(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 August 2015 (13.08.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/120011 A1

(51) **International Patent Classification**:
B32B 5/02 (2006.01)

(21) **International Application Number**:
PCT/US2015/014399

(22) **International Filing Date**:
4 February 2015 (04.02.2015)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
61/935,445 4 February 2014 (04.02.2014) US

(71) **Applicant**: **N12 TECHNOLOGIES, INC.** [US/US]; 85 Bolton Street, Cambridge, Massachusetts 02140 (US).

(72) **Inventors**: **WILLIAMS, Ryan**; 85 Bolton Street, Cambridge, Massachusetts 02140 (US). **DEGTIAROV, David**; 85 Bolton Street, Cambridge, Massachusetts 02140 (US). **GOULDSTONE, Christopher**; 85 Bolton Street, Cambridge, Massachusetts 02140 (US). **JAROSZ, Paul**; 85 Bolton Street, Cambridge, Massachusetts 02140 (US). **KENNEDY, Thomas J. III**; 85 Bolton Street, Cambridge, Massachusetts 02140 (US).

(74) **Agents**: **KENNEDY, Brendan** et al.; Hunter Clark PLLC, Suite 213-T, 900 Cummings Center, Beverly, Massachusetts 01915 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: ARTICLES AND METHODS FOR MANUFACTURE OF NANOSTRUCTURE REINFORCED COMPOSITES

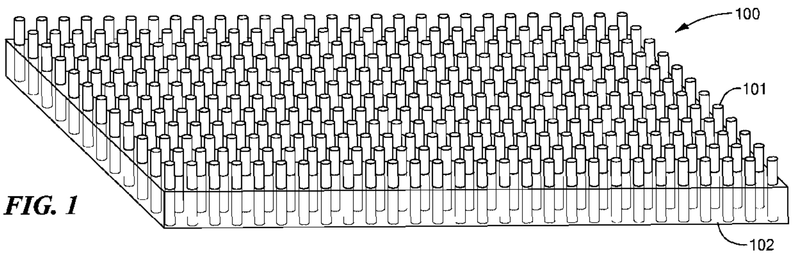

FIG. 1

(57) **Abstract**: An article includes a hybrid nanocomposite product, which includes a nanostructure array and a resin matrix contained among and/or around the nanostructure array. The array/matrix is placed in between layers of dry or resin-infused fiber composite to permit formation of a composite structure. The nanostructure array and/or the resin matrix may be disposed in an abutting relationship with other layers of a composite. The array/matrix can provide reinforcement of the composite in the z-direction. Transfer of resin into dry fiber forms may be provided when the array/matrix acts as a resin transfer medium. Nanostructure arrays with a resin matrix can be prepared to form a resin film product. Methods are presented for infusing composites via resin-transfer molding (RTM), vacuum-assisted resin transfer molding (VARTM), resin film infusion (RFI), or injection molding wherein a resin matrix film substantially maintains alignment and position of the nanostructure array during the infusion process.

TITLE

ARTICLES AND METHODS FOR MANUFACTURE OF NANOSTRUCTURE REINFORCED COMPOSITES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Application No. 61/935,445, filed February 4, 2014, entitled "ARTICLES AND METHODS FOR MANUFACTURE OF NANOSTRUCTURE REINFORCED COMPOSITES," the entire contents of which is hereby incorporated herein by reference.

BACKGROUND

[0002] The addition of nanostructures to fiber reinforced composites can enhance the mechanical, thermal, electrical, and electromagnetic properties of the composite article. In particular, carbon nanostructures such as vertically aligned carbon nanotubes (VACNTs) have been shown to enhance the material properties. The incorporation of micron scale fibers in aligned, woven, and randomly-oriented geometries allows control over the properties of the resulting material. Precise control over the degree of anisotropy in the composite material offers substantial design freedom to the composite fabricator. Similarly, the aligned, woven, or random orientation of nanostructures heavily influences the properties and anisotropy of the material.

[0003] The addition of nanostructured materials to a conventional fiber reinforced polymer composite results in what is called a hierarchical material. That is, a material where the macro, micro, and nanoscale arrangement of the constituent materials results in new and often surprising composite material properties. It is well understood that the physical and chemical properties of nanomaterials are often quite different than that of their micro- and macro-scale bulk counterparts. The addition of nanostructures to fiber reinforced composites in controlled geometries, alignments, and arrangements may provide for enhanced mechanical, thermal, electrical, and electromagnetic properties. However, incorporation of the nanostructures in controlled geometries remains a fabrication challenge.

SUMMARY

[0004] An article includes hybrid nanocomposite product, which includes a nanostructure array and a resin matrix contained among and/or around the nanostructure array. The product is placed in between layers of dry or resin-infused fiber composite to permit formation of a composite structure. The nanostructure array and/or the resin matrix may be disposed in an abutting relationship with other layers of a composite. The product can provide reinforcement of the composite in the z-direction. Transfer of resin into dry fiber forms may be provided when the product acts as a resin transfer medium. Nanostructure arrays with a resin matrix can be prepared to form a resin film composition. Methods are presented for infusing composites via resin-transfer molding (RTM), vacuum-assisted resin transfer molding (VARTM), resin film infusion (RFI), or injection molding using a resin matrix film that substantially maintains alignment and position of the nanostructure array during the infusion process.

[0005] According to some example configurations, an article is composed of a nanostructure array with at least some of the nanostructures having a length of at least 1 micron and/or a diameter less than 100 nm. The long axes of the nanostructures are substantially aligned relative to each other from top to bottom. A resin matrix is provided among, interior to the nanostructures themselves and/or around the nanostructure array. The nanostructures may have a density of at least $10^8/\text{cm}^2$.

[0006] The resin matrix may contain a nanoparticle that enhances the conductivity of resin matrix. The resin matrix may include a conducting polymer. The resin matrix may include an insulating polymer. The resin matrix may include a self-healing agent. The resin matrix may include a ceramic precursor. The matrix may include a ceramic material. The resin matrix may include a precursor to a graphite as in a carbon-carbon composite.

[0007] The resin matrix may be composed of one or more of a polythiophene, a polypyrrole, a polyacetylene, a polyphenylene, polypyrrole, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(thiophene-3-acetic acid) (PTAA), or copolymers thereof; TEFLON®, poly(glycidyl methacrylate), poly(maleic anhydride-alt-styrene), poly[maleic anhydride-co-dimethyl acrylamide-co-di(ethylene glycol) divinyl ether], poly(furfuryl methacrylate), poly(vinyl pyrrolidone), poly(para-xylylene), poly(dimethylaminomethyl styrene), poly(propargyl methacrylate), poly(methacrylic acid-co-ethyl acrylate), poly(perfluoroalkyl ethyl methacrylate), poly(perfluorodecyl acrylate), poly(trivinyltrimethoxycyclotrisiloxane), poly(furfuryl methacrylate), poly(cyclohexyl methacryateco-ethylene glycol dimethacrylate), poly(pentafluorophenyl methacrylate), poly(pentafluorophenyl methacrylate co-ethylene glycol diacrylate), poly(methacrylic acid-co-ethylene glycol dimethacrylate), poly(methyl methacrylate) and/or poly(3,4-ethylenedioxythiophene) and/or common fiber reinforced composite polymer systems such as epoxides, phenolics, polyesters, polyurethanes, bis-maleimides, polyimides, and silicones.

[0008] The resin matrix may include a B-stage resin or partially cured resin, a hardener, cross-linking agent, coefficient of thermal expansion matching agent, erosion resistance agent, toughener, accelerator and/or flame retardant. The resin matrix may include a material that chemically reacts to form liquid or gaseous species that dissolves in or is removed from the final cured composite.

[0009] The article may be provided as a resin film and may be provided on at least one backing or release material associated with the nanostructure array that could be used for shipping and then removed. The article may be provided on at least one backing or release material associated with the nanostructure array that is not removed and contains a polymer that is used in the composite. The backing or release material may act as a support material and may include a monomer, a polymer, a fiber, or a metal. The nanostructure array may be arranged on a substrate, pre-preg, or semi-preg.

[0010] The nanostructure array may include nanotubes, nanofibers, nanowires or nanostructures. The volume fraction of the nanostructures within the article may be at least between 0.1% and 78%. The nanostructures may have an average diameter between 1 nm and 100 nm. The average distance between the nanostructures is less than between 5 nm and 100 nm.

[0011] The resin matrix may assist in maintaining alignment of the nanostructure array. The nanostructure array may be substantially perpendicular to the plane of a resin matrix material. The nanostructures may act or be caused to act or be used like tools within the matrix to permit selective absorption of specific frequencies and/or reduce the amount of energy used during curing. The nanostructures may be used to enhance heat transfer into or out of the curing composite. The nanostructures may be connected to a power supply and used as electrical resistance heaters to assist the resin curing reaction. The nanostructures may be used to detect the state of the curing reaction and/or the endpoint. The nanostructures may be used to inspect the cured article for damage.

[0012] The nanostructure array with the resin matrix may include a polymeric material and can be placed atop or below a single layer of substrate, particularly a fiber layer, and/or placed in between two layers of substrate, pre-preg, semi-preg, or fiber. The nanostructure array may be grown or placed on a surface of a substrate, particularly a fiber layer, wherein the long axes of the nanostructures are substantially aligned and non-parallel to the substrate surface, to form an assembly of nanostructures having a thickness defined by the long axes of the nanostructures. The nanostructure array may be provided with a resin matrix over a portion of the surface area of the nanostructures. In some cases, the resin matrix is a uniform thickness. The nanostructure array may be a relatively large-area nanostructure array with a tailored thickness along the X and Y axes.

[0013] The alignment of the nanostructure array may be maintained while being incorporated into the resin matrix. The nanostructure array may be aligned perpendicular to a thin plane of the resin matrix. The resin matrix may have a thickness that deviates from a height of the nanostructure array less than 1000% or between 1% and 1000%.

[0014] The resin matrix may be heated, placed under vacuum and/or have pressure applied to assist in adhesion between the resin matrix and nanostructure array. The resin matrix may be infused into the nanostructure array through capillary action. The resin matrix may be arranged into a thin plane and/or introduced to the nanostructure array as an aerosol spray and/or with resin Chemical Vapor Deposition (CVD).

[0015] The article may be used to fabricate a composite where a nanostructure array with a resin matrix contained among and/or around the nanostructure array is placed in alternating layers with a sequence of fiber layers. The article may be provided as a resin film on a backing film or material, which backing film or material may be removed after adhesion of the resin film to an underlying substrate or fiber layer. The nanostructure array in resin matrix may be placed at all or some of the laminar interfaces or in selective areas of the interfaces. The nanostructure array in resin matrix may be joined to the surface of a fiber layer, as in a semi-preg. The composite may be fabricated by forming a sequence of semi-preg layers. The nanostructure array may be joined to fiber plies without a resin matrix. The nanostructure array may substantially penetrates one or more of the abutting fiber layers above or below, so as to fix or anchor the position and alignment of the nanostructures.

[0016] The assembled layer structure may be prepared for a resin infusion process such as resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM), resin film infusion (RFI), or injection molding. The assembly may be used with a configuration that may include tool plates (mold), preforms, distribution mediums, breather layers, bleeder layers, vacuum bags, peel plies, reinforcement layers, structured honeycombs, and/or sealant tapes. The assembly layer structure may be infused with resin, either perpendicular or parallel to the ply interfaces. The assembly may be heated to control the viscosity of the infusing resin and/or resin film. Vacuum and/or pressure may be applied to influence the flow of the resin, as in vacuum assisted resin transfer molding (VARTM).

[0017] The resin film provides mechanical stability to maintain alignment and positioning of the nanostructure array during the infusion process. The resin film may be composed of a resin the same or different from the infusing resin. The resin film may have a viscosity that is substantially higher than the infusing resin. The resin film with nanostructure array may serve as a source for all or some of the resin for the finished composite, as in a resin film infusion (RFI) process.

[0018] The infused assembly may be consolidated and cured under heat and/or positive or negative pressure using an autoclave, hot press, or other conventional method. The composite assembly may be heated at high temperature sufficient to form a ceramic material. The composite assembly may be heated in a reducing atmosphere to form a graphitic structure in a carbon-carbon composite.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The presently disclosed compositions and techniques are described in greater detail below with reference to the accompanying drawings, in which:

[0020] Fig. 1 is a depiction of a carbon nanotube array where a resin is infused on one side of the array;

[0021] Fig. 2 is a depiction of a carbon nanotube array where a resin matrix is infused in a planar center of a carbon nanotube array;

[0022] Fig. 3 is a depiction of a carbon nanotube array where resin matrix is infused in a planar center of a carbon nanotube array;

[0023] Fig. 4 is a depiction of a carbon nanotube array where the entire array is infused with a resin;

[0024] Fig. 5 is a depiction of a carbon nanotube array that is infused by a resin matrix beyond an extent of a length of the carbon nanotubes;

[0025] Fig. 6 is a depiction of a carbon nanotube array that is partially infused with a resin matrix and coupled with a pre-preg matrix;

[0026] Fig. 7 shows the process of incorporating a partially resin infused nanotube array that is incorporated between two sheets of dry fiber material;

[0027] Fig. 8 shows the process of incorporating a fully resin infused carbon nanotube array that is incorporated between two sheets of dry fiber material;

[0028] Fig. 9 is a depiction of a fully resin infused carbon nanotube array that is sandwiched between two layers of resin infused fiber pre-preg material; and

[0029] Fig. 10 is a depiction of the incorporation of a fully resin infused carbon nanotube array onto one side of a resin infused fiber pre-preg.

DETAILED DESCRIPTION

[0030] Methods for the production of composite articles incorporating nanostructures in controlled arrangements, alignments, and geometries, as well as products using the methods are described herein. These methods and products are particularly well-suited for use with infusion-based processes for composite construction, including such infusion-based processes as resin-transfer molding (RTM), vacuum-assisted resin transfer molding (VARTM), and resin film infusion (RFI). Composite materials, including such items such as fibers, can be provided in unidirectional, woven, and randomly oriented composites, including fiber reinforced composites. Nanostructures can be introduced in controlled geometries to influence the underlying properties both of material used in composite construction as well as final composite products.

[0031] Aligned nanostructures have been shown to enhance the mechanical, thermal, electrical, and electromagnetic properties of composite materials. In particular, the placement of vertically aligned carbon nanotubes at the inter-laminar ply interfaces of carbon fiber reinforced polymer composites has demonstrated substantial enhancement of the mechanical toughness, as well as enhancement of other mechanical properties. The placement of aligned carbon nanostructures at ply interfaces has also been demonstrated in glass, alumina, basalt, and other fiber materials in fiber reinforced polymer composites. Additionally, the placement of these aligned nanostructures has been shown to increase the thermal and electrical conductivity of the composite, enabling them to be used as multifunctional materials, e.g. a mechanical structure that also conducts electricity. These multifunctional properties can be used for applications such as structural health monitoring, de-icing heaters, out-of-autoclave polymer curing, polymer cure detection, embedded electrical heaters, electromagnetic signature modification, and manufacturing quality control and parts inspection.

[0032] The placement of aligned nanostructures in composite materials has been demonstrated primarily with pre-preg material, that is, material such as fibers that is impregnated with thermoset or thermoplastic polymer resin formed in sheets. The sheets typically have a backing paper on one or both sides. The sheets can be cut into shapes and used to form a composite article by laying successive layers with different orientations (e.g. 0°, +/-45°, 90°) to construct the final part. The part is then heated, which causes the resin to flow as a liquid resin and cure into a solid polymer, typically through a cross-linking reaction for thermosets. The heating process can be combined with mechanical or fluid pressure in a mechanical press, vacuum oven, or autoclave.

[0033] The term pre-preg describes pre-impregnated composite fibers where a material, such as epoxy or unsaturated polyester, is already present. The resin matrix is only partially cured to allow easy handling. This configuration is called B-Stage material and typically requires cold storage to prevent complete curing although room temperature pre-pregs have been developed. Composite structures built of pre-pregs will mostly require an oven or autoclave to come to a final cure. In pre-preg based methods, the tacky resin allows the aligned nanostructures to adhere to the pre-preg, maintaining their position at the ply interface, preserving their alignment, and serving as a source of resin to fully encapsulate the aligned nanostructures. During consolidation and curing of the composite part, the flowing resin travels relatively short distances, on the order of less than the ply thickness, because the plies are already impregnated with resin.

[0034] However, many composite structures are not manufactured using pre-preg materials. Infusion-based methods such resin-transfer molding (RTM), vacuum-assisted resin transfer molding (VARTM), and resin film infusion (RFI) are widely used in the composite construction industry. These methods present a significant challenge for the incorporation of sheets of aligned nanostructures at the ply interfaces. Typically, infusion-based methods use fiber layers that are laid up dry with no resin. In RTM and VARTM, the layer structure is typically encapsulated (“bagged”) in polymer film and resin is allowed to flow and infuse through the dry fibers. The whole structure is then baked to cure or set the polymer. In resin film infusion (RFI), the dry fiber layers are alternated with polymer sheets of resin film. Heat is applied and the resin begins to soften and flow through the dry fiber layers to form the consolidated composite. In another variation, these resin films may be bonded to the surface sheets of fiber in a product format called semi-preg.

[0035] The above-described infusion-based composite molding techniques present a challenge when aligned nanostructures are desired at the ply interfaces for mechanical reinforcement or other property enhancement. For example, the dry aligned nanostructures are difficult to join with the dry fiber layers. The aligned nanostructures may be placed at the interface, but there is little to no adhesion of the dry nanostructures to a dry fiber layer. It is furthermore difficult to maintain the coherence, alignment, and positioning of the aligned nanostructures. With infusion-based methods the resin travels substantially through the entire volume of the composite, from an inlet to an outlet. The bulk flow of the resin typically displaces the nanostructures, moving them away from ply interfaces and disrupting their alignment. The accumulation and entanglement of the nanostructures within the resin may also negatively impact the flow pattern and lower the viscosity of the resin resulting in non-uniform distribution of both the resin and the nanostructures.

[0036] The methods and products discussed herein provide for aligned nanostructures that can be integrated with infusion-based composite construction methods while preserving the alignment and placement of the nanostructures. In an example embodiment, aligned nanostructure films, here, sheets of VACNTs, are joined to a sheet of resin film. The resin film may be a thermoset or thermoplastic material. The aligned nanostructure films may be provided on a particular carrier material such as a metal foil, polymer film, or paper backing. The joining may be accomplished by heating the resin film and/or applying both vacuum and/or pressure to increase the tackiness of the resin to enhance transfer of the aligned nanostructure film. The thickness of this resulting film may be less than, equal to, or substantially greater than the thickness (height) of the aligned nanostructure film. The result is a film of aligned nanostructures partially or fully embedded within the polymer. The aligned nanostructure resin films may be applied by being placed in alternating layers or patterns with dry fiber layers. The aligned nanostructure resin films need not be placed at every ply interface and may be placed selectively at different interfaces or in limited areas of particular interfaces. The aligned nanostructure resin films may be tapes, sheets, or patches of material. The aligned nanostructure resin films may be partially bonded to layers of dry fiber in a semi-preg configuration.

[0037] The VACNT material may be pretreated with a surface tension modifying material or a compatibalizing material, such as maleic anhydride, so that the resin flows more easily into the VACNT forest. The VACNT forest may also be functionalized with an organic or inorganic moiety to improve the adhesion of the VACNT forest to the resin matrix.

[0038] In an example RTM or VARTM compatible configuration, one or more aligned nanostructure resin films may be placed within a dry fiber stack. The aligned nanostructure resin films may be connected to each other and/or the dry fibers or dry fiber stack in a conventional configuration, which may include tool plates (mold), preforms, distribution mediums, breather layers, bleeder layers, vacuum bags, peel plies, reinforcement layers, structured honeycombs, and sealant tapes. There may be one or more inlets and outlets for the infused resin. The infused resin may be identical, similar, or different in composition to the resin film. In some example embodiments, the aligned nanostructure resin film may include a high viscosity resin, while the infused resin may have a lower viscosity to permit the infused resin to flow around the aligned nanostructures. In some example embodiments, the aligned nanostructure resin film may include a low viscosity resin, while the infused resin may have a higher viscosity to permit the infused resin to flow around and through the aligned nanostructures. Management of the relative viscosity of the two films allows for design of infusion methods that maintain the alignment and positioning of the nanostructures. Upon application of heat, pressure, and/or vacuum, the infused resin flows through the composite structure, filling the bulk of the volume with resin and encapsulating both the fibers and the aligned nanostructures. The resin in the resin film maintains the alignment and position of the aligned nanostructures during the relatively aggressive infusion process. The direction of the bulk resin flow may be parallel, perpendicular, or randomly oriented to the alignment direction of the nanostructures. In some embodiments, the bulk resin flow is parallel to the direction of the nanostructures to minimize forces that may disrupt the position and alignment of the nanostructures.

[0039] In a resin film infusion (RFI) configuration, the aligned nanostructures resin films are the source for all or most of the resin in the final composite structure. A composite layer, or ply, that includes the aligned nanostructures resin films may be placed in a configuration that may include tool plates (mold), preforms, distribution mediums, breather layers, bleeder layers, vacuum bags, peel plies, reinforcement layers, structured honeycombs, and sealant tapes. The entire assembly is heated, allowing the resin to flow and encapsulate both the fiber and aligned nanostructure layers. The alignment and placement of the aligned nanostructures is wholly or substantially maintained during the heating, curing, and consolidation process

[0040] In any of the infusion methods, once the composite structure has been impregnated with resin, the entire assembly may be consolidated and cured in an autoclave, hot press, or other conventional approach. In another configuration, the nanostructures layers are connected to an external power source and used as embedded heaters to heat the composite part and cure the resin, either with or without the assistance of an autoclave, hot press, cold press, or other consolidation method. The resin material may utilize a single or dual cure polymerization process for thermoset materials. For a thermoplastic resin material, the heating process may encourage the resin to flow and consolidate with or without initiating a reaction.

[0041] The resin matrix may be composed of a polythiophene, a polypyrrole, a polyacetylene, a polyphenylene, polypyrrole, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(thiophene-3-acetic acid) (PTAA), or copolymers thereof. In addition, or alternatively or in combination, the resin matrix may be composed of at least one of TEFLON®, poly(glycidyl methacrylate), poly(maleic anhydride-alt-styrene), poly[maleic anhydride-co-dimethyl acrylamide-co-di(ethylene glycol) divinyl ether], poly(furfuryl methacrylate), poly(vinyl pyrrolidone), poly(para-xylylene), poly(dimethylaminomethyl styrene), poly(propargyl methacrylate), poly(methacrylic acid-co-ethyl acrylate), poly(perfluoroalkyl ethyl methacrylate), poly(perfluorodecyl acrylate), poly(trivinyltrimethoxycyclotrisiloxane), poly(furfuryl methacrylate), poly(cyclohexyl methacryateco-ethylene glycol dimethacrylate), poly(pentafluorophenyl methacrylate), poly(pentafluorophenyl methacrylate co-ethylene glycol diacrylate), poly(methacrylic acid-co-ethylene glycol dimethacrylate), poly(methyl methacrylate) and/or poly(3,4-ethylenedioxythiophene).

[0042] In an example embodiment, nanostructure arrays or vertically aligned carbon nanotubes (VACNTs) or VACNT arrays or nano-fiber arrays are produced in a continuous process at ambient or near ambient pressure. In such an embodiment, nanostructure arrays with or without a resin matrix may be transferred to a second substrate such that the nanostructure arrays, if without the resin matrix, would have a resin matrix form added in a second processing step.

[0043] According to some embodiments, a resin is introduced into the nanostructure arrays such that a cohesive sheet is formed of a resin matrix on a transfer substrate for shipping and handling during fabrication of composites. The transfer substrate may be a release paper that has been treated with a low energy coating, like a polydimethyl siloxane, to facilitate the release and subsequent incorporation of the resin / VACNT matrix into a composite structure. The resin may be an epoxy resin such as a b-staged bis-phenol A / epichlorohydrin with a blocked polyamide or polyamine.

[0044] In some configurations, the matrix material could be a ceramic precursor such as a sol-gel precursor. In these and previous configurations, the composite structure may be heated at a high temperature to form a ceramic material or in a high-temperature reducing atmosphere to pyrolize the resin matrix, as in a carbon-carbon composite. The incorporation of the resin matrix into the carbon nanotube array may be performed by various processes that include lamination, dipping, flow coating, spraying, gravure, vapor deposition and the like.

[0045] In some configurations, the matrix material for the nanostructures may be a material that is commonly formulated in pre-preg or resin films, such as hardeners, cross-linking agents, coefficient of thermal expansion matching agents, erosion resistance agents, tougheners, accelerators, or flame retardants. In some configurations, the matrix material for the nanostructures may be a material that chemically reacts and forms a liquid solvent or gaseous species that is subsequently dissolved within or removed from the final cured composite.

[0046] Fig. 1 is a view of a composite 100 that is comprised of a resin matrix form 102 at a base of a nanostructure array 101. Resin matrix 102 may also be positioned at a top of nanostructure array 101, or composite 100 may be rotated 180 degrees. It should be understood that any orientation of composite 100 is possible, where resin matrix 102 extends from an end of the nanostructures in nanostructure array 101 to a substantially uniform length along the nanostructures. Resin matrix form 102 can be 1%-99.9999999% of the height of nanostructure array 101. Nanostructure array 101 is between 1 micron and 2000 microns in height.

[0047] Fig. 2 is a view of a composite 200 comprised of a resin matrix form 202 between a top and a base of a nanostructure array 201. Resin matrix form 202 can be 50%-99% of the height of nanostructure array 201. Ends of nanostructure array 201 are not covered by resin matrix form 202, but are rather exposed. Nanostructure array 201 is between 1 micron and 2000 microns in height.

[0048] Fig. 3 is a view of a composite 300 comprised of a resin matrix form 302 between a top and a base of a nanostructure array 301. Resin matrix form 302 can be 1%-50% of the height of nanostructure array 301. Ends of nanostructure array 301 are not covered by resin matrix form 302, but are rather exposed. Nanostructure array 301 is between 1 micron and 2000 microns in height.

[0049] Fig. 4 is a view of a composite 400 comprised of a resin matrix form 402 entirely encapsulating a nanostructure array 401 and is at least 100% of the height of nanostructure array 401. Accordingly, resin matrix form 402 has at least a height and position that permits resin matrix form 402 to extend from end to end of the nanostructures in nanostructure array 401. Nanostructure array 401 is between 1 micron and 2000 microns in height.

[0050] Fig. 5 is a view of a composite 500 comprised of a resin matrix form 501 entirely encapsulating a nanostructure array 502 and is from 100% to 500% of the height of nanostructure array 502. Thus, resin matrix form 501 extends beyond at least one end of the nanostructures, and may extend beyond both ends of the nanostructures in nanostructures array 502. Nanostructure array 502 is between 1 micron and 2000 microns in height.

[0051] Fig. 6 is a view of a composite 600 comprised of a nanostructure array 601 on top of a resin impregnated fiber layer 603 also called “pre-preg.” Nanostructure array 601 is between 1 micron and 2000 microns in height and resin matrix 602 is between 100% and 500% of the height of the nanostructure array. Ends of the nanostructures in nanostructure array 601 may be covered by resin matrix 602, or may be exposed on one or more ends.

[0052] Fig. 7 is a depiction of a process 700 for fabricating a composite structure. A nanostructure array 702 with resin matrix 704, which may be implemented collectively as composite 100 (Fig. 1), composite 200 (Fig. 2), composite 300 (Fig. 3) or composite 400 (Fig. 4), as examples, is placed on top of a fiber layer 701, which may or may not include impregnated resin. Another layer of fibers 703, with or without impregnated resin, is placed on top nanostructure array 702 with resin matrix 704. The fibers could be in any direction in any layer with any size or type including alumina fibers, glass fibers or carbon fibers.

[0053] Fig. 8 is a depiction of a process 800 for fabricating a composite structure. A composite 803 composed of a nanostructure array with resin matrix, which may be implemented as composite 500 (Fig. 5) is placed on top of a fiber layer 802, which is without impregnated resin. Another fiber layer 802 without impregnated resin is placed on top of composite 803. At least some of the resin matrix in composite 803 transfers to fiber layers 802 during curing, forming fiber layers with resin matrix 804. The fibers in fiber layers 802 can be in any direction in any layer with any size or type including alumina fibers, glass fibers or carbon fibers.

[0054] Fig. 9 is a view of a composite 900 comprised of a resin matrix form 905 entirely encapsulating a nanostructure array 902. Resin matrix form 905 is at least 100% of the height, and covers at least one end of the nanostructures in nanostructure array 902. Nanostructure array 902 is between 1 micron and 1000 microns in height and is embedded into two sheets of pre-impregnated layers of fibers 901 and 903 otherwise known as pre-preg.

[0055] Fig. 10 is a view of a composite 1000 comprised of a resin matrix form 1003 entirely encapsulating a nanostructure array 1002. Resin matrix form 1003 is at least 100% of the height, and covers at least one end of the nanostructures in nanostructure array 1002. Nanostructure array 1002 is between 1 micron and 100 microns in height and is embedded into one sheet of pre-impregnated layer of fibers 1001 otherwise known as pre-preg.

[0056] Although Figs. 1-10 illustrate certain examples of implementations or techniques, it should be understood that other variations are included within the scope of the disclosed products, articles or processes. For example, while Figs. 1-10 show a generally planar geometry for the resin matrix and the nanostructure array, other variations are understood to be contemplated. The resin matrix and/or the nanostructure array may be provided with a height gradient, for example, or other geometries that can be specified in accordance with a desired application. In such examples, some nanostructures in an array may be free of the resin matrix and/or be partially covered within the resin matrix and/or have one or both ends covered by the resin matrix and/or be wholly covered by the resin matrix.

[0057] Other examples and implementations are within the scope and spirit of the disclosure and appended claims. Features implementing functions may also be physically located at various positions, including being distributed such that portions of functions are implemented at different physical locations. Also, as used herein, including in the claims, “or” as used in a list of items prefaced by “at least one of” indicates a disjunctive list such that, for example, a list of “at least one of A, B, or C” means A or B or C or AB or AC or BC or ABC (i.e., A and B and C), or combinations with more than one feature (e.g., AA, AAB, ABBC, etc.).

[0058] As used herein, including in the claims, unless otherwise stated, a statement that a function or operation is “based on” an item or condition means that the function or operation is based on the stated item or condition and may be based on one or more items and/or conditions in addition to the stated item or condition. The methods, systems, products and articles discussed above are examples. Various configurations may omit, substitute, or add various procedures or components as appropriate. For instance, in alternative configurations, the methods may be performed in an order different from that described, and that various steps may be added, omitted, or combined. Also, features described with respect to certain configurations may be combined in various other configurations. Different aspects and elements of the configurations may be combined in a similar manner. Also, technology evolves and, thus, many of the elements are examples and do not limit the scope of the disclosure or claims.

[0059] Specific details are given in the description to provide a thorough understanding of example configurations (including implementations). However, configurations may be practiced without these specific details. For example, well-known processes, structures, products, articles and techniques have been shown without unnecessary detail to avoid obscuring the configurations. This description provides example configurations only, and does not limit the scope, applicability, or configurations of the claims. Rather, the preceding description of the configurations provides a description for implementing described techniques. Various changes may be made in the function and arrangement of elements without departing from the spirit or scope of the disclosure.

[0060] Also, configurations may be described as a process which is depicted as a flow diagram or block diagram. Although each may describe the operations as a sequential process, some of the operations may be performed in parallel or concurrently. In addition, the order of the operations may be rearranged. A process may have additional stages or functions not included in the figure.

[0061] Having described several example configurations, various modifications, alternative constructions, and equivalents may be used without departing from the spirit of the disclosure. For example, the above elements may be components of a larger system, wherein other techniques may take precedence over or otherwise modify the application of the invention. Also, a number of operations may be undertaken before, during, or after the above elements are considered. Accordingly, the above description does not bound the scope of the claims.

[0062] Further, more than one invention may be disclosed.

CLAIMS

We claim:

1. An article, comprising:

a nanostructure array at least some of which has a length of at least 1 micron, the long axes of the nanostructures being substantially aligned relative to each other from top to bottom; and a resin matrix contained among, interior to the nanostructures themselves and/or around the nanostructure array.

2. An article, comprising:

a nanostructure array at least some of which have a diameter less than 100 nm, the long axes of the nanostructures being substantially aligned relative to each other; and a resin matrix contained among and/or around the nanostructure array.

3. An article, comprising:

a nanostructure array, wherein the long axes of the nanostructures are substantially aligned relative to each other and the nanostructures have a density of at least $10^8/cm^2$; and a resin matrix contained among and/or around the nanostructure array

4. An article as in any preceding claim, wherein the resin matrix contains a nano-particle that enhances the conductivity of resin matrix.

5. An article as in any preceding claim, wherein the resin matrix comprises a conducting polymer.

6. An article as in any preceding claim, wherein the resin matrix comprises an insulating polymer.

7. An article as in any preceding claim, wherein the resin matrix comprises a self-healing agent.

8. An article as in any preceding claim, wherein the resin matrix comprises a ceramic precursor.

9. An article as in any preceding claim, wherein the matrix comprises a ceramic material.

10. An article as in any preceding claim, wherein the resin matrix comprises a precursor to a graphite as in a carbon-carbon composite

11. An article as in any preceding claim, wherein the resin matrix comprises a polythiophene, a polypyrrole, a polyacetylene, a polyphenylene, polypyrrole, poly(3,4-ethylenedioxythiophene) (PEDOT), poly(thiophene-3-acetic acid) (PTAA), or copolymers thereof.

12. An article as in any preceding claim, wherein the resin matrix comprises at least one of TEFLON®, poly(glycidyl methacrylate), poly(maleic anhydride-alt-styrene), poly[maleic anhydride-co-dimethyl acrylamide-co-di(ethylene glycol) divinyl ether], poly(furfuryl methacrylate), poly(vinyl pyrrolidone), poly(para-xylylene), poly(dimethylaminomethyl styrene), poly(propargyl methacrylate), poly(methacrylic acid-co-ethyl acrylate), poly(perfluoroalkyl ethyl methacrylate), poly(perfluorodecyl acrylate), poly(trivinyltrimethoxycyclotrisiloxane), poly(furfuryl methacrylate), poly(cyclohexyl methacryateco-ethylene glycol dimethacrylate), poly(pentafluorophenyl methacrylate), poly(pentafluorophenyl methacrylate co-ethylene glycol diacrylate), poly(methacrylic acid-co-ethylene glycol dimethacrylate), poly(methyl methacrylate), poly(3,4-ethylenedioxythiophene), epoxides, phenolics, polyesters, polyurethanes, bis-maleimides, polyimides and silicones.

13. An article as in any proceeding claim, wherein the resin matrix comprises a B-stage resin or partially cured resin.

14. An article as in any proceeding claim, wherein the resin matrix comprises a hardener, cross-linking agent, coefficient of thermal expansion matching agent, erosion resistance agent, toughener, accelerator, or flame retardant.

15. An article as in any proceeding claim, wherein the resin matrix comprises a material that chemically reacts to form liquid or gaseous species that dissolves in or is removed from the final cured composite.

16. An article as in any preceding claim, further comprising at least one backing or release material associated with the nanostructure array that could be used for shipping and then removed.

17. An article as in any preceding claim, further comprising at least one backing or release material associated with the nanostructure array that is not removed and contains a polymer that is used in the composite.

18. An article as in any preceding claim, wherein the support material comprises a monomer, a polymer, a fiber, or a metal.

19. An article as in any preceding claim, wherein the nanostructure array is arranged on a substrate, pre-preg, or semi-preg.

20. An article as in any preceding claim, wherein the nanostructure array comprise nanotubes, nanofibers, nanowires or nanostructures.

21. An article as in any preceding claim, wherein the volume fraction of the nanostructures within the article is at least between 0.1% and 78%.

22. An article as in any preceding claim, wherein the nanostructures have an average diameter between 1 nm and 100 nm.

23. An article as in any preceding claim, wherein the average distance between the nanostructures is less than between 5 nm and 100 nm.

24. An article as in any preceding claim, wherein the matrix assists in maintaining alignment of the nanostructure array.

25. An article as in any preceding claim, comprised of a nanostructure array that is substantially perpendicular to the plane of a matrix material.

26. An article as in any preceding claim, wherein the nanostructures act like tools within the matrix that use selective absorption of specific frequencies and/or reduce the amount of energy used during curing.

27. An article as in any proceeding claim, wherein the nanostructures enhance heat transfer into or out of the curing composite.

28. An article as in any proceeding claim, wherein the nanostructures are connected to a power supply and used as electrical resistance heaters to assist the resin curing reaction.

29. An article as in any proceeding claim, wherein the nanostructures are used to detect the state of the curing reaction and/or the endpoint.

30. An article as in any proceeding claim, wherein the nanostructures are used to inspect the cured article for damage.

31. A method of producing a material, comprising:

providing a nanostructure array at least some of which have a length of at least 1 micron, the long axes of the nanostructures being substantially aligned relative to each other; and forming, a nanostructure array with a resin matrix comprising a polymeric material where the nanostructure array infused with a resin matrix can be placed on top or bottom of a single layer of substrate, particularly a fiber layer, and/or placed in between two layers of substrate, pre-preg, semi-preg, or fiber.

32. A method as in any preceding method claim, wherein providing a nanostructure array comprises: growing or placing a nanostructure array on a surface of a substrate, particularly a fiber layer, wherein the long axes of the nanostructures are substantially aligned and non-parallel to the substrate surface, to form an assembly of nanostructures having a thickness defined by the long axes of the nanostructures.

33. A method as in any preceding method claim, wherein the nanostructures comprise nanotubes, nanofibers, nanowires or nanostructures.

34. A method as in any preceding method claim, wherein the nanostructures comprise carbon-based nanostructures.

35. A method as in any preceding method claim, wherein the carbon-based nanostructures comprise carbon nanotubes.

36. A method as in any preceding method claim, wherein the nanostructures have an average diameter between 1 nm and 100 nm.

37. A method as in any preceding method claim, a resin matrix is placed in the nanostructure array

38. A method as in any preceding method claim, wherein the nanostructure array has a resin matrix over a portion of the surface area of the nanostructures.

39. A method as in any preceding method claim, wherein the resin matrix has a uniform thickness.

40. A method as in any preceding method claim, a large-area nanostructure array having a tailored thickness along the X and Y axes.

41. A method as in any preceding method claim, wherein the alignment of the nanostructure array is maintained while incorporated into the resin matrix.

42. A method as in any preceding method claim, wherein the nanostructure array is aligned perpendicular to a thin plane of the resin matrix.

43. A method as in any preceding method claim, further comprising providing a resin matrix with a thickness that deviates from a height of the nanostructure array less than 1000%.

44. A method as in any preceding method claim, further comprising providing a resin matrix with a thickness that deviates from a height of the nanostructure array between 1% and 1000%.

45. A method as in any preceding method claim, wherein the resin matrix is heated to assist in adhesion between the resin matrix and nanostructure array

46. A method as in any preceding method claim, wherein the resin matrix is covered and placed under vacuum to assist in adhesion between the resin matrix and nanostructure array

47. A method as in any preceding method claim, wherein the resin matrix is covered and pressure applied to assist in adhesion between the resin matrix and nanostructure array

48. A method as in any preceding method claim, wherein the resin matrix is placed under a combination of heat, vacuum, and/or pressure to assist in adhesion between the resin matrix and nanostructure array

49. A method as in any preceding method claim, wherein the resin matrix is infused into the nanostructure array through capillary action.

50. A method as in any preceding method claim, wherein the resin matrix is arranged into a thin plane.

51. A method as in any preceding method claim, wherein the resin matrix is introduced to the nanostructure array as an aerosol spray.

52. A method as in any preceding method claim, wherein the resin matrix is introduced to the nanostructure array with resin Chemical Vapor Deposition (CVD).

53. A method of producing a material, comprising:

fabricating a composite where a nanostructure array with a resin matrix contained among and/or around the nanostructure array is placed in alternating layers with a sequence of fiber layers.

54. A method as in claim 53, wherein a backing film or material is removed from the resin film after adhesion to the underlying substrate or fiber layer.

55. A method as in any of claims 53-54, wherein the nanostructure array in resin matrix can be placed at all or some of the laminar interfaces or in selective areas of the interfaces.

56. A method as in any of claims 53-55, wherein the nanostructure array in resin matrix is joined to the surface of a fiber layer, as in a semi-preg.

57. A method as in any of claims 53-56, wherein a sequence of semi-preg layers are placed to form a composite component.

58. A method as in any of claims 53-57, wherein a nanostructure array is joined to fiber plies without a resin matrix.

59. A method as in any of claims 53-58 wherein the nanostructure array substantially penetrates one or more of the abutting fiber layers above or below, so as to fix or anchor the position and alignment of the nanostructures.

60. A method as in any of claims 53-59, wherein the assembled layer structure is then prepared for a resin infusion process such as resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM), resin film infusion (RFI), or injection molding.

61. A method as in any of claims 53-60, wherein the assembly is placed in a configuration that may include tool plates (mold), preforms, distribution mediums, breather layers, bleeder layers, vacuum bags, peel plies, reinforcement layers, structured honeycombs, and/or sealant tapes.

62. A method as in any of claims 53-61, wherein the layer structure is then infused with resin, either perpendicular or parallel to the ply interfaces.

63. A method as in any of claims 53-62, wherein the assembly is heated to control the viscosity of the infusing resin and/or resin film.

64. A method as in any of claims 53-63, wherein vacuum and/or pressure are applied to influence the flow of the resin, as in vacuum assisted resin transfer molding (VARTM).

65. A method as in any of claims 53-64, wherein the resin film provides mechanical stability to maintain alignment and positioning of the nanostructure array during the infusion process.

66. A method as in any of claims 53-65, wherein the resin film is comprised of a resin that is the same or different from the infusing resin.

67. A method as in any of claims 53-66, wherein the resin film has a viscosity that is substantially higher than the infusing resin.

68. A method as in any of claims 53-67, wherein the resin film with nanostructure array serves as a source for all of the resin for the finished composite, as in a resin film infusion (RFI) process.

69. A method as in any of claims 53-68, wherein the resin film with nanostructure array provides some of the resin for the finished composite.

70. A method as in any of claims 53-69, wherein the infused assembly is then consolidated and cured under heat and/or pressure using an autoclave, hot press, or other conventional method.

71. A method as in any of claims 53-70, wherein the composite assembly is heated at high temperature to form a ceramic material

72. A method as in any of claims 53-71, wherein the composite assembly is heated in a reducing atmosphere to form a graphitic structure in a carbon-carbon composite.

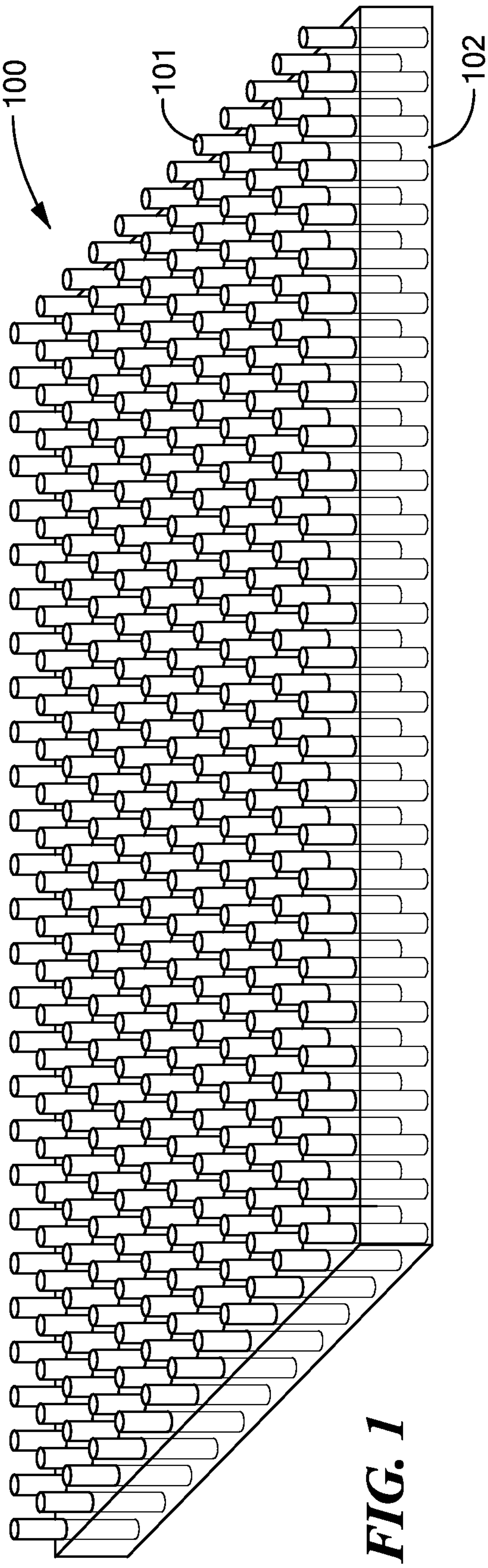

FIG. 1

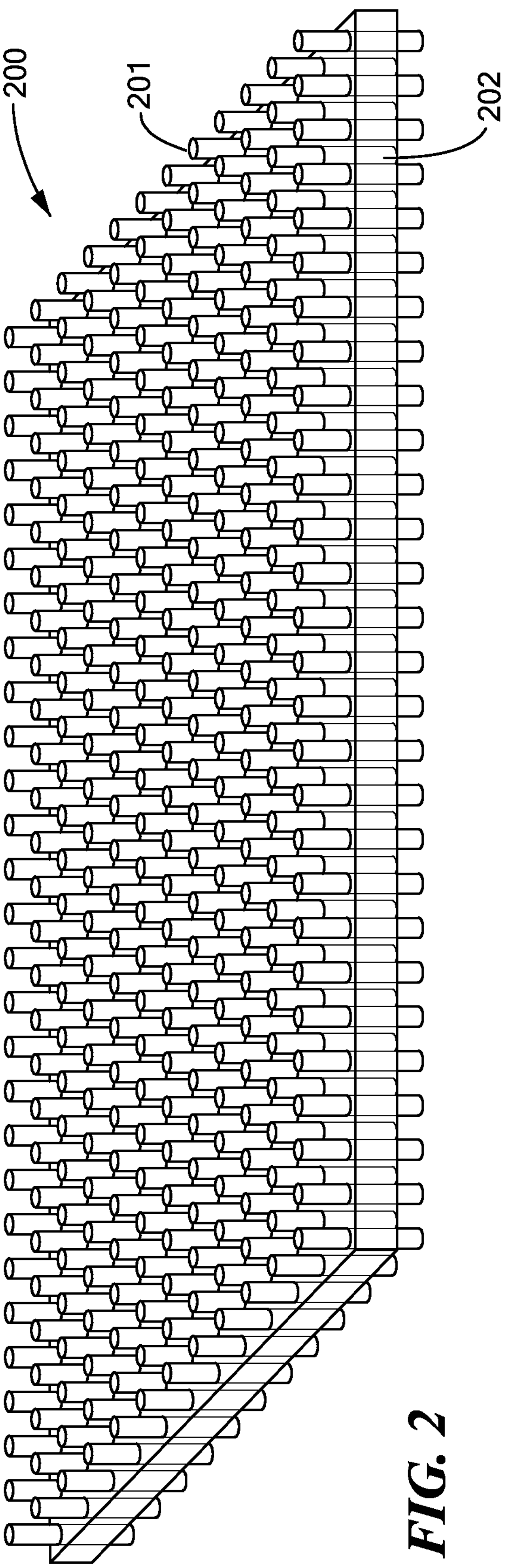

FIG. 2

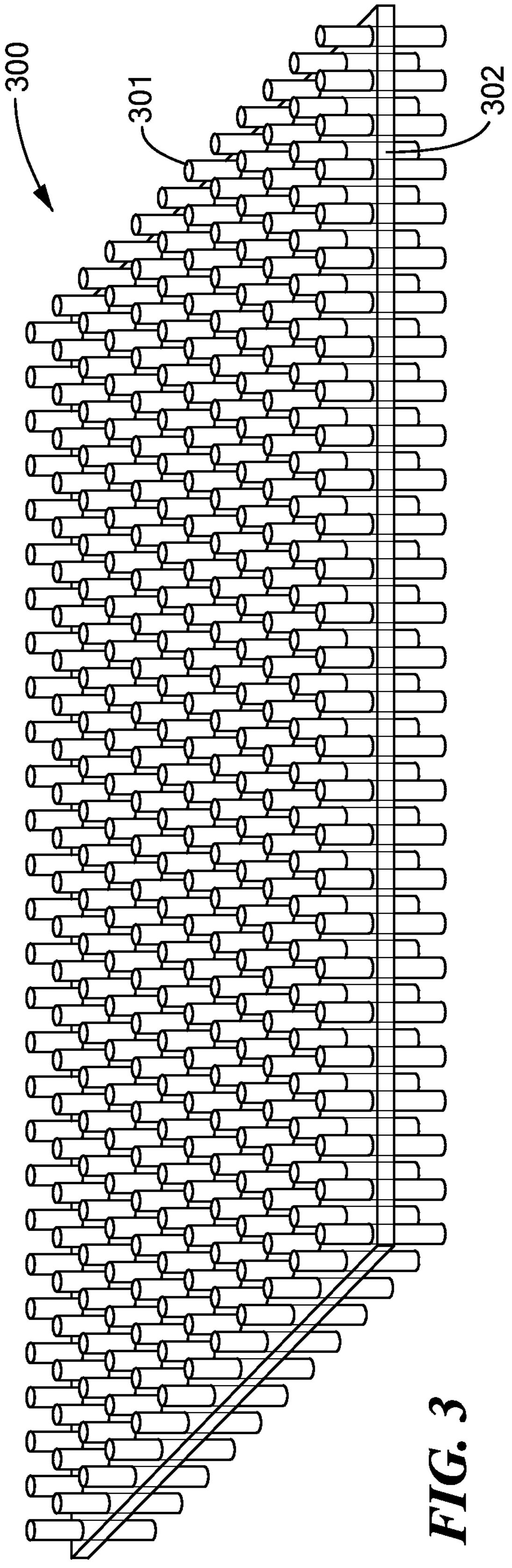

FIG. 3

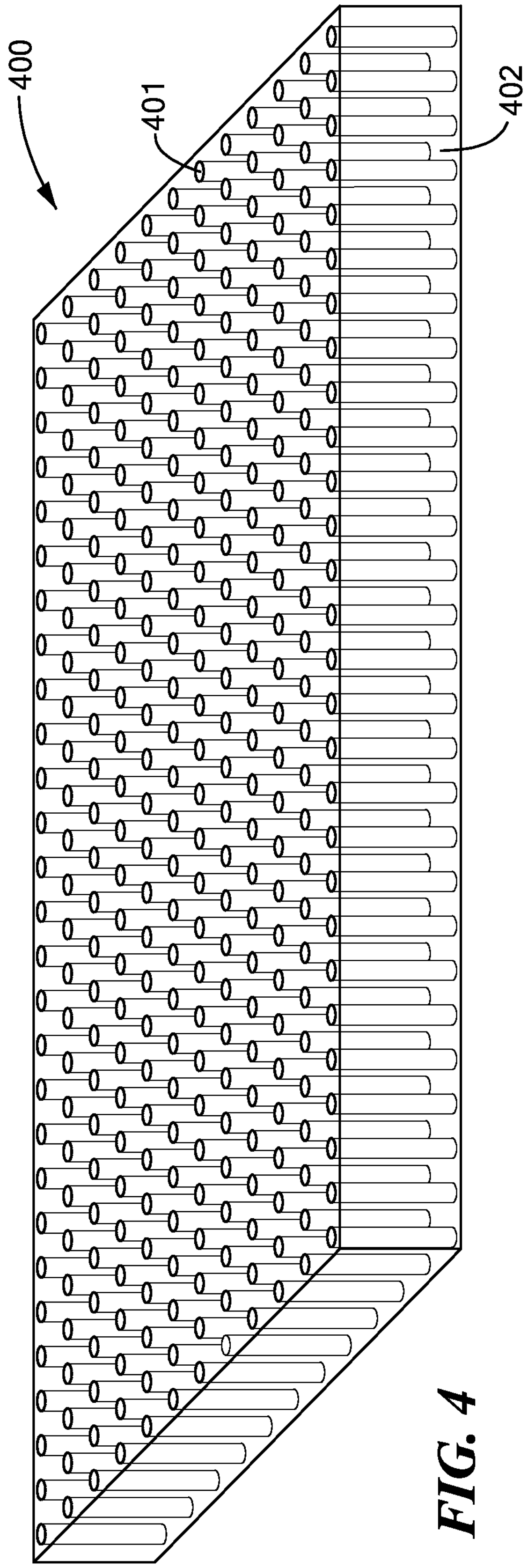

FIG. 4

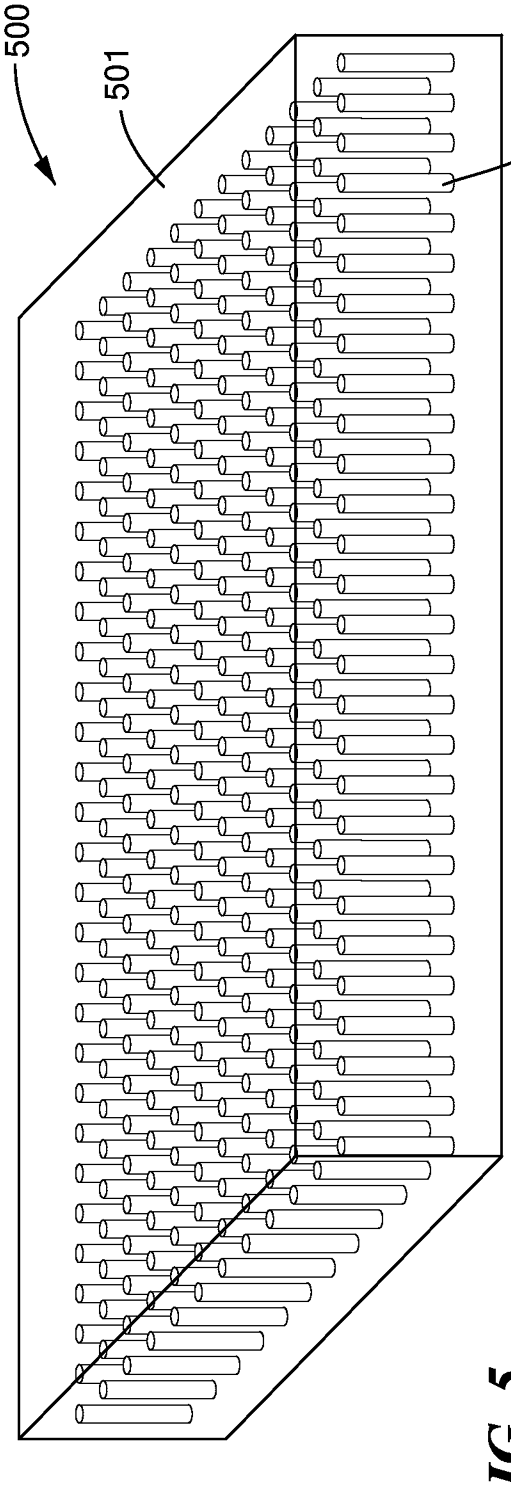

FIG. 5

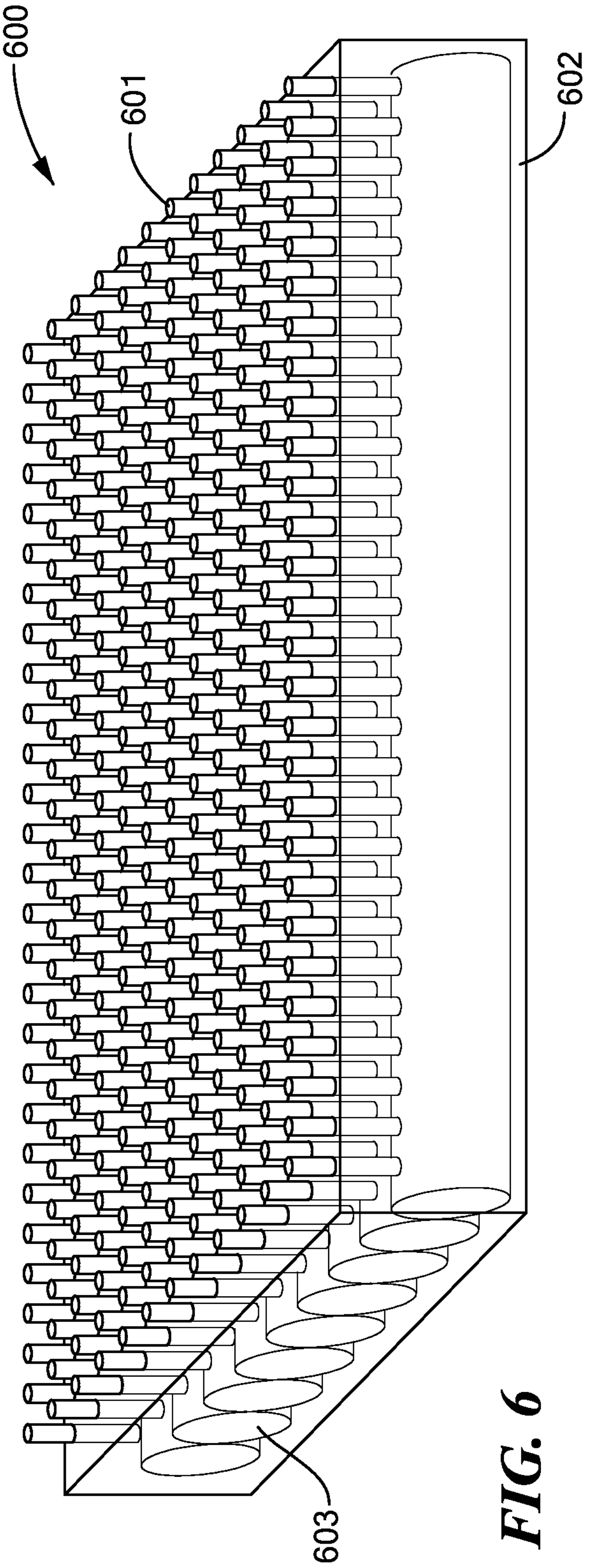

FIG. 6

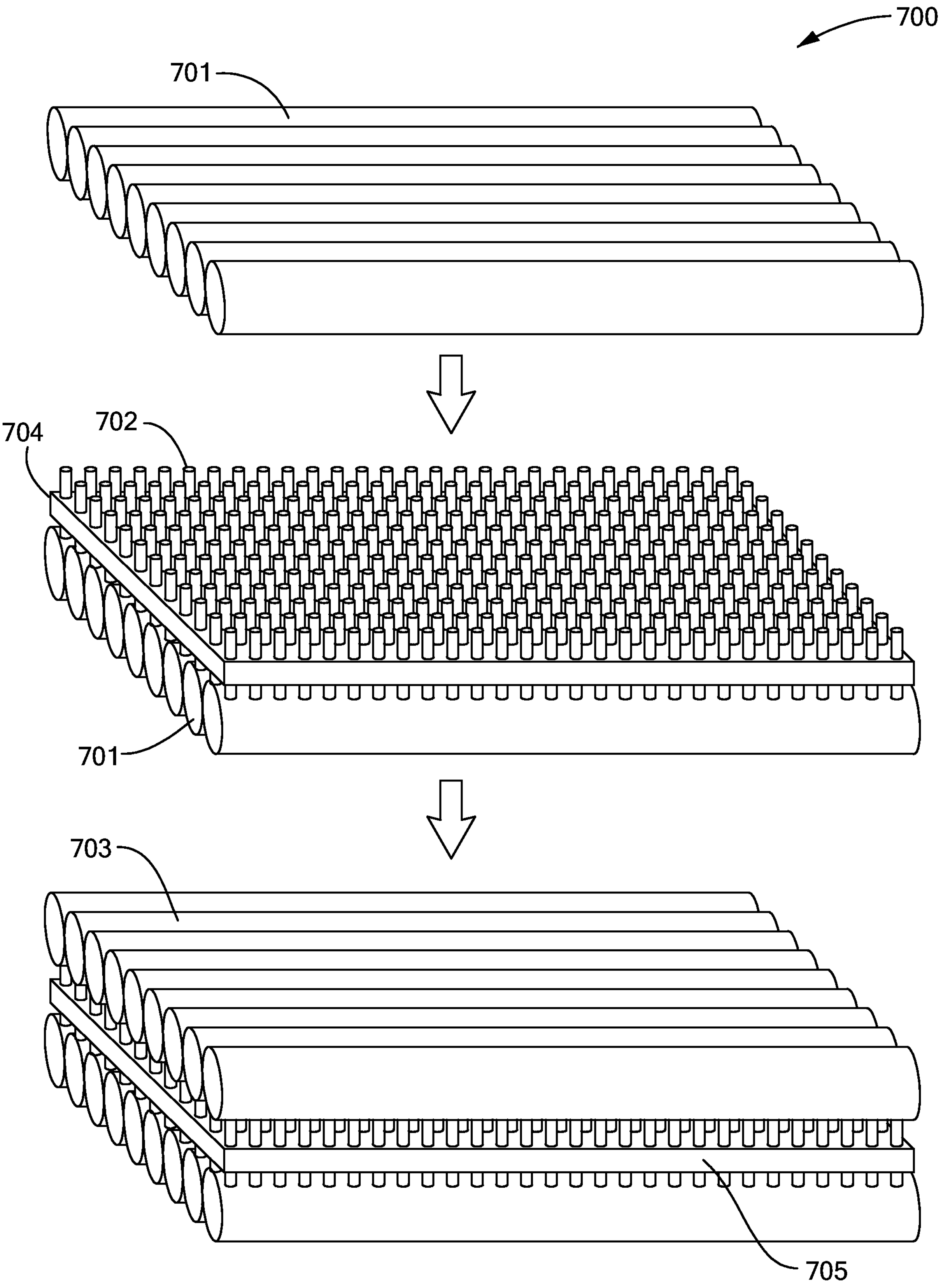

FIG. 7

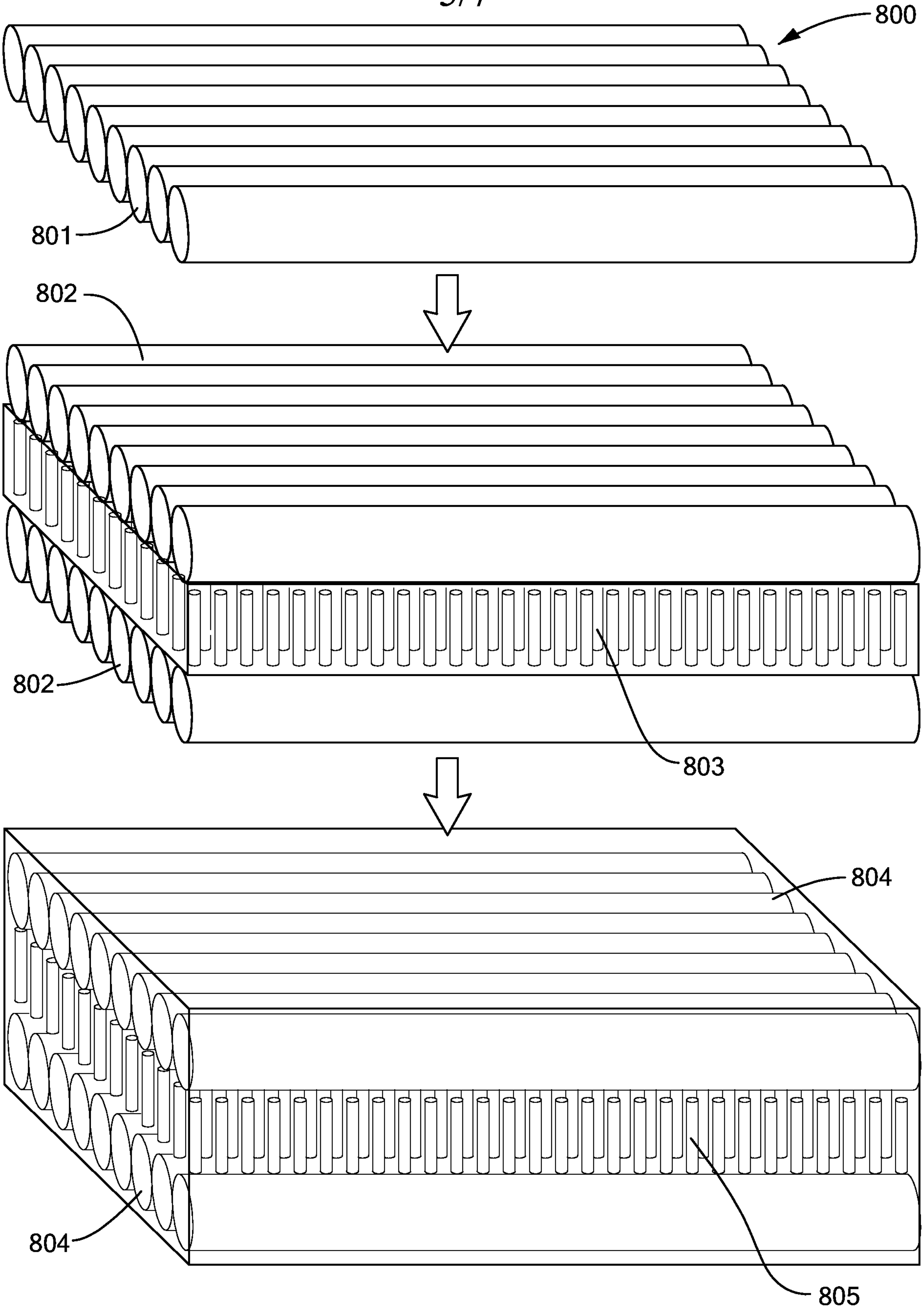

FIG. 8

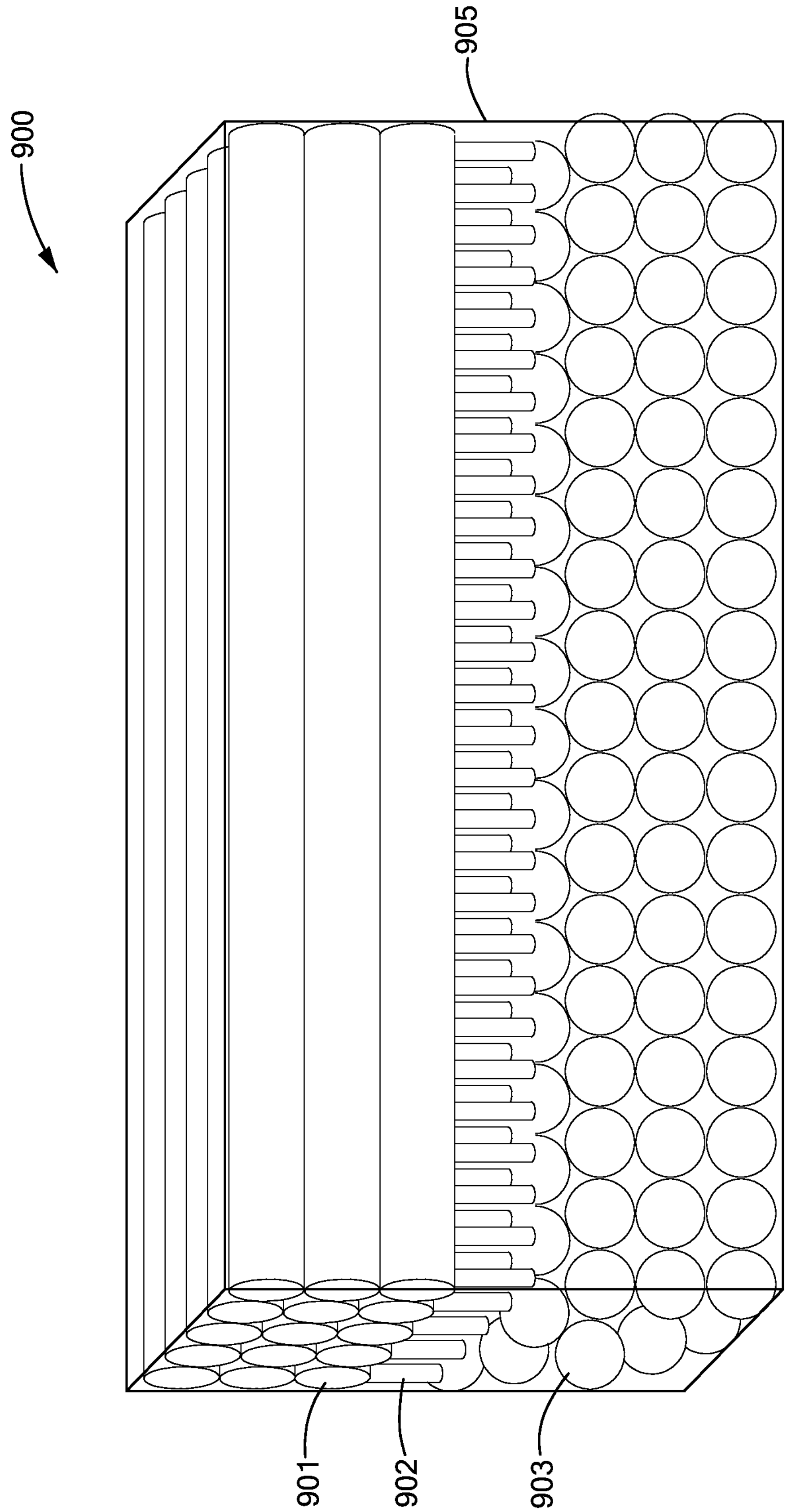

FIG. 9

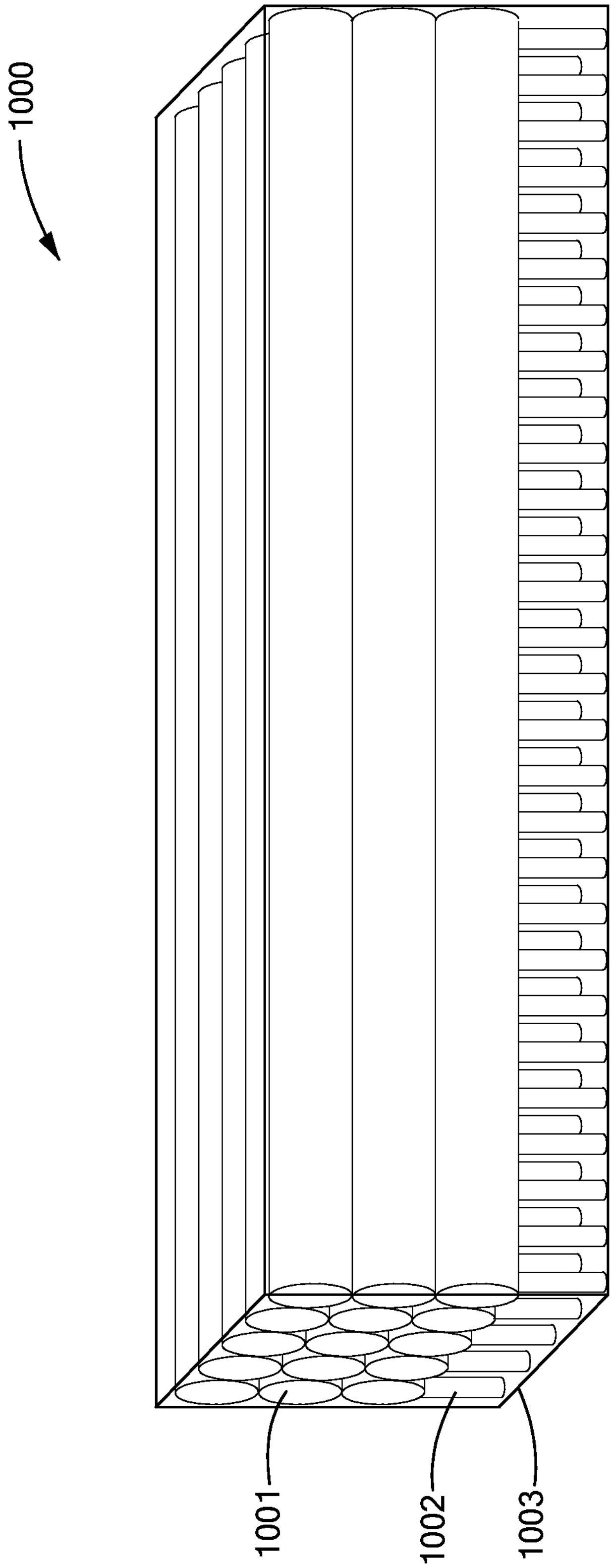

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/014399

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B32B 5/02 (2015.01)
CPC - B32B 5/12 (2015.01
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)
IPC(8) - B32B 5/02, 5/14, 5/26; B82Y 30/00, 40/00 (2015.01)
CPC - B32B 5/12, 5/26, 5/28, 2250/20, 2250/42, 2260/023, 2260/046, 2262/106, 2305/076, 2305/77, 2307/202; B82Y 30/00, 40/00 (2015.01) (keyword delimited)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 428/338, 401; 977/742, 762, 789 (keyword delimited)

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

Orbit, Google Scholar
Search terms used: article, nanostructure, array, resin, matrix, density, conductivity, backing film

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/0164903 A1 (WARDLE et al) 28 June 2012 (28.06.2012) entire document	1-3, 31-33, 53, 55
Y		4, 54
Y	US 2013/0071565 A1 (MALECKI et al) 21 March 2013 (21.03.2013) entire document	4
Y	US 2013/0216811 A1 (UNIVERSITY OF HAWAII) 22 August 2013 (22.08.2013) entire document	54
A	US 2011/0192233 A1 (AIZENBERG et al) 11 August 2011 (11.08.2011) entire document	1-4, 31-33, 53-55
A	US 8,257,678 B2 (STEINER III et al) 04 September 2012 (04.09.2012) entire document	1-4, 31-33, 53-55
A	US 7,968,273 B2 (CHEN et al) 28 June 2011 (28.06.2011) entire document	1-4, 31-33, 53-55
A	US 8,557,507 B2 (JANG et al) 15 October 2013 (15.10.2013) entire document	1-4, 31-33, 53-55
A	US 2013/0101495 A1 (PETERSON et al) 25 April 2013 (25.04.2013) entire document	1-4, 31-33, 53-55

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"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 06 April 2015	Date of mailing of the international search report 07 MAY 2015
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. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/014399

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.: 5-30, 34-52, 56-72
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:

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.:

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.