inorganic materials fabricated in examples 1-4 are applied to polymeric foils or fibers, woven and non-woven, and used as packaging materials for food or any goods that require protection against humidity or environmental gases such as oxygen. The self-healing materials provide additional protection and extend the shelf-life of those goods.

CLAIMS

1. A self-healing organic-inorganic material comprising:
   - a polymeric substrate,
   - a coating layer directly on the surface of the polymeric substrate, and
   - an infiltrated layer within the polymeric substrate;

   wherein the coating layer and the infiltrated layer comprise at least a metal, semimetal or semiconductor element;

   wherein said at least a metal, semimetal or semiconductor element is the same in the coating and infiltrated layers; and

   wherein the polymeric substrate or the infiltrated layer within the polymeric substrate comprises a halogen.

2. The self-healing organic-inorganic material according to claim 1, wherein the halogen is selected from a chlorine, fluorine, iodine, bromine or a mixture thereof; preferably is chlorine.

3. The self-healing organic-inorganic material according to any of claims 1 or 2, wherein the polymeric substrate is selected from organosilicon polymers, polyurethanes, polyamides, polyxylylenes, parylenes, polyamines, polyimides, polyalkylenes, polyacrylates, polymethacrylates, polyalcohols, polyethers, polyesters, polyvinyls, polyvinylidenes, halopolymers, polypyrroles, polythiophenes, polystyrenes, polyaromatic hydrocarbons, polysaccharides, polypeptides, polysiloxanes, polysilazanes, polyketones, and mixtures thereof.

4. The self-healing organic-inorganic material according to any one of claims 1 to 3, wherein the polymeric substrate is a halogen-containing polymeric substrate; preferably poly(chloro-p-xylylene), polyvinyl chloride, chlorinated polyvinyl chloride, polyvinylidene chloride, poly(Iodine-p-xylylene), polyvinyl Iodine, iodate polyvinyl iodine, polyvinylidene Iodine, polyvinyl bromide, polyvinylidene bromide, polyvinyl fluoride, polyvinylidene fluoride, poly(fluoro-p-xylene), poly(difluoro-p-xylene), poly (tetrafluoro-p-xylene), poly(dichloro-p-xylylene), poly(tetrachloro-p-xylylene), poly(bromo-p-xylene), poly(dibromo-p-xylene), poly(tetrabromo-p-xylene), and combinations thereof.

5. The self-healing organic-inorganic material according to any one of claims 1 to 4, wherein the metal, semimetal or semiconductor element is selected from In, Zn, Al, As,

Bi, B, Ca, Cr, Co, Cu, Ga, Ge, Hf, Fe, La, Mg, Mn, Mo, Ni, Pt, Re, Sb, Si, Se, Ti, Ta, Te, Tm, Sn, W, V, Y, Zr and/or Li; preferably is selected from In, Zn, Al, Si, and/or Ti; more preferably is Zn or In.

6. The self-healing organic-inorganic material according to any one of claims 1 to 5, wherein the coating and/or infiltrated layer comprise oxides, nitrides, halides, sulfides, phosphides, phosphates, salts, halogen-containing organic compounds or mixtures thereof of the metal, semimetal or semiconductor element.

7. The self-healing organic-inorganic material according to any one of claims 1 to 6, wherein the coating layer and the infiltrated layer comprise an oxide of the metal, semimetal or semiconductor element;
wherein the metal, semimetal or semiconductor element is selected from In, Zn, Al, Si, or Ti; and
optionally wherein the infiltration layer has a thickness of at least 50 nm.

8. The self-healing organic-inorganic material according to claim 7; wherein the infiltrated layer further comprises a halogen-containing compound of the metal, semimetal or semiconductor element selected from an halide, oxyhalide, hydroxyhalide or a mixture thereof of the metal, semimetal or semiconductor element.

9. A process for the preparation of self-healing organic-inorganic materials according to any one of claims 1 to 8, comprising the steps of:
   i) providing a polymeric substrate in a reaction chamber;
   ii) if the polymeric substrate of step (i) does not comprise a halogen, pulsing a precursor comprising a halogen into the reaction chamber followed by an exposure time and then, purging of the reaction chamber,
   to obtain the polymeric substrate of step (i) infiltrated and optionally coated;
   iii) pulsing a precursor comprising a metal, semimetal or semiconductor element into the reaction chamber followed by an exposure time and then, purging of the reaction chamber; and
   pulsing a co-reactant into the reaction chamber followed by an exposure time and then purging of the reaction chamber, wherein the co-reactant reacts with at least part of the precursor comprising a metal, semimetal or semiconductor element,
   to obtain the polymeric substrate of step (i) or of step (ii) coated and infiltrated;

wherein the exposure time between the pulsing and the purging of step (ii) and/or of step (iii) is at least 5 seconds.

10. Process according to claim 9, wherein the exposure time between the pulsing and the purging is at least 10 seconds and/or wherein steps (ii) and (iii) are performed at a temperature between 25 and 300ºC; preferably between 180 and 250ºC.

11. Process according to any one of claims 9 to 10, wherein steps (ii) and (iii) are repeated; preferably wherein steps (ii) and (iii) are repeated a different number of times; more preferably wherein the process comprises at least a cycle that consist of

    - repeating step (ii) a number of times “n”; and

    - repeating step (iii) a number of times larger than “n”.

12. Process according to any one of claims 9 to 11,

    wherein the pulsing time of step (ii) and/or step (iii) is between 0.1 and 100 seconds;

    wherein the exposure time between the pulsing and the purging of step (ii) and/or of step (iii) is at least 10 seconds;

    wherein steps (ii) and (iii) are performed at a temperature of between 25 and 350ºC;

    wherein the precursor of the metal, semimetal or semiconductor compound comprises the metal, semimetal or semiconductor element as defined on claim 5; and

    wherein the precursor comprising a halogen is selected from hydrogen halides, phosphoryl halides, acyl halides, thionyl halides or mixtures thereof.

13. A self-healing organic-inorganic material obtainable by the process according to any one of claims 9 to 12.

14. A device comprising:
    - at least a layer of the self-healing organic-inorganic material according to any of claims 1-8 or 13; and
    - an Organic light-emitting device (OLED) comprising at least one electrode;

    wherein the layer of the self-healing organic-inorganic material is coating the at least one electrode.

15. Use of the self-healing organic-inorganic material as defined in any of claims 1 to 8 or 13, in the fabrication of electronic materials, optoelectronic materials, absorbent materials, personal safety equipment, sport equipment, construction and building materials, textiles, packaging, automotive and aircraft materials.

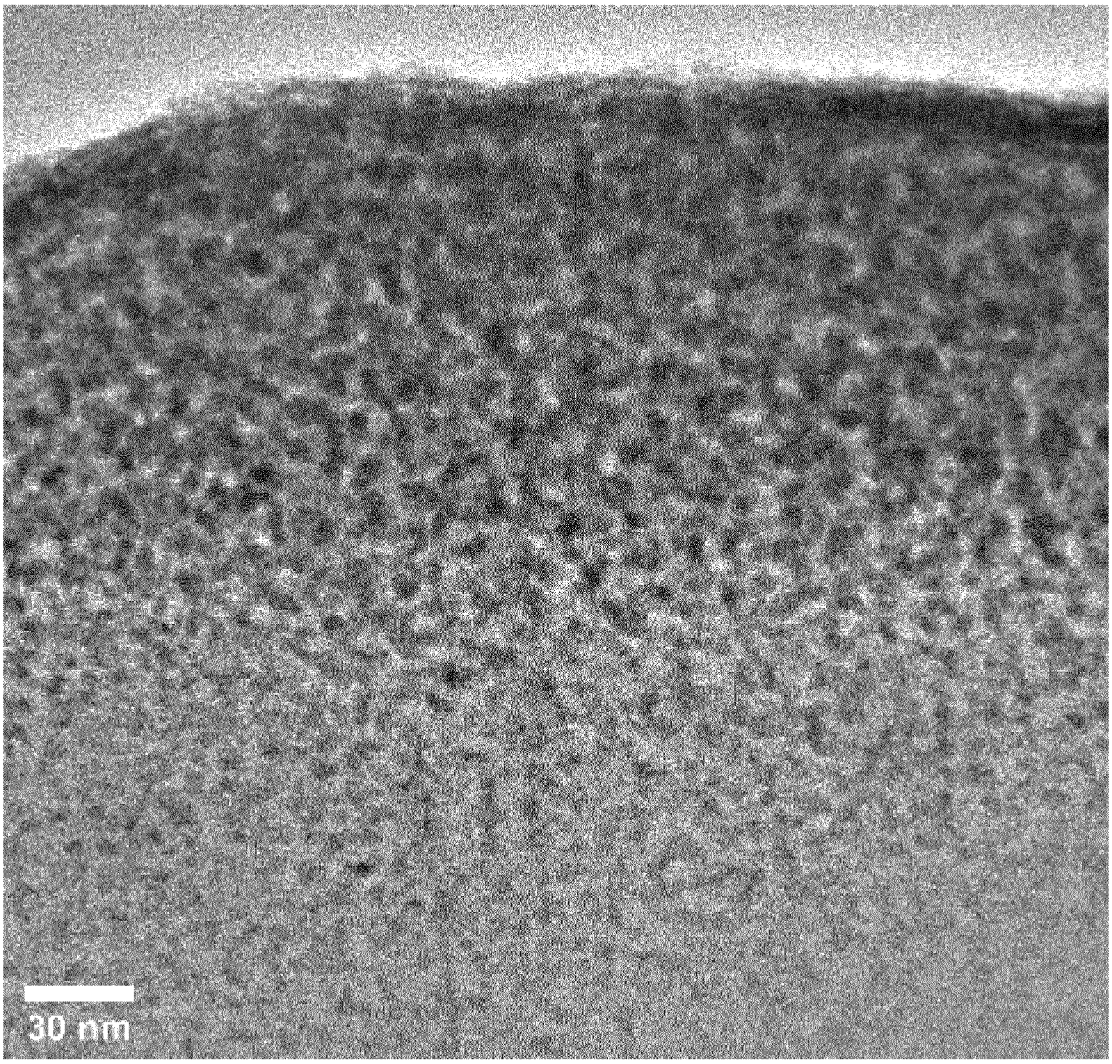

FIG. 1

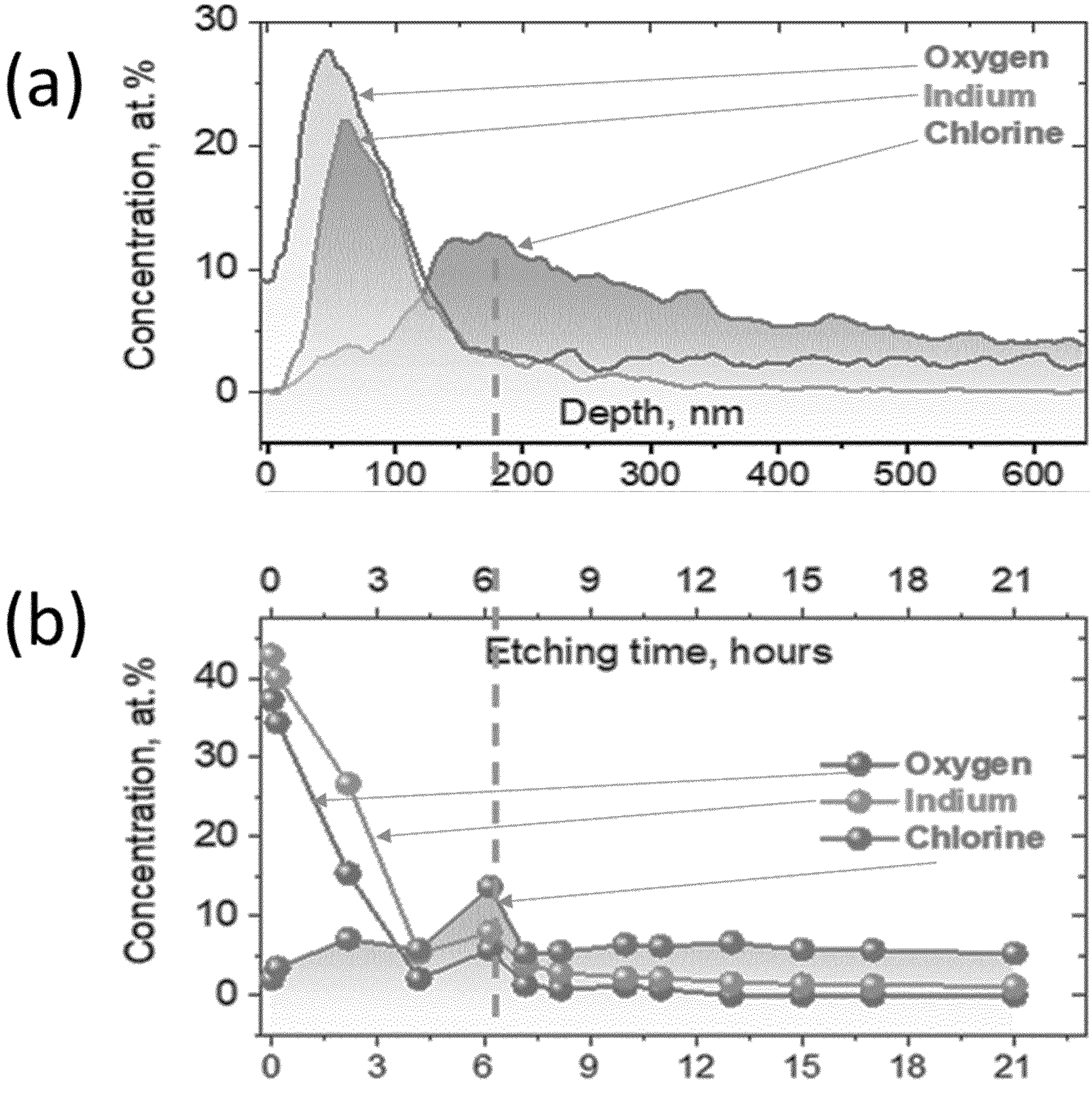
(a)
Concentration, at.%
30
20
10
0
Oxygen
Indium
Chlorine
Depth, nm
0
100
200
300
400
500
600
(b)
0
3
6
9
12
15
18
21
Etching time, hours
Concentration, at.%
40
30
20
10
0
Oxygen
Indium
Chlorine
0
3
6
9
12
15
18
21

FIG. 2

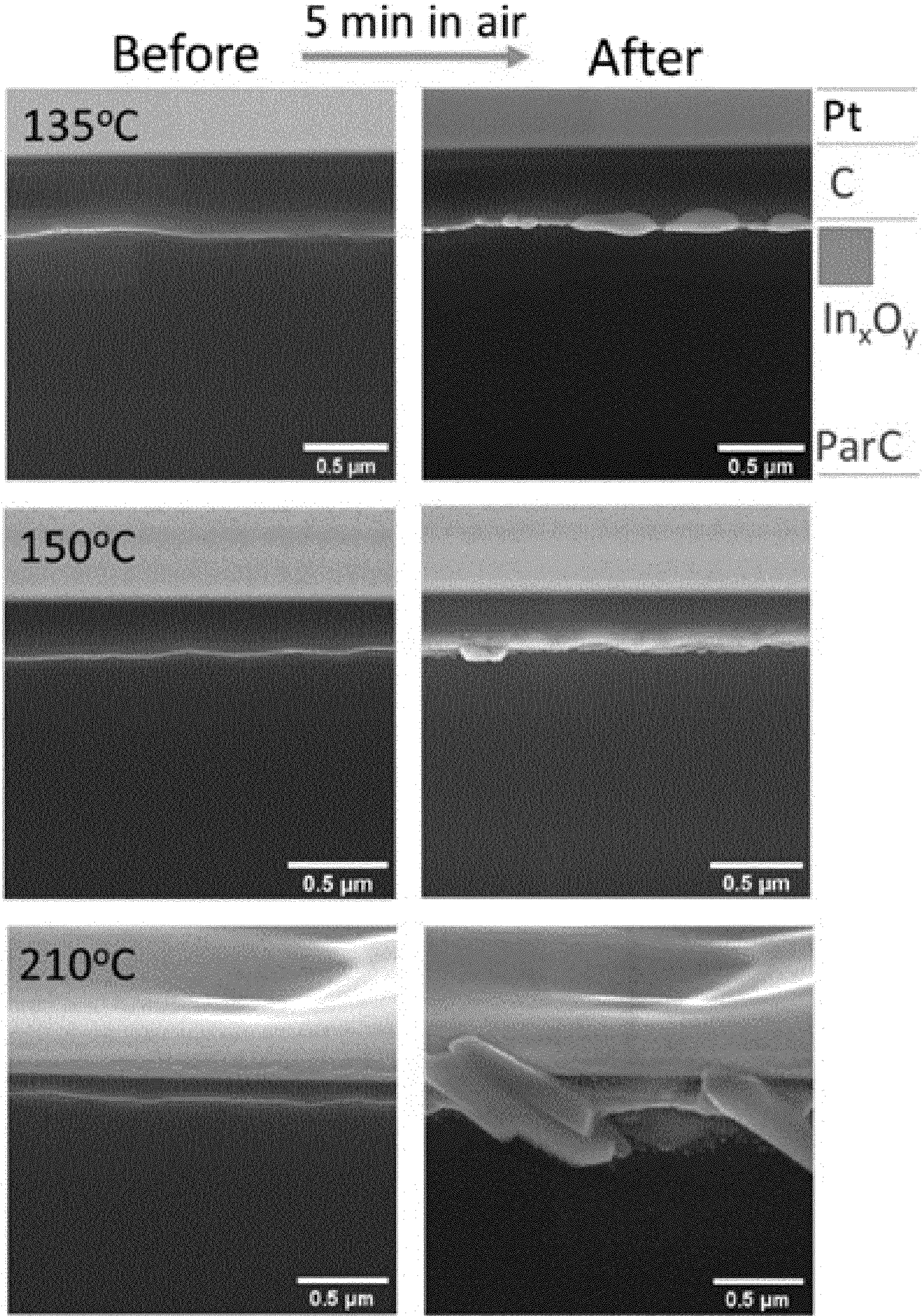

FIG. 3

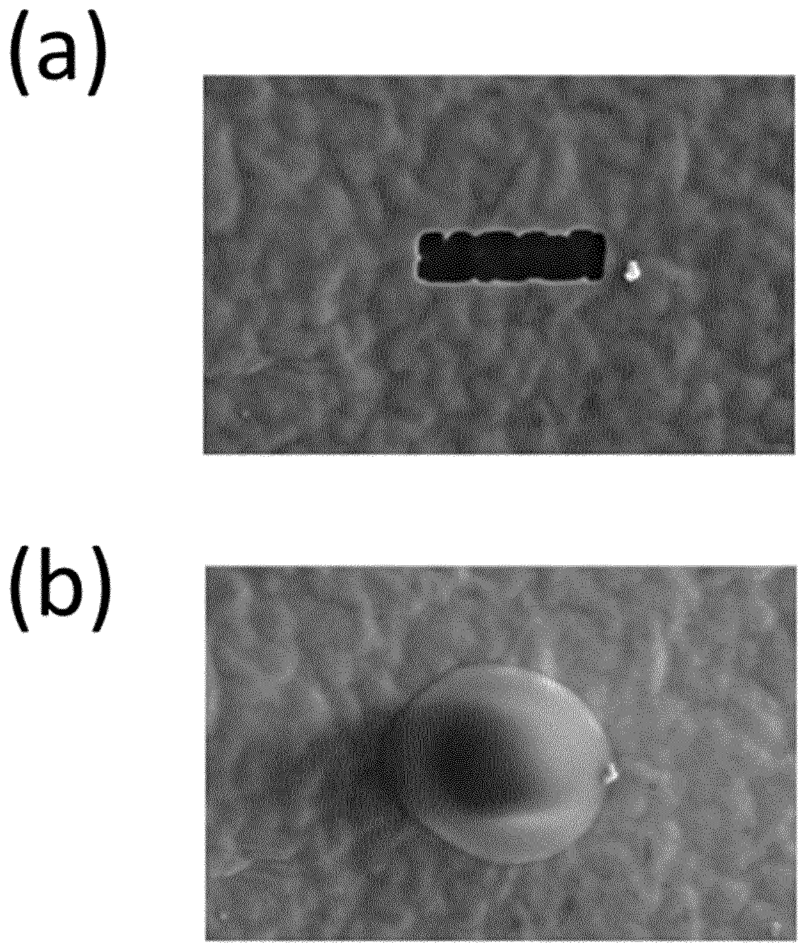

FIG. 4

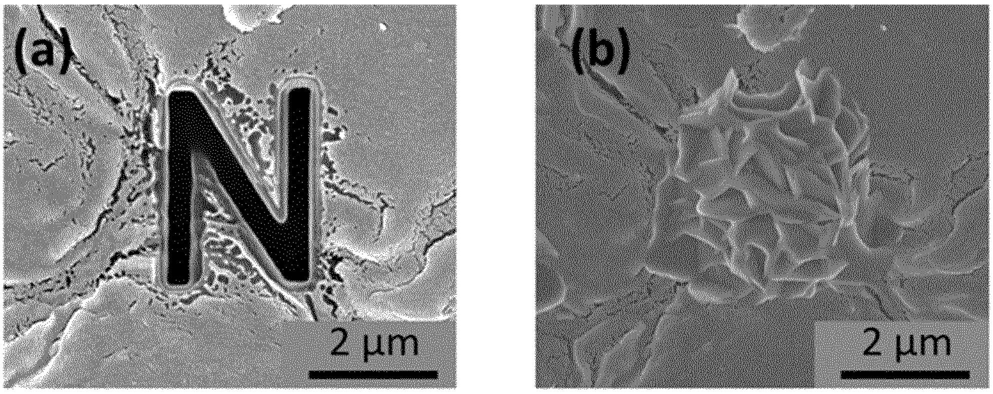

FIG. 5

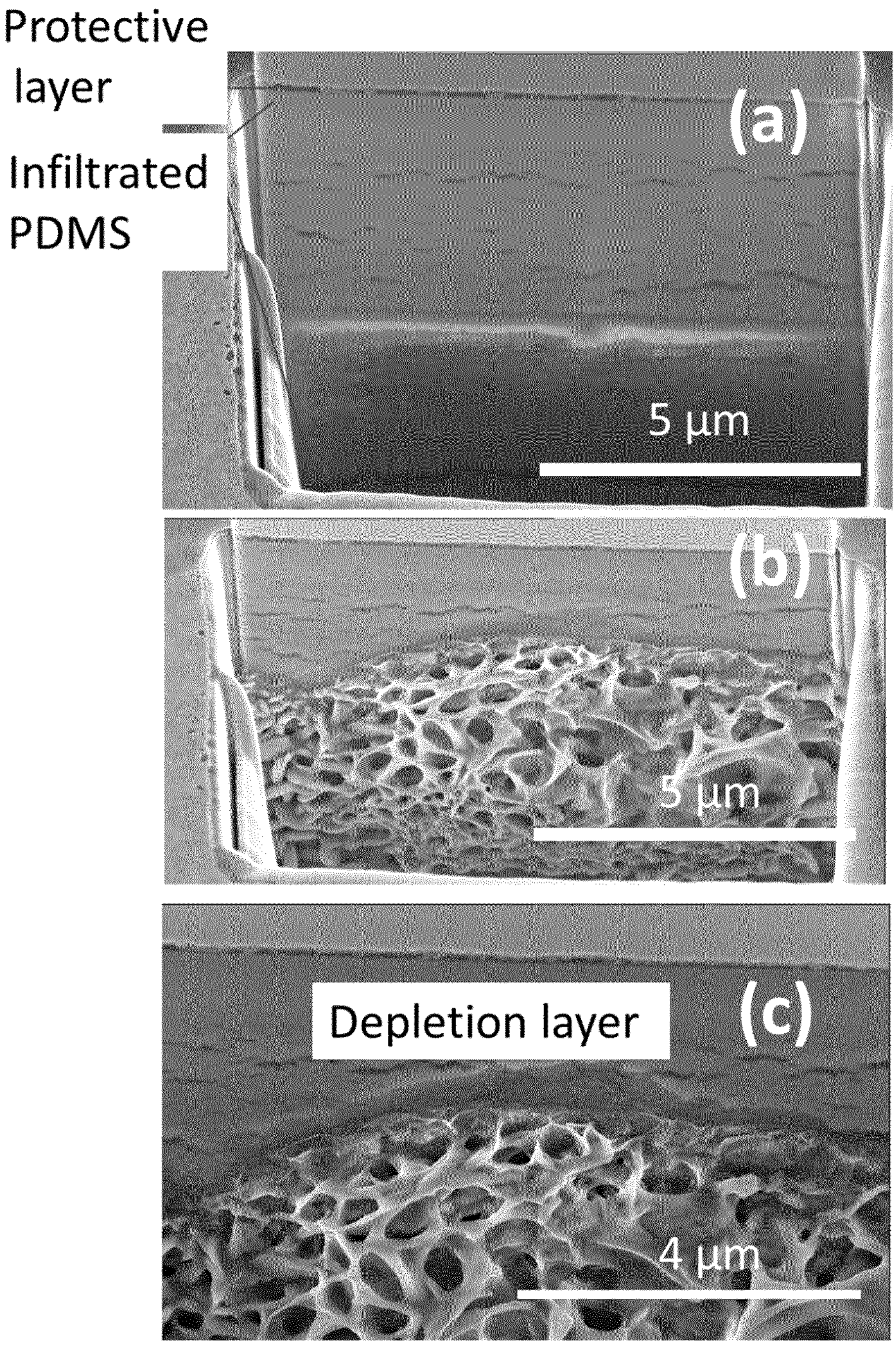
Protective layer
Infiltrated PDMS
(a)
5 µm
(b)
5 µm
Depletion layer
(c)
4 µm

FIG. 6

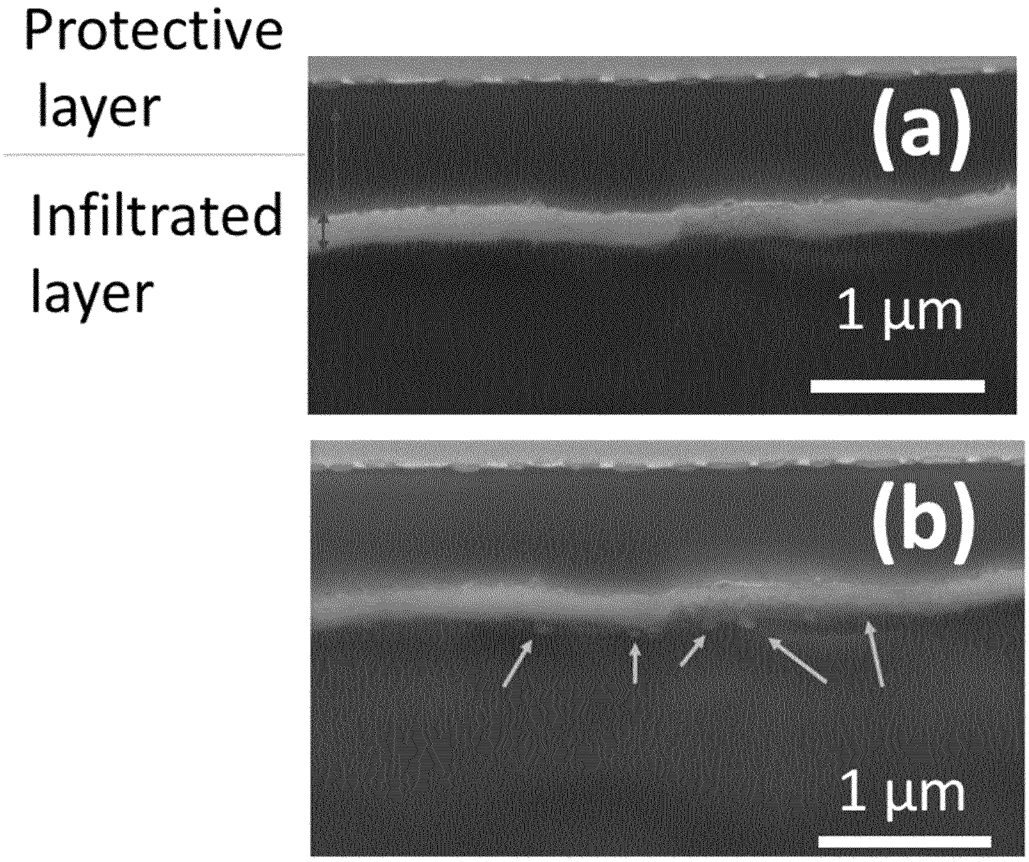

FIG. 7

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2022/079300

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D5/00 C09D5/02

ADD.

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)

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 practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2021/105349 A1 (LUXEMBOURG INST SCIENCE & TECH LIST [LU]) 3 June 2021 (2021-06-03) page 3, line 10 - page 5, line 23 abstract; figures 1-13; examples 1-9 -----	1-15
A	WO 2015/199791 A2 (PENN STATE RES FOUND [US]) 30 December 2015 (2015-12-30) paragraph [0004] - paragraph [0010] abstract; claims 1-51; figures 1-29; tables 1-3 -----	1-15
A	US 2013/017405 A1 (BENKOSKI JASON J [US] ET AL) 17 January 2013 (2013-01-17) paragraph [0008] - paragraph [0012] abstract; claims 1-18; figures 1-6 ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 25 January 2023	Date of mailing of the international search report 10/02/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Glomm, Bernhard

1

International application No
PCT/EP2022/079300

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/166542 A1 (BRAUN PAUL V [US] ET AL) 19 July 2007 (2007-07-19) paragraph [0038] - paragraph [0045] abstract; figures 1-6; examples 1-8; table 1 -----	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2022/079300

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		WO 2007082153 A2	19-07-2007