

METALLIZATION OF THREE-DIMENSIONAL PRINTED STRUCTURES

Cross-Reference To Related Application

[0001] This application claims the benefit of priority of Singapore Patent Application
5 No. 10201811217R, filed 14 December 2018, the content of it being hereby
incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The present disclosure relates to methods of electroless deposition of a metal
10 on a three-dimensional polymeric structure. The present disclosure also relates to a
composition for electroless deposition of a metal on a three-dimensional polymeric
structure.

Background

15 [0003] The design and manufacture of three-dimensional (3D) complicated structures
have been rendered easier due to advanced 3D printing technology. The most
fundamental method for 3D printing, conventionally, is to melt plastic, such as
acrylonitrile butadiene styrene (ABS), at the tip of a nozzle to deposit the melted
plastic, according to a design, at a defined site.

20 [0004] Typically, the 3D printed structure is made entirely of plastic or metal as the
difference in melting point of plastic and metal is too significant for such materials to
be melted at the nozzle tip for 3D printing. To render a shiny appearance or a
conductive layer on a certain part of or over the entire 3D printed plastic structure, a
metallization technique that selectively coats a metal onto an area thereon may be
25 required. Dry or vacuum metallization processes such as sputtering and evaporation,
however, tend to be unsuitable for coating metal onto a 3D printed structure due to
poor coverage. Dipping metallization and solution-based processes where a substrate
may be immersed into a solution to deposit metal, may be suitable as the solution is a
liquid that can flow to cover the entire surface area of a 3D structure. For example, in
30 electroplating and electroless plating, the substrate may be dipped into a solution
having a metal ion, wherein the metal ion may undergo reduction to form one or more
metal layers on the substrate.

[0005] Particularly, electroless deposition may be more suitable for coating metal on the non-conductive plastic surface, as an external power source to provide electrons may not be required since a reducing agent may be utilized in the solution to serve as the source of electrons. For electroless deposition to occur, the substrate may be pre-dipped into catalyzation solutions, where two solutions respectively containing palladium (Pd) ions and a reducing agent (e.g. SnCl_2) are used. The substrate may be dipped into these solutions in an alternate manner to deposit Pd nanoparticles or colloids thereon. The Pd nanoparticles may serve as a catalyst to induce electroless deposition. In this connection, electroless deposition for an ABS substrate tends to be carried out by first dipping the ABS substrate into chromic acid to pre-etch the surface before the Pd catalyzation process, so as to trap the Pd nanoparticles and produce high adhesion of the electroless plated metal on the ABS substrate. That said, use of chromic acid has been refrained due to demand for usage reduction of hexavalent chromium out of health concerns. Also, it is undesirable to have the surface or any part of the 3D printed plastic structure etched as the structure is already precisely designed and manufactured by the 3D printer.

[0006] In light of the above, there is a need to provide for a solution that ameliorates one or more of the abovementioned limitations to deposit metal onto 3D structures. The solution of the present disclosure at least provides for deposition of metal over 3D printed structure without pre-etching.

Summary

[0007] In one aspect, there is provided for a method of electroless deposition of a metal on a three-dimensional polymeric structure, the method comprising:

providing a composition comprising one or more organic solvents having a polymer and a metal catalyst precursor homogeneously dissolved therein;

fabricating the three-dimensional polymeric structure from the composition;
and

forming the metal on the three-dimensional polymeric structure, wherein the one or more organic solvents comprise acetone.

[0008] In another aspect, there is provided for a method of electroless deposition of a metal on a three-dimensional polymeric structure, the method comprising:

providing a solid composition comprising a polymer and metal ions homogeneously distributed therein;

fabricating the three-dimensional polymeric structure having one or more regions formed of the solid composition; and

5 forming the metal on the one or more regions.

[0009] In another aspect, there is provided for a method of forming a composition for electroless deposition of a metal on a three-dimensional polymeric structure, the method comprising:

10 mixing a polymer and a metal catalyst precursor in one or more organic solvents to form the composition, wherein the one or more organic solvents comprise acetone.

[0010] In another aspect, there is provided for a composition for electroless deposition of a metal on a three-dimensional polymeric structure, the composition comprising:

15 a polymer;
a metal catalyst precursor; and
one or more organic solvents comprising the polymer and the metal catalyst precursor homogeneously dissolved therein, wherein the one or more organic solvents comprise acetone.

20 **[0011]** In another aspect, there is provided for a solid composition for electroless deposition of a metal on a three-dimensional polymeric structure, wherein the solid composition is generated from a composition comprising:

a polymer;
a metal catalyst precursor; and
one or more organic solvents comprising the polymer and the
25 metal catalyst precursor homogeneously dissolved therein,
wherein the one or more organic solvents comprise acetone,

wherein the solid composition comprises:

the polymer; and
metal ions homogeneously distributed therein.

Brief Description of the Drawings

[0012] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various embodiments of the present disclosure are described with reference to the following drawings, in which:

[0013] FIG. 1 shows the various solvents tested for dissolving an acrylonitrile butadiene styrene (ABS) (top row images) and for dissolving PdCl₂ (bottom row images).

[0014] FIG. 2A shows a scanning electron microscopy (SEM) image of ABS fibers after Pd/Sn catalyzation and Ni deposition. The fibers are obtained by conventional electroless plating, and are not uniform in that the metal coating on the fibers are uneven. The scale bar denotes 10 μm.

[0015] FIG. 2B shows the resultant fibers after Ni electroless deposition on Pd ion loaded ABS fibers. The metal is evenly coating on the fibers. The scale bar denotes 10 μm.

[0016] FIG. 3 shows a three-dimensional (3D) printed structure (1 cm³ dice) having three dots on one of the surfaces deposited with metal via a mask-less area-selective electroless plating without catalyzation and pre-etching. The scale bar denotes 5 mm.

Detailed Description

[0017] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0018] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations

and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

5 [0019] The present disclosure provides for methods of electroless deposition of a metal onto a three-dimensional (3D) polymeric structure. The methods may involve the use of a composition having metal ions loaded in a polymer. The metal ions may be, for example, palladium (Pd) ions. The polymer may be, for example, acrylonitrile butadiene styrene (ABS). Both the Pd ions and ABS may be dissolved in one or more organic solvents to form the composition. Said differently, the present disclosure
10 relates to palladium (Pd) ions loaded into ABS for forming metal (i.e. metallization) on three-dimensional (3D) polymeric structures. The 3D polymeric structures may be 3D plastics. The 3D polymeric structures may be 3D printed structures. The 3D polymeric structures may be 3D fibers. The metal may be formed by electroless deposition, such as electroless plating.

15 [0020] Advantageously, the present methods and composition circumvent etching of the 3D polymeric structure (e.g. a 3D printed ABS structure). The present methods and composition also circumvent masking for electroless deposition of a metal on a selected region (e.g. surface area) on the 3D printed structures. Moreover, even without any post-activation steps (i.e. to activate a surface for electroless deposition of
20 metal) such as heating or wet treatment, the loaded metal ions (e.g. Pd ions) may be reduced into a metal (e.g. Pd), which serves as a catalyst for electroless plating, by a reducing agent contained in an electroless plating bath. The electroless plating may then be induced by the metal (e.g. Pd) catalyst and proceed to form a metal (e.g. nickel) at selected areas (e.g. areas coated with the Pd ions loaded ABS).

25 [0021] With the above in mind, the present methods and composition, and their various embodiments, are described as follow.

[0022] Various embodiments in one aspect provide for a method of electroless deposition of a metal on a three-dimensional polymeric structure. The method may comprise providing a composition comprising one or more organic solvents having a
30 polymer and a metal catalyst precursor homogeneously dissolved therein, fabricating the three-dimensional polymeric structure from the composition, and forming the

metal on the three-dimensional polymeric structure, wherein the one or more organic solvents comprise acetone.

[0023] The composition may comprise one or more organic solvents that include an acetone. This is advantageous as the acetone dissolves both the polymer and metal catalyst precursor. For example, using ABS as the polymer, acetone is able to break the butadiene linkage in ABS for ABS to dissolve. At the same time, acetone dissolves the metal catalyst precursor. Hence, even if one type of organic solvent is used, which is acetone, two different components of the composition may be dissolved, translating to cost saving of materials. On the other hand, another organic solvent such as methyl ether ketone may dissolve ABS but does not dissolve the metal catalyst precursor. Other solvents for dissolving the metal catalyst precursor, such as water and ethanol, may undesirably cause the dissolved polymer to precipitate and solidify, which renders the composition unsuitable for subsequent steps of the present methods.

[0024] In the present method, providing the composition may include dissolving the polymer in the acetone to generate a polymer solute, and dissolving the metal catalyst precursor in the acetone to form metal ions. As already mentioned, the acetone is advantageous not just because it can dissolve the polymer, but also dissolve the metal catalyst precursor to produce metal ions. The polymer may be dissolved in the acetone to form a polymer solution containing the polymer solute.

[0025] In various embodiments, providing the composition may comprise mixing the polymer solute and the metal ions in the acetone to form the composition. That is to say, the polymer dissolved in acetone forms a first acetone solution. The metal catalyst precursor may be dissolved in acetone, separately, to form a second acetone solution. The first acetone solution contains the polymer solute. The second acetone solution contains the metal ions. The metal ions are produced from dissolution of the metal catalyst precursor. The first acetone solution and second acetone solution may then be mixed to form the composition. As such, the composition may be deemed to comprise metals ions loaded in a polymer or polymer solution, or with the polymer solute. Advantageously, the polymer solute and the metal ions may be compatibly mixed as the same organic solvent of acetone is used. Mixing of the polymer solute and metal ions in the presence of different organic solvents may adversely render

precipitation of the polymer solute and/or metal ions, such that the composition may not properly formed. Alternatively, either the polymer or the metal catalyst precursor may be first dissolved in acetone, and the other component (i.e. metal catalyst precursor or polymer, respectively) is then added for dissolving therein.

5 **[0026]** In various embodiments, the metal ions may comprise or consist of palladium ions. To produce the palladium ions, the metal catalyst precursor used may comprise or consist of palladium chloride. The palladium ions, and hence palladium chloride, are advantageous because the ions are stable and hence preserve the catalytic activity needed for subsequent electroless deposition. In other words, the palladium ions do
10 not get easily reacted away in the presence of any chemicals.

[0027] In various embodiments, the polymer may comprise or consist of acrylonitrile butadiene styrene or polylactic acid (PLA). Such polymers are suitable for 3D printing, as they may be conveniently formed into a solid filament fittable into 3D printing apparatus. They also do not require high melting temperature to be printed
15 into 3D structures. Such polymers are also versatile in that they can be used for electrospinning to form polymeric fibers.

[0028] The present method may comprise fabricating the three-dimensional polymeric structure from the composition. Fabricating the three-dimensional polymeric structure may comprise electrospinning the composition to form the three-
20 dimensional polymeric structure. The three-dimensional polymeric structure may comprise or may be polymeric fibers. The polymeric fibers may have the metal ions homogeneously distributed therein. The polymeric fibers may be ABS fibers or PLA fibers, respectively. The metal ions may comprise or consist of palladium ions.

[0029] To fabricate the three-dimensional polymeric structure from the composition,
25 the composition may be ejected by air pressure onto a substrate. The substrate may be a glass substrate. The glass substrate may be combined with an electrically conductive metal substrate for the polymeric fibers to be electrospun onto the glass substrate. For example, the composition may be filled in a syringe and air may be exerted to eject the composition from the syringe onto the substrate.

30 **[0030]** After the composition gets formed into the three-dimensional polymeric structure, the metal may be formed thereon. This includes forming the metal on a surface area of the three-dimensional polymeric structure. In various embodiments,

forming the metal on the three-dimensional polymeric structure may comprise contacting the three-dimensional polymeric structure with an alkaline bath comprising a reducing agent. For example, the alkaline bath may have a pH of more than 7, more than 8, more than 9, more than 10, more than 11, more than 12, more than 13, or a pH
5 of 14. The pH may be adjusted by adding a base to the bath, non-limiting examples of which may include sodium hydroxide.

[0031] In various embodiments, the reducing agent may comprise or consist of sodium hypophosphite. As the reducing agent comes into contact with the metal ions deposited at the three-dimensional polymeric structure (e.g. the polymeric fibers), it
10 converts the metal ions into a metal catalyst. The metal catalyst aids in electroless deposition of a metal thereon, thereby forming the metal on the three-dimensional polymeric structure. In various embodiments where the metal catalyst precursor used is palladium chloride, the metal catalyst formed is then palladium.

[0032] Advantageously, with the metal ions homogeneously loaded in the three-dimensional polymeric structure, the metal catalyst and the metal formed may adhere
15 more strongly compared to metal catalysts and metals formed from metal ions (e.g. in an aqueous medium) that were merely coated on (i.e. not loaded therein) a polymeric substrate, as the metal ions in the present method may at least be embedded into the surface of the three-dimensional polymeric structure (or polymeric fibers).

[0033] In various embodiments, the metal may comprise or consist of nickel. Other metals that can be deposited suitably by electroless deposition may be used. The electroless deposition may be electroless plating.
20

[0034] The present disclosure also provides for a method of electroless deposition of a metal on a three-dimensional polymeric structure according to another aspect. The
25 method may comprise providing a solid composition comprising a polymer and metal ions homogeneously distributed therein, fabricating the three-dimensional polymeric structure having one or more regions formed of the solid composition, and forming the metal on the one or more regions. This method differs from the method of the above aspect in that the composition is in a solid form, which is to say, providing the
30 solid composition may comprise generating the solid composition from a composition comprising one or more organic solvents having the polymer and a metal catalyst precursor homogeneously dissolved therein, wherein the one or more organic solvents

may comprise acetone. Embodiments and advantages described for the method in the above aspect are analogously valid for the present method as described herein, and vice versa.

[0035] For the sake of brevity, where embodiments and advantages of the present method are analogous to embodiments and/or advantages of the method in the above aspect, they shall not be iterated as they have already been described above in various embodiments of the above aspect. For example, it has already been described above that to obtain the composition, the steps may comprise dissolving the polymer in the acetone to generate a polymer solute, and dissolving the metal catalyst precursor in the acetone to form metal ions. It is also already described above there may be mixing of the polymer solute and the metal ions in the acetone to form the composition.

[0036] Similarly, the metal ions in the present method may comprise or may consist of palladium ions. The polymer may comprise or may consist of acrylonitrile butadiene styrene or polylactic acid. The metal catalyst precursor may comprise or may consist of palladium chloride. Advantages of these have already been discussed in the method of the above aspect.

[0037] In the present method, the composition may be converted to a solid composition. In other words, generating the solid composition, from the composition, may comprise filling the composition into a mold, removing the one or more organic solvents to form the solid composition configured with a shape based on the mold, and separating the solid composition from the mold. Removal of the one or more organic solvents may comprise evaporating the one or more organic solvents. The one or more organic solvents may comprise or consist of acetone. The mold may be a silicone tube. By filling the composition into the mold, the composition conforms to the shape of the mold, e.g. silicone tube. When the composition dries, it forms a solid composition having a shape imparted by the silicone tube. To separate the solid composition from the mold, the mold (e.g. silicone tube) may be cut and peeled off therefrom. The solid composition may comprise the polymer having metal ions loaded therein. Such a solid composition may be termed herein as a “filament”, as it is of a form usable for 3D printing and thermal printing to form three-dimensional printed structures.

[0038] In the present method, the solid composition may then be heated. Said differently, the solid composition may be fitted to a nozzle of a 3D printer, where the heating may be carried out thereat (i.e. localized heating). Heating the solid composition (e.g. at the nozzle) may comprise melting the solid composition at a temperature of 300°C or less, 250°C or less, 200°C or less, or 150°C or less, to form the melted composition.

[0039] In the present method, fabricating the three-dimensional polymeric structure may comprise 3D printing of the three-dimensional polymeric structure entirely from the solid composition, wherein the one or more regions may be defined as the entire surface area of the three-dimensional polymeric structure. For this step, the solid composition may be used to form the entire three-dimensional polymeric structure via 3D printing. Accordingly, the entire three-dimensional polymeric structure, including all of its surface, may be formed of the solid composition (i.e. the one or more regions may be formed of the solid composition). Advantageously, this step circumvents the adhesion issue experienced when solely metal ions (in an aqueous medium) are coated on a polymeric surface, as the entire three-dimensional polymeric structure is already formed of the solid composition, i.e. the metal ions in the present method may at least be embedded in the surface.

[0040] In certain embodiments, the three-dimensional polymeric structure need not be entirely formed of the solid composition. In other words, a pre-formed three-dimensional polymeric structure may be used for depositing the solid composition on one or more surface areas of the pre-formed three-dimensional polymeric structure. As such, one or more regions of the three-dimensional polymeric structure may be defined by or formed of the solid composition deposited thereon. Accordingly, in certain embodiments, fabricating the three-dimensional polymeric structure may comprise depositing the solid composition on one or more surface areas of a pre-formed three-dimensional polymeric structure, wherein the one or more regions are defined by the solid composition deposited on the one or more surface areas. Depositing the solid composition may comprise 3D printing of the solid composition on one or more surface areas of the pre-formed three-dimensional polymeric structure. The pre-formed three-dimensional polymeric structure may be absent of (not loaded with) the metal ions. For example, a pre-formed three-dimensional polymeric

structure may be 3D printed from ABS or polylactic acid, and this ABS or polylactic acid does not contain metal ions. The surface of this pre-formed three-dimensional polymeric structure may then be entirely or partly deposited with the solid composition. Where one or more parts of the surface are to be deposited with the solid composition, the one or more parts of the surface may be pre-determined or pre-defined (e.g. marked-out) for depositing the solid composition thereon. The one or more parts of the surface may be any shape. This also advantageously circumvents the adhesion issue experienced with solely coating an aqueous solution of metal ions thereon. With the metal ions loaded in the solid composition to be deposited thereon, the metals ions may adhere more strongly at the one or more regions (i.e. one or more parts of the surface). Adhesion of the metal ions at the one or more regions may be improved further when the solid composition comprises the same polymer as that of the pre-formed three-dimensional structure. This may be because the same polymers may adhere together more compatibly than different polymers.

[0041] In various embodiments, the one or more regions may comprise one or more surface areas, or the entire surface, of the three-dimensional polymeric structure.

[0042] Similar to the method described in various embodiments of the above aspect, forming the metal on the one or more regions, in the present method, may comprise contacting the one or more regions with an alkaline bath comprising a reducing agent.

The entire three-dimensional polymeric structure may be contacted with the alkaline bath, or one or more parts (e.g. one or more surface areas) of the three-dimensional polymeric structure may be contacted with the alkaline bath. The reducing agent may comprise or consist of sodium hypophosphite. The pH of the alkaline bath and adjustment of the bath's pH shall not be iterated as they have already been described in the method of the above aspect.

[0043] The metal may comprise or consist of nickel. Further examples and embodiments are already described in the method of the first aspect and shall not be iterated for brevity.

[0044] The present disclosure further provides for a method of forming a composition for electroless deposition of a metal on a three-dimensional polymeric structure. The method may comprise mixing a polymer and a metal catalyst precursor in one or more organic solvents to form the composition, wherein the one or more organic solvents

may comprise acetone. Embodiments and advantages described in the context of the method of either one or both aspects mentioned above are analogously valid for the present method of forming the composition as described herein, and vice versa.

5 [0045] In the present method, mixing the polymer and the metal catalyst precursor may comprise dissolving the polymer in the acetone to generate a polymer solute, and dissolving the metal catalyst precursor in the acetone to form metal ions. Embodiments and advantages of this step have already been described in the methods of both aspects mentioned above.

10 [0046] In various embodiments, the metal ions may comprise or consist of palladium ions. The polymer may comprise or consist of acrylonitrile butadiene styrene or polylactic acid. The metal catalyst precursor may comprise or consist of palladium chloride. As embodiments and advantages of these have already been described in the method of either one or both aspects mentioned above, they shall not be iterated for brevity.

15 [0047] The present disclosure, in another aspect, provides for a composition for electroless deposition of a metal on a three-dimensional polymeric structure. The composition may comprise or consist of a polymer, a metal catalyst precursor, and one or more organic solvents comprising the polymer and the metal catalyst precursor homogeneously dissolved therein, wherein the one or more organic solvents may
20 comprise or consist of acetone. The metal catalyst precursor may be dissolved to form metal ions. The metal ions may comprise or consist of palladium ions. Embodiments and advantages described in the context of the present methods are analogously valid for the present composition as described herein, and vice versa.

25 [0048] The polymer may comprise or consist of acrylonitrile butadiene styrene or polylactic acid. The metal catalyst precursor may comprise or consist of palladium chloride. Advantages of these components have already been discussed above.

[0049] In certain embodiments, the composition may be formable into a solid composition for 3D printing. In other embodiments, the composition may be in the form of a solution. The composition is versatile in that it can be prepared in either
30 forms for depositing the metal ions loaded polymer on a polymer surface.

[0050] The present disclosure, in another aspect, provides for a solid composition for electroless deposition of a metal on a three-dimensional polymeric structure. The solid

composition may be generated from the composition described above, wherein the composition may comprise a polymer, a metal catalyst precursor, and one or more organic solvents comprising the polymer and the metal catalyst precursor homogeneously dissolved therein. The one or more organic solvents may comprise acetone. Embodiments and advantages described in the context of the methods and composition mentioned above are analogously valid for the present solid composition as described herein, and vice versa.

[0051] The present solid composition may comprise the polymer and metal ions homogeneously distributed therein. Said differently, the metal ions may be homogeneously distributed in the polymer.

[0052] In various embodiments of the solid composition, the polymer may comprise or consist of acrylonitrile butadiene styrene or polylactic acid. The metal catalyst precursor may comprise or consist of palladium chloride. The metal ions may comprise or consist of palladium ions. Advantages of these components have already been discussed above.

[0053] In the context of the present disclosure, the word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

[0054] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0055] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance. The variance may be $\pm 0.1\%$, $\pm 0.5\%$, $\pm 1\%$, $\pm 5\%$, or even $\pm 10\%$.

[0056] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0057] Unless specified otherwise, the terms “comprising” and “comprise”, and grammatical variants thereof, are intended to represent “open” or “inclusive” language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[0058] While the methods described above are illustrated and described as a series of steps or events, it will be appreciated that any ordering of such steps or events are not to be interpreted in a limiting sense. For example, some steps may occur in different orders and/or concurrently with other steps or events apart from those illustrated and/or described herein. In addition, not all illustrated steps may be required to implement one or more aspects or embodiments described herein. Also, one or more of the steps depicted herein may be carried out in one or more separate acts and/or phases.

Examples

[0059] The present disclosure relates to metal ions pre-loaded polymer for area selective plating and a method of plating metal selectively on a surface area.

[0060] The metal ions pre-loaded polymer can be formed into a filament for 3D printing, wherein the pre-loaded polymer includes metal ions homogeneously distributed therein. The metal ions pre-loaded polymer can be in the form of a solution comprising a solvent having a dissolved polymer and metal ions homogeneously distributed therein. The metal ions pre-loaded polymer can be in the form of electrospun fibers comprising a polymer having metal ions homogeneously distributed.

[0061] The method of plating can comprise: (a) providing a 3D printing filament having metal ions homogeneously distributed therein, (b) printing the filament on a pre-determined area for electroless plating, and (c) performing plating using a plating bath comprising a reducing agent for reducing the metal ions to metal.

[0062] The method of plating can comprise: (a) providing a coating solution comprising a solvent having a dissolved polymer and metal ions homogeneously distributed, (b) coating the solution on a pre-determined area for electroless plating, (c) evaporating the solvent from the coating, and (d) performing plating using a plating bath comprising a reducing agent for reducing the metal ions to metal.

[0063] A non-limiting example of the polymer, solvent, and metal ions, can be ABS, acetone, and palladium (Pd) ions, respectively.

[0064] Details of the present metal ions pre-loaded polymer and method of plating, are discussed, by way of non-limiting examples, as set forth below.

[0065] Example 1A: Present Method - Compatibility of ABS and Different Organic Solvents

[0066] ABS was mixed with deionized (DI) water. This was repeated for mixing with ethanol, glacial acetic acid, toluene, o-xylene, methyl ethyl ketone (MEK), and acetone, to observe compatibility of the ABS with each of the different solvents.

[0067] PdCl₂ solubility in each of the different solvents was tested by adding 10 mg of PdCl₂ powder into 1 mL of DI water, ethanol, glacial acetic acid, toluene, O-xylene, MEK, and acetone, respectively.

[0068] Example 1B: Present Method - Synthesis of Pd Ion Loaded ABS Microfibers by Electrosin

[0069] 2 g of ABS (Plasil, FA17510WT) was dissolved in 2 g of acetone (Wako Pure Chemical, 016-00346), and 1 g of PdCl₂ (Kanto Chemical, 32009-60) was dissolved in 4 g of acetone. These acetone solutions were left overnight, then mixed together and filled into a polypropylene syringe (17 mm in diameter and 82 mm in length, 10 ml in capacity) with a sharp nozzle (polyethylene, 0.25 mm in inside diameter and 0.51 mm in outer diameter and 31 mm in length). To eject the mixed solution (Pd ion + ABS in acetone) by electrosin, an enamel-coated wire (electrode) was inserted into the solution, and air pressure was exerted using another syringe. The metal surface at the other end of the wire was exposed by polishing off the enamel, and the exposed metal tip was connected to the positive end-terminal of a high-voltage power supply (Green Techno, GS30). This unit was set on a stage so that the nozzle points vertically down to the stage. A metal plate (100 mm x 100 mm, 1 mm thick) was placed on the stage, and connected to the ground of the high-voltage power supply. A glass plate (18 mm x 18 mm, 0.17 mm thick) was set on the metal plate with 25 mm gap (working distance) between its top surface and the tip of the nozzle. The power supply was turned on to apply a voltage of 9.0 V between the mixed solution and metal plate to drive the electrosin and form Pd ion loaded ABS microfibers on the glass plate.

[0070] Example 1C: Present Method - Pd Ion Loaded ABS Coating on 3D Printed ABS Structure

[0071] The mixed solution (Pd ion + ABS in acetone) described in the former example was prepared and filled into a syringe in the same way. The solution was

injected from the syringe into a silicone tube (1000 mm in length, 2 mm in diameter). Two hours were given to evaporate the acetone of the filled tube, and then, a cycle of the injection and the evaporation was repeated another two times to fill the tube with Pd ion loaded ABS. The filled tube was completely dried up overnight, and then, the solidified Pd ion loaded ABS was taken up as a filament by cutting and removing the tube. The filament was set to a 3D printer where its tip was heated at 230°C to locally melt and deposit Pd ion loaded ABS onto a pre-determined area to form a pre-designed 3D structure or to form the entire 3D structure.

[0072] In another example, a pure ABS filament (no Pd ion loading, Plasil, FA17510WT) was also used for 3D printing to form a 3D ABS structure, having pre-determined areas loaded with Pd ion from the Pd ion loaded ABS filament. This was used to form a dice (a 1 cm³ cube) having three dot-domains loaded with Pd ion. In other words, the mixed solution (Pd ion + ABS in acetone) was directly used to coat a Pd ion loaded ABS layer on pre-determined areas of a pre-formed 3D ABS structure.

[0073] The mixed solution (Pd ion + ABS in acetone) can be used as ink in an electrospinning set up to fabricate electrospun fibers having homogeneously distributed Pd ions.

[0074] Example 1D: Present Method - Electroless Nickel Plating

[0075] The nickel bath for electroless nickel deposition contained 0.2 M sodium citrate, 0.5 M boric acid, 15 g/L nickel (II) sulphate hexahydrate and 25 g/L sodium hypophosphite monohydrate. Also, pH of the nickel bath was adjusted to 9.0 by sodium hydroxide, and the temperature was maintained at 60°C during the electroless plating.

[0076] The prepared Pd ion loaded ABS sample (microfiber or 3D structure) was washed by DI water, followed by electroless nickel plating thereon.

[0077] For comparison, the pure ABS sample (microfiber or 3D structure) was also used for electroless plating. It was washed by DI water first, catalyzed by conventional Pd/Sn catalyst, which involves: (1) dipping into 1.5 mM palladium (II) chloride for 2 mins, (2) washing with DI water to prevent contamination, (3) followed by dipping in 0.2 M tin (II) chloride for 2 mins, (4) washing with DI water to prevent contamination, (5) immersing into 1 M NaOH for 3 mins to help accelerate the plating process, (6) washing with DI water to remove excess solution on the substrate surface.

After Pd/Sn catalyzation, the ABS samples were dipped in the bath for electroless nickel plating.

[0078] Example 2A: Results And Discussion – Selection of Acetone as Solvent For ABS Resin and Pd Catalyst Precursor

5 **[0079]** As demonstrated above, acetone was chosen as the solvent to dissolve both the ABS resin and Pd catalyst precursor (e.g. PdCl₂). Other solvents shown in FIG. 1 have also been tested.

[0080] Acetone, as well as methyl ethyl ketone (MEK), works as a polar protic solvent that breaks the butadiene linkage in ABS to generate ABS solute. On the other
10 hand, PdCl₂ is partially dissolved in acetone but does not dissolve in MEK. DI water and ethanol are usable as a solvent for PdCl₂, but both solidify the ABS solute once they contact with the acetone which the ABS solute is present in. Glacial acetic acid, toluene and o-xylene swell the ABS solute but show poor solubility of PdCl₂. Particularly, glacial acetic acid causes solidification of the ABS solute in the acetone.
15 Based on the above compatibility tests for both PdCl₂ and the ABS solute, acetone was chosen.

[0081] Example 2B: Results And Discussion - Pd Ion Loaded ABS Acetone Solution For Electrospinning and Electroless Deposition

[0082] Electrospinning of the Pd ion loaded in ABS acetone solution produced Pd ion
20 loaded ABS fibers. Electroless deposition was then utilized for subsequent metal coating.

[0083] Metal coating on polymer or organic nanofibers is a technique to provide electrical conductivity, catalytic activity, and/or mechanical stiffness to the fibers. Methods based on vacuum deposition, e.g. sputtering and evaporation, suffer from
25 uneven, or even defective, deposition of metal on the fibers' surface, as fibers are three-dimensional structures and tangled, such that some fibers cover the surface of others. For the same reason, solution deposition techniques based solely on dipping fibers into solution may also be difficult for uniform deposition of metal on fibers surface. Moreover, the fibers may be piled up over substrate which renders it difficult
30 for the fibers to be uniformly coated with metal, not just in terms of having all fibers coated, but also having the surface of each fibers uniformly coated.

[0084] In conventional electroless deposition, the fibers are functionalized with Pd nanoparticles, which act as a catalyst for electroless deposition, by alternatively dipping the fibers in a Pd ion solution and a reducing agent solution (e.g. PdCl₂ and NaH₂PO₂, respectively). In this instance, the uniform deposition of Pd nanoparticles on the fibers is necessary for uniform electroless deposition of metal on the fibers. However, this does not address the issue of uniform metal coating mentioned above, which is neither simple nor easy to resolve. For example, fibers disposed on a substrate have one side facing the substrate and another side facing away from the substrate. The side of fibers facing away from the substrate may get a higher loading of Pd nanoparticles deposited thereon than the side of fibers facing the substrate.

[0085] In fact, as seen in FIG. 2A, in conventional electroless deposition where fibers are dipped in catalyzation solutions prior to electroless deposition, the metal deposited on the fibers was not uniform, and the metal even got deposited in spaces between fibers (i.e. not on fibers), probably due to residue of Pd ions or Pd nanoparticles.

[0086] On the other hand, the present method where Pd ions are pre-loaded into the ABS solution render the Pd ions to be contained in the ABS fibers, so that every individual fiber got uniformly coated as seen in FIG. 2B.

[0087] Example 2C: Results And Discussion – Area-Selectivity of Electroless Plating on ABS Surfaces Coated with Pd Ion Loaded ABS

[0088] The electroless plating was induced selectively on surfaces of an ABS coated with Pd ion loaded ABS. To test the success of electroless plating on surfaces already coated with Pd ion loaded ABS, three 3D ABS structure samples of different catalyst coating methods were tested: (A) by thermal 3D printing of the Pd ion loaded ABS filament, (B) by air-pressure ejection of the Pd ion loaded ABS solution, (C) by dipping in Pd ion solution (PdCl₂ solution). Coating methods (A) and (B) have already been described in example 1C.

[0089] As for the sample from coating method (B), the electroless plating successfully occurred only at Pd ion loaded domains and the plated metal (Ni) had sufficient adhesion (FIG. 3). This indicates that the loaded Pd ion was reduced into Pd metal by the reducing agent (sodium hypophosphite monohydrate) in the electroplating bath and the Pd metal works as catalyst for subsequent deposition of Ni.

[0090] As for the sample from coating method (C), the electroless plating actually occurred but the plated Ni was easily peelable during or after the plating due to poor adhesion. This is in line with the observation for conventional metallization of ABS surface, wherein ABS is usually etched with chromic acid to roughen the surface to have sufficient adhesion of electroless plated metal. This etching process is not environment friendly due to use of chromic acid. Notably, the present method of metallization using Pd ion + ABS solution for coating metal over ABS is more environment friendly and cost less as it avoids chromic acid etching process. For the method producing sample from (C), such method may be useful in applications where the plated Ni needs to be subsequently removed.

[0091] The present method is an “area-selective” method, wherein only certain surface areas of a structure induce electroless plating. The present method also provides for strong adhesion of metal on a plastic. The present method provides for an environment friendly metallization (electroless plating) of 3D printed structures, for example, using Pd ion loaded ABS solution.

[0092] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method of electroless deposition of a metal on a three-dimensional polymeric structure, the method comprising:

5 dissolving a polymer and a metal catalyst precursor in one or more organic solvents to generate a composition having a polymer solute and metal ions, respectively, wherein the polymer solute and the metal ions are homogeneously dissolved in the one or more organic solvents;

 removing the one or more organic solvents to form a solid composition
10 comprising the polymer and the metal ions homogeneously distributed therein, wherein the metal ions are derived from the metal catalyst precursor;

 fabricating the three-dimensional polymeric structure having one or more regions formed of the solid composition;

 contacting the one or more regions with an alkaline bath comprising a
15 reducing agent to form a metal catalyst from the metal ions; and

 contacting the metal catalyst with a solution configured for electroless deposition of the metal on the one or more regions,

 wherein the one or more organic solvents comprise acetone,

 wherein the polymer comprises acrylonitrile butadiene styrene or polylactic
20 acid.

2. The method of claim 1, wherein dissolving the polymer and the metal catalyst precursor in the one or more organic solvents comprises:

 separately dissolving each of the polymer and the metal catalyst precursor in a
25 first acetone and a second acetone, respectively, and then mixing the first acetone containing the polymer solute and the second acetone containing the metal ions to form the composition; or

 dissolving the polymer and the metal catalyst precursor together in acetone.

30 3. The method of claim 1 or 2, wherein the metal catalyst precursor comprises palladium chloride.

4. The method of any one of claims 1 to 3, wherein the metal ions comprise palladium ions.
- 5 5. The method of any one of claims 1 to 4, wherein forming the solid composition comprises:
 - filling the composition into a mold;
 - evaporating the one or more organic solvents to form the solid composition configured with a shape based on the mold; and
 - 10 separating the solid composition from the mold.
6. The method of any one of claims 1 to 5, wherein fabricating the three-dimensional polymeric structure comprises 3D printing of the three-dimensional polymeric structure entirely from the solid composition, wherein the one or more
15 regions are defined as entire surface area of the three-dimensional polymeric structure.
7. The method of any one of claims 1 to 5, wherein fabricating the three-dimensional polymeric structure comprises depositing the solid composition on one or
20 more surface areas of a pre-formed three-dimensional polymeric structure, wherein the one or more regions are defined by the solid composition deposited on the one or more surface areas.
8. The method of claim 1, wherein the reducing agent comprises sodium
25 hypophosphite.
9. The method of any one of claims 1 to 8, wherein the metal comprises nickel.
10. A method of electroless deposition of a metal on a three-dimensional
30 polymeric structure, the method comprising:

dissolving a polymer and a metal catalyst precursor in one or more organic solvents to provide a composition comprising one or more organic solvents having a polymer solute and metal ions homogeneously dissolved therein;

fabricating the three-dimensional polymeric structure from the composition;

5 contacting the three-dimensional polymeric structure with an alkaline bath comprising a reducing agent to form a metal catalyst from the metal ions;

 contacting the metal catalyst with a solution configured for electroless deposition of the metal on the three-dimensional polymeric structure,

 wherein the one or more organic solvents comprise acetone,

10 wherein the polymer comprises acrylonitrile butadiene styrene or polylactic acid.

11. The method of claim 10, wherein dissolving the polymer and the metal catalyst precursor in the one or more organic solvents comprises:

15 separately dissolving each of the polymer and the metal catalyst precursor in a first acetone and a second acetone, respectively, and then mixing the first acetone containing the polymer solute and the second acetone containing the metal ions to form the composition; or

 dissolving the polymer and the metal catalyst precursor together in acetone.

20

12. The method of claim 10 or 11, wherein the metal ions comprise palladium ions.

13. The method of any one of claims 10 to 12, wherein the metal catalyst precursor comprises palladium chloride.

25

14. The method of any one of claims 10 to 13, wherein fabricating the three-dimensional polymeric structure comprises electrospinning the composition to form the three-dimensional polymeric structure, wherein the three-dimensional polymeric structure comprises polymeric fibers having metal ions homogeneously distributed therein.

30

15. The method of any one of claims 10 to 14, wherein fabricating the three-dimensional polymeric structure comprises ejecting the composition by air pressure onto a substrate.
- 5 16. The method of any one of claims 10 to 15, wherein forming the metal on the three-dimensional polymeric structure comprises forming the metal on a surface area of the three-dimensional polymeric structure.
17. The method of claim 10, wherein the reducing agent comprises sodium
10 hypophosphite.
18. The method of any one of claims 10 to 17, wherein the metal comprises nickel.
- 15 19. A method of forming a composition for electroless deposition of a metal on a three-dimensional polymeric structure, the method comprising:
dissolving a polymer and a metal catalyst precursor in one or more organic solvents to form the composition having a polymer solute and metal ions, respectively, wherein the one or more organic solvents comprise acetone, wherein the
20 polymer comprises acrylonitrile butadiene styrene or polylactic acid.
20. The method of claim 19, wherein dissolving the polymer and the metal catalyst precursor in the one or more organic solvents comprises:
separately dissolving each of the polymer and the metal catalyst precursor in a
25 first acetone and a second acetone, respectively, and then mixing the first acetone containing the polymer solute and the second acetone containing the metal ions to form the composition; or
dissolving the polymer and the metal catalyst precursor together in acetone.
- 30 21. The method of claim 19 or 20, wherein the metal ions comprise palladium ions.

22. The method of any one of claims 19 to 21, wherein the metal catalyst precursor comprises palladium chloride.

5 23. A composition for electroless deposition of a metal on a three-dimensional polymeric structure, the composition comprising:

a polymer;

a metal catalyst precursor; and

one or more organic solvents comprising the polymer and the metal catalyst precursor homogeneously dissolved therein, wherein the one or more organic solvents
10 comprise acetone, and

wherein the polymer comprises acrylonitrile butadiene styrene or polylactic acid.

15 24. The composition of claim 23, wherein the metal catalyst precursor comprises palladium chloride.

25. The composition of claim 23 or 24, wherein the composition is formable into a solid composition for 3D printing.

20

26. A solid composition for electroless deposition of a metal on a three-dimensional polymeric structure, wherein the solid composition is generated from a composition comprising:

a polymer;

25 a metal catalyst precursor; and

one or more organic solvents comprising the polymer and the metal catalyst precursor homogeneously dissolved therein, wherein the one or more organic solvents comprise acetone,

wherein the solid composition comprises:

30 the polymer; and

metal ions homogeneously distributed therein, and

wherein the polymer comprises acrylonitrile butadiene styrene or polylactic acid.

27. The solid composition of claim 26, wherein the metal catalyst precursor
5 comprises palladium chloride.

28. The composition of claim 26 or 27, wherein the metal ions comprise palladium ions.