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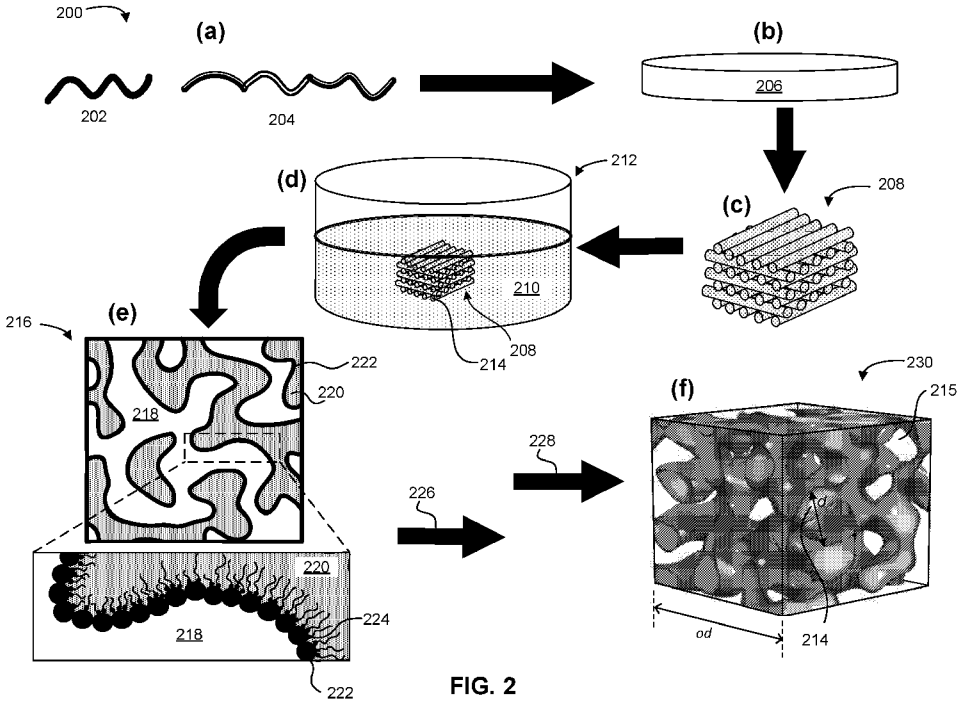

FIG. 2

(57) Abstract: An ink includes a polymer precursor, a copolymer, a catalyst, and a solvent. A product includes a three-dimensional printed structure having ligaments, where an average diameter of the ligaments is in a range of about 10 microns to about 500 microns.

[Continued on next page]

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ADDITIVE MANUFACTURE OF HIERARCHICALLY POROUS MATERIALS WITH HIGH RESOLUTION

[0001] The United States Government has rights in this invention pursuant to Contract No. DE-AC52-07NA27344 between the United States Department of Energy and Lawrence Livermore National Security, LLC for the operation of Lawrence Livermore National Laboratory.

FIELD OF THE INVENTION

[0002] The present invention relates to additive manufacturing of hierarchically porous materials, and more particularly, this invention relates to an ink system for additive manufacturing of hierarchically porous materials with high resolution, use thereof, and resulting products.

BACKGROUND

[0003] Porous materials including polymer, ceramic, and metal have been of great interest in a variety of applications, such as catalyst technology, energy storage and

conversion, structure supporting scaffold and light-weight materials with high performance. A hierarchically porous structure has advantages over regular porous structures in terms of more efficient mass transport and accessibility to different pores.

[0004] Three-dimensional (3D) printing provides the ability to create an orderly structure to tune a mass flow.

SUMMARY

[0005] In one aspect of an inventive concept, an ink includes a polymer precursor, a copolymer, a catalyst, and a solvent.

[0006] In another aspect of an inventive concept, a method includes printing a three-dimensional structure using an ink that includes a polymer precursor, a block copolymer, a catalyst, and a solvent, immersing the printed three-dimensional structure in a second solvent for forming a gel, and drying the printed three-dimensional structure.

[0007] In yet another aspect of an inventive concept, a product includes a three-dimensional printed structure having ligaments, where an average diameter of the ligaments is in a range of about 10 microns to about 500 microns.

[0008] Other aspects and advantages of the present invention will become apparent from the following detailed description, which, when taken in conjunction with the drawings, illustrate by way of example the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. **1** is a flowchart of a method, according to one approach.

[0010] FIG. **2** is a schematic drawing of a method, according to one approach.

[0011] FIG. **3** is a series of scanning electron microscope images of a bicontinuous porous carbonized structure using a low content resol-like polymer precursor, according to one approach. The image of part **(a)** is the lowest magnified view of the structure. The image of part **(b)** is a magnified view of a portion of the image of part **(a)**. The image of part **(c)** is a magnified view of a portion of the image of part **(b)**.

[0012] FIG. **4** is a series of scanning electron microscope images of a hierarchically porous carbonized structure using a high content resol-like polymer precursor, according to one approach. The image of part **(a)** is the lowest magnified view of the structure. The image of part **(b)** is a magnified view of a portion of the image of part **(a)**.

[0013] FIG. **5** is a scanning electron microscope image of a printed three-dimensional structure, according to one approach.

[0014] FIG. **6A** is series of scanning electron microscope images of a bicontinuous hierarchically porous silica structure before pyrolysis, according to one approach. The image of part **(a)** is the lowest magnified view of the structure. The image of part **(b)** is a magnified view of a portion of the image of part **(a)**. The image of part **(c)** is a magnified view of a portion of the image of part **(b)**.

[0015] FIG. **6B**, part **(a)** is an image of a pyrolyzed 3D porous silica structure, according to one approach.

[0016] FIG. **6B**, parts **(b)** and **(c)** are a series of scanning electron microscope images of the carbonized porous silica structure of part **(a)**, according to one approach. The image of part **(c)** is a magnified view of a portion of the image of part **(b)**.

DETAILED DESCRIPTION

[0017] The following description is made for the purpose of illustrating the general principles of the present invention and is not meant to limit the inventive concepts claimed herein. Further, particular features described herein can be used in combination with other described features in each of the various possible combinations and permutations.

[0018] Unless otherwise specifically defined herein, all terms are to be given their broadest possible interpretation including meanings implied from the specification as well as meanings understood by those skilled in the art and/or as defined in dictionaries, treatises, etc.

[0019] It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless otherwise specified.

[0020] As also used herein, the term "about" denotes an interval of accuracy that ensures the technical effect of the feature in question. In various approaches, the term "about" when combined with a value, refers to plus and minus 10% of the reference value. For example, a thickness of about 10 nm refers to a thickness of 10 nm ± 1 nm, a temperature of about 50 °C refers to a temperature of 50 °C ± 5 °C, etc.

[0021] The nanoscale is defined as between 1 nanometer and about 500 nanometers.

[0022] For the purposes of this description, macropores are defined as having an average diameter of greater than 1 millimeter (mm). Mesopores are defined as having an average diameter of less than 1 mm and greater than about 10 microns (μm). Micropores

are defined as having an average diameter less than about 10 μm and greater than about 100 nanometers (nm). Nanopores are defined as having an average diameter less than 1 μm and greater than 0 nanometers. These ranges are approximate and may overlap, e.g., a large nanopore may also be defined as a small micropore.

[0023] It is also noted that, as used in the specification and the appended claims, wt% is defined as the percentage of weight of a particular component is to the total weight/mass of the mixture. Vol% is defined as the percentage of volume of a particular compound to the total volume of the mixture or compound. Mol% is defined as the percentage of moles of a particular component to the total moles of the mixture or compound. Atomic % (at%) is defined as a percentage of one type of atom relative to the total number of atoms of a compound.

[0024] The present disclosure includes several descriptions of exemplary "inks" used in an additive manufacturing process to form the inventive concepts described herein. It should be understood that "inks" (and singular forms thereof) may be used interchangeably and refer to a composition of matter comprising a plurality of particles coated with/dispersed throughout a liquid phase such that the composition of matter may be "written," extruded, printed, or otherwise deposited to form a layer that substantially retains its as-deposited geometry and shape with perhaps some, but preferably not excessive, sagging, slumping, or other deformation, even when deposited onto other layers of ink, and/or when other layers of ink are deposited onto the layer. As such, skilled artisans will understand the presently described inks to exhibit appropriate rheological properties to allow the formation of monolithic structures via deposition of

multiple layers of the ink (or in some cases multiple inks with different compositions) in sequence.

[0025] The following description discloses several preferred structures formed via direct ink writing (DIW), extrusion freeform fabrication, or other equivalent techniques and therefore exhibit unique structural and compositional characteristics conveyed via the precise control allowed by such techniques. The physical characteristics a structure formed by DIW may include having lower layers of the structure are slightly flattened, slightly disfigured from original extrusion (e.g., see slight droop of the filament in FIG. 6), etc. by weight of upper layers of structure, due to gravity, etc. The three-dimensional structure formed by DIW may have a single continuous filament that makes up at least two layers of the 3D structure.

[0026] The following description discloses several preferred aspects of an inventive concept of hierarchically porous materials and/or related additive manufacturing systems, methods, and products formed by the same.

[0027] In one general aspect of an inventive concept, an ink includes a polymer precursor, a copolymer, a catalyst, and a solvent.

[0028] In another general aspect of an inventive concept, a method includes printing a three-dimensional structure using an ink that includes a polymer precursor, a block copolymer, a catalyst, and a solvent, immersing the printed three-dimensional structure in a second solvent for forming a gel, and drying the printed three-dimensional structure.

[0029] In yet another general aspect of an inventive concept, a product includes a three-dimensional printed structure having ligaments, where an average diameter of the ligaments is in a range of about 10 microns to about 500 microns.

[0030] A list of acronyms used in the description is provided below.

3D	Three-dimensional
C	Celsius
cm	centimeter
CO_2	Carbon dioxide
DIW	Direct ink writing
M	Molar
mg	milligram
mm	millimeter
nm	nanometer
SEM	Scanning electron microscope
TEOS	Tetraethoxyl silane
TPP	Two-photon polymerization
μm	micron
Wt%	weight percent

[0031] Conventional 3D printing processes form structures with limited ligament sizes dependent on particle size and concentration in the inks for direct-ink writing. According to various approaches described herein, an ink system for direct-ink writing enables creation of hierarchically porous structures via 3D printing by a method of phase-separation and sol-gel process. According to one aspect of an inventive concept, an ink is powder free and enables printing of an ultrafine 3D structure. In some approaches, the average ligament size of the ultrafine structure may be less than 100 microns (μm). The pores of the formed 3D structure have an average diameter in a range from about a few

nanometers to hundreds of microns. Various aspects described herein provide a feasible way to fabricate highly-order hierarchically porous carbon, ceramic, and metal hybrid-materials.

[0032] Additive manufacturing techniques using light initiated processes, such as two-photon polymerization (TPP) laser printing generate small features, but the disadvantage of these processes is the parts are very small as well. Using the ink in additive manufacturing techniques such as direct ink writing (DIW) allows printing of structures with fine resolution. In some approaches, the ink may be used in a nozzle having an extrusion diameter in a range of less than 800 μm to about 10 μm. According to various approaches described herein, a particle-free ink as described allows the DIW process of additive manufacturing generate large parts on the order of centimeters to tens of centimeters having features having an average fine resolution in a range of less than 100 μm to about 30 μm, and may be smaller.

[0033] According to one approach, an ink includes a polymer precursor, a copolymer, a catalyst, and a solvent. Preferably, the ink is substantially free of particles. In some approaches, the solvent may be a solvent mixture.

[0034] In some approaches, the polymer precursor may include a formaldehyde resin. Illustrative examples of formaldehyde resins include: phenol formaldehyde resin, urea formaldehyde resin, resorcinol formaldehyde, melamine formaldehyde resin, etc. In other approaches, the polymer resin may include an epoxy resin.

[0035] In various approaches, a different formulation of the polymer precursor in the ink may yield a different final morphology of the final porous pyrolyzed structure. In some approaches, a low content resol-like polymer precursor may yield a bicontinuous

hierarchically porous pyrolyzed structure, where a bicontinuous hierarchically porous structure may be defined as having two distinct phases that are continuous and coexist in the structure. In other approaches, a high content resol-like polymer precursor may yield a hierarchically porous pyrolyzed structure, where a hierarchically porous structure (having no indication of the continuous nature of the pores) may be defined as having pores separated by a carbon backbone and the pores may or may not be continuous.

[0036] In one approach, the copolymer is a triblock copolymer. Illustrative examples of a triblock copolymer include Pluronic® F127, P105, F68, etc. According to another approach, the copolymer may be a non-block polymer. An illustrative example of a non-block polymer may be a poly(acrylamide) (PAM).

[0037] In various approaches, the ratio by weight of the polymer precursor to the copolymer may be less than about 1:8. In a preferred approach, the ratio by weight of the polymer precursor to the copolymer may be about 1:3. In another approach, the ratio by weight of the polymer precursor to the copolymer may be about 1:1. In one approach, the range of ratios of polymer precursor to copolymer may be from about 1:1 to about 1:11.

[0038] In one approach, the catalyst may be an acid catalyst. Illustrative examples of acid catalysts include hydrochloric acid (HCl), nitric acid, sulfuric acid, etc.

[0039] In other approaches, the catalyst may be a base catalyst. Illustrative examples of base catalysts include sodium carbonate, ammonia, ammonium carbonate, potassium carbonate, sodium hydroxide, etc.

[0040] In various approaches, the concentration of the catalyst may be in a range of about 1 weight% (wt%) to about 2 wt% of a total weight of the ink.

[0041] In one approach, the solvent of the ink may be water. In some approaches, the solvent may be a combination of water and an organic solvent. Illustrative examples of organic co-solvents include ethanol, methanol, isopropanol, etc. In an exemplary approach, the solvent includes a combination of water and ethanol.

[0042] In one approach, the ink may include a precursor of a ceramic component. Illustrative examples of the precursor of the ceramic component include titanium isopropoxide, titanium diisopropoxide bis(acetylacetonate), copper nitrate , aluminum chloride ($AlCl_3$), iron (III) chloride ($FeCl_3$), nickel nitrate, cobalt nitrate, copper(II) chloride ($CuCl_2$), etc. .In one exemplary approach, the precursor of the ceramic component in the ink may be tetraethoxyl silane (TEOS). A ratio by weight of ceramic component to polymer precursor in the ink may be about 1:1.

[0043] In some approaches, the ink may include an additional component. For example, an additional component may be silicon oxide, titanium oxide, nickel oxide, etc. In some approaches, an effective amount of the additional component may be present to result in a discernable change in a target characteristic of the ink, printed structure, and/or final product in which the component is present. In one approach, the additional component may preferably result in a change of characteristic to within a desired range. One skilled in the art, now armed with the teachings herein, would be able to readily determine an effective amount of a particular component without having to resort to undue experimentation.

[0044] FIG. **1** shows a method **100** for printing a three-dimensional (3D) structures using an ink, in accordance with one aspect of an inventive concept. As an option, the present method **100** may be implemented to form structures such as those shown in the

other FIGS. described herein. Of course, however, this method **100** and others presented herein may be used to provide applications which may or may not be related to the illustrative approaches listed herein. Further, the methods presented herein may be carried out in any desired environment. Moreover, more, or less steps than those shown in FIG. **1** may be included in method **100**, according to various approaches. It should also be noted that any of the aforementioned features may be used in any of the approaches described in accordance with the various methods.

[0045] Step **102** of method **100** includes printing a three-dimensional (3D) structure using an ink, where the ink includes a polymer precursor, a block copolymer, a catalyst, and a solvent. In one approach, the solvent may be a composition of two or more solvents, e.g., water and an organic solvent. The ink may have any composition described herein, e.g., it may be one of the inks described above.

[0046] In one approach, the printing of the 3D structure is performed by a DIW technique. The DIW method includes a nozzle having an extrusion diameter in a range of about 10 μm to less than 800 μm. In some approaches, the ink may be used in a nozzle having a diameter of less than 250 μm. In some approaches, the ink may be used in a nozzle with a diameter of 50 μm or less. In other approaches, the ink may be used in a nozzle with a diameter of 30 μm or less. In yet other approaches, the ink may be used in a nozzle having an extrusion diameter of about 10 μm.

[0047] In some approaches, the ink may be mixed prior at adding the ink to the nozzle for DIW. In other approaches components of the ink may be mixed in the nozzle during printing by DIW.

[0048] Step **104** of method **100** includes immersing the 3D structure in a solvent for forming a gel at an elevated temperature. The temperature for gelation of the 3D structure may be in a range of greater than 60°C to about 100°C. In some approaches, the immersing results in transforming the ink of the printed 3D structure to a wet gel. Preferably, the solvent is not miscible with water. Also, preferably, the solvent has a boiling point greater than the temperature of the heating during gelation of the 3D structure. For example, in one approach, forming the gel may at 80°C, then the solvent would preferably have a boiling point greater than 80°C, and more preferably greater than 100°C.

[0049] Gelation of the 3D structure may include immersion of the 3D structure in a solvent such as iso-octane. In other approaches, gelation of the 3D structure may include immersion of the 3D structure in a solvent such as one of the following: decane, undecane, tridecane, etc.

[0050] Step **106** of method **100** includes drying the 3D structure. In one approach, the drying includes freeze drying the 3D structure. In one approach, the 3D structure may be freeze dried under liquid nitrogen. In one approach, the 3D structure may be freeze dried under the solid form of carbon dioxide (i.e., dry ice). Methods of freeze drying the 3D structure are generally known by one skilled in the art.

[0051] In another approach, step **106** of method **100** includes super critical drying the 3D structure. Before super critical drying, the wet gel of the 3D structure preferably is soaked in acetone to exchange all previous solvents from the structure to acetone. Methods of super critical drying are generally known by one skilled in the art.

[0052] An optional step **108** of method **100** includes heating the dried 3D structure in an inert atmosphere, in open air, etc. for forming a pyrolyzed 3D structure. Pyrolysis techniques known by one generally skilled in the art may be used for heating the 3D structure. In some approaches, in which pyrolysis of the 3D structure may result in carbonization of the 3D structure when conducting in an inert atmosphere. In other approaches, pyrolysis of the 3D structure may result in a 3D structure having only inorganic components when conducting in open air.

[0053] FIG. **2** shows a schematic drawing of a method **200** for printing a three-dimensional (3D) structures using an ink, in accordance with one aspect of an inventive concept. As an option, the present method **200** may be implemented to form structures such as those shown in the other FIGS. described herein. Of course, however, this method **200** and others presented herein may be used to provide applications which may or may not be related to the illustrative approaches listed herein. Further, the methods presented herein may be carried out in any desired environment. Moreover, more, or less steps than those shown in FIG. **2** may be included in method **200**, according to various approaches. It should also be noted that any of the aforementioned features may be used in any of the approaches described in accordance with the various methods.

[0054] FIG. **2** represents a schematic drawing of the synthesis route and proposed mechanism of method **200**, according to one approach. The method **200** begins in part **(a)** with a resol-like polymer precursor **202** component and a triblock copolymer **204** component. These components form a homogenous mixture **206** in part **(b)** that includes an acid catalyst, and solvent, e.g., water and ethanol (EtOH).

[0055] The homogenous mixture **206** may be used as an ink to form a 3D structure **208** by direct ink writing (DIW) techniques as shown in part **(c)**. As depicted, the DIW process allows the ink of the homogenous mixture to form a geometric shape, e.g., a log pile formation having channels extending along the length of the 3D shape. In addition, the DIW process is an engineered process of forming a 3D structure **208**, where each ligament and feature is engineered to a predetermined dimension.

[0056] As shown in part **(d)**, the 3D structure **208** is immersed in a solvent **210** for transforming the ink of the 3D structure into a wet gel through a gelation process **212**. The 3D structure **208** may be immersed, soaked, submerged, etc. in the solvent **210** at an elevated temperature, for example, about 80°C for a duration of time until the material of the 3D structure transforms into a wet gel. In some approaches, the 3D structure may be immersed in the solvent at an elevated temperature for about 3 to 7 days.

[0057] Part **(e)** shows a magnified representation of a bicontinuous structure **216** present in the ligaments **214** of the 3D structure **208** (*see* part **(d)**). Following evaporation of part of the solvent of the ink used to form the homogenous mixture **206** (*see* part **(b)**), the bicontinuous structure **216** may include an immiscible continuous water-rich phase **218** and a resol-rich phase **220** formed during phase separation that occurs during immersion of the 3D structure **208** in the solvent **210** (*see* part **(d)**). As shown, the bicontinuous nature of the bicontinuous structure **216** shows two distinct phases, the water-rich phase **218** and the resol-rich phase **220**, that may coexist in the structure thereby resulting in a bicontinuous structure.

[0058] A magnified view of the pores in part **(e)** shows that the cross-linked polymers **222** that include block copolymer components **224** may stabilize the phase separated bicontinuous structure **216**.

[0059] The structure is dried **226** thereby forming micropores (pores having an average diameter greater than 200 nm and less than 10 μm) and mesopores (pores having an average diameter greater than about 10 μm and less than about 1 mm) in the structure. In some applications, the dried structure may be heated in a pyrolysis process **228** under inert atmosphere or air to form smaller pores, such as nanopores (pores having an average diameter less than approximately 200 nm, in some instances as small as 10 nm) in the resulting carbonized 3D structure **230**.

[0060] Part **(f)** shows a schematic drawing of a portion of a carbonized 3D structure **230.** The ligaments **214** of the carbonized 3D structure **230** may have an average diameter ***d*** less than 100 μm. The carbonized 3D structure **230** of the bicontinuous structure **216** may represent a final bicontinuous porous structure where the two phases, **222**, **218** of part **(e)** result in carbon ligaments **214** and pores **215**, respectively.

[0061] In one approach, a product includes a 3D printed structure having ligaments, where an average diameter of the ligaments may be in a range of about 10 μm to about 500 μm. In one approach the average diameter of the ligaments may be in a range of 20 μm to about 250 μm.

[0062] In one approach, the 3D structure may have at least one outer dimension greater than about one centimeter. In some approaches, as shown in FIG. **2**, the carbonized 3D structure **230** has an outer dimension ***od*** as defined as the length from one edge of the structure to the opposite edge of the structure in a longitudinal direction. In

some approaches, the 3D structure may have at least one outer dimension ***od*** in a range of greater than one millimeter to less than about one centimeter. In some approaches, the 3D structure may have at least one dimension greater than 10s of centimeters.

[0063] In one approach, the product may be essentially free of particles, for example, the product may be greater than 99% free of particles. Particles may be defined as components with an average diameter greater than 1 nanometer (nm). In some approaches, the product may be essentially free of any component with an average diameter greater than 1 nm.

[0064] In one approach, the product has a plurality of pores defined by the ligaments. The average diameter of the pores may be less than 100 nanometers (nm).

[0065] **Experiments**

[0066] In a typical procedure, a pre-prepared polymer precursor 0.5 g was mixed with 3 g Pluronic F127 (Sigma-Aldrich, St. Louis, MO), 3 g water, 0.4 g ethanol and 0.03 g 2 M HCl to afford clear polymer ink. Any other ceramic precursors such as tetraethoxyl silane (TEOS) can be introduced to generate homogeneous ink system. The prepared ink was then direct-ink written onto a substrate. The printed object was then immersed into isooctane and cured at 80°C. After gelation, the wet gel was washed by acetone and water. Afterwards the gel was freeze-dried and treated to pyrolysis to form a carbonized structure.

[0067] FIG. **3** shows a series of scanning electron microscopy (SEM) images of a bicontinuous porous carbonized structure formed using a low concentration of resol-like polymer precursor and a method described herein. A bicontinuous structure may include two distinct phases that are continuous and co-exist. Part **(a)** is a low magnification SEM

image of the porous carbonized structure formed with a low concentration of resol-like polymer precursor. Part **(b)** is a higher magnification of a portion of the image in part **(a)**. Part **(c)** is a higher magnification of a portion of the image in part **(b)**.

[0068] FIG. **4** shows a series of SEM images of a hierarchically porous carbonized structure using a high concentration of resol-like polymer precursor and a method described herein. A high concentration of resol-like polymer precursor may yield a final structure having pores separated by a carbon backbone and thus the pore structure may not be continuous. In various approaches, a different formulation of the polymer precursor may yield a different final morphology of the porous carbonized structure. For example, a low concentration of resol-like polymer precursor may yield a bicontinuous porous carbonized structure (*see* FIG. **3**) and a high concentration of resol-like polymer precursor may yield a hierarchically porous carbonized structure (FIG. **4**). Part **(a)** of FIG. **4** is a low magnification SEM image of the porous carbonized structure formed with a high concentration of resol-like polymer precursor. Part **(b)** is a higher magnification of a portion of the image in part **(a)**.

[0069] FIG. **5** is an image of a printed 3D structure using a method as described herein. The image demonstrates high resolution of the ligaments of the structure using the method of 3D printing as described. As shown, a ligament **502** has an average diameter of approximately 30 μm. Moreover, the printed 3D structure has substantially uniform ligaments **502**, for example, where a first set of ligaments extends along the length of the structure in a longitudinal direction and a second set of ligaments extend along the structure in a direction orthogonal to the first set of ligaments. A printed 3D structure may have a plurality of sets of ligaments.

[0070] FIG. **6A** shows a series of SEM images of a bicontinuous porous silica precursor 3D structure aerogel before pyrolysis, according to one approach. Part **(a)** is a low magnification of the bicontinuous porous silica 3D structure. Part **(b)** is a higher magnification of a portion of the image in part **(a)**. Part **(c)** is a higher magnification of a portion of the image in part **(b)**.

[0071] FIG. **6B**, part **(a)** is an image of the carbonized bicontinuous porous silica 3D structure after the pyrolysis step of a method, according to one approach. Part **(b)** is a SEM image of the carbonized structure of part **(a)**. Part **(c)** is a magnified view of a portion of the SEM image in part **(b)**.

[0072] **In Use**

[0073] Various aspects of an inventive concept described herein may be used for energy storage, for example, super capacitors and lithium-ion batteries. Some approaches may be used for catalysts supporting. Some approaches may be used for water purification, sensors, CO_2 reduction, flow batteries and water splitting devices.

[0074] The inventive concepts disclosed herein have been presented by way of example to illustrate the myriad features thereof in a plurality of illustrative scenarios, approaches, and/or implementations. It should be appreciated that the concepts generally disclosed are to be considered as modular, and may be implemented in any combination, permutation, or synthesis thereof. In addition, any modification, alteration, or equivalent of the presently disclosed features, functions, and concepts that would be appreciated by a person having ordinary skill in the art upon reading the instant descriptions should also be considered within the scope of this disclosure.

[0075] While various approaches have been described above, it should be understood that they have been presented by way of example only, and not limitation. Thus, the breadth and scope of an approach of the present invention should not be limited by any of the above-described exemplary approaches but should be defined only in accordance with the following claims and their equivalents.

CLAIMS

What is claimed is:

1. An ink, comprising:

a polymer precursor;

a copolymer;

a catalyst; and

a solvent.

2. The ink as recited in claim 1, comprising a precursor of a ceramic component.

3. The ink as recited in claim 2, comprising an additional component, wherein the additional component is selected from the group consisting of: silicon oxide, titanium oxide, and nickel oxide.

4. The ink as recited in claim 2, wherein the precursor of the ceramic component is tetraethoxyl silane (TEOS).

5. The ink as recited in claim 1, wherein the polymer precursor includes a formaldehyde resin selected from the group consisting of: phenol formaldehyde resin, urea formaldehyde resin, resorcinol formaldehyde, and melamine formaldehyde resin.

6. The ink as recited in claim 1, wherein the copolymer is at least one copolymer selected from the group consisting of: a triblock copolymer and a non-block copolymer.

7. The ink as recited in claim 1, wherein a ratio by weight of the polymer precursor to the copolymer is in a range from about 1:1 to about 1:11.

8. The ink as recited in claim 1, wherein the catalyst is an acid catalyst.

9. The ink as recited in claim 1, wherein the catalyst is a base catalyst.

10. The ink as recited in claim 1, wherein a concentration of the catalyst is in a range of about 1 weight% to about 2 weight % of a total weight of the ink.

11. A method, comprising:

printing a three-dimensional structure using an ink, wherein the ink comprises:

a polymer precursor,

a block copolymer,

a catalyst, and

a solvent;

immersing the printed three-dimensional structure in a second solvent for forming a gel; and

drying the printed three-dimensional structure.

12. The method as recited in claim 11, wherein the printing is performed by a direct-ink writing method.

13. The method as recited in claim 12, wherein the direct-ink writing method includes a nozzle having an extrusion diameter in a range of about 10 microns to less than 800 microns.

14. The method as recited in claim 11, wherein the drying includes freeze drying.

15. The method as recited in claim 11, wherein the drying includes super critical drying.

16. The method as recited in claim 11, comprising heating the dried printed three-dimensional structure for forming a pyrolyzed three-dimensional structure.

17. A product, comprising:
a three-dimensional printed structure having ligaments, wherein an average diameter of the ligaments is in a range of about 10 microns to about 500 microns.

18. The product as recited in claim 17, wherein the three-dimensional printed structure has at least one outer dimension greater than about one centimeter.

19. The product as recited in claim 17, wherein the three-dimensional printed structure is essentially free of particles.

20. The product as recited in claim 17, wherein the product has a plurality of pores defined by the ligaments, wherein an average diameter of the pores is less than 100 micrometers.

21. The product as recited in claim 17, wherein the three-dimensional printed structure is a pyrolyzed 3D printed structure.

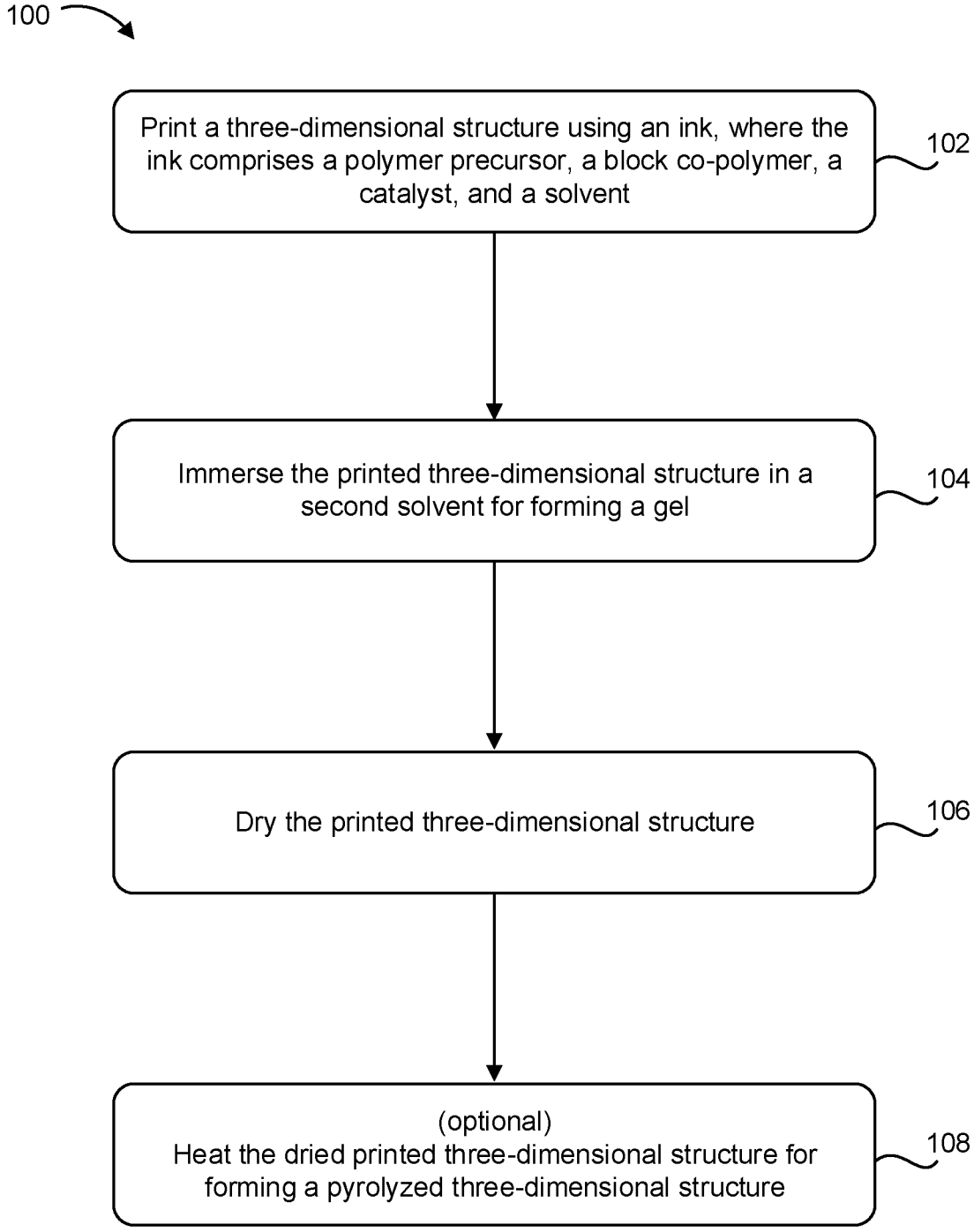
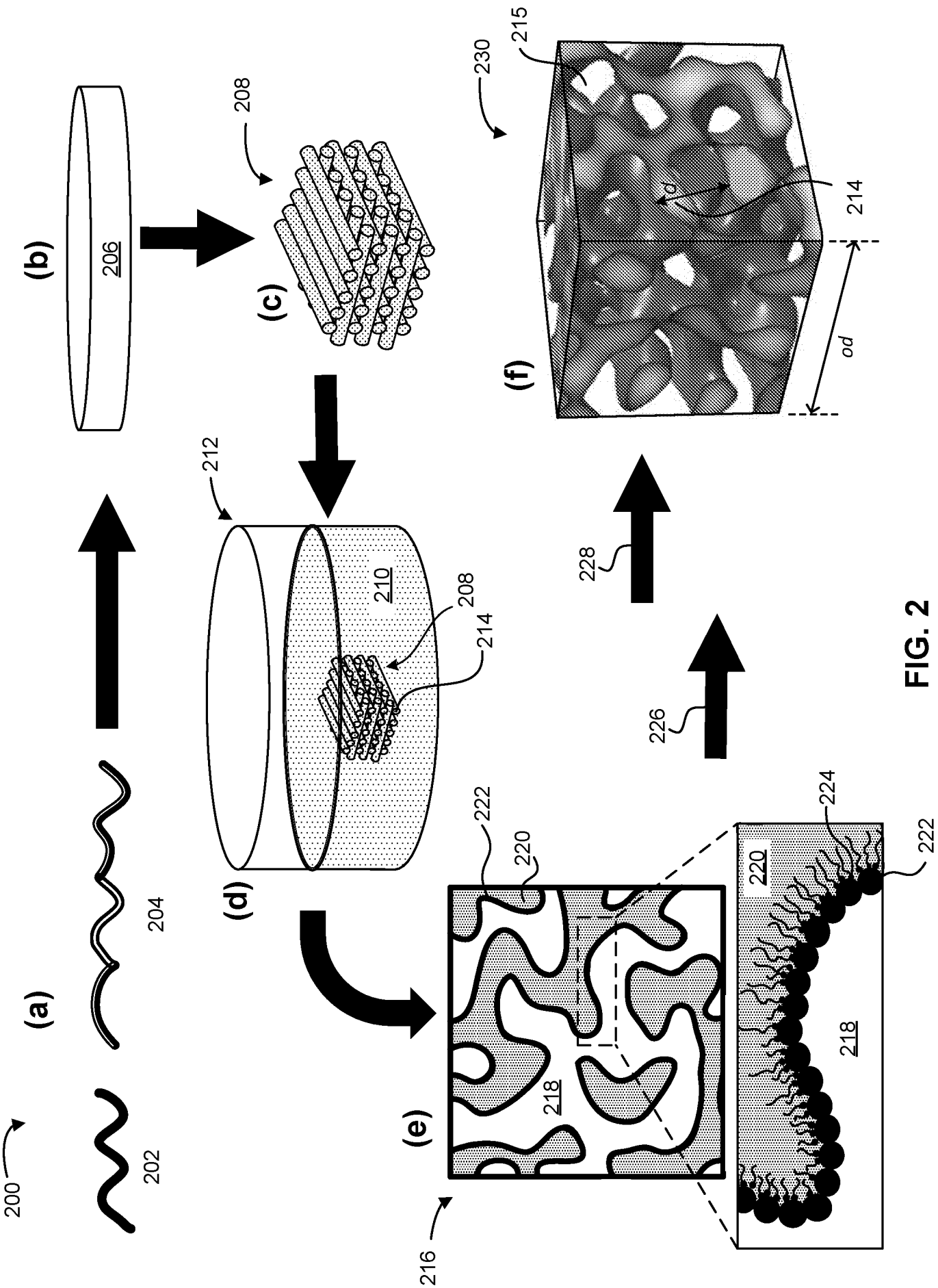

100
Print a three-dimensional structure using an ink, where the ink comprises a polymer precursor, a block co-polymer, a catalyst, and a solvent
102
Immerse the printed three-dimensional structure in a second solvent for forming a gel
104
Dry the printed three-dimensional structure
106
(optional)
Heat the dried printed three-dimensional structure for forming a pyrolyzed three-dimensional structure
108

FIG. 1


200
202
(a)
204
206
(b)
208
(c)
212
210
208
214
(d)
216
218
222
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(e)
224
222
220
218
226
228
230
215
214
d
od
(f)

FIG. 2

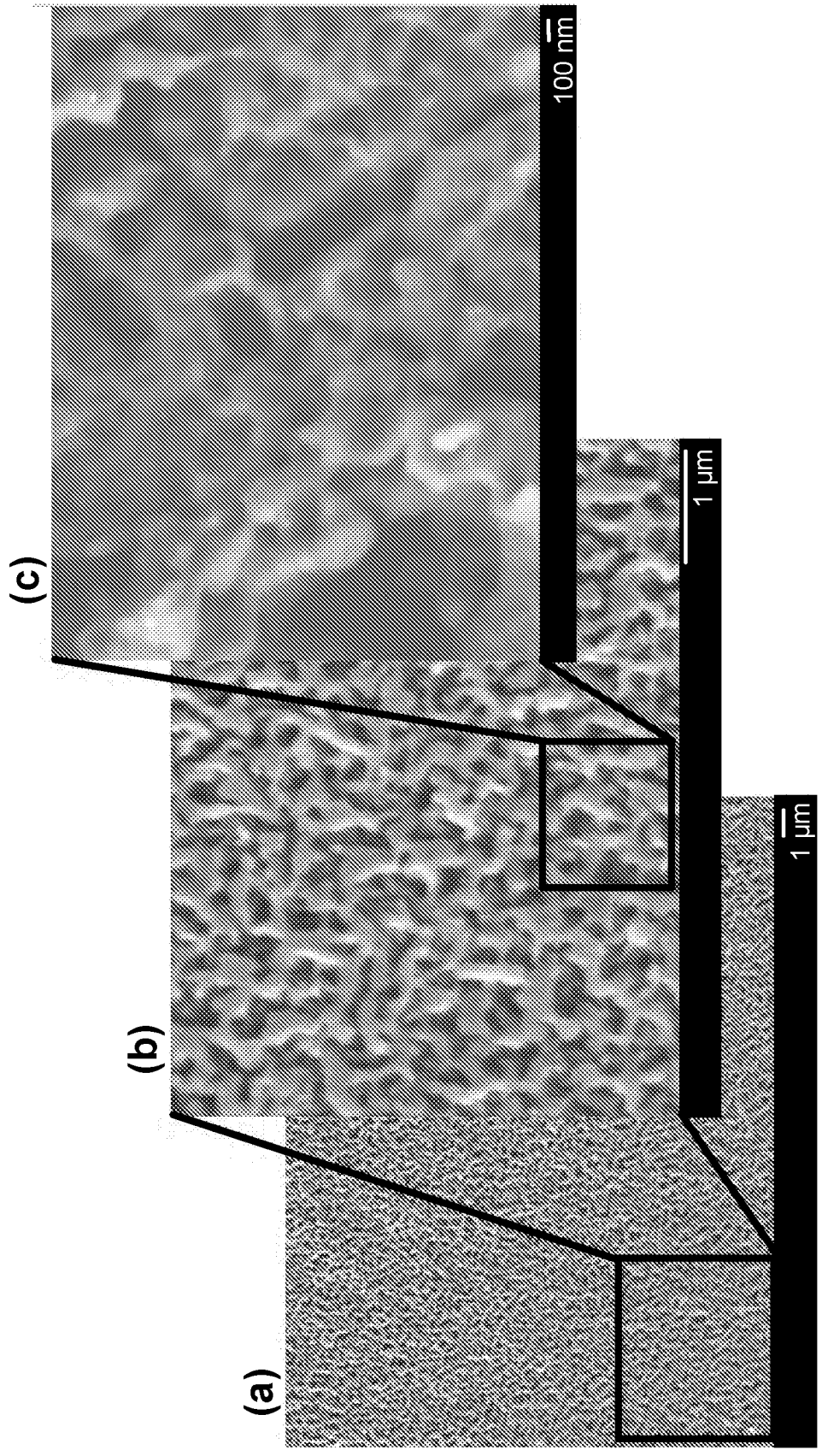

FIG. 3

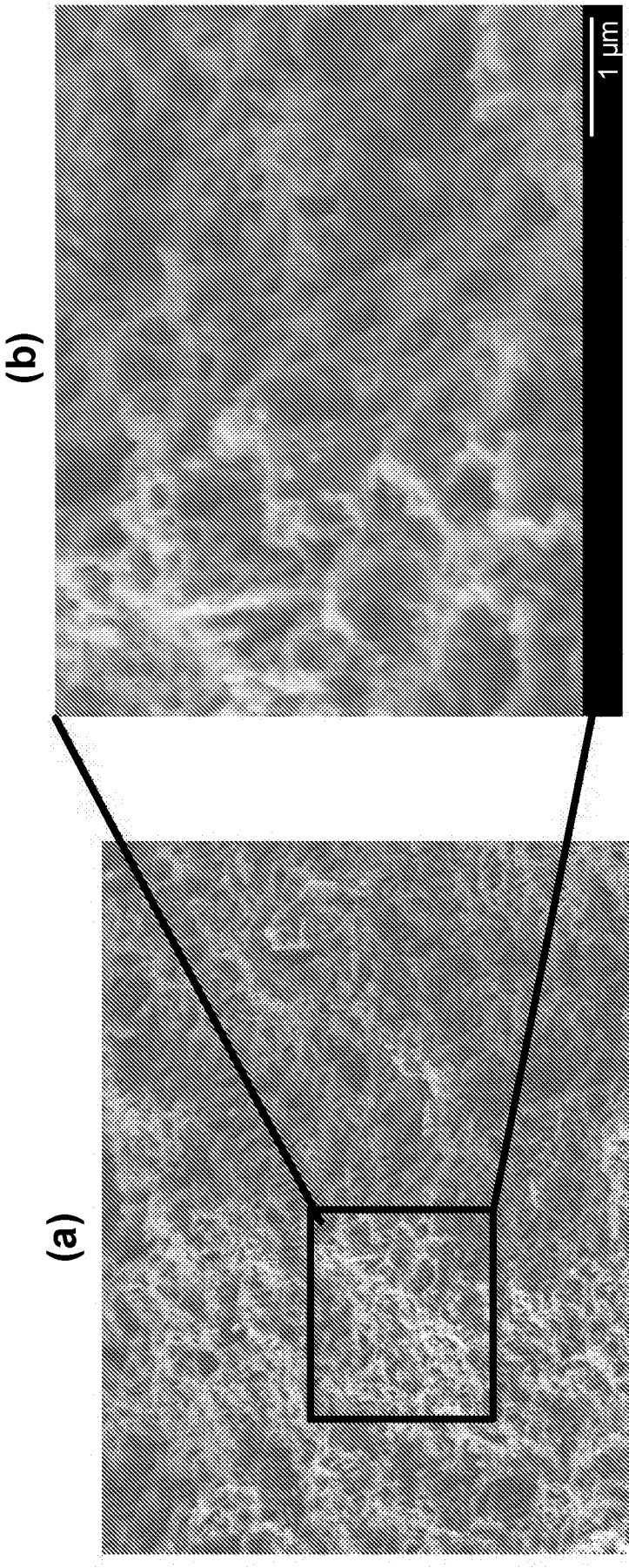

FIG. 4

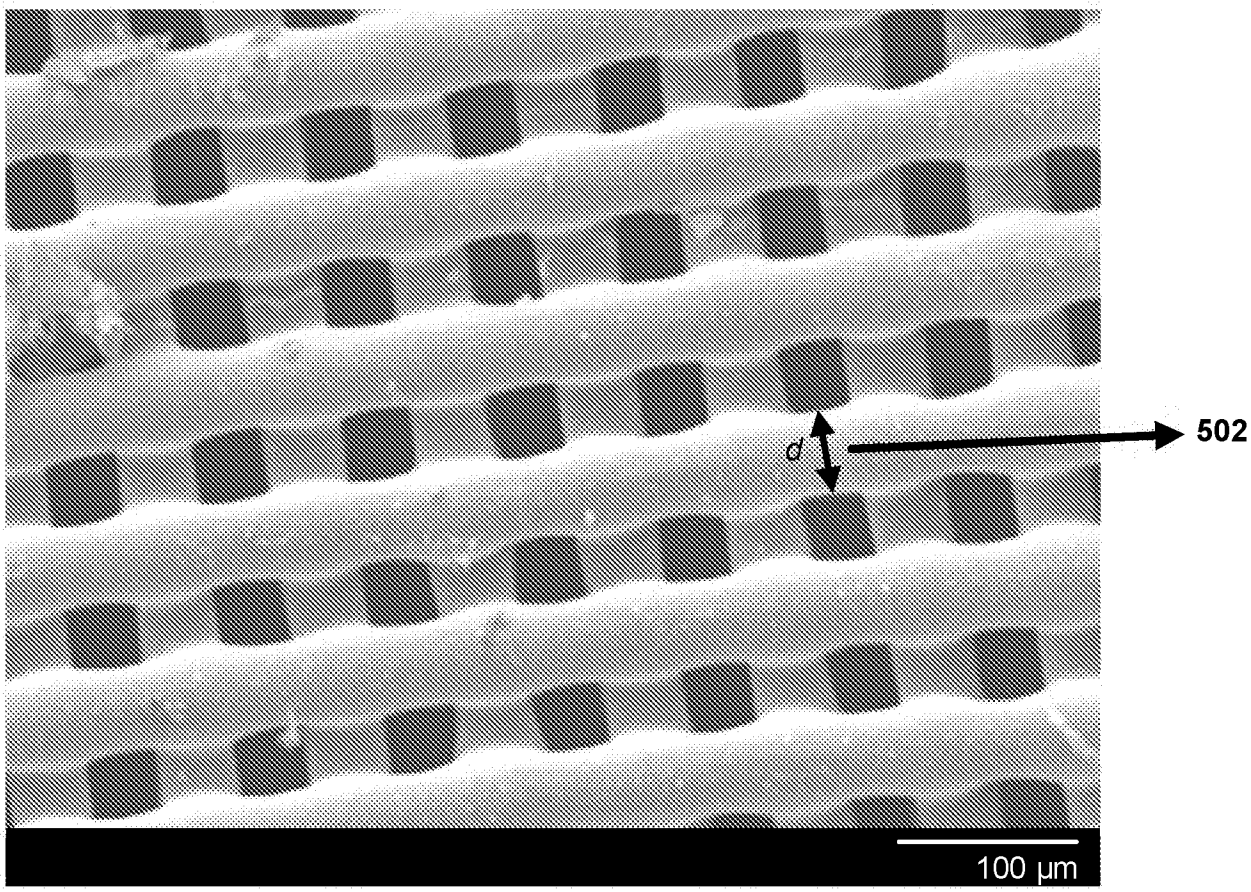

FIG. 5

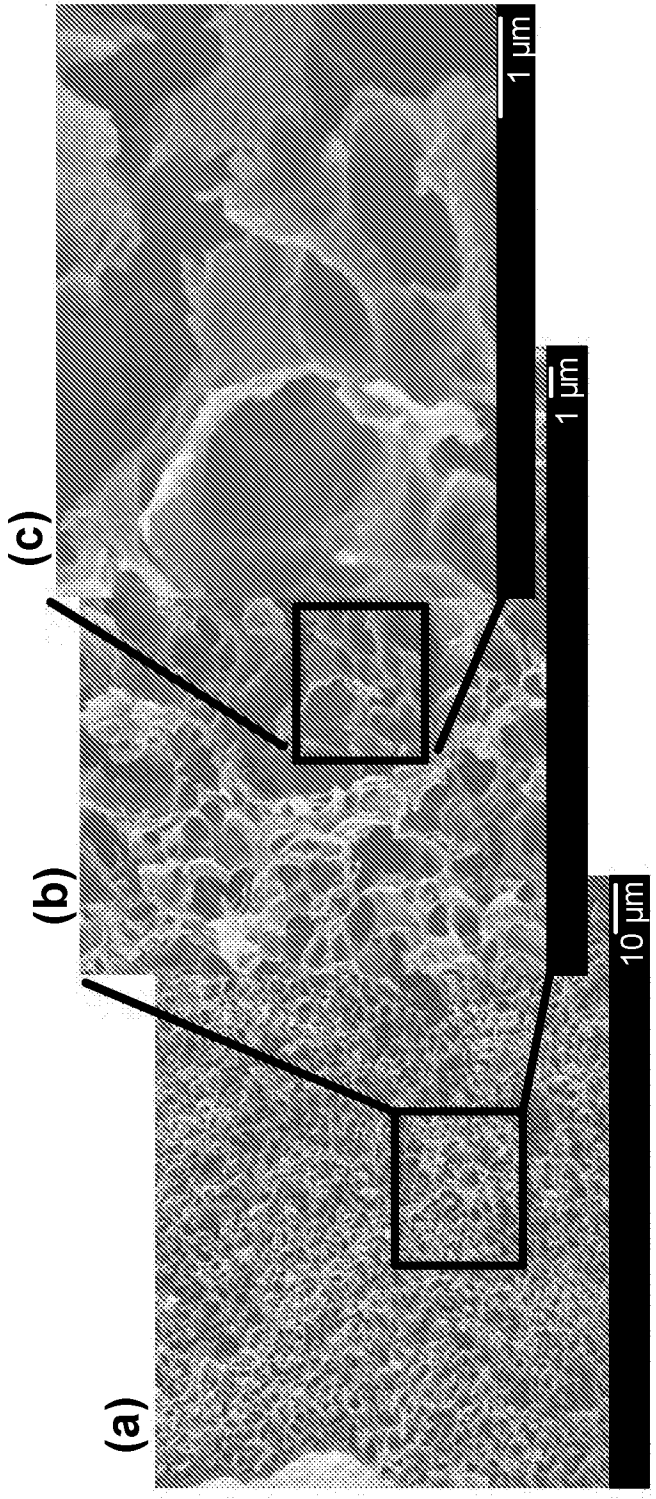

FIG. 6A

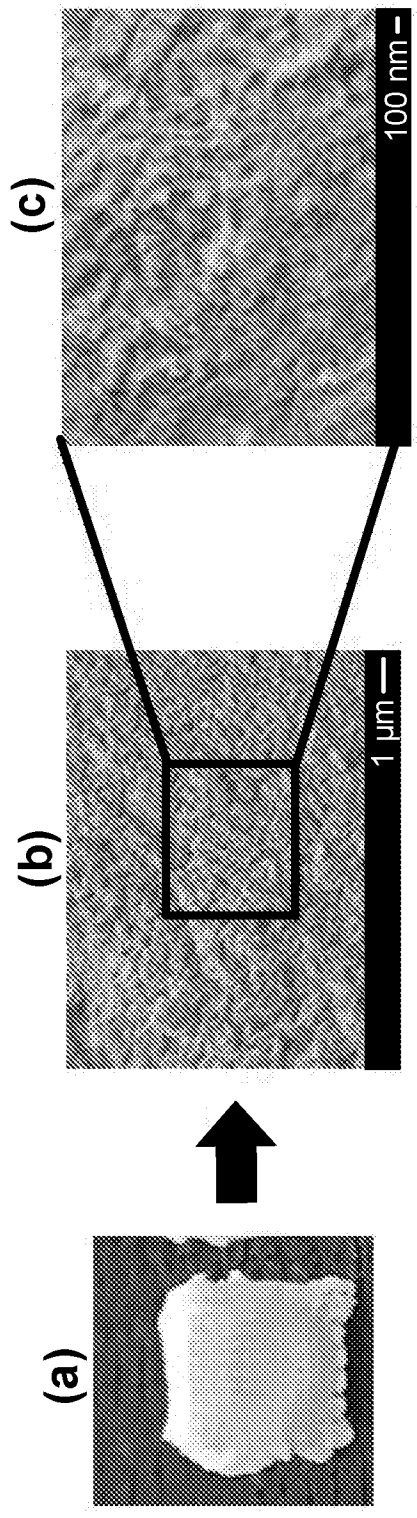

FIG. 6B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/23844

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B29C 64/10, C09D 11/00 (2020.01)

CPC - B29C 64/10, C09D 11/103, C09D 11/102; C09D 11/38, B28B 1/001, B28B 1/007, C08J 9/0042, B32B 2266/126, B32B 2266/057, B33Y 10/00, C04B 2235/483, C04B 2235/606

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2009/0110843 A1 (HALAHMI et al.) 30 April 2009 (30.04.2009), para [0010], [0019], [0020], [0033], [0034], [0057], [0114]	1, 5-8, 10
X --- Y	US 2006/0171990 A1 (ASGARI) 03 August 2006 (03.08.2006), para [0008], [0041], [0045], [0052], [0055], [0065], [0072], [0079], [0085], [0091], [0092], [0113]; claim 19	1-4, 9, 11, 15 ---------- 12-14, 16
Y	US 2013/0084449 A1 (LEWIS et al.) 04 April 2013 (04.04.2013), para [0006]-[0008], [0050], [0052], [0055]	12, 13
Y	US 2016/0067891 A1 (LAWRENCE LIVERMORE NATIONAL SECURITY, LLC) 10 March 2016 (10.03.2016), para [0006], [0026]	14
Y	US 2018/0251645 A1 (YISSUM RESEARCH DEVELOPMENT COMPANY OF THE HEBREW UNIVERSITY OF JERUSALEM LTD) 06 September 2018 (06.09.2018), para [0019], [0051], [0090], [0092]	16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 July 2020	07 AUG 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/23844

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III *Observations where unity of invention is lacking (Continuation of item 3 of first sheet)*

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-16 drawn to an ink and method for printing.

Group II: Claims 17-21, drawn to a product.

--see extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-16

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/23844

Continuation of box No. III -- Observations where unity of invention is lacking

The inventions listed in the above-mentioned groups do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features
Group I includes the special technical feature of a polymer precursor; a copolymer; and a catalyst, not included in the other group.

Group II includes the special technical feature of a three-dimensional printed structure having ligaments, not included in the other group.

Common Technical Features:
The only technical feature shared by Groups I and II that would otherwise unify the groups, is 3d printing. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is disclosed by US 20180/320008 A1 to President and Fellows of Harvard College et al. (hereinafter Harvard).

Harvard discloses 3D printing (abstract).

As the common technical feature was known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups.

Therefore, Groups I-II lack unity under PCT Rule 13.