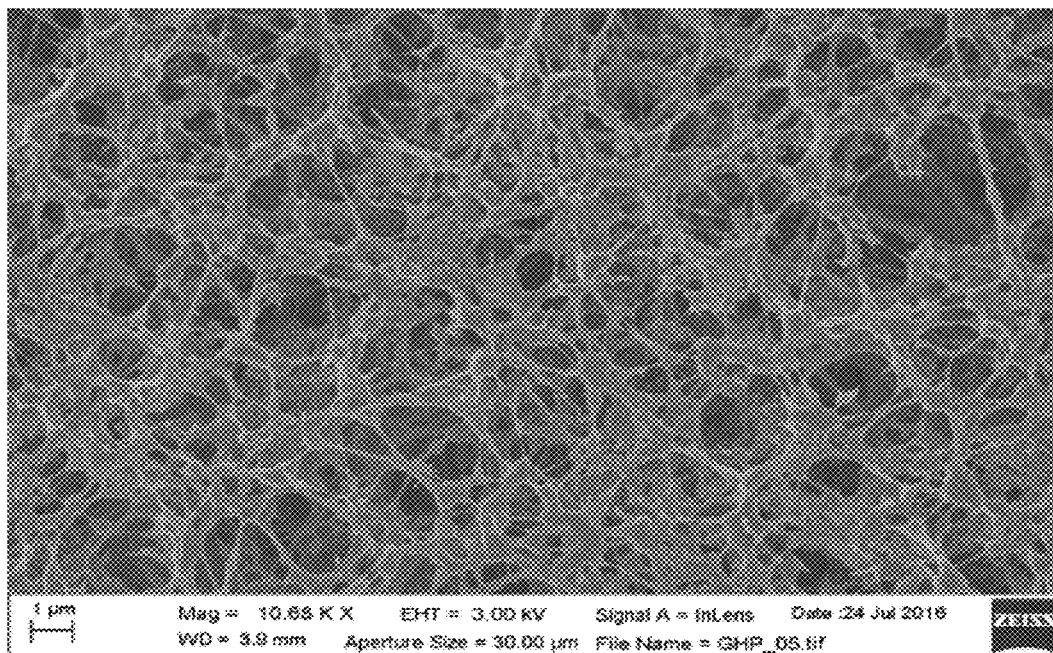




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ZAMOSHCHIK et al.(10) **Pub. No.: US 2019/0211455 A1**(43) **Pub. Date: Jul. 11, 2019**(54) **METAL ACTIVE COMPONENT FORMATION
IN HYBRID MATERIALS**(60) Provisional application No. 62/393,403, filed on Sep.
12, 2016, provisional application No. 62/537,215,
filed on Jul. 26, 2017.(71) Applicant: **OrelTech Ltd.**, Rehovot (IL)(72) Inventors: **Natalia ZAMOSHCHIK**, Rehovot
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Yana SHEYNIN, Rehovot (IL)(73) Assignee: **OrelTech Ltd.**, Rehovot (IL)(21) Appl. No.: **16/298,028**(22) Filed: **Mar. 11, 2019****Related U.S. Application Data**(63) Continuation of application No. PCT/US2017/
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(2013.01); **C23C 18/1682** (2013.01); **C23C**
18/1667 (2013.01)(57) **ABSTRACT**

A method for forming a metal active component in a hybrid material is provided. The method includes applying a metal precursor formulation on a substrate; and exposing the metal precursor formulation applied on the substrate to a low-energy plasma, wherein the low-energy plasma is operated according to a set of exposure parameters.



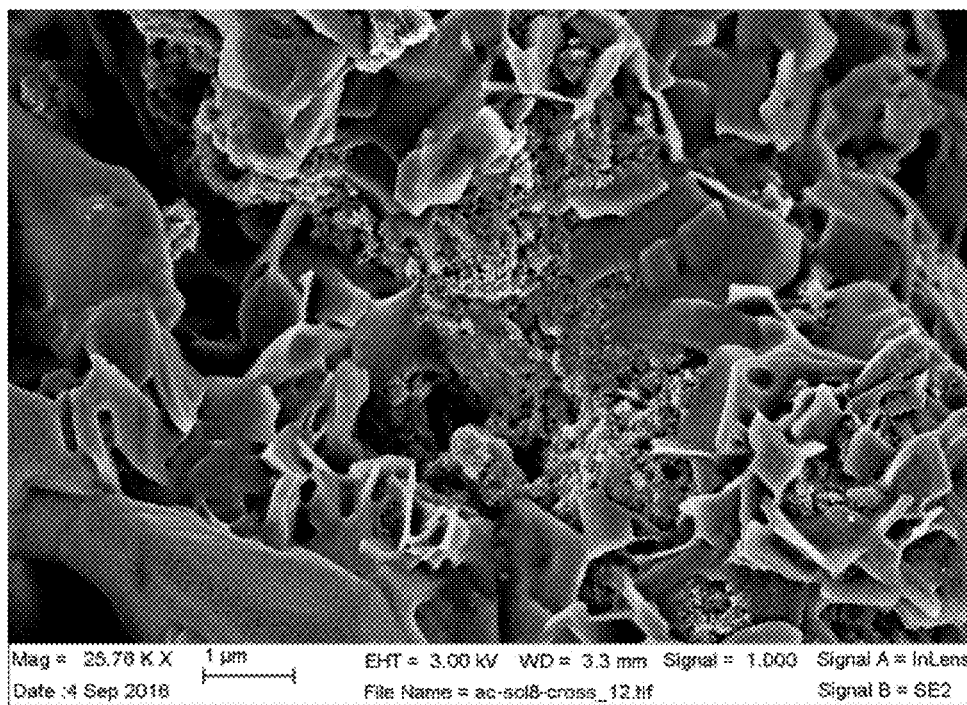


FIG. 1

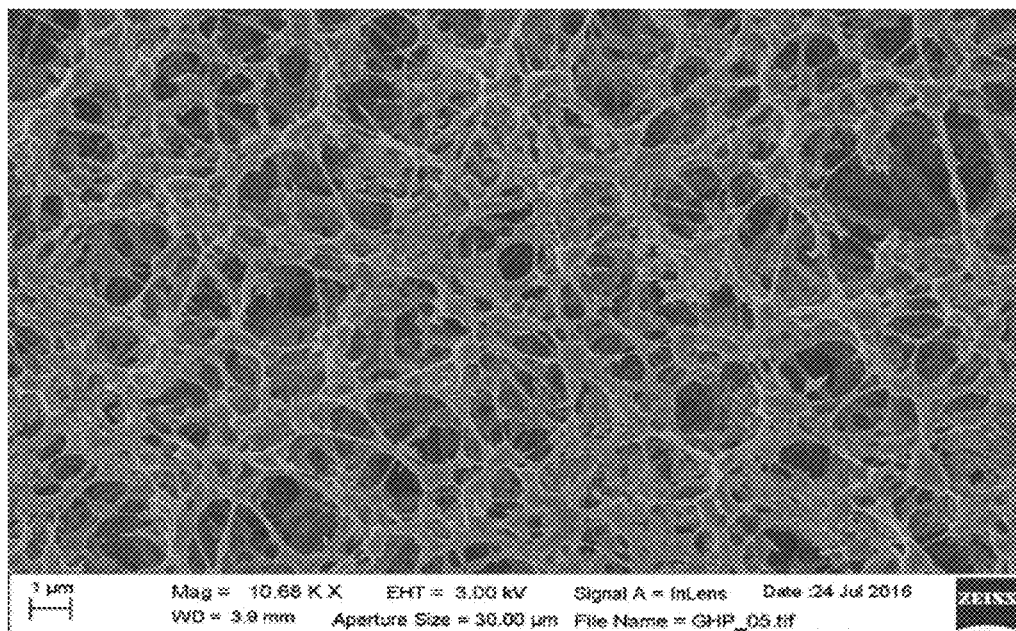


FIG. 2

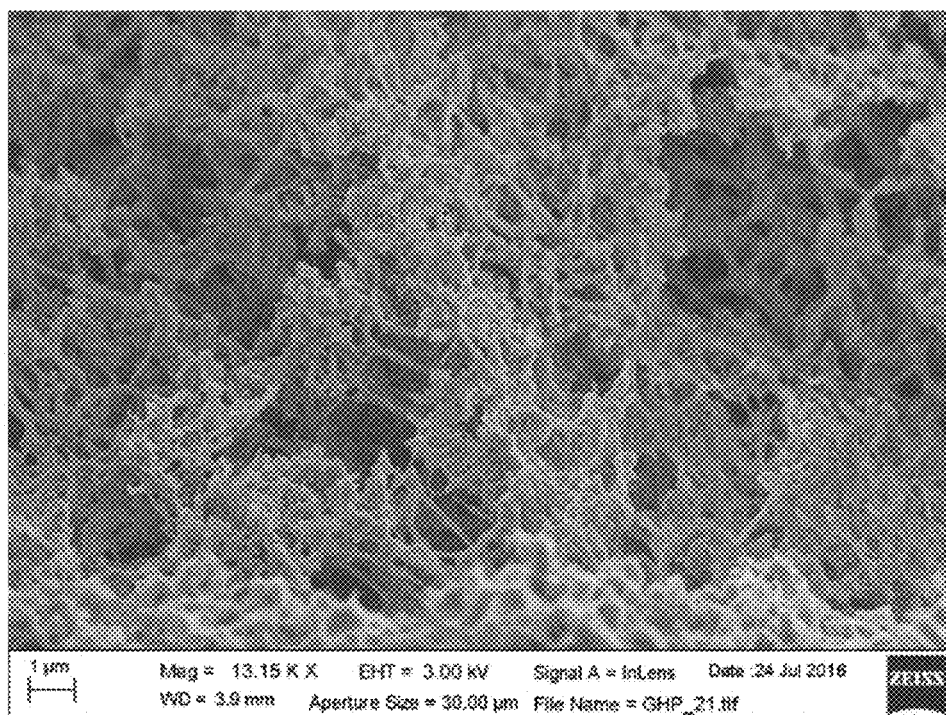


FIG. 3

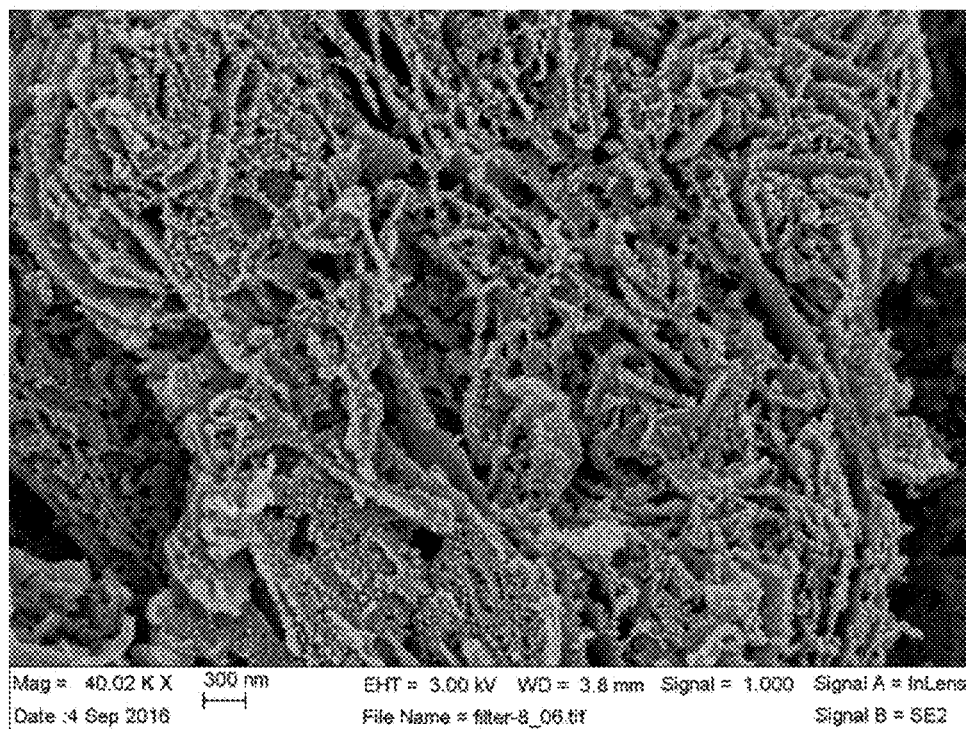


FIG. 4

METAL ACTIVE COMPONENT FORMATION IN HYBRID MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of International Application PCT/US2017/050951 filed Sep. 11, 2017, which claims the benefit of U.S. Provisional patent application Nos. 62/393,403 filed on Sep. 12, 2016 and of U.S. Provisional patent application No. 62/537,215 filed Jul. 26, 2017, the contents of which are hereby incorporated by reference.

TECHNICAL FIELD

[0002] The disclosure generally relates to techniques and a solution composition for in-situ formation of metal nanocrystal coating in compounds of various shapes.

BACKGROUND

[0003] Hybrid compounds are defined as composite materials that consist of two or more chemically different constituents (e.g., a first part and a second part) that possess at least one property that does not exist in either constituent separately. Typically, a hybrid compound can be described as any of organic-inorganic, block copolymer networks, hydrogels inorganic-inorganic, sol-gels. In a hybrid compound, the first part provides the hybrid compound's shape (such as, for example, shape-defining organic ligands in a MOF), and the second part provides the hybrid's function (such as heterogeneous catalysis in zeolites).

[0004] Generally, a suitable framework for the hybrid compounds is a porous network. Such a framework can be utilized in many applications, as it provides high surface areas and easy access to the active sites of the compound. An additional advantage of hybrid compounds is the ability to control the optical, electronic, magnetic, chemical or mechanical properties of the compound by changing only one of the constituents through relatively mild synthetic conditions (e.g., temperature, etc.). The most primitive example of a hybrid compound is a flat substrate with an active material coating. As an example, the flat substrate may include a polymer or ceramic surface and the active material may include catalytically active metal nanocrystals.

[0005] There are many possible applications for utilizing porous hybrid materials discussed in the related art. Such applications are typically used as various membranes and filters. For example, a water filtration/purification process can be performed with porous hybrid material due to their high porosity and a possibility of filtration based on chemical affinity as well as size and antibacterial filtration.

[0006] The porosity and functionalization characteristics of the hybrid materials allow for use of such materials as effective fuel (i.e., hydrogen) and gas (i.e., CO₂) storage devices and possible candidates for controlled drug delivery, as well as ion exchange materials. Additional applications based on the same principles include gas/electrochemical sensors; composite electrolyte materials (for example, solid-state lithium batteries or supercapacitors) and various composite devices for electronic and optoelectronic applications including light-emitting diodes, photodiodes, solar cells, and field effect transistors.

[0007] Applications for porous hybrid compounds include heterogeneous catalysis, which often requires an active

metallic or organometallic moiety inside a large-surface area porous framework. One of the most prominent examples of such systems is an automobile catalytic converter. All those applications require a presence of an inorganic, typically metal, active species embedded into the porous scaffold. Common metals employed in these kinds of applications are silver, gold, platinum, and palladium.

[0008] One existing technique for producing porous hybrid compounds includes separately preparing the structural units of hybrid constituents and then combining them together, typically using either organic or inorganic synthesis. This technique is often referred to as "building blocks strategy." The major disadvantages of this technique are relatively low process control capabilities and relatively low variety of the possible structural units.

[0009] Another existing technique for producing porous hybrid compounds includes preparation of one constituent separately and then forming the second one in situ. In this technique, there are two main approaches: in situ formation of the scaffold and in situ formation of the active component. In situ formation of the scaffold usually includes preparation of the active component (for example, metal nanoparticles) as a precursor, and then using it as a template for the formation of an organic network. This approach has similar disadvantages: structures that are built on or around nanoparticles usually have a low structural variability. Additionally, using the nanoparticles as a precursor limits their choice to those with templating capabilities.

[0010] In situ formation of the active component includes first preparing the scaffold (organic or inorganic) and then impregnating the scaffold with the active particles or moieties. The disadvantages of this techniques typically include shallow particle permeation with unequal distribution, and harsh conditions often required for the particle formation. The latter limits the choice of the scaffolding constituent predominantly to inorganic ones (zeolites or sol-gels) and limits the choices of the active constituents to those resistive to high temperatures or invasive chemical reagents.

[0011] A common technique for in situ synthesis of metal nanoparticles in polymer scaffolds includes thermal annealing of a metal-ion embedded in a polymer thin film. In both cases, the polymer acts as a reducing agent, whereby an electron is extracted from the polymer and donated to the metal-ion. This irreversible oxidation of the polymer scaffold leads to degradation, which has detrimental effects on the whole system's stability and durability.

[0012] It would be therefore advantageous to provide a non-destructive technique for in situ formation of an active component that overcome the deficiencies noted above.

SUMMARY

[0013] A summary of several example embodiments of the disclosure follows. This summary is provided for the convenience of the reader to provide a basic understanding of such embodiments and does not wholly define the breadth of the disclosure. This summary is not an extensive overview of all contemplated embodiments, and is intended to neither identify key or critical elements of all embodiments nor to delineate the scope of any or all aspects. Its sole purpose is to present some concepts of one or more embodiments in a simplified form as a prelude to the more detailed description that is presented later. For convenience, the term "some embodiments" may be used herein to refer to a single embodiment or multiple embodiments of the disclosure.

[0014] The various aspects of the disclosed embodiments provide non-destructive method for in situ formation of active component coating either inside or on top of heterogeneous compound with high nanoparticle loading and high control of nanoparticles size distribution and metal layer thickness. The in-situ formation may be of metal nanocrystal coating in compounds of various shape, ranging from flat to porous. The coating can be of various densities, ranging from a uniform polycrystalline layer to a coating of separate nanocrystals (nanoparticles) on a surface of a substrate.

[0015] Some example embodiments include a method for forming a metal active component. The method includes applying a metal precursor formulation on a substrate; and exposing the metal precursor formulation applied on the substrate to a low-energy plasma, wherein the low-energy plasma is operated according to a set of exposure parameters.

[0016] Some example embodiments include metal active component comprising: a metal precursor formulation; and a substrate at least partially covered by the metal precursor formulation, wherein the metal precursor formulation is applied on the substrate, wherein the metal precursor formulation applied on the substrate is exposed to a low-energy plasma, wherein the low-energy plasma is operated according to a set of exposure parameters.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The subject matter disclosed herein is particularly pointed out and distinctly claimed in the claims at the conclusion of the specification. The foregoing and other objects, features, and advantages of the disclosed embodiments will be apparent from the following detailed description taken in conjunction with the accompanying drawings.

[0018] FIG. 1 is a cross-section scanning electron microscope (SEM) image of gold nanoparticles formed on an activated carbon 3D matrix. (Example I)

[0019] FIG. 2 is a SEM image of silver nanoparticles formed on a polypropylene filter. (Example II)

[0020] FIG. 3 is another SEM image of silver nanoparticles formed on a polypropylene filter. (Example II)

[0021] FIG. 4 is a SEM image of silver nanoparticles formed on a polytetrafluoroethylene (PTFE) filter. (Example III)

DETAILED DESCRIPTION

[0022] It is important to note that the embodiments disclosed herein are only examples of the many advantageous uses of the innovative teachings herein. In general, statements made in the specification of the present application do not necessarily limit any of the various claimed embodiments. Moreover, some statements may apply to some inventive features but not to others. In general, unless otherwise indicated, singular elements may be in plural and vice versa with no loss of generality. In the drawings, like numerals refer to like parts through several views.

[0023] According to the disclosed embodiments, a non-destructive method for in situ formation of metallic coatings is provided. The disclosed method allows the in situ formation with precise control over metal layer thickness or density of separate nanocrystals. The substrate for the coating may be, for example, a flat substrate, a porous material, and the like.

[0024] The porous substrates may be membranes and filters utilized in applications, such as fuel and gas storage devices, ion exchange materials, gas/electrochemical sensors, composite electrolyte materials (e.g., solid-state lithium batteries or supercapacitors), various composite devices for electronic and optoelectronic applications (e.g., LEDs, photodiodes, solar cells, FETs, etc.), and heterogeneous catalysis (e.g., an automobile catalytic converter).

[0025] The substrate can be formed of materials including, but not limited to, macroporous polymers, foams, MOFs, COFs, zeolites, metal oxide networks, sol-gels, activated 3D carbon, commercial filters, and membranes. In an embodiment, the substrate may be pre-treated for better adhesion.

[0026] According to the disclosed embodiments, the metal active component formation method utilizes growth of metallic nanocrystals. The nanocrystals can be grown to be interconnected, thereby forming a network or a uniform layer; or they can remain as separate nanostructures on a surface. The density of the nanostructures, as well as the thickness of the metal layer, can be precisely controlled. The active component formation method is performed using a low temperature technique that allows a wide choice of substrates (both organic and inorganic) and a wide choice of metals as active component material. Further, the method operates with any type of substrate material, including commercial plastics, glass, and ceramics. The precursor for the metal component is a solution of organic solvents and metal salts. As such, the disclosed active component formation method is cost-efficient and practical.

[0027] For a typical procedure, a substrate (either organic or inorganic) is covered with a solution (formulation) of a metal precursor. In an embodiment, applying the solution may be performed using printing, drop-casting, spin-coating, smearing, dip-coating or any other conventional deposition method. The substrate is then placed in the plasma apparatus under a low vacuum and exposed to plasma radiation at a preconfigured power and exposure duration. Some examples are provided below.

[0028] It should be appreciated that, under plasma irradiation conditions, the metal precursor undergoes a reduction process, and metal nanocrystals are formed on soaked surfaces of either flat substrate or surface areas of the porous material. The behavior of the nanocrystals is governed by the precursor formulation and concentration. As such, in low concentrations, the nanocrystals remain relatively small and remain scattered on a surface. In higher precursor concentrations, the nanocrystals grow large and interconnect, forming a network of crystals or a uniform polycrystalline layer. The particles are attached to the substrate via physical adsorption and/or intramolecular chemical bonds.

[0029] In an embodiment, the plasma utilized by the formation method is a low energy plasma, such as a radio frequency (RF) plasma or another non-thermal plasma. The use of low energy plasma enables the conduction of a chemical reaction without creating high temperatures on the surface of the porous substrate/compound/scaffold. Thus, the disclosed process would not thermally damage or otherwise harm the surface or deeper layers of the substrate. It should be noted that the metal nanoparticles include any metal feature that can be adhered or bounded to the porous materials. Furthermore, "metal" of the metal nanoparticles as referred to herein includes any metal alloys, bi-metal alloys, mixtures of various types of metals, or combinations thereof.

[0030] The formation is performed by exposing the substrate to a low-energy and non-thermal plasma, a gas such as Argon, Nitrogen, Oxygen, Hydrogen, Air, and the like. To this end, the substrate is placed in a chamber and exposed to a gas plasma (such as, for example, Argon and Nitrogen plasma) as determined by a set of exposure parameters including, for example, power, RF frequency, gas flow rate, and time duration for the exposure. The values of the set of exposure parameters are determined based, in part, on the type of the substrate, precursor solution, gas type, the means of application, or a combination thereof.

[0031] In an embodiment, the values of the set of exposure parameters may be as follows: the power is between 5 W (watt) and 600 W, the plasma RF frequency is between 50 Hz and 5 GHz, the gas flow rate is between 2 SCCM (standard cubic centimeter per minute) and 50 SCCM, and the exposure time is between 1 second and 30 minutes.

[0032] In an embodiment, the precursor solution is applied by a means including, but not limited to, drop-casting, spray-coating, immersion, and the like.

[0033] According to the disclosed embodiments, the precursor solution may be composed of different metal cations, and different contractions thereof. The resulting metal active component may include of various types of metals, bi-metals, alloys, or a combination thereof.

[0034] In an embodiment, in its basic form, the precursor solution includes metal cations with at least one type of solvent. The metal cations include any of $M(NO_3)_n$, $M(SO_4)_n$, MCl_n , and $HmMCl_{n+m}$, and MN , where “M” is a metal atom (or any appropriate metal alloy) with a valence of “n”, H is hydrogen, NO_3 is nitrate, SO_4 is sulfate, Cl is chloride, “N” is alkyl-, alyl-, aceto-, and other organic moieties, and “m” is a valence of the counter ion. The metal cation may be in the form of organic and inorganic salts of gold, silver, platinum, palladium, copper, nickel, or a combination thereof, to get metallic and bimetallic nanoparticles. Further, the metal cations may be provided in gels, colloids, suspensions, dispersions, organic-inorganic compounds, and so on. The metal cations may be stabilized by a counter ion, e.g., forming an organometallic complex, such that they are connected by coordinate bonds rather than by ionic bonds.

[0035] In this embodiment, the precursor solution may be in a form of solution, dispersion, suspension, gel, or colloid.

[0036] The solvents that may be used in the precursor solution include, but are not limited to, alcohols, water, toluene, dioxane, cyclohexanol, dimethyl sulfoxide (DMSO), formamides, ethylamines, glycols, glycol ethers, glycerol, propylene carbonate, and acetonitrile. In some embodiments, the precursor solution can contain other additives such as, but not limited to, organic molecules, polymers, conductive polymers, carbon nanotubes (CNT), densifiers, surfactants, and the like. Such additives can be used to change the viscosity and surface tension.

[0037] The resulting metal active component may be in the form of metal particles in the range of 1-100 nm (nanometer) and up to 10 μ m (micrometer). The particle size can be controlled by the choice of substrate material, choice of solvent/solvent mixture, precursor concentration, gas flow, and processing time. According to the disclosed embodiments, the particle shape can be controlled by changing the choice of substrate material and the choice of precursor type.

[0038] In an embodiment, the arrangement of the particles into separate nanocrystals or interconnected metallic poly-

crystalline layers can be controlled by the solution formulation and metal precursor concentration. The nanocrystal distribution, density layer thickness, or a combination thereof, can be controlled by the choice of solvent/solvent mixture, precursor concentration, gas type, gas flow, and processing time.

[0039] Following are a few non-limiting examples for precursor solutions and forming active component using such solutions.

Example I

[0040] The solution includes the metal precursor $HAuCl_4$ in the concentration of 10 percentage by weight (wt. %) in a mixture including water in the concentration of 10 wt. %, propylene glycol in the concentration of 20 wt. %, and ethylene glycol in the concentration of 60 wt. %. Activated carbon 3D substrate is immersed in the precursor solution for 1 min to soak the solution inside the scaffold. Then, the activated carbon substrate with solution is placed in a vacuum chamber and exposed to argon plasma. The chamber is set with the following exposure parameters: RF frequency, power, gas flow rate, and time; having the values: 13.56 MHz, 50 W, 20 SCCM gas flow rate, and 15 minutes, respectively. The pressure at the chamber is 0.6 mbar. As a result, an activated carbon substrate is filled inside and covered outside by gold nanoparticles of 20 nm size. A cross-section SEM image of the gold nanoparticles formed on an activated carbon 3D matrix is shown in FIG. 1.

Example II

[0041] The solution includes metal precursor $AgNO_3$ in the concentration of 20 wt. % in a mixture including water in the concentration of 52 wt. %, propylene glycole in the concentration of 22 wt. % and n-propanol in the concentration of 6 wt. %. A polypropylene network substrate is immersed in the precursor solution for 1 min to soak the solution inside the scaffold. Then, the polypropylene network substrate with solution is placed in a vacuum chamber and exposed to argon plasma. The chamber is set with the following exposure parameters: RF frequency, power, gas flow rate, and time; having the values: 13.56 MHz, 100 W, 40 SCCM gas flow rate, and 10 minutes, respectively. The pressure at the chamber is 0.8 mbar. As a result, a polypropylene substrate is filled inside and covered outside by silver nanoparticles of 60 nm size. A SEM image of silver nanoparticles formed on a polypropylene filter are shown in FIGS. 2 and 3.

Example III

[0042] The solution includes metal precursor $PtCl_2$ in the concentration of 20 wt. % in a mixture including water 10 wt. %, n-propanol in the concentration of 20 wt. %, and dipropylene glycol methyl ether in the concentration of 50 wt. %. A polytetrafluoroethylene (PTFE) substrate immersed in the precursor solution for 1 min to soak the solution inside the scaffold. Then, the PTFE substrate with solution is placed in a vacuum chamber and exposed to argon plasma. The chamber is set with the following exposure parameters: RF frequency, power, gas flow rate, and time; having the values: 13.56 MHz, 150 W, 25 SCCM gas flow rate, and 15 minutes, respectively. The pressure at the chamber is 0.8 mbar. As a result, a PTFE substrate is filled inside and covered outside by platinum nanoparticles of 5 nm size. A

SEM image of silver nanoparticles formed on a polytetrafluoroethylene (PTFE) filter is shown in FIG. 4.

Example IV

[0043] The solution includes a metal precursor chloroplatinic acid $[H_3O]PtCl_6$ in the concentration of 0.01 wt. % in a mixture including water in the concentration of 10 wt. %, propylene glycol in the concentration of 20 wt. %, and ethylene glycol in the concentration of 60 wt. %. A droplet of the solution is deposited on a polyethylene terephthalate (PET) slide and smeared. Then, the composition of the substrate with the solution is placed in a vacuum chamber and exposed to nitrogen plasma. The chamber is set with the following exposure parameters: RF frequency, power, gas flow rate, and time; having the values 13.56 MHz, 50 W, 20 SCCM gas flow rate, and 15 minutes, respectively. The pressure at the chamber is 0.3 mbar. As a result, the substrate is coated by a non-continuous coating of separate platinum nanoparticles of 20-40 nm size, and is later used for catalytic reaction in an organic photovoltaic cell.

[0044] It should be understood that any reference to an element herein using a designation such as “first,” “second,” and so forth does not generally limit the quantity or order of those elements. Rather, these designations are generally used herein as a convenient method of distinguishing between two or more elements or instances of an element. Thus, a reference to first and second elements does not mean that only two elements may be employed there or that the first element must precede the second element in some manner. Also, unless stated otherwise, a set of elements comprises one or more elements.

[0045] As used herein, the phrase “at least one of” followed by a listing of items means that any of the listed items can be utilized individually, or any combination of two or more of the listed items can be utilized. For example, if a system is described as including “at least one of A, B, and C,” the system can include A alone; B alone; C alone; A and B in combination; B and C in combination; A and C in combination; or A, B, and C in combination.

[0046] All examples and conditional language recited herein are intended for pedagogical purposes to aid the reader in understanding the principles of the disclosed embodiment and the concepts contributed by the inventor to furthering the art, and are to be construed as being without limitation to such specifically recited examples and conditions. Moreover, all statements herein reciting principles, aspects, and embodiments of the disclosed embodiments, as well as specific examples thereof, are intended to encompass both structural and functional equivalents thereof. Additionally, it is intended that such equivalents include both currently known equivalents as well as equivalents developed in the future, i.e., any elements developed that perform the same function, regardless of structure.

What is claimed is:

1. A method for forming a metal active component, comprising:

applying a metal precursor formulation on a substrate; and exposing the metal precursor formulation applied on the substrate to a low-energy plasma, wherein the low-energy plasma is operated according to a first set of exposure parameters.

2. The method of claim 1, wherein the substrate is any one of: an organic substrate and an inorganic substrate.

3. The method of claim 1, wherein the low-energy plasma is a gas plasma.

4. The method of claim 3, wherein the gas plasma is any one of: Argon, Nitrogen, Oxygen, Hydrogen, and Air.

5. The method of claim 1, wherein the set of exposure parameters includes at least one of: radio frequency (RF), power, gas flow rate, and exposure time.

6. The method of claim 5, wherein the RF frequency is between 50 Hertz (Hz) and 5 Giga Hertz (GHz), inclusive.

7. The method of claim 5, wherein the power is between 5 watts (W) and 600 W, inclusive.

8. The method of claim 5, wherein the gas flow rate is between 2 standard cubic centimeters per minute (SCCM) and 50 SCCM, inclusive.

9. The method of claim 5, wherein the exposure time is between 1 second and 30 minutes, inclusive.

10. The method of claim 1, wherein applying the metal precursor formulation is performed via at least any of: drop-casting, spin-coating, smearing, dip-coating, immersing and printing.

11. The method of claim 5, wherein exposing the metal precursor formulation applied on the substrate further comprises:

placing the substrate in a low vacuum chamber for an amount of time equal to the exposure time.

12. The method of claim 1, further comprising:

treating a surface of the substrate to create a pre-treated substrate, wherein the metal precursor formulation is applied on the pre-treated substrate.

13. The method of claim 1, wherein the metal precursor formulation consists of an organic solvent and metal salts.

14. The method of claim 13, wherein the metal precursor formulation includes metal cations with at least one type of solvent.

15. The method of claim 14, wherein the metal cations are selected from the group consisting of: $M(NO_3)_n$, $M(SO_4)_n$, MCl_n , and $HmMCl_{n+m}$, and MN ; wherein “M” is a metal atom with a valence of “n”, H is hydrogen, NO_3 is nitrate, SO_4 is sulfate, Cl is chloride, “N” is alkyl-, alyl-, aceto-, and other organic moiety, and “m” is a valence of the counter ion.

16. The method of claim 14, wherein the metal cations are inorganic cations selected from the group consisting of: gold, silver, platinum, palladium, copper, nickel, and a combination thereof.

17. The method of claim 14, wherein the metal precursor solution is any of a substance form of a solution, a dispersion, a suspension, a gel, and a colloid.

18. The method of claim 1, wherein the substrate any one of: a membrane, a filter, a catalyst, a porous scaffold, a surface of various roughness.

19. A metal active component, comprising:

a metal precursor formulation; and

a substrate at least partially covered by the metal precursor formulation, wherein the metal precursor formulation is applied on the substrate, wherein the metal precursor formulation applied on the substrate is exposed to a low-energy plasma, wherein the low-energy plasma is operated according to a set of exposure parameters.

20. The metal active component of claim 19, wherein the metal precursor formulation consists of an organic solvent and metal salts.

21. The metal active component of claim **20**, wherein the metal precursor formulation includes metal cations with at least one type of solvent.

22. The metal active component of claim **21**, wherein the metal cations are selected from the group consisting of: $M(NO_3)_n$, $M(SO_4)_n$, MCl_n , and $HmMCl_{n+m}$, and MN ; wherein “M” is a metal atom with a valence of “n”, H is hydrogen, NO_3 is nitrate, SO_4 is sulfate, Cl is chloride, “N” is alkyl-, alyl-, aceto-, and other organic moieties, and “m” is a valence of the counter ion.

23. The metal active component of claim **21**, wherein the metal cations are inorganic cations selected from the group consisting of: gold, silver, platinum, palladium, copper, nickel, and a combination thereof.

24. The metal active component of claim **19**, wherein the metal precursor solution is any of a solution, a dispersion, a suspension, a gel, and a colloid.

25. The metal active component of claim **1**, wherein the substrate includes any one of: a membrane, a filter, a catalyst, a porous scaffold, a surface of various roughness.

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