

MAGNETICALLY ASSISTED DROP-ON-DEMAND 3D PRINTING OF MICROSTRUCTURES

The present application claims priority to the Singapore patent application no. 10202106292P, the entire disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

[0001] The present disclosure relates to the field of additive manufacturing, and more particularly to additive manufacturing of microstructures.

BACKGROUND

[0002] Three-dimensional (3D) printing is a manufacturing technology that generates freeform 3D structures using layer-by-layer deposition. Traditionally, 3D printing is used for small batch prototyping with limited material compatibilities. It remains a challenge to fabricate microstructures by 3D printing owing to the complex anisotropy and structural issues involved in forming layers of dissimilar materials.

SUMMARY

[0003] In one aspect, the present application discloses a method of 3D printing, the method comprising: printing a droplet of ink, the ink including a plurality of microplatelets in a liquid, the plurality of microplatelets being configured to be magnetically responsive; subjecting the printed droplet of ink to a rotating magnetic field; and providing a period of drying in which at least a portion of the liquid is evaporated from the printed droplet of ink to form an at least partially dried droplet, the at least partially dried droplet being characterized by the plurality of microplatelets being in alignment with one another, wherein the plurality of microplatelets in alignment defines a corresponding plurality of at least partially un-filled gaps between the plurality of microplatelets.

[0004] The method recited above, in which the at least partially dried droplet has a final concentration of the microplatelets, and wherein the final concentration is higher than a maximum concentration of the droplet, wherein the droplet at the maximum concentration is saturated with the plurality of microplatelets. Optionally, prior to the period of drying, the

droplet of ink has an initial concentration that is lower than the maximum concentration. The at least partially dried droplet has a final concentration that is higher than the initial concentration.

[0005] Optionally, the method may further comprise providing a polymer after forming the at least partially un-filled gaps, wherein the polymer is received by the at least partially un-filled gaps to form a composite. Optionally, the method may include subjecting the printed droplet of ink with the at least partially un-filled gaps to a heat treatment to bind the plurality of microplatelets, such that the plurality of microplatelets consolidate into an at least partially porous inorganic scaffold. Optionally, the method may further comprise controllably heating the substrate before the period of drying ends. The rotating magnetic field may be configured with a magnetic field strength higher than a capillary flow action in a drying droplet. The liquid may be one of or a combination of an aqueous solution and an organic solvent. Optionally, the liquid may comprise a binder. Each of the plurality of microplatelets may be characterized by at least one anisotropic property.

[0006] The method may comprise printing a subsequent droplet of ink adjacent the printed droplet of ink, wherein the subsequent droplet of ink is printed prior to the printed droplet of ink becoming fully dried.

[0007] Optionally, the method may comprise, before the printing, decorating the plurality of microplatelets with superparamagnetic iron oxide nanoparticles.

[0008] According to another aspect, a product formed by a method of drop-on-demand 3D printing, the product comprises: one or more units, each of the one or more units including a plurality of microplatelets disposed on a substrate or on another of the one or more units, the plurality of microplatelets being configured to be magnetically responsive, the plurality of microplatelets of a same unit being in alignment with an alignment orientation, wherein the adjacent ones of the plurality of microplatelets in alignment define an at least partially un-filled gap such that the plurality of microplatelets in alignment define a corresponding plurality of the at least partially un-filled gaps.

[0009] Each of the one or more units is formed by an ink, and wherein at least one of the one or more units is characterized by a final concentration of the microplatelets that is higher

than a maximum concentration, wherein the maximum concentration of the ink corresponds to the ink being saturated with the plurality of microplatelets. The ink has an initial concentration prior to forming the one or more units, and the initial concentration may be lower than the maximum concentration. The final concentration may be higher than the initial concentration.

[0010] Optionally, the product may further comprise a polymer, wherein the polymer is disposed in the plurality of the at least partially un-filled gaps to form a composite. The one or more units may be characterized by at least one anisotropic property. Optionally, before polymer infiltration in the partially un-filled gaps, the product may be submitted to a heat treatment to bind the plurality of microplatelets. The printed droplet of ink or the plurality of microplatelets consolidate to form a composite or to yield a porous self-standing structure (e.g., an inorganic scaffold).

[0011] The plurality of microplatelets may be selected from one of the following: titania-decorated aluminum oxide microplatelets decorated with superparamagnetic iron oxide, aluminum oxide microplatelets decorated with superparamagnetic iron oxide, graphite microplatelets, boron nitride microplatelets decorated with superparamagnetic iron oxide, and a combination of any thereof. Preferably, each microplatelet is made magnetically responsive prior to its employment in the composition. Said magnetically responsive modification can be plural, including coating with superparamagnetic iron oxide nanoparticles. Before the printing, each of the plurality of microplatelets may be decorated with superparamagnetic iron oxide nanoparticles. The terms “coated” and “decorated”, or the like, are used interchangeably, and refer to the surfaces of a microplatelet having magnetically responsive material adhered, adsorbed, attached, or otherwise disposed thereon.

[0012] According to another aspect, the present disclosure provides a method of 3D printing, the method comprising: preparing an ink, the ink comprising a slurry of microplatelets in a liquid, the microplatelets being magnetically responsive and characterized by a degree of magnetic responsiveness and a microplatelet size; printing a droplet of the ink; subjecting the droplet to a rotating magnetic field, the rotating magnetic field being characterized by a magnetic field strength and a rotation frequency; and

providing a period of drying in which at least a portion of the liquid is evaporated from the droplet to form an at least partially dried droplet, the at least partially dried droplet comprising an array of the microplatelets oriented at an alignment angle, wherein the array of the microplatelets are in alignment and define a corresponding plurality of at least partially un-filled gaps between neighbouring ones of the microplatelets, wherein the alignment angle is configurable by controlling one or more of the slurry concentration, the magnetic field strength, and the rotation frequency, and wherein the slurry concentration corresponds to a quantity of the microplatelets in an unit of the ink prior to the printing. Optionally, the at least partially dried droplet has a final concentration, and wherein the final concentration is higher than a saturated slurry concentration, the saturated slurry concentration corresponding to a maximum quantity of the microplatelets in the unit of the ink prior to the printing. Optionally, prior to the period of drying, the droplet has an initial concentration that is lower than the saturated slurry concentration. Preferably, the at least partially dried droplet has a final concentration that is higher than the slurry concentration.

[0013] According to another aspect, the present disclosure provides a capacitor comprising: a dielectric layer; and two graphite layers disposed on either side of the dielectric layer, each of the two graphite layers being printed by the method of 3D printing disclosed herein such that each of the two graphite layers includes the plurality of microplatelets with an alignment angle of 90 degrees relative to a plane of an interface between the dielectric layer and any of the two graphite layers. The dielectric layer may comprise a scaffold of second microplatelets, the second microplatelets being magnetically responsive and aligned at a second alignment angle relative to the plane of the interface between the dielectric layer and any of the two graphite layers. Preferably, the second alignment angle is 90 degrees. Optionally, the second microplatelets comprises one of the following: barium titanate microplatelets decorated with superparamagnetic iron oxide nanoparticles, titania-decorated aluminum oxide decorated with superparamagnetic iron oxide nanoparticles, and a combination thereof.

[0014] According to yet another aspect, a piezoresistive device comprises: an active layer disposed between two electrodes, the active layer being printed by the method of 3D printing disclosed herein such that the active layer includes: graphite microplatelets in alignment and defining a corresponding array of gaps; and polydimethylsiloxane infiltrated into gaps

between the graphite microplatelets.

BRIEF DESCRIPTION OF DRAWINGS

[0015] Fig. 1A is an electron micrograph showing a cross-section of a printed droplet according to one embodiment of the present disclosure;

[0016] Fig. 1B is an electron microscope image (electron micrograph) of the surface of functionalized microplatelets in an ink of the present disclosure;

[0017] Fig. 2A is an optical image of droplets with differently oriented microstructures, and Figs. 2B and 2C are electron micrographs of droplets with differently oriented microstructures;

[0018] Fig. 3 is a flow chart schematically illustrating a method of magnetically assisted drop-on-demand 3D printing of microstructures according to embodiments of the present disclosure;

[0019] Fig. 4A is a schematic diagram showing a set-up for magnetically assisted alignment of microstructures in a droplet;

[0020] Fig. 4B is a schematic diagram illustrating a product formed according to embodiments of the present disclosure;

[0021] Figs. 5A and 5B are electron micrographs showing the effect of capillary flows, and Fig. 5C is a plot of threshold magnetic field strength in relation to the capillary forces;

[0022] Fig. 6A is an optical image of a droplet with a relatively high contact angle and Fig. 6B is a corresponding electron micrograph of a cross section of the dried droplet;

[0023] Fig. 7A is an optical image of a droplet with a relatively low contact angle and Fig. 7B is a corresponding electron micrograph of a cross section of the dried droplet;

[0024] Fig. 8 are electron micrographs of microstructures formed from droplets of different volumes and from droplets of similar volumes and different ink compositions;

[0025] Figs. 9A to 9D are electron micrographs showing the resulting microplatelet

alignment angles from different ink concentrations;

[0026] Figs 10A to 10D are schematic diagrams illustrating changes in a printed droplet;

[0027] Fig. 11A shows optical images and plots of microplatelet concentration at different time instances;

[0028] Fig. 11B is a plot showing a variation of final concentration, droplet radius and contact angle of the droplet for three different substrates;

[0029] Fig. 11C is a plot showing relation between initial concentration and final concentration on copper and glass substrates;

[0030] Fig. 12 is a plot showing variations of microplatelet alignment deviations as a function of the final concentration;

[0031] Fig. 13 shows cross-sectional electron micrographs of droplets of different final concentrations;

[0032] Figs. 14A and 14B are perspective views of schematic representations of voxelated structures;

[0033] Fig. 15A shows optical images of droplets configurable for forming voxelated structures;

[0034] Fig. 15B shows a schematic diagram of a multilayer structure with varying microplatelet alignment angles θ in each layer and electron micrographs of the corresponding multilayer structure;

[0035] Fig. 15C shows a schematic diagram of a 3 x 3 voxelated sample printed with varying microplatelet orientations and the electron micrograph of a cross-section of the corresponding structure after infiltration with a polymeric matrix;

[0036] Fig. 16A is a plot showing variation in electrical resistance anisotropy in a graphite structure as a function of the alignment angle θ ;

[0037] Fig. 16B is a plot showing variation in cooling rates of hBN deposits as a function

of the alignment angle θ ;

[0038] Fig. 16C is a plot showing variation in Young's modulus and Vicker's hardness of sintered titania-decorated aluminum oxide droplets as a function of the alignment angle θ ;

[0039] Fig. 16D is an electron micrograph showing a crack deflection event in a multilayer titania-decorated aluminum oxide-epoxy composite;

[0040] Fig. 17A shows electron micrograph of the cross-section of a printed graphite-titania-decorated aluminum oxide-graphite capacitor and Fig. 17B is an optical image of the same;

[0041] Fig. 17C shows the variation of measured capacitance with respect to alumina microplatelet orientations of the capacitor of Fig. 17A;

[0042] Fig. 17D shows the discharge characteristics of the capacitor of Fig. 17A;

[0043] Fig. 18A shows the stress-strain plots of a printed graphite-polydimethylsiloxane (PDMS) piezoresistive pressure sensor; and

[0044] Fig. 18B are plots of the measured electrical response of the sensors of Fig. 18A.

DETAILED DESCRIPTION

[0045] Reference throughout this specification to "one embodiment", "another embodiment" or "an embodiment" (or the like) means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearance of the phrases "in one embodiment" or "in an embodiment" or the like in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the described features, structures, or characteristics may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided to give a thorough understanding of embodiments. One skilled in the relevant art will recognize, that the various embodiments be practiced without one or more of the specific details, or with other methods, components, materials, etc. In other instances, some or all known structures, materials, or operations may not be shown or described in detail to avoid obfuscation.

[0046] The word “exemplary” is used herein to mean “serving as an example, instance, or illustration.” Any embodiment described herein as “exemplary” is not necessarily to be construed as preferred or advantageous over other embodiments. As used herein, the singular ‘a’ and ‘an’ may be construed as including the plural “one or more” unless apparent from the context to be otherwise.

[0047] Terms such as “first” and “second” are used in the description and claims only for the sake of brevity and clarity, and do not necessarily imply a priority or order, unless required by the context. The terms “about” and “approximately” as applied to a stated numeric value encompasses the exact value and a reasonable variance as will be understood by one of ordinary skill in the art, and the terms “generally” and “substantially” are to be understood in a similar manner, unless otherwise specified.

[0048] Embodiments of the present disclosure provide a product 400 formed by a method 700 of 3D printing. One example of the product 400 is shown in the electron micrograph of Fig. 1A. The product 400 includes a plurality of microstructures 110 substantially in alignment with one another. The microstructures 110 may include microplatelets. The term “microplatelet” and “microstructure” may be used interchangeably in the present disclosure to refer to a relatively thin piece of material having two opposing major surfaces. As shown in Fig. 1B, the microplatelet may be substantially in the form of a flake or a thin piece of material 114, such that the microplatelets may be described as “two-dimensional” (2-D) or substantially planar in shape. The linear dimensions of the major surfaces may be in the order of micrometers (μm). The product 400 is characterized by the plurality of microplatelets 110 being oriented with respective major surfaces substantially parallel to one another, or with the major surfaces oriented at similar angles to a substrate. Capillary action can be observed in prototypes of the product 400, i.e., the product 400 is characterized by a degree of porosity (or an ability to absorb a liquid) consistent with the presence of at least a partial air gap between pairs of neighboring or adjacent microplatelets. That is, the product 400 is formed with a plurality of microplatelets 110 in which the microplatelets 110 are spaced apart from one another, forming a corresponding plurality of gaps 130 therebetween. The microplatelets are configured to be magnetically responsive. Optionally, if a base material of the microplatelet is not magnetically responsive, the microplatelets may be functionalized to be magnetically responsive. For example, the microplatelets in Fig. 1B

are functionalized by decorating the major surfaces of the microplatelets with iron oxide particles 112. In the following, it will be understood that the terms “microplatelets” and “magnetically-responsive microplatelets” are used interchangeably for the sake of brevity. The present method may include providing (including but not limited to acquiring) microplatelets in a form in which the microplatelets are characterized by a magnetically responsive property (for example but not limited to microplatelets made of magnetic materials, graphite microplatelets coated with iron oxide, etc.). The present method may include providing magnetically responsive microplatelets by coating or decorating microplatelets with magnetically responsive materials (e.g., titania-decorated aluminum oxide, aluminum oxide, graphite, boron nitride, or any combination thereof, each of which being decorated with magnetically responsive nanoparticles). The present method may also include providing microplatelets by additionally coating or decorating microplatelets with one or more types of magnetically responsive materials, in which the microplatelets before the additional coating process were already magnetically responsive. In other words, the provision of microplatelets include providing microplatelets with a target degree of magnetic responsiveness or a selected degree of magnetic responsiveness, as will be understood from the various embodiments described herein. The microplatelets may undergo one or a plurality of magnetic responsive modifications. The microplatelets may be decorated with more than one type of magnetically responsive nanoparticles. Examples of magnetically responsive microplatelets include but are not limited to microplatelets which have been decorated with superparamagnetic iron oxide nanoparticles.

[0049] Fig. 2A is an optical image of droplets 300 formed by the method 700 of the present disclosure, using the same ink composition. Droplets 301 and droplets 302 appear to be of different shades or colors, suggesting that the microplatelets in a droplet 301 are differently oriented from the microplatelets in a droplet 302. This is verified by electron micrographs of Figs. 2A and 2B. Fig. 2A is an electron micrograph of a top view of the droplets 301 and Fig. 2B is an electron micrograph of a top view of the droplets 302. Fig. 2B shows that the product 400 can be formed with the plurality of microstructures 110 aligned in a substantially “vertical” orientation or an alignment angle of about 90 degrees relative to a substrate. Fig. 2C shows that the product 400 can alternatively be formed with the plurality of microplatelets 110 aligned in a substantially “horizontal orientation”, i.e., with an

alignment angle of about zero relative to the substrate. In other words, the method 700 can configure the orientation of the plurality of microplatelets in the product 400.

[0050] Fig. 2B also demonstrates that, surprisingly, when dried, the microplatelets can maintain the desired orientation with gaps 130 between neighboring microplatelets or adjacent microplatelets, even if the desired orientation corresponds to an alignment angle of about 90 degrees. The gaps 130 are substantially air gaps or substantially unfilled gaps. In other words, the gaps 130 do not need to be filled with filler materials in order to maintain a desired orientation. The gaps 130 remain in the product 400 upon formation of the product 400, as evidenced by the capillary behavior observed of the product 400. As shown in Fig. 2B, the product 400 may be formed with a plurality of substantially parallel channels, where each channel is flanked or defined by similarly oriented microplatelets.

[0051] Fig. 3 is a flow chart schematically illustrating the method 700 of forming the product 400 by 3D printing, according to embodiments of the present disclosure. The term “3D printing” (three-dimensional printing) and “additive manufacturing” may be used interchangeably. Preferably, the method 700 includes an ink-based 3D printing method, such as a method of drop-on-demand (DOD) 3D printing. Preferably, the method 700 includes selecting or providing an aqueous slurry ink, in which the ink includes magnetically responsive microplatelets in an aqueous carrier (705). Optionally, this may include, before printing, coating each of the plurality of microplatelets with superparamagnetic iron oxide nanoparticles. Preferably, the method 700 includes depositing an amount of ink in the form of one or more droplets 300 on a substrate 230 or on a previously formed part (710). For the sake of brevity, in the present disclosure, reference to the term “substrate” may be understood to apply similarly to a previously formed part. The method 700 includes subjecting the deposited ink (droplet of ink) 300 to a magnetic field before the deposited ink fully dries (720). The method 700 includes providing a period of drying after the deposition of the deposited ink, during which the deposited ink is permitted to fully dry or partially dry (730). If a second/subsequent droplet of ink 300 is to be deposited on or adjacent to an earlier deposited/a first droplet of ink, the second droplet of ink 300 is preferably deposited before the first droplet of ink has fully dried. After the deposited ink has substantially dried or fully dried 400/300d, the method 700 optionally includes introducing a matrix material 140 to the gaps 130 between the microplatelets. The method 700 optionally includes selecting or

configuring a combination of ink, substrate, and/or printing parameters to form a plurality of microplatelets substantially aligned to a desired alignment angle (705). Optionally, the method 700 may include infiltrating or filling the gaps 130 with a filler such as a polymer or epoxy resin (740). The introduction of the polymer occurs after at least some liquid has evaporated away from the printed droplet, so that the gaps 130 or capillary channels in between the microplatelets 110 are un-filled or at least partially un-filled (132), and capable of receiving the polymer.

[0052] The method 700 includes subjecting the deposited ink 300 to a rotating magnetic field 222, in which the magnetic field is configured to rotate about an axis of rotation 80. Figs. 4A and 4B schematically illustrate a configuration of the magnetic field for the purpose of aligning the microplatelets in a target alignment angle. The orientation of the axis of rotation 80 may be selected according to a target alignment angle of the microplatelets. In some examples, each microplatelet 110 may generally define a respective longitudinal axis 118 that is substantially parallel to a major surface of the microplatelet. The alignment angle or the microplatelet alignment angle may be defined as an angle between the longitudinal axis 118 and a plate of the substrate 230. The alignment angle θ may alternatively be defined as an angle between a major surface of the microplatelet and the substrate. In some examples, the axis of rotation 80 of the magnetic field (Fig. 4A) may be oriented substantially parallel to a target alignment angle (Fig. 4B). In the experiments conducted, the magnetic field is rotated at a frequency of at least about 1 Hz (hertz). The period of time during which a deposited ink is subjected to the rotating magnetic field is referred to as the alignment time. In the experiments, the alignment time can be shorter than about 5 seconds. For the purpose of illustrating small features, the schematic diagram of Fig. 4B is not to-scale. In an actual product 400, the aligned microplatelets 110 are observed to be close to one another such that they are able to maintain a target alignment angle without further support from a polymer matrix, and yet spaced apart to exhibit capillary action or a degree of porosity in drawing other materials into the gaps 130.

[0053] The method 700 may include selecting a strength of the magnetic field to apply during the alignment time. Figs. 5A and 5B are electron micrographs of cross-sections of products 400 formed using the method 700, using droplets deposited on similar glass substrates. The ink used in both experiments of similar ink composition of initial

concentration of 5 vol%. In both experiments, the target alignment angle is 90 degrees, i.e., with the microplatelets oriented “vertically” relative to the substrate. In the method of Fig. 5A, the magnetic field strength was 7.5 mT (milli Tesla) and in the method of Fig. 5B, the magnetic field strength was 15 mT. It can be observed that the microplatelets of Fig. 5B are oriented more closely to the target alignment angle than those of Fig. 5A. Fig. 5C compares experimental values with estimated values of threshold magnetic field strength. The agreement of the experimental values with the calculated estimates suggests that the droplet can be described in terms of a combination of mathematical models for capillary flows in sessile droplets and magnetic torques during magnetic alignment. Within a drying sessile deposit or droplet 300, capillary flows and resulting torque forces (τ_{cap}) may act on the microplatelets in radially outward directions. Preferably, the magnetic field strength applied is stronger than a threshold magnetic field strength (B_{crit}) to counteract the capillary flow-induced torque forces. The capillary flows within a droplet are in turn dependent on the contact angle of the droplet and a rate at which the solvent or the liquid in the droplet evaporates.

[0054] The method 700 may include selecting a combination of ink composition and substrate material such that the ink deposited on the substrate 230 forms a droplet 300 characterized by a contact angle. The contact angle may affect the final alignment of the microplatelets. A relatively low contact angle does not preclude the microplatelets from aligning with a relatively high alignment angle. A range of different alignment angles can be obtained using the present method 700. Fig. 6A is an image of a droplet 300 deposited on a copper substrate, in which the droplet 300 is characterized by a contact angle of about 79.7° (degrees) or 79.8°. Fig. 6B shows an electron micrograph of a bottom edge of the product 400 resulting from the droplet of Fig. 6A. The alignment angle of the microstructures in Fig. 5B is relatively large. In another example, an ink of a similar composition is deposited on a substrate of glass. Fig. 7A shows another example in which the droplet 300 is characterized by a contact angle of about 37.8° (degrees) and as shown in Fig. 7B, the product 400 resulting from the droplet 300 includes microplatelets with a different alignment angle.

[0055] The method 700 may include selecting any one or more of the following: an ink composition, an initial ink concentration, and a volume of ink in one droplet as it is deposited

(before significant evaporation or drying as occurred).

[0056] The ink composition consists essentially of microplatelets 110 in a liquid 120. The liquid 120 may be an aqueous solution or an organic solvent, including but not limited to an alcohol solvent, a non-alcohol solvent, or any combination or mixture thereof. The liquid 120 is selected to be one in which the microplatelets 110 may be dispersed or suspended without chemically reacting therewith, and the liquid 120 is also selected to be one which can evaporate from the deposited droplets (e.g., under mild temperature and pressure). Preferably, the liquid 120 is water. Optionally, a binder may be included to provide the ink with a suitable viscosity for 3D printing. One example of the binder includes but is not limited to polyvinylpyrrolidone (PVP) aqueous solution of 1 wt%. Preferably the ink composition does not include photocurable polymer inks.

[0057] The ink may be characterized by an initial concentration, e.g., in terms of the loading of microplatelets (solid) in a volume of the ink at the time of depositing a droplet (before significant drying of the deposited droplet has occurred). Fig. 8 shows electron micrographs of cross-sections of deposited alumina microplatelets using droplets of increasing volume, and the electron micrographs of different types of microplatelets printed with droplets of the same volume.

[0058] The ink may be described as a slurry which may require agitation or stirring to feed a series of droplets of relatively consistent ink concentration. The microplatelets may be selected from magnetically responsive materials. Microplatelets which are originally not magnetically responsive may be decorated with magnetic particles thereon. Examples of microplatelets include but are not limited to one of the following or any combination of more than one of the following: aluminum oxide microplatelets, titania-decorated aluminum oxide microplatelets, graphite particles, boron nitride particles, etc. Examples of inks according to embodiments of the present disclosure are listed in Table 1 below.

Table 1: Examples of inks

Microplatelets	Microplatelet dimensions (average)	Volume % of microplatelets	Weight % of binder	Liquid	Magnetic field strength (mT)
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Aluminum Oxide	Diameter: ~10 to ~20 μm Thickness: ~200 nm	5% to 7%	1wt% PVP	Water	15
Graphite	Diameter: ~4 μm to ~7 μm Thickness: ~300 nm	10%	1wt% PVP	Water	15
Boron Nitride	Diameter: ~7 μm to ~12 μm Thickness: ~300 nm	10%	1wt% PVP	Water	15

[0059] The microplatelets 110 may be characterized by anisotropic material/physical properties. In other words, the microplatelets 110 may be configured with direction-dependent material/physical properties. For example, the thermal conductivity of a microplatelet 110 along the longitudinal axis 115 may be higher than the thermal conductivity along a lateral axis 119 (the lateral axis being substantially transverse to the longitudinal axis). For the purpose of the present disclosure, the microplatelets 110 may be described as exhibiting anisotropic properties along the respective longitudinal axis.

[0060] The method 700 may include selecting an ink having an initial concentration (ϕ_i). In the present disclosure, ink concentrations refer to the amount of microplatelets in a unit of the ink and may be expressed in terms of the volume percent of microplatelets. As illustrated below, for a selected combination of ink composition and substrate material, the initial concentration of the ink may be used to determine the achievable alignment angle (of the microplatelets relative to a plane of the substrate) and the density of the microstructures in the final product 400.

[0061] Figs. 9A-9D are electron micrographs of cross-sections of products 400 formed using the same method 700 using with inks of different initial concentrations of 1.75 vol%, 2.5 vol%, 3.5 vol%, and 5 vol% respectively. For the sake of convenient reference, an optimum ink concentration refers to the initial ink concentration that produces the smallest alignment deviation from the target alignment angle (target alignment orientation). In this example, the vertical line in each image indicates the target alignment orientation, and the arrowed line indicates the actual alignment orientation. All other parameters being equal, the optimum ink concentration in this case is around 3.5 vol%, as the corresponding microplatelets show a microplatelet alignment orientation that is closest to the target alignment orientation. The optimum ink concentration can also be defined in terms of the

initial ink concentration that produces the highest density of the microstructures (microstructure density). In this example, the product 400 corresponding to an initial ink concentration of 3.5 vol% shows the most amount of microstructures packed in a unit space. The method 700 does not preclude the selection of an initial ink concentration that is different from the optimum ink concentration. Rather, by selecting the initial ink concentration, a product with a target microstructure density and a target alignment deviation (relative to the orientation of the rotating magnetic field) can be controllably reproduced for a given ink composition and substrate material.

[0062] The maximum concentration refers to the maximum microplatelet content that can be suspended or dispersed in a unit volume of the ink. Using conventional methods, the product with the highest concentration of solid content is the product 3D printed using the ink or the extrudate material with the maximum concentration. Unexpectedly, the method 700 according to embodiments of the present disclosure makes it possible to form products 400 in which the density of the microplatelets (also referred to as “final concentration” (ϕ_f) of the microplatelets) is far higher than the maximum concentration (ϕ_{max}) of the microplatelets in the ink. This opens up exciting new possibilities, such as a broader range of applications and products with higher levels of performance, for products formed using the present method 700 are not constrained by ϕ_{max} .

[0063] To aid understanding and not to be limited by the model described, the terms initial concentration ϕ_i and final concentration ϕ_f are described with reference to Figs. 10A to 10D. Fig. 10A is a schematic diagram illustrating a droplet of ink upon being printed or deposited. The concentration of the microplatelets in the droplet at this time instant is referred to as the initial concentration ϕ_i . Physically, there is a limit to the amount of microplatelets that can be loaded in the liquid, and the initial concentration ϕ_i is limited by the maximum concentration ϕ_{max} for the ink composition. Fig. 10B represents an alignment time when the rotating magnetic field is applied to align the microplatelets 110 in the droplet 300.

[0064] In the course of the experiments, it was observed that deposition of a droplet 300/300a with an ink composition that consists essentially of microplatelets 110 in an aqueous solution 120 provides the suspended microplatelets with the freedom to align with

the applied magnetic field (Fig. 10B, 300b), while concurrently sedimentation of the microplatelets occurs with evaporation of liquid from the droplet (Fig. 10c). In embodiments of the present disclosure, the ink composition and/or the ink concentration are formulated/selected to promote sedimentation. Sedimentation refers to a settling of the solid parts of the ink such that the microparticles are mostly found at the base of the droplet 300c/300d. The present disclosure takes a radically different approach from tradition. Conventionally, printing inks are formulated to avoid sedimentation because sedimentation is well known to result in uneven printing quality.

[0065] Fig. 10D is a schematic diagram illustrating the droplet 300 after a time of concurrent alignment and sedimentation, i.e., the droplet 300 being an at least partially dried droplet 300d. It is believed that this process enables the formation of a final concentration ϕ_f that is much higher than the maximum concentration ϕ_{max} . Further drying of the droplet may not increase the concentration or density of the microplatelets at the base of the droplet. The final concentration is thus used as an indicator of how densely the microstructures are packed in the fully dried product, or an indicator of a resolution of the aligned microstructures and/or channels formed therebetween. Advantageously, further evaporation of the liquid will result in the formation of at least partially unfilled gaps (air gaps) 130 between the microplatelets. Surprisingly, the microstructures remain packed and in alignment, i.e., the product remains characterized by the final concentration ϕ_f , even when the product is no longer under the rotating magnetic field and/or when the product is fully dried.

[0066] The present method 700 does not preclude the addition of a polymer to form a matrix surrounding the microplatelets. Optionally, according to some embodiments of the present disclosure, after sufficient liquid has evaporated away to expose the at least partially unfilled gaps 130 between the microplatelets, a polymer or a matrix material may be introduced to the partially or fully fill the gaps 130. Depending on the polymer selected, curing may be performed such that a composite of the microstructures embedded in the polymer matrix is formed. Optionally, before the polymer matrix is provided, the method 700 includes subjecting the printed droplet of ink having the at least partially un-filled gaps 130 to a heat treatment to bind the plurality of microplatelets, such that the plurality of microplatelets

consolidate into an at least partially porous inorganic scaffold 400/500. Consolidation refers to the forming of a unitary or integrated structure (e.g., a scaffold) 400/500 from previously separate particles (e.g., microplatelets).

[0067] In another example, titania-decorated alumina (titania-decorated aluminum oxide) microplatelets are used to illustrate the effect of initial concentration (ϕ_i) on ink densification and microplatelet alignment. titania-decorated aluminum oxide microplatelets have a reflective platelet surface which allows easy identification of alignment. The drying behavior of a single droplet was used as the basis for evaluation. Due to the relatively large platelet dimensions, the maximum concentration (ϕ_{max}) is approximately 10.5 vol%. Ink composition deposits/droplets with initial concentration (ϕ_i) of 5 vol% were deposited on two different substrates: copper and glass, respectively. The samples were subjected to magnetic fields similarly oriented in the vertical direction. The deposited profiles were observed using an optical microscope as shown in Fig. 11A. It can be seen in Fig. 11A that the shiny titania-decorated aluminum oxide microplatelets initially dispersed within the droplet begin to vertically align to the magnetic field. After some time, the titania-decorated aluminum oxide microplatelets start to exhibit sedimentation. The profile of the dried droplet shows a relatively flatter upper surface, in contrast to the hemispherical or dome profile of a newly deposited or printed droplet. This is consistent with the evaporation of the liquid and the occurrence of sedimentation.

[0068] By tracking the volume of the droplet, the change in the ink concentration (concentration of microplatelets) may be estimated. The microplatelet concentration increased with time from the initial concentration (ϕ_i) of 5 vol% to a final concentration (ϕ_f) of 17.5 vol% for the copper substrate and 13 vol% for the glass substrate. These values of final concentration (ϕ_f) are higher than both the initial concentration (ϕ_i) of 5 vol% and the maximum concentration (ϕ_{max}) of 10.5 vol%. Table 2 shows some exemplary data for titania-decorated aluminum oxide microplatelets (with relatively large sizes, diameter of $\sim 15\text{-}20\text{ }\mu\text{m}$).

Table 2

Initial concentration (vol%)	1.75	2.5	3.5	5	7
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Final concentration (vol%)	11.3	13.6	15.6	17.8	22.3
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[0069] The difference in the final concentrations (ϕ_f) observed between the copper substrate and glass substrate may be attributed to differences in the contact angles. This was verified by depositing the same ink composition onto gold-sputtered glass substrates (sputtered Au) which formed droplets of a lower contact angle than the copper substrate and the glass substrate as shown in Fig. 11B. The final concentration (ϕ_f) increases with the contact angle. This suggests that some embodiments of the method 700 may include selecting the material of the substrate to controllably form products of the desired final concentrations.

[0070] Experimental values for the titania-decorated aluminum oxide inks of different final initial concentrations and the corresponding final concentrations are shown in Fig. 11C. The titania-decorated aluminum oxide microplatelet ink is characterized by an optimum ink concentration. For initial concentrations beyond the optimum ink concentration, the final concentration does not increase. In the case of the titania-decorated aluminum oxide microplatelet ink, the highest achievable final concentration (ϕ_f) is around 22.5 vol%, corresponding to an optimum concentration or initial concentration (ϕ_i) of 7.5 vol%.

[0071] The product 400 according to embodiments of the present disclosure may advantageously be characterized by a relatively high final concentration that is associated with good alignment of the microplatelets. This is shown in Fig. 12 which plots the experimental results of microplatelet alignment deviation for different final concentrations (ϕ_f).

[0072] The electron micrographs in Fig. 13 illustrates the displacement of the titania-decorated aluminum oxide microplatelets under the action of capillary forces. For final concentrations (ϕ_f) greater than about 14 vol%, the titania-decorated aluminum oxide microplatelets are well aligned to the target alignment orientation. It is observed that the sustainability of the alignment angle is more dependent on the final concentration (ϕ_f) than on the choice of substrate material.

[0073] In some embodiments, the size of the microplatelet 110 may also have an effect on

the achievable final concentration (ϕ_f) of the microplatelets 110. For example, microplatelets 110 with smaller sizes may achieve a higher final concentration (ϕ_f).

[0074] According to another aspect of the present disclosure, the product 400 formed may include a voxelated structure 500. Fig. 14A is a schematic diagram of a voxelated structure 500. The structure 500 may be formed from printing a plurality of ink droplets 400a/400b/400c sequentially on a substrate. Adjacent droplets may be formed with differently oriented microplatelets. For example, each of the ink droplets 400a/400b/400c may include respective microplatelets 110a/110b/110c with differing alignment angles. The ink composition deposits 400a/400b/400c may be deposited to form a 2D voxelated structure 500 (with a linear dimension corresponding to a single droplet), or a 3D voxelated structure 500 (with linear dimensions corresponding to multiple droplets) as shown in Fig. 14B.

[0075] In some embodiments, the structure 500 may include a plurality of first microplatelets 110a magnetically aligned along a first direction. Each of the first microplatelet 110a forms an air gap with an adjacent first microplatelet 110a, to provide a porous structure 500 with a first anisotropic property along the first direction. The structure 500 may further include a plurality of second microplatelets 110b magnetically aligned along a second direction. Each of the second microplatelet 110b forms an air gap with an adjacent second microplatelet 110b, to provide the porous structure 500 with a second anisotropic property along the second direction. In some embodiments, a polymer matrix is disposed between adjacent first microplatelet 110a and second microplatelet 110b to hold them together.

[0076] To create voxelated structures 500, consecutive deposition of droplets 400a/400b/400c may be carried out to form a continuous structure 500. Preferably, there is an interval provided between each deposition to provide for newly printed droplets to bind with a previously printed droplet. Preferably, a droplet 300 is printed adjacent a previously printed droplet before the previously printed droplet is entirely dry. In some embodiments, the method 700 may include depositing a second row of ink droplets 300 on a previously deposited row of ink droplets, before the previously deposited row of ink droplets has completed evaporation. The drying time of each ink droplet deposit may be modulated by

the provision of an external heating or cooling source and/or by way of controlling the environmental humidity. Table 3 shows some illustrative and non-limiting examples of drying time for titania-decorated aluminum oxide microplatelets.

Table 3: Drying time for titania-decorated aluminum oxide microplatelets

Droplet volume (microliter)	Drying time without heating (minutes)	Drying time with heating ~50°C (minutes)
2	4.67	1.33
4	10.5	3
7	18	4.5

[0077] The product 400/500 formed by the method 700 may include one or more units 410. Each of the one or more units 410 includes a plurality of microplatelets 110 disposed on a substrate 230 or on another of the one or more units 410. The microplatelets 110 are configured to be magnetically responsive. The microplatelets 110 of a same unit 410 are in generally in alignment with another and aligned with about the same alignment orientation. Neighbouring or adjacent ones of the microplatelets 110 in alignment define an at least partially un-filled gaps 130 such that the microplatelets 110 in the same unit 410 define a corresponding plurality of at least partially un-filled gaps 130.

[0078] Each of the one or more units 410 may be formed by ink that is characterized by a final concentration of the microplatelets 110. The final concentration in a unit 410 may be higher than a maximum concentration. The maximum concentration of the ink corresponds to the concentration of the ink when it is saturated with the plurality of microplatelets 110. The ink has an initial concentration prior to forming the one or more units 410. In some examples, the initial concentration may be lower than the maximum concentration. The final concentration in a unit 410 may be higher than the initial concentration.

[0079] Optionally, the product 400/500 may include a polymer disposed in the plurality of the at least partially un-filled gaps 130 to form a composite. The one or more units 410 may be characterized by at least one anisotropic property. Optionally, before polymer infiltration in the partially un-filled gaps 130, the product 400/500 may be submitted to a heat treatment to bind the plurality of microplatelets 110. The printed droplet 300 of ink or the plurality of microplatelets 110 consolidate to form a composite or to yield a porous self-standing structure (e.g., an inorganic scaffold) 400/500.

[0080] The plurality of microplatelets 110 may be selected from one of the following: titania-decorated aluminum oxide microplatelets decorated with superparamagnetic iron oxide, aluminum oxide microplatelets decorated with superparamagnetic iron oxide, graphite microplatelets, boron nitride microplatelets decorated with superparamagnetic iron oxide, and a combination of any thereof. Preferably, each microplatelet is made magnetically responsive prior to its employment in the composition. Said magnetically responsive modification can be plural, including coating with superparamagnetic iron oxide nanoparticles. Before the printing, each of the plurality of microplatelets may be decorated with superparamagnetic iron oxide nanoparticles. The terms “coated” and “decorated”, or the like, are used interchangeably, and refer to the surfaces of a microplatelet having magnetically responsive material adhered, adsorbed, attached, or otherwise disposed thereon.

[0081] Fig. 15A shows the different orientations achievable in an individual ink droplet 300, to form the basis 410 of a voxelated structure 500. The electron micrographs of Fig. 15A show the surface morphology (middle column of images) and the cross-section (right column of images) of the corresponding ink droplets. The arrows on the surface morphology images represent the normal vector of the microplatelets, which is indicative of their lateral directions. The cross-sectional electron micrographs show that the microplatelet alignment angle θ may be varied as desired from about 0° to about 90° . The microplatelet orientation in the lateral direction may also be varied as shown in the surface morphology images.

[0082] In some embodiments, the magnetic alignment of microplatelets 110 may produce a substantially flat top surface for building additional voxelated structures thereon, although this is not necessary in all cases. The alignment angle of a previously printed layer 510 does not prevent a subsequent or additional layer 510 of droplets from being printed therein. Preferably the subsequently printed droplets 300/layers 510 are printed adjoining previously printed droplets/layers before the previously printed droplets/layers have completely dried. In other words, a subsequently printed droplet is preferably printed before evaporation has formed gaps (capillary channels) in a neighboring previously printed droplet, or only after the gaps have been filled by impregnation with a filler material. This is to mitigate the capillary effect of the porous dried deposits/structures and minimize disruption to the alignment of microstructures in the subsequently deposited droplet.

[0083] Fig. 15B shows a schematic diagram of a multilayer structure with varying microplatelet angles θ in each layer. Fig. 15B also shows the corresponding electron micrograph of a cross-section of the printed structure after infiltration with a resin. The structure was printed with repeating microplatelet alignment angles in a predetermined order of 0° , 45° , -45° and 90° . In this example, the printed structure was infiltrated with an epoxy to form a composite material. From the micrograph of the cross-section, the microplatelet alignment was unperturbed by the infiltration and the varying alignment was apparent in each distinct layer. By printing such micropillar structures adjacent to each other, fully voxelated structures may be formed. Fig. 15C illustrates a demonstration of printing a 3×3 unit voxelated structure with alternating 0° and 90° aligned microplatelet voxels. The voxels may be printed laterally or vertically before the existing structure completely dries, in prevention of the buildup of capillary pressure.

[0084] As the printed voxelated structure 500 is formed by individual ink composition deposits 300, the lateral and vertical (height direction) printing resolution is determined by the dimensions of the dried ink composition deposit 400. This may be controlled by the contact angle of the ink composition with the substrate as well as the volume dispensed in each deposit. An increase in contact angle decreases the ink composition deposit diameter and increases the ink composition deposit height. The volume of the ink composition deposit may be varied by changing the nozzle diameter and the input pressure of the nozzle. A larger ink droplet volume may be used to increase both the diameter and height of the deposit. It may be appreciated that the final concentration of microplatelets is not affected by or independent from the deposit volume. As an example, the lateral and vertical printing resolution achievable using the titania-decorated aluminum oxide microplatelets based ink composition on a copper substrate is approximately 0.7 millimeter (mm) and 50 micrometers (μm) respectively. The printing resolution may theoretically be improved by tens of micrometers (μm) using nozzles with a smaller diameter or by incorporating techniques such as electrohydrodynamic printing. In some embodiments, multiple ink compositions may be deposited or printed, i.e., by use of multiple nozzles, to create multimaterial structures with individual layers or voxels comprising different microplatelet orientations. A variety of microplatelets dimensions and materials may be deposited to form a multimaterial structure. In one example, individual deposits of magnetically responsive

graphite microplatelets, magnetically responsive hexagonal boron nitride (hBN) microplatelets and magnetically responsive copper microplatelets collective form a structure. Despite having different physical properties such as dimensions and densities, the microplatelets in each ink composition deposit may be independently deposited and magnetically aligned. Smaller microplatelets like graphite microplatelets and hBN microplatelets require a higher initial concentration to achieve alignment and could attain a higher final concentration, for example around 50 vol%. In addition, anisotropic nature of these functional microplatelets may be harnessed to provide anisotropic properties in the 3D deposited structures. A variety of printed structure properties may be obtained by the different combination of microplatelet alignment angle and microplatelet material properties.

[0085] Fig. 16A illustrates an example of tunable electrical properties achieved by printing graphite droplets with varying alignment angles θ . In the experiments, graphite deposits with varying alignment angles θ of 0° , 20° , 45° , 70° , 90° and diameter of ~ 4 mm and heights of ~ 0.2 mm were printed on glass substrates. Three samples of each alignment angle were printed, and the electrical resistance measurements were taken using a two-probe multimeter. The electrical resistances along the directions x and y are denoted by R_x and R_y respectively. The plot of a ratio R_x/R_y against θ shows that R_x/R_y increases as the alignment angle θ of the graphite microplatelets is increased from 0° to 90° . This is consistent with the anisotropic properties of a graphite microplatelet, e.g., it is characterized by a higher conductivity parallel to the microplatelet surface than through its thickness. As the graphite microplatelet orientation changes, where the alignment angle increases from 0° to 90° , the relative degree of conduction through the microplatelet thickness increases for R_x . Conversely, R_y remained relatively constant regardless of alignment angle θ which causes R_x/R_y to increase with alignment angle θ .

[0086] Fig. 16B illustrates another example of tunable anisotropic thermal properties of hexagonal boron nitride (hBN) microplatelet deposits/droplets. The microplatelet of hBN has a higher thermal conductivity along the surface of the microplatelet than in a direction directed through the thickness of the microplatelet. Hexagonal boron nitride (hBN) droplets with alignment angle θ at 0° and at 90° were printed on silicon substrates to emulate their use as thermal management material in electronics. The samples were heated to 70°C and

cooled down to room temperature, with the temperature and cooling rates captured using a thermal imaging camera. Fig. 16B shows the different cooling rates for samples with different microplatelet alignment angles. This suggests potential applications for engineering products with different thermal properties.

[0087] In another example as shown in Fig. 16C, titania-decorated aluminum oxide deposits demonstrated tunable mechanical properties. Here, titania-decorated aluminum oxide microplatelet structures were printed and aligned at different alignment angles θ before being sintered at 1600°C to form ceramic samples. As shown in Fig. 16C, both the Young's modulus and Vicker's hardness of the ceramics increase with alignment angle θ , from 22 GPa and 0.26 GPa respectively, for horizontally aligned samples to 60 GPa and 0.68 GPa respectively, for vertically aligned. This demonstrates the feasibility of tunable mechanical stiffness and resistance to elastic deformation solely through the control of microplatelets alignment angles.

[0088] Referring to Fig. 16D, ceramic-polymer composites with varying microplatelet orientations in adjacent layers may be used to engineering material properties of the composite. A crack that propagates at an interface between the microplatelet and a polymer matrix filler would change direction when crossing between layers (of differently oriented microplatelets). This increases the toughness of the structure as energy is dissipated by the increased crack length and debonding at the microplatelet-matrix interfaces.

[0089] As an example of measuring the mechanical properties of sintered titania-decorated aluminum oxide structures, titania-decorated aluminum oxide droplets with varying alignment angles were printed onto alumina plates as the substrate to form micropillars with diameter of approximately 4 mm and height of 1 mm. Once the droplets were dried, they were sintered in a high temperature furnace first at 500 °C for 1 hour for binder removal and then at 1600 °C for 2 hours for sintering. Once the samples were cooled back to room temperature, they were cold mounted in an epoxy resin for subsequent preparation for further characterization. The mounted samples were first grinded using sandpapers with increasing grits of 400, 800, 1200 and 2400. This was followed by polishing using OPS solution. The mechanical properties of the polished samples were characterized using nanoindentation and Vicker's hardness tester. The nanoindentation tests were performed

using a Berkovich tip with a loading rate of 1 mN/s to a maximum load of 100 mN and dwell time of 10seconds. 20 indents were made on each sample. For the Vicker's hardness test, a load of 1 kg was applied for 10seconds. 9 indents were made on each sample.

[0090] In one illustrative and non-limiting example, a parallel plate capacitor was fabricated using the method 700 of the present disclosure. The capacitor may be formed in layers, with each layer formed according to the present method 700. As shown in Fig. 17A, the product includes conductive graphite layers sandwiching a dielectric titania-decorated aluminum oxide layer. The dielectric layer may be described as a scaffold of second microplatelets. The second microplatelets are configured to be magnetically responsive. The second microplatelets are at an alignment angle relative to a plate of the interface between the dielectric layer and any of the two graphite layers. Each of the graphite layer has an alignment angle θ of 90° to ensure high conductivity between the dielectric layer and the electrical contacts. From the electron micrographs of Fig. 17A and the optical image of Fig. 17B (insert), the graphite layers and titania-decorated aluminum oxide layer are clearly distinguishable. The capacitance of the printed capacitor (~ 3 mm diameter, < 1 mm high) is in the range of 0.1 nano-farad (nF). The capacitance of parallel plate capacitors is determined by the area of the capacitor (A), dielectric constant (ϵ) and height of the dielectric layer (d) through the relation:

$$C = \frac{\epsilon A}{d} \quad (\text{Equation 1})$$

[0091] The height and alignment of the titania-decorated aluminum oxide layer may be tuned to increase the resultant capacitance. The capacitance decreases with increasing titania-decorated aluminum oxide layer height as shown in Fig. 17C. Capacitor devices with vertically aligned titania-decorated aluminum oxide layer (second alignment angle θ of about 90°) consistently exhibits a higher capacitance compared to devices with horizontally aligned titania-decorated aluminum oxide layer (alignment angle θ of about 0°).

[0092] The capacitors were further tested for their discharging behavior to verify their functionality, by using a resistance-capacitor (RC) circuit. The capacitors were first charged using a power supply and then discharged while monitoring the potential difference across the respective capacitors. An array of capacitors with titania-decorated aluminum oxide

thickness down to ~70 micrometer (μm) was printed to achieve a combined capacitance of up to ~120 nF. Fig. 17D illustrates two discharging curves for different combinations of RC values. The discharging results match the theoretical behavior described by:

$$\frac{V}{V_0} = e^{\frac{-t}{RC}} \quad (\text{Equation 2})$$

where V is the voltage across the capacitor, V_0 is the voltage across the charged capacitor, R is the resistance of the circuit and C is the capacitance of the capacitor.

[0093] The results demonstrate that the present method 700 is an effective way of performing multimaterial printing with good control on the deposition of different materials to create functionalities. In addition, the results highlight the strength of microstructural control in improving capacitor device performances. The capacitance may be further boosted by using microplatelets with higher dielectric constant (ϵ) such as barium titanate (BaTiO_3) in the dielectric layer, or by using ink compositions that lead to higher final concentration (ϕ_f). Aside from the capacitance, the microstructure may also be used to tune other aspects of the capacitor, such as the breakdown voltage. As grain boundaries are known to impede dielectric breakdown, samples may be configured with a dielectric layer oriented at the second alignment angle θ of 0° for a higher dielectric strength.

[0094] Embodiments of the present method were successfully implemented to fabricate functional arrays of microstructures as an active layer for a piezoresistive device, such as a piezoresistive pressure sensor. In these illustrative and non-limiting examples, arrays of graphite microplatelets were formed using the method 700. After the porous product 400 is formed, the gaps between the graphite microplatelets were infiltrated with polydimethylsiloxane (PDMS). The composite structure may be sandwiched between electrodes (e.g., formed of conductive layers such as copper tapes, etc.)

[0095] Examples of the piezoresistive pressure sensor with different sensitivities were fabricated by forming microstructures of different microplatelet alignment angles. As shown in the stress-strain graphs of Fig. 18A, a stiffer structure can be obtained by configuring the alignment angle θ to be about 90° , and a less stiff structure can be obtained by configuring the alignment angle θ at about 0° . The printed structure is highly elastic and can exhibit

elastic deformation under deformation pressures of up to 1.5 MPa (mega Pascals), as shown by the unloading curves of Fig. 18A. In other experiments, the electrical response from small, applied pressures are observed. The piezoresistive device exhibited consistent and repeatable changes in resistance in experiments to verify its reliability.

[0096] The piezoresistive pressure sensor was further tested with a wider range of applied pressures, applying an increasing pressure to the sensor while monitoring the electrical resistance. The sensitivity, S of the sensor may be calculated using the following formula:

$$S = \frac{\Delta I / I_0}{\Delta P} \quad (\text{Equation 3})$$

where I_0 is the current through the sensor material when no pressure is applied and ΔI is the change in the current through the sensor when a pressure of ΔP is applied. Fig. 18B shows the measured electrical response of the piezoresistive sensors with different alignment angles of the microstructures. The sensitivity of the substantially horizontally aligned samples (alignment angles about 0 degrees) was approximately 0.92 kPa^{-1} , which is higher than that of the substantially vertically aligned samples (alignment angles about 90 degrees) with a sensitivity of 0.42 kPa^{-1} . The conventional flexible piezoresistive sensors typically work within a limited pressure range of $<2.5 \text{ kPa}$. Advantageously, the piezoresistive pressure sensor of the present has a far wider sensing range up to 350 kPa , enabling its use in a broader range of applications. This is possible due to high microplatelet content of the printed product and its structures, such that they are characterized by high strength and robust mechanical properties and can withstand high pressures without being damaged.

[0097] In some examples, the piezoresistive sensors may be tuned based on required performances. For instance, the sensitivity of the sensors may potentially be increased by decreasing the graphite microplatelet loading, which may bring the composite material closer to a percolation threshold to create larger variations in resistance. At the same time, a lower graphite microplatelet content may enable the resulting structure to be more compliant, increasing the pressure-induced strain, which further increases the resistance change with applied pressure. In addition, the microstructure and device geometry may also be adapted to make the sensor more responsive to other types of stress such as shear and bending stresses.

[0098] It can be understood from the above description that, given the amount of magnetic response of the microplatelets 110 used and their dimensions, an optimum ink can be produced to achieve the desired/target orientation/alignment by using the process/method 700 presented herein. This can be achieved by tuning the slurry concentration, the magnetic field strength, and the rotation frequency of the magnetic field. In other words, the present disclosure provides a method of 3D printing, in which the method includes configuring an ink composition or preparing the ink. The ink includes a slurry of microplatelets 110 in a liquid 120, in which the microplatelets are magnetically responsive and characterized by a degree of magnetic responsiveness and a microplatelet size. The method 700 includes printing a droplet 301 of the ink and subjecting the droplet 301 to a rotating magnetic field. The rotating magnetic field may be characterized by a magnetic field strength and a rotation frequency. The method 700 includes providing a period of drying in which at least a portion of the liquid is evaporated from the droplet 301 to form an at least partially dried droplet. The at least partially dried droplet includes an array of the microplatelets oriented at an alignment angle, in which the array of the microplatelets 110 is in alignment and define a corresponding plurality of at least partially un-filled gaps 130 between neighbouring ones of the microplatelets 110. The alignment angle of the microplatelets 110 in the product 400 formed is configurable by controlling one or more of the slurry concentration, the magnetic field strength, and the rotation frequency. The slurry concentration corresponds to a quantity of the microplatelets 110 in a unit 410 of the ink prior to the printing. Optionally, the at least partially dried droplet has a final concentration, and wherein the final concentration is higher than a saturated slurry concentration, the saturated slurry concentration corresponding to a maximum quantity of the microplatelets in the unit 410 of the ink prior to the printing. Optionally, prior to the period of drying, the droplet 301 has an initial concentration that is lower than the saturated slurry concentration. Advantageously, the at least partially dried droplet has a final concentration that can be higher than the slurry concentration.

[0099] All examples described herein, whether of apparatus, methods, materials, or products, are presented for the purpose of illustration and to aid understanding and are not intended to be limiting or exhaustive. Various changes and modifications may be made by one of ordinary skill in the art without departing from the scope of the invention as claimed.

CLAIMS

1. A method of 3D printing, the method comprising:
 - printing a droplet of ink, the ink including a plurality of microplatelets in a liquid, the plurality of microplatelets being configured to be magnetically responsive;
 - subjecting the printed droplet of ink to a rotating magnetic field; and
 - providing a period of drying in which at least a portion of the liquid is evaporated from the printed droplet of ink to form an at least partially dried droplet, the at least partially dried droplet being characterized by the plurality of microplatelets being in alignment with one another, wherein the plurality of microplatelets in alignment define a corresponding plurality of at least partially un-filled gaps between the plurality of microplatelets.
2. The method according to claim 1, wherein the at least partially dried droplet has a final concentration of the microplatelets, and wherein the final concentration is higher than a maximum concentration of the droplet, wherein the droplet at the maximum concentration is saturated with the plurality of microplatelets.
3. The method according to claim 2, wherein prior to the period of drying, the droplet of ink has an initial concentration that is lower than the maximum concentration.
4. The method according to claim 2, wherein the at least partially dried droplet has a final concentration that is higher than the initial concentration.
5. The method according to any one of claims 1 to 4, further comprising: providing a polymer after forming the at least partially un-filled gaps, wherein the polymer is received by the at least partially un-filled gaps to form a composite.
6. The method according to any one of claims 1 to 5, further comprising: subjecting the printed droplet of ink having the at least partially un-filled gaps to a heat treatment to bind the plurality of microplatelets, such that the plurality of microplatelets consolidate into an at least partially porous inorganic scaffold.

7. The method according to any one of claims 1 to 6, further comprising controllably heating the substrate before the period of drying ends.
8. The method according to any one of claims 1 to 7, wherein the rotating magnetic field is configured with a magnetic field strength higher than a capillary flow action in a drying droplet.
9. The method according to any one of claims 1 to 8, wherein the liquid is one of or a combination of an aqueous solution and an organic solvent.
10. The method according to claim 9, wherein the liquid comprises a binder.
11. The method according to any of claims 1 to 9, wherein each of the plurality of microplatelets is characterized by at least one anisotropic property.
12. The method according to any one of claims 1 to 11, comprising:
 - printing a subsequent droplet of ink adjacent the printed droplet of ink, wherein the subsequent droplet of ink is printed prior to the printed droplet of ink becoming fully dried.
13. The method according to any one of claims 1 to 12, further comprising: before the printing, decorating the plurality of microplatelets with superparamagnetic iron oxide nanoparticles.
14. A product formed by a method of drop-on-demand 3D printing, the product comprising:
 - one or more units, each of the one or more units including a plurality of microplatelets disposed on a substrate or on another of the one or more units, the plurality of microplatelets being configured to be magnetically responsive, the plurality of microplatelets of a same unit being in alignment with an alignment orientation, wherein the adjacent ones of the plurality of microplatelets in alignment define an at least partially un-filled gap such that the plurality of microplatelets in alignment define a corresponding plurality of the at least partially un-filled gaps.

15. The product according to claim 14, wherein each of the one or more units is formed by an ink, and wherein at least one of the one or more units is characterized by a final concentration of the microplatelets that is higher than a maximum concentration, wherein the maximum concentration of the ink corresponds to the ink being saturated with the plurality of microplatelets.

16. The product according to claim 15, wherein the ink has an initial concentration prior to forming the one or more units, and wherein the initial concentration is lower than the maximum concentration.

17. The product according to claim 15, wherein the final concentration is higher than the initial concentration.

18. The product according to any one of claims 14 to 17, further comprising a polymer, wherein the polymer is disposed in the plurality of the at least partially un-filled gaps to form a composite.

19. The product according to any one of claims 14 to 18, wherein the one or more units are characterized by at least one anisotropic property.

20. The product according to any one of claims 14 to 19, wherein the plurality of microplatelets is selected from one of the following: titania-decorated aluminum oxide microplatelets decorated with superparamagnetic iron oxide, aluminum oxide microplatelets decorated with superparamagnetic iron oxide, graphite microplatelets, boron nitride microplatelets decorated with superparamagnetic iron oxide, and a combination of any thereof.

21. A method of 3D printing, the method comprising:

preparing an ink, the ink comprising a slurry of microplatelets in a liquid, the microplatelets being magnetically responsive and characterized by a degree of magnetic responsiveness and a microplatelet size;

printing a droplet of the ink;

subjecting the droplet to a rotating magnetic field, the rotating magnetic field being characterized by a magnetic field strength and a rotation frequency; and

providing a period of drying in which at least a portion of the liquid is evaporated from the droplet to form an at least partially dried droplet, the at least partially dried droplet comprising an array of the microplatelets oriented at an alignment angle, wherein the array of the microplatelets are in alignment and define a corresponding plurality of at least partially un-filled gaps between neighboring ones of the microplatelets, wherein the alignment angle is configurable by controlling one or more of the slurry concentration, the magnetic field strength, and the rotation frequency, and wherein the slurry concentration corresponds to a quantity of the microplatelets in an unit of the ink prior to the printing.

22. The method according to claim 21, wherein the at least partially dried droplet has a final concentration, and wherein the final concentration is higher than a saturated slurry concentration, the saturated slurry concentration corresponding to a maximum quantity of the microplatelets in the unit of the ink prior to the printing.

23. The method according to claim 22, wherein prior to the period of drying, the droplet has an initial concentration that is lower than the saturated slurry concentration.

24. The method according to claim 21, wherein the at least partially dried droplet has a final concentration that is higher than the slurry concentration.

25. A capacitor comprising:

a dielectric layer; and

two graphite layers disposed on either side of the dielectric layer, each of the two graphite layers being printed by the method of 3D printing according to any one of claims 1 to 13 such that each of the two graphite layers includes the graphite microplatelets aligned with an alignment angle of 90 degrees relative to a plane of an interface between the dielectric layer and any of the two graphite layers.

26. The capacitor according to claim 25, wherein the dielectric layer comprises a scaffold of second microplatelets, the second microplatelets being magnetically responsive and aligned at a second alignment angle relative to the plane of the interface between the dielectric layer and any of the two graphite layers.

27. The capacitor according to claim 26, wherein the second alignment angle is 90 degrees.

28. The capacitor according to claim 26, wherein the second microplatelets comprises one of the following: barium titanate microplatelets decorated with superparamagnetic iron oxide nanoparticles, titania-decorated aluminum oxide decorated with superparamagnetic iron oxide nanoparticles, and a combination thereof.

29. A piezoresistive device comprising: an active layer disposed between two electrodes, the active layer being printed by the method of 3D printing according to any one of claims 1 to 13 such that the active layer includes:

graphite microplatelets in alignment and defining a corresponding array of gaps; and
polydimethylsiloxane infiltrated into gaps between the graphite microplatelets.