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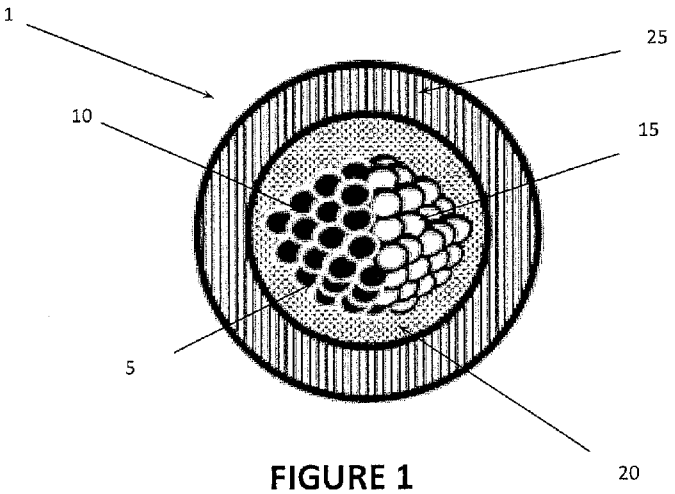


FIGURE 1

(57) Abstract: A smart ink, comprising microparticles, with each microparticle comprising: a) an exterior shell; b) a liquid encapsulated within the shell; and c) a Janus microparticle suspended in the liquid, wherein the Janus microparticle either comprises: i) two or more distinct assemblies of particles; or ii) a core loaded with particles, the core having a first surface portion and a second surface portion that is functionally distinct from the first surface portion. An apparatus and method for production of the microparticles are also provided.

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MICROPARTICLES AND APPARATUS FOR SMART INK PRODUCTION

The present disclosure relates to microparticles. In particular, it relates to a smart ink comprising microparticles that provide covert security features, along with apparatus and methods to produce such microparticles.

Digital printing technology represents a counterfeiting threat as digital reproduction methods are increasingly being used to produce holographic and printed features similar to those on banknotes and other security documents. With the advancement in digital printing, the quality of printed features could become indistinguishable from gravure printing, intaglio printing, offset printing and holograms. While optically active devices and inks have proven useful in slowing counterfeiters, security document and feature designers need more tools to stay ahead of counterfeiters.

Particles are frequently used to impart security features to high-value items. These security features are typically derived from the chemical composition of the particles and include luminescent materials, magnetic, optically variable pigments, thermo-chromic materials, and the like. Since most of these particles are produced by traditional processes, the counterfeit deterrence is limited.

The development of efficient methods for fabricating and actuating multifunctional asymmetric microparticles plays an important role in the advancement of the next generation of functional materials. These materials can serve as "intelligent" building blocks of smart inks,

compartmentalized drug carriers, optical, electronic, and sensor devices. For instance, anisotropic microparticles possessing two sides of distinct composition, commonly called Janus particles, have shown potential as emulsions stabilizers, in inks for electronic paper, or in solar cell compositions.

In the case of electronic inks, Janus particles with oppositely-charged hemispheres have a large dipole moment that allows for their remote positioning in an electric field. The particles are typically then suspended in a carrier gel or oil, sandwiched between two substrates that enclose the floating particles. The function of the enclosure is twofold: it contains electrodes required for particle actuation; and it prevents evaporation of carrier oil surrounding the particle. Examples of patent documents that disclose Janus particles, their production, incorporation in displays and applications include U.S. Patent Numbers 8,501,272; 8,068,271; 8,049,954; 5,914,805; 5,891,479; 5,754,332; 5,717,514; 5,344,594; 5,262,098; 4,810,431; 4,438,160; 4,315,720; and 4,143,103, all of which are incorporated herein by reference.

The advancement in the development of electrically anisotropic Janus particles and enclosure devices has fueled numerous applications in the display technology field, and these particles have been commercialized. However, the requirement for the specialized enclosure substrates for their actuation has prevented their use as printing inks that can be deposited directly on the printed substrate.

Currently available Janus particle production processes are limited to production of simple Janus particles which then require specialized enclosure devices to enable their actuation. The following documents disclose examples of such processes:

1) Andreas Walther and Axel H. E. Müller, *Chemical Reviews* 2013 *113* (7), 5194;
2) Nie, Z.; Li, W.; Seo, M.; Xu, S.; Kumacheva, E. *J. Am. Chem. Soc.* 2006, 128, 9408;
3) Kim, S.-H.; Jeon, S.-J.; Jeong, W. C.; Park, H. S.; Yang, S.-M. *Adv. Mater.* 2008, 20, 4129; and
4) T. Nisisako, T. Torii, T. Takahashi, Y. Takizawa, *Adv. Mater.* 2006, 18, 1152.

The requirement for specialized enclosure devices prevents direct use of Janus particles in multifunctional smart inks that can be printed directly on any substrate and subsequently actuated to generate security features.

There is a need for a new and difficult-to-reproduce fabrication method that can generate microparticles with multifunctional features, without the limitation of specialized enclosure devices.

The microparticle, the apparatus and method used in the production thereof, in their general forms will first be described, and then there implementation in terms of embodiments will be detailed hereafter. These embodiments are intended to demonstrate the principles of the microparticle, the apparatus and method used in the production thereof, and the manner of implementation. The microparticle, the apparatus and method used in the production thereof, in the broadest and more specific forms will then be further described, and defined, in each of the individual claims which conclude this specification.

In one aspect of the present invention, there is provided a microparticle comprising: a) an exterior shell; b) a liquid encapsulated within the shell; and c) a Janus microparticle suspended in the liquid, wherein the Janus microparticle either comprises: i) two or more distinct assemblies of particles; or ii) a core loaded with particles, the core having a first surface portion and a second surface portion that is functionally distinct from the first surface portion.

In a further aspect of the present invention, there is provided a microparticle ink comprising the microparticles.

In another aspect of the present invention, there is provided a method of fabricating the microparticle using a flow-focusing microfluidic system, comprising the steps of: dispersing the Janus microparticle into the liquid in a first microfluidic channel of the microfluidic system to form a dispersion; injecting the dispersion into a first junction intercepted by two monomer microfluidic channels, each monomer microfluidic channel carrying a continuous phase of a monomer towards the first junction, thereby forming a double emulsion composed of droplets surrounded by the continuous phase of the monomer, each droplet comprising the Janus microparticle encapsulated by the liquid; flowing the double emulsion through a second junction intercepted by two liquid microfluidic channels, each liquid microfluidic channel carrying a continuous phase of a second liquid, the second liquid immiscible with the liquid, thereby forming a triple emulsion composed of the Janus particle immersed in the liquid encapsulated by the monomer surround by a continuous phase of the second liquid; and applying a UV source to the triple emulsion thereby polymerizing the monomer to form the external shell.

In yet a further aspect of the present invention there is provided a microparticle ink made by the above method.

In yet a further aspect of the present invention, there is provided a microfluidic device for fabrication of the microparticle comprising: a first microfluidic channel that simultaneously intersects a second and third microfluidic channel at a first flow-focus junction leading to a fourth microfluidic channel; and the fourth microfluidic channel simultaneously intersects a fifth and sixth microfluidic channel at a second flow-focus junction leading to a seventh microfluidic channel.

The Janus particle may comprise two distinct assemblies of particles; with each assembly of particles embedded in a polymer; and the particles are selected from the group consisting of dyes, pigments and functional nanoparticles. The particles may comprise matter that is transparent, opaque, dyed, reflective, fluorescent, plasmonic, magnetic or electrically-charged. In one example of the above, the first assembly comprises a polymerized first monomer loaded with fluorescent silica nanoparticles and the second assembly comprises a polymerized second monomer loaded with plasmonic magnetic nanoparticles, where the second monomer is miscible with the first monomer.

In another example, the first assembly comprises a polymerized first monomer loaded with fluorescent silica nanoparticles and the second assembly comprises a polymerized second monomer loaded with plasmonic magnetic nanoparticles, where the second monomer is immiscible with the first monomer.

In either example, the plasmonic magnetic nanoparticles can be gold-silica coated iron oxide nanoparticles.

Alternatively, the Janus particle may comprise a core, wherein the core is either a homogenous polymer or inorganic, and the core is loaded with particles selected from the group consisting of dyes, pigments and functional nanoparticles. The first and/or second surface portions can be coated with either: a) a thin film; or b) a monolayer of nanoparticles that is subsequently covered with a thin optical film. In either case, the thin film or the nanoparticles may be magnetic. Furthermore, the first surface portion may be covered with a thin film of electroless-deposited metal, which may be nickel.

The exterior shell of the microparticle may comprise an exterior polymeric or inorganic shell. For example, the exterior shell may comprise silica.

The liquid of the microparticle can be selected from an aqueous solution, oil, lubricant, ionic liquid and a resin. Such a liquid may have low volatility, for example, a volatility of less than 23 torr at room temperature. The Janus microparticle itself may have a size of from 1 nm to 1000 microns, which orients in response to an applied external field.

With regards to the method of fabricating the microparticle described above, one manner in which the Janus microparticle can be formed is by prior to step (a), injecting a first monomer composition into a first inlet; injecting a second monomer composition different from the first monomer composition into a second inlet and co-flowing the first and second inlets to a

prejunction that is intercepted by two channels, each channel carrying the liquid, thereby forming uncured Janus microparticles composed of the first and second monomer compositions dispersed in a continuous phase of the liquid; and polymerizing the first and second monomer compositions in step (d). The first monomer composition may comprise nanoparticles, dyes, pigments or any combination thereof; and the second monomer composition may comprise nanoparticles, dyes, pigments or any combination thereof. In one example, the first monomer composition comprises magnetic gold nanoparticles and the second monomer composition comprises fluorescent nanoparticles.

With regards to the method of fabricating the microparticle described above, another manner in which the Janus microparticle can be formed is prior to step (a) by: loading the core with particles that may be selected from the group consisting of nanoparticles, dyes, colorants and any combination thereof; and depositing a thin film on the first surface portion. The thin film can be an electroless deposited metal, for example, nickel.

With regards to the method of fabricating the microparticle described above, a third manner in which the Janus microparticle can be formed is prior to step (a) by: dispensing a nanoparticle suspension onto the first surface portion of the core; evaporating solvent from the dispensed nanoparticles suspension thereby forming a monolayer of nanoparticles on the first surface portion; and depositing a color-absorbing thin film onto the monolayer of nanoparticles. The nanoparticles suspension may be magnetic.

When fabricating the microparticles using the method described above, the liquid may be a non-volatile liquid selected from an aqueous solution, oil, an ionic liquid and resin. In one example, the liquid is an ionic liquid or an aqueous solution, while the second liquid is oil. In another example, the liquid is an oil while the second liquid is an ionic liquid or an aqueous solution.

With regards to the microfluidic device, the first flow-focus junction can have a height and width that is less than a height and width of the fourth microfluidic channel; while the second flow-focus junction can have a height and width that is less than a height and width of the seventh microfluidic channel. In general, each flow-focus junction can have an aspect ratio of between 0.5 and 2.

The microfluidic device may further comprise a UV source applied after the seventh microfluidic channel. In addition, a dispersion of the Janus microparticle in the liquid can flow in the first microfluidic channel; a continuous phase of a monomer can flow in the second and third microfluidic channels; a double emulsion of droplets can flow in the fourth microfluidic channel; a second liquid immiscible with the liquid can flow in the fifth and sixth microfluidic channels; and a triple emulsion can flow in the seventh microfluidic channel, wherein the double emulsion comprises droplets of the Janus microparticle in the liquid surrounded by the continuous phase of the monomer; and the triple emulsion comprises the Janus particle immersed in the liquid encapsulated by the monomer surround by a continuous phase of the second liquid.

In general, the microfluidic device may further comprise a prejunction prior to the first microfluidic channel, with the prejunction consisting of the intersection of a plurality of

additional microfluidic channels. In this arrangement, a first monomer composition flows in a first additional microfluidic channel, a second monomer composition different from the first monomer composition flows in a second additional microfluidic channel; the liquid flows in a third and fourth additional microfluidic channels; a dispersion of the Janus microparticle comprising the first and second monomer compositions dispersed in the liquid flows in the first microfluidic channel; a continuous phase of a third monomer flows in the second and third microfluidic channels; a double emulsion of droplets flows in the fourth microfluidic channel; a second liquid immiscible with the liquid flows in the fifth and sixth microfluidic channel; and a triple emulsion flows in the seventh microfluidic channel, wherein the double emulsion comprises droplets of the Janus microparticle in the liquid surrounded by a continuous phase of the third monomer; and the triple emulsion comprises the Janus particle immersed in the liquid encapsulated by the third monomer surround by a continuous phase of the second liquid.

In general, the plurality of channels and flow-focused junctions of the microfluidic device can be made from material selected from the group consisting of silicon, glass, polydimethylsiloxane, a thermoplastic polymer, a thermoplastic elastomer and any combinations thereof. The thermoplastic polymer can be selected, for example, from cyclic olefin copolymer, polymethyl methacrylate, polycarbonate, polyurethane, polyimide and polystyrene.

In general, the microfluidic channels, the additional microfluidic channels, the and flow-focused junctions of the microfluidic device can be made using a method selected from the group consisting of photolithography, wet etching, dry etching, soft-lithography, hot-embossing, nano-imprinting and injection-molding.

Wherever ranges of values are referenced within this specification, sub-ranges therein are intended to be included within the scope of the microparticle, the apparatus and method used in the production thereof, unless otherwise indicated. Where characteristics are attributed to one or another variant of the microparticle, the apparatus and method used in the production thereof, unless otherwise indicated, such characteristics are intended to apply to all other variants where such characteristics are appropriate or compatible with such other variants.

BRIEF DESCRIPTION OF FIGURES

Figure 1 illustrates an embodiment of the microparticle.

Figures 2A to 2C illustrate the microparticle of Fig. 1 in response to an external field.

Figures 3A to 3C illustrate an example of an optical effect obtained by smart ink printing on a substrate.

Figures 4A to 4D illustrate examples of a microparticle assembly with sharp and blurring fluorescence effects without and with the application of a magnetic field.

Figure 5 illustrates another embodiment of the microparticle.

Figure 6 illustrates a Janus particle used in the embodiment of Fig. 5.

Figures 7A to 7C illustrate the response of the microparticle in Fig. 5 to an external field.

Figures 8A and 8B illustrates the effect of a magnetic field on microparticles of the second embodiment.

Figure 9 illustrates an embodiment of a microfluidic device for production of a microparticle.

Figure 10 illustrates a method to produce microparticles of either the first or second embodiment.

Figures 11A and 11B illustrate methods to produce Janus microparticles used in the second embodiment.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

First embodiment

Figure 1 illustrates an embodiment of the microparticle (1). The microparticle comprises a Janus microparticle (5) suspended in a non-evaporating liquid (20) that is encapsulated by a hard polymer shell (25).

The Janus microparticle (5) comprises two portions (10, 15) that are chemically or structurally distinct. Each portion (10, 15) may be hemispherical, thereby leading to an overall spherical shape of the Janus microparticle (5). Alternatively, each portion (10, 15) can be partly spherical, thereby giving the Janus microparticle (5) the semblance of a dumbbell shape. Other shapes and configurations are possible, giving rise to (asymmetric) Janus microparticles that can be used in the microparticle (1).

In the embodiment shown in Fig. 1, each distinct portion (10, 15) comprises a polymerized assembly of particles. As an example, these particles can be selected from pigments, dyes, nanoparticles and any combination thereof. In addition, the particles can be transparent, reflective, fluorescent, plasmonic, magnetic or electrically charged.

As an example, the first portion (10) of the Janus particle (5) can consist of fluorescent silica nanoparticles embedded in a polymer, while the second portion (15) can consist of magnetic and

plasmonic gold-coated silica-iron-oxide nanoparticles. As further sub-examples, the first portion (10) of can consist of polymerized Polyethylene (glycol) Diacrylate (PEG-DA) loaded with fluorescent silica nanoparticles, while the second portion (15) can consist of polymerized PEG-DA loaded with the plasmonic magnetic nanoparticles. Alternatively, the first portion (10) of can consist of polymerized ethoxylated trimethylolpropane triacrylate (EPTPA) loaded with fluorescent silica nanoparticles, while the second portion (15) can consist of polymerized PEG-DA loaded with the plasmonic magnetic nanoparticles. The fluorescent portion of the Janus microparticle (5) can be visible to the naked eye. This visual feature is enhanced when there are a multitude of such Janus microparticles (5).

The non-evaporating liquid (20) can be an aqueous solution, ionic liquid, oil, lubricant or a resin. The liquid can also contain surfactants and/or dispersion agents known in the art that favor particle dispersion and emulsion stabilization. In an example, the liquid and the surfactant of the microparticle can be selected from the perfluorinated polyether (PFPE) fluid family.

The polymer shell (25) can be made of monomers that allow for dispersion of the microparticle (1) in aqueous solutions or solvents such that the microparticle (1) can be directly printed on a substrate of choice.

The overall size of microparticle (5) ranges from 1 nm to 1000 μm.

Figures 2A – 2C illustrate the response of the microparticle in Fig. 1 to an external field. Without an applied external field, as shown in Fig. 2A, the encapsulated Janus microparticle (5) is randomly oriented within the liquid (20) encapsulated by the shell (25). However, in the

presence of an external field (30) that acts on portion (10) and/or portion (15), as shown in Fig. 2B, the suspended Janus microparticle (5) can be oriented within the liquid (20) in the direction of the applied external field. The external field can be magnetic, electric, optical or gravitational. Fig. 2C provides an example in which the external field is a magnetic field provided by an external magnet (35), and portion (15) comprises magnetic and plasmonic gold-coated silica-iron-oxide nanoparticles. The magnetic particles within portion (15) cause the Janus microparticle (5) to orient within the liquid (20) in the direction as shown. Such an embodiment can be used to make covert security features.

Figures 3A to 3C illustrate an example of an optical effect obtained by smart ink printing on a substrate. The smart ink comprises microparticles in which the first portion comprises an assembly of silica nanoparticles with florescence dye doping, while the second portion comprises an assembly of gold-coated-silica-shell-iron-oxide nanoparticles.

In Figure 3A, by applying a magnetic field during printing, microparticles are oriented on the surface of the substrate, and by subsequent selective UV exposure through a mask pattern or by laser writing, the aligned microparticles are permanently set in a polymerized middle liquid. The gold-coated nanoparticles in the Janus microparticle provide image color of a design (40) (red flower colors; in Fig. 3A, this is shown as a dark shaded portion of the design (40)). The non-exposed area of the printed image contains randomly oriented microparticles, thus providing a blurring effect of the (flower) design (40). Once printed, covert features are seen when applying a second magnetic field, revealing bright yellow features of the design (40) (shown as the sharp light-coloured outlines of the flower petals in Fig. 3B), which provide a sharpened image.

Finally, as an additional covert security feature, under UV light, the particles fluoresce and/or provide a specific plasmonic signature as illustrated in Figure 3C, where the design (40) changes in colour from the original red hue (or dark features in Fig. 3B) to a fluorescent yellow (light features shown in Fig. 3C).

An example of microparticle assembly with sharp and blurring fluorescence effects without and with the application of a magnetic field are shown in Figures 4A to 4D. Figs. 4A and 4C are sample images of faint (or blurred) fluorescence without an external magnetic field, where the Janus microparticles are randomly oriented, and thus the fluorescence effects are dampened due to destructive interference. Figures 4B and 4D are sample images of intense (or sharpened) fluorescence in the presence of an external magnetic field. Here, the Janus microparticles are no longer randomly oriented, but rather, aligned with the external magnetic field due to magnetic nanoparticles in the Janus microparticle. The fluorescence effect is thus more intense, as the fluorescent portions of the Janus microparticles are aligned, rather than randomly oriented.

Second embodiment

Figure 5 illustrates another embodiment of the microparticle (100), while Figure 6 illustrates a Janus particle (45) used in the embodiment of Figure 5.

As in the first embodiment shown in Figure 1, microparticle (100) comprises a Janus microparticle (45) suspended in a non-evaporating liquid (20) that is encapsulated by a hard polymer shell (25). The Janus microparticle (45), shown in greater detail in Figure 6, can consist of a homogeneous polymer core (50) that can be loaded with functional nanoparticles (silica,

fluorescent, plasmonic or composite thereof), dyes or colorants. While a spherical core is shown in Figure 6, it is understood that the polymer core (50) may take other suitable shapes. The surface of one hemisphere of the polymer core (50) is coated with a layer of material acting as a hemispherical shell (55) in order to impart a separate functionality. This can be achieved using, for example, deposited thin magnetic films or assembly of a monolayer of magnetic nanoparticles deposited using solvent evaporation and self-assembly. This hemisphere can be subsequently covered with an optically absorbing thin film (60) to provide color contrast from the uncoated hemisphere.

In particular, one advantage of Janus microparticles (45) having a hemisphere coated with electroless-deposited Nickel or an assembly of nanoparticles covered by thin absorbing films (60), is the retention of a low remnant magnetic moment in the Nickel layer which enables switchability of visual optical effect by applying and removing the magnetic field without any chain formation or agglomeration.

As examples of this embodiment, the polymer core (50) of the microparticle can be composed of a polymer loaded with fluorescent dye, nanoparticles or colorant or any combination thereof. An example of suitable polymers includes PEGDA, ETPTA, polystyrene, PMMA and other polymers known in the art. The assembly of nanoparticles (55) can consist, for example, of superparamagnetic nanoparticles such as iron-oxide nanoparticles or silica-coated iron-oxide nanoparticles. The absorbing thin film (60) can be a combination of dielectric and metallic thin films such as gold, chromium, nickel, titanium, silicon dioxide and silicon nitride. In an

embodiment, the absorbing thin film (60) can consist of sequential layers of: chromium, gold, nickel, chromium, silicon dioxide, chromium and silicon dioxide.

Figures 7A to 7C illustrate the response of a microparticle (100) shown in Fig. 5 to an external field. Without an applied external field, as shown in Fig. 7A, the encapsulated Janus microparticle (45) is randomly oriented within the liquid (20) encapsulated by the shell (25). However, as illustrated in Figure 7B, in the presence of an external field (30), the suspended Janus microparticle (45) can be oriented within the liquid (20) in the direction of the applied external field. The external field (30) can be magnetic, electric, optical or gravitational. Fig. 7C provides an example in which the external field is a magnetic field provided by an external magnet (35).

As with the first embodiment, an ink comprises a plurality of these microparticles (100), which is printed on a surface of a substrate. Without the presence of an external field, the encapsulated Janus microparticles are randomly oriented within the liquid encapsulated by the shell. As such, the collective optical effect of the printed microparticles is random. However, by applying an external field (for example, a permanent magnet), the suspended Janus microparticles can be oriented within the liquid in the direction of the applied field thus exhibiting the desired optical effect.

As an example, the magnetic manipulation of microparticles, each with an encapsulated Janus microparticle exhibiting one hemisphere that is fluorescent and a second hemisphere that is magnetic is demonstrated in Figure 8FIGS. 8A-B. The microparticle (150) comprises a polymer

shell (165), fluid (160) and the Janus microparticle (155). The fluid (160) is a liquid monomer. The Janus microparticle core is composed of PEGDA loaded with a fluorescent dye. One hemisphere of the microparticle is covered by magnetic and absorbing thin film consisting of Ni (30 nm) - Au (80 nm) – Cr (2 nm) - SiO_2 (80 nm) - Cr (10 nm) - SiO_2 (80 nm). The particle is suspended in PFPE fluid (Galden HT 200 liquid) containing PFPE surfactant (Krytox). The shell consists of photopolymerized ETPTA. In Fig. 8A, there is an absence of an applied magnetic field, whereas in Fig. 8B, a magnetic field is turned on. In FIG. 8B, the Janus microparticle (50) orients in alignment with the applied magnetic field. This is seen by the light color of the aligned Janus microparticle (50) in FIG. 8B, compared to the dark color of the non-aligned Janus microparticle (50) in FIG. 8A.

Method of manufacture

The fabrication of microparticles can be achieved by use of microfluidic technology in which a microemulsion system is implemented. The microfluidic device can be fabricated from, for example, silicon, glass, PDMS, thermoplastic polymers such as COC, PMMA, PC, PS or thermoplastic elastomer using photolithography, wet or dry etching, soft-lithography, hot-embossing, nanoimprinting, injection-molding etc. An example of a microfluidic system (200) is shown in Figure 9. The microfluidic device (200) consists of three flow-focusing junctions that are used to generate microdroplets in microfluidic channels (explained in greater detail in Fig. 10). The dimensions of the device can be 2cm by 5cm, although other dimensions are possible.

By flowing aqueous solution as a dispersed phase and oil solution as a continuous phase, water-in-oil emulsions can be obtained. Similarly, by flowing oil solutions as a dispersed phase and

aqueous solutions as a continuous phase, oil-in-water emulsions can be obtained. Therefore, by connecting three junctions in parallel and alternating aqueous solutions (monomers) and oil solutions, a triple emulsion is generated. By changing the flow velocity of continuous and dispersed phases and the size of a given junction, various droplet sizes can be obtained (for example, from 1 to 1000 μm).

The microfluidic device utilizes a flow focusing method to create triple emulsion droplets, as illustrated in Figure 10. For generation of Janus droplets of the first embodiment, monomer A (61) and monomer B (65) compositions are injected in the first two inlets (70, 75) respectively and co-flow to a junction (80). As an example, monomer A can contain magnetic-gold nanoparticles while monomer B can contain fluorescent nanoparticles. The junction is intercepted perpendicularly by two channels (85, 90) that carry the non-evaporating liquid (95) (ionic liquid, oil or resin) which enables the creation of Janus droplets (105) through flow-focusing. The non-evaporating liquid (95) then carries the generated Janus droplets (105) to a second junction (110) which is intercepted by two channels (115, 120) flowing monomer C (125).

Alternatively, in the case of Janus particles of the second embodiment, fabricated using electroless Nickel deposition or self-assembled solvent evaporated magnetic nanoparticles (see, for example, Figures 11A and 11B), the particles are directly dispersed in the non-evaporating liquid (95) and injected into the second junction (110) illustrated in the Figure 10, thereby bypassing the first junction (80). After junction (110), a double emulsion (130) composed of Janus droplet encapsulated in the non-evaporating liquid surrounded by monomer C continuous phase is created. Finally, monomer C is flowed through a third junction (135) and intercepted by

two channels (140, 145) carrying the continuous oil (or aqueous) phase (150). The resulting triple-emulsion (155) is generated composed of a Janus droplet immersed in the non-evaporating liquid that is encapsulated in the monomer C surrounded by continuous oil phase. A UV point source (160) near the third junction is then used to expose and polymerize monomers A, B and C, resulting in a smart microparticle (165).

Alternatively, as illustrated in Figures 11A and 11B, the Janus microparticle can be fabricated starting with a homogeneous microparticle core (300), followed by deposition of a thin film (305) (as in Fig. 11A) or deposition of an assembly of nanoparticles (310) over one hemisphere of the microparticle core (300) (as in Fig. 11B).

The microparticle core (300) can be composed of a polymer loaded with fluorescent dye, nanoparticles or colorant or any combination thereof. An example of suitable polymers includes PEGDA, ETPTA, polystyrene, PMMA and others known in the art.

In Fig. 11A, a solution (315) of polymer microparticles dispersed in aqueous solution or solvent is deposited on a substrate (316) and solvent is evaporated. Upon solvent evaporation, microparticle cores create a densely packed monolayer of particles. The thin film (305) is subsequently deposited over the monolayer of microparticle cores. As illustrated in Figure 11A, electroless Nickel solution is added drop-wise to the substrate containing a monolayer of microparticle cores (300). The substrate resides on a hot plate which initiates electroless Nickel deposition (305) on the surface of the microparticle cores (300). Following electroless Ni deposition, the deposited Nickel is further coated with an absorbing coating (320). The absorbing

thin film (320) can be a combination of dielectric and metallic thin films such as gold, chromium, nickel, titanium, silicon dioxide and silicon nitride.

In an embodiment, the absorbing thin film (320) can consist of chromium, gold, nickel, chromium, silicon dioxide, chromium and silicon dioxide. For example, the absorbing coating can consist of Au (80 nm) – Cr (2 nm) - SiO_2 (80 nm) - Cr (10 nm) - SiO_2 (80 nm) deposited using sputtering or evaporation.

As illustrated in Fig. 11B, superparamagnetic functionality can be imparted to the Janus microparticle by deposition of superparamagnetic nanoparticles (310) on one hemisphere of the polymer microparticle core (300). The superparamagnetic nanoparticles (310) can consist of iron-oxide nanoparticles, silica-coated iron-oxide nanoparticles or gold-silica iron-oxide nanoparticles. As illustrated in Figure 11B, a solution (325) containing superparamagnetic nanoparticles (310) is added dropwise to the substrate (316) containing a monolayer of microparticle cores (300). Following evaporation of nanoparticle solution, a monolayer of superparamagnetic nanoparticles (310) is formed on one hemisphere of the microparticle cores (300). Subsequently, thin absorbing film (320) is deposited to ensure that nanoparticles (310) are embedded in the newly formed Janus particle. The absorbing thin film (320) can be a combination of dielectric and metallic thin films such as gold, chromium, nickel, titanium, silicon dioxide and silicon nitride.

In an embodiment, the absorbing thin film (320) can consist of chromium, gold, nickel, chromium, silicon dioxide, chromium and silicon dioxide. For example, the absorbing coating

can consist of Au (80 nm) – Cr (2 nm) - SiO_2 (80 nm) - Cr (10 nm) - SiO_2 (80 nm) deposited using sputtering or evaporation.

It will be appreciated by persons skilled in the art that the foregoing disclosure constitutes a description of specific embodiments of the microparticles, an ink comprising the microparticles, as well as, an apparatus and methods for producing the microparticles. These embodiments are only exemplary and are not meant to limit the disclosure to what has been particularly shown and described herein above. A variety of modifications and variations are possible in light of the above teachings without departing from the scope of the present disclosure. The ink comprising the microparticles, as well as, an apparatus and methods for producing the microparticles are further described and defined in the claims which now follow.

CLAIMS:

1. A microparticle comprising: a) an exterior shell; b) a liquid encapsulated within the shell; and c) a Janus microparticle suspended in the liquid, wherein the Janus microparticle either comprises:

    i) two or more distinct assemblies of particles; or

    ii) a core loaded with particles, the core having a first surface portion and a second surface portion that is functionally distinct from the first surface portion.

2. The microparticle of claim 1, wherein the Janus particle comprises two distinct assemblies of particles; each assembly of particles is embedded in a polymer; and the particles are selected from the group consisting of dyes, pigments, functional nanoparticles and any combination thereof.

3. The microparticle of claim 2, wherein the particles comprise matter that is transparent, opaque, dyed, reflective, fluorescent, plasmonic, magnetic or electrically-charged.

4. The microparticle of claim 2 or 3, wherein a first assembly comprises a polymerized first monomer loaded with fluorescent silica nanoparticles and a second assembly comprises a polymerized second monomer loaded with plasmonic magnetic nanoparticles, the second monomer miscible with the first monomer.

5. The microparticle of claim 2 or 3, wherein a first assembly comprises a polymerized first monomer loaded with fluorescent silica nanoparticles and the second assembly comprises a polymerized second monomer loaded with plasmonic magnetic nanoparticles, the second monomer immiscible with the first monomer.

6. The microparticle of claim 4 or 5, wherein the plasmonic magnetic nanoparticles are gold-silica coated iron oxide nanoparticles.

7. The microparticle of claim 1, wherein the Janus particle comprises a core, the core is either a homogenous polymer or inorganic, and the core is loaded with particles selected from the group consisting of dyes, pigments, functional nanoparticles and any combination thereof.

8. The microparticle of clam 7, wherein at least one of the first and second surface portions are coated with either: a) a thin film; or b) a monolayer of nanoparticles that is subsequently covered with a thin optical film.

9. The microparticle of clam 7, wherein the first surface portion is coated with either: a) a thin film; or b) a monolayer of nanoparticles that is subsequently covered with a thin optical film.

10. The microparticle of claim 8 or 9, wherein the thin film is magnetic.

11. The microparticle of claim 8 or 9, wherein the nanoparticles are magnetic.

12. The microparticle of any one of claims 8 to 10, wherein the first surface portion is covered with a thin film of electroless-deposited metal.

13. The microparticle of claim 12 wherein the metal is nickel.

14. The microparticle of any one of claims 1 to 13 comprising an exterior polymeric or inorganic shell.

15. The microparticle of claim 14, wherein the exterior shell comprises silica.

16. The microparticle of any one of claims 1 to 15, wherein the liquid is selected from an aqueous solution, oil, lubricant, ionic liquid and a resin.

17. The microparticle of claim 16, wherein the liquid has volatility of less than 23 torr at room temperature.

18. The microparticle of any one of claims 1 to 17, wherein the Janus microparticle has a size of from 1 nm to 1000 microns.

19. The microparticle of any one of claims 1 to 18, wherein the Janus particle orients in response to an applied external field.

20. A method of fabricating the microparticle of claim 1 using a flow focusing microfluidic system, comprising the steps of:

i) dispersing the Janus microparticle into the liquid in a first microfluidic channel of the microfluidic system to form a dispersion;

ii) injecting the dispersion into a first junction intercepted by two monomer microfluidic channels, each monomer microfluidic channel carrying a continuous phase of a monomer towards the first junction, thereby forming a double emulsion composed of droplets surrounded by the continuous phase of the monomer, each droplet consisting of the Janus microparticle encapsulated by the liquid;

iii) flowing the double emulsion through a second junction intercepted by two liquid microfluidic channels, each liquid microfluidic channel carrying a continuous phase of a second liquid, the second liquid immiscible with the liquid, thereby forming a triple emulsion composed of the Janus particle immersed in the liquid encapsulated by the monomer surround by a continuous phase of the second liquid; and

iv) applying a UV source to the triple emulsion thereby polymerizing the monomer to form the external shell.

21. The method of claim 20, wherein the Janus microparticle is formed in the microfluidic system by:

i) prior to step (a), injecting a first monomer composition into a first inlet; injecting a second monomer composition different from the first monomer composition into a second inlet and co-flowing the first and second inlets to a prejunction that is intercepted by two channels, each channel carrying the liquid, thereby forming uncured Janus microparticles composed of the first and second monomer compositions dispersed in a continuous phase of the liquid; and

ii) polymerizing the first and second monomer compositions in step (d).

22. The method of claim 21, wherein the first monomer composition comprises nanoparticles, dyes, pigments or any combination thereof; and the second monomer composition comprises nanoparticles, dyes, pigments or any combination thereof.

23. The method of claim 22, wherein the first monomer composition comprises magnetic gold nanoparticles and the second monomer composition comprises fluorescent nanoparticles.

24. The method of claim 20, wherein the Janus microparticle is fabricated prior to step (a) by:

i) loading the core with particles selected from the group consisting of nanoparticles, dyes, colorants and any combination thereof; and

ii) depositing a thin film on the first surface portion.

25. The method of claim 24, wherein the thin film is an electroless deposited metal.

26. The method of claim 25, wherein the metal is nickel.

27. The method of claim 20, wherein the Janus microparticle is fabricated prior to step (a) by:

i) dispensing a nanoparticle suspension onto the first surface portion of the core;

ii) evaporating solvent from the dispensed nanoparticles suspension thereby forming a monolayer of nanoparticles on the first surface portion; and

iii) depositing a color-absorbing thin film onto the monolayer of nanoparticles.

28. The method of claim 27, wherein nanoparticle suspension is magnetic.

29. The method of any one of claims 20 to 28, wherein the liquid is a non-volatile liquid selected from an aqueous solution, oil, an ionic liquid and resin.

30. The method of claim 29, wherein the liquid is an ionic liquid or an aqueous solution and the second liquid is an oil.

31. The method of claim 29, wherein the liquid is an oil and the second liquid is an ionic liquid or an aqueous solution.

32. A microfluidic device for fabrication of the microparticle of claim 1 comprising: a first microfluidic channel that simultaneously intersects a second and third microfluidic channel at a first flow-focus junction leading to a fourth microfluidic channel; and the fourth microfluidic channel simultaneously intersects a fifth and sixth microfluidic channel at a second flow-focus junction leading to a seventh microfluidic channel .

33. The microfluidic device of claim 32, wherein the first flow-focus junction has a height and width that is less than a height and width of the fourth microfluidic channel; and the second flow-focus junction has a height and width that is less than a height and width of the seventh microfluidic channel.

34. The microfluidic device of claim 32 or 33, wherein each flow-focus junction has an aspect ratio of between 0.5 and 2.

35. The microfluidic device any one of claims 32 to 34, further comprising a UV source applied after the seventh microfluidic channel.

36. The microfluidic device of any one of claims 32 to 35, wherein a dispersion of the Janus microparticle in the liquid flows in the first microfluidic channel; a continuous phase of a monomer flows in the second and third microfluidic channels; a double emulsion of droplets flows in the fourth microfluidic channel; a second liquid immiscible with the liquid flows in the fifth and sixth microfluidic channels; and a triple emulsion flows in the seventh microfluidic channel, wherein the double emulsion comprises droplets of the Janus microparticle in the liquid surrounded by the continuous phase of the monomer; and the triple emulsion comprises the Janus particle immersed in the liquid encapsulated by the monomer surround by a continuous phase of the second liquid.

37. The microfluidic device of any one of claims 32 to 35, further comprising a prejunction prior to the first microfluidic channel, the prejunction consisting of the intersection of a plurality of additional microfluidic channels.

38. The microfluidic device of claim 37, wherein a first monomer composition flows in a first additional microfluidic channel, a second monomer composition different from the first monomer composition flows in a second additional microfluidic channel; the liquid flows in a third and fourth additional microfluidic channels; a dispersion of the Janus microparticle comprising the first and second monomer compositions dispersed in the liquid flows in the first microfluidic channel; a continuous phase of a third monomer flows in the second and third microfluidic channels; a double emulsion of droplets flows in the fourth microfluidic channel; a second liquid immiscible with the liquid flows in the fifth and sixth microfluidic channel; and a triple emulsion flows in the seventh microfluidic channel, wherein the double emulsion comprises droplets of the Janus microparticle in the liquid surrounded by a continuous phase of the third monomer; and the triple emulsion comprises the Janus particle immersed in the liquid encapsulated by the third monomer surround by a continuous phase of the second liquid.

39. The microfluidic device of any one of claims 32 to 38, wherein the plurality of channels and flow-focused junctions is made from material selected from the group consisting of silicon, glass, polydimethylsiloxane, a thermoplastic polymer, a thermoplastic elastomer and any combinations thereof.

40. The microfluidic device of claim 39, wherein the thermoplastic polymer is selected from cyclic olefin copolymer, polymethyl methacrylate, polycarbonate and polystyrene.

41. The microfluidic device of any one of claims 32 to 40, wherein the microfluidic channels, the additional microfluidic channels, the and flow-focused junctions are made using a method selected from the group consisting of photolithography, wet etching, dry etching, soft-lithography, hot-embossing, nanoimprinting and injection-molding.

42. A microparticle ink comprising the microparticle of any one of claims 1 to 19.

43. A microparticle ink made by the method of any one of claims 19 to 31.

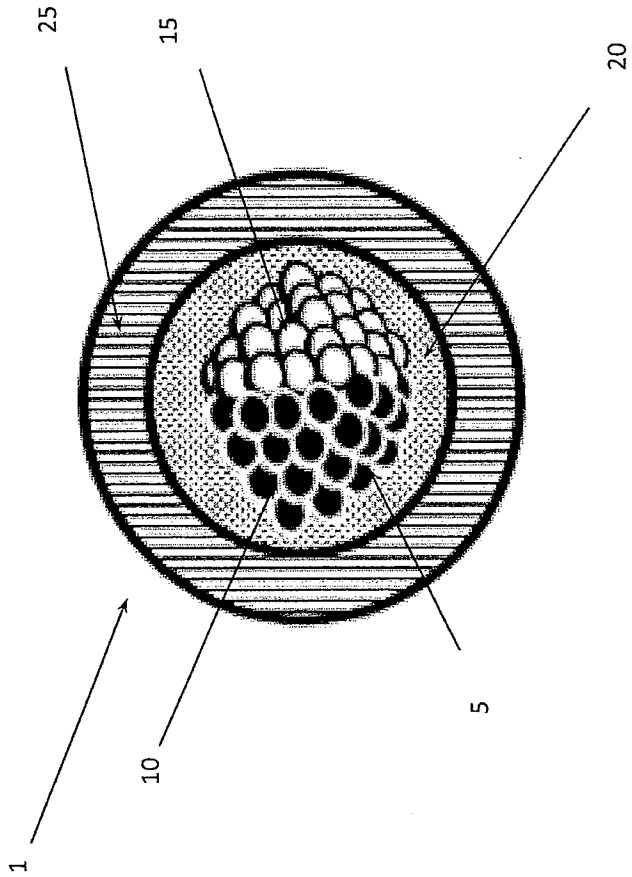


FIGURE 1

FIG 2A

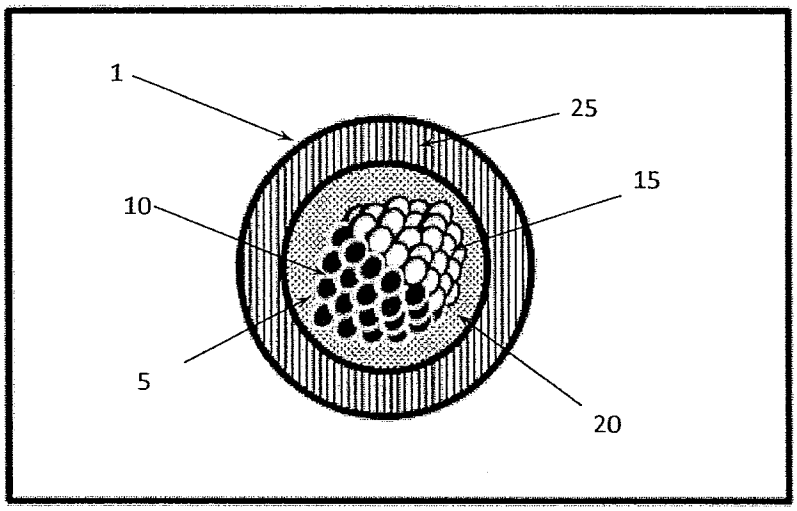


FIG 2B

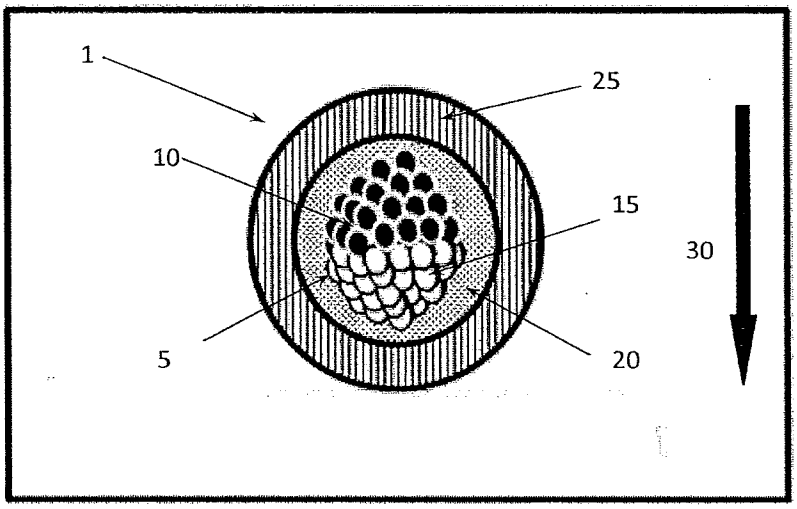
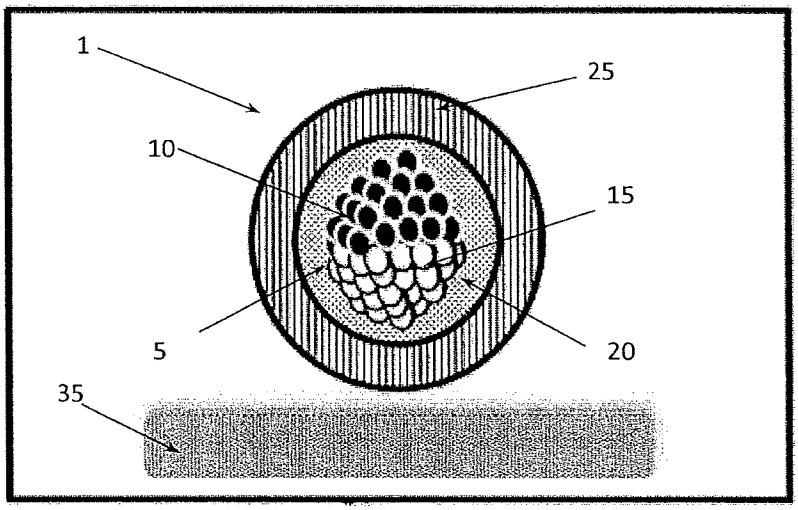


FIG 2C



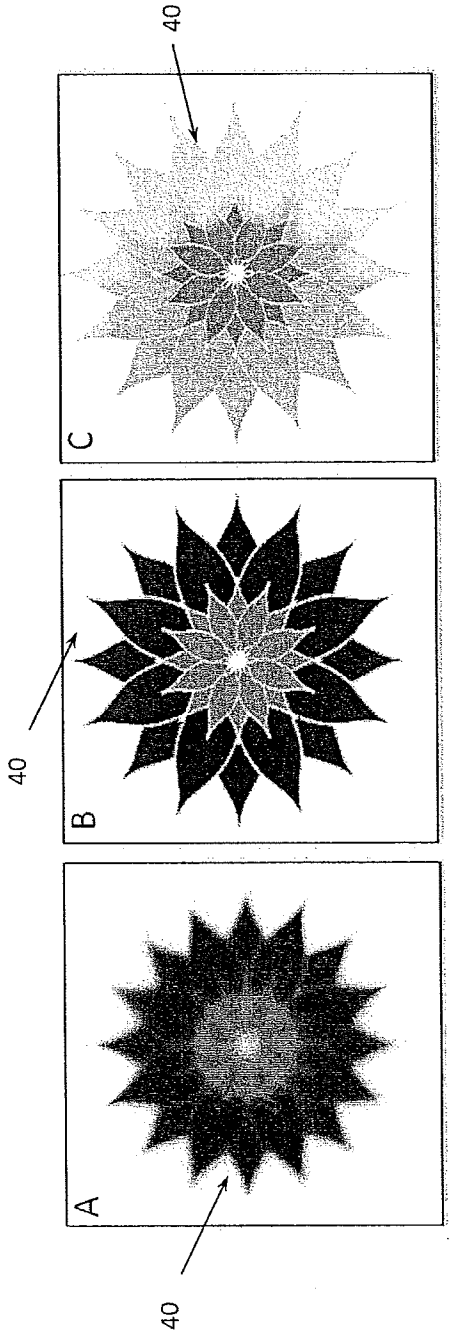


FIG. 3C

FIG. 3B

FIG. 3A

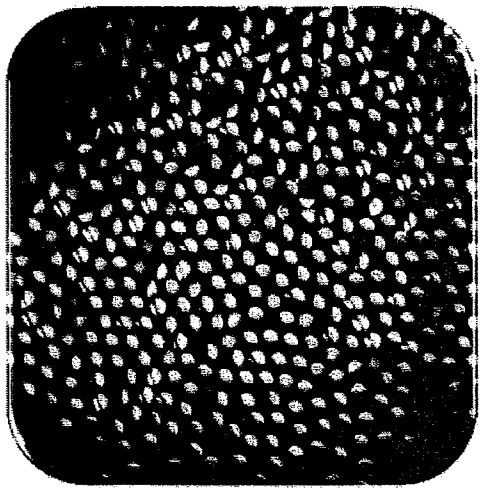


FIG. 4B

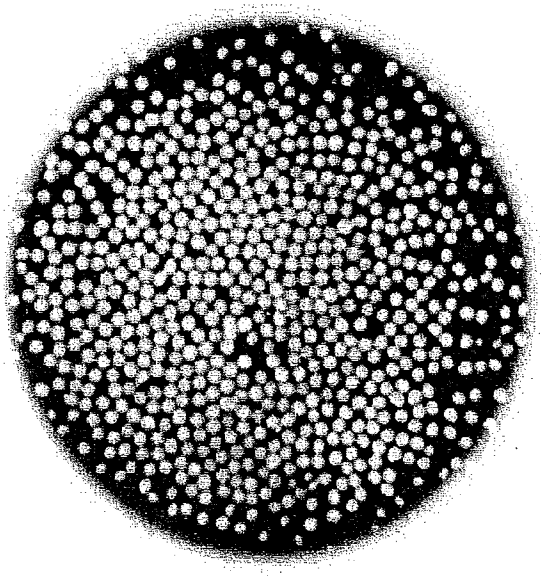


FIG. 4D

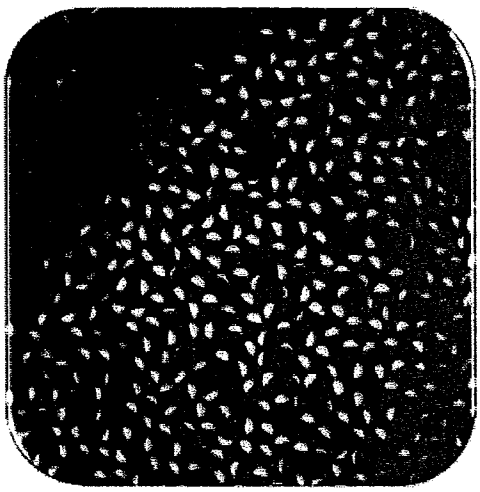


FIG. 4A

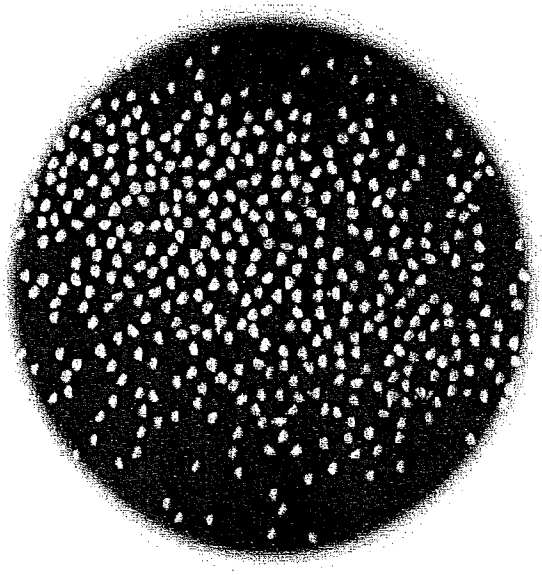


FIG. 4C

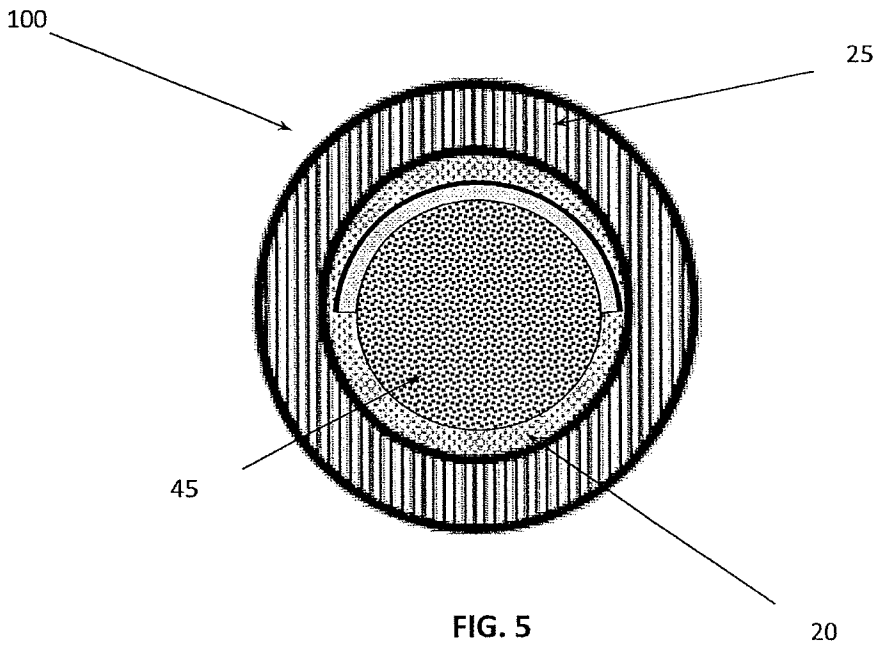


FIG. 5

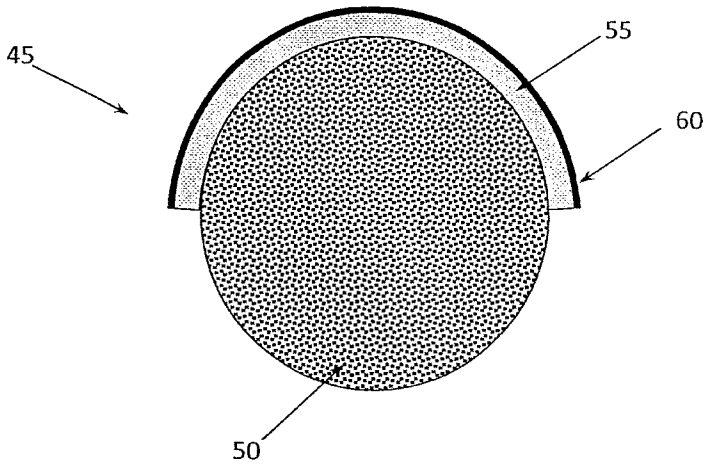


FIG. 6

FIG 7A

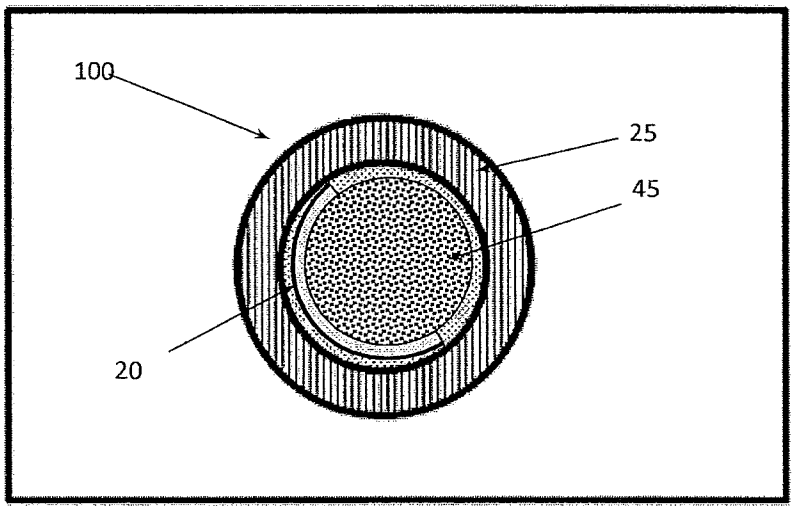


FIG 7B

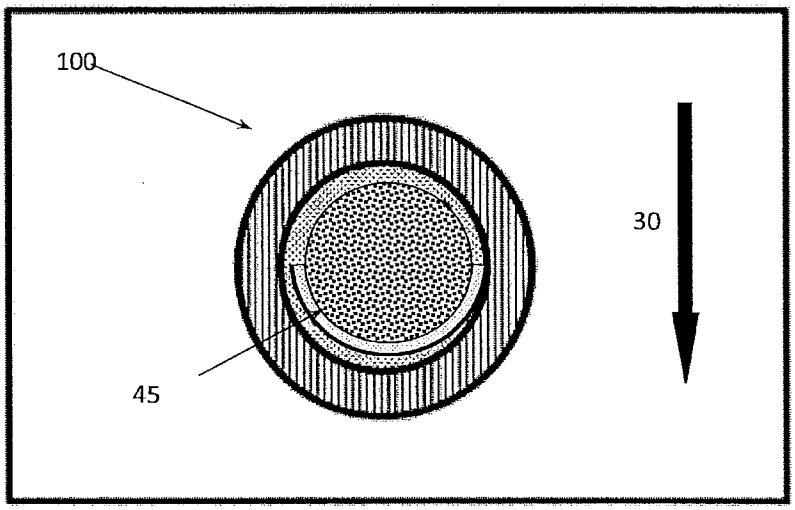
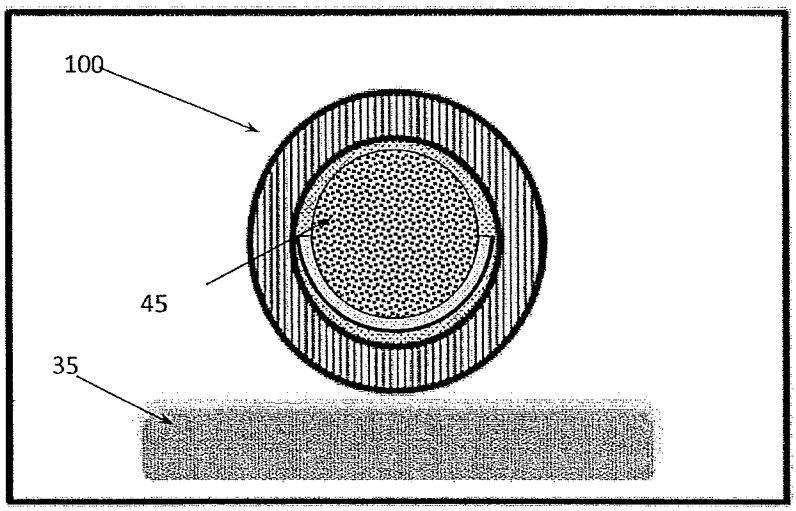


FIG 7C



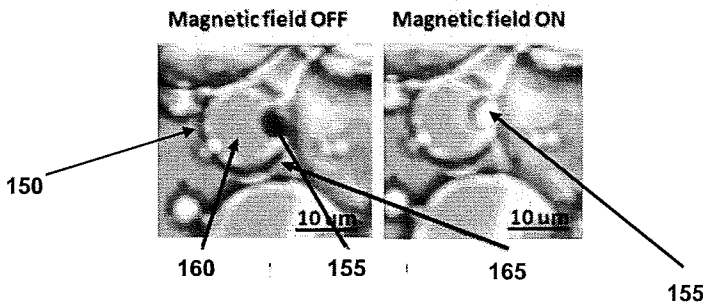

Magnetic field OFF
Magnetic field ON
150
10 µm
10 µm
160
155
165
155

FIG. 8A FIG. 8B

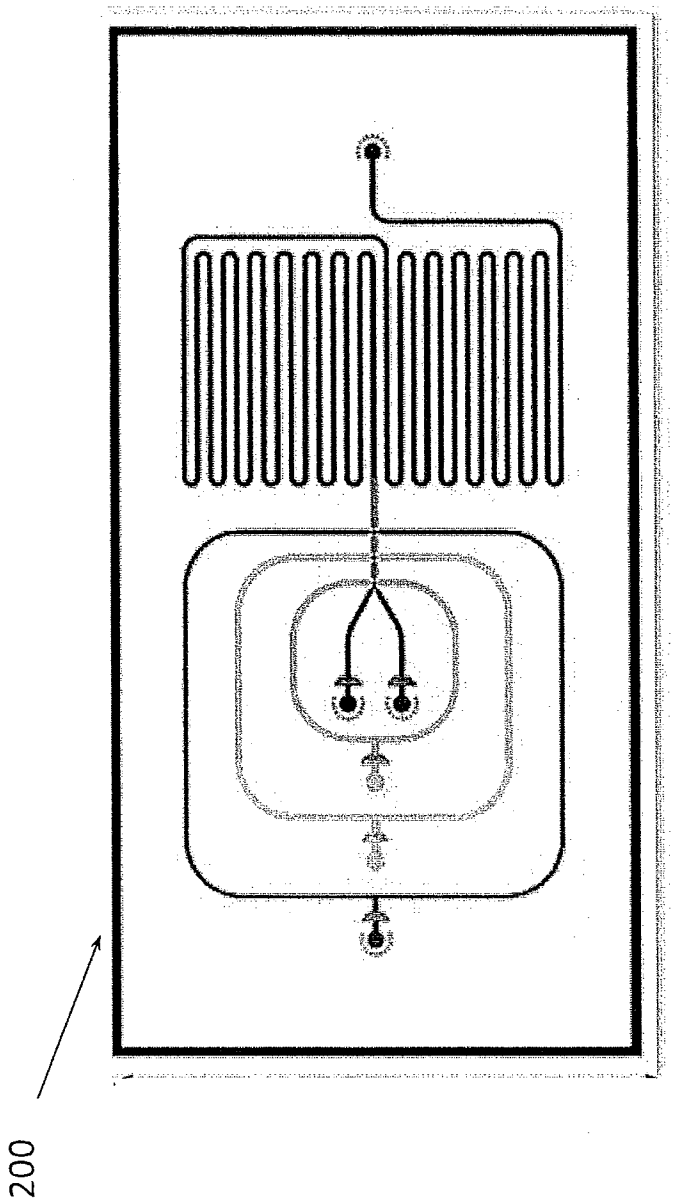


FIG. 9

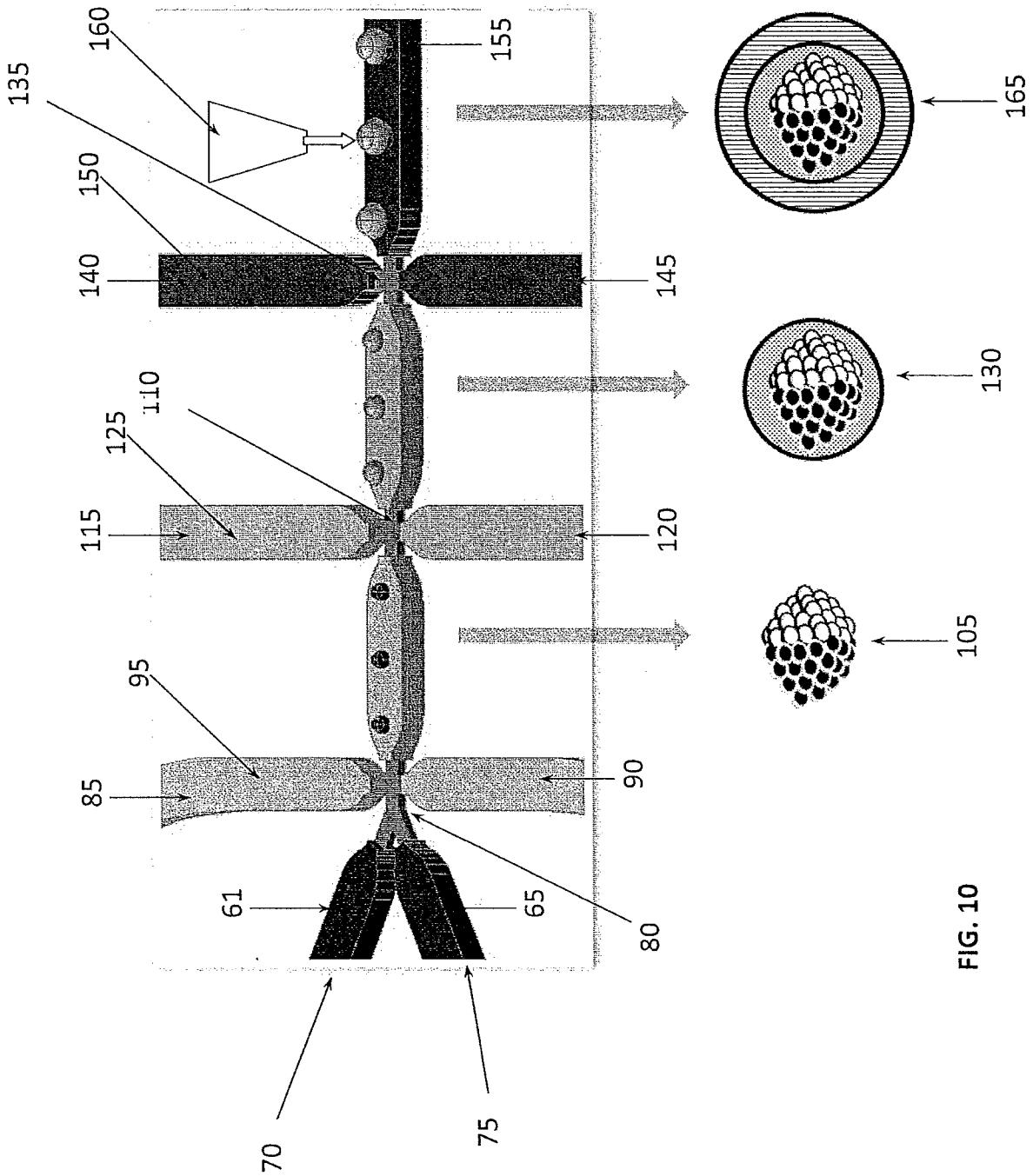

160
155
135
165
150
140
145
130
110
125
115
120
105
95
85
90
61
65
80
70
75

FIG. 10

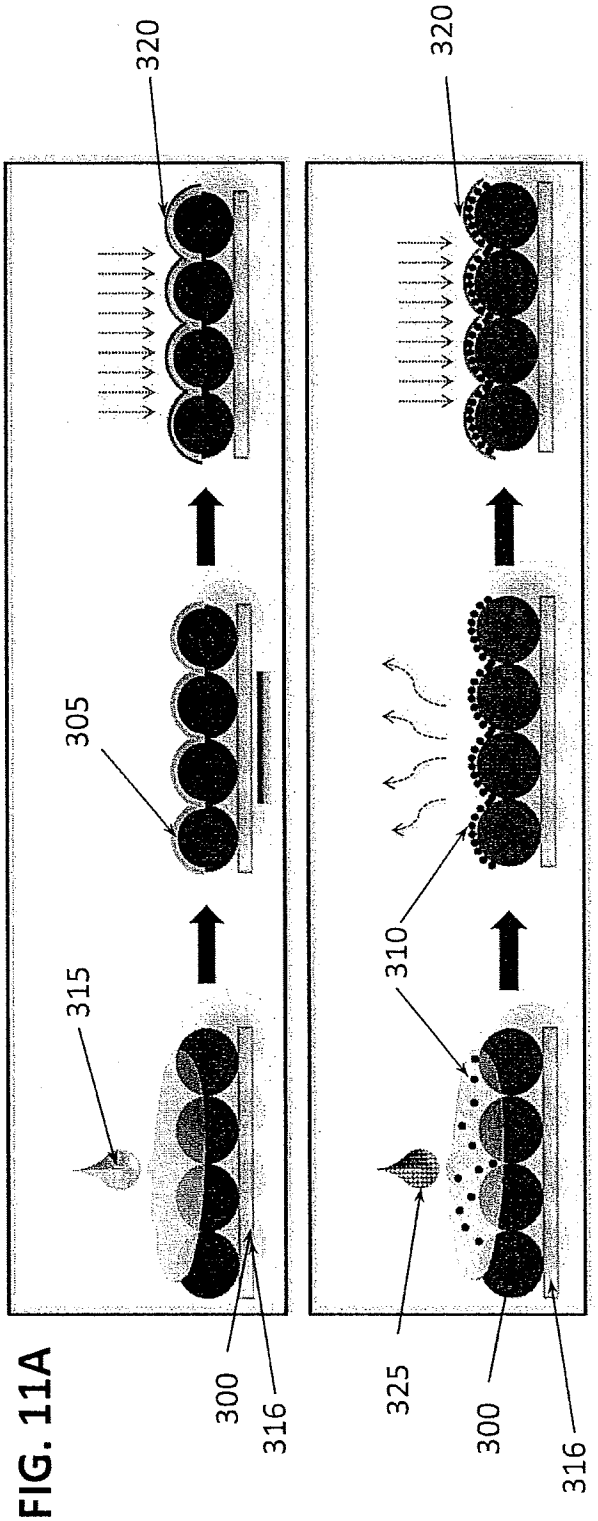


FIG. 11A

FIG. 11B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2015/051373

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C09D 11/03*** (2014.01), ***B41M 3/14*** (2006.01), ***B82Y 30/00*** (2011.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: ***C09D 11/03*** (2014.01), ***B41M 3/14*** (2006.01), ***B82Y 30/00*** (2011.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Databases : Questel-Orbit (PlusPat, FamPat), STN Caplus, West Station, Canadian Patent Database, CIPO Library Discovery Tool
Keywords : Printing inks, Janus particle, microparticle, encapsulation anisotropy, plasmonic, microfluid, polyethylene glycol, PEG

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HU, J. ZHOU, S., SUN, Y., FANG, X AND WU, L. Fabrication, Properties, and Applications of Janus Particles, 2012, Chem. Soc. Rev., Vol. 41, pages 4356 – 4378. Whole document.	1-43
A	DHANAJAY, D., and PATRIC S. D. The Synthesis and Assembly of Polymeric Microparticles Using Microfluidics, Adv. Mater. 2009, Vol. 21, pages 1-16. Whole document.	1-43
A	CHEN, C-H. SHAH, R. K., ABATE, A. R., and WEITZ, D. A. Janus Particles Templated from Double Emulsion Droplets Generated Using Microfluidics, 2009, Langmuir, Vol. 25 (8), pages 4320 – 4323. Whole document	1-43

☐ 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
"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 02 March 2016 (02-03-2016)	Date of mailing of the international search report 08 March 2016 (08-03-2016)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer Muqtar Mohammed (819) 639-9341