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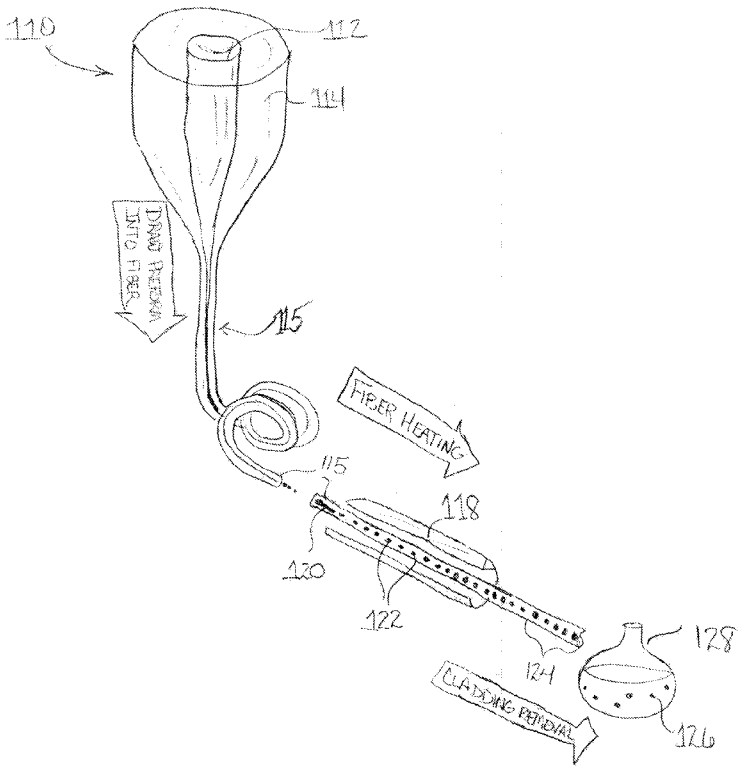
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[Continued on next page]

(54) Title: IN-FIBER PARTICLE GENERATION



(57) Abstract: A fiber is provided, including a cladding material that is disposed along a longitudinal-axis fiber length. A plurality of spherical particles are disposed as a sequence along a longitudinal line parallel to the longitudinal fiber axis in at least a portion of the fiber length. Each spherical particle is of a spherical particle material that is interior to and different than the fiber cladding material. The spacing between adjacent spherical particles in the sequence of particles is greater than the spherical particle diameter. Each spherical particle can be provided as a core- shell particle that includes a spherical core that is surrounded by at least one spherical shell. Each spherical particle can be provided with a plurality of azimuthal sections of at least two distinct materials.

WO 2013/192368 A2

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IN-FIBER PARTICLE GENERATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 61/663,032, filed June 22, 2012, the entirety of which is hereby incorporated by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with Government support under Contract No. DMR-0819762, awarded by the National Science Foundation; under Contract No. ECCS-1002295, awarded by the National Science Foundation; under Contract No. FA-9550-12-1-0148, awarded by the Air Force Office of Scientific Research, and under Contract No. W911NF-07-D-0004, awarded by the Army Research Office. The Government has certain rights in the invention.

BACKGROUND

[0003] This invention relates generally to particle fabrication, and more particularly relates to structured microparticles and nanoparticles.

[0004] Known so-called 'bottom-up' approaches for forming particles, such as nanoparticles, generally rely on nucleation, chemical reactions, or self-assembly processes. The particles produced using such approaches are typically characterized by a large dispersion in size and shape distributions, and are generally hampered by particle coalescence and agglomeration during particle growth. Conversely, so-called 'top-down' approaches, such as microfluidics, lithography, and imprint lithography, typically yield larger, mono-disperse particles, but each such approach is generally suited only to a specific material and particle size range that is determined by the underlying kinetics of the process.

SUMMARY

The many historical limitations in micro-scale and nano-scale particle geometry and controllability are overcome with an arrangement of nanoparticles that employs a fiber. The fiber includes a cladding material that is disposed along a longitudinal-axis fiber length. A plurality of spherical particles are disposed as a sequence along a longitudinal line parallel to the longitudinal fiber axis in at least a portion of the fiber length. Each spherical particle is of a spherical particle material that is interior to and different than the fiber cladding material.

[0005] With this arrangement, the spacing between adjacent spherical particles in the sequence of particles is greater than the spherical particle diameter. Each spherical particle can be provided as a core-shell particle that includes a spherical core that is surrounded by at least one spherical shell. Additionally, each spherical particle can be provided with a plurality of azimuthal sections of at least two distinct materials.

[0006] The spherical particles can be prespecified as geometrically complex and well-defined micro-scale and nano-scale structures that are well-ordered, controllably oriented, and immobilized. An enormous range of applications, e.g., from the fields of chemistry, physics, and biology, are addressed by the particles. For example, three-dimensional optical and acoustic meta-materials can be produced, optical-resonance-based sensitive detection of chemical species and pathogens can be enabled, and sophisticated controlled-release drug delivery systems can be realized. Many applications requiring precisely controlled particle formation can be enabled in a cost-effective and well-controlled environment. Other features and advantages will be apparent from the following description and accompanying figures, and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1A is a flow chart that shows steps in an example method for the efficient and scalable fabrication of spherical particles such as spherical microparticles or nanoparticles, according to an example embodiment;

[0008] Figure 1B is a schematic perspective view of materials being processed in the steps of the flow chart of Figure 1A;

[0009] Figure 1C is a plot of fiber core diameter, D_{core}, and spherical particle break up time, τ, as a function of fiber thermal processing temperature, for a single fiber core material of As_2Se_3, and a fiber cladding of PES, in an example analysis for determining requisite particle break up time;

[0010] Figure 2A shows an example fiber tapering setup;

[0011] Figure 2B is a scanned optical micrograph of a fiber cross section with a 20-μm core diameter;

[0012] Figure 2C a scanned image of a typical fiber taper;

[0013] Figure 2D shows a magnified scanned image of the taper center corresponding to the dotted box in Figure 2C, showing the core broken into a periodic string of core droplets oriented along the axial (drawing) direction, according to example embodiments;

[0014] Figure 3A is a schematic perspective view of a fiber preform including concentric core materials for production of a spherical core-shell particle;

[0015] Figure 3B is a schematic cross-sectional view of a spherical core-shell particle produced with a fiber drawn from the preform of Figure 2A;

[0016] Figure 3C is a schematic cross-sectional view of a spherical core-shell particle including a plurality of spherical shells;

[0017] Figure 3D is a schematic perspective view of a fiber preform including concentric core materials for production of a spherical core-shell particle having four nested shells;

[0018] Figure 3E is a schematic perspective view of one hemisphere of a core-shell particle produced with a fiber drawn from the preform of Figure 3D;

[0019] Figure 4A is a schematic, perspective, cut-away view of a fiber including two half-cylinder core materials for production of a spherical Janus particle;

[0020] Figure 4B is a schematic cross-sectional view of a spherical Janus particle produced with the fiber of Figure 4A;

[0021] Figure 5A is a schematic, perspective, cut-away view of a fiber including an azimuthal arrangement of core material sections for production of a spherical 'beach ball' compartmentalized particle;

[0022] Figure 5B is a schematic cross-sectional view of a spherical 'beach ball' particle produced with the fiber of Figure 5A;

[0023] Figure 5C is a schematic, perspective, cut-away view of a fiber including an azimuthal arrangement of core material sections for production of a non-symmetric spherical compartmentalized particle;

[0024] Figure 5D is a schematic view of a spherical particle produced with the fiber of Figure 5C;

[0025] Figure 5E is a schematic, perspective, cut-away view of a fiber including concentric core materials for production of a spherical core-shell particle with azimuthal control of materials in a particle core and in the shell layers;

[0026] Figure 5F is a schematic view of a spherical core-shell particle produced with the fiber of Figure 5E;

[0027] Figure 5G is a schematic, perspective, cut-away view of a fiber including concentric core materials for production of a spherical core-shell particle having daughter spheres within a central core mother sphere;

[0028] Figure 5H is a schematic cross-sectional view of a spherical core-shell particle including daughter particles within a central core mother sphere produced with the fiber of Figure 5G;

[0029] Figures 6A-6E are scanned optical micrographs of the side view of fiber tapers produced at different temperatures, but with the same tapering speed (2 mm/s) and tapering distance (15 mm) showing different stages of the core breakup process, according to example embodiments;

[0030] Figures 7A and 7B are scanned SEM micrograph of 12 20 micro-diameter intact glass cores exposed from a 1-mm-outer-diameter fiber cross section;

[0031] Figure 8 is a scanned high-magnification SEM micrograph of a fiber including 27,000 cores each of 200 nm in diameter, with stacked fibers in the preform producing a hexagonal lattice (see dashed lines), and at each lattice site 80 200-nm glass cores located as shown in the inset;

[0032] Figure 9A is a scanned SEM micrograph of a 1-mm-diameter fiber cross section containing 80 7 μm-diameter cores, with P= polyethersulfone (PES);

[0033] Figure 9B is a higher-magnification scanned SEM micrograph of the 80 cores of Figure 9A, with G=As_2Se_3;

[0034] Figure 9C is a scanned transmission optical micrograph of the side view of the fiber of Figures 9A-9B, before break-up (via global heating); and

[0035] Figure 9D is a scanned transmission optical micrograph of the side view of the fiber of Figures 9A-9B after break-up of the cores via global heating, showing that the resulting spatial distribution of particles immobilized in the cladding (scaffold) is well-ordered in all 3 dimensions.

DETAILED DESCRIPTION

[0036] In this Description, referring to the attached figures, like reference numerals are used throughout the figures to designate similar or equivalent elements. The figures are not drawn to scale and they are provided merely to illustrate the disclosed embodiments. Several aspects are described below with reference to example applications for illustration. It should be understood that numerous specific details, relationships, and methods are set forth to provide a full understanding of the disclosed embodiments. One having ordinary skill in the relevant art, however, will readily recognize that the subject matter disclosed herein can be practiced without one or more of the specific details or with other methods. In other instances, well-known structures or operations are not shown in detail to avoid obscuring structures or operations that are not well-known. This Description is not limited by the illustrated ordering of acts or events, as some acts may occur in different orders and/or concurrently with other acts or events. Furthermore, not all illustrated acts or events are required to implement a methodology in accordance with this Disclosure.

[0037] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of this Disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Moreover, all ranges disclosed herein are to be understood to encompass any and all sub-ranges subsumed therein. For example, a range of "less than 10" can include any and all sub-ranges between (and including) the minimum value of zero and the maximum value of 10, that is, any and all sub-ranges having a minimum value of equal to or greater than zero and a maximum value of equal to or less than 10, e.g., 1 to 5.

[0038] Disclosed embodiments include methods applied to multi-material fibers for the efficient and scalable fabrication of microparticles or

nanoparticles. Disclosed methods include a thermally-based process applied to an extended multi-material fiber having an extended core , that results in the extended core breaking up into a plurality of microparticles or nanoparticles that are embedded in a cladding layer of the fiber.

[0039] Figure 1A is a flow chart that shows steps in an example method 100 for the efficient and scalable in-fiber fabrication of microparticles or nanoparticles, according to an example embodiment. Step 101 comprises providing a multi-material fiber preform having at least one core comprising a first material and including at least an outer first cladding layer comprising a second material different from the first material outside the core. The first and second materials generally have similar softening temperatures that allow for the first and second materials to be consolidated together and then co-drawn from the same fiber preform, such as a softening temperature within 50°C of one another. Step 101 can comprise assembling a multi-material macroscopic preform with a core assembled from the intended particle constituent materials encased in a scaffold material that provides a cladding material.

[0040] Step 102 comprises thermal drawing of the multi-material fiber preform to form an extended multi-material fiber having an extended core that is parallel to the longitudinal-axis length of the fiber, such that the core diameter (or other cross-sectional core dimension) in the extended core is reduced to approach the diameter of particles which are to be formed in a subsequent step with the core material or materials. To ensure the integrity of the fiber core, the fiber preform is preferably thermally drawn in a high-viscosity regime, e.g., > 10^6 Pa s, and the fiber drawing temperature selected is preferably sufficiently high to allow for the preform to be drawn continuously into a fiber. The fiber can be rapidly cooled (e.g., with active cooling) after fiber drawing to arrest the development of axial instability. The fiber drawing can optionally include two or more fiber drawing steps. This fiber drawing process can produce an axially stable fiber core having a diameter from, e.g., 3

nm to > 1 mm, e.g., between about 1 mm and less than 100 nm, setting the lower and upper limits on the sizes of particles to be subsequently formed. These steps of preform production and consolidation, and fiber drawing are described in U.S. No. 7,295,734, issued November 13, 2007, to Bayindir et al., the entirety of which is hereby incorporated by reference.

[0041] Step 103 comprises thermally treating the extended multi-material fiber under conditions (e.g., temperature, time, and for some applications, tapering speed) that cause an axial breaking up of the continuous extended core to form a plurality of core particles embedded in the cladding. The maximum temperature utilized in step 103 is generally higher than the maximum temperature used in step 102, such as by a temperature higher by at least 10 °C. In this step the thermal treatment of the drawn fiber controllably induces the break-up of the extended core(s). In a typical embodiment the extended core breaks up into an orderly (periodic) sequence of oriented, smooth-surfaced structured spherical particles held immobile in the fiber cladding; the cladding material engulfs the particles and holds the particles separated from each other. The thermal treatment can comprise holding a temperature fixed along a longitudinal fiber axis of the multi-material fiber, and using a sufficient heating time to form the plurality of core particles.

[0042] In contrast to the rapid cooling that is preferred after fiber drawing, here it is preferred to maintain an elevated temperature along the fiber axis for an extended time period that produces the break-up of the fiber core into droplets, as described in detail below. In another embodiment the thermal treating can comprise applying a temperature gradient along a fiber axis of the multi-material fiber. In either process, the resulting droplets are frozen *in situ* upon cooling to produce a sequence of particles along a longitudinal line that is parallel to the longitudinal fiber axis, with the particles interior to the fiber cladding material.

[0043] In optional step 104, the resulting core particles are released from the cladding. For example, the core particles embedded in the cladding may be released by dissolving the cladding material in a suitable solvent that preferably does not affect the core particles. For example, given an organic polymer cladding, e.g., polyethersulphone (PES), this polymer cladding can be dissolved in a solution of, e.g., dimethylacetamide (DMAC), in applications in which the particles are formed of an inorganic material such as an inorganic glass. In general, for arrangements in which the core materials are inorganic, the fiber polymer can be dissolved using a standard organic solvent, which retains the resulting particles intact.

[0044] But for many applications the core particles can be employed held immobilized in the fiber cladding material, rather than released from the cladding. While embedded in the fiber cladding, the particles are isolated from each other and therefore cannot agglomerate in the manner often occurring in conventional nanoparticle synthesis. Being disposed interior to, or internal to, the fiber cladding material, each particle is provided with a buffer between it and all other particles, even for very large particle density. Thereby, this arrangement of embedded particles within a fiber cladding layer can be employed for applications, e.g., in which there is required a three-dimensional distribution of particles in a uniform matrix.

[0045] The in-fiber particle fabrication process is schematically represented in Figure 1B. A fiber preform 110 is assembled with the materials selected for particle production, e.g., a selected preform core material 112 corresponding to a desired particle composition, and one or more cladding or other fiber preform layers 114 that are different than the core material. During the fiber drawing process, the fiber preform 110 is thermally drawn down to a fiber 115, of an extended longitudinal-axis length; the drawn fiber can be many hundreds of meters in length.

[0046] After fiber drawing, the cooled drawn fiber 115 is heated by a selected heating source 118 at a heating temperature, T, for a heating

duration, *t*, that is sufficient to reduce the viscosity of the core material(s) to a level that causes instability in the core material(s) due to perturbations at the core-cladding interface. This instability causes the core 120 of the drawn fiber to break-up into uniformly-sized droplets 122. The heating source can be local or global, and the representation in the figure is for clarity only and not meant to be limiting. The core material droplets are solidified upon cooling of the fiber, producing a longitudinal sequence of spherical particles 124 disposed along line that is parallel to the longitudinal fiber axis, in at least a portion of the fiber length, with the particles being engulfed and separated from each other by the cladding material. For some applications, there can be imposed uniform spacing between the particles, and with a spacing between particles being greater than particle diameter. If desired, after particle production, the fiber cladding can then be removed, e.g., in solution, providing released particles 126 for use in a given application, e.g., as-suspended in a solution 128.

[0047] Although not necessary to practice disclosed embodiments, the breaking up of the extended core(s) of the drawn multi-material fiber into a plurality of particles is believed to be based on Plateau-Rayleigh (PR) capillary instability during the thermal treating of the drawn fiber. In one particular embodiment the fiber core can comprise a glass and the cladding comprises an amorphous thermoplastic polymer. PR instability is believed to be manifested in the breakup of the core into a periodic string of size-tunable micro-scale droplets embedded along the fiber axis. As disclosed above, size tuning can be provided by fiber drawing, or can be provided by fiber tapering, described below, such that the extended core(s) has a cross sectional dimension (e.g., a diameter) that approaches the desired particle size.

[0048] In the fiber core break-up into spherical particles, the heating temperature, *T*, is applied for a duration, *t*, that is sufficient to cause the development of a sinusoidal modulation at the core-cladding interface due to the PR capillary instability. In contrast to the rapid cooling that is employed

in conventional fiber drawing processes, including the prior draw process employed to draw the fiber being thermally treated, in the thermal treatment the fiber is maintained at the elevated heating temperature, T, for the duration, t, that allows for the core break-up as the instability progresses. At break-up, the core is a high-viscosity fluid that forms the uniform droplets, which subsequently become spherical particles upon cool down from the heating temperature, T. As a result of this spherical particle formation process, the spherical particles are uniform, with a uniform particle diameter, and are arranged as a linear sequence of particles along the fiber axis, with uniform spacing between the spherical particles and the spacing between the spherical particles being greater than the particle diameter.

[0049] The conditions required to produce the spherical particles in-fiber can be analyzed by modeling the fiber core at the elevated heating temperature, T, as a viscous thread having a viscosity, μ_{core}, and a diameter, D_{core}, that is surrounded by an infinitely extended viscous cladding, having a viscosity, μ_{clad}. Based on the classical Tomotika linear stability theory, the instability growth time, τ, i.e., the time scale determining the growth of a corresponding capillary instability wavelength, λ, of the fiber core, is given as:

$$\tau = \frac{D_{core}\mu_{core}}{\gamma[(1-x^2)\Phi\left(x,\frac{\mu_{core}}{\mu_{clad}}\right)]}; \quad (1)$$

where γ is the surface tension between the core and cladding materials and $x = \pi D_{core}/\lambda$.

The function $\Phi(x)$is given by:

$$\Phi(x) = \frac{N(x)}{D(x)}, \quad (2)$$

where

$$N(x) \equiv I_1(x)\Delta_1 - \{xI_0(x) - I_1(x)\}\Delta_2, \text{ and}$$

$$D(x) \equiv \left(\mu_{core}/\mu_{clad}\right)\{xI_0(x) - I_1(x)\}\Delta_1 - \left(\mu_{core}/\mu_{clad}\right)\{(x^2+1)I_1(x) - xI_0(x)\}\Delta_2 - \{xK_0(x) + K_1(x)\}\Delta_3 - \{(x^2+1)K_1(x) + xK_0(x)\}\Delta_4, \quad (3)$$

where $I_n(x)$ and $K_n(x)$ are the modified Bessel functions of the nth order, and μ_{core}/μ_{clad} is the viscosity ratio between the fiber core and the surrounding fiber material, such as fiber cladding.

[0050] In Expression (3), Δ_1, Δ_2, Δ_3, and Δ_4 are all functions of x expressed in determinantal forms as follows:

$$\Delta_1 = \begin{vmatrix} xI_0(x) - I_1(x) & K_1(x) & -xK_0(x) - K_1(x) \\ I_0(x) + xI_1(x) & -K_0(x) & -K_0(x) + xK_1(x) \\ (\mu_{core}/\mu_{clad})xI_0(x) & K_1(x) & -xK_0(x) \end{vmatrix},$$

$$\Delta_2 = \begin{vmatrix} I_1(x) & K_1(x) & -xK_0(x) - K_1(x) \\ I_0(x) & -K_0(x) & -K_0(x) + xK_1(x) \\ (\mu_{core}/\mu_{clad})I_1(x) & K_1(x) & -xK_0(x) \end{vmatrix},$$

$$\Delta_3 = \begin{vmatrix} I_1(x) & xI_0(x) - I_1(x) & -xK_0(x) - K_1(x) \\ I_0(x) & I_0(x) + xI_1(x) & -K_0(x) + xK_1(x) \\ (\mu_{core}/\mu_{clad})I_1(x) & (\mu_{core}/\mu_{clad})_1 xI_0(x) & -xK_0(x) \end{vmatrix}, \text{ and}$$

$$\Delta_4 = \begin{vmatrix} I_1(x) & xI_0(x) - I_1(x) & K_1(x) \\ I_0(x) & I_0(x) + xI_1(x) & -K_0(x) \\ (\mu_{core}/\mu_{clad})I_1(x) & (\mu_{core}/\mu_{clad})_1 xI_0(x) & K_1(x) \end{vmatrix},$$

[0051] In one technique for determining a suitable heating time for producing spherical droplets out of a fiber core material or materials, the fastest growing instability wavelength, λ, is determined for a selected value of fiber core diameter, D_{core}, and a selected heating temperature, T, by numerically evaluating the following expression based on the expressions given above:

$$\max_{\lambda}[(1\text{-}x^2)\Phi(x, \mu_{core}/\mu_{clad})]. \quad (4)$$

[0052] The shortest, or fastest, instability growth time, $\tau_{fastest}$, is determined by the evaluation of Expression (4) above, and corresponds to the fastest growing instability wavelength. If the fiber is subjected to the heating

temperature, T, for a time, t, that is at least as long as $\tau_{fastest}$, ($t \geq \tau_{fastest}$), then the capillary instability of the core can drive the continuous core to break-up into droplets, for the given fiber materials, selected core diameter, and selected heating temperature. For heating times less than the determined value of the smallest instability growth time, $\tau_{fastest}$, ($t < \tau_{fastest}$) the core will remain intact and not break-up.

[0053] Thus, in determining the process conditions for achieving fiber core break-up, iterative analysis with various process and material parameters can be employed to obtain a suitable process that produces spherical particles out of selected materials. Figure 1C is an example plot for such an analysis. In this example, there is selected a fiber arrangement including a single core material of As_2Se_3, which has a viscosity that is temperature-dependent and therefore obtained from an empirical Arrhenius formula, and an outer cladding layer of polyethersulfone (PES), having a viscosity of 10^5 Pa s. The surface tension between As_2Se_3 and PES is 0.1 N/m. With these parameters, the expressions above can be evaluated as a function of heating temperature, T, and core material diameter, D_{core}. In general, the shortest instability growth time, $\tau_{fastest}$, at which break-up of the core will occur, corresponding to the fastest growing instability wavelengths, λ, is linearly proportional to the core diameter, D_{core}, and linearly dependent on the core viscosity, which is a function of the heating temperature, T. In this model, a fiber core will break-up, for any fixed heating temperature, T, after heating for a duration that is sufficient for the requisite PR instability to be initiated.

[0054] For the As_2Se_3 example fiber core material being considered here, with a selected heating temperature of 270 °C, the viscosity of the As_2Se_3 core material is about 10^5 Pa s. For a As_2Se_3 core diameter of 10 μm, the smallest calculated PR capillary instability time, $\tau_{fastest}$, determined by evaluation of the expression above, is given as about 150 seconds. Thus, in this example, when the As_2Se_3-PES fiber is heated at a temperature of 270 °C for at least about 150 seconds, the As_2Se_3 core will break-up into uniform spherical particles.

The plot of Figure 1C demonstrates how this required heating duration shifts based on fiber core diameter and on heating temperature. Thus, there can be determined a heating duration that will produce spherical particles for a selected set of fiber materials, fiber core diameter, and heating temperature.

[0055] The thermal treatment of a fiber to produce in-fiber spheres can be implemented in any suitable manner. In a first example implementation, a section of a drawn fiber is locally heated in a relatively short heating zone, e.g., about 7.5 mm-long, resulting in the production of particles having a diameter that is equal to that of the fiber core created only in the localized heating section. In this process, sections of the fiber can be heated in sequence, down the length of fiber. In a second example implementation, an extended fiber length is globally heated in a furnace. In this global heating technique, particles are produced having a diameter that is about twice the diameter of the fiber core along the whole fiber length. Although this global heating technique generally produces larger particles, the global heating technique enables the simultaneous production of particles along extended fiber lengths, and given a more uniform temperature distribution along the length of the fiber being thermally treated, reduces the size dispersion in particles produced.

[0056] In the localized-heating scenario, the tension in the heating section is released, from that tension that was employed during thermal fiber drawing, and the fiber narrows at the expense of the fiber materials, such as the polymer, accumulating at the edges of the hot zone. The reduction in diameter of the fiber on average is in this case by a factor of about 2. In the global-heating approach, the whole fiber is placed in a furnace. The fiber tension is also released from that during fiber drawing, and the core diameter resulting after heating is typically a factor 1–1.5 larger than the initial diameter, depending on the tension during the fiber drawing process. Accordingly, the diameter of the particles after fiber core material break-up is 2-3 times larger than those produced by localized heating. These factors may

be pre-compensated for by producing an appropriate core diameter in a preform and corresponding drawn fiber.

[0057] In a further heating scenario, there can be employed a fiber tapering process. Fiber tapering is a process that allows for obtaining a wider range of parameters as compared to fiber drawing. Referring to Figure 2A, steps for heating a fiber in an example fiber tapering apparatus are shown. In fiber tapering, a fiber 115 is inserted in a movable heating zone 118 for a fixed (predetermined) time before both ends of the fiber are pulled symmetrically in opposite directions by the motor 130 together with rollers 132, cabling 133 and end holders 134 as shown in Figure 2A.

[0058] There are generally at least three controllable fiber tapering parameters that may be used for process control during the fiber heating . A first parameter is the temperature, T, which determines the viscosity of the respective fiber materials. The second parameter is the tapering distance, L, which is defined as the length by which the fiber is elongated after softening, that determines the final diameter (or other cross sectional area) of the fiber taper. A third parameter is the tapering speed, v, which determines the dwelling time in the heating zone 118. Once the tapering ends, the heating zone is removed and the extended fiber can be cooled, such as in air. Alternatively, active cooling may be used.

[0059] In the example fiber described above, with a glassy chalcogenide semiconductor As_2Se_3 core having a diameter in the range 5 μm - 20 μm with a thermoplastic polymer cladding comprising PES having an outer diameter of 1 mm, such can be employed in a fiber taper process as depicted in Figure 2B. An example of a typical taper is shown in Figure 2C, with the central tapered section 230 observed after the continuous and uniform extended glass core evolved into a periodic string of core droplet particles 237 as depicted in Figure. 2D. It is noted that the apparent size of the core in Figure 2C and the droplets in Figure 2D are larger than their actual sizes due to magnification resulting from the curvature of the fiber outer surface.

[0060] With these thermal processes for treating a fiber to produce particles in the fiber, there can be produced substantially perfectly spherical particles having an exquisitely smooth-surfaced external morphology. Such can be produced over an extremely broad range of particle dimension, e.g., with a starting fiber core diameter ranging from millimeters down to nanometers, for example, ranging from 2 mm down to 20 nm or down to 10 nm. This size span corresponds to five orders of magnitude in linear dimension, and fifteen in volume, from about 8 mm^3 to about 8,000 nm^3.

[0061] A wide range of particle structures can be produced by these thermal processes. In a first example, homogeneous spheres of fiber core material can be produced, of electrically conducting, electrically semiconducting, or electrically insulating material. Alternatively, the spherical particles can include nonhomogeneous regions of materials, i.e., a plurality of distinct materials can be included as compartments in the spherical particle, in any suitable arrangement.

[0062] For example, the produced spheres can exhibit a core-shell construction; i.e., the produced particles can be fabricated as spherical cores each surrounded by one or more spherical shells. Referring to Figure 3A, in a fiber preform 150 for producing such core-shell spherical particles, there is provided a fiber core 152, e.g., a polymer core material or a glass core material, or other suitable material, having a core diameter, D_1. A cladding layer 154, e.g., a glass cladding layer or polymer cladding layer, is provided around the core 152, having a diameter D_2, with $D_2 \approx 2.5 \times D_1$. A scaffolding outer cladding layer 156, e.g., a polymer layer, is provided around the structure. After consolidation, this preform is drawn down to a fiber having the corresponding core-cladding-scaffold arrangement.

[0063] Then, when subjected to a post-draw thermal process as described above, the core and inner cylindrical layer 154 undergo a correlated PR-driven break-up that results in the formation of core-shell particles along the length of fiber, with the core-shell particles held immobilized in the polymer scaffold

fiber cladding material. Figure 3B is a cross-sectional view of such a core-shell sphere, including a spherical core of fiber core material 152 having a cladding material 154 as a concentric spherical shell around the core. The materials employed for the core and shell components are not limited to polymer core and glass shell example just described. Any combination of materials that are thermally compatible for fiber co-drawing and for thermally-induced break up into the core-shell formation can be employed.

[0064] Referring to Figure 3C, this geometry and process can be extended to produce spheres including any reasonable number of concentric, nested, spherical shells, e.g., three shells 154a, 154b, 154c, surrounding a spherical core 152. In this case, multi-layered spherical particles are produced. Here, the fiber preform is assembled including nested layers of appropriate thicknesses of layers around a central cylindrical core material. The preform is then drawn into a fiber of desired diameter, and exposed to a post-draw thermal process that causes the break-up of the cylindrical layers and central core materials into spherical particles each produced by an evolution of concentric shells around a spherical core.

[0065] This paradigm can be extended for control over spherical radial structure to any suitable degree. For example, as shown in Fig. 3D, there can be assembled a preform 156 including a central cylinder 158 around which are provided four or more cylindrical layers 159a, 159b, 159c, 159d for production of a highly-nested spherical core-shell geometry. A fiber cladding layer 161 of suitable geometry is provided. After fiber drawing, heating in the manner described above is conducted to form the highly-nested particles in the arrangement set by the preform geometry. A hemispherical cross-section of such a highly-nested sphere 163 is shown in Fig. 3E. It is to be recognized that the Plateau-Rayleigh capillary instability (PRI) phenomena employed during fiber heating for producing such highly-nested core-shell particles places constraints on the relative diameters of the different shell layers to ensure that the PRI break up results in particles of the intended nested structure. In

general, during heating of the fiber, the inner core cylinder undergoes break up first, while embedded in a surrounding layer of the adjacent material layer, which in turn subsequently undergoes break up, and so on. Therefore, if one of the concentric cylindrical layers has a much smaller diameter than the adjacent layers, it is possible that spheres of the smaller-diameter layer material could be formed embedded within one of the particle shells or even the particle core. For example, so long as the diameter of the core is not significantly smaller than the outer diameter of the adjacent shell layer, a shell will form around a spherical core. At some point, a transition in the system occurs, based on the viscosities and surface tension of adjacent materials, beyond which particles are formed

[0066] A second example of a structured particle that can be produced by the post-draw thermal processing described herein is a broken-symmetry, spherical Janus particle, comprising two hemispheres of different materials, e.g., two different optical glasses, such as As_2S_3 and $((As_2Se_3)_{99}Ge_1)$, that can be co-drawn with a polymer into a fiber. Figure 4A is a schematic cut-away view of such a fiber 160 arranged for Janus particle production. In formation of the fiber, there is assembled a preform including a half cylinder of each of the selected core materials, wrapped in a selected polymer material. After fiber draw, the fiber includes a first half cylinder core 62 and a second half cylinder core 164 of the two selected core materials, surrounded by a fiber cladding layer 166.

[0067] Thermal processing of the fiber is then conducted to cause formation of Janus particles out of the fiber core. Referring to Fig. 4B, the thermally-induced break-up of the core materials produces spherical Janus particles 168 having a first hemisphere 170 and a second hemisphere 172, corresponding to the first half cylinder 162 and the second half cylinder 164, respectively, in the fiber. The figure is a cross-sectional view; each Janus particle is a three-dimensional, two-compartment, spherical structure. The Janus particles are held immobilized along the length of the fiber, within the

polymer cladding, all with the same orientation of materials along the fiber length.

[0068] In the successful production of Janus particles by the thermal methods described herein, it can be preferred, for glassy core materials, that the selected glasses be characterized by a relatively low glass-glass surface tension, and the core and cladding be characterized by a similar glass-polymer surface tension. With these considerations, the two-compartment Janus particle spheres are produced along the length of a fiber. As with the core-shell particles described above, the materials employed Janus particle components are not limited to this particular example, here glasses. Any combination of materials that are thermally compatible for fiber co-drawing and for thermally-induced break up into the Janus particle formation can be employed.

[0069] The two-compartment particle design can be extended to a general azimuthal design. In one example of such, as shown in Figure 5A, a fiber 180 is first produced including a core of a selected number of wedge-shaped azimuthal sections, e.g., six wedge-shaped sections, of selected materials, such as sections 182, 184, 186, and 188, 190 192, employing, e.g., the two glasses employed in the Janus particle example above, or other arrangement of glasses or other materials that can be co-drawn. A polymer cladding 194 is disposed around the core arrangement. With this fiber configuration, there can be produced, as shown in Figure 5B, a 'beach ball' particle 200, a cross section of which is shown. The particle 200 is a three-dimensional, six-compartment, spherical structure, having six distinct azimuthal compartments 202, 204, 206, 208, 210, and 212.

[0070] Symmetry is not required for the azimuthal control of particles, and indeed, for many applications it can be desired to enforce lack of symmetry. For example, as shown in Fig. 5C, there can be formed a fiber 215 having a fiber core 216 that includes multiple distinct regions arranged in a geometry that lacks rotational symmetry. A suitable cladding 218, e.g., a

polymer cladding, is provided around the core. This fiber, when subjected to the thermal processes described above, produces corresponding spherical particles 220 each having multiple distinct material regions 221, 222, 223, 224, and lacking rotational symmetry.

[0071] These sectional particles and the core-shell particles described above are just a few examples of the structures from which more complex geometries can be constructed based on the post-draw thermal processing described herein. Having an understanding of the PRI fiber core break up phenomena, the fiber core can be reverse-engineered to produce particles with a selected structure in a manner that pre-compensates for the PRI deformation process. As a result, there can be achieved combined elements of both radial and azimuthal control over particle geometry. For example, multilayer particles can be produced including a core of nested cylindrical shells of appropriate thicknesses, and within the central core, azimuthal compartments can be provided by arranging the core with azimuthal sections. Similarly, each in a series of nested shells can be independently provided with distinct azimuthal material arrangements. i.e., each distinct radial layer can include multiple distinct azimuthal sections. Each of the cylindrical shells and each of the azimuthal sections can be provided as distinct materials, or selected materials can be alternated or otherwise arranged in a selected configuration for the particle.

[0072] For example, as shown in Fig. 5E, there can be formed a fiber 225 including a core 226 having a two-material inner cylinder 228 surrounded by a first cylindrical layer 230 also of two materials and having a material junction that is offset from that of the inner cylinder arrangement by a selected angle, e.g., 90°. Any suitable number of additional cylindrical layers can be provided around the first. For example, a second cylindrical layer of two or more materials and having a material junction offset from that of the first cylindrical layer can be included in the fiber. A suitable fiber cladding 234 is provided around the core. Upon thermal processing in the manner described

above, the fiber core breaks up into particles 240 each having a core 242 and at least one shell 244 that each are arranged with multiple materials in a pre-selected orientation to adjacent layers, as shown in Fig. 5F. Thereby is achieved control of the orientation of broken-symmetry layers with respect to each other, with each layer and the core including any number of distinct materials that are compartmentalized within the three-dimensional volume of the particle.

[0073] In a further example of radial and azimuthal control, there can be produced particles that include a plurality of sub-particle arrays, in a mother-daughter particle arrangement. An example of such is shown in Figs. 5G-5H. A drawn fiber 245 is provided including a cylindrical mother core 246 in which are disposed a plurality of cylindrical daughter cores 248. Such can be achieved by, e.g., drawing a fiber having one or more cores and cladding and then cutting and stacking the drawn fiber in a selected arrangement to position the drawn cores with additional cladding material surrounding the stacked cores. Then one or more cylindrical layers 250 can be arranged radially outwardly, and a cladding layer 252 further disposed radially outwardly. As described below, a fiber preform can be produced with a corresponding arrangement for drawing into the fiber of Fig. 5G. The structure is then drawn into a fiber, and with this drawn fiber geometry, exposure to the thermal processes described above produces a core-shell sphere having a core in which a plurality of daughter spheres are disposed. Fig. 5H is a cross section of a mother-daughter particle 255 including a plurality of daughter spherical particles 256 within a mother spherical core 258. There can be included one or more spherical shells 260 around the core 258. The arrangement of the daughter spheres 256 within the mother core sphere 258 is set by the configuration of daughter core cylinders in the fiber preform, prior to fiber drawing, and the corresponding drawn fiber. To ensure that the particle arrangement occurs during particle break-up, the daughter cores 248 are preferably much smaller than the diameter of the mother core 246. Based on the PRI break up phenomena given above, the diameter of the daughter cores

is selected based on the viscosity and surface tension of the materials, for selected thermal processing temperature and duration, to ensure production of the daughter spherical particles.

[0074] While this example includes one spherical shell around the mother spherical core 258, such is not required. Mother-daughter spherical particle arrangements can be constructed with no outer spherical shells, or with any suitable number of nested shells. Each of the mother core particle and shell layers can be formed of multiple materials, further including azimuthal control as well as radial control of multiple materials in the particles, in the manner of Figs. 5D and 5F, if desired.

[0075] In the production of these many examples of particle geometries, a fiber preform is assembled that exhibits the corresponding macro-scale arrangement of materials. For example, in the production of spherical particles, a selected core material for producing spheres of, for example, As_2Se_3, is provided, e.g., as a 10 mm-diameter, 10 cm-long cylindrical rod. Such can be produced by, e.g., melt-quenching a commercial glass, available from, e.g., Amorphous Materials, Inc., Garland, TX. A thin cladding material, e.g., a 75 μm-thick layer of PES, is then rolled around the rod, to produce a preform for the thermal production of homogeneous As_2Se_3 spheres. The resulting preform is consolidated, e.g., under vacuum at a suitable temperature for the given preform materials, e.g., 225°C. The preform is then thermally drawn into a fiber; drawing a preform with diameter D_o and length L_o by a factor N results in a fiber of diameter D_o/N and length N^2L_o. Where multiple cores are to be provided within a single fiber, a selected number of drawn fibers, each including one or more fiber cores, are stacked as a preform assembly, consolidates, and drawn together to form a composite, multi-core fiber. The drawing and stacking of cores can be reiterated as-desired.

[0076] In the formation of the core-shell particles like that in Figures 3A-3E, a preform can be produced by, e.g., extruding a cylindrical billet, such as a 30 mm-diameter cylindrical billet, through a circular die, e.g., a 12 mm-

diameter die. An example of such a billet consists of three discs: a first, top disc is polymer, a middle disc is glass, and a bottom disc is again polymer, with heights of, e.g., 30 mm, 20 mm, and 20 mm, respectively. The billet is heated to above the softening temperature and then pushed vertically downward through the die under pressure. The resulting extruded rod can then be employed as a preform to draw a fiber for production of a core-shell particle.

[0077] In the formation of Janus particles or other azimuthally-structured particles such as the 'beach ball' particle of Figure 5B, there is arranged in a corresponding fiber preform the requisite materials having an arrangement of shapes for production of particle compartments. For example, in production of the Janus particle of Figure 4B, a preform is assembled by providing two half-cylinders, e.g., two 12 mm-diameter, 30 mm-long structures, provided with selected materials, e.g., with melt-quenched glasses. Here it is preferred that the two materials, e.g., two optical glasses, have approximately similar viscosities at the target particle break-up temperature, ~ 350°C – 400°C. A cylinder can be formed from the two half-cylinders and then arranged as the core of a preform by rolling a cladding layer, e.g., a thin layer of PES, around the two half cylinders. The preform is then consolidated under vacuum. The preform is then drawn into a fiber for thermal Janus particle fabrication.

[0078] A multi-section 'beach ball' particle like that of Figure 5B can be produced from a preform arrangement corresponding to the fiber structure shown in Figure 5A. The preform core can be assembled from six sections, for example, three each from two different glasses. In this example, the two glasses can be extruded, e.g., using a die with the shape of the desired 60° 'pie' sections, to produce the requisite core arrangement of materials. Any number of sections can be employed. A cladding layer, e.g., a thin layer of PES, is then rolled around the assembled sections, and the preform is consolidated under vacuum. The preform is then drawn into a fiber for thermal particle fabrication. These are but a few example preform assembly processes that

enable the construction of any number of sections that are controlled radially and azimuthally to produce particles having corresponding radial and azimuthal control.

[0079] After thermal particle formation, the various structures can be released from the fiber matrix, e.g., the fiber cladding phase of the fiber, by removing the cladding material. If the fiber matrix is an organic material, such as a polymer, and the particle materials are all inorganic, then an organic solvent can be employed to dissolve the polymer. For example, the fiber can be placed in, e.g., a watch glass filled with N, N-Dimethylacetamide (DMAC), e.g., having a 99% concentration at room temperature, to dissolve the polymer, with fresh DMAC replacement as the dissolving proceeds. With four or five iterations, the polymer matrix is substantially completely removed. For applications in which a large quantity of particles is required, a large number of particle-embedded fibers are placed into a suitable vessel, e.g., a beaker, for an extended duration, e.g., 1-2 hours, at room temperature. With this duration, the particles are completely released from the fiber cladding matrix. No particular particle release process is required, and any suitable method that removes fiber cladding material can be employed.

[0080] Whatever particle release method is employed, there can further be carried out surface passivation of the particles to prevent agglomeration of the particles. One particular advantage of the particle formation processes described herein is the function of the fiber cladding phase to isolate each particle so that particles embedded in a fiber, as-produced, cannot agglomerate in the fiber. To preserve this highly-desirable particle isolation, the particles can be processed during release from the fiber, can be processed at the time of release from the fiber, or processed subsequent to release from the fiber. For example, the particles can be coated with a selected spray species, e.g., a polymer spray, to form a layer on the particles as the fiber cladding material is dissolved or otherwise removed. Alternatively, the fiber cladding removal can be conducted in a flowing solution that includes a high concentration of a

particle-coating material. Here the flow of the solution can be employed to maintain spacing between the particles as the particles are released from the fiber. Further, the particles can be exposed to a passivating agent, such as an oxidizing environment, that prevents agglomeration. These examples demonstrate that a wide range of processes can be applied to prevent agglomeration of particles upon release from the fiber.

[0081] Disclosed embodiments also include compositions of matter comprising a plurality of core particles embedded in a scaffold. In one embodiment an embedded particle arrangement comprises a multi-material fiber having a length ≥ one hundred times its cross sectional area, where the multi-material fiber includes a cladding material providing a continuous phase for said multi-material fiber, and a plurality of particles along at least a portion of the fiber length embedded in the cladding material. The plurality of particles are separated from one another, have a median size of any suitable diameter, e.g., from 5 nm to 1 mm, are spherical in shape, and can be molecularly smooth.

[0082] The cladding material in one embodiment comprises a polymer, such as a thermoplastic polymer. For embodiments corresponding to use of performs including a plurality of cores, the plurality of particles are arranged in a three dimensional distribution. The three-dimensional distribution of particles can include periodicity providing a standard deviation of center-to-center particle spacing <5% of the average center to center particle spacing in at least a first and a second dimension transverse to the length dimension of the multi-material fiber. As described above, the transverse periodicity is controllable at the fabrication stage through the stack-and-draw process. A periodicity of < 15% (such as about 10%) of the average center-to-center particle spacing can also be provided in the length dimension of the multi-material fiber. The plurality of particles can be uniformly sized providing a <10% standard deviation in particle size with respect to an average (mean) size of the particles. The mean particle size depends on the core diameter of the

fiber employed in particle production. The particle size distribution around a mean therefore depends on several factors, including the uniformity of the core diameter along the fiber axis; this factor can be optimized by careful control of fiber drawing parameters. In addition, the uniformity of the temperature distribution in the heating zone of the furnace employed in post-draw thermal break-up of the core impacts the particle size distribution. Optimization of furnace geometry can be preferred to carefully control furnace temperature. Finally, it is found that statistical fluctuations that initiate the fiber core break-up process result in residual fluctuations in the particle size distribution.

[0083] Disclosed particles can comprise spherical particles including a first hemisphere comprising a first material and a second hemisphere comprising a second material different from the first material. In this embodiment the first material can comprise a first glass and the second material a second glass different from the first glass to provide "Janus particles" that are generally defined as spherical glass particles with one of the hemispheres being one material and the other hemisphere being another material. Disclosed processing may also be extended to multiple sectors (e.g., 3, 4, 5 ...) of a cylinder to form spherical particles with more sophisticated sub-structure.

[0084] Applications for disclosed particles are numerous. Example applications include cosmetics, biomedical, chemical and biological catalysts, and paints (particles are held as a colloid in a solution).

EXAMPLES

[0085] Disclosed embodiments are further illustrated by the following specific Examples, which should not be construed as limiting the scope or content of this Disclosure in any way.

[0086] Example parameters tested include an initial As_2Se_3 core diameter of 40 μm and PES cladding tapered at a fixed speed v=2 mm/s and tapering distance d=15 mm, but with varying temperature, T. As_2Se_3 is known

to have a melting point of about 360°C and a glass transition temperature of about 180°C. The PES used had a glass transition temperature of about 230°C. When the fiber temperature rises sufficiently above both of the glass transition temperatures and the viscosity decreases sufficiently, PR instability is believed to be initiated through perturbations at the core/cladding interface.

[0087] Referring to Figures 6A and 6B, it was found that at relatively low temperatures, such as 261°C and 264°C, respectively, the viscosity of the As_2Se_3 core is relatively large and the extended core remained intact during tapering, so that no core droplets were observed. However, as the temperature was increased, a gradual growth in the PR instability shown began at about 268°C apparently resulting in the periodic string of periodic core droplets shown being formed, as shown in Figures 6C-E.

[0088] Static heating was also studied. Static heating as used herein refers to the only parameter being varied is the temperature (no pulling/tapering). The instability breakup time, τ, of the core, was measured over the range of temperatures for fibers with an initial core diameter, where τ was measured from the start of heating until initiation of breakup.

[0089] In order to analyze these results quantitatively, there was adopted as a model the linear stability analysis of Tomotika [S. Tomotika, Proc. Roy. Soc. Lond. A 150, 322 (1935)], which describes a stationary viscous thread embedded in an unbound viscous fluid, as described above. According to this analysis, as previously explained, perturbations at the interface between the two fluids (core and cladding here) grow on a time-scale, τ, that depends on the perturbation wavelength λ, the viscosities of the two fluids, core viscosity, μ_{core}, and cladding viscosity, μ_{clad}, the thread diameter (core diameter, D_{core}, assuming an unbound cladding for simplicity), and surface tension, γ. The wavelength with the largest growth rate, and minimum τ, $\tau_{fastest}$, defined previously above, quickly dominates the instability and results in the fiber core breaking up into a periodic sequence of droplets with separation λ. The following values of the parameters were used in

calculations: D =10 μm, surface tension between As_2Se_3 and PES, γ = 0.1 N/m, and η_p = 10^5 Pa·s for PES. While the temperature dependence of μ_{clad} over the temperature range of interest was ignored, μ_{core} for As_2Se_3 changes considerably over the same range and was obtained from an empirical Arrhenius formula. Using these values the instability growth time as a function of temperature was calculated and the results compared the results to the experimental data. The predictions of the Tomotika model are in quantitative agreement with the data of about 150 s for a temperature of 270 °C. Further was calculated the break-up time, τ, over the same temperature range for other initial core diameters. To a reasonable degree of accuracy, it was found that τ depends linearly on D at a fixed temperature.

[0090] Further, the breakup wavelength λ is proportional to the fiber core diameter at the time of core breakup. From the Tomotika linear stability model, λ is related to the core diameter D through $\lambda = \pi D/\eta$, where η is a dimensionless constant that depends on the relative viscosities of the fiber core and cladding materials. Assuming incompressible flow of the core material, the diameter, D_p, of a droplet being formed and the core diameter at breakup, D_{core}, are related through $D_p = \sqrt[3]{3\pi/2\eta}\, D_c$. For $\eta = 0.6$, which is typical for the example materials described herein, $D_p \approx 2D_c$. If the fiber initial core diameter is D, this implies that $D_p \approx D$ for the localized heating process, and $D_p \approx 2D - 3D$ for the global heating process. As a result, the diameter of the produced particles can be, e.g., less than about 1 mm, less than about 1 micron, and less than about 100 nm.

[0091] Also examined was the effect of each fiber tapering parameter (L, T, and v) while holding the other two parameters fixed. A simple model for this system is based on a quasi-static extension to the static Tomotika model. This model decouples the effect of heating on the core from the dynamics of tapering. The static results for the temperature-dependent instability time, τ, was therefore employed with the added geometric effect of size change during tapering. This model yielded results in quantitative agreement with

observations despite its simplicity within the margin of error in the measurements performed.

[0092] The effect of tapering distance, L while holding the velocity, v = 1 mm/s and T = 285°C was studied. The static results indicated that breakup occurs after about 80 s at this temperature with the initial core diameter D_{core} = 10 μm. As the diameter decreases during tapering, τ decreases accordingly. It was found that the core remains intact until L = 21 mm at which point it breaks up into a series of droplets with an average separation of 7.1 μm. After breakup has occurred in the taper, further elongation was found to only increase the droplet separation.

[0093] Making use of the above-described quasi-static model, and making use of the approximately linear relation between τ and diameter D, an estimate for D at the moment of breakup can be generated. Taking τ = 21 s, $D_{final} \sim 2.6$ μm is estimated. This estimate depends only on the measured instability time and the assumptions of the static Tomotika' model. An independent estimate was also achieved from a different route. Geometric considerations coupled with the simplifying but reasonable assumption that the temperature of the heating zone is uniform and the taper material exiting the heating zone cools down immediately lead to the initial and final core diameters being related by a factor of the form $e^{-L/h}$, where h is the length of the heating zone. Thus $D_{final} = De^{-L/h} = 10\ e^{\{-21/17\}} \sim 2.9$ μm, consistent with the considerations described above. The last data point (at L = 27μm) was higher than expected since the fiber undergoes rapid plastic deformation before mechanical fracture with further tapering.

[0094] The effect of T for fixed v = 1 mm/s and d = 23 mm was next considered where the final taper diameter remains approximately constant. At low temperatures, the viscosity of the core was found to be relatively large and the core to remain intact. As the temperature increased, the PR instability grows until droplets are formed and the average period of the droplets increases with temperature. This may be understood as follows: viscosity

decreases exponentially with temperature and the Tomotika model indicates that lower viscosity leads to linearly shorter instability time. The instability thus develops quickly at a larger diameter corresponding to a longer period. The period hence will exponentially increase with temperature. Furthermore, if the breakup occurs early on in the tapering process at higher temperature, then further tapering leads to further separation between the core droplets.

[0095] The effect of v while holding d = 23 mm and T = 285°C was next considered. The final diameter of the fiber taper is also approximately constant. At high speeds, the dwelling time may be less than τ for the final core diameter, and the core thus remains intact. At lower speeds, the fiber dwells for a longer time in the heating zone thus having the opportunity to reach τ and thus breakup. The breakup of the larger-diameter core during tapering results in longer period, and then the droplets further separate if the tapering process continues. The period was found to be inversely proportional with the drawing speed.

[0096] As noted above disclosed methods may be used to fabricate microparticles or nanoparticles. The particle size as disclosed herein may be tuned by adjusting the tapering parameters, and the physical process described here hence offers an unconventional non-lithographic, top-down approach to fabricating micro and nano-structures using non-traditional materials combinations. To demonstrate control over particle size, there were produced core particles at three different sizes, namely, 5 μm, 2 μm, and 1 μm, where particle size was tuned by varying the tapering speed.

[0097] There are a number of advantageous features of the disclosed in-fiber particle fabrication methods. First, the methods are amenable to a wide range of materials. The particles that are produced in the fiber can be electrically conducting, electrically insulating, or electrically semiconducting, and therefore can be provided as a metal, an insulator, or a semiconductor. Suitable materials include, e.g., glassy inorganic materials, such as

chalcogenide glasses, and low-melting-temperature metals, and other materials, preferably that can be co-drawn into a fiber.

[0098] Generally, a wide range of metals and metal alloys, both above their melting temperature, including, e.g., tin, indium, bismuth, cadmium, lithium, or other low melting-temperature metal, and alloys such as Sn-Ag, Sn-Sb, Sn-Cu, and other alloys can be employed, as well as suitable amorphous glassy metals. With these suitable metals employed in the processes described above, there can be formed metal and metal alloy spheres.

[0099] No particular material combination is required in the sphere production processes. The viscosities of the materials to be co-drawn into a fiber are preferably compatible for fiber drawing, e.g., the viscosities of the materials can for some applications preferably be less than about 10^6 Poise at a fiber draw temperature while maintaining the material integrity of the materials; such compatible materials in general exhibit an overlap in softening temperature.

[00100] Secondly, since the process can start from a macroscopic preform, including, e.g., a rod or cylinder, that is drawn into a fiber, particles of complex structure may be obtained through assembly of the rod with the prescribed structure. Janus particles, nested spherical particles, and complicated nonhomogeneous particles of different material segments can be produced. Thirdly, although the process described herein is generally not efficient in producing particles in terms of volume conversion, the efficiency may be increased by using multi-core fibers, i.e., fibers including a plurality of cores, e.g., three different cores, all of which can undergo break-up into particles.

[00101] One may further increase the number of cores until they become hydrodynamically coupled during tapering and the assumption of an unbound cladding breaks down. But in general, for a fiber of 1 mm outer diameter to be processed by a non-tapering heating scenario, there can be provided, e.g., 12 20-μm cores, 4,000 500-nm cores, or even 27,000 200-nm cores. In principle there could be provided 10^8 50-nm cores in such a fiber, with 25% fill factor, all

of which can be subjected to heat treatment for production of particles. This particle production technique far exceeds parallelization capabilities of particle production approaches such as microfluidics-based approaches. Furthermore, the resulting spatial distribution of particles produced from a large plurality of fiber cores is held immobilized in the fiber cladding scaffold and is well-ordered in three dimensions. The axial directions of the particles are ordered because the instability growth is dominated by a single wavelength. In the transverse dimensions, order is imposed on the fiber cores during the preform assembly process.

[00102] As disclosed above, the size of particles that may be fabricated using disclosed methods extends over a very wide range, such as extending from 1 mm down to less than 100 nm, and even as small as nanometers. The particles can be highly spherical particles. Moreover, the same procedure may be used with a wide variety of materials. For example, the above-described processes were demonstrated with a polymer core and polymer cladding. The same particle generation phenomena occur with polymer cores that occur with glass cores. Therefore, disclosed processes can also be used to fabricate micro- and nano-particles of polymers. The PR-driven breakup process is universal in the sense that it does not rely on the chemistry of the materials in the fiber to produce particles, but relies only on the physical parameters of viscosity and surface tension.

[00103] In an example of particle production from an all-polymer fiber structure, there can be provided a polymer fiber core, e.g., the polymer cyclic olefin copolymer (COC), while the fiber cladding, or scaffold matrix, can also be provided as a polymer, e.g., polycarbonate (PC). For some applications, it can be preferred to select a fiber core material that is biocompatible, such as a biocompatible polymer. Both COC and PC are examples of polymers that are biocompatible. With such an all-polymer fiber system, the breakup dynamics of the fiber core into particles are similar to those for, e.g., a glass-polymer fiber material system, with the dynamic range of polymer particles produced

being similar to that for glass particles. Such an all-polymer system is particularly well-suited for, e.g., biomedical applications and in controlled-release drug delivery. Any suitable polymer combination can be employed, e.g., polyetherimide (PEI) and polysulfone (PSu), or other suitable polymer combination, including cyclic olefin polymer, poly-ether sulfone, poly-methyl methacrylate, and other such polymers. This demonstrates one example in which the spherical particles that are produced in the fiber are biocompatible. Any such biocompatible particle material having the requisite characteristics for the in-fiber production processes described herein can be employed for a wide range of biomedical and health-related applications.

[00104] Since the disclosed particle generation processes are top-down approaches that start from a structure at the macroscopic scale, the shape of the fiber preform, e.g., cylinder of the material, can be selected that is to be drawn into a fiber for break-up into particles. For example, as described above, two hemi-spheres of different materials can be used. The result is "Janus-particles", which are particles formed of two hemispheres of different core materials. The process may also be extended to multiple sectors of a preform cylinder to form spherical particles with a sophisticated sub-structure.

[00105] Disclosed embodiments include methods to form high-density macroscopic arrays of well-ordered nanowires that can range from nanometers to 1 mm. A centimeter-scale macroscopic cylindrical preform containing the nanowire material in the core encased in a polymer scaffold cladding was thermally drawn in the viscous state to a fiber. By cascading several iterations of the fiber drawing process, continuous reduction of the diameter of an amorphous semiconducting chalcogenide glass was demonstrated. Starting from a 10-mm-diameter rod thermally drawing was used to generate hundreds of meters of continuous sub-5-nm-diameter nanowires. Using this approach, macroscopic lengths of high-density, well-ordered, globally-oriented fiber core nanowire arrays can be produced.

[00106] Experimental results are provided below described relative to Figures 7A-9D which demonstrate the production of spherical particles following disclosed processing applied to a fiber preform including a large number of glass cores encased in a polymer cladding. In the axial (longitudinal-axis length) direction the resulting particles are ordered since the instability growth is dominated by a single wavelength. In the transverse dimensions particle order is imposed upon the cores during the stacking process to form the preform.

[00107] Figures 7A and 7B are scanned SEM micrograph of a 12-core fiber, with each core of 20 μm in diameter, for producing particles by a post-draw thermal process. In the figures, G represents the glass, As_2Se_3, and P represents the polymer, PES. Periodicity of the glass in the transverse directions is demonstrated.

[00108] Figure 8 is a scanned high-magnification SEM micrograph of a portion of a fiber including 27,000 cores each of 200 nm in diameter. The stacked fibers in the preform were found to produce a hexagonal lattice (see dashed lines). At each lattice site 80 200-nm glass cores are located as shown in the inset. After break-up of these cores by thermally-induced PR, there is produced a three-dimensional arrangement of particles in the polymer cladding matrix that is periodic in all three dimensions. The periodicity in the two transverse dimensions is imposed by the stacking process, and the longitudinal periodicity of each core is an inherent result of the PR process.

[00109] Figures 9A-D are scanned SEMs demonstrating the resulting well-ordered, three-dimensional particle emulsion that can be produced held in the polymer cladding. Figure 9A is a scanned SEM micrograph of a 1-mm-diameter fiber cross section containing 80 7-μm-diameter cores. Figure 9B is a higher-magnification scanned SEM micrograph of the 80 cores, G = As_2Se_3 and P = PES. Figures 9C and 9D are scanned transmission optical micrographs of the fiber side view before and after breakup (via global heating), respectively,

showing the resulting spatial distribution of particles held immobilized in the cladding (scaffold) is well-ordered in all 3 dimensions.

[00110] The description above makes clear that the post-draw thermal processing of fibers for in-fiber spherical particle generation enables the controllable production of complex and well-defined structures. These scalable thermal processes, in which there are first assembled disparate components that fit together, as a macro-scale preform, for scalable production of size-tunable structured spherical particles, enable a wide range of applications. The well-ordered, oriented, and immobilized particles that are produced by the thermal processing within a fiber scaffold layer can be employed for three-dimensional optical and acoustic meta-materials; the surface-tension-driven smooth spherical surface morphology of the particles enables optical-resonance-based sensitive detection of chemical species and pathogens; and three-dimensional structural control over such particles that are impregnated with drugs, e.g., in the preform stage, enable the realization of sophisticated controlled-release drug delivery systems.

[00111] While various disclosed embodiments have been described above, it should be understood that they have been presented by way of example only, and not limitation. Numerous changes to the subject matter disclosed herein can be made in accordance with this Disclosure without departing from the spirit or scope of this Disclosure. In addition, while a particular feature may have been disclosed with respect to only one of several implementations, such feature may be combined with one or more other features of the other implementations as may be desired and advantageous for any given or particular application.

[00112] Thus, the breadth and scope of the subject matter provided in this Disclosure should not be limited by any of the above explicitly described embodiments. Rather, the scope of this Disclosure should be defined in accordance with the following claims and their equivalents.

[00113] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. As used herein, the singular forms "a," "an," and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. Furthermore, to the extent that the terms "including," "includes," "having," "has," "with," or variants thereof are used in either the detailed description and/or the claims, such terms are intended to be inclusive in a manner similar to the term "comprising."

[00114] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which embodiments of the invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[00115] We claim:

1. A fiber comprising:

a cladding material disposed along a longitudinal-axis fiber length; and

a plurality of spherical particles disposed as a sequence along a longitudinal line parallel to the longitudinal fiber axis in at least a portion of the fiber length, each spherical particle comprising a spherical particle material that is interior to and different than the fiber cladding material, and each spherical particle comprising a core-shell particle including a spherical core that is surrounded by at least one spherical shell.

2. The fiber of claim 1 wherein the spherical shell comprises a plurality of nested spherical shells.

3. The fiber of claim 1 wherein each core-shell spherical particle includes a spherical core including at least two distinct materials in the spherical core.

4. The fiber of claim 1 wherein the spherical shell includes at least two distinct materials in the spherical shell.

5. The fiber of claim 1 wherein each core-shell spherical particle includes a spherical core including at least two distinct materials in the spherical core and the spherical shell includes at least two distinct materials in the spherical shell.

6. The fiber of claim 1 wherein each core-shell spherical particle includes a spherical core that is a mother spherical particle including a plurality of daughter spherical particles within the mother spherical particle.

7. A fiber comprising:

a cladding material disposed along a longitudinal-axis fiber length; and

a plurality of spherical particles disposed as a sequence along a longitudinal line parallel to the longitudinal fiber axis in at least a portion of the fiber length, and comprising a spherical particle material that is interior to and different than the fiber cladding material, each spherical particle comprising a plurality of azimuthal sections of at least two distinct materials.

8. The fiber of claim 7 wherein the spherical core is surrounded by at least one spherical shell.

9. The fiber of claim 7 wherein each spherical particle has no rotational symmetry.

10. The fiber of claim 7 wherein each spherical particle is a mother spherical particle including a plurality of daughter spherical particles within the mother spherical particle.

11. A fiber comprising:

a cladding material disposed along a longitudinal-axis fiber length; and

a plurality of spherical particles disposed as a sequence along a longitudinal line parallel to the longitudinal fiber axis in at least a portion of the fiber length, each spherical particle comprising a spherical particle material that is interior to and different than the fiber cladding material, and each spherical particle having a particle diameter, with spacing between adjacent spherical particles in the sequence of particles being greater than the spherical particle diameter.

12. The fiber of claim 11 wherein the fiber cladding material and the spherical particle material are each characterized by a viscosity that is less than about 10^6 Poise, while maintaining material integrity, at a common fiber draw temperature.

13. The fiber of claim 11 wherein the fiber cladding material comprises a polymer material selected from the group consisting of poly-ether imide, poly-ether sulfone, polycarbonate, polysulfone, cyclic olefin polymer, cyclic olefin copolymer, and poly-methyl methacrylate.

14. The fiber of claim 11 wherein the spherical particle material comprises an electrically semiconducting material.

15. The fiber of claim 11 wherein the spherical particle material comprises an electrically insulating material.

16. The fiber of claim 11 wherein the spherical particle material comprises an electrically conducting material.

17. The fiber of claim 16 wherein the spherical particle material comprises a material selected from the group consisting of metals and metal alloys.

18. The fiber of claim 17 wherein the spherical particle material comprises a material selected from the group consisting of tin, indium, bismuth, cadmium, lithium, lead, zinc, Sn-Ag alloys, Sn-Sb alloys, and Sn-Cu alloys.

19. The fiber of claim 11 wherein each spherical particle is a mother spherical particle including a plurality of daughter spherical particles within the mother spherical particle.

20. The fiber of claim 11 wherein each spherical particle comprises a biocompatible polymer material.

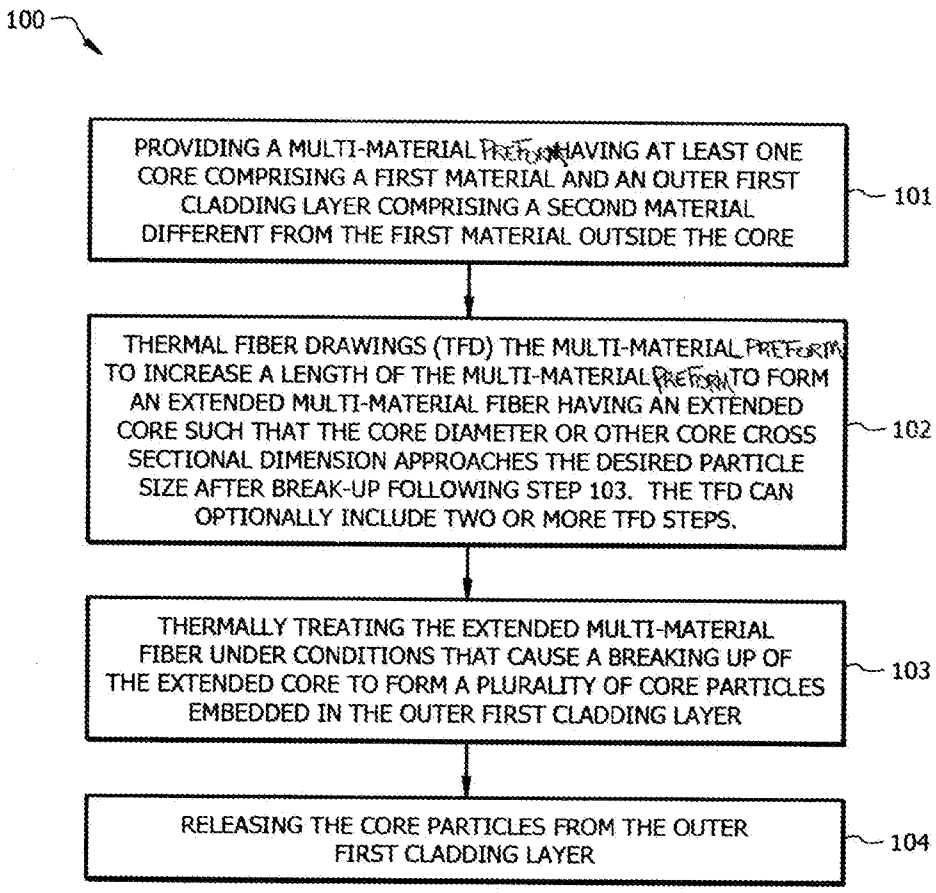

100
PROVIDING A MULTI-MATERIAL PREFORM HAVING AT LEAST ONE CORE COMPRISING A FIRST MATERIAL AND AN OUTER FIRST CLADDING LAYER COMPRISING A SECOND MATERIAL DIFFERENT FROM THE FIRST MATERIAL OUTSIDE THE CORE
101
THERMAL FIBER DRAWINGS (TFD) THE MULTI-MATERIAL PREFORM TO INCREASE A LENGTH OF THE MULTI-MATERIAL PREFORM TO FORM AN EXTENDED MULTI-MATERIAL FIBER HAVING AN EXTENDED CORE SUCH THAT THE CORE DIAMETER OR OTHER CORE CROSS SECTIONAL DIMENSION APPROACHES THE DESIRED PARTICLE SIZE AFTER BREAK-UP FOLLOWING STEP 103. THE TFD CAN OPTIONALLY INCLUDE TWO OR MORE TFD STEPS.
102
THERMALLY TREATING THE EXTENDED MULTI-MATERIAL FIBER UNDER CONDITIONS THAT CAUSE A BREAKING UP OF THE EXTENDED CORE TO FORM A PLURALITY OF CORE PARTICLES EMBEDDED IN THE OUTER FIRST CLADDING LAYER
103
RELEASING THE CORE PARTICLES FROM THE OUTER FIRST CLADDING LAYER
104

FIG. 1A

FIG. 1B

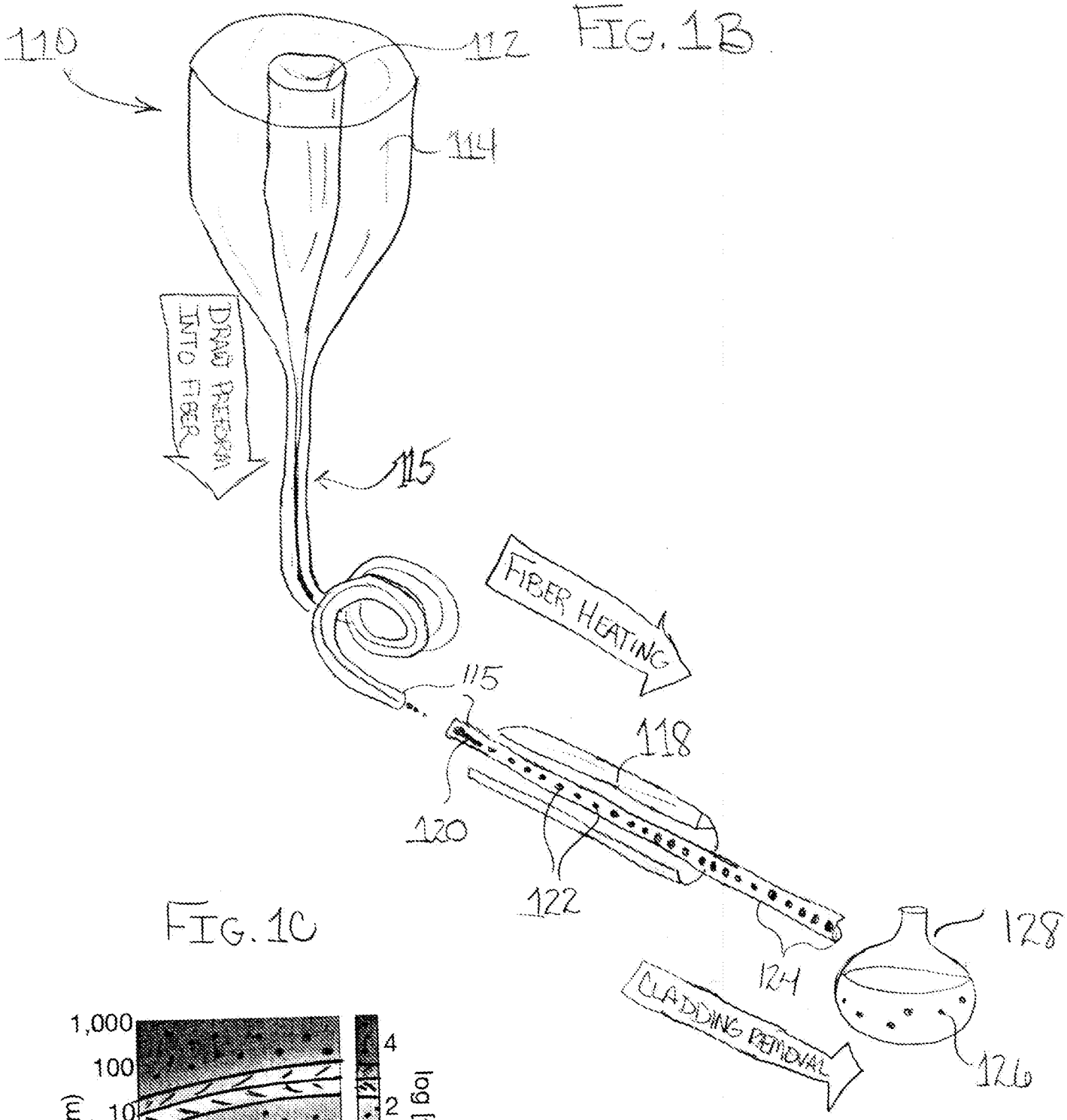
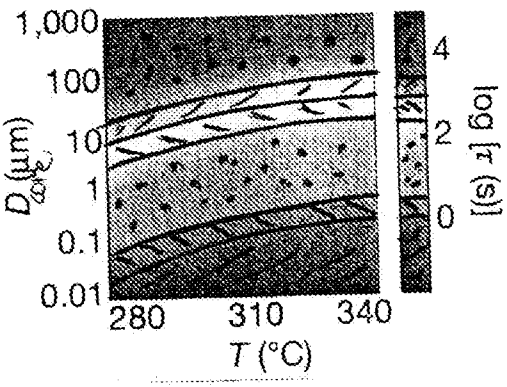

110
112
114
DRAW PREFORM INTO FIBER
115
FIBER HEATING
115
118
120
122
124
128
CLADDING REMOVAL
126

FIG. 1C


1,000
100
10
1
0.1
0.01
$D_{\alpha\alpha}$ (μm)
280
310
340
T (°C)
4
2
0
log [τ (s)]

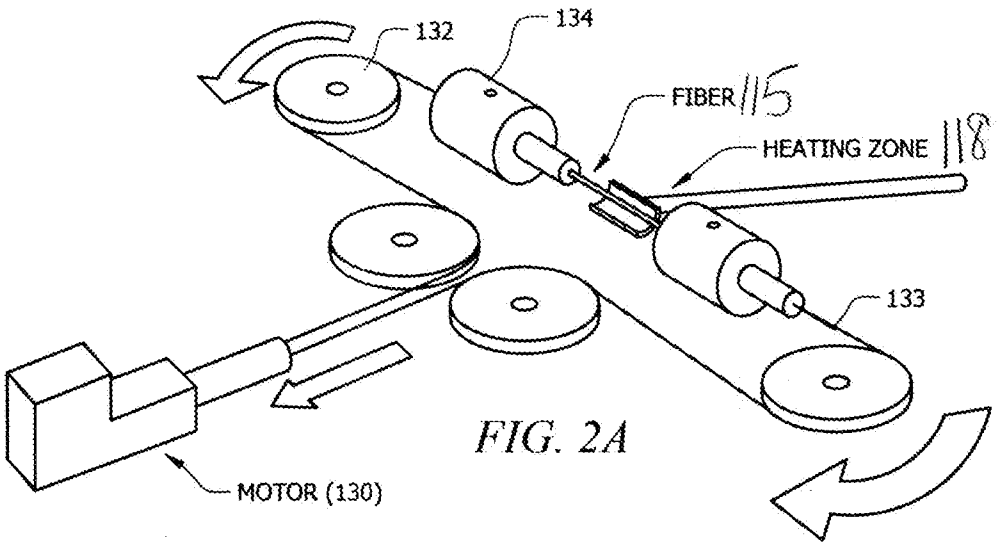


FIG. 2A

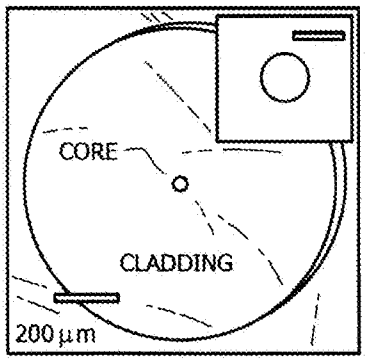


FIG. 2B

FIG. 2C

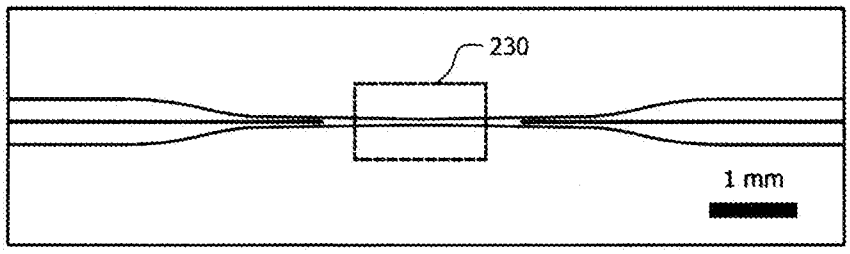


FIG. 2D

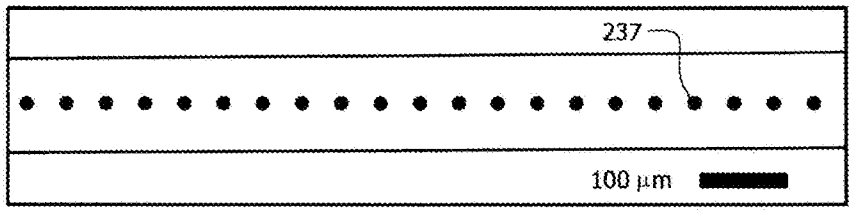


FIG. 3A

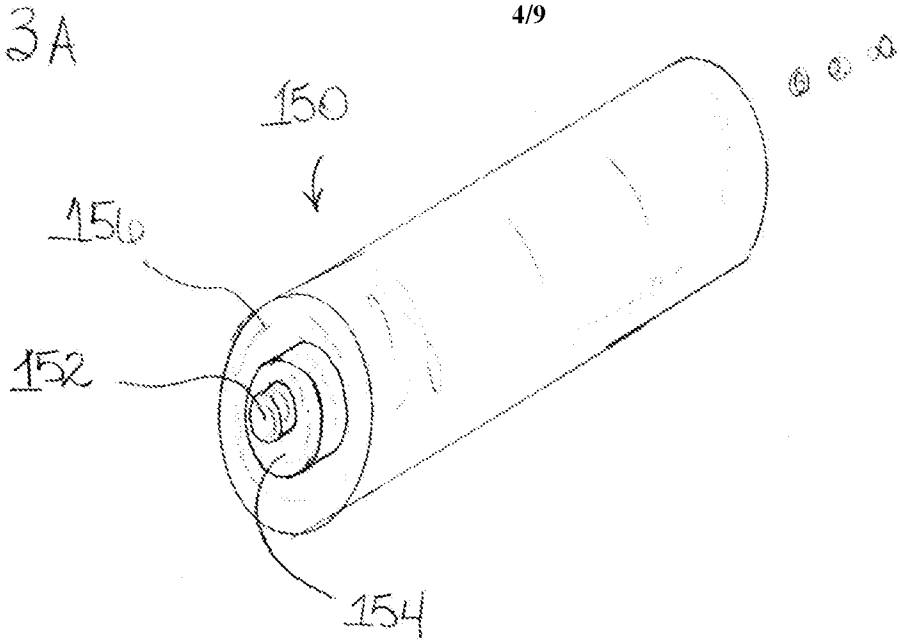


FIG. 3B

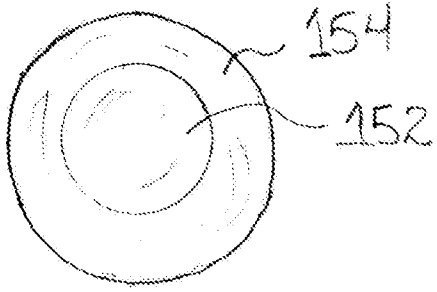


FIG. 3C

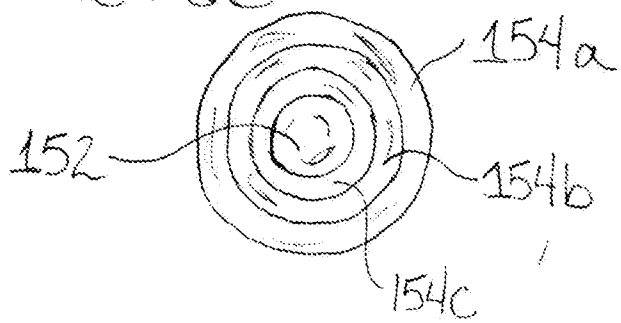


FIG. 3D

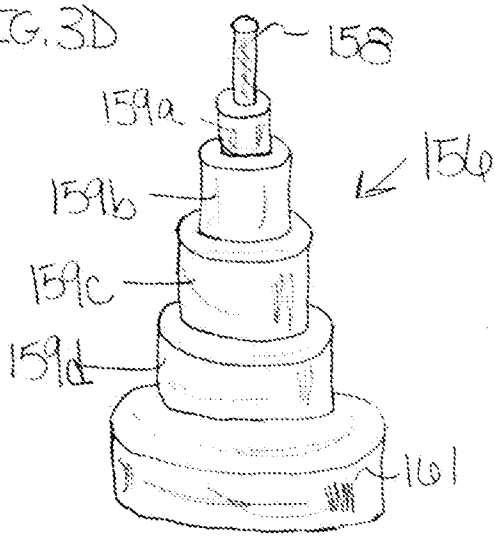


FIG. 3E

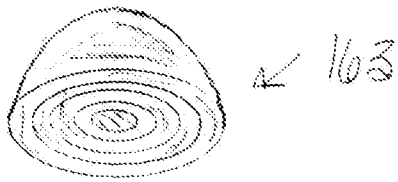
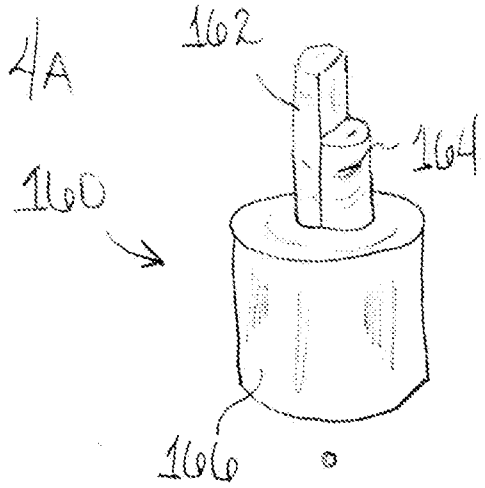


FIG. 4A



168

FIG. 4B

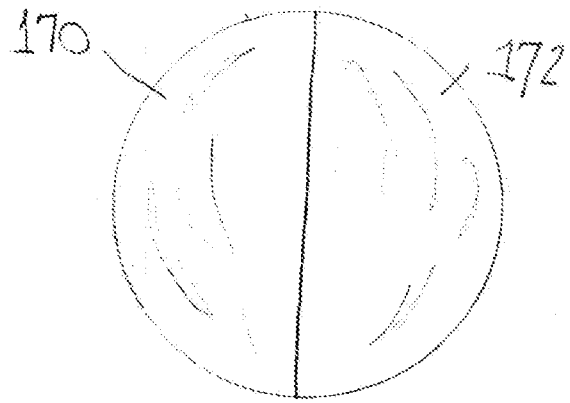


FIG. 5A

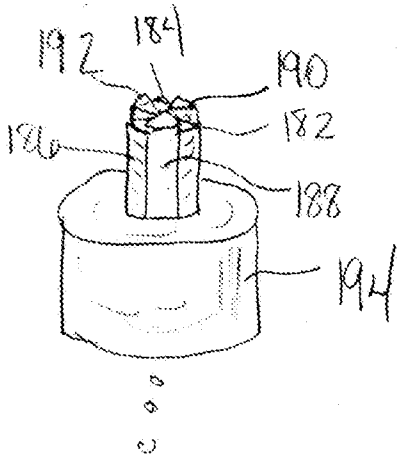


FIG. 5B

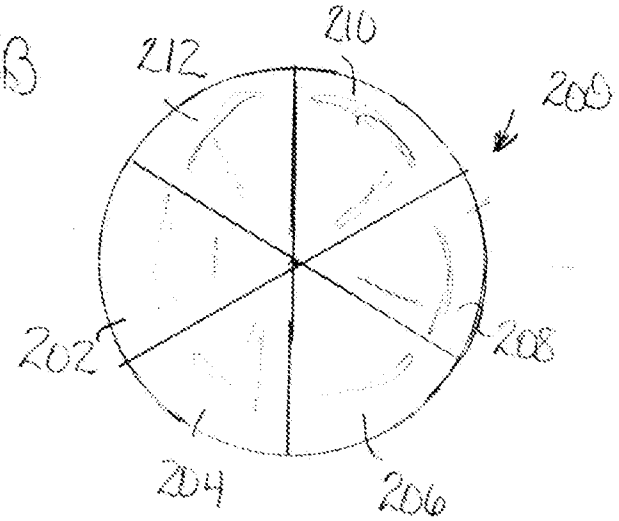


FIG. 5C

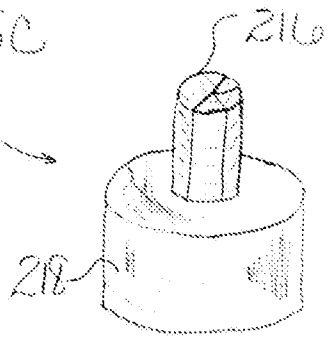


FIG. 5D

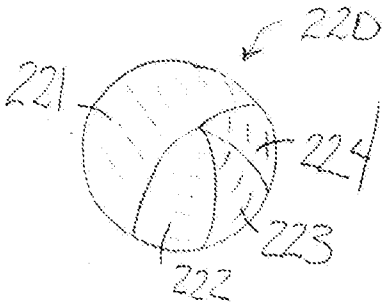


FIG. 5E

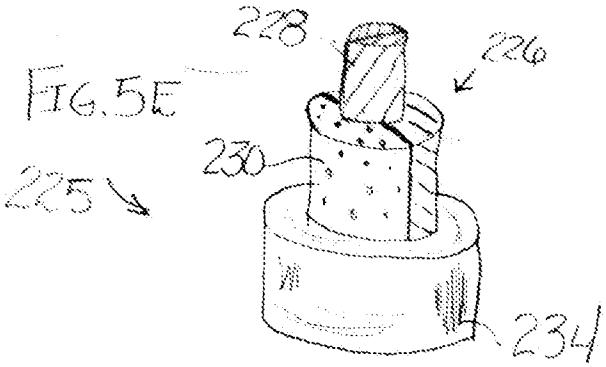


FIG. 5F

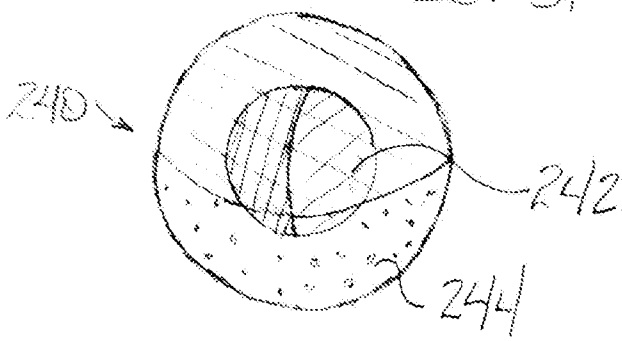


FIG. 5G

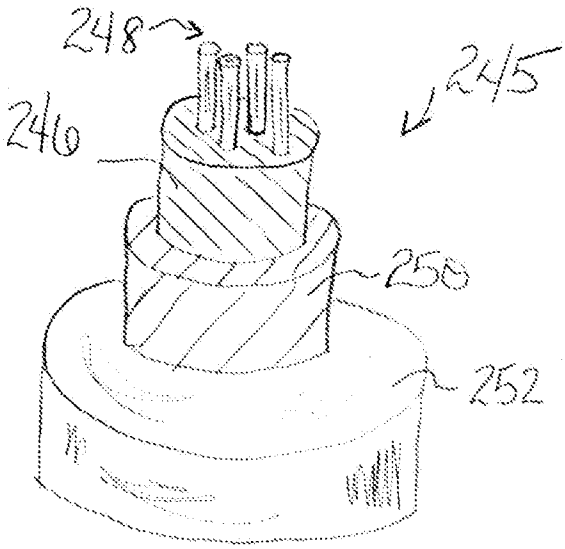
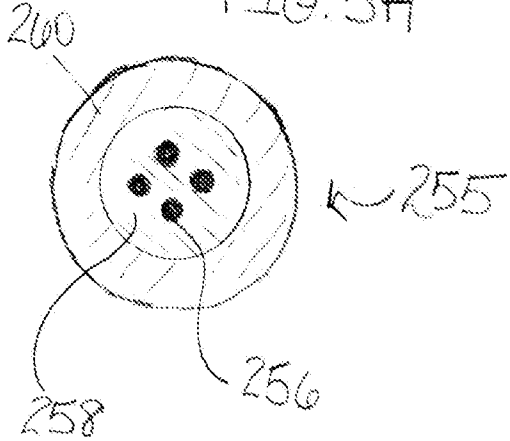


FIG. 5H



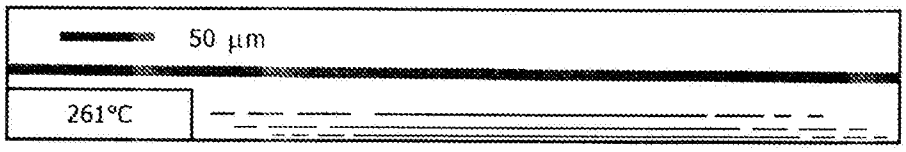


FIG. 6A

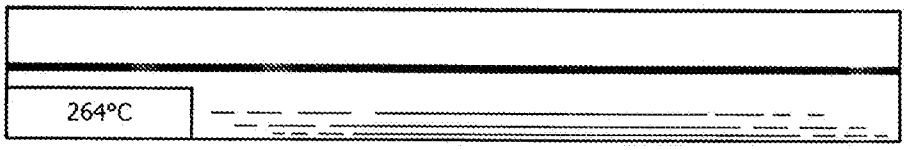


FIG. 6B

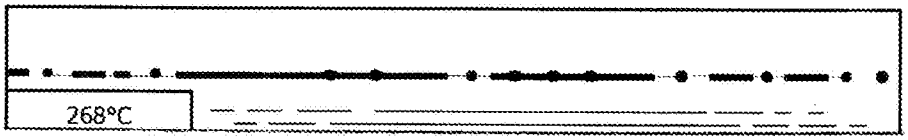


FIG. 6C

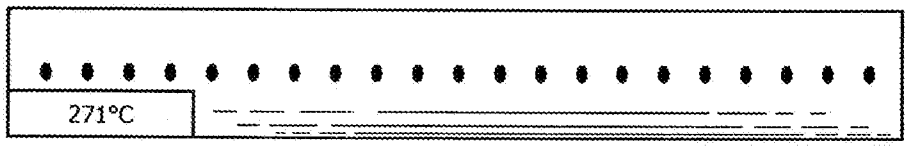


FIG. 6D

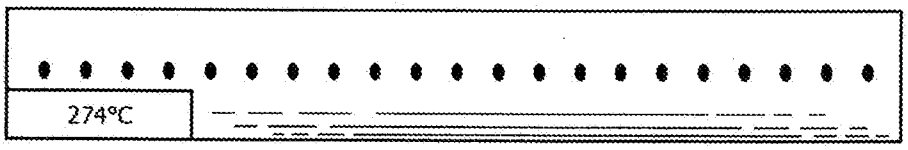


FIG. 6E

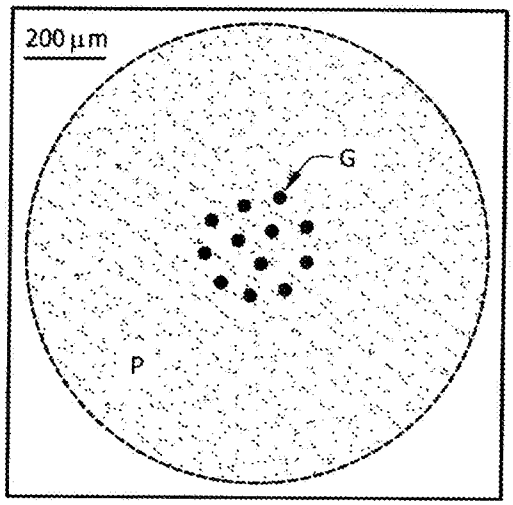


FIG 7A

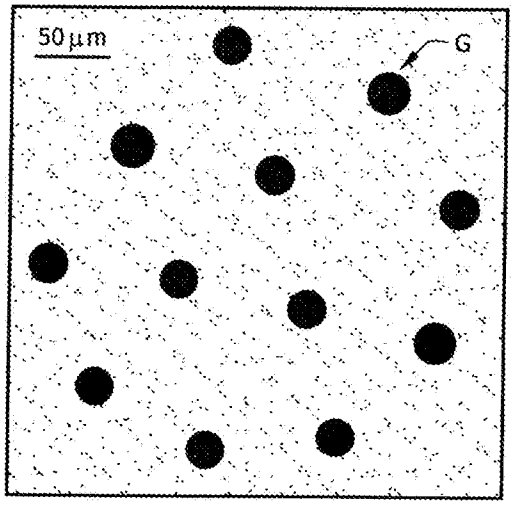


FIG 7B

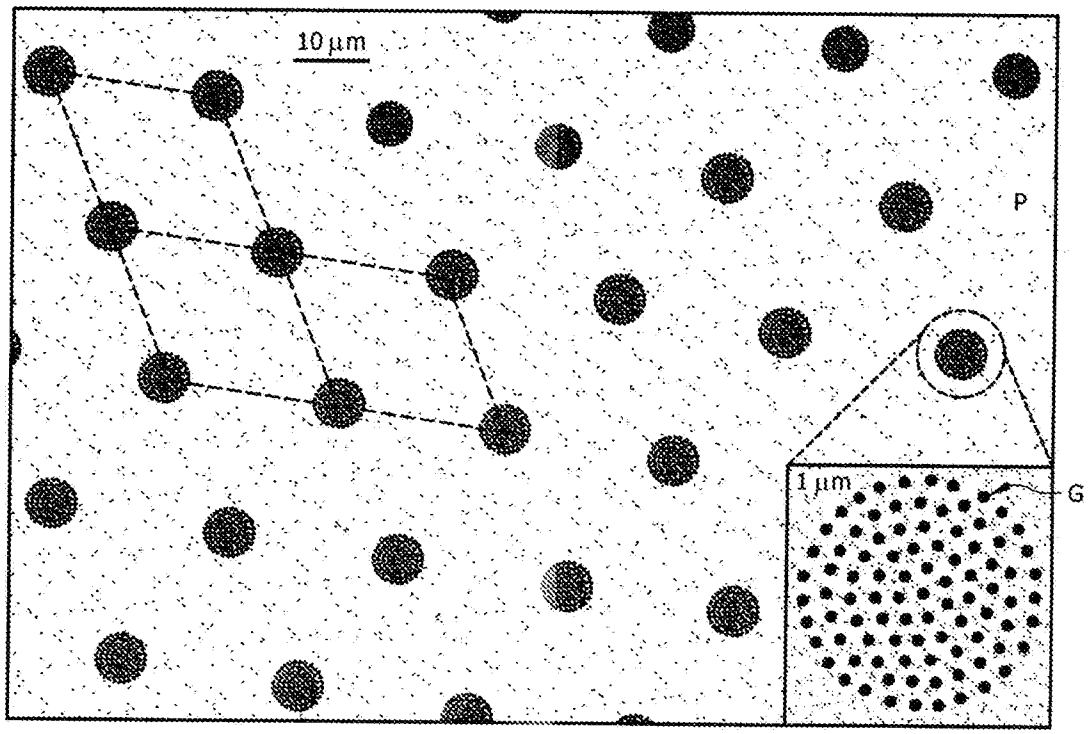


FIG. 8

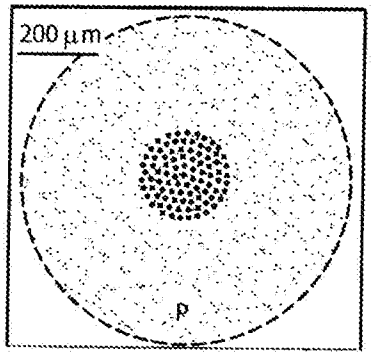


FIG. 9A

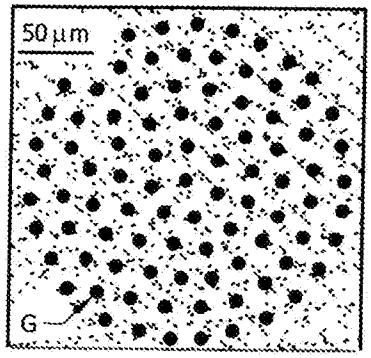


FIG. 9B

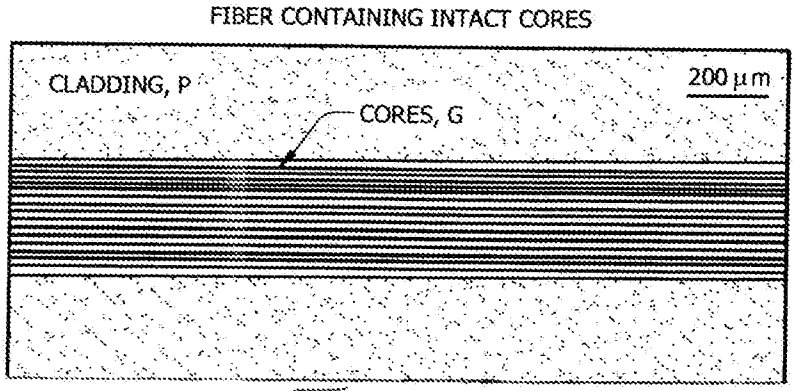


FIG. 9C

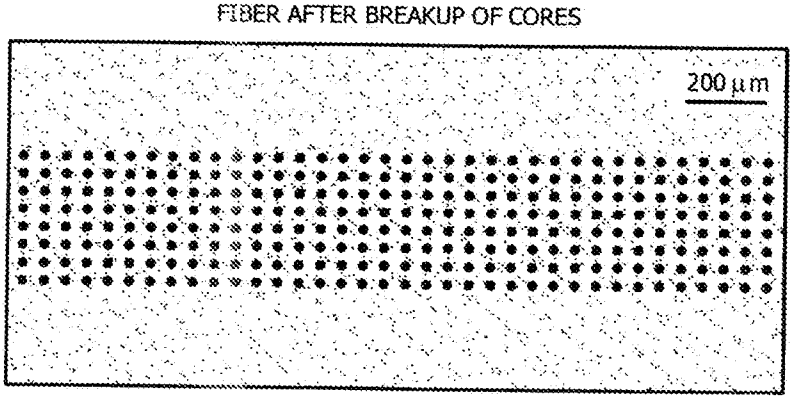


FIG. 9D