

ADDITIVE MANUFACTURING SYSTEM, METHODS OF FORMING THE SAME AND OF FORMING A COMPOSITE STRUCTURE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application No. 10202103820Q filed April 14, 2021, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various aspects of this disclosure relate to an additive manufacturing system. Various aspects of this disclosure relate to a method of forming an additive manufacturing system. Various aspects of this disclosure may provide a method of forming a composite structure according to various embodiments.

BACKGROUND

[0003] The formation of specific metal patterns on three-dimensional (3D) plastic parts has attracted a great deal of research interest because of potential applications in 3D smart electronics, telecommunication technology, micro/nano-sensors, microelectromechanical systems (MEMS) and even quantum science. In contrast to traditional two-dimensional (2D) printed circuit boards (PCBs), 3D metal-plastic composite functional devices have more complex and sophisticated structures with higher degrees of design freedom and higher integration. The selective construction of metallized layouts in specific regions of 3D substrates can allow the fabrication of interconnecting devices having a variety of complicated geometric shapes. These 3D metal-plastic structures greatly reduce size requirements relative to standard planar printed electronics and thus permit the further miniaturization of functional devices. Even so, it is difficult to build interconnected metal patterns on the surfaces of more complex 3D parts using traditional microfabrication techniques such as lithography, deposition, etching and release. As the manufacturing of 3D metal-plastic components requires laser direct structuring (LDS), the fabrication of such parts can be expensive and may involve long production cycle, a high degree of complexity and low design flexibility.

[0004] The combination of computer aided design (CAD) and 3D printing (3DP) allows the manufacture of a wide range of complex shapes via a layer-by-layer manufacturing process. Despite the greater design flexibility and superior processing capability of 3DP, this technology

has not reached its full potential regarding the formation of 3D metal-plastic structures due to the limited materials that can be utilized. To address this issue, researchers have focused on combining 3DP with metallization techniques to create conductive structures. Several studies have attempted to replace 3D metal-plastic structures used in areas such as electronics with various conductive materials, including metallic nanoparticles, graphene, multi-walled carbon nanotubes and carbon black. These substances are often used as conductive fillers to obtain modified materials that can be applied to 3DP. Although several types of micro-structured circuits have been successfully fabricated using this approach, these fillers are typically expensive, and the modified materials tend to exhibit reduced printing accuracy and performance after molding. In addition, the complex preparation process associated with this technology tends to result in slow method development. In contrast, most research has examined the metallization of 3D printed parts via electroplating (EP), electroless plating (ELP), vacuum evaporation (VE) and sputtering. In this manner, complex 3D printed structures having surfaces with metallic properties have been obtained. Among these methods, ELP is the most cost-effective technique for the deposition of metal onto non-metallic structures. ELP is based on simple wet chemical processing and allows the deposition of a uniform metal coating onto the surface of a part without applying an external electrical potential. However, although many researchers have fabricated microstructures with specific functions using 3DP and ELP, most of these parts do not meet the complex topological requirements of 3D metal-plastic parts intended to serve as non-conductive or conductive substrates. For this reason, multi-material 3DP (MM3DP) technology has been proposed as a means of achieving pattern selective ELP. Using MM3DP, materials having special functions can be applied at any location of a part to form interconnected 3D patterns that can be used to activate the ELP process. An activation-sensitization pre-treatment is required prior to performing ELP, and this necessity has been exploited to achieve patterned plating. The most straightforward approach to this process is to coarsen specific regions on the material surface by creating microstructures. This technique takes advantage of the change in the capacity of the roughened surfaces to adsorb activating/sensitizing palladium (Pd) catalyst which induces subsequent ELP reaction. However, although selective metallization can be achieved in this manner, the resulting accuracy and resolution are still not satisfactory. Consequently, some researchers have prepared materials with electrode properties that allow more accurate adsorption of activated Pd^{2+} and Ag^+ seeds, based on generating structures having opposite charges. This method improves the plating accuracy to some extent, although the electrode regions may react with

ions in the processing solution when ELP is performed. In contrast to these indirect activation routes, other methods directly add activation seeds including ions such as Pd^{2+} and Ag^+ to the material to fabricate metal-plastic composite structures. Unfortunately, problems related to activator dispersion in the material restrict the application of this technique to just a few 3DP processes. In addition, the quality of the resulting coatings is poor, as is the adhesion of plated metal to the substrate material. Thus, there are remaining challenges related to achieving the fabrication of metallized parts having complex structures in conjunction with high accuracy and performance.

SUMMARY

[0005] Various embodiments may provide an additive manufacturing system for forming a composite structure. The system may include a first pool including or configured to include an active solution or mixture to form a first printed portion of a workpiece, the active solution or a mixture including a solvent, an activation seed soluble in the solvent, and a light curable resin. The system may also include a second pool including or configured to include a further light curable resin to form a second printed portion of the workpiece. The system may additionally include a light source configured to provide light. The system may further include a mask configured to be arranged such that the light provided by the light source is irradiated onto the workpiece through the mask. The system may also include a third pool including or configured to include a cleaning solution or mixture for cleaning the workpiece. The first printed portion including the activation seed may be configured to form a metallic layer via an electroless deposition process, thereby forming the composite structure.

[0006] Various embodiments may provide a method of forming an additive manufacturing system for forming a composite structure. The method may include providing a first pool including or configured to include an active solution or mixture to form a first printed portion of a workpiece, the active solution or mixture including a solvent, an activation seed soluble in the solvent, and a light curable resin. The method may also include providing a second pool including or configured to include a further light curable resin to form a second printed portion of the workpiece. The method may further include providing a light source configured to provide light. The method may additionally include providing or arranging a mask such that the light provided by the light source is irradiated onto the workpiece through the mask. The method may also include providing a third pool including or configured to include a cleaning solution or mixture for cleaning the workpiece. The first printed portion including the

activation seed is configured to form a metallic layer via an electroless deposition process, thereby forming the composite structure.

[0007] Various embodiments may provide a method of forming a composite structure. The method may include depositing an active solution or mixture to form a first printed portion of a workpiece, the active solution including a solvent, an activation seed soluble in the solvent, and a light curable resin. The method may also include depositing a further light curable resin to form a second printed portion of the workpiece. The method may additionally include irradiating light provided by a light source onto the workpiece through a mask. The method may also include dispensing a cleaning solution or mixture for cleaning the workpiece. The method may further include forming a metallic layer on the first printed portion via an electroless plating process due to the activation seed included in the first printed portion, thereby forming the composite structure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

FIG. 1 shows a general illustration of an additive manufacturing system according to various embodiments for forming a composite structure.

FIG. 2 shows a general illustration of a method of forming an additive manufacturing system for forming a composite structure.

FIG. 3 shows a general illustration of a method of forming a composite structure according to various embodiments.

FIG. 4 is a schematic illustrating the multi-material digital light processing three-dimensional printing (MM-DLP3DP) process according to various embodiments.

FIG. 5 shows (a) a multi-material digital light processing three-dimensional printing (MM-DLP3DP) apparatus according to various embodiments, and (b) numerical processing of multi-material models in which the slicing data are obtained by treating different material topologies in the same part as units with separate slicing according to various embodiments.

FIG. 6 is a schematic showing an arbitrary complex multi-material model and the printing process of printing the model according to various embodiments.

FIG. 7 shows (a) a plot of absorption as a function of wavelength (in nanometres or nm) showing the ultraviolet spectra of a rigid light-cured resin before and after modification with palladium (Pd^{2+}) ions according to various embodiments; and (b) a plot of absorption as a function of wavelength (in nanometres or nm) showing the ultraviolet spectra of a flexible light-cured resin before and after modification with palladium (Pd^{2+}) ions according to various embodiments.

FIG. 8 shows (a) three micro-structured metallized surfaces each with a thickness of 200 μm : circular with a radius of 200 μm , ortho-hexagonal with an inner circle radius of 200 μm , and circular groove with a groove width of 400 μm using the process according to various embodiments; (b) a skeletonized ball structure with a circular base that has been covered with Ni metal using the process according to various embodiments; (c) an Eiffel Tower with a microfine structure in which selected parts have been uniformly covered with nickel (Ni) plating using the process according to various embodiments; (d) a five-sided structure with a complex nickel (Ni) metal distribution and multi-material nesting between layers and within layers using the process according to various embodiments; (e) a dome structure with an arc-shaped metal distribution using the process according to various embodiments; (f) a U-shaped tube with an internal metal mesh having a thickness of 1 mm and square hexagons each with a 500 μm inner diameter using the process according to various embodiments, demonstrating the construction and metallization of a small structure within the resin; (g) a double-layer 3D hollow nesting part, a large ball (radius 15 mm.) with triangular hollow holes wrapping a small ball (radius 8 mm) with regular hexagon hollow holes and selectively deposited with nickel (Ni) using the process according to various embodiments; (h) a flexible carbon nanotube structure with selective three dimensional (3D) metallization using the process according to various embodiments, showing a lack of fracture after deformation; and (i) a wearable structure with a complex shape and nickel (Ni) plating that remains tightly bonded to the flexible substrate after deformation formed by the process according to various embodiments.

FIG. 9 shows (a) an light emitting diode (LED) stereo circuit with complex nickel (Ni) metal wire topology using the process according to various embodiments; (b) a double-layer three-dimensional (3D) circuit structure with a complex three-dimensional (3D) copper wire structure using the process according to various embodiments, and which is difficult to fabricate by traditional processes; and (c) a plot of impedance (in ohms or Ω) as a function of frequency as a function of frequency (in hertz or Hz) showing the impedance of nickel (Ni) and copper (Cu) coatings formed using the process according to various embodiments.

FIG. 10 shows (a) nickel (Ni)-plated structures with widths of 1 mm, 500 μm and 100 μm and with widths of 50 and 40 μm formed by the process according to various embodiments; and (b) a circuit board part having a width of 1 mm incorporating 500 μm copper wires formed by the process according to various embodiments. FIG 10(a) shows images of Ni wires having widths of 1 mm, 500 μm , 100 μm , 50 μm , and 40 μm . High-magnification microscopy showed that the Ni was precisely distributed on these active precursor wires, thus showing exceptional resolution of the printing method and the effectiveness of selective metal deposition. The Cu plating on the circuit board shown in FIG. 10(b) shows that various embodiments may provide a manufacturing resolution of at least 40 μm , which is sufficient to meet the processing requirements of most electronic products.

FIG. 11 shows (a) a standard flat nickel (Ni) plating according to various embodiments; (b) and (c) scanning electron microscopy (SEM) images of the indicated area in (a) with different magnifications according to various embodiments; (d) a nickel (Ni) plating on the surface of a circular microstructure according to various embodiments; (e) and (f) scanning electron microscopy (SEM) images of the indicated area in (d) with different magnifications according to various embodiments; (g) a nickel (Ni) plating on the surface of an annular groove microstructure according to various embodiments; (h) and (i) scanning electron microscopy (SEM) images of the indicated area in (g) with different magnifications according to various embodiments; (j) a nickel (Ni) plating on the surface of an ortho-hexagonal microstructure according to various embodiments; (k) – (l) scanning electron microscopy (SEM) images of the indicated area in (j) with different magnifications according to various embodiments; (m) a flexible sample with nickel (Ni) plating; and (n) – (o) scanning electron microscopy (SEM) images of the indicated area in (m) with different magnifications according to various embodiments.

FIG. 12 shows (a) a cross-sectional transmission electron microscopy (TEM) image indicating the resin layer, the conjunction layer, and the nickel layer of the composite structure according to various embodiments; (b) an energy-dispersive X-ray spectroscopy (EDS) image showing the distribution of iron according to various embodiments; (c) an energy-dispersive X-ray spectroscopy (EDS) image showing the distribution of palladium according to various embodiments; and (d) an energy-dispersive X-ray spectroscopy (EDS) image showing the distribution of nickel according to various embodiments.

FIG. 13 shows (a) a schematic of a three-dimensional (3D) printed integrated strain gauge according to various embodiments on the measured object; (b) images of the strain gauge

according to various embodiments and a schematic on the measurement of the strain gauge according to various embodiments; (c) an image showing the bending deformation of the gauge under stress according to various embodiments; (d) a plot of voltage (in volts or V) as a function of load (in grams or g) showing the voltage measurement characteristics of the strain gauge according to various embodiments; (e) a plot of strain as a function of load (in grams or g) showing the strain characteristics of the strain gauge according to various embodiments calculated from experiment data; and (f) a plot of deformation (in millimetres or mm) as a function of load (in grams or g) showing the experimental deformation data of the strain gauge according to various embodiments.

FIG. 14 shows (a) schematics illustrating the operation principles of a three-dimensional (3D) printed piezoelectric sensor according to various embodiments; (b) images showing the piezoelectric sensor according to various embodiments being bent at bending angles 30°, 60°, 90° and 120°; (c) a plot of voltage (in volts or V) as a function of time (in seconds or s) showing the voltage waveforms generated by the piezoelectric sensor according to various embodiments at 30°, 60°, 90° and 120°; and (d) a plot of voltage (in volts or V) as a function of deformation (in nanometers or nm) showing the voltage generated by the piezoelectric sensor according to various embodiments in tension as a function of deformation.

FIG. 15 shows (a) a schematic showing a measurement system including three-dimensional (3D) electrocardiogram (ECG) electrodes formed according to various embodiments; (b) images showing the device components of the system including the electrodes formed according to various embodiments; (c) a plot showing five electrocardiogram (ECG) signals measured by the electrodes formed according to various embodiments based on random measurements of a subject at rest; and (d) a plot showing electrocardiogram (ECG) signals measured by the electrodes formed according to various embodiments based on measurements when the subject is swing an arm, clicking a computer mouse, and writing.

DETAILED DESCRIPTION

[0009] 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 practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, and logical 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.

[0010] Embodiments described in the context of one of the methods or additive manufacturing system are analogously valid for the other methods or additive manufacturing systems. Similarly, embodiments described in the context of a method are analogously valid for a system, and vice versa.

[0011] 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.

[0012] 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.

[0013] 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.

[0014] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0015] Various embodiments may relate to a simple means of fabricating metal-plastic functional devices with complex shapes based on a multi-material digital light processing 3DP (MM-DLP3DP) process. This technique may allow the fabrication of microstructures containing active precursors and substrate materials having specific 3D spatial distributions that can selectively activate ELP. The active precursors may be prepared by adding a saturated aqueous solution of Pd^{2+} ions to water-washable light-cured resins (either rigid or flexible). Subsequently, complex microstructures with specific topological distributions of material properties (comprising combinations of standard resin with the active precursor) may be fabricated using a MM-DLP3DP apparatus with multiple workstations. After a simple cleaning process, the materials were directly plated and metallized with 3D patterns using ELP. Pd^{2+} ions may be homogeneously dispersed throughout the active precursor, and irradiation of the treated resin with patterned UV light caused a photo-initiator to generate free radicals. These radicals may initiate a double-bond cross-linking reaction between the monomer and the low-molecular-weight polymer that produced a rigid cured structure in which the Pd^{2+} ions were embedded. In the plating bath, the Pd^{2+} ions exposed at the surface of the material may be

reduced by NaH_2PO_2 to Pd and may serve as catalytic nuclei after forming Pd particles, following which they induced the targeted metal deposition. This method may produce a conjunction layer where the deposited metal is microscopically embedded in the plastic layer. This technique may simplify the production process and may reduce costs while providing the capability to manufacture various complex 3D structures with special metal patterns.

[0016] FIG. 1 shows a general illustration of an additive manufacturing system according to various embodiments for forming a composite structure. The system may include a first pool 102 including or configured to include an active solution or mixture to form a first printed portion of a workpiece, the active solution or a mixture including a solvent, an activation seed soluble in the solvent, and a light curable resin. The system may also include a second pool 104 including or configured to include a further light curable resin to form a second printed portion of the workpiece. The system may additionally include a light source 106 configured to provide light. The system may further include a mask 108 configured to be arranged such that the light provided by the light source 106 is irradiated onto the workpiece through the mask. The system may also include a third pool 110 including or configured to include a cleaning solution or mixture for cleaning the workpiece. The first printed portion including the activation seed may be configured to form a metallic layer via an electroless deposition process, thereby forming the composite structure.

[0017] In other words, the additive manufacturing system may include a first pool 102, a second pool 104, and a third pool 110 for storing an active solution or mixture, a further light curable resin and a cleaning solution or mixture respectively. The additive manufacturing system may also include a light source 106 and a mask 108.

[0018] For avoidance of doubt, FIG. 1 seeks to illustrate an additive manufacturing system having certain features according to various embodiments, and is not intended to limit the arrangement, size, shape, orientation etc. of the features.

[0019] In various embodiments, the activation seed may be a catalyst or a catalyst precursor. The catalyst precursor may include metallic ions such as palladium ion or silver ion. The catalyst may include metals such as palladium metal or silver metal.

[0020] In various embodiments, the light curable resin and the further light curable resin may be of a same material. In various other embodiments, the light curable resin and the further light curable resin may be of different materials.

[0021] Generally speaking, the light may be any light that is able to cure the light curable resin and the further light curable resin. The light source 106 may be chosen based on the ability

of light emitted by the light source 106 to cure the resins. In various embodiments, the light may be ultraviolet light or visible light. However, in various other embodiments, the light may be any other light that is able to cure the light curable resin and the further light curable resin.

[0022] The mask 108 may be any suitable mask. The mask 108 may be configured to allow light to pass through to irradiate certain portions of the first printed portion and/or second printed portion, while blocking the light from irradiating other portions, thereby forming masking patterns. For instance, the mask 108 may be a liquid crystal display (LCD) mask.

[0023] In various embodiments, the additive manufacturing system may also include a controller in electrical connection with the first pool 102, the second pool 104, the third pool 110, the light source 106, and the mask 108.

[0024] Various embodiments may relate to printing using the multi-material nested topology. In various embodiments, the controller may be configured to control the first pool 102 to deposit the active solution or mixture onto a predetermined position of a substrate or an underlying layer to form the first printed portion. The controller may be configured to control the mask 108 to generate a first masking pattern, or to position or arrange the mask 108 having the first masking pattern. The controller may be further configured to control the light source 106 to irradiate the light onto the first printed portion through the first masking pattern, thereby curing at least a slice of the first printed portion. The controller may be further configured to control the third pool 110 to dispense the cleaning solution or mixture for cleaning the first printed portion and to remove a remaining uncured slice of the first printed portion. The controller may also be configured to control the second pool 104 to deposit the further light curable resin onto another predetermined position of the substrate or the underlying layer to form the second printed portion. The controller may be also configured to control the mask 108 to generate a second masking pattern, or to position or arrange a further mask having the second masking pattern. The controller may also be configured to control the light source 106 to irradiate the light onto the second printed portion through the second masking pattern, thereby curing at least a slice of the second printed portion. The controller may be further configured to control the third pool 110 to dispense the cleaning solution or mixture for cleaning the second printed portion and to remove a remaining uncured slice of the second printed portion.

[0025] Various embodiments may relate to printing using the interlayer multi-material stacking topology. In various embodiments, the controller may be configured to control the first pool 102 to deposit the active solution or mixture onto a substrate or an underlying layer to form the first printed portion. The controller may be configured to control the mask 108 to

generate a first masking pattern, or to position or arrange the mask having the first masking pattern. The controller may also be further configured to control the light source 106 to irradiate the light onto the first printed portion through the first masking pattern, thereby curing at least a slice of the first printed portion, the cured slice of the first printed portion forming a first layer. The controller may be further configured to control the third pool 110 to dispense the cleaning solution or mixture for cleaning the first printed portion and to remove a remaining uncured slice of the first printed portion. The controller may also be configured to control the second pool 104 to deposit the further light curable resin onto the cured slice of the first printed portion to form the second printed portion. The controller may also be configured to control the mask 108 to generate a second masking pattern, or to position or arrange a further mask having the second masking pattern. The controller may be further configured to control the light source 106 to irradiate the light onto the second printed portion through the second masking pattern, thereby curing at least a slice of the second printed portion, the cured slice of the second printed portion forming a second layer on the first layer. The controller may also be configured to control the third pool 110 to dispense the cleaning solution or mixture for cleaning the first printed portion and the second printed portion and to remove a remaining uncured slice of the second printed portion.

[0026] In various embodiments, the additive manufacturing system may also include one or more additional pools including the cleaning solution or mixture for cleaning the workpiece. The cleaning solution or mixture may be a liquid including water, an alcohol and/or an acid. The cleaning solution or mixture may, for instance, including ethanol, acetone and sulfuric acid. The cleaning solution or mixture may be configured to wash the substrate and/or the printed portion(s). Additionally, the cleaning solution or mixture may be further configured to remove uncured resin. In various embodiments, the first pool 102, the second pool 104, the third pool 110, and the one or more additional pools may each be a container or tank.

[0027] In various embodiments, the additive manufacturing system may including a printer including the first pool 102, the second pool 104 and the third pool 110. The printer may also include the one or more additional pools including or configured to include the cleaning solution or mixture. The printer may also include the light source 106, the mask 108 and/or the controller. The printer may also be referred to as a multi-material digital light processing three-dimensional printing (MM-DLP3DP) apparatus.

[0028] In various embodiments, the additive manufacturing system may include a plating bath for forming the metallic layer via the electroless plating process. The plating bath may be

a standalone component, or may be included in a fourth pool of the printer. In other words, the plating bath may be integrated together with the printer, or may be separate from the 3D printer.

[0029] In various embodiments, the metallic layer may include a metal or a metal alloy. For instance, the metallic layer may include nickel metal, copper metal, gold metal, cobalt metal, silver metal, platinum metal or an alloy including any combination thereof.

[0030] In various embodiments, the metallic layer may be formed on or over the first printed portion. In various embodiments, a conjunction layer may be formed between the metallic layer and the first printed portion. The conjunction layer may be formed by the interaction or diffusion between the metal or metal alloy of the metallic layer, and the active solution or mixture included in the material(s) included in the first printed portion. In various embodiments, the composite structure may be a strain gauge, a piezoelectric sensor, or an electrocardiogram (ECG) electrode.

[0031] FIG. 2 shows a general illustration of a method of forming an additive manufacturing system for forming a composite structure. The method may include, in 202, providing a first pool including or configured to include an active solution or mixture to form a first printed portion of a workpiece, the active solution or mixture including a solvent, an activation seed soluble in the solvent, and a light curable resin. The method may also include, in 204, providing a second pool including or configured to include a further light curable resin to form a second printed portion of the workpiece. The method may further include, in 206, providing a light source configured to provide light. The method may additionally include, in 208, providing or arranging a mask such that the light provided by the light source is irradiated onto the workpiece through the mask. The method may also include, in 210, providing a third pool including or configured to include a cleaning solution or mixture for cleaning the workpiece. The first printed portion including the activation seed is configured to form a metallic layer via an electroless deposition process, thereby forming the composite structure.

[0032] In other words, the method may include providing the first pool, the second pool, and the third pool as well as the mask and the light source.

[0033] For avoidance of doubt, FIG. 2 is not intended to limit the sequence of the various steps. For instance, step 202 can occur before, during, or after step 204.

[0034] In various embodiments, the method may include providing or forming a controller in electrical connection with the first pool, the second pool, the third pool, the light source, and the mask. The method may include electrically connecting the controller with the first pool, the second pool, the third pool, the light source, and the mask.

[0035] In various embodiments, the method may also include providing one or more additional pools including the cleaning solution or mixture for cleaning the workpiece.

[0036] The first pool, the second pool and the third pool may be part of a printer. The printer may also include the light source, the mask and/or the controller. The printer may also include the one or more additional pools including the cleaning solution or mixture.

[0037] In various embodiments, the method may additionally include providing a plating bath for forming the metallic layer via the electroless plating process. The plating bath may be a standalone component, or may be included in a fourth pool of the printer. In other words, the plating bath may be integrated together with the printer, or may be separate from the printer.

[0038] FIG. 3 shows a general illustration of a method of forming a composite structure according to various embodiments. The method may include, in 302, depositing an active solution or mixture to form a first printed portion of a workpiece, the active solution including a solvent, an activation seed soluble in the solvent, and a light curable resin. The method may also include, in 304, depositing a further light curable resin to form a second printed portion of the workpiece. The method may additionally include, in 306, irradiating light provided by a light source onto the workpiece through a mask. The method may also include, in 308, dispensing a cleaning solution or mixture for cleaning the workpiece. The method may further include, in 310, forming a metallic layer on the first printed portion via an electroless plating process due to the activation seed included in the first printed portion, thereby forming the composite structure.

[0039] For avoidance of doubt, FIG. 3 is not intended to limit the sequence of the various steps. For instance, step 302 can occur before, during, or after step 304.

[0040] In various embodiments, the activation seed may be a catalyst or a catalyst precursor.

[0041] In various embodiments, the light curable resin and the further light curable resin may be of a same material. In various other embodiments, the light curable resin and the further light curable resin may be of different materials.

[0042] In various embodiments, the light may be any light that is able to cure the light curable resin and the further light curable resin, e.g. ultraviolet light or visible light.

[0043] In various embodiments, the mask may be any suitable mask, such as a liquid crystal display (LCD) mask.

[0044] Various embodiments may relate to printing using the multi-material nested topology. In various embodiment, the active solution or mixture may be deposited onto a predetermined position of a substrate or an underlying layer to form the first printed portion.

The method may include generating a first masking pattern using the mask, or arranging or positioning the mask having the first masking pattern. The light may be irradiated onto the first printed portion through the first masking pattern, thereby curing at least a slice of the first printed portion. The cleaning solution or mixture may be dispensed for cleaning the first printed portion and to remove a remaining uncured slice of the first printed portion. The further light curable resin may be deposited onto another predetermined position of the substrate or the underlying layer to form the second printed portion. The method may include generating a second masking pattern using the mask, or arranging or positioning a further mask having the second masking pattern. The light may be irradiated onto the second printed portion through the second masking pattern, thereby curing at least a slice of the second printed portion. The cleaning solution or mixture may be dispensed for cleaning the second printed portion and to remove a remaining uncured slice of the second printed portion.

[0045] Various embodiments may relate to printing using the interlayer multi-material stacking topology. In various embodiments, the active solution or mixture may be deposited onto a substrate or an underlying layer to form the first printed portion. The method may include generating a first masking pattern using the mask, or arranging or positioning the mask having the first masking pattern. The light may be irradiated onto the first printed portion through the first masking pattern, thereby curing at least a slice of the first printed portion, the cured slice of the first printed portion forming a first layer. The cleaning solution or mixture may be dispensed for cleaning the first printed portion and to remove a remaining uncured slice of the first printed portion. The further light curable resin may be deposited onto the cured slice of the first printed portion to form the second printed portion. The method may also include generating a second masking pattern using the mask, or arranging or positioning a further mask having the second masking pattern. The light may be irradiated onto the second printed portion through the second masking pattern, thereby curing at least a slice of the second printed portion, the cured slice of the second printed portion forming a second layer on the first layer. The cleaning solution or mixture may be dispensed for cleaning the first printed portion and the second printed portion and to remove a remaining uncured slice of the second printed portion.

[0046] In various embodiments, the cleaning solution or mixture may include water, an alcohol and an acid.

[0047] In various embodiments, the electroless plating process may be carried out by immersing the workpiece in a plating bath.

[0048] In various embodiments, the metallic layer may include a metal or a metal alloy.

[0049] In various embodiments, the metallic layer may be formed on or over the first printed portion. In various embodiments, a conjunction layer may be formed between the metallic layer and the first printed portion. The conjunction layer may be formed by the interaction or diffusion between the metal or metal alloy of the metallic layer, and the active solution or mixture included in the material(s) included in the first printed portion.

[0050] Preparation of active precursors

[0051] As noted, the technique described herein may enable the indirect fabrication of metal-plastic composite structures via the selective three-dimensional (3D) deposition of active precursors that subsequently promote electroless plating (ELP) reactions. Precursors exhibiting high catalytic activity and positive stability were obtained by adding activation seeds to standard photocurable resins.

[0052] Light-curable resins may usually be modified by incorporating nano-powders with specific desired properties as fillers, along with dispersants that ensure the uniform distribution of these fillers. However, it has been found that the stability of modified resins prepared in this manner is low because the filler tends to eventually settle, such that the material becomes inhomogeneous. In addition, the dispersants required for different fillers can be incompatible and may degrade the physical properties of the original substrate materials. To mitigate these issues, various embodiments may make use of the ability of certain water-washable light-cured resins to form homogeneous mixtures with low concentrations (<10%) of aqueous solutions. The addition of an aqueous solution containing active seeds directly to the resin may provide a well-mixed and stable active precursor after sufficient agitation.

[0053] Palladium (Pd^{2+}) ions may provide superior catalytic activity during ELP and may often be used as activation seeds. Various embodiments as described herein may be based on the solubility of metal ions, such as Pd^{2+} ions, in aqueous solutions containing chloride (Cl^-) ions by employing an activation solution containing PdCl_2 powder and NH_4Cl . The activated precursors may be obtained by homogeneously mixing the activation solution with various resins. This method may both be simple and versatile, and may be applicable to most of the resins in which a polyurethane is the primary component.

[0054] Crystalline NH_4Cl was purchased from the FUJIFILM Wako Pure Chemical Corporation while PdCl_2 nano-powder (purity: 99.0%) was obtained from the Kanto Chemical Company, Inc. White rigid (Washable, 405 nm, ASIN: JP206000BK510.) , green transparent rigid (405 nm, ASIN: B07CQF6QNM.) , acrylic (405 nm, model: PMMA-like, ASIN: B07SKCNMZX.) , dark gray flexible (405nm, model: SK01F, ASIN:

B08T929XVW.) and light gray flexible light-cured resins (405nm, model: SK02F, ASIN: B08T929RXB.) were purchased from the Nova Robot Technology Co., Ltd., Elegoo Co., Ltd., eSun Co., Ltd., Siraya Tech Co. Ltd. and Japan SK Honpo Co., Ltd., respectively. These resins are denoted by resins #1 through 5. Each active precursor was prepared at room temperature (20 °C) by dissolving 3.7 g of NH_4Cl in 10 ml of deionized water, to which 50 mg PdCl_2 was added and dissolved with agitation. This produced 10 ml of a saturated activation solution. This solution was allowed to stand for some time, after which a 5 ml portion of the upper, clear part of the solution was removed. Subsequently, a 45 ml quantity of one of the light-cured resins was transferred into a vessel with a magnetic stirrer turning at 1000 revolutions per minute (rpm), and 5 ml of the activation solution was added dropwise. Following this addition, the mixture was stirred at 1200 rpm for a further 30 min to obtain 50 ml of an active precursor solution.

[0055] Fabrication of multi-material nested complex structures via MM-DLP3DP

[0056] Compared with direct writing 3DP (DW3DP) and fused deposition modeling 3DP (FDM3DP), DLP3DP may allow surface molding with higher resolution, so that parts with smoother surfaces, higher molding accuracy and fill rates can be obtained.

[0057] FIG. 4 is a schematic illustrating the multi-material digital light processing three-dimensional printing (MM-DLP3DP) process according to various embodiments. During this process, the 3DP of a standard resin (serving as the substrate) and of an active solution containing an active precursor may form a part having the desired 3D topology.

[0058] After cleaning and drying, the surface on which the active precursor is exposed may exhibit catalytic activity. During the subsequent ELP process, the deposition of metal particles from solution may be promoted by catalytic ions (e.g. Pd^{2+}) ions in the active precursor, and selective deposition may occur to form the desired metal pattern.

[0059] FIG. 5 shows (a) a multi-material digital light processing three-dimensional printing (MM-DLP3DP) apparatus according to various embodiments, and (b) numerical processing of multi-material models in which the slicing data are obtained by treating different material topologies in the same part as units with separate slicing according to various embodiments.

[0060] To enable the manufacturing of multi-material 3D printed parts containing both standard resin and the active precursor, an MM-DLP3DP device incorporating three stations or pools may be developed as shown in FIG. 5(a). The apparatus may include a printer platform. The printing platform may be able to select from three pools (referred to as material pool A, material pool B and the cleaning pool), and the printing platform can move in both the x and y

directions to switch between the different pools to form the work piece. By dipping into the different pools, the initial layers of the work piece may be formed adhered to or suspended from the printing platform. The material pools A, B and cleaning pool hold the standard light-cured resin, the active precursor, and cleaning solution or mixture, respectively. The partially formed work piece may be held or suspended by the printing platform using adhesion, and by continuously switching and dipping into the various pool, the remaining layers of the work piece may be formed.

[0061] The right-hand diagram in FIG. 5(a) summarizes the structural features of the printer. To ensure sufficient molding accuracy and resolution, a 2K black-and-white liquid crystal display (LCD) mask may be used to provide transmissive graphics masking. Ultraviolet (UV) light at 405 nm was passed through a mask to form light fields related to specific slice patterns, thus enabling layered curing and molding of parts. The LCD mask may be capable of moving in the x and y directions together with along the z-axis of the printer.

[0062] The entire 3D printed workpiece may be moved as one piece, thus enabling material switching and ensuring that different material topologies in the same part had precise interpositional relationships. Acquiring digital model data for the multi-material part may be an critical initial step, even though there are currently no mature multi-material slicing software programs that enable the labeling of material properties in conjunction with specific and complex topologies. In various embodiments, this issue may be addressed by using a modeling-assembly-disassembly-slicing method to assist in the numerical processing of multi-material models (FIG. 5(b)). In this process, topologies having the same physical properties may be created as a single unit and then converted to the standard template library (STL) format. The slicing software assembled units with different properties according to the desired topological relationships, following which these parts may be sliced separately to obtain the respective slice data. As the different parts had defined positional relationships in the part coordinate system, the slice data for the different materials may incorporate the required topological relationships. Various embodiments may use specially developed control software for slice data processing, the setting of printing parameters and the control of the MM-DLP3DP system. The manufacturing of multi-material parts with 3D active precursors may be made possible by performing a series of cycles in which material A was applied, followed by cleaning, followed by the application of material B.

[0063] FIG. 6 is a schematic showing an arbitrary complex multi-material model and the printing process of printing the model according to various embodiments. As shown in FIG. 6,

each multi-material part having an arbitrarily complex structure, regardless of its structural characteristics, may be analyzed in terms of the different material topologies. This analysis may involve both the interlayer multi-material stacking topology and multi-material nested topology. In the case of the former, the various materials may be nestled between layers, thus eliminating the need for the printer to perform a cleaning and material switching process at each slice. However, when processing the latter topology, the printer had to cycle through printing of material A, printing of material B and a cleaning process for each slice. Since all materials used in the part had the topological characteristics described above, various embodiments may allow the fabrication of various complex parts, although it should be noted that the fabrication of certain components required the assistance of support structures. The multi-material model of an arbitrary complex structure may be divided into interlayer multi-material stacking and multi-material nested topologies according to the desired distributions of the material topologies.

[0064] Selective 3D metallization using ELP

[0065] During processing, the printed part may be firmly adhered to the printing platform and so, because the platform was made of metal, a small amount of metal residue may remain on the base of the part after it was removed. This residue may promote the precipitation of nickel (Ni) and so degrade the accuracy of subsequent selective ELP and interrupt the metal distribution pattern. In addition, uncured resin remaining on the surface of the part could obscure Pd^{2+} ions inside the resin and so affect the catalytic activity of the active precursor during plating. For these reasons, it was vital to clean parts after the 3DP. In various embodiments, the cleaning solution may be composed of 40 % ethanol (analysis pure), 50 % acetone (analysis pure) and 10 % dilute sulfuric acid (40 wt %) in volume. The alcohol and acetone in this mixture may dissolve any uncured resin on the part surface (both the standard resin substrate and the active precursor) while the sulfuric acid may remove residual metal powder adhering to the bottom of the part.

[0066] Unlike the ELP processes used in other studies, various embodiments may not require the cleaned finished parts to be roughened or sensitized. Consequently, the cleaned and dried parts may be directly immersed in the plating bath.

[0067] The Ni plating bath employed in this process may have the primary components summarized in Table 1.

Table 1 Electroless Ni plating bath composition and operating conditions

Component	Concentration [mmol/L]
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NiSO ₄ ·6H ₂ O	60
NaH ₂ PO ₂ ·H ₂ O	240
C ₆ H ₅ Na ₃ O ₇ ·2H ₂ O	200
H ₃ BO ₃	500
H ₂ SO ₄	pH adjustment
NaOH	
pH	9.0
Temperature	70 °C

[0068] The plating bath may have a pH of 9 and may be held at 70 °C. Within each printed multi-material part, the active precursor (in which Pd²⁺ ions were homogeneously dispersed) may be distributed on the resin substrate in a specific 3D topology. Upon immersion of the part in the bath, the exposed Pd²⁺ ions on the surface may initially be reduced to Pd monomers that served as catalytically active metal nuclei to initiate the ELP reaction in specific microscopic regions, and so achieve targeted Ni metal deposition.

[0069] The reactions may be illustrated by Equations (1) – (4) below:



[0070] The reactions shown in equations (1)-(4) may include the mechanism by which the reactive precursor catalyze the directed deposition of Ni metal. In this process, hypophosphite may be oxidized in solution to generate adsorbed hydrogen atoms on the surface of the substrate. Immediately afterwards, these hydrogen atoms may reduce Ni ions in the solution. As hydrogen atoms are adsorbed on the substrate surface, the reduced Ni may naturally be deposited on the same surface after 5-10 min to form a coating. In addition, since Pd²⁺ ions are embedded on the surface of the active precursor portions of the part, there may be no overflow or deviated deposition of the plating layer due to migration of the catalyst during the ELP process. As the time-consuming pretreatment of the part surfaces is not required, the original surface morphology may be maintained and so a more accurate plating pattern can be obtained.

[0071] Properties of reactive precursors combined with commercial photocured resins

[0072] After modification, resin #1 changed from its original white color to a light yellow. The uniform distribution of this coloration indicated that Pd²⁺ ions were homogeneously dispersed throughout the material. Similarly, the #5 resin changed from gray to yellow gray. After three days of standing, neither material exhibited precipitation, indicating the high stability of these precursors.

[0073] FIG. 7 shows (a) a plot of absorption as a function of wavelength (in nanometres or nm) showing the ultraviolet spectra of a rigid light-cured resin before and after modification with palladium (Pd^{2+}) ions according to various embodiments; and (b) a plot of absorption as a function of wavelength (in nanometres or nm) showing the ultraviolet spectra of a flexible light-cured resin before and after modification with palladium (Pd^{2+}) ions according to various embodiments.

[0074] FIG. 7(a) shows the UV absorption spectra obtained from the #1 resin before and after modification. Both spectra are basically about equivalent with peak absorbance at approximately 405 nm. These results may demonstrate that the addition of the Pd^{2+} solution does not change the basic properties of the resin, especially the molding properties, and does not decrease the light sensitivity of the original resin. Similar results were obtained from the analysis of the #4 resin before and after it was modified, as shown in FIG. 7(b).

[0075] Complex 3D metal-plastic composite structures

[0076] Circuit boards are traditionally made from flat modules or a combination of multiple flat modules such that the processing surfaces are 2D planes or combinations of such planes. These structures are relatively simple and so the manufacturing process is not complex but has limited applications. The demands for more structurally complex parts with regular cylindrical or freeform processing surfaces requires improved manufacturing capabilities. To illustrate the fabrication capabilities of our new approach, metal-plastic composite parts having representative structures were fabricated and then processed via ELP. Compared with multi-material 3DP using multiple nozzles, the technique demonstrated herein may provide higher resolution, and may thus allow the construction of micro-structured surfaces with special functions. This may be important because metallized micro-structured surfaces have numerous potential applications.

[0077] FIG. 8 shows (a) three micro-structured metallized surfaces each with a thickness of 200 μm : circular with a radius of 200 μm , ortho-hexagonal with an inner circle radius of 200 μm , and circular groove with a groove width of 400 μm using the process according to various embodiments; (b) a skeletonized ball structure with a circular base that has been covered with Ni metal using the process according to various embodiments; (c) an Eiffel Tower with a microfine structure in which selected parts have been uniformly covered with nickel (Ni) plating using the process according to various embodiments; (d) a five-sided structure with a complex nickel (Ni) metal distribution and multi-material nesting between layers and within layers using the process according to various embodiments; (e) a dome structure with an arc-

shaped metal distribution using the process according to various embodiments; (f) a U-shaped tube with an internal metal mesh having a thickness of 1 mm and square hexagons each with a 500 μm inner diameter using the process according to various embodiments, demonstrating the construction and metallization of a small structure within the resin; (g) a double-layer 3D hollow nesting part, a large ball (radius 15 mm.) with triangular hollow holes wrapping a small ball (radius 8 mm) with regular hexagon hollow holes and selectively deposited with nickel (Ni) using the process according to various embodiments; (h) a flexible carbon nanotube structure with selective three dimensional (3D) metallization using the process according to various embodiments, showing a lack of fracture after deformation; and (i) a wearable structure with a complex shape and nickel (Ni) plating that remains tightly bonded to the flexible substrate after deformation formed by the process according to various embodiments. The micro-sized hollow or complex heterogeneous structures as shown in FIG. 8 may be as small as 400 μm , confirming the precision manufacturing that is possible utilizing this method.

[0078] FIG. 8(a) shows three different surface structures constructed on circular substrates. These include a circular microstructure with a radius of 200 μm , an ortho-hexagonal microstructure with an inner circle radius of 200 μm and a circumferential groove microstructure with a groove width of 400 μm . After printing and cleaning, these microstructures could be clearly seen under a high magnification microscope. After plating, metallic Ni uniformly covered the microstructure surface and a 3D profile consistent with the active precursor was obtained.

[0079] FIG. 8(b) shows metal skeleton ball structure with a circular base has also been fabricated using this process. This microfine structure may be interconnected in an irregular manner and, after plating, the skeleton may be covered with Ni metal. The structure was evenly plated inside and outside and had a metallic luster with no under-plating or missing plating.

[0080] FIG. 8(c) shows a 3D printed Eiffel Tower model with the tip and middle part made of the active precursor material, and the rest made of standard resin. After plating, Ni metal was precisely deposited on both the tip and central surface of the tower. The original hollow microstructure remained intact and that the interior and exterior of the hollow structure in the middle of the tower were covered with Ni metal having a metallic luster. The manufacturing of these multi-material nested parts may demonstrate the capabilities of the MM-DLP3DP as described herein.

[0081] Additionally, FIG. 8(d) shows a multi-material five-sided part with a specific metal topology distributed on four faces. This structure is highly complex, with the metal portions

and the resin substrate nested within one another such that there are both interlayer and intralayer nesting. Despite this complexity, clear boundaries are evident between these portions of the part, confirming that precise selective metallization was achieved. There was a uniform plating distribution and no spillage or contamination of the Ni plating.

[0082] FIG. 8(e) shows a dome structure with six curved metal bands evenly distributed around its surface, while FIG. 8(f) shows a U-tube part having an internal hexagonal mesh made of Ni. The U-tube part with internal mesh structure shown in FIG. 8(f) is particularly difficult to fabricate by most other manufacturing technologies. This highly complex part could not be fabricated by conventional methods using laser etching or 3DP, but was obtainable based on slicing and material switching that permitted deposition of the active precursor inside the U-tube. During the ELP process, the plating solution was able to flow into the tubular part to form the mesh in the cavity via the deposition of Ni. The right-hand side of this figure indicates the intricate structure of the metal mesh after removal from the part. The mesh had a thickness of 1 mm and contained hexagonal holes each with an inner diameter of 500 μm .

[0083] Furthermore, FIG. 8(g) shows a double-layer 3D hollow part in which the large ball (radius 15 mm) with triangular hollow holes wrapped around the small ball (radius 8 mm) with regular hexagon hollow holes. In this part, the plating solution enters through the holes of the outer large ball, so that the selective Ni deposition of the inner small ball can be successfully achieved. The enlarged image (right of FIG. 8(g)) shows the metallic luster of the inner ball and illustrates a good Ni coating. These two parts demonstrate the possibility of manufacturing items with complex internal metal structures, thus broadening the potential applications of this technology.

[0084] Various embodiments may also be used to manufacture flexible 3D electronics. The present surface molding 3DP process maintains the manufacturing success rate of flexible parts, as no support is required to obtain the desired flexible structure. FIG. 8(h) demonstrates a flexible carbon nanotube structure, the central part of which was selectively applied using ELP. The high-resolution image shows the junction between the metal and resin in this item. The metal plating was evidently uniformly distributed and the boundaries between the different materials are well defined, indicating the effective formation of a flexible metal-plastic composite structure using this method. After being stressed, the Ni metal plating remained intact and did not break. FIG. 8(i) shows a flexible wearable hoop-shaped structure. The enlargement demonstrates the precise deposition of the metal plating on the surface of the knotted part. This item was found to be highly flexible, and the metal structure did not break

in response to bending deformation. In addition to the above parts, various 3D stereoscopic circuits to replace conventional PCB circuits were designed and fabricated, thus illustrating the potential of the process as described herein for application in the field of 3D micro-nano electronics.

[0085] FIG. 9 shows (a) an light emitting diode (LED) stereo circuit with complex nickel (Ni) metal wire topology using the process according to various embodiments; (b) a double-layer three-dimensional (3D) circuit structure with a complex three-dimensional (3D) copper wire structure using the process according to various embodiments, and which is difficult to fabricate by traditional processes; and (c) a plot of impedance (in ohms or Ω) as a function of frequency as a function of frequency (in hertz or Hz) showing the impedance of nickel (Ni) and copper (Cu) coatings formed using the process according to various embodiments.

[0086] FIG. 9(a) shows diagrams and a photographic image of a light-emitting diode (LED) circuit with an irregular 3D structure. The circuit board model in the figure shows that the substrate had an irregular surface profile while the wires had a complex 3D alignment. After printing, soldering, and powering up at 3.3 V, the LED was found to function with a normal level of brightness. This result confirmed that the metal wire structure distributed on the substrate was suitably conductive. FIG. 9(b) shows a double-layer 3D circuit with a through-hole structure in which the width of the conductor was 800 μm . The diameter of the through hole was 500 μm and the inner wall was covered with copper (Cu) metal that connected the inner and outer layers of the circuit. This circuit had a complicated 3D wire distribution that reduced the size of the device compared with a standard circuit and increased the electron transmission efficiency. These improvements may be expected to increase the extent of integration in 3D electronic devices, and may have numerous practical applications. FIG. 9(c) shows a plot summarizing the impedance characteristics of Cu and Ni plating obtained using the process as described herein and may confirm that the resulting 3D metal wires exhibited electrical conductivity that meets the requirements for use in electronic devices.

[0087] Sample parts with very small components were also designed and manufactured to examine the accuracy and resolution achievable via selective metallization. FIG. 10 shows (a) nickel (Ni)-plated structures with widths of 1 mm, 500 μm and 100 μm and with widths of 50 and 40 μm formed by the process according to various embodiments; and (b) a circuit board part having a width of 1 mm incorporating 500 μm copper wires formed by the process according to various embodiments. FIG 10(a) shows images of Ni wires having widths of 1 mm, 500 μm , 100 μm , 50 μm , and 40 μm . High-magnification microscopy showed that the Ni

was precisely distributed on these active precursor wires, thus showing exceptional resolution of the printing method and the effectiveness of selective metal deposition. The Cu plating on the circuit board shown in FIG. 10(b) shows that various embodiments may provide a manufacturing resolution of at least 40 μm , which is sufficient to meet the processing requirements of most electronic products.

[0088] Microscopic characterization of 3D selective metal topologies

[0089] The effectiveness of ELP induced by active precursors and the quality of the resulting plating was assessed by fabricating samples having dimensions of 20 mm (length) $\times$ 10 mm (width) $\times$ 5 mm (height). These specimens had planar, circular, ortho-hexagonal, and annular grooved micro-nano structures with metallic coatings.

[0090] FIG. 11 shows (a) a standard flat nickel (Ni) plating according to various embodiments; (b) and (c) scanning electron microscopy (SEM) images of the indicated area in (a) with different magnifications according to various embodiments; (d) a nickel (Ni) plating on the surface of a circular microstructure according to various embodiments; (e) and (f) scanning electron microscopy (SEM) images of the indicated area in (d) with different magnifications according to various embodiments; (g) a nickel (Ni) plating on the surface of an annular groove microstructure according to various embodiments; (h) and (i) scanning electron microscopy (SEM) images of the indicated area in (g) with different magnifications according to various embodiments; (j) a nickel (Ni) plating on the surface of an ortho-hexagonal microstructure according to various embodiments; (k) – (l) scanning electron microscopy (SEM) images of the indicated area in (j) with different magnifications according to various embodiments; (m) a flexible sample with nickel (Ni) plating; and (n) – (o) scanning electron microscopy (SEM) images of the indicated area in (m) with different magnifications according to various embodiments.

[0091] FIGS. 11(a) – (c) present microscopic characterization results for a planar sample after a 5 min plating process. The sample was uniformly covered with Ni and a metallic luster can be observed in the low-magnification light microscope image (right side of the FIG. 11 (a)). SEM images acquired with a 100 μm scale bar show the surface profile of the Ni layer, which is flat in most places, in agreement with the planar profile of the active precursor. Some minor protrusions are evident due to the accumulation of Ni metal caused by high local Pd^{2+} concentrations. Higher magnification shows that the Ni metal particles were closely packed together with a more even distribution of crystals and less discontinuity. FIGS. 11(d) – (f)

present images of the specimen obtained after a 6 min plating of a circular surface having a radius of 200 μm and a depth of 200 μm .

[0092] FIGS. 11(g) – (i) show the plating on the surface of an annular groove with a width of 200 μm and a depth of 200 μm , while FIGS. 11(j) – (l) show images of a plated hexagonal microstructure having an inner radius of 200 μm and a depth of 200 μm . All three-parts exhibit complete and uniform plating with a metallic luster. The SEM images with a 100 μm scale bar demonstrate that the Ni metal particles all grew along the surface profile in a uniform manner. The plating did not make the original surface structure unclear due to uneven thickness, again demonstrating the uniformity of the plating. SEM images with the 500 nm scale bar clearly demonstrate the morphology and distribution of the Ni metal particles. The distribution of Ni crystals on the surfaces of these microstructure samples was more disordered than on the planar specimens but was still compact. In the active precursor regions, Pd^{2+} ions were embedded in the cured resin, but the bonding interactions between the molecules in flexible resin were not as strong in these resins compared with the rigid resins after curing. Therefore, the Pd^{2+} ions in the flexible active precursors precipitated more easily during plating such that shorter plating times were required. FIGS. 11(m)-(o) show the results for 3 min Ni plating of a flexible active precursor specimen. The resulting metalized microstructure not only increased the functionality of the part but also strengthened the bond between the plating and the substrate. Tape tests showed that Ni metal on microstructure surfaces exhibited a higher bonding force compared with metal on flat surfaces, as a consequence of the higher roughness associated with the microstructures. Compared with the rigid samples, the flexible samples showed more consistent plating with higher integrity, and with 100 μm scale bar SEM observations indicated that the latter had much rougher surfaces. This phenomenon was attributed to corrosion of the flexible surface by the acidic component of the plating solution. Corrosion is also evident in the 500 nm scale bar SEM images, which show a significant increase in the number of Ni metal particles in the same area, with continuous and tight clusters of crystals. This occurred because more Pd^{2+} ions were exposed when the sample was inadvertently roughened.

[0093] Various embodiments may involve incorporating catalytic seeds into standard resins, which allow metal layers with higher confinement and bonding strength to be obtained. Ni-plated samples were processed using a focused ion beam to obtain cross sections allowing better examination of the microstructures at the metal-resin junctions. Analyses by transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were subsequently performed. FIG. 12 shows (a) a cross-sectional transmission electron

microscopy (TEM) image indicating the resin layer, the conjunction layer, and the nickel layer of the composite structure according to various embodiments; (b) an energy-dispersive X-ray spectroscopy (EDS) image showing the distribution of iron according to various embodiments; (c) an energy-dispersive X-ray spectroscopy (EDS) image showing the distribution of palladium according to various embodiments; and (d) an energy-dispersive X-ray spectroscopy (EDS) image showing the distribution of nickel according to various embodiments.

[0094] FIG. 12(a) presents a TEM image acquired at the boundary between the resin and the Ni metal layer. The cross section shows the Ni metal, conjunction, and resin layers after plating. FIG. 12(b) indicates the distribution of carbon along the cross section containing the resin boundary. Carbon was more abundant in the resin layer and significantly less abundant in the intermediate layer, such that the partition between these two phases is highly consistent with the image shown in FIG. 12(a). This result supports the existence of a conjunction layer. During the ELP process, the sodium hypophosphite in the plating solution reduced Pd^{2+} ions to Pd particles that were attached to the surface. The Pd in the interlayer catalyzed the deposition of Ni such that the Ni metal migrated into the resin to generate an interlayer of Ni embedded in the material. This effect improved the adhesion of the Ni plating.

[0095] 3D printed metal-plastic composite parts for electronic devices

[0096] Various embodiments may relate to combining non-metallic materials having different functions with specific metal patterns to generate metal-plastic composite parts.

[0097] 3D printed strain gauge

[0098] A metal-based resistance strain gauge works on the principle of the resistance strain effect. Specifically, when a Cu wire is subjected to stress, its resistance will change in proportion to the degree of stretching or compression. In conventional strain gauges, a resistive measurement grid is usually laminated between a carrier and cover film, and this foil strain gauge is bonded using an adhesive to the component being assessed. Strain in the component is transferred to the measurement grid via two intermediate layers. In principle, the measurement grid should be placed as close as possible to the component surface in order to avoid force transmission losses. In such devices, variations in bonding thickness will be reflected in the degree of force transmission, meaning that the response of the strain gauge may change.

[0099] Various embodiments may relate to printing a strain gauge on an object to be measured. Various embodiments may allow strain gauges to be printed inside complex parts. This may not only ensure consistent mechanical deformation between the strain gauge and the

measured object, but may also enable the design and manufacture of specific strain gauges that match the actual 3D shape of the object. FIG. 13 shows (a) a schematic of a three-dimensional (3D) printed integrated strain gauge according to various embodiments on the measured object; (b) images of the strain gauge according to various embodiments and a schematic on the measurement of the strain gauge according to various embodiments; (c) an image showing the bending deformation of the gauge under stress according to various embodiments; (d) a plot of voltage (in volts or V) as a function of load (in grams or g) showing the voltage measurement characteristics of the strain gauge according to various embodiments; (e) a plot of strain as a function of load (in grams or g) showing the strain characteristics of the strain gauge according to various embodiments calculated from experiment data; and (f) a plot of deformation (in millimetres or mm) as a function of load (in grams or g) showing the experimental deformation data of the strain gauge according to various embodiments.

[00100] FIG. 13(a) shows a strain gauge according to various embodiments that is integrated with the measured object. The overall part is a cuboid with openings, and the strain gauge is in the interior of the base. Electrical signals generated when the internal strain gauge is deformed are extracted via a hole in the device. FIG. 13(b) presents images indicating the structure of the internal strain gauge. Using a 3D printing and copper (Cu) plating process, metal electrodes having a pitch and width of 500 μm may be formed. When the strain gauge was bent and deformed as the object being tested was subjected to force, the overall length of the through-electrode changed and so its resistance was varied. By measuring the change in voltage, the strain and thus the amount of deformation could be calculated. FIG. 13(c) provides a photographic image of the strain gauge after it has been deformed. As an acrylic-type UV resin was used, the strain gauge was highly flexible and so did not break when bent. FIG. 13(d) plots the voltage generated by the strain gauge as a function of the load, as obtained using a star-shaped circuit. FIGS. 13(e) – (f) summarize the calculated strain and deformation values, respectively. When the load is 10 g, the strain value of the sensor obtained through the experiment is 0.003. This data is basically consistent with the result of the simulation calculation (the upper left corner of FIG. 13(e)), which verifies the effectiveness of the sensor. This device may therefore be used to perform strain measurements when correcting for variations in temperature and material properties.

[00101] 3D printed piezoelectric sensor

[00102] Various embodiments may allow the construction of metal wires on the surfaces of various functional materials. In various embodiments, the polymer polyvinylidene fluoride-

trifluoroethylene (PVDF-TrFE) may be added to an elastic light-cured resin to produce a material with piezoelectric properties that could also be used as the active precursor. FIG. 14 shows (a) schematics illustrating the operation principles of a three-dimensional (3D) printed piezoelectric sensor according to various embodiments; (b) images showing the piezoelectric sensor according to various embodiments being bent at bending angles 30° , 60° , 90° and 120° ; (c) a plot of voltage (in volts or V) as a function of time (in seconds or s) showing the voltage waveforms generated by the piezoelectric sensor according to various embodiments at 30° , 60° , 90° and 120° ; and (d) a plot of voltage (in volts or V) as a function of deformation (in nanometers or nm) showing the voltage generated by the piezoelectric sensor according to various embodiments in tension as a function of deformation. The 3D printed piezoelectric sensor includes a thin film substrate made of a piezoelectric material and comb electrodes. When this type of sensor is subjected to an external force along its sensitive axis, electric charges of opposite polarity are generated on the two adjacent electrodes, corresponding to an electric charge source (that is, an electrostatic generator). The piezoelectric effect allows the device to sense deformation and thus can be used to measure deformation, strain, angular changes, and other variables. FIG. 14(b) provides photographic images showing the device being bent at various angles, while the resulting voltage values are presented in the oscilloscope trace in FIG. 14(c). FIG. 14(d) shows a plot indicating the piezoelectric effect for the sensor in the stretched state. As the amount of deformation was increased (that is, the length of the central axis of the upper surface increased), the voltage generated via the piezoelectric effect also increased. This voltage was directly correlated with specific variables and could provide accurate measurements with the support of additional filtering and amplifier circuits. Using this principle, accurate measurement of certain physical quantities may be achieved. Compared with conventional piezoelectric sensors, piezoelectric sensors made by 3DP may require a less complex manufacturing process that can be integrated with that for the object being examined to permit a wider range of applications.

[00103] Wearable 3D printed flexible ECG electrodes

[00104] An electrocardiogram (ECG) may provide information regarding the electrical activity of the heart and is widely used for the diagnosis and analysis of many diseases. Typically, a complete ECG measurement system is primarily made of electrodes, digital processing circuits and data analysis terminals. Among these, the electrodes may be the key components that affect the quality of the electrical signals received from the heart. Various embodiments may relate to forming a wearable flexible 3D printed ECG electrode.

[00105] FIG. 15 shows (a) a schematic showing a measurement system including three-dimensional (3D) electrocardiogram (ECG) electrodes formed according to various embodiments; (b) images showing the device components of the system including the electrodes formed according to various embodiments; (c) a plot showing five electrocardiogram (ECG) signals measured by the electrodes formed according to various embodiments based on random measurements of a subject at rest; and (d) a plot showing electrocardiogram (ECG) signals measured by the electrodes formed according to various embodiments based on measurements when the subject is swing an arm, clicking a computer mouse, and writing.

[00106] The measurement system shown in FIG. 15(a) may use a dual-lead measurement method in which the host ECG electrode and vice ECG electrode may be worn on the right and left wrists of the subject, respectively. The electrodes may acquire the ECG signal and send the acquired signal to a computer via a Bluetooth module attached to the host ECG, and the computer may in turn process and display the signal. FIG. 15(b) shows images of the 3D printed strap-like wearable device having a specially patterned metal electrode, a circuit for connecting with a portable battery, and the Bluetooth module. This configuration eliminated measurement errors and inconvenience caused by wires and made it easier to measure ECG signals while the subject was in motion. FIG. 15(c) shows plots of five different ECG signals obtained with the proposed ECG electrode with the subject in the resting state. The five plots essentially overlap and that the waveforms reflected the expected ECG waveforms of a normal human heart. FIG. 15(d) shows the measurement signals obtained with the ECG electrode during writing, swinging of one arm and clicking of a computer mouse. Compared with a conventional ECG, the electrode may offer an easier measurement process together with efficient output of the resulting data.

[00107] Various embodiments may relate to an approach to construct precise metal patterns on the surfaces or interiors of 3D plastic parts with arbitrary complex shapes, along with potential applications. By modifying standard resins, active precursors that were able to promote the ELP process may be prepared. Various embodiments may relate to an MM-DLP3DP apparatus to permit the fabrication of micro-nano 3D metal-plastic component structures. The method according to various embodiments had been employed to fabricate various parts as a demonstration of manufacturing capability. These parts were primarily multi-material and involved nesting layers, including microporous and small hollow structures with the smallest size being 40 μm . A 3D circuit with a double-sided structure connected by a

through hole was manufactured to illustrate the manufacturing capabilities of the proposed technology. Further, a series of sensors operating on different principles (a 3D printed strain gauge, 3D printed piezoelectric sensor and wearable 3D printed flexible ECG electrodes) were fabricated to illustrate the superiority of this technique. Compared with conventional processes, various embodiments may allow integrated manufacturing of the sensor and the object, thus avoiding measurement errors and complex processes caused by assembly. As more specialized light-cured resins (such as acrylonitrile-butadiene-styrene, acrylic and silicon materials) become available, it may be possible to fabricate 3D structures with unique properties. In addition, a variety of metals (including Ni, Co, Cu, Au, Ag and Pt) may potentially be deposited in targeted patterns by means of active precursor-induced plating. This process may enable the 3D nesting of a variety of composites and thus has promising applications, especially in micro-electromechanical systems (MEMS), sensors and robotics, wearable devices, and 3D precision electronics.

[00108] 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. An additive manufacturing system for forming a composite structure, the additive manufacturing system comprising:
 - a first pool comprising an active solution to form a first printed portion of a workpiece, the active solution comprising a solvent, an activation seed soluble in the solvent, and a light curable resin;
 - a second pool comprising a further light curable resin to form a second printed portion of the workpiece;
 - a light source configured to provide light;
 - a mask configured to be arranged such that the light provided by the light source is irradiated onto the workpiece through the mask; and
 - a third pool comprising a cleaning solution for cleaning the workpiece;wherein the first printed portion comprising the activation seed is configured to form a metallic layer via an electroless deposition process, thereby forming the composite structure.
2. The additive manufacturing system according to claim 1,
 - wherein the activation seed is a catalyst or a catalyst precursor.
3. The additive manufacturing system according to claim 1,
 - wherein the activation seed is palladium metal, silver metal, palladium ion or silver ion.
4. The additive manufacturing system according to any one of claims 1 to 3,
 - wherein the light curable resin and the further light curable resin are of a same material.
5. The additive manufacturing system according to any one of claims 1 to 3,
 - wherein the light curable resin and the further light curable resin are of different materials.
6. The additive manufacturing system according to any one of claims 1 to 5,

wherein the light is ultraviolet light or visible light.

7. The additive manufacturing system according to any one of claims 1 to 6,
wherein the mask is a liquid crystal display (LCD) mask.
8. The additive manufacturing system according to any one of claims 1 to 7, further comprising:
a controller in electrical connection with the first pool, the second pool, the third pool, the light source, and the mask.
9. The additive manufacturing system according to claim 8,
wherein the controller is configured to control the first pool to deposit the active solution onto a predetermined position of a substrate or an underlying layer to form the first printed portion;
wherein the controller is configured to control the mask to generate a first masking pattern;
wherein the controller is further configured to control the light source to irradiate the light onto the first printed portion through the first masking pattern, thereby curing at least a slice of the first printed portion;
wherein the controller is further configured to control the third pool to dispense the cleaning solution for cleaning the first printed portion and to remove a remaining uncured slice of the first printed portion;
wherein the controller is also configured to control the second pool to deposit the further light curable resin onto another predetermined position of the substrate or the underlying layer to form the second printed portion;
wherein the controller is also configured to control the mask to generate a second masking pattern;
wherein the controller is also configured to control the light source to irradiate the light onto the second printed portion through the second masking pattern, thereby curing at least a slice of the second printed portion; and
wherein the controller is further configured to control the third pool to dispense the cleaning solution for cleaning the second printed portion and to remove a remaining uncured slice of the second printed portion.

10. The additive manufacturing system according to claim 8,
- wherein the controller is configured to control the first pool to deposit the active solution onto a substrate or an underlying layer to form the first printed portion;
 - wherein the controller is configured to control the mask to generate a first masking pattern;
 - wherein the controller is further configured to control the light source to irradiate the light onto the first printed portion through the first masking pattern, thereby curing at least a slice of the first printed portion, the cured slice of the first printed portion forming a first layer;
 - wherein the controller is further configured to control the third pool to dispense the cleaning solution for cleaning the first printed portion and to remove a remaining uncured slice of the first printed portion;
 - wherein the controller is also configured to control the second pool to deposit the further light curable resin onto the cured slice of the first printed portion to form the second printed portion;
 - wherein the controller is also configured to control the mask to generate a second masking pattern;
 - wherein the controller is further configured to control the light source to irradiate the light onto the second printed portion through the second masking pattern, thereby curing at least a slice of the second printed portion, the cured slice of the second printed portion forming a second layer on the first layer;
 - and
 - wherein the controller is also configured to control the third pool to dispense the cleaning solution for cleaning the first printed portion and the second printed portion and to remove a remaining uncured slice of the second printed portion.
11. The additive manufacturing system according to any one of claims 1 to 10, further comprising:
- one or more additional pools comprising the cleaning solution for cleaning the workpiece.

12. The additive manufacturing system according to any one of claims 1 to 11,
wherein the cleaning solution is a liquid.
13. The additive manufacturing system according to any one of claims 1 to 12,
wherein the cleaning solution comprises water, an alcohol and an acid.
14. The additive manufacturing system according to any one of claims 1 to 13, further
comprising:
a plating bath for forming the metallic layer via the electroless plating process.
15. The additive manufacturing system according claim 14,
wherein the plating bath is a standalone component, or a fourth pool of a
printer comprising the first pool, the second pool and the third pool.
16. The additive manufacturing system according to any one of claims 1 to 15,
wherein the metallic layer comprises a metal or a metal alloy.
17. The additive manufacturing system according to any one of claims 1 to 16,
wherein the metallic layer comprises nickel metal, copper metal, gold metal,
or an alloy comprising any combination thereof.
18. A method of forming an additive manufacturing system for forming a composite
structure, the method comprising:
providing a first pool comprising an active solution to form a first printed
portion of a workpiece, the active solution comprising a solvent, an activation
seed soluble in the solvent, and a light curable resin;
providing a second pool comprising a further light curable resin to form a
second printed portion of the workpiece;
providing a light source configured to provide light;
arranging a mask such that the light provided by the light source is irradiated
onto the workpiece through the mask; and

providing a third pool comprising a cleaning solution for cleaning the workpiece;

wherein the first printed portion comprising the activation seed is configured to form a metallic layer via an electroless deposition process, thereby forming the composite structure.

19. A method of forming a composite structure, the method comprising:
 - depositing an active solution to form a first printed portion of a workpiece, the active solution comprising a solvent, an activation seed soluble in the solvent, and a light curable resin;
 - depositing a further light curable resin to form a second printed portion of the workpiece;
 - irradiating light provided by a light source onto the workpiece through a mask;
 - dispensing a cleaning solution for cleaning the workpiece; and
 - forming a metallic layer on the first printed portion via an electroless plating process due to the activation seed comprised in the first printed portion, thereby forming the composite structure.
20. The method according to claim 19,
 - wherein the activation seed is a catalyst or a catalyst precursor.
21. The method according to claim 19 or claim 20,
 - wherein the light curable resin and the further light curable resin are of a same material.
22. The method according to claim 19 or claim 20,
 - wherein the light curable resin and the further light curable resin are of different materials.
23. The method according to any one of claims 19 to 22,
 - wherein the light is ultraviolet light or visible light.
24. The method according to any one of claims 19 to 23,

wherein the mask is a liquid crystal display (LCD) mask.

25. The method according to any one of claims 19 to 24,

wherein the active solution is deposited onto a predetermined position of a substrate or an underlying layer to form the first printed portion;

wherein the method comprises generating a first masking pattern using the mask;

wherein the light is irradiated onto the first printed portion through the first masking pattern, thereby curing at least a slice of the first printed portion;

wherein the cleaning solution is dispensed for cleaning the first printed portion and to remove a remaining uncured slice of the first printed portion;

wherein the further light curable resin is deposited onto another predetermined position of the substrate or the underlying layer to form the second printed portion;

wherein the method comprises generating a second masking pattern using the mask;

wherein the light is irradiated onto the second printed portion through the second masking pattern, thereby curing at least a slice of the second printed portion; and

wherein the cleaning solution is dispensed for cleaning the second printed portion and to remove a remaining uncured slice of the second printed portion.

26. The method according to any one of claims 19 to 24,

wherein the active solution is deposited onto a substrate or an underlying layer to form the first printed portion;

wherein the method comprises generating a first masking pattern using the mask;

wherein the light is irradiated onto the first printed portion through the first masking pattern, thereby curing at least a slice of the first printed portion, the cured slice of the first printed portion forming a first layer;

wherein the cleaning solution is dispensed for cleaning the first printed portion and to remove a remaining uncured slice of the first printed portion;

wherein the further light curable resin is deposited onto the cured slice of the first printed portion to form the second printed portion;
wherein the method comprises generating a second masking pattern using the mask;
wherein the light is irradiated onto the second printed portion through the second masking pattern, thereby curing at least a slice of the second printed portion, the cured slice of the second printed portion forming a second layer on the first layer; and
wherein the cleaning solution is dispensed for cleaning the first printed portion and the second printed portion and to remove a remaining uncured slice of the second printed portion.

27. The method according to any one of claims 19 to 26,
wherein the cleaning solution comprises water, an alcohol and an acid.
28. The method according to any one of claims 19 to 27, further comprising:
wherein the electroless plating process is carried out by immersing the workpiece in a plating bath.
29. The method according to any one of claims 19 to 28,
wherein the metallic layer comprises a metal or a metal alloy.