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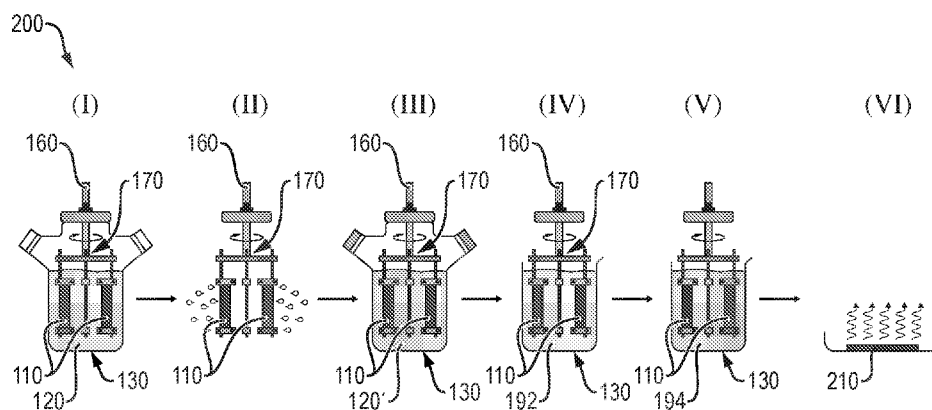


FIG. 2

(57) Abstract: The present disclosure is directed to synthesizing a nanomaterial-polymer composite via in situ interfacial polymerization. A nanomaterial is exposed to a solution having a first solute dissolved in an aqueous solvent to uniformly, or substantially uniformly, distribute the solvent throughout the porosity of the network of the nanomaterial. The nanomaterial is then exposed to a second solution having a second solute dissolved in an organic solvent, which is substantially immiscible with the first solvent, with the first solute reacting with the second solute. The first and second solutions can be stirred, or otherwise moved with respect to each other, to facilitate transport of the second solution throughout the nanomaterial to promote reaction of the polymer within the nanomaterial to produce a polymer composite having uniform morphology.



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SYSTEMS, DEVICES, AND METHODS FOR PROMOTING IN SITU POLYMERIZATION WITHIN NANOMATERIAL ASSEMBLIES

CROSS REFERENCE TO RELATED APPLICATION

[0001] The present disclosure claims priority to U.S. Provisional Application No. 62/749,751, entitled “In Situ Polymerization within Nanomaterial Assemblies,” which was filed on October 24, 2019, and which is incorporated by reference herein in its entirety.

GOVERNMENT RIGHTS

[0002] This invention was made with Government support under Grant No. NNX17AJ32G awarded by NASA. The Government has certain rights in the invention.

10 FIELD

[0003] The present disclosure relates to systems, devices, and methods for synthesizing a polymer inside of a nanoporous medium, and more particularly relates to formation of highly-loaded nanomaterial-polymer composites by in situ interfacial polymerization to achieve substantially uniform or uniform morphology within nanomaterial structures.

15 BACKGROUND

[0004] Composite materials combining nanoporous materials, have been widely sought to achieve high strength, high toughness, and in some cases multifunctional performance. One example of such nanoporous materials are carbon nanotubes (CNTs), which exhibit outstanding mechanical, electrical, and thermal properties, and their nanometer-scale diameter and high aspect ratio enables load transfer to polymers via van der Waals, π interactions, or covalent bonding. Despite the focus of conventional techniques on using CNTs as a filler to polymer matrices at low loadings, recent emphasis has been placed on processing methods that leverage organized CNT assemblies, such as forests, sheets, or fibers, to achieve highly loaded CNT composites via polymer infiltration.

25 [0005] Infiltration of polymers into neat CNT structures, such as sheets and yarns, has proven effective to enhance CNT-CNT load transfer, and hence create a composite with improved Young's modulus and tensile strength as compared to the neat CNT structure. CNTs are commonly used as a reinforcement phase in composite systems because they are

small (typically having diameters approximately in the range of about 1 nm to about 10 nm) and lightweight (*e.g.*, having a density of approximately 1.3 g/cm^3), and exhibit extreme stiffness and strength (*e.g.*, having a stiffness of approximately -1 TPa; *e.g.*, having a strength of approximately >100 GPa) substantially greater than the properties of any carbon fiber or metal. Common methods of creating CNT/polymer composites involve dispersing CNTs in a monomer or polymer solution, a time-and-energy-intensive process that can damage the CNT structure, degrading its mechanical properties. Moreover, such methods are typically limited to a maximum content of approximately 1-10 wt.% CNTs for the final composite material, and are prone to aggregation of the CNTs.

[0006] The common method used to obtain composite systems with a higher CNT content involves infiltrating a nanoporous CNT structure, such as a yarn or sheet obtained by floating catalyst chemical vapor deposition (CVD) synthesis, with a polymer dissolved at low concentration in a solvent, an uncured resin, or a polymer melt. Because the size of the oligomer or polymer chains is typically on the same order of magnitude as the porosity within the CNT structure, the macromolecules typically have low mobility into the CNT structure. For example, typical resins and polymers used in composite processing have characteristic molecular size comparable to CNT diameters, therefore making infiltration a slow process (sometimes involving soaking for hours or even days) that can be highly dependent on parameters such as polymer chain length, molecular structure, as well as the chemical interaction with its surroundings (CNTs, additional solvent, etc.). This approach results in highly heterogeneous structures with phase separation between polymer-rich and CNT-rich regions, as well as incomplete filling of the initial porosity. Agglomeration during infiltration of pre-made polymers or oligomers, as well as the creation of sub-micron voids acting as stress concentrators in the structure, contribute to significant weakening of the characteristics of the resultant composite system, often inhibiting its mechanical and electrical properties. Commercially, CNT-based composites are notably suited to complement existing carbon fiber (CF) composites such as by interlaminar toughening and grafting of CNTs on CFs.

[0007] Numerous techniques for fabrication of CNT-polymer composites exist for formation of polymers in a nonporous network, with each technique, despite having benefits, also having significant shortcomings. Melt processing is a widespread industrial technique and has been used to produce low-loading CNT composites at large scale, such as by bulk

mixing. In melt processing, dedicated steps to remove impurities or solvents are not needed, and controlling the cooling rate also enables adjustment of the degree of crystallinity of the polymer, particularly in an interphase region. In the case of polypropylene and CNT forests with low density, melt infiltration can induce enhanced crystallization by a combination of shear stress occurring in the initial stage of infiltration multi-walled carbon nanotube (MWCNT) arrays by flowing molten polymer, and template-based growth of crystallites. Such enhanced crystallization due to shear stress results in a highly crystalline polymer and improved tensile properties for the final composite. However, composites obtained through polymer melt infiltration often feature poor mechanical properties. The high viscosity of the melt causes the CNTs to aggregate and/or results in occasional voids and polymer-rich regions that limit the composite strength. Partial infiltration is usually a consequence of the low mobility of the organic molecules forming a highly entangled melt, while phase separation is the result of CNT agglomeration due to capillary forces.

[0008] Alternate methods for fabricating CNT-polymer composites include pre-polymer infiltration in which fiber composite systems utilize pre-polymer mixtures that are subsequently mixed with a filler (nanoparticle, fibers, etc.) and cured. For instance, carbon fiber composites are typically processed by infiltration of resins that comprise monomers and short-chain polymers (oligomers), as well as smaller crosslinking agents and additives, in which the resin chemistry and thermal curing processes can be optimized for high modulus and tensile strength. Compared to direct melt infiltration, CNT composites that utilize this approach exhibit faster diffusion of the reactive species compared to melt infiltration. For example, a CNT network can be impregnated by the liquid resin for several hours before being cured at elevated temperature. However, the viscosity of pre-polymer resins is still quite high, and the resulting forces exerted during infiltration can cause CNT aggregation and phase separation. This can be highly dependent on the resin system used, and it is often difficult to predict whether a resin system will wet a CNT network well. Moreover, some epoxy-based resins have exhibited poor wetting of a CNT network, and capillary forces during evaporation of solvents may lead to voids in the composite. Moreover, the presence of a large amount of CNTs can influence the curing process by sterically hindering interaction between the monomers/oligomers and the curing agents, which can lead to heterogeneities of the composite where monomers at the vicinity of a CNT may polymerize at a different rate, resulting in a broad molecular weight distribution for the final polymer. However, the presence of CNTs may result in an acceleration or a slowdown of the

polymerization reaction through a decrease or increase in the steric hindrance effect respectively. Moreover, introducing CNTs in the resin can result in faster thermal curing due to excellent CNT thermal conductivity, or catalytic effect due to the surface chemistry of the CNT. Lastly, some polymers exhibit significant shrinkage while curing, therefore disturbing the morphology of the CNT network.

[0009] Yet another approach of CNT composite fabrication by polymer infiltration uses a polymer dissolved in a solvent as the liquid phase. In this approach, the lower viscosity of polymer solutions, compared to polymer melts or pre-polymer resins, allows the polymer to be more easily infiltrated through the CNT network by immersion or spray coating.

Additionally, adjusting the choice of solvent, as well as the polymer concentration and molecular weight allows tuning of the mobile phase viscosity. However, deficiencies of this approach include that the solvent being used as a carrier phase for polymer infiltration must be removed *a posteriori*, while use of a solvent can cause CNT aggregation during solvent evaporation due to capillary forces (*e.g.*, elastocapillary aggregation) exerted by the receding meniscus. Further, heterogeneity of the final composite structure on the micrometer to millimeter scale is therefore a big challenge arising from polymer solution infiltration.

[0010] Accordingly, there is a need to create systems, devices, and methods for rapid and scalable synthesis of highly loaded nanomaterial-polymer composites having uniform morphology. Moreover, there is a further need for techniques that improve the properties of these composites due to local voids in the composite, phase separation, and lack of optimization of hierarchical load transfer between the polymer and any nanoporous materials, including CNTs.

SUMMARY

[0011] In one exemplary embodiment of a method of synthesizing a polymer within a nanoporous medium, the method includes exposing a nanoporous substrate to a first solvent having a first solute dissolved in the first solvent to allow the first solvent and solute to infiltrate the nanoporous substrate, and exposing the nanoporous substrate to a second solvent having a second solute dissolved in the second solvent to allow the second solvent and solute to travel through the porosity of the nanoporous substrate to react the second solute with the first solute to form the polymer. The second solvent is sufficiently immiscible with the first solvent.

[0012] The method can also include stirring the substrate while the substrate is exposed to the second solvent to assist the transport of the second solvent through the substrate where the first solute reacts with the second solute to form the polymer. The polymer can be formed at the interface between the first and second solvents or at the interface between the substrate and the second solvent while the substrate is disposed in the second solvent. A spacing between adjacent nanostructures in the nanoporous substrate can be approximately in the range of about 1 nanometer to about 100 nanometers, or more particularly approximately in the range of about 1 nanometer to about 10 nanometers.

[0013] The first solute and/or the second solute can include one or more of a monomer, a mixture of monomers, an oligomer, a mixture of oligomers, or a mixture of a monomer and an oligomer. In some embodiments, the first solvent can include water and the second solvent can include an organic solvent. The reaction of the first and second solutes can occur within the second solvent. In some embodiments, the second solvent can wet the substrate after the substrate is disposed in the second solvent to substantially displace the first solvent.

[0014] The second solvent can travel through the porosity of the nanoporous substrate faster than the first solvent travels through the porosity of the nanoporous substrate. In at least some embodiments, the substrate can be dried between exposure to the first solvent and exposure to the second solvent.

[0015] The method can include drying the substrate after removing the substrate from the first solvent and prior to disposing the substrate in the second solvent. The substrate can include one or more of cellulose, ceramic, metal, polymer, carbon nanotubes, graphene, silicon nanowires, or boron nitride nanotubes, in the form of a powder, foam, lattice, sheet, or yarn.

[0016] The method can further include rinsing the substrate in one or more additional solvents to remove byproduct or unreacted solutes from the substrate. The one or more additional solvents can include acetone and/or water. The method can also include collecting the polymer composite and trying the polymer composite. The first solute can be soluble in the second solvent.

[0017] The method can include disposing the substrate in the first bath for at least about 10 minutes and/or disposing the substrate in the second bath for at least about 5 minutes. In some embodiments, the method includes repeatedly disposing the substrate into the first bath

and/or the second bath to increase a final polymer content of the polymer within a nanoporous medium.

[0018] In some embodiments, the method can include a mechanical force being applied to the substrate during or after disposing the substrate in the first solvent or in the second solvent. The mechanical force can be tensile or compressive.

[0019] One exemplary embodiment of a method of synthesizing a polymer composite includes disposing a nanomaterial substrate having a porous structure in a first bath that contains a first solvent, the first solvent having a first solute dissolved in the first solvent, removing the substrate from the first bath, and disposing the substrate in a second bath that contains a second solvent, the second solvent having a second solute dissolved in the second solvent. Disposing the substrate in the second bath reacts the first and second solutes to form a polymer composite. The second solvent is sufficiently immiscible with the first solvent.

[0020] The method can also include stirring the substrate in the second bath to assist the transport of the second solvent through the substrate, and to react the first solute with the second solute to form the polymer composite. The polymer composite can form at the interface between the first and second solvents or at the interface between the substrate and the second solvent while the substrate is disposed in the second solvent. A spacing between adjacent nanostructures in the nanomaterial substrate can be approximately in the range of about 1 nanometer to about 100 nanometers, or more particularly approximately in the range of about 1 nanometer to about 10 nanometers.

[0021] The first solute and/or the second solute can include one or more of a monomer, a mixture of monomers, an oligomer, a mixture of oligomers, or a mixture of a monomer and an oligomer. In some embodiments, the first solvent can include water and the second solvent can include an organic solvent. The reaction of the first and second solutes can occur within the second solvent. In some embodiments, the second solvent can wet the substrate after the substrate is disposed in the second solvent to substantially displace the first solvent.

[0022] The method can include drying the substrate after removing the substrate from the first solvent and prior to disposing the substrate in the second solvent. The substrate can include one or more of cellulose, ceramic, metal, polymer, carbon nanotubes, graphene, silicon nanowires, or boron nitride nanotubes, in the form of a powder, foam, lattice, sheet, or yarn.

[0023] The method can further include rinsing the substrate in one or more additional solvents to remove byproduct or unreacted solutes from the substrate. The one or more additional solvents can include acetone and/or water. The method can also include collecting the polymer composite and trying the polymer composite. The first solute can be soluble in the second solvent.

[0024] The method can include disposing the substrate in the first bath for at least about 10 minutes and/or disposing the substrate in the second bath for at least about 5 minutes. In some embodiments, the method includes repeatedly disposing the substrate into the first bath and/or the second bath to increase a final polymer content of the polymer composite.

[0025] In some embodiments, the method can include a mechanical force being applied to the substrate during or after disposing the substrate in the first bath or in the second bath. The mechanical force can be tensile or compressive.

[0026] One exemplary polymer composite can include a nanoporous material having a polymer substantially uniformly distributed throughout a structure of the material. The polymer is formed from a reaction of a first solute and a second solute within pores of the nanoporous material at a liquid-liquid interface within the nanoporous material

[0027] In some embodiments, the solute includes one or more of a monomer, a mixture of monomers, an oligomer, a mixture of oligomers, and a mixture of a monomer and an oligomer. The first solute can include one or more of amines, piperazines, thiols, diols, acid halides (*e.g.*, acyl chloride, or acid chloride, acyl fluoride, acyl bromide, or carbon suboxides). The nanoporous material can include one or more of cellulose, ceramics, metal foam, polymer fiber mat or foam, sheet, fiber, or yarn comprising carbon nanotubes, boron nitride nanotubes, or graphene. The polymer can include one or more of a polyamide, a polyurea, or nylon. In some embodiments, the nanoporous material can have a porosity approximately in the range of about 1 nanometer to about 10 nanometers.

BRIEF DESCRIPTION OF DRAWINGS

[0028] This disclosure will be more fully understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

[0029] FIG. 1A is a perspective view of one exemplary embodiment of a system of synthesizing a polymer composite, the system including a flask;

[0030] FIG. 1B is a perspective view of a carousel used in the flask of FIG. 1A, the carousel having a plurality of substrates attached thereto;

5 [0031] FIG. 1C is a side view of a substrate disposed within the carousel of FIG. 1B;

[0032] FIG. 2 is a schematic side view of one exemplary embodiment of a sequence of steps of one exemplary method of synthesizing a polymer composite using the devices of FIGS. 1A-1C;

10 [0033] FIG. 3 is a schematic illustration that shows the impact of low polarity and high polarity solvents and low and high solute concentration on a resulting polymer composite;

[0034] FIG. 4A is a plot illustrating polymer distribution across a thickness of a bare CNT ribbon;

[0035] FIG. 4B is a plot illustrating polymer distribution across a thickness of a polymer composite ribbon obtained using chloroform;

15 [0036] FIG. 4C is a plot illustrating polymer distribution across a thickness of a polymer composite ribbon obtained using cyclohexanone;

[0037] FIG. 5A is a graph illustrating stress-strain curves for a bare CNT structure as well as CNT-polymer composites;

20 [0038] FIG. 5B is a graph illustrating values of elastic modulus as a function of polymer content with respect to the compounds of FIG. 4A;

[0039] FIG. 5C is a graph illustrating values of tensile strength as a function of polymer content with respect to the compounds of FIG. 4A;

[0040] FIG. 6 is a schematic side view of an exemplary embodiment of a continuous process of synthesizing a polymer composite;

25 [0041] FIG. 7 is a schematic detailed illustration of the nanomaterial network throughout a process of synthesizing the polymer composite; and

[0042] FIG. 8 is a schematic illustration of a solute diffusing across the interface between two immiscible liquids to engage in a polymerization reaction.

DETAILED DESCRIPTION

[0043] Certain exemplary embodiments will now be described to provide an overall understanding of the principles of the structure, function, manufacture, and use of the systems, devices, and methods disclosed herein. One or more examples of these embodiments are illustrated in the accompanying drawings. Those skilled in the art will understand that the systems, devices, and methods specifically described herein and illustrated in the accompanying drawings are non-limiting exemplary embodiments and that the scope of the present disclosure is defined solely by the claims. The features illustrated or described in connection with one exemplary embodiment may be combined with the features of other embodiments. Such modifications and variations are intended to be included within the scope of the present disclosure.

[0044] To the extent a term like “nanoporous” is used herein without a structural modifier, a person skilled in the art, in view of the present disclosure, will understand that it includes a nanomaterial having a porous network, with the porosity of the network typically being variable and/or uniform throughout the nanomaterial. Additionally, to the extent the terms “substrate” and “material” are described in the present disclosure, a person skilled in the art will recognize that these terms are used interchangeably. Further to the extent the terms “solutions” and “phases” are described in the present disclosure, a person skilled in the art will recognize that these terms are used interchangeably. Still further, to the extent compounds, sides, or steps are described as being “first” or “second,” such numerical ordering is generally arbitrary, and thus such numbering can be interchangeable. For example, the terms “first solute” and “second solute” can refer to the order in which the substrate is exposed to solutes, with the terms “first” and “second” being able to be applied to various compounds, some of which can be interchanged in different embodiments so as to be a “first solute” in a given embodiment and a “second solute” in an alternate embodiment. Still further, in the present disclosure, like-numbered components of various embodiments generally have similar features when those components are of a similar nature and/or serve a similar purpose. The present disclosure includes some illustrations and descriptions that include prototypes or bench models. A person skilled in the art will recognize how to rely

upon the present disclosure to integrate the techniques, systems, devices, and methods provided for into a product in view of the present disclosures.

[0045] The present disclosure generally relates to systems, devices, and methods for promoting in situ interfacial polymerization to synthesize a polymer within a nanoporous medium to form a polymer composite. Interfacial polymerization can be used synthesize a polymer within a network via a reaction that occurs at a liquid-liquid interface within the network to form a polymer composite that is dense, lightweight, and strong, and in some embodiments, having an attractive combination of one or more of mechanical strength, stiffness, electrical conductivity, thermal conductivity, and/or low density. In an exemplary embodiment of synthesizing a polymer composite, solutes can travel, transport, or infiltrate, through a nanoscale porosity of the nanoporous medium to subsequently react and form the polymer. Once the solutes fill the porosity, they can polymerize, *e.g.*, react with one or more solutes, within the porosity to form the polymer composite. By starting from solutes, which can be approximately 10,000 times smaller than polymer macromolecules formed after polymerization, the materials can travel throughout the porosity of the nanomaterial to form a polymer composite having a tailored polymer content. A person skilled in the art will recognize that the tailored polymer content can establish uniform loading, though, in some embodiments, the volume fraction of the polymer content can vary from approximately 10% to approximately 100%.

[0046] One exemplary embodiment of a process for synthesizing the polymer composite can include exposing a nanomaterial substrate, or a nanoporous material, to a solution of a solvent having a solute dissolved therein to allow the solution to infiltrate the network to wet the substrate while carrying the solute throughout the porosity of the nanomaterial. The wet substrate can then be exposed to a second solution that includes another solvent, this solvent being immiscible with the previous solvent and having another solute dissolved therein. The solution can be stirred or otherwise mixed to increase the speed of travel of the second solution through the substrate. As the second solution enters the substrate, the solutes can react with one another within the nanomaterial to form a polymer composite. The polymer composite can then be removed from the solution, washed and dried to remove the solutions, byproducts, and unreacted solute therefrom, and dried to produce the final polymer composite. Alternate embodiments of the process can include a continuous process in which the substrate is disposed within multiple baths of solutions causing the polymer composite to

be formed. Other ways of processing substrates by causing a first solute to react with a second solute to form a polymer composite in view of the present disclosures are also possible without departing from the spirit of the present disclosure.

[0047] FIGS. 1A-1C illustrate an exemplary embodiment of a system 100 for synthesizing a nanomaterial-polymer composite. The system 100 can include one or more ribbons, or substrates, 110 disposed in a container for mixing with a solution 120. The system 100 can be configured to dispose, such as, by ways of non-limiting examples, dipping or soaking, the one or more substrates 110 in the solution 120 to expose the substrates 110 to the solution, which allows the solution to infiltrate the substrate 110.

[0048] As shown, the system 100 can include a flask 130 for retaining the solution 120 therein. The flask 130 can include a single solution, as shown, though in some embodiments, the flask 130 can retain a plurality of solutions therein. A person skilled in the art will recognize that the volume of the flask 130 can vary, though in some embodiments the flask 130 can have a volume that is large enough to allow multiple substrates 110 to be submerged therein. For example, as shown, the flask 130 can include six substrates 110 disposed therein, though five or less, or seven or more, substrates can be disposed therein. The substrates 110 can be fully or substantially fully submerged, as shown, to allow the solution to travel throughout the entirety of the network, though in some embodiments only portions of the substrate can be submerged if the composite is desired to be formed in only a portion of the substrate.

[0049] The solution 120 can include one or more solvents that include a substance therein. For example, the solution 120 can include one or more of water, glycerol, ethylene glycol, and/or an organic solvent (*e.g.*, cyclohexanone, hexane, chloroform, tetrahydrofuran, benzene, carbon tetrachloride, and so forth) having the substances dissolved therein. The substances can be dissolved substantially uniformly, though in some embodiments a dispersion can be formed.

[0050] The solution 120 can include one or more solute(s) or therein. The solute(s) can include a monomer, a mixture of monomers, an oligomer, a mixture of oligomers, and/or a mixture of a monomer and an oligomer, and so forth. A person skilled in the art will recognize that the oligomers can include reactive groups at one or more ends thereof that have the same functional groups as those of the monomers, thereby promoting reaction with

the monomers and/or other oligomers. The monomers can be dissolved and/or dispersed in the solvent to form the solution of varying solubility. Some non-limiting examples of monomers include amines, piperazines, thiols, diols, acid halides (*e.g.*, acyl chloride, or acid chloride, acyl fluoride, acyl bromide, and/or carbon suboxides) Moreover, to the extent that the instant disclosure discusses the compounds in the solvents as monomers herein, other solutes such as (*e.g.*, sodium carbonate, sodium chloride, sodium hydroxide, trihydroxy titanium stearate) and surface-active agents (*e.g.*, sodium lauryl sulfate) can be used in lieu of, and/or in addition to, monomers.

[0051] The flask 130 can include a stirrer 140 for agitating the solution. For example, the flask 130 can be coupled to an overhead stirrer 140 for rotating the substrates 110 relative to the solution to facilitate transport of the solution throughout the substrates 110. Stirring of the solution when the substrates are disposed therein can assist with the transport of the solution through the substrates and/or facilitate in situ polymer formation within the substrate network, as described further below. A person skilled in the art will recognize that transport phenomena such as convection, diffusion, and/or imbibition can apply to the solution and the monomer that travel and/or infiltrate the network of the substrate 110. Although the illustrated embodiment uses a stirrer, carousel, and rotary shaft, a person skilled in the art will understand that there exist a multitude of alternate conditions under which the substrates can be exposed to the solution, including ultrasonication, vortex stirring, or tumbling. In some embodiments, the flask 130 can include a gasket 150. The gasket 150 can hold the carousel in place by engaging the rotary shaft 160, which allows rotation of the flask while keeping the solution sealed.

[0052] The stirrer 140 can be coupled to a rotary shaft 160 associated with the substrate that spins the substrates within the flask relative to the solution, as shown and discussed in FIG. 1B in greater detail below. More specifically, FIG. 1B illustrates an exemplary embodiment of a carriage or carousel 170 configured to attach to the stirrer 140 and to be rotated. The carousel 170 can include the rotary shaft 160 and one or more sample holders 180 that extend through a length of the carousel 170. Each of the sample holders 180 can be coupled to a substrate 110 for introduction into the flask 130. As shown, the carousel 170 can include six sample holders 180, each having a substrate 110 attached thereto, though it will be appreciated that five or fewer or seven or more sample shafts can be used. The

sample holders 180 can be spaced apart from one another to prevent overlap between the substrates in instances where no overlap is desired.

[0053] FIG. 1C illustrates the substrate 110 used to form the nanomaterial-polymer composite attached to each sample holders 180 in greater detail. As shown, the nanomaterial can be disposed between clamps 190 of the sample shaft to suspend, and optionally stretch, the substrate 110 therebetween. CNTs, when formed into a network such as a sheet, yarn, mat, or other assembly, are one example of a nanoporous material which can be processed to create a composite article, resulting in a highly loaded nanomaterial-polymer composite. A person skilled in the art will recognize that although the instant disclosure discusses printing systems, devices, and methods of synthesizing CNT-polymer composites, the systems, devices, and methods generally discussed herein can be applied to any nanomaterial, regardless of its physical properties, assembled form, or surface chemistry to synthesize nanomaterial-polymer composites. For example, the nanomaterial can include nanotubes and/or nanowires of carbon, silicon, graphene oxide, graphene, boron nitride, cellulose, and so forth, to synthesize composites such as film, yarn, fiber, 'bucky paper', sponge, forests, materials with and without surface functionalization and/or coating, and other three-dimensional assemblies that include the nanostructures discussed above. It will be appreciated that depending on the choice of nanomaterial, its surface functionalization, and the combination of solutes, it is possible to chemically bond formed polymer chains to the surface of the nanomaterial. Further, in the case where the scaffold material is a CNT network, a high nanotube content can allow for the formation of polymers with properties differing from when they are synthesized bulk, including higher crystallinity and/or higher tensile strength.

[0054] The nanomaterial that makes up the substrate 110 can have a characteristic pore size that may span a wide range of values, and be either uniform or have a distribution of pore sizes locally or within the span of the material. For example, the substrate 100 can have an average pore size of about 100 nanometers or less, though, in some embodiments, the average pore size can be about 10 nanometers or less, of about 5 nanometers or less, of about 3 nanometers or less, and/or of about 1 nanometer or less. The small pore size can enhance the ability of the nanomaterial to retain solutes and/or other substances therein, though larger substances and compounds may have difficulties entering the substrate at smaller porosity

values. Similarly, the substrate 110 can have an average pore size larger than 10 nanometers which allows compounds to travel more easily through the substrate.

[0055] FIG. 2 illustrates an exemplary embodiment of a method 200 for synthesizing a polymer inside a nanoporous medium, *e.g.*, the substrate 110. As shown in (I), the carousel 170 is disposed within the flask 130 such that the substrates 110 are substantially immersed in the first bath of solute solution 120 to allow for transport of the solution throughout the nanomaterial. The carousel 170 can be rotated with respect to the flask, and thus the solution, either via the rotary shaft 160 coupled to the stirrer 140 of the flask 130 or manually, to increase the dynamic nature of the process to expedite transport of the solution through the nanomaterial. Nevertheless, it will be appreciated that in some embodiments the diffusion can be performed statically. It will further be appreciated while the solution travels through the substrate, the solute contained within the solvent 120 can become entrapped within the porosity of the substrate 110 so as to become substantially uniformly distributed from the walls to the center of the substrate.

[0056] The time spent in the bath 120 is defined by the duration necessary for the solute to substantially diffuse through the nanoporous structure, where substantial diffusion is at least 95% of the initial porosity is filled with the solution. The amount of time that the substrate 110 is exposed to the solution 120 can vary based, at least in part, on the material of the substrate 110, content of the solution 120, a temperature of the solution 120, ambient temperature, the stirring conditions that can contribute to convection, the solute concentration, and/or the salt content in solution (*e.g.*, pH in the case of an aqueous phase), and so forth. For example, in the case of a CNT substrate immersed in an aqueous solution, the substrate can be disposed in the solution or bath for about 10 minutes, though in some embodiments, the exposure time can be up to about 15 minutes, up to about 20 minutes, up to about 30 minutes, or any amount of time that is sufficient for the solvent 120 to travel throughout the substrate 110, which may include less than 10 minutes, such as about 5 minutes.

[0057] Once the solvent has sufficiently transported throughout the substrate 110, the substrate 110 and/or the carousel 170 can be removed from the solution 120 and dried to remove excess liquid from the substrate, while the first solution having the first solute is retained within the network. As shown in (II), the substrates 110 can be removed from the solution 120 and spun or rotated to remove excess solution therefrom, though it will be

appreciated that drying can occur in a variety of ways known to one skilled in the art in view of the present disclosures, including by heating, shaking, evaporating, squeezing, and so forth. To minimize drying time, rotating the carousel can effectively substantially remove unwanted solution, though any of the above-mentioned processes can be used.

5 [0058] After the substrate(s) 110 are sufficiently dried, the substrates 110 and/or the carousel 170 can be immersed in a second solvent 120'. For example, the wet substrate(s) 110 having the first solute entrapped within its porosity can be disposed within the second solvent 120' having the second solute therein, as discussed above. The substrates 110 can be stirred while in the solution 120', as shown in (III) to increase the transport of the solution
10 120' throughout the substrates 110. As the second solvent 120' travels throughout the substrates 110, the first solute within the porosity of the substrates 110 can react with the second solute in the solution 120' to form a polymer within the porous nanostructure of the substrates, as described in greater detail below. In some embodiments, a mechanical force can be applied to the substrate 110 during or after disposing the substrate 110 in the first
15 solvent 120 or in the second solvent 120'. The mechanical force can be tensile or compressive.

[0059] The polymerization reaction of the two solutes occurring in situ within the porosity of the substrate 110 can allow the polymer to be more uniformly distributed throughout the nanomaterial. The porosity of the network within the nanomaterial can be narrow, as
20 discussed above, which can prevent polymers from passing therethrough at least because polymer chains can be sized larger than the pores. Moreover, even if the polymer can be introduced through the walls of the substrate 110, it can be difficult to creep the polymer through the body of the nanomaterial into the center at least because the sponge-like shape of many nanomaterials has varying pore sizes and crevices that can hinder movement. A person
25 skilled in the art will recognize that movement of polymer chains through the substrate 110 would likely be slow, as it would take a lot of time polymer chains that contain many monomer units to navigate the inner walls of the substrate. For example, for short oligomers (molar mass approximately 1 kg/mol or less), it can take minutes to reach an infiltration depth of approximately 50 μm into a nanoporous network with a pore size of approximately 10
30 nanometers, while for longer polymer chains (molar mass approximately 100 kg/mol or more, typical for polystyrene, polyethylene, or polypropylene), infiltrating the same network can take up to a week, or a day if the pore size is larger, e.g., approximately 50 nanometers.

These times, while approximate, underscore the challenge of implementing polymer infiltration into nanoporous networks at rates that are practical for industrial processing. It will be appreciated that the above-described infiltration into nanoporous networks follows reputation theory and can be applied to any nanoporous network, *e.g.*, CNTs and the like.

5 Monomers, on the other hand, can be sized on the order of angstroms, which can allow passage through the porosity of the network of the nanomaterial with little resistance.

[0060] It will be appreciated that an organic solvent can be used in the solvent 120' when the first solvent 120 is aqueous such that the polymerization reactions takes place between two immiscible solvents. Immiscibility of the solvents allows the solutes contained therein to
10 react quickly and faster than either of the solutes react with the solvents. It will be appreciated that in the case of two miscible solvents, one or more of the solutes would react with the solvent to form a non-reactive species, which will neutralize the solute, thereby preventing a polymerization reaction between the solutes. For example, in a miscible solvent, acyl chloride can react to form a carboxylic acid, which is significantly less reactive and
15 would not polymerize. Moreover, a person skilled in the art will recognize that a polymerization reaction can be a slow-occurring process, which presents challenges for broader applicability and scalability. By undergoing interfacial polymerization, as provided for herein, which is a rapid chemical reaction through which a polymer is formed at the interface between two immiscible phases (liquid-liquid or liquid-solid), the polymerization
20 reaction can happen much more quickly due to the reactivity of the solutes. For example, diamine and acyl chloride are unstable compounds, resulting in a polymerization reaction that occurs substantially instantaneously to form the polymer, which can be orders of magnitude faster than conventional polymerization reactions.

[0061] Interfacial polymerization can be used in the textile industry, for example, to produce
25 continuous fibers from polymer systems obtained by poly-condensation, or for coating of wool fabric. Examples of polymers that can be formed through this method include polyamides, polyureas, and polyimides. The polymers can have a high aspect ratio (chain length) and a high degree of crystallinity. In interfacial polymerization reactions, polymers can form a film that synthesizes additional polymer film as the film is pulled and/or collected. Additional details
30 about interfacial polymerization are provided for in U.S. Patent Application No. 2,708,617, the disclosure of which is incorporated by reference herein in its entirety. A person skilled in the art understands the processes and techniques used in interfacial polymerization, and thus a detailed description is omitted for the sake of brevity.

[0062] Stirring of the solvents 120, 120' can promote interfacial polymerization at a liquid-liquid interface within the porosity of the nanomaterial, and prevent unwanted buildup of the polymer on the edges of the substrate 110. In some embodiments, the polymer can form at the interface between the substrate and the second solvent 120' and/or onto walls of the pores of the nanoporous substrate 110. Stirring can assist in the transport of the second solvent 120' through the porosity of the network of the nanomaterial, thereby preventing the polymer from forming *on* the nanoporous substrate 110, such as methods known to one skilled in the art for making desalination membranes, and rather allows for polymer formation *inside* the substrate to create a phase separated system within the nanoporous substrate. A person skilled in the art will recognize that implementations of interfacial polymerization to form polymer composites has not been previously implemented in combination with stirring. For example, formation of polymer-infiltrated CNT composites rapidly and in a scalable manner has previously relied on infiltration with a monomer followed by in-situ polyaddition. In such embodiments, polymerization can be thermally initiated by using benzoyl peroxide or 2,2'-azobisisobutyronitrile as an initiator, and monomers that undergo free radical bulk polymerization, such as methyl methacrylate (MMA), or styrene can be used.

[0063] Moreover, the relationship between solutes and their respective solvents can be chosen based on a type of reaction and/or a desired location of the polymerization reaction within the nanomaterial. For example, formation of the nanomaterial-polymer composite via polymerization of the two immiscible solvents occurs inward such that the polymer is formed within the nanomaterial. Further, in some embodiments, the solute of the first solution 120 has a stronger chemical affinity with the second solution 120' so that the solute can diffuse through the interface of the immiscible liquids and react with the second solute in the organic phase. Diffusivity of the solute of the first solution 120 into the organic phase is faster than the diffusivity of the solute of the second solution 120' into the aqueous phase. It will be appreciated that, in addition to the higher diffusivity values of the solute of the first solution 120 into the organic phase, little to no reaction occurs in the aqueous phase because when the solute of the second solution 120' enters the aqueous phase, it becomes neutralized and no polymerization reaction occurs between the solutes, as discussed in further detail below.

[0064] A person skilled in the art will recognize that use of two immiscible solvents refers to a process in which a solvent in the second solution 120' does not, or substantially does not, form a uniform solution with the solvent of the first solution 120 that remains in the

substrates 110. While the term “immiscible” is used to describe the relationship between the two solvents, immiscibility is a relative relationship between two solvents based mainly on the relative polarity of the solvents, and thus the term “immiscible” can encompass situations in which the solvents are substantially immiscible, sufficiently immiscible so as to form a liquid-liquid interface within the nanoporous network when the solvents contact one another, and/or be able to sit on top of one another when mixed such that a definitive boundary exists between the two solvents.

[0065] For example, chloroform and cyclohexanone, each of which can be used as the solvent of the organic phase, can produce composites with different solid structures due to their varying degrees of miscibility with the aqueous solvent of the first solution 120.

Chloroform is an example of a low polarity solvent, which makes it more immiscible with water, and cyclohexanone is an example of a high polarity solvent, which makes it less immiscible with water. FIG. 3 illustrates these two materials at varying concentrations of solute to illustrate the relationship between the immiscibility of solvents and/or solute concentrations on the formed polymer composite, though it will be appreciated that the figure can be applied to any two solvents of varying miscibility with water or each other. As shown in (i), when an aqueous phase (A) is mixed with a low polarity organic phase (B) that is strongly immiscible with water, *e.g.*, chloroform, in the presence of a low concentration of solute, the resultant polymer (P) composite forms only droplets within the nanomaterial network and does not exhibit uniform distribution throughout the network. In such embodiments, the low composite content can be attributed to low availability of solute to polymerize. In (ii), while the concentration of solute is high, the presence of substantial immiscibility of the organic phase (B) with the aqueous phase (A) results in formation of the polymer closer towards the outer surface of the nanomaterial discussed above, or a crust, due to polymer precipitation which is faster than the organic phase transport speed through the network. The presence of substantial immiscibility between the aqueous and organic phases can result in only partial polymer distribution/infiltration, with little to no polymer being formed closer to the center of the network. In (iii), on the other hand, when an aqueous phase (A) is mixed with a high polarity organic phase (B) that is more miscible with water, *e.g.*, cyclohexanone, in the presence of a high concentration of solute, the resultant polymer (P) is uniformly, or substantially uniformly, distributed throughout the nanomaterial network, as the more miscible organic phase transport is faster than polymer precipitation.

[0066] FIGS. 4A-4C illustrate EDS plots of polymer distribution across a bare CNT structure (A) and composite ribbons obtained using chloroform (B), and cyclohexanone (C). A person skilled in the art will recognize that tracking nitrogen (N) can provide polymer distribution across a thickness of a sample. As shown in FIG. 4B, chloroform (B), as compared to the bare CNT structure (A), shown in FIG. 4A, and cyclohexanone (C), shown in FIG. 4C, has a greater polymer composition at lower depth on either side of the sample. That is, the chloroform does not penetrate through the network, but rather only travels approximately 5 μm through the network before the polymer closes the porosity, unlike cyclohexanone, which has a uniform polymer distribution throughout the network, as shown by the nitrogen line remaining substantially flat throughout the distance shown in FIG. 4C.

[0067] FIGS. 5A-5C illustrate the effects that chloroform, and cyclohexanone have on various properties of the final nanomaterial-polymer composites. For example, FIG. 4A illustrates a stress-strain comparison for a bare CNT structure (I), chloroform (II), and cyclohexanone (III). As shown, cyclohexanone (III) has a higher stress than either of chloroform (II) and the bare CNTs (I). FIGS. 4B and 4C show the evaluation of the elastic modulus and the tensile strength, respectively, graphed along the y-axis against polymer content for each of the three compounds of FIG. 4A, shown graphed on the x-axis.

[0068] A person skilled in the art will recognize that although the first solvent 120 and the second solvent 120' discussed herein are water and an organic solvent, respectively, in some embodiments the organic solvent can be the first solvent and the aqueous solvent can be the second solvent. The solvent can be chosen based on one or more parameters of the system, including but not limited to the desired rate of the reaction, the type of substrate and nanomaterial network, and so forth. For example, when the nanomaterial is hydrophobic, such as carbon nanotubes (CNTs) or hydrophobic polymer nanofibers (*e.g.*, polyvinylidene fluoride, and polyacrylonitrile), and so forth, the second solvent being the organic solvent allows it to travel through the hydrophobic medium faster, thereby increasing the rate of the polymerization reaction while allowing the second solvent to quickly infiltrate the substrate to result in polymer composite with uniform morphology. A quick transport is one in which the solvent travels through the nanomaterial network at a rate greater than the rate of interfacially polymerized polymer precipitation. A person skilled in the art will recognize that the latter-introduced solvent into the nanomaterial network should be the solvent that travels through the network faster. As the solvent is introduced, the solutes between the

solvents react in a polymerization reaction. The surface energy of the second solvent 120' is lower than the energy of the first solvent 120 with respect to the network so that the second phase can completely fill the nanoporous network before the precipitated polymer closes the porosity. In embodiments in which the solvent travels at a slower rate, the speed of the polymerization reaction would form polymers more quickly than the solvent transports through the network, preventing uniform distribution of the polymer throughout the network and/or resulting in formation of a crust that is more akin to formation of desalination membranes, as discussed above. Alternatively, when forming a polymer composite using cellulose, which is hydrophilic, as the substrate, the organic phase is introduced prior to the aqueous phase at least because the increased speed of transport of the aqueous phase through the hydrophilic network.

[0069] With respect to cellulose, the cellulose molecule can be a linear polymer with a repeating unit that includes two anhydroglucose rings, $(C_6H_{10}O_5)_n$ where $n = 10,000$ to $15,000$, that can be linked by covalent bonds. Cellulose can a preferred material because it is the primary reinforcement phase of many biological organisms, including trees, plants, algae, some sea creatures, and bacteria, and is also the most abundant organic polymer on Earth.

[0070] One having skill in the art will appreciate that in some embodiments, cellulose acetate, which is a functionalized form of cellulose, can be used instead of cellulose. Both cellulose and cellulose acetate are biocompatible, biodegradable, pleasant to the touch, and inexpensive. Both molecules are also compostable, dry quickly, are shrink, mildew, and moth resistant, are washable or dry cleanable, and are easily dyed. Cellulose acetate differs from cellulose in that approximately $2/3$ of the hydroxyl groups on the cellulose molecule have been replaced by acetate groups. While this can reduce the number of hydrogen bonds in the material, and thus its tensile strength, the cellulose acetate is hydrophilic, has high surface area, and absorbs organics, allowing it to be used to produce specially structured separation membranes or even implantable sensors/filtration devices. It is also strongly dielectric and can be used to produce actuators in prostheses, as well as in robotics or haptic interfaces.

[0071] The use of interfacial polymerization as an in situ polymerization method within nanomaterial assemblies provides versatility in the choice of the formed polymer and its properties. For example, the solute systems used in interfacial polymerization can be tuned independently. By way of further example, using two aromatic polymers can produce a fully

aromatic polyamide with a high degree of crystallinity, very high thermal stability, and strong mechanical properties, while swapping one of those aromatic solutes for an aliphatic compound would contribute to improving the ductility of the final composite. Interfacial polymerization can also result in tunability of the polymer content and porosity of the final composite. Indeed, by
5 adjusting the solute concentration in the two solutions, the temperature of the baths, and the immersion time, a wide range of hierarchical nanomaterials-based composites with morphologies ranging from partially infiltrated, nanoporous networks up to dense, fully infiltrated, and homogeneous composite systems, *e.g.*, CNT/polyamide composites featuring >70 wt.% CNTs uniformly coated and infiltrated with polymer can be formed. By way of further example, the
10 reaction rate of the polymerization reaction can be tuned by adjusting the nature of the functional groups of the reacting solutes. For example, in some embodiments, such as those in which the hydrophilicity/hydrophobicity of the nanomaterial prevents rapid transport through the network, bromine functional groups can be used instead of chlorine functional groups to reduce the speed of the polymerization reaction.

[0072] In some embodiments, one or more rate constants can be tuned to affect a final composition of the polymer composite as desired. For example, for substantially uniform polymer distribution throughout the network, akin to cyclohexanone, a rate constant of solvent transport can be set at a value greater than a rate constant of polymerization. In such
15 embodiments, the solvent can travel through the network faster than the speed at which polymerization occurs, allowing the polymer to form throughout the nanoporous network. Alternatively, for non-uniform polymer distribution throughout the network, akin to chloroform, the rate constant of polymerization can be set at a value greater than a value of a rate constant of solvent transport, aggregating a larger amount of polymer on the edges of the
20 network while the center remains substantially free from polymer.

[0073] The polycondensation reaction occurs when the two solute phases are in contact as the material goes through the second bath, *e.g.*, bath containing the second solvent 120'. The time spent in the second bath 120' can affect the final degree of polymerization of the obtained macromolecules. As discussed above, reaction time and final molecular weight can be adjusted by tuning the temperature and stirring condition of the bath, the solute types and concentrations in
25 both solutions, as well as the nature of the solvents. For example, referring to FIG. 2, the amount of time that the substrate is exposed to the organic solvent can vary based, at least in part, on the material of the substrate, content of the solution, a temperature of the solvent, ambient temperature, and so forth. For example, in the case of a CNT substrate immersed in
30

an aqueous solution, the substrate can be disposed in the first bath for about 5 minutes, though in some embodiments, the exposure time can be up to about 7 minutes, up to about 8 minutes, up to about 10 minutes, or any amount of time that is sufficient for the organic solvent to travel throughout the substrate and react with the first solute to form the composite.

5 [0074] A person skilled in the art will recognize that although the instantly illustrated process shows the substrates 110 being immersed in each of the solvents 120, 120' a single time, in some embodiments the substrates can be disposed in one or more of the solvents a plurality of times to form the composite. For example, the instantly disclosed process can include repeatedly exposing the substrate to one or more of the first solvent 120 or the second
10 solvent 120' to increase a final polymer content of the polymer composite. The substrate 110 can be exposed to multiple aqueous solvents sequentially by dipping the substrate into a single bath a plurality of times, reintroducing the substrate into the first solvent 120 after being removed from the second solvent 120', and/or a combination of dipping the substrate into a single bath a plurality of times and reintroducing the substrate into the first solvent 120
15 after being removed from the second solvent 120'.

[0075] Once the polymerization reaction between the solutes has occurred, the substrates 110 can be removed from the organic solvent and cleaned. Cleaning can be performed in one or several steps in which the composite is exposed to compounds that remove any byproducts and/or unreacted solutes remaining within the composite. For example, as shown, the
20 composite can be immersed in an aqueous bath 192, *e.g.*, in water, to remove any byproduct, as shown in (IV), and/or immersed in an acetone bath 194 to remove any untreated solutes, as shown in (V). As with the previous steps discussed with respect to this method, the amount of time that the substrates 110 are exposed to the second solvent 120' can vary based, at least in part, on the material of the substrate, content of the solution, a temperature of the solvent,
25 ambient temperature, and so forth. After the unwanted substances are removed, the composite 210 can be placed in the ambient environment to dry in air, as shown in (VI).

[0076] In some embodiments, interfacial polymerization can be scaled and integrated in a roll-to-roll production line. This can be beneficial in view of the speed at which chemical reactions can occur during interfacial polymerization. For example, FIG. 6 illustrates an
30 embodiment of a continuous process that can be performed with high scalability to produce nanomaterial-polymer composites through *in situ* interfacial polymerization. A person skilled in the art will recognize that a continuous process refers to a process in which a

substrate can be escorted from a dispensing source through various baths and/or solvents provided herein. While the term “continuous” can be used to describe this process, a person skilled in the art will understand that instances in which the source can stop and start to pause the exposure time of the substrate in a particular bath or to refill may be desirable, and thus the term “continuous” can encompass situations in which the substrate stops or is paused for a time needed to promote the reaction and/or install a new roll of substrate to be delivered throughout the system.

[0077] For example, the process shown in FIG. 6 illustrates a roll-to-roll production line or an automated dipping mechanism. As shown, the nanoporous material 310 can be dispensed continuously from a ribbon or wheel 302 and cycled through sequential dipping and drying steps to create meters of composite. In some embodiments, the production line can follow a pre-programmed sequence. For example, in some embodiments, the diffusion of the solute through the material 310 and/or the reaction on the solutes can be set at the time taken for the substrate to pass through the baths 320, 320', 320''.

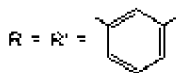
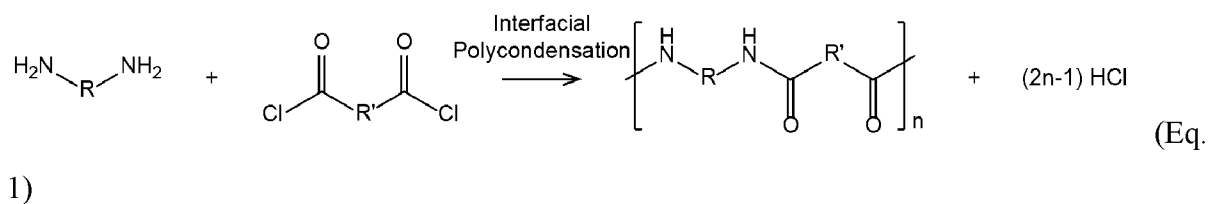
[0078] As shown, in the continuous process 300, a CNT nanoporous material 310 (*e.g.*, fiber, ribbon, bucky paper, or weave) can be run from the ribbon 302 to a collecting roll 304. The material 310 can be first run successively through two baths containing two solute solutions 320, 320' used for interfacial polymerization. The material 310 can be run multiple times through the two solute baths to increase the final polymer content of the composite. The process 300 can include one or more drying rolls 306 disposed therebetween for drying the material 310 before disposing it in a subsequent solvent. In some embodiments, the material 310 can be run through a third solution 320'' having a variation of one or more of the first solvent and/or the first solute. Subsequently, the obtained composite system is run through one or more rinsing baths 392 before being collected and left to dry.

[0079] In an exemplary embodiment for the polymerization of an aromatic polyamide at room temperature within a CNT sheet, one bath features an aqueous solution containing about 10 mg/mL of *m*-phenylene diamine, while the other bath contains an organic phase containing about 10 mg/mL of trimesoyl chloride in hexane. The CNT starting material can be first dipped in the aqueous bath for about 20 minutes, or another time sufficient to ensure that the first solution travels through the porosity. The material can be taken out of the first bath and excess liquid at the surface can be removed before transferring the wet CNT material to the second bath, where it is left to react for about 20 minutes, or another time sufficient for the first and second solutes to

react with one other. The final composite then undergoes subsequent rinses, which can occur for a few seconds or more in hexane and ethanol, before being left to dry at room temperature for about three hours or longer (although shorter drying times are also possible). The sequence of baths (from the dipping in the diamine solution to the drying at room temperature) can be repeated several times, *e.g.*, three or more, to obtain a dense CNT/polymer composite having up to 91wt.% CNTs.

[0080] A person skilled in the art will recognize that the number of baths can depend, at least in part, on the desired architecture of the final composite, *e.g.*, featuring one polymer or more, partially or fully infiltrated network. For example, composite systems involving more than one polymer system can be fabricated by dipping the scaffold material in an initial set of two solute baths to form a first polymer, followed by another dipping cycle in a second set of two solute baths to synthesize an additional polymer. In some embodiments, the additional solute baths can allow for cycling the nanoporous material through the same two solute baths to increase the polymer content of the final composite. The temperature of each bath, and the temperature of the nanoporous material, may be varied throughout the process, with the temperature of the nanoporous material being able to be controlled independently of the bath. Multiple polymers may be synthesized sequentially in such a continuous process and directed fluid flows and/or electric fields may be used to assist infiltration and/or accelerate or moderate the polymerization process.

[0081] The graphic in FIG. 7 illustrates an embodiment of the polymerization reaction disclosed in FIG. 2 in greater detail. For example, an in situ interfacial polycondensation reaction in the formation of polyamides can proceed as follows:



where C_6H_4 , though it will be appreciated that each of R and R' can represent a different compound, or in some embodiments, can be different compounds from one another. It will be appreciated that although the process will be described in view of the above solutes

and solvents, the disclosure can generally be applied to any of a variety of solutes and solvents, unless indicated otherwise, to produce various polymers, *e.g.*, polyurea, polyimide, and so forth.

[0082] As shown in (I) of FIG. 7, the aqueous solution (Aq) of diamine monomer can be distributed throughout the nanomaterial such that the monomer is dispersed throughout the porosity. When the nanomaterial is exposed to the organic solution (Or) that contains acyl chloride monomer dissolved in the organic solvent, the organic solvent can displace the water and the polymerization reaction can begin to occur. As shown in (II), the diamine monomer and the acyl chloride monomer can react substantially immediately to form the polyamide (P) within the nanomaterial. It will be appreciated that the polymerization reaction occurs in the organic solvent, and the organic solvent is chosen such that the diamine monomer, or any solute that is used in the aqueous solvent, can diffuse into the organic solvent. Further, it will be appreciated that the organic solvent can be selected to be immiscible with the aqueous solvent of the diamine monomer solution for reasons discussed above. The solubility of the diamine monomer in the organic solvent can allow the diamine to pass into the organic solvent to polymerize therein, as shown in greater detail in FIG. 8.

[0083] More specifically, FIG. 8 illustrates a phase separated system formed between two immiscible liquids. For example, when water (A) and the organic solvent (B), *e.g.*, hexane, are mixed together, they do not mix, instead forming a liquid-liquid interface within the nanoporous network, as shown. The solubility of the diamine monomer (Dm) in the organic solvent allows the diamine (Dm) to travel across the phase separated system, or interface between the solvents, into the organic solvent (B) to react with the acyl chloride monomer (Am) contained therein. The travel of the diamine monomer (Dm) into the organic solvent (B) can create a reaction zone Rx within the organic solvent (B), as shown, with the polymer reaction and the resulting polymer being formed within the reaction zone.

[0084] Referring to Eq. 1, the polymerization reaction can produce hydrochloric acid and/or other impurities (F) as a byproduct of the reaction in addition to the polyamide polymer. As exposure time to the organic solvent increases, increased amounts of the diamine react with the acyl chloride to form polymer (P) within the network, as shown in (III). Once the reaction has progressed to substantial completion, the polymer composite can be rinsed in water to eliminate the byproduct and any unreacted monomers to produce the

polymer composite, as shown in (IV). The polymer composite can then be dried to remove any excess solvents, *e.g.*, water, acetone, and so forth.

[0085] The illustrated and described systems, devices, methods, configurations, shapes, and sizes are in no way limiting. A person skilled in the art, in view of the present
5 disclosures, will understand how to apply the teachings of one embodiment to other embodiments either explicitly or implicitly provided for in the present disclosures. Further, a person skilled in the art will appreciate further features and advantages of the present disclosure based on the above-described embodiments. Accordingly, the disclosure is not to be limited by what has been particularly shown and described, except as indicated by the
10 appended claims. All publications and references cited herein, including the aforementioned document and provisional application, are expressly incorporated herein by reference in their entirety.

What is claimed is:

1. A method of synthesizing a polymer within a nanoporous medium, comprising:
exposing a nanoporous substrate to a first solvent having a first solute dissolved
therein to allow the first solvent and solute to infiltrate the nanoporous substrate; and
5 exposing the nanoporous substrate to a second solvent having a second solute
dissolved therein to allow the second solvent and solute to travel through the porosity of the
nanoporous substrate to react the second solute with the first solute to form the polymer,
wherein the second solvent is sufficiently immiscible with the first solvent.
2. The method of claim 1, wherein the second solvent travels through the porosity of the
10 nanoporous substrate faster than the first solvent travels through the porosity of the
nanoporous substrate.
3. The method of claim 1 or 2, wherein at least one of the first solute or the second
solute comprises one or more of a monomer, a mixture of monomers, an oligomer, a mixture
of oligomers, or a mixture of a monomer and an oligomer.
- 15 4. The method of any of claims 1 to 3, further comprising stirring the substrate while the
substrate is exposed to the second solvent to assist the transport of the second solvent through
the substrate where the first solute reacts with the second solute to form the polymer.
5. The method of any of claims 1 to 4, wherein the polymer is formed at the interface
between the first and second solvents or at the interface between the substrate and the second
20 solvent while the substrate is disposed in the second solvent.
6. The method of any of claims 1 to 5, wherein the reaction of the first and second
solutes occurs within the second solvent.
7. The method of any of claims 1 to 6, further comprising rinsing the substrate in one or
more additional solvents to remove byproduct or unreacted solutes therefrom.
- 25 8. The method of claim 7, wherein the one or more additional solvents comprises at least
one of acetone or water.
9. The method of claim 7 or 8, further comprising collecting the polymer composite and
drying the polymer composite.

10. The method of any of claims 1 to 9, wherein the substrate is dried between exposure to the first solvent and exposure to the second solvent.
11. The method of any of claims 1 to 10, further comprising repeatedly exposing the substrate to at least one of the first solvent or the second solvent to increase a final polymer content of the polymer within a nanoporous medium.
12. The method of any of claims 1 to 11, wherein the first solute is soluble in the second solvent.
13. The method of any of claims 1 to 12, wherein the first solvent comprises water and the second solvent comprises an organic solvent.
14. The method of any of claims 1 to 13, wherein the substrate is disposed in the first solvent for at least about 10 minutes.
15. The method of any of claims 1 to 14, wherein the substrate is disposed in the second bath for at least about 5 minutes.
16. The method of any of claims 1 to 15, further comprising drying the substrate after removing the substrate from the first solvent and prior to disposing the substrate in the second solvent.
17. The method of any of claims 1 to 16, wherein the substrate comprises one or more of cellulose, ceramic, metal, polymer, carbon nanotubes, graphene, silicon nanowires, or boron nitride nanotubes, in the form of a powder, foam, lattice, sheet, or yarn.
18. The method of any of claims 1 to 17, wherein a spacing between adjacent nanostructures in the nanoporous substrate is approximately in the range of about 1 nanometer to about 100 nanometers.
19. The method of claim 18, wherein the spacing between adjacent nanostructures of the polymer composite is approximately in the range of about 1 nanometer to about 10 nanometers.
20. A method of synthesizing a polymer composite, comprising:
disposing a nanomaterial substrate having a porous structure in a first bath that contains a first solvent, the first solvent having a first solute dissolved therein;

removing the substrate from the first bath; and
disposing the substrate in a second bath that contains a second solvent, the second solvent having a second solute dissolved therein to react the first and second solutes to form a polymer composite,

5 wherein the second solvent is sufficiently immiscible with the first solvent.

21. The method of claim 20, wherein at least one of the first solute or the second solute comprises one or more of a monomer, a mixture of monomers, an oligomer, a mixture of oligomers, or a mixture of a monomer and an oligomer.

10 22. The method of claim 20 or 21, wherein the polymer composite forms at the interface between the first and second solvents or at the interface between the substrate and the second solvent while the substrate is disposed in the second solvent.

23. The method of any of claims 20 to 22, wherein the reaction of the first and second solutes occurs within the second solvent.

15 24. The method of any of claims 20 to 23, further comprising rinsing the substrate in one or more additional solvents to remove byproduct or unreacted solutes therefrom.

25. The method of claim 24, wherein the one or more additional solvents comprises at least one of acetone or water.

26. The method of claim 24 or 25, further comprising collecting the polymer composite and drying the polymer composite.

20 27. The method of any of claims 20 to 26, further comprising repeatedly disposing the substrate into at least one of the first bath or the second bath to increase a final polymer content of the polymer composite.

28. The method of any of claims 20 to 27, wherein the first solute is soluble in the second solvent.

25 29. The method of any of claims 20 to 28, wherein the first solvent comprises water and the second solvent comprises an organic solvent.

30. The method of any of claims 20 to 29, wherein the substrate is disposed in the first bath for at least about 10 minutes.

31. The method of any of claims 20 to 30, further comprising stirring the substrate in the second bath to assist the transport of the second solvent through the substrate and to react the first solute with the second solute to form the polymer composite.
32. The method of any of claims 20 to 31, wherein the substrate is disposed in the second bath for at least about 5 minutes.
33. The method of any of claims 20 to 32, further comprising drying the substrate after removing the substrate from the first solvent and prior to disposing the substrate in the second solvent.
34. The method of any of claims 20 to 33, wherein the nanomaterial substrate comprises cellulose, ceramic, metal, polymer, carbon nanotubes, graphene, silicon nanowires, or boron nitride nanotubes, in the form of a powder, foam, lattice, sheet, or yarn.
35. The method of any of claims 20 to 34, wherein a spacing between adjacent nanostructures in the nanomaterial substrate is approximately in the range of about 1 nanometer to about 100 nanometers.
36. The method of claim 35, wherein the spacing between adjacent nanostructures of the polymer composite is approximately in the range of about 1 nanometer to about 10 nanometers.
37. The method of any of claims 20 to 36, wherein a mechanical force is applied to the substrate during or after disposing the substrate in the first bath or in the second bath.
38. The method of claim 37, wherein the mechanical force is tensile or compressive.
39. The method of any of claims 20 to 38, wherein the second solvent wets the substrate after the substrate is disposed therein, causing the first solvent to be substantially displaced from the substrate.
40. A polymer composite, comprising:
a nanoporous material having a polymer substantially uniformly distributed throughout a structure thereof, the polymer being formed from a reaction of a first solute and a second solute within pores of the nanoporous material at a liquid-liquid interface within the nanoporous material.

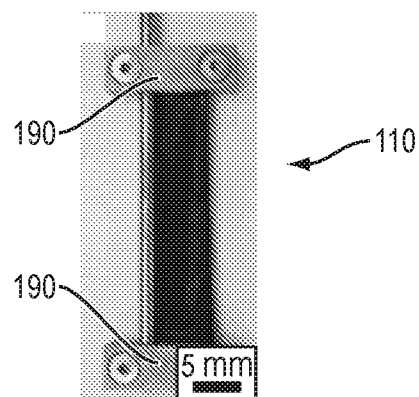
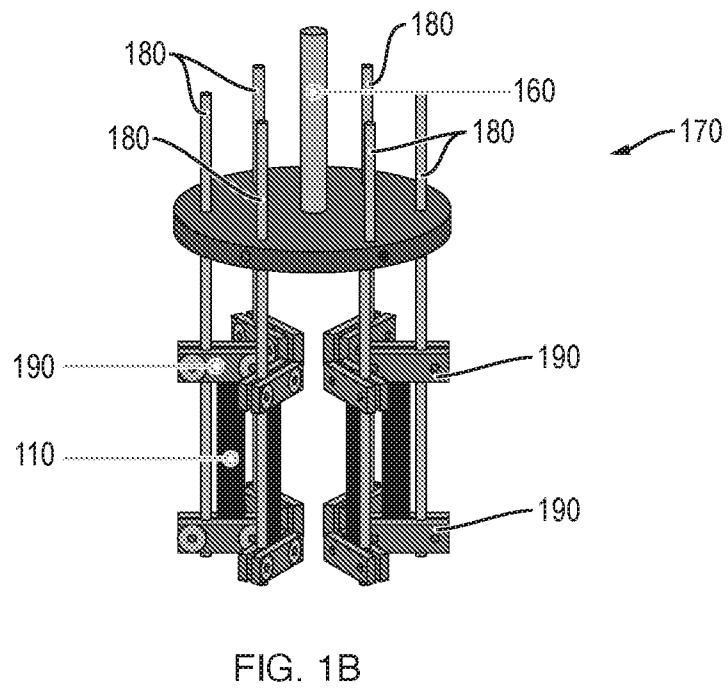
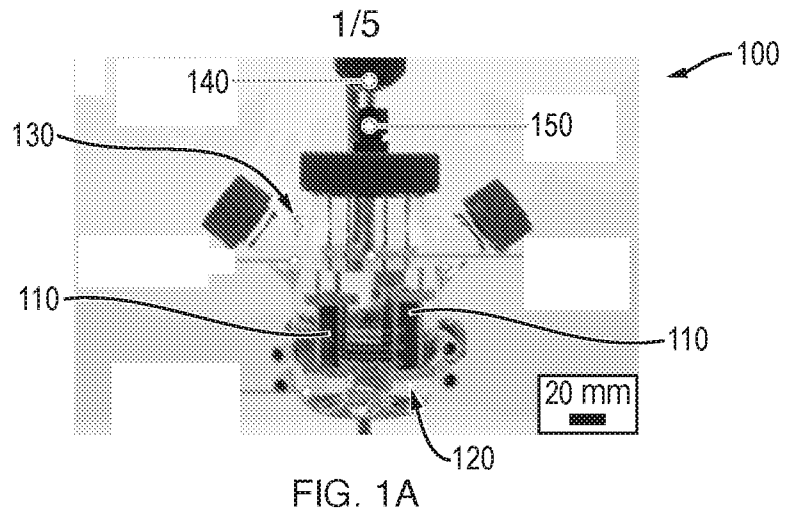
41. The composite of claim 40, wherein the solute comprises one or more of a monomer, a mixture of monomers, an oligomer, a mixture of oligomers, and a mixture of a monomer and an oligomer.

5 42. The composite of claim 40 or 41, wherein the first solute comprises one or more of amines, piperazines, thiols, diols, acid halides (*e.g.*, acyl chloride, or acid chloride, acyl fluoride, acyl bromide, or carbon suboxides).

43. The composite of any of claims 40 to 42, wherein the nanoporous material comprises one or more of cellulose, ceramics, metal foam, polymer fiber mat or foam, sheet, fiber, or yarn comprising carbon nanotubes, boron nitride nanotubes, or graphene.

10 44. The composite of any of claims 40 to 43, wherein the nanoporous material has a porosity approximately in the range of about 1 nanometer to about 10 nanometers.

45. The composite of any of claims 40 to 44, wherein the polymer comprises one or more of a polyamide, a polyurea, or nylon.



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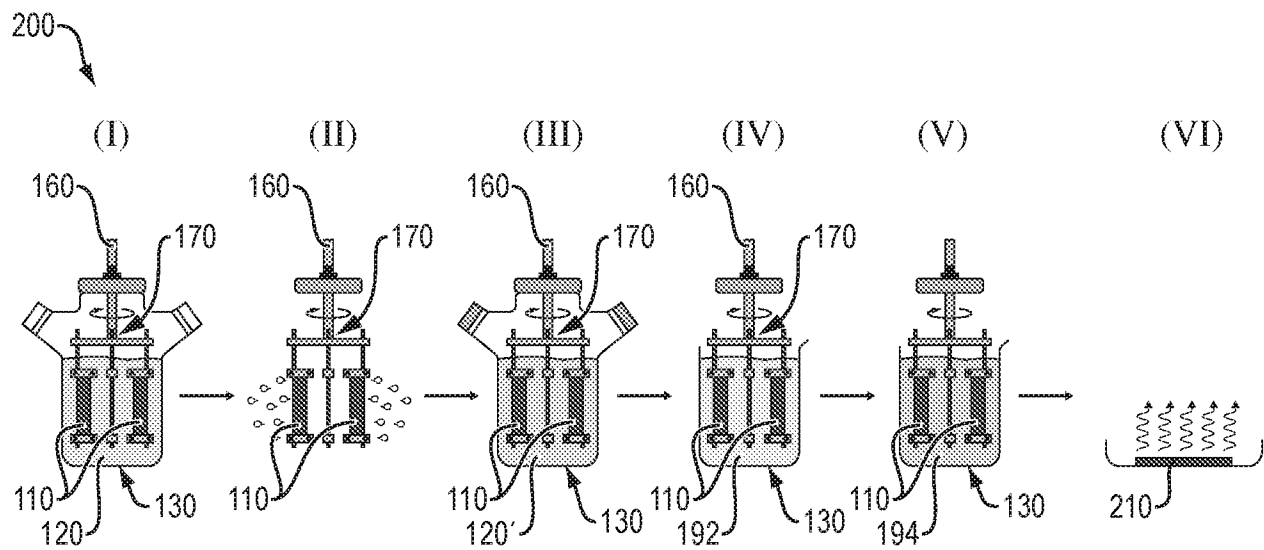


FIG. 2

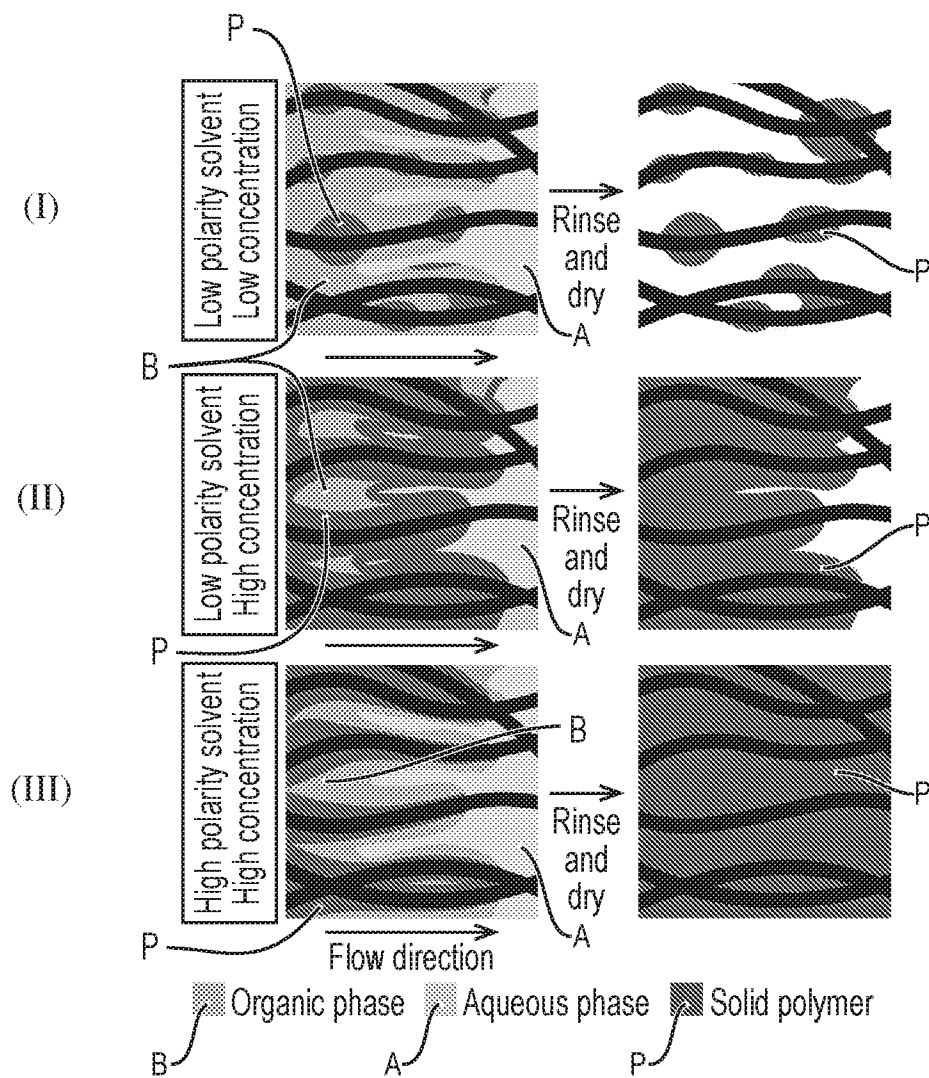


FIG. 3

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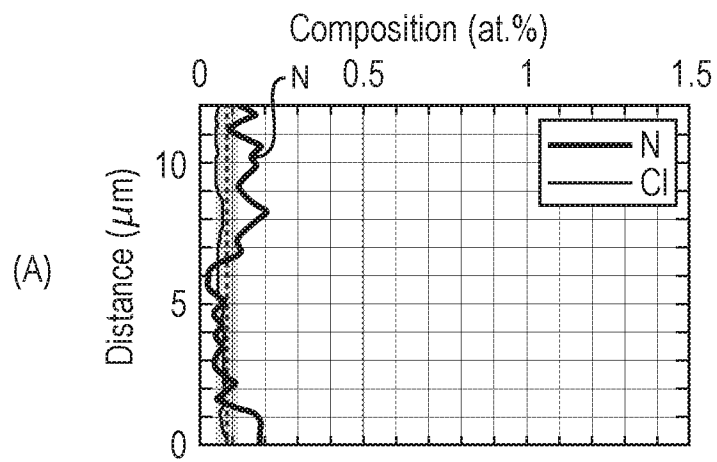


FIG. 4A

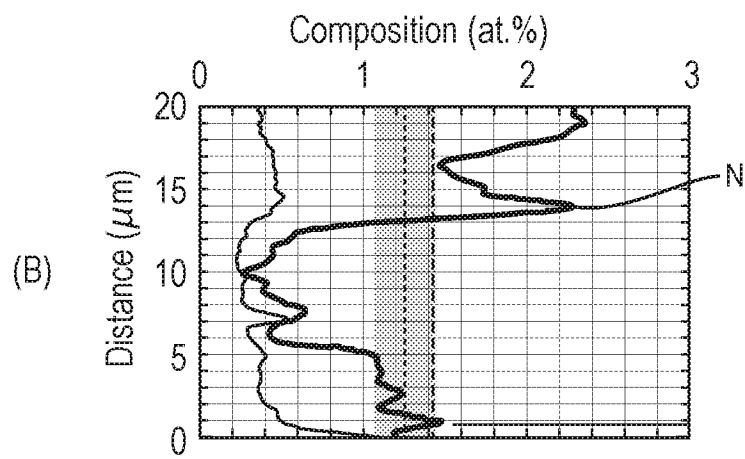


FIG. 4B

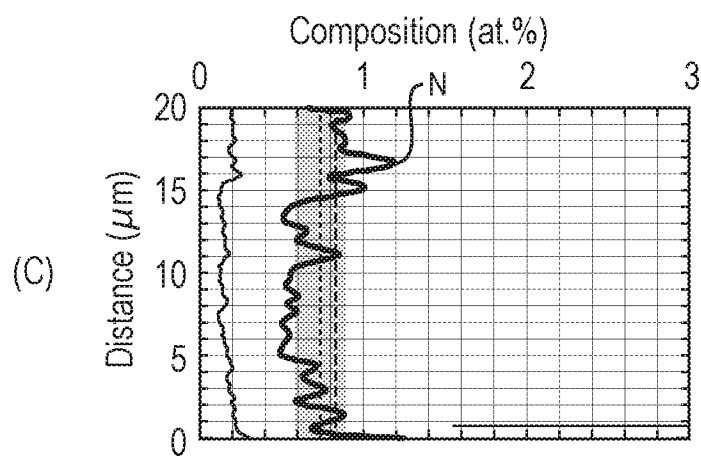


FIG. 4C

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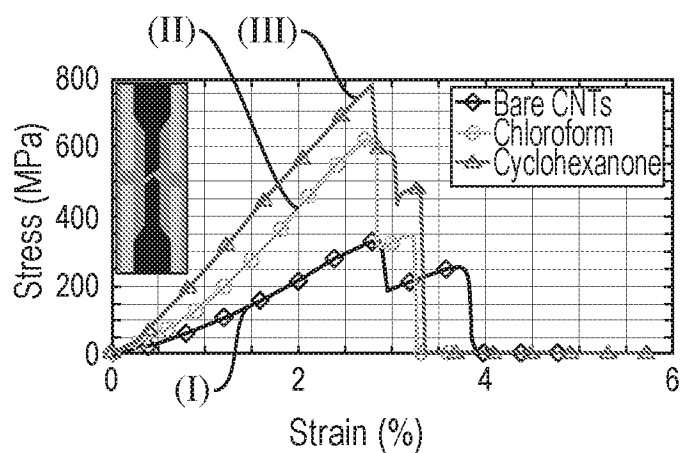


FIG. 5A

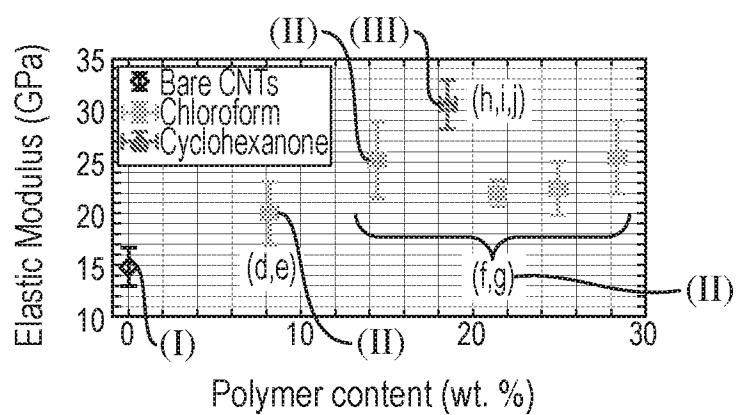


FIG. 5B

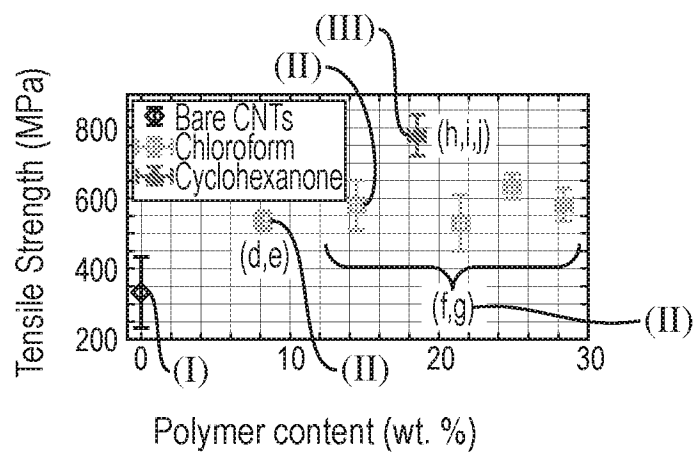


FIG. 5C

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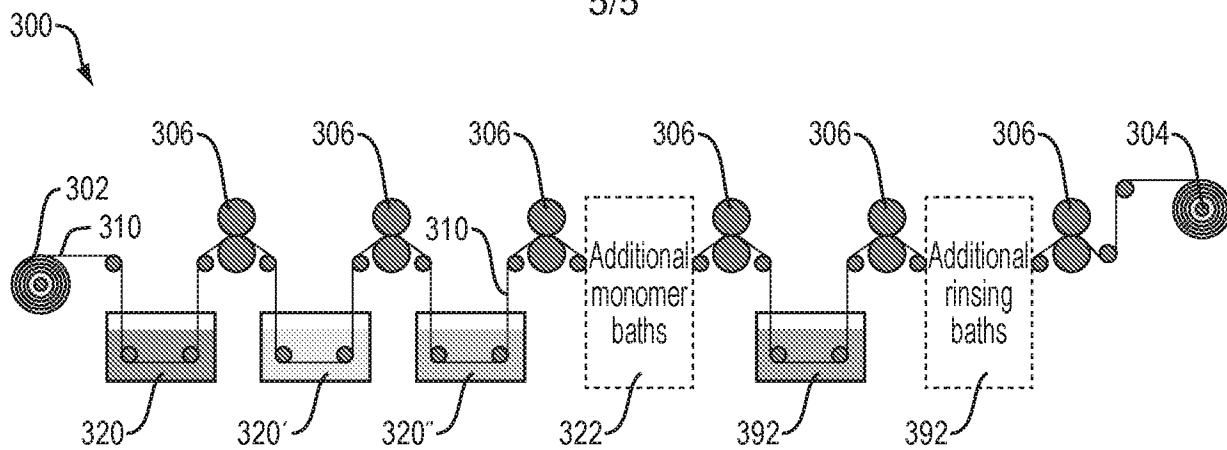


FIG. 6

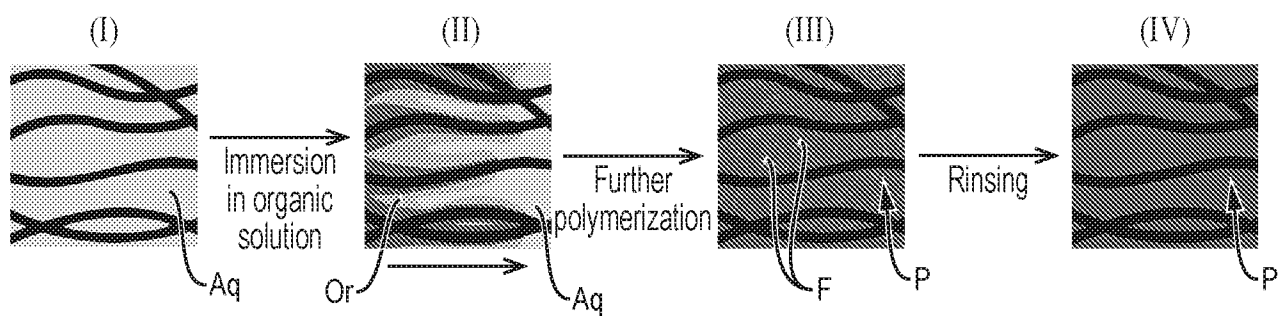


FIG. 7

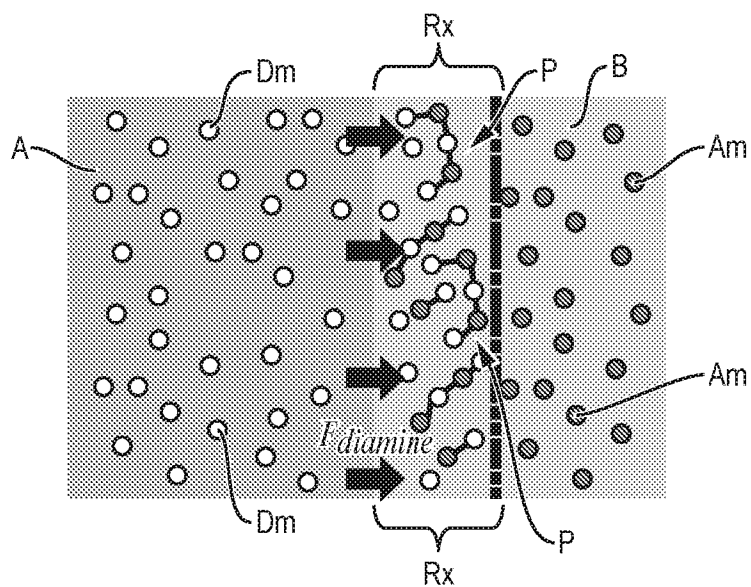


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/57966

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B05D 5/12; B32B 3/26; H01L 21/308 (2020.01)

CPC - B01D 69/02; B01D 69/141; B01D 71/80; B05D 5/00; B81C 1/00031; B82Y 30/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/0180526 A1 (Winey et al.) 25 September 2003 (25.09.2003) Para [0002]; [0009]; [0012]; [0014]; [0015]	20-22
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Y		1-3 and 40-42
Y	US 2011/0024698 A1 (Worsley et al.) 03 February 2011 (03.02.2011) Para [0033]; [0047]; [0049]; [0050]	1-3 and 40-42
A	US 2012/0282453 A1 (Wang et al.) 08 November 2012 (08.11.2012) entire document	1-3, 20-22, and 40-42
A	US 8,262,943 B2 (Meng et al.) 11 September 2012 (11.09.2012) entire document	1-3, 20-22, and 40-42
E/X	US 2020/0131326 A1 (Massachusetts Institute of Technology) 30 April 2020 (30.04.2020) Para [0003]; Para [0011]; [0019]; [0045]; Para [0059]; [0060]	1-3, 20-22, and 40-42

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

23 June 2020

Date of mailing of the international search report

15 JUL 2020

Name and mailing address of the ISA/US

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Facsimile No. 571-273-8300

Authorized officer

Lee Young

Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/57966

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.: 4-19, 23-39, and 43-45
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.