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(54) Title: FLOW PROCESSING AND CHARACTERIZATION OF METAL-ORGANIC FRAMEWORK (MOF) MEMBRANES IN HOLLOW FIBER AND TUBULAR MODULES

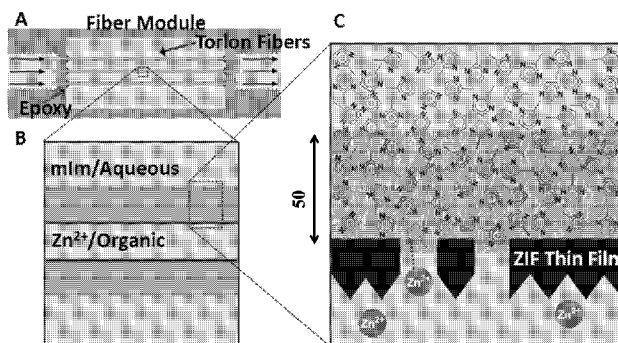


FIG. 15

(57) Abstract: A reactor cell for measuring gas and liquid permeation is disclosed. The reactor cell comprises a reactor module having a reactor chamber and a cover. A first hole extends into the reactor chamber from a first surface, a second hole opposing the first hole extends into the reactor chamber from a second surface, a third hole extends into the reactor chamber from a third surface and a fourth hole opposing the third hole extends into the reactor chamber from a fourth surface. A hollow fiber is supported by and sealed into the first and second holes of the reactor module. The first and second ends of the hollow fiber are sealed with a sealing solution. Methods for making and using the reactor cell are also disclosed. As made and used, the reactor cell further comprises a molecular sieving membrane grown on an inner bore surface of the hollow fiber.

FLOW PROCESSING AND CHARACTERIZATION OF METAL-ORGANIC FRAMEWORK (MOF) MEMBRANES IN HOLLOW FIBER AND TUBULAR MODULES

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TECHNICAL FIELD

This invention relates to a scalable, *in situ* flow-processing method to synthesize metal-organic framework (MOF) membranes on or inside hollow fiber and tubular modules and to characterize their molecular transport properties.

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BACKGROUND OF THE INVENTION

Molecular sieving membranes have generated great interest as high-performance separation systems for production of clean and renewable fuels, building block chemicals, and specialty chemicals. Compared to thermodynamically-driven separation methods, membrane-based processes can significantly reduce the energy and capital costs of separating molecules on a large scale. For example, energy-intensive methods such as cryogenic distillation are commonly used to separate hydrocarbons because of their quite similar thermodynamic properties. Membranes composed of molecular sieving materials such as zeolites,¹ layered zeolites,² or metal-organic frameworks³ (MOFs) have intrinsic advantages over polymeric membranes such as a simultaneously high permeability and selectivity. Despite their performance limitations, polymeric membranes have continued to dominate industrial membrane separations due to their relative ease of processing into morphologies such as hollow fibers.⁴ The greatest scientific challenge facing molecular sieving membranes is the lack of an easily scalable, reliable, and benign fabrication process.⁵ This limitation has been particularly severe for zeolite membranes, which are typically fabricated by hydrothermal synthesis on high-cost support materials.

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While substantive progress is being made in gradually reducing the barriers to economical zeolitic membranes,⁶⁻⁷ the advent of metal-organic framework (MOF) molecular sieves has created potential for more scalable membrane fabrication processes under relatively benign conditions.⁸ MOFs consist of metal centers connected by coordination bonds to organic linker molecules, and have been used to grow crystalline membranes through techniques similar to those developed for zeolitic membranes. The zeolitic imidazolate framework (ZIF) subclass of MOFs is of particular interest for membrane fabrication, because of its tunable pore size and chemistry,⁹ and relatively good thermal and chemical stability.¹⁰⁻¹¹ In an early demonstration of scalable ZIF membrane processing, we

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recently demonstrated the growth of ZIF-90 membranes on the outer surfaces of porous polymeric poly(amide-imide) (Torlon®) hollow fibers (~250 µm outer diameter) by a seeded growth process¹² at mild conditions (65°C in methanol solutions). Molecular sieving membranes on the inner surfaces of the hollow fibers are much more challenging to grow but better suited for scalable fabrication and industrial uses, due to the ability to be bundled in close proximity while avoiding membrane-membrane contact points and interfaces that lead to defects during synthesis.

It has been shown that free-standing MOF films and spheroids can be synthesized at the interfaces between two immiscible solvents.¹³ However, the growth of defect-controlled membranes on the inner surfaces of microscale hollow fibers (50-300 µm inner (bore) diameter) is a key, and more challenging, advance. As the bore size (and hence volume) is decreased to microscopic dimensions, the likelihood of reactant depletion and local inhomogeneity increase, leading to loss of control over membrane continuity and defect density.¹⁴

Thus, a new reactor cell design and processing strategy for preparing defect-controlled molecular sieving membranes on the inner surfaces of microscale hollow fibers is needed to improve performance in gas and liquid separations.

SUMMARY OF THE INVENTION

Zeolite and MOF membranes are typically synthesized in a reactor, and then removed for washing and mounting in a separate module. However, in this invention we demonstrate an *in situ* flow process to synthesize a membrane on or inside hollow fiber and tubular modules at a controlled location, and to subsequently activate the membrane and measure separation properties *in situ* without having to remove the membrane. Furthermore, damage to membranes during module construction and handling are eliminated. Lastly, this reactor cell design is capable of providing continuous flow in the bore and shell side of the hollow fiber or tubular module to allow for reagent recycling and to homogenize membrane thickness along the length. By using a single module for synthesis and characterization, membrane growth variables and post-treatments can be controlled accurately. This device also allows *in situ* characterization of the permeation properties of the module after each treatment step to determine cause and effect.

In other words, this reactor cell design facilitates a scalable and generalizable method of processing molecular sieving membranes (specifically, ZIF-8 membranes) referred to as an Interfacial Microfluidic Membrane Processing (IMMP) approach. The IMMP approach

combines three key concepts: first, a two-solvent interfacial approach that can be tuned to achieve positional control over membrane formation (at inner and outer surfaces, as well as inside the bulk, of the porous fiber); second, supply, replenishment, and recycling of reactants at microfluidic conditions in the hollow fiber bore; and third, membrane synthesis *in situ* directly in the membrane module, which also functions as a membrane synthesis reactor.

Although our IMMP approach can be applied to other MOF materials, we demonstrate our key findings with the ZIF-8 membrane, which has been identified as a promising candidate for critical separations such as hydrogen from hydrocarbons, hydrogen from propane and propylene from propane.^{3,15}

These and other objects, features, and advantages will become apparent as reference is made to the following detailed description, preferred embodiments, and examples, given for the purpose of disclosure, and taken in conjunction with the accompanying drawings and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee.

For a further understanding of the nature and objects of the present inventions, reference should be made to the following detailed disclosure, taken in conjunction with the accompanying drawings, in which like parts are given like reference numerals, and wherein:

FIG. 1A illustrates a side perspective view of a hollow fiber or tubular membrane module showing location of a bore and a shell;

FIG. 1B illustrates a cross-sectional view of a hollow fiber or tubular membrane module showing location of a bore and a shell;

FIG. 2 illustrates an upper, right front perspective view of a reactor according to an embodiment of the present invention;

FIG. 3 illustrates a photograph of a polyamide-imide (e.g., TORLON®) hollow fiber epoxy-sealed inside a reactor according to an embodiment of the present invention;

FIG. 4 illustrates a photograph of a reactor connected to cycling peristaltic pump according to an embodiment of the present invention;

FIG. 5A illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on an outer (shell) side surface of a seeded polyamide-imide (e.g., TORLON®) hollow fiber;

FIG. 5B illustrates a top-view of a SEM micrograph of a ZIF-8 membrane grown on outer (shell) side surface of a seeded polyamide-imide (e.g., TORLON®) hollow fiber;

FIG. 6A illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on a polyamide-imide (e.g., TORLON®) hollow fiber under aqueous flow conditions;

FIG. 6B illustrates a detailed cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on a polyamide-imide (e.g., TORLON®) hollow fiber under aqueous flow conditions;

FIG. 7A illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on a polyamid-imide (e.g., TORLON®) hollow fiber under 1-octanol flow conditions;

FIG. 7B illustrates a detailed cross-sectional view of a SEM micrograph of ZIF-8 membrane grown on a polyamide-imide (e.g., TORLON®) hollow fiber under 1-octanol flow conditions;

FIG. 8A illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on a polyamide-imide (e.g., TORLON®) hollow fiber using an Interfacial Microfluidic Membrane Processing (IMMP) approach with 2mL/min flow rate of a Zn^{+2} /1-octanol bore solution and an aqueous 2-methyl imidazole (mIm) shell solution according to an embodiment of the present invention;

FIG. 8B illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on a polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP approach with 1 μ L/min flow rate of a Zn^{+2} /1-octanol bore solution and an aqueous mIm shell solution according to an embodiment of the present invention;

FIG. 9 illustrates a X-ray Diffraction (XRD) chart of 2Theta (°) vs. Intensity for simulated and experimental ZIF-8 membranes, confirming structure of supported ZIF-8 membranes;

FIG. 10 illustrates an Energy Dispersive X-ray Spectroscopy (EDS) Zinc line profile scan chart of Distance from membrane surface (μm (microns)) vs. Intensity, depicting thickness of membrane to be $\sim 3 \mu\text{m}$;

FIG. 11 illustrates a chart of Time vs. Flow Rate for static and continuous flow conditions, showing static growth conditions;

FIG. 12 illustrates a chart of Time vs. Flow Rate for pulsed flow conditions, showing growth and replenishment conditions;

FIG. 13 illustrates a chart of Time (min.) vs. Flow Rate ($\mu\text{L}/\text{hour}$) for pulsed flow conditions, showing growth, static growth and replenishment conditions;

FIG. 14 illustrates a X-ray Diffraction (XRD) chart of 2θ ($^\circ$) vs. Intensity for simulated and experimental ZIF-8 membranes on polyamide-imide (e.g., TORLON®) hollow fiber, confirming formation and structure of supported ZIF-8 membranes on inner (bore) side surface of hollow fiber;

FIG. 15 illustrates a schematic of the IMMP approach: (A) depicts a side view of a plurality of hollow fibers (orange) mounted in a reactor cell, (B) depicts an exploded side view of hollow fiber support during synthesis, showing Zn^{2+} ions being supplied by a 1-octanol solution (light red) flowing through the bore of the hollow fiber and methylimidazole linkers being supplied on the outer (shell) side of the hollow fiber in an aqueous solution (light blue), and (C) depicts a further exploded view of hollow fiber support during synthesis, showing the membrane forming on the inner surface of the hollow fiber by reaction of the two precursors to form a polycrystalline ZIF-8 layer (dark blue);

FIG. 16 illustrates a schematic of steady-state gas permeation measurement apparatus, with the reactor cell functioning as the permeation cell;

FIG. 17A illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in polyamide-imide (e.g., TORLON®) hollow fiber on the inner (bore) side surface by manipulating the location of the two reactants (i.e., zinc nitrate hexahydrate and mIm) and the two solvents (i.e., deionized water (DI) and 1-octanol) as in Example 1;

FIG. 17B illustrates an EDS elemental maps of carbon (red) and superimposed zinc (green) showing the localization of the ZIF-8 membrane on the inner (bore)

side surface of the polyamide-imide (e.g., TORLON®) hollow fiber as in Example 1;

FIG. 18A illustrates a chart of Time (minutes) vs. Flow Rate ($\mu\text{L}/\text{hour}$), showing static, continuous and intermittent flow conditions used to synthesize ZIF-8 membranes on the inner (bore) side surface of a polyamide-imide (e.g., TORLON®) hollow fibers as in Example 1;

FIG. 18B illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP approach with a static flow of a $\text{Zn}^{+2}/1\text{-octanol}$ bore solution, depicting a discontinuous particle coating on the inner (bore) side surface of the hollow fiber;

FIG. 18C illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP approach with a continuous flow of a $\text{Zn}^{+2}/1\text{-octanol}$ bore solution, depicting a continuous ZIF-8 membrane ($\sim 3\ \mu\text{m}$ thick) on the inner (bore) side surface of the hollow fiber;

FIG. 18D illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP approach with an intermittent flow of a $\text{Zn}^{+2}/1\text{-octanol}$ bore solution, depicting a continuous ZIF-8 membrane ($\sim 8\ \mu\text{m}$ thick) on the inner (bore) side surface of the hollow fiber;

FIG. 19 illustrates an XRD pattern confirming crystal structure of ZIF-8 membrane grown on a polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP approach with intermittent flow of a $\text{Zn}^{+2}/1\text{-octanol}$ bore solution as in Example 1;

FIG. 20A illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber closer to an inner (bore) side surface by manipulating the location of the two reactants (i.e., zinc nitrate hexahydrate and mIm) and the two solvents (i.e., DI and 1-octanol) as in Example 2;

FIG. 20B illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber closer to an inner (bore) side surface by manipulating the location of the two

reactants (i.e., zinc nitrate hexahydrate and mIm) and the two solvents (i.e., DI and 1-octanol) as in Example 3;

FIG. 20C illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber closer to an outer (shell) side surface by manipulating the location of the two reactants (i.e., zinc nitrate hexahydrate and mIm) and the two solvents (i.e., DI and 1-octanol) as in Example 4;

FIG. 20D illustrates a cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber closer to an outer (shell) side surface by manipulating the location of the two reactants (i.e., zinc nitrate hexahydrate and mIm) and the two solvents (i.e., DI and 1-octanol) as in Example 5;

FIG. 21A illustrates a chart of Temperature (°C) vs. Permeance (G.P.U.) and Separation Factor, showing binary H_2/C_3H_8 permeation characteristics for equimolar feed mixtures on a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP system and capping ends of the hollow fiber with poly(dimethylsiloxane) (PDMS);

FIG. 21B illustrates a chart of Temperature (°C) vs. Permeance (G.P.U.) and Separation Factor, showing binary C_3H_6/C_3H_8 permeation characteristics for equimolar feed mixtures on a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP system and capping ends of the hollow fiber with PDMS;

FIG. 22A illustrates a chart of Temperature (°C) vs. Permeance (G.P.U.) and Separation Factor, showing binary permeation characteristics for an equimolar H_2/C_3H_8 feed mixture on a ZIF-8 membrane grown in polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP system;

FIG. 22B illustrates a chart of Temperature (°C) vs. Permeance (G.P.U.) and Separation Factor, showing binary permeation characteristics for an equimolar C_3H_6/C_3H_8 feed mixture on a ZIF-8 membrane grown in polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP system;

FIG. 23A illustrates a chart of Temperature (°C) v. Permeance (G.P.U.) and Separation Factor, showing binary permeation characteristics for equimolar H_2/C_3H_8 feed mixtures on ZIF-8 membranes grown simultaneously in three (3)

polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP system and sealing the ends of the fibers with PDMS;

FIG. 23B illustrates a chart of Temperature (°C) v. Permeance (G.P.U.) and Separation Factor, showing binary permeation characteristics for an equimolar C₃H₆/C₃H₈ feed mixture on ZIF-8 membranes grown simultaneously in three (3) polyamide-imide (e.g., TORLON®) hollow fiber using the IMMP approach and sealing the ends of the fibers with PDMS;

FIG. 24A illustrates a schematic showing feed gas molecules bypassing the ZIF-8 membrane through the hollow fiber ends;

FIG. 24B illustrates a schematic showing suppression of the bypass effect in FIG. 24A by capping the hollow fiber ends with a PDMS film;

FIG. 25A illustrates a SEM cross-section image of the inner-surface ZIF-8 membrane after end-capping by penetration of PDMS; and

FIG. 25B illustrates an EDS elemental map of Si (red) showing the penetration of PDMS into the pores of a polyamide-imide (e.g., TORLON®) hollow fiber.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The following detailed description of various embodiments of the present invention references the accompanying drawings, which illustrate specific embodiments in which the invention can be practiced. While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains. Therefore, the scope of the present invention is defined only by the appended claims, along with the full scope of equivalents to which such claims are entitled.

In this invention, we demonstrate an *in situ* flow process to synthesize a membrane on or inside a hollow fiber or tubular membrane module at a controlled location, and to subsequently activate the membrane and measure separation properties *in situ* without having to remove the membrane. By using a single module for synthesis and characterization,

membrane growth variables and post-treatments can be controlled accurately. This device also allows *in situ* characterization of the permeation properties of the module after each treatment step to determine cause and effect.

Hollow Fiber or Tubular Membrane Module Detail

5 In an embodiment of the present invention, a membrane was synthesized on or inside a hollow fiber or tubular membrane module. A side perspective view of a hollow fiber or tubular membrane module **100** is depicted in FIG. 1A. As shown in FIG. 1A, the hollow fiber or tubular membrane module **100** comprises a shell **105** and a bore **110**.

10 A cross-sectional view of a hollow fiber or tubular membrane module **100** is depicted in FIG. 1B. As shown in FIG. 1B, the hollow fiber or tubular membrane module **100** comprises a shell **105** and a bore **110**. In an embodiment, the hollow fiber or tubular module may have an inner (bore) diameter of about 50 μm to about 5000 μm . In an embodiment, the hollow fiber or tubular module may have an inner (bore) diameter of about 50 μm to about 300 μm .

Design Considerations/Machining Detail for Reactor Cell

15 A reactor cell of the present invention may be cubic-, rectangular-, cylindrical- or cylindrical-like shaped (e.g., elliptical base), and the like. In an embodiment, a reactor module **200** was fabricated to have a base shape and a first height, and a reactor module cover **420** was fabricated to have the same base shape as the reactor module **200** and a second height. In an embodiment, the base shape may be selected from the group consisting of square, rectangular, circular and ellipse.

25 Suitable materials for the reactor module and/or cover include any metal, or any plastic compatible with an adhesive (e.g., epoxy), alcohol solvents and water. In an embodiment, the metal may be selected from the group consisting of stainless steel, stainless steel alloys such as MONEL® (Special Metals Corp.) and HASTALLOY® (Haynes International, Inc.), and the like. In an embodiment, the plastic may be selected from the group consisting of polyether ketone (PEEK), polymethylene (e.g., DELRIN® (DuPont Co.)), polytetrafluorethylene (PTFE) (e.g., TEFLON® (DuPont Co.)), and the like. In an embodiment, stainless steel 304 was used to fabricate the reactor module **200** and cover **420**.

30 Although a rectangular reactor module **200** and cover **420** are depicted in FIGS. 2-4, a person of ordinary skill in the art could easily adapt these teachings to cubic, cylindrical and cylindrical-like reactor modules and covers. Accordingly, although the rectangular reactor

module **200** and cover **420** are discussed in detail below, this discussion should not be interpreted to exclude cubic, cylindrical and cylindrical-like reactor modules and covers.

Although the reactor module and cover were machined from metal blocks, a person of ordinary skill in the art (POSITA) could easily adapt these teaching to other suitable methods of fabricating parts. In an embodiment, the fabrication method may be selected from machining, molding, printing and combinations thereof. For example, if a plastic material is used, the reactor module and cover may molded by compression or injection molding or printed on a 3-D printer as customary in the art. Accordingly, although machining is discussed in detail below, this discussion should not be interpreted to exclude molding and printing techniques.

An upper, right front perspective view of a reactor module **200** is depicted in FIG. 2. As shown in FIG. 2, the reactor module **200** has a first length **205**, a second length **210** and a third length **215**. Further, the reactor module **200** has an upper surface **220**, a first side surface **225**, a second side surface **230** (not shown), a third side surface **235** and a fourth side surface **240** (not shown). The reactor module **200** may be constructed from a metal or a plastic as discussed above. In an embodiment, the reactor module **200** was constructed from stainless steel 304.

The reactor module **200** has a reactor chamber **245** with a reactor chamber diameter **250** and reactor chamber depth **255** (not shown) extending into the reactor module **200** from the upper surface **220**. Further, the reactor module **200** has an O-ring groove **260** extending into the reactor module **200** from the upper surface **220** and surrounding the reactor chamber **245**.

In an embodiment, the reactor chamber may be cylindrical. In such cylindrical embodiment, the inner diameter of the O-ring groove **260** is slightly larger than and offset from the reactor chamber diameter **250**.

In an embodiment, the reactor chamber may not be cylindrical. For such non-cylindrical embodiments, an O-ring groove with an inner dimension slightly larger than and offset from an outer dimension of the reactor chamber may be machined in the upper surface of the reactor module.

In an embodiment, the reactor module **200** has a temperature probe chamber **290** (not shown) with a temperature probe diameter **295** (not shown) and a temperature probe depth (not shown) extending into the reactor module **200** from the upper **220** or first side **225**,

second side **230**, third side **240**, fourth side **245** surface. Suitable temperature probes **490** include resistance temperature detectors (RTDs), thermocouples, thermometers, and the like.

The reactor module **200** has a plurality of holes **285** extending into the reactor module **300** material from the upper surface **225** to attach a reactor module cover (not shown). In an embodiment, if the temperature probe chamber **290** extends into the reactor module **200** from the upper surface **220**, the reactor module cover **420** will have a temperature probe hole with a temperature probe diameter **295** extending through the reactor module cover **420** and aligning with the temperature probe diameter **295** of the temperature probe chamber **290** in the reactor module **200**. The reactor module cover **420** may be constructed from a metal or a plastic as discussed above. In an embodiment, the reactor module **200** was constructed from stainless steel **304**.

The reactor module **200** has a first hole **265** extending into the reaction chamber **245** from a first side surface **225**, a second hole **270** extending into the reaction chamber **245** from a second side surface **230** (not shown), a third hole **275** extending into the reaction chamber **245** from a third side surface **235**, and a fourth hole **280** extending into the reaction chamber **245** from a fourth side surface **240** (not shown).

In an embodiment, the first **265** and second **270** holes may extend only partially into the first **225** and second **230** side surfaces, respectively, of the reactor chamber **245** such that a first and second smaller hole may extend into the reaction chamber **245** to accept a hollow fiber or tubular membrane module **100** as shown in FIG. 3. In an embodiment, the hollow fiber or tubular membrane module **100** may be held (and sealed) in place in the first and second smaller holes with an adhesive such as an epoxy. In an embodiment, the first **265**, second **270**, third **275** and fourth **280** holes are threaded to accept various fittings as are customarily used in the art.

In an embodiment, the third **275** and fourth **280** holes extending into the third **235** and fourth **240** side surfaces of the reactor module **200** (i.e., surfaces perpendicular to the mounted hollow fiber or tubular membrane module **100**) may be slightly offset either vertically or horizontally from each other to facilitate mixing during flow conditions.

For example, a laboratory-scale reactor module **300** was constructed from a rectangular stainless steel block with a first length **305** of about 3-inches, a second length **310** of about 3-inches and a third length **315** of about 1.5-inches as depicted in FIGS. 3-4. A reactor chamber **345** with reactor chamber diameter **350** of about 2-inches and a depth of about 1.38-inches was machined into the center of the stainless steel block.

Next, first **365**, second **370**, third **375** and fourth **380** holes were drilled for 1/8-inch NPT fittings through the first **325** (not shown), second **330** (not shown), third **335** (not shown) and fourth **340** (not shown) side surfaces of the stainless steel block. Although 1/8-inch NPT fittings were used, a POSITA could easily adapt this teaching to other fittings. Accordingly, although the 1/8-inch NPT fittings are disclosed, this disclosure should not be interpreted to exclude other fittings.

The first **365** and second **370** holes extended only partially into the first **325** and second **330** side surfaces, respectively, of the reactor chamber **345** such that a first and second smaller holes with a diameter of about 0.5 mm extended into the reaction chamber **345** to accept a hollow fiber or tubular membrane module **100** as shown in FIG. 3. In an embodiment, the first **365** and second **370** holes extended into the first **325** and second **330** side surfaces, respectively, at a height of about 1-inch such that about 0.1-inch wall remained and second smaller holes with a diameter of about 0.02-inch were drilled through the 0.1-inch wall to create an aperture for mounting the hollow fiber or tubular membrane module **100**. These smaller holes may be used to support the hollow fiber or tubular membrane module **100**. The hollow fiber or tubular membrane module **100** may be mounted (and sealed) in place in the first and second smaller holes with an adhesive such as an epoxy.

Although the smaller holes were used to support the hollow fiber or tubular membrane, a person of ordinary skill in the art (POSITA) could easily adapt these teachings to use an insert to support the hollow fiber or tubular membranes(s) or to bundle the hollow fiber or tubular membranes such that the smaller holes are unnecessary. Accordingly, although smaller holes are discussed in detail above, this discussion should not be interpreted to exclude other techniques of the supporting the hollow fiber or tubular membrane.

The third **375** and fourth **380** holes extending into the third **335** and fourth **340** side surfaces, respectively, of the reactor module **300** (i.e., surfaces perpendicular to the mounted hollow fiber or tubular membrane module **100**) were offset vertically from each other by about 1/8 to 1/4-inch to facilitate mixing during flow conditions. In an embodiment, the third **375** and fourth **380** holes extended into the third **335** and fourth **340** sides, respectively, at a height of about 1 1/8-inch such that the third **375** and fourth **380** holes extended into the reactor chamber **345**.

In an embodiment (not shown), the first hole **365** may extend into the reactor chamber **345** from the first side surface **325**, the second hole **370** opposing the first hole **365** may extend into the reactor chamber **345** from the second surface **330**, the third hole **375** may

extend into the reactor chamber **345** from the first surface **325** and the fourth hole **380** opposing the third hole **375** may extend into the reactor chamber **345** from the second surface **330**.

In an embodiment (not shown), the first hole **365** may extend into the reactor chamber **345** from the first side surface **325**, the second hole **370** opposing the first hole **365** may extend into the reactor chamber **345** from the second surface **330**, the third hole **375** may extend into the reactor chamber **345** from an upper surface of a reactor module cover **420** and the fourth hole **380** opposing the third hole **375** extends into the reactor chamber **345** from a bottom surface of the reactor chamber **345**.

Although a few possible alternative configurations for an inlet (i.e., third hole **375**) and an outlet (i.e., fourth hole **380**) for an outer (shell) side solution have been discussed above, a POSITA could easily adapt this teaching to other designs. For example, the inlet and the outlet of the outer (shell) side solution may be positioned to create turbulent flow.

As depicted in FIG. 4, the reactor module **400** must be airtight to be used to measure gas and liquid permeation. To provide an airtight seal, an O-ring groove **360** with a diameter of about 2 1/4-inches and cross-section of about 0.06-inches (AS568-035) was machined in the upper surface **320** of the reactor module **300** to receive an O-ring (see FIG. 3).

In an embodiment, the reactor chamber may not be cylindrical. For such non-cylindrical embodiments, an O-ring groove with an inner dimension slightly larger than and offset from an outer dimension of the reactor chamber may be machined in the upper surface of the reactor module.

A plurality of threaded holes **385** were machined into each corner of the upper surface **320** of the reactor module **300**, **400** about 0.35-inches away from the O-ring groove **360** to receive a plurality of 10-32 hexagonal screws **485** as shown in FIGS. 3-4. Although 10-32 hexagonal screws were used to secure a reactor module cover **420** (see FIG. 4) to the reactor module **300**, a POSITA could easily adapt this teaching to other fasteners. Accordingly, although the 10-32 hexagonal screws are discussed in detail, this discussion should not be interpreted to exclude other fasteners.

A temperature probe chamber **290** with temperature probe diameter **295** was machined in the reactor module **300**, **400** outside of the O-ring groove **360** to receive a temperature probe **490** as shown in FIGS. 2-4. As shown in FIG. 4, the temperature probe **490** (e.g., heat probe, thermometer) is inserted in the temperature probe chamber **290**.

Suitable temperature probes **490** include heat probe, resistance temperature detectors (RTDs), thermocouples, thermometers, and the like.

A rectangular block was used to fabricate a reactor module cover **420**. A photograph of a reactor module **400** and cover **420** is depicted in FIG. 4. As shown in FIG. 4, the reactor module cover **420** has a first length **425** of about 3-inches, a second length **430** (not shown) of about 3-inches and a third length **435** (not shown) of about 1/4-inch. A plurality of holes (not shown) was machined in the reactor module cover **420** extending through the cover **420** and aligning with the diameters of the threaded holes **385** in the reactor module **400**. In an embodiment, the reactor module cover **420** was constructed from stainless steel 304.

A temperature probe hole (not shown) was machined in the reactor module cover **420** extending through the cover **420** and aligning with the temperature probe diameter **295** of the temperature probe chamber **290** in the reactor module **400**. As illustrated in FIG. 4, the temperature probe **490** (e.g., heat probe, thermometer) is inserted in the temperature probe hole (not shown) of the cover **420** and into the temperature probe chamber **290** (not shown) of the reactor module **400**. Suitable temperature probes **490** include heat probes, resistance temperature detectors (RTDs), thermocouples, thermometers, and the like.

The reactor module cover **420** provides a flange-seal by tightening the cover **420** onto the reactor module **400** via the plurality of 10-32 hexagonal screws **485**.

Temperature Control of Reactor Cell/Module

The reactor module **400** may be heated and/or cooled to a temperature between about 0°C and about 200°C. As shown in FIG. 4, the laboratory-scale reactor module **400** was placed on a stir plate, and heated to about 30°C with a temperature probe **490**. In an embodiment, the temperature probe **490** was set at about 30°C and inserted into the temperature probe chamber **290** of the reactor module **400**.

Although a temperature probe **490** was used to heat the reactor module **400**, a POSITA could easily adapt this teaching to other heating and/or cooling methods. Accordingly, although the temperature probe heating method is discussed in detail, this discussion should not be interpreted to exclude other heating and/or cooling methods. For example, suitable heaters include temperature probes, hot plates, heating coils, enclosure heaters, silicone rubber heaters, polyester heaters, polyimide heaters, strip heaters, band heaters, tubular heaters, cartridge heaters, and the like. For example, suitable coolers include liquid baths, cooling coils, enclosure coolers, thermoelectric coolers, thermoelectric chillers, heat sinks, fans, and the like.

The temperature of the reactor module **400** may be set with a temperature probe **490** or measured with a thermometer. Although a temperature probe **490** was used, a POSITA could easily adapt this teaching to other combinations of heaters (discussed above) and temperature probes. Suitable temperature probes **490** include resistance temperature detectors (RTDs), thermocouples, thermometers, and the like.

Mounting/Sealing Hollow Fiber in Reactor Cell/Module

A length of a hollow fiber or tubular membrane module **100** may be threaded through the first and second smaller holes in the reactor module **200, 300**. In an embodiment, a porous polyamide-imide (e.g., TORLON® (Solvay Advanced Polymers)) hollow fiber **100** with a length of about 4-inches was threaded through the first and second smaller holes of the reactor module **200, 300**.

The hollow fiber or tubular membrane module **100** may be mounted (and sealed) in place in the first and second smaller holes with an adhesive such as an epoxy. In an embodiment, the hollow fiber **100** was held (and sealed) in place in the first and second smaller holes with a small drop of epoxy on the shell of each fiber where the fiber passes through the aperture. After the epoxy was allowed to cure for about 90 minutes, the excess fiber ends were removed with tweezers, taking care not to crush or block the fiber ends. In an embodiment, a plurality of hollow fibers **100** may be mounted (and sealed) using this same method.

To ensure that the mounted hollow fiber(s) **100** was/were properly sealed and that the ends were not crushed or blocked, the reactor module **400** should be tested for use as a permeation cell by measuring the leak rate and the N₂ permeances of the mounted fiber(s), as discussed below.

Performance as Permeation Cell

The reactor module **400** was tested for use as a permeation cell by measuring the leak-rate and the permeance of a known standard. Using a porous polyamide-imide (e.g., TORLON®) hollow fiber as a standard, a N₂ permeance of 53,000 GPU, which is consistent with the reported values in the literature, was measured with the reactor cell **400**.^{12,16} Based on flow-based leak tests, the leak-rate was determined to be less than 0.1 psi/hour.

Constant Flow Synthesis of ZIF-8 Membranes

Using a macroporous polyamide-imide (e.g., TORLON®) hollow fiber and the material ZIF-8 as an archetype for a hollow fiber or tubular membrane synthesis, a series of constant flow membrane synthesis experiments were performed. Several examples of ZIF-8

membrane fabrication using this reactor module **400** are described below, and their results are shown in the SEM micrographs of FIGS. 5-8.

Performance in Membrane Synthesis: Static Conditions

Starting with a seeded polyamide-imide (e.g., TORLON®) hollow fiber **100** mounted
5 in the reactor module **400**,¹² an aqueous synthesis gel consisting of about 0.22g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL of deionized water (DI) (about 0.018 mol/L) and about 9g 2-methyl imidazole (mIm) in about 80 mL deionized water (DI) (about 1.37 mol/L) was poured on the outer (shell) side surface **105** of the hollow fiber **100**. After 6 hours at 30°C, the shell solution was removed and the hollow fiber **100** was thoroughly rinsed with
10 deionized water (DI) and methanol.

A cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on an outer (shell) side surface of a seeded polyamide-imide (e.g., TORLON®) hollow fiber is shown in FIG. 5A; and a top view of a SEM micrograph of the ZIF-8 membrane grown on the outer (shell) side surface **105** of the seeded polyamide-imide (e.g., TORLON®) hollow fiber is
15 shown in FIG. 5B. Based upon FIGS 5A-5B, the ZIF-8 membrane is formed on the outer (shell) side surface **105** of the hollow fiber **100**.

Performance in Membrane Synthesis: Flow Conditions

Reactions that are performed under flowing conditions are easier to control and allow recycling; therefore, ZIF-8 membranes were grown by flowing reagents through the bore **110**
20 of the hollow fiber **100** (see FIGS. 6-7).

First, an aqueous Zn^{+2} solution containing about 0.22g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL deionized water (DI) (about 0.018 mol/L) was flowed through the bore **110** at 2mL/min while an aqueous mIm solution containing 9g mIm in about 80 mL deionized water (DI) (about 1.37 mol/L) was poured on the outer (shell) side surface **105**. The reaction was
25 stopped after 6 hours and the hollow fiber **100** was rinsed with deionized water (DI) and methanol.

A cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown under aqueous flow conditions is shown in FIG. 6A; and a detailed (10X) cross-sectional view of the SEM micrograph of the ZIF-8 membrane grown under aqueous flow conditions is shown
30 in FIG. 6B. Based upon FIGS. 6A-6B, the ZIF-8 membrane is formed on the inner (bore) side surface **110** of the hollow fiber **100**.

To determine the effect of solvent, the aforementioned experiment was repeated using a different solvent (i.e., 1-octanol).

Second, a Zn^{+2} /1-octanol solution containing about 0.22g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL 1-octanol (about 0.018 mol/L) was flowed through the bore **110** at 2mL/min while a mIm/1-octanol solution containing about 9g mIm in about 80 mL 1-octanol (about 1.37 mol/L) was poured on the outer (shell) side surface **105**. The reaction was stopped after 6 hours and the hollow fiber **100** was rinsed with deionized water (DI) and methanol.

A cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown under 1-octanol flow conditions is shown in FIG. 7A; and a detailed (10X) cross-sectional view of the SEM image of the ZIF-8 membrane grown under 1-octanol flow conditions is shown in FIG. 7B. Based upon FIGS. 7A-7B, the ZIF-8 membrane is formed on the inner (bore) side surface **110** of the hollow fiber **100**.

Accordingly, for both the aqueous (see FIG. 6) and 1-octanol (see FIG. 7) flow systems, the ZIF-8 membrane growth was observed in the inner (bore) side surface **110** of the hollow fiber **100** instead of on the outer (shell) side surface **105**.

Performance in Membrane Synthesis: Interfacial Synthesis

The next experiment involved using interfacial synthesis technique whereby immiscible solvents are used as a means to physically separate the organic and inorganic precursors. Specifically, a Zn^{+2} /1-octanol solution containing about 0.22g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL 1-octanol (about 0.018 mol/L) was flowed at 2mL/min through the bore **110** while an aqueous mIm solution containing about 9g mIm in about 80 mL deionized water (DI) (about 1.37 mol/L) was poured into the reactor chamber **345** immersing the outer (shell) side surface **105** of the hollow fiber **100**. The reaction was stopped after 6 hours and the hollow fiber **100** was flushed with neat 1-octanol, heptane, and deionized water (DI).

To determine the effect of flow rate, the aforementioned experiment was repeated using a slower flow rate (1 μ L/min).

A cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown under 1-octanol flow conditions of 2mL/min bore flow rate, using an interfacial system is shown in FIG. 8A; and a cross-sectional view of the SEM micrograph of the ZIF-8 membrane grown under 1-octanol flow conditions of 1 μ L/min bore flow rate, using the interfacial system is shown in FIG. 8B.

Accordingly, for the interfacial system, both the 2mL/min (see FIG. 8A) and 1 μ L/min (see FIG. 8B) bore flow rates, the ZIF-8 membrane growth was observed in the interior

(bore) side surface **110** of the hollow fiber **100** instead of on the outer (shell) side surface **105**.

Table 1 shows the measurement of single-component gas permeation properties of three of the ZIF-8 membranes using the reactor module **400**. The entire process of membrane formation and permeation measurement can be done *in situ* within the same pre-fabricated reactor module **400**, thereby avoiding the difficulties associated with previous membrane fabrication processes.

Table 1. Measurement of Single-Component Gas Permeation Properties for *In-Situ* grown ZIF-8 Membrane

Example	Support	Flow Rate	Thickness (μm)	Permeance (GPU)		Selectivity N_2/SF_6
				N_2	SF_6	
ZIF-8_Outer (see FIGS. 5A-5B)	Torlon Tube	Static	3	800	430	1.9
ZIF-8_Inner_1 (see FIG. 8A)	Torlon Tube	2mL/min	5-15	240	100	2.4
ZIF-8_Inner_2 (see FIG. 8B)	Torlon Tube	1 μL /min	2-3	320	60	5.3

An X-ray Diffraction (XRD) chart of 2Theta ($^\circ$) vs. intensity for simulated and experimental ZIF-8 membranes, confirming the structure of supported ZIF-8 membranes is shown in FIG. 9.

An EDS Zinc line profile scan of distance from membrane surface (μm (microns)) vs. intensity, depicting the thickness of the ZIF-8 membrane to be about 3 μm is shown in FIG.

Performance in Membrane Synthesis: Static, Continuous and Pulsed Flow Conditions

In an embodiment, ZIF-8 membranes were grown by flowing reagents through the bore **110** of the hollow fiber **100** (see FIGS. 6-7, 18B-18C) under static, continuous and pulsed flow conditions. See FIGS. 11-12 & 18A.

First, a Zn^{+2} /1-octanol solution containing about 0.22g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL 1-octanol (about 0.018 mol/L) was continuously flowed through the bore **110** at about 60 μL /hour while an aqueous mIm solution containing about 9g mIm in about 80 mL deionized water (DI) (about 1.37 mol/L) was poured on the outer (shell) side surface **105**.

The reaction was stopped after about 9 hours and the hollow fiber **100** was rinsed with 1-octanol, heptanes, deionized water (DI) and methanol.

Second, a Zn^{+2} /1-octanol solution containing about 0.22g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL 1-octanol (about 0.018 mol/L) was held static in the bore **110** while an aqueous mIm solution containing about 9g mIm in about 80 mL deionized water (DI) (about 1.37 mol/L) was poured on the outer (shell) side surface **105**. The reaction was stopped after about 9 hours and the hollow fiber **100** was rinsed with 1-octanol, deionized water (DI), heptanes and methanol.

A chart of Time vs. Flow Rate static and continuous flow through the bore **110** of the hollow fiber **100** is illustrated in FIG. 11. No continuous ZIF-8 membrane was formed on the inside of the bore **110** of the hollow fiber **100** under static conditions. In contrast, a continuous ZIF-8 membrane was formed on the inside of the bore **110** of the hollow fiber **100** by continuously flowing bore solution at about 60 μ L/hour, however, the membrane had a low $\text{H}_2/\text{C}_3\text{H}_8$ selectivity.

A chart of Time vs. Flow Rate for pulsed flow conditions through the bore **110** of the hollow fiber **100** is illustrated in FIG. 12. Under pulsed flow conditions, a ZIF-8 membrane was formed on the inside of the bore **110** of the hollow membrane **100**, and, further, the pulsed-flow membrane had a higher $\text{H}_2/\text{C}_3\text{H}_8$ selectivity than the continuous-flow membrane discussed above.

To further test the effect of flow conditions, the aforementioned experiment was repeated using a one phase aqueous solvent system, a single phase organic solvent system (1-octanol), and a biphasic interfacial solvent system (aqueous/1-octanol), respectively.

First, an aqueous Zn^{+2} solution containing about 0.22g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL deionized water (DI) (about 0.018 mol/L) was flowed through the bore **110** at about 10 μ L/hour while an aqueous mIm solution containing about 9g mIm in about 80 mL deionized water (DI) (about 1.37 mol/L) was poured on the outer (shell) side surface **105**. After about 2 hours of bore solution flow, the pump was stopped for about 3.5 hours to provide a static growth step. After about 3.5 hours, the pump was continued for about 20 minutes. After about 20 minutes, the pump was stopped for another 3.5 hours to provide another static growth step. The reaction was stopped after about 9 hours and the hollow fiber **100** was rinsed with deionized water (DI) and methanol.

Second, a Zn^{+2} /1-octanol solution containing about .022g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL 1-octanol (about 0.018 mol/L) was flowed through the bore **110** at

about 10 μ L/hour while a mIm/1-octanol solution containing about 9g mIm in about 80 mL 1-octanol (about 1.37 mol/L) was poured on the outer (shell) side surface **105**. After about 2 hours of bore solution flow, the pump was stopped for about 3.5 hours to provide a static growth step. After about 3.5 hours, the pump was continued for about 20 minutes. After
5 about 20 minutes, the pump was stopped for another 3.5 hours to provide another static growth step. The reaction was stopped after about 9 hours and the hollow fiber **100** was rinsed with 1-octanol, deionized water (DI), heptanes and methanol.

Third, a Zn⁺²/1-octanol solution containing about 0.11g Zinc nitrate hexahydrate (Zn⁺²) in about 40 mL 1-octanol (about 0.018 mol/L) was flowed through the bore **110** at
10 about 10 μ L/hour while an aqueous mIm solution containing about 9g mIm in about 80 mL deionized water (DI) (about 1.37 mol/L) was poured on the outer (shell) side surface **105**. After about 2 hours of bore solution flow, the pump was stopped for about 3.5 hours to provide a static growth step. After about 3.5 hours, the pump was continued for about 20 minutes. After about 20 minutes, the pump was stopped for another 3.5 hours to provide
15 another static growth step. The reaction was stopped after about 9 hours and the hollow fiber **100** was rinsed with 1-octanol, deionized water (DI), heptanes and methanol.

A chart of Time vs. Flow Rate summarizing the examined static, continuous and pulsed flow conditions through the bore **110** of the hollow fiber **100** is illustrated in FIG. 18A.

A cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown in a polyamide-imide (e.g., TORLON®) hollow fiber with a static flow of a Zn⁺²/1-octanol bore solution is illustrated in FIG. 18B. As shown in FIG. 18B, static growth conditions produce dense, non-continuous coatings of ZIF-8 particles in the inner (bore) side surface **110** of the hollow fiber **100**. This is due to the lack of sufficient Zn²⁺ ions available in the microscale
25 bore of the hollow fiber **100** to sustain the film growth after the initial nucleation and growth of ZIF-8 crystals at the inner (bore) side surface **110** of the hollow fiber **100**.

A cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on a polyamide-imide (e.g., TORLON®) hollow fiber with continuous flow of a Zn⁺²/1-octanol bore solution is illustrated in FIG. 18B. As shown in FIG. 18C, continuous flow growth
30 conditions produced a thin, continuous membrane (about 3 μ m thickness) that was formed in the inner (bore) side surface **110** of the hollow fiber **100**. This is due to the relatively rapid transport of reactants to the interface under continuous flow, leading to rapid formation and closure of the ZIF-8 layer. The growing membrane itself becomes a barrier between the two

immiscible solvents, and confines the liquid-liquid interface into the gaps and interstices between the ZIF-8 crystals. *See* FIG. 15.

A cross-sectional view of a SEM micrograph of a ZIF-8 membrane grown on a polyamide-imide (e.g., TORLON®) hollow fiber with intermittent flow of a Zn^{+2} /1-octanol bore solution is illustrated in FIG. 18D. As shown in FIG. 18D, intermittent flow growth conditions produced a thicker, continuous membrane (about 8 μm thickness) that was formed in the inner (bore) side surface **110** of the hollow fiber **100**. The flow profile included an initial continuous growth step, followed by a static growth step interrupted by a brief reactant replenishment step. In an embodiment, the flow profile included an initial continuous growth step of about 10 μL /hour of a Zn^{+2} /1-octanol bore solution for about 2 hours, followed by a static growth step of about 0 μL /hour of the bore solution for about 3.5 hours, followed by a replenishment step of about 10 μL /hour of bore solution for about 20 minutes and followed by another static growth step of about 0 μL /hour of bore solution for about 3.5 hours. *See* FIG. 18A: flow profile 2.

Additionally, FIG. 17A shows lower-magnification images of ZIF-8 membranes formed on two hollow fibers **100**; and FIG. 17B shows the zinc elemental mapping, confirming the localization of the membrane to the inner (bore) side surface **110** of the hollow fiber **100**. X-ray diffraction confirmed the ZIF-8 crystal structure of the film. *See* FIG. 19.

Performance in Membrane Synthesis: Pulsed Flow Synthesis

Table 2 shows measurement of gas and liquid permeation properties for various supported ZIF-8 membranes.

Table 2. Measurement of Gas and Liquid Permeation Properties

Reference	Support	Thickness (μm)	Permeance (GPU)						
			H_2	CO_2	CH_4	C_3H_8	C_6H_{14}	C_6H_{12}	C_6H_6
Y. Pan	YSZ Tube	2.5	4400	1200	360	4			
Y. Pan	Al_2O_3 Disk	2.5	1100	390	240	2			
AJB	Torlon®	8	2900	500	270	60	2600	600	290

A X-ray Diffraction (XRD) chart of 2Theta (°) vs. intensity for simulated and experimental ZIF-8 membranes and polyamide-imide (e.g., TORLON®) hollow fiber, confirming formation and structure of supported ZIF-8 membranes on the bore **110** of the hollow fiber **100** is shown in FIG. 14.

5 Performance in Membrane Synthesis: Pulsed Flow and Stirred Synthesis

Table 3 shows the single-component gas permeation properties of a ZIF-8 membrane measured *in situ* using the reactor module **400** and gently stirring the outer (shell) side **105** solution.

Table 3. Measurement of Single-Component Gas Permeation Properties for grown ZIF-8

10 Membrane

Sample	Support	Flow Rate	Thickness (μm)	Permeance (GPU)			Selectivity
				H ₂	CH ₄	C ₃ H ₈	H ₂ /C ₃ H ₈
ZIF-8_10μL/hour Pulsed	Torlon®	10μL/hour	8	4200	400	35	120

Table 4 shows measurement of gas permeation properties of a ZIF-8 membrane when the mixture feed consisted of a 1:1 H₂/C₃H₈ mixture.

Table 4. Measurement of Mixed Gas Permeation Properties

Sample	Support	Thickness (μm)	Permeance (GPU)		Selectivity
			H ₂	C ₃ H ₈	H ₂ /C ₃ H ₈
Y. Pan	YSZ Tube	2.5	2000	4	470
ZIF-8_1010μL/hour	Torlon®	8	2250	26.4	85

Y. Pan, *et al.*, J. MEMBR. SCI. 421 (2012) 292.

15 Pulsed-Flow Synthesis of ZIF-8 Membranes

Using a macroporous polyamide-imide (e.g., TORLON®) hollow fiber and the material ZIF-8 as an archetype for a hollow fiber or tubular membrane synthesis, a series of

pulsed flow membrane synthesis experiments were performed. Table 5 shows combinations of precursor solutions and locations (bore/shell) tested to synthesize ZIF-8 membranes using a reactor module 400. Several examples of ZIF-8 membrane fabrication using the reactor module 400 are described below, and their results are shown in the SEM micrographs of FIGS. 17A-17B, 18A-18D and 20A-20D. For the experiments, a temperature probe 490 set at 30°C was inserted into the reactor module 400 during membrane growth.

Table 5. Combinations of Precursor Solutions Tested to Synthesize ZIF-8 Membranes Using IMMP Approach

Example	Bore Solution	Shell Solution	Molar Ratio $\text{Zn}^{+2}/\text{mIm}$	Membrane Location
1 (see FIGS. 17A-17B and 18A-18D)	0.018 mol/L Zn^{+2} in 1-octanol	1.37 mol/L mIm in DI	75	Bore (inner surface)
2 (see FIG. 20A)	0.018 mol/L Zn^{+2} in 1-octanol	1.37 mol/L mIm in DI	75	In fiber, closer to bore surface
3 (see FIG. 20B)	0.018 mol/L Zn^{+2} in 1-octanol	1.37 mol/L mIm in DI	75	In fiber, closer to bore surface
4 (see FIG. 20C)	1.37 mol/L mIm in DI	0.018 mol/L Zn^{+2} in 1-octanol	75	Shell (outer surface)
5 (see FIG. 20D)	1.37 mol/L mIm in DI	0.018 mol/L Zn^{+2} in 1-octanol	75	Shell (outer surface)

Example 1

First, about 10 mL of neat 1-octanol solvent was flowed through a bore 110 using a syringe pump.

Second, about 3 mL of a Zn^{+2} /1-octanol solution containing 0.11g Zinc nitrate hexahydrate (Zn^{+2}) in about 40 mL 1-octanol (about 0.018 mol/L) was flowed through the bore 110 of a horizontal hollow fiber 100 at a flow rate of about 10 $\mu\text{L}/\text{hour}$. In an embodiment, a limited Zn^{+2} /1-octanol solution containing about 0.005 mol/L to about 0.1 mol/L Zn^{+2} in 1-octanol may be used. In an embodiment, a limited Zn^{+2} /1-octanol solution containing about 0.01 mol/L to about 0.03 mol/L Zn^{+2} in 1-octanol may be used. Increasing the Zn^{+2} concentration to about 0.03 mol/L leads to reduction of the membrane thickness and increase in crystal nucleation.

About 70 mL of an aqueous mIm solution containing about 9g mIm in about 80 mL deionized water (DI) (about 1.37 mol/L) was slowly poured into the reactor module 400, immersing the outer (shell) side surface 105 of the hollow fiber 100. In an embodiment, an

excess aqueous mIm solution containing about 0.5 mol/L to about 10 mol/L mIm in deionized water (DI) may be used, provided that the mIm concentration is in excess. In an embodiment, an excess aqueous mIm solution containing about 1.2 mol/L to about 1.6 mol/L mIm in deionized water (DI) may be used.

5 The aqueous mIm (shell) solution was gently stirred at about 60 rpm to prevent the formation of local concentration gradients. In an embodiment, the aqueous mIm solution may be stirred at about 40 rpm to about 80 rpm.

 After about 2 hours of bore solution flow, the pump was stopped for about 3.5 hours to provide a static growth step. After about 3.5 hours, the pump was continued for about 20
10 minutes. After about 20 minutes, the pump was stopped for another 3.5 hours to provide another static growth step. In an embodiment, the bore solution flows at a first flow rate for a first period, the bore solution is stopped for a second period, the bore solution flows at a second flow rate for a third period and the bore solution is stopped for a fourth period. In an
15 embodiment, the first and second flow rate is about 10 μ L/hour to about 100 μ L/hour. In an embodiment, the first period is about 1 hour to about 3 hours, the second period is about 3 hours to about 4 hours, the third period is about 10 minutes to about 30 minutes and the fourth period is about 3 hours to about 4 hours.

 To stop the reaction, about 10 mL of neat 1-octanol solvent was pushed through the bore 110 while the outer (shell) side surface 105 was soaked in about 70 mL of neat DI (and
20 replaced three times) to remove the excess Zn^{+2} . Next, about 10 mL heptanes were pushed through the bore 110 while the outer (shell) side surface 105 was soaked in about 70 mL heptanes to remove the 1-octanol. Next, about 10 mL of hexane was pushed through the bore 110 while the outer (shell) side surface 105 was soaked in hexane to remove the heptanes. Then, about 20 mL methanol was flowed through the bore 110 while the outer (shell) side
25 surface 105 was soaked in about 70 mL methanol to remove the DI. The reactor module 400 was allowed to air dry at least 4 days before permeation testing.

Example 2

 First, about 10 mL DI was first flowed through the bore 110 followed by about 3 mL of an aqueous Zn^{+2} (bore) solution (about 0.018 mol/L). About 70 mL of an aqueous mIm
30 solution (about 1.37 mol/L) was added to the outer (shell) side surface 105 (i.e., slowly poured into the reactor module 400 and was gently stirred at about 60 rpm to prevent the formation of local concentration gradients) while the aqueous Zn^{+2} (bore) solution was flowed at about 10 μ L/hour for about 2 hours. After about 2 hours of bore solution flow, the

pump was stopped for about 3.5 hours to provide a static growth step. After about 3.5 hours, the pump was continued for about 20 minutes. After about 20 minutes, the pump was stopped for another 3.5 hours to provide another static growth step.

To stop the reaction, about 20 mL DI was flowed through the bore **110** while the outer (shell) side surface **105** was soaked in about 70 mL of neat DI (and replaced three times) to remove the excess Zn^{+2} . Then, about 20 mL methanol was flowed through the bore **110** while the outer (shell) side surface **105** was soaked in about 70 mL methanol to remove the DI. The reactor cell **400** was allowed to air dry at least 4 days before permeation testing.

Example 3

First, about 10 mL 1-octanol was first flowed through the bore **110** followed by about 3 mL of a Zn^{+2} /1-octanol (bore) solution (about 0.018 mol/L). About 70 mL of an mIm/1-octanol solution (about 1.37 mol/L) was added to the outer (shell) side surface **105** while the Zn^{+2} /1-octanol (bore) solution was flowed at about 10 $\mu\text{L}/\text{hour}$ for about 2 hours. After about 2 hours of bore solution flow, the pump was stopped for about 3.5 hours to provide a static growth step. After about 3.5 hours, the pump was continued for about 20 minutes. After about 20 minutes, the pump was stopped for another 3.5 hours to provide another static growth step.

To stop the reaction, about 10 mL neat 1-octanol solvent was pushed through the bore **110** while the outer (shell) side surface **105** was soaked in about 70 mL of neat 1-octanol solvent. Then, about 10 mL of heptanes were pushed through the bore **110** while the outer (shell) side surface **105** was soaked in about 70 mL of heptanes to remove the 1-octanol. Then, about 10 mL of hexane was pushed through the bore **110** while the outer (shell) side surface **105** was soaked in about 70 mL of hexane to remove the heptanes. Then, about 10 mL of methanol was pushed through the bore **110** while the outer (shell) side surface **105** was soaked in about 70 mL of methanol. The reactor module **400** was allowed to air dry at least 4 days before permeation testing.

Example 4

First, about 10 mL neat 1-octanol solvent was flowed through the bore **110** followed by about 3 mL of mIm/1-octanol (bore) solution (about 1.37 mol/L).

Second, About 70 mL of an aqueous Zn^{+2} solution (about 0.018 mol/L) was added to the outer (shell) side surface **105** while the mIm/octanol (bore) solution was flowed at about 10 $\mu\text{L}/\text{hour}$ for about 2 hours. After about 2 hours of bore solution flow, the pump was stopped for about 3.5 hours to provide a static growth step. After about 3.5 hours, the pump

was continued for about 20 minutes. After about 20 minutes, the pump was stopped for another 3.5 hours to provide another static growth step.

To stop the reaction, about 10 mL of neat 1-octanol solvent was pushed through the bore 110 while the outer (shell) side surface 105 was soaked in about 70 mL of neat DI (and replaced three times) to remove the excess Zn^{+2} . Next, about 10 mL heptanes were pushed through the bore 110 while the outer (shell) side surface 105 was soaked in about 70 mL heptanes to remove the 1-octanol. Next, about 10 mL of hexane was pushed through the bore 110 while the outer (shell) side surface 105 was soaked in hexane to remove the heptanes. Then, about 20 mL methanol was flowed through the bore 110 while the outer (shell) side surface 105 was soaked in about 70 mL methanol to remove the DI. The reactor module 400 was allowed to air dry at least 4 days before permeation testing.

Example 5

First, about 10 mL DI was flowed through the bore 110 followed by about 3 mL of an aqueous mIm solution (about 1.37 mol/L).

Second, about 70 mL of a Zn^{+2} /1-octanol solution (about 0.018 mol/L) was added to the outer (shell) side surface 105 while the aqueous mIm (bore) solution was flowed at about 10 $\mu\text{L}/\text{hour}$ for about 2 hours. After about 2 hours of bore solution flow, the pump was stopped for about 3.5 hours to provide a static growth step. After about 3.5 hours, the pump was continued for about 20 minutes. After about 20 minutes, the pump was stopped for another 3.5 hours to provide another static growth step.

The reaction was stopped by flowing about 20 mL DI through the bore 110 and exchanging the outer (shell) side surface 105 solution with neat 1-octanol solvent. Then, about 10 mL heptanes were flowed through the bore 110 while the outer (shell) side surface 105 was soaked in about 70 mL of heptanes. Then, about 10 mL hexane was flowed through the bore 110 while the outer (shell) side surface 105 was soaked in about 70 mL of hexane. Then, about 20 mL methanol was flowed through the bore 110 while the outer (shell) side surface 105 was soaked in about 70 mL of methanol.

Capping of Hollow Fiber Ends

A capping solution containing poly(dimethylsiloxane) (PDMS) (e.g., SYLGARD® 184 (Corning)) in a solvent may be used as a filler material to cap both ends of the hollow fiber 100. In an embodiment, a capping solution containing about 9 wt% PDMS in heptane was heated at about 90 °C with vigorous stirring for about 4 hours to thermally crosslink the

PDMS. In an embodiment, a capping solution of about 8 wt% to 10 wt% PDMS in heptane may be used.

After cooling to about 25 °C, about 2 µL droplet was applied from a pipette to each hollow fiber **100** end. Immediately upon applying the sealing solution, Argon gas was immediately flowed through the inner (bore) side **110** and followed by curing at about 120 °C for about 2 hours.

Performance of ZIF-8 Membranes Made Using IMMP Reactor Cell/Module

The separation properties of the ZIF-8 membrane grown on the inner bore of the polyamide-imide (e.g., TORLON®) hollow fiber **100** were characterized by hydrogen (H₂)/propane (C₃H₈) and propylene (C₃H₆)/propane (C₃H₈) binary equimolar mixture permeation as a function of temperature, with the reactor module **400** directly acting as a permeation cell. *See* FIG. 16. In an embodiment, the feed mixture may be selected from the group consisting of hydrogen/hydrocarbons, hydrogen/propane, propylene/propane and butenes/butanes.

A steady-state Wicke Kallenbach technique was used to test binary H₂/C₃H₈ and C₃H₆/C₃H₈ mixtures. Specifically, 1:1 feed mixtures were flowed through a bore **110** of the ZIF-8 membrane grown on the polyamide-imide (e.g., TORLON®) hollow fiber **100** at about 20 mL/min while an argon sweep gas was flowed across an outer (shell) side surface **105** of the hollow fiber **100** at about 20 mL/min. *See e.g.*, FIGS. 21A-21B, 22A-22B and 23A-23B. In FIGS. 21A-21B, 22A-22B and 23A-23B, the error bars were estimated from characterization of three independent ZIF-8 membrane samples.

A gas chromatograph with TCD and FID detectors was used to determine the composition of permeate. At least 3 GC injections were collected (median permeance values were reported) at each temperature after waiting 30 minutes for steady-state conditions.

The ZIF-8 membranes in polyamide-imide (e.g., TORLON®) hollow fibers **100** were formed using the reaction conditions of Example 1 under intermittent flow conditions (see FIG. 18A: flow profile 2). The as-made ZIF-8 membranes on polyamide-imide (e.g., TORLON®) hollow fibers **100** exhibited clear molecular sieving properties: high H₂ permeances, sharp H₂/C₃H₈ separation factors as high as 125 at 120°C (see FIG. 22A), and strong temperature dependence of H₂ permeance with temperature, indicating activated molecular transport through the ZIF-8 pores. Further, the example ZIF-8 membrane on polyamide-imide (e.g., TORLON®) hollow fiber **100** proved to be robust showing no decline in permeation properties after six weeks of testing and multiple heating/cooling cycles.

While the permeation properties were dominated by molecular sieving, the C₃ isomer (especially C₃H₈) permeances were much larger than those expected from previous studies^{8, 17-20} and prevented a high C₃H₆/C₃H₈ separation factor. *See* FIG. 23B. It was hypothesized that the high C₃ isomer permeances were due to both molecular transport through the ZIF-8 membrane as well as due to bypassing of the ZIF-8 membrane by the feed molecules through the ends of the fiber. *See* FIG. 24A.

To suppress this membrane bypass, we include a capping step to the IMMP approach, accomplished by applying a controlled amount of a solution containing poly(dimethylsiloxane) (PDMS) to the ends of the mounted hollow fibers **100**. *See* FIG. 24B.

The PDMS solution is readily absorbed by capillary action into the hollow fiber **100**, and blocks the pores of the hollow fiber **100** support. *See* FIGS. 25A and 25B. SEM cross-sectional imaging (see FIG. 25A) and EDX mapping (see FIG. 25B) indicated that the fiber matrix is completely covered by PDMS while the bore remains unblocked. Since the permeances of the feed gases through PDMS are 3 orders of magnitude lower than through the macroporous hollow fiber **100** support, the C₃H₈ flux should decrease substantially after capping. After curing the PDMS-sealed hollow fibers **100**, the H₂/C₃H₈ separation factor is now much higher (370 at 120°C) (see FIG. 21A) and the C₃H₆/C₃H₈ separation factor is also higher (12 at 25°C) (see FIG. 21B), consistent with previously reported ZIF-8 membranes with low defect densities.^{8, 17-20} Notably, the C₃H₈ permeance decreased by a factor of 10 after capping. This indicates that most of the propane was previously bypassing the ZIF-8 layer and that the addition of the capping step to the IMMP largely shuts down this non-selective permeation path. The permeate stream contains 92% C₃H₆/8% C₃H₈, which is a significant upgrade from the equimolar feed stream.

Performance of Bundle of ZIF-8 Membranes Made Using IMMP Reactor Cell/Module

In large-scale gas separations with hollow fiber membranes, high membrane areas per unit module volume are achieved by bundling large numbers of fibers in the permeation module. The present invention has the advantage of being inherently a modular approach that should allow independent processing of membranes in each fiber constituting a bundle.

To demonstrate this concept, we applied reactor module **400** to the simultaneous processing of three polyamide-imide (e.g., TORLON®) hollow fiber **100** supports. The processing conditions were identical to the case of the single-fiber membranes, except that the total feed solution initially introduced to the bore and the flow rate on the bore side was increased by a factor of 3 so that the flow rate through individual hollow fibers **100** was

maintained constant in relation to the single-fiber membrane fabrication described earlier. The ends of the hollow fibers **100** were capped in a similar manner as described earlier.

FIGS. 23A and 23B show that the H_2/C_3H_8 and C_3H_6/C_3H_8 separation behavior is near-identical to the single-fiber membranes (see FIGS. 21A and 21B), thereby clearly demonstrating the potential for scalability of the IMMP approach. We also note that the separation factor values of the ZIF-8 membranes are very sensitive to the small permeance of C_3H_8 (~2.5 GPU in the present invention). With further improvements in the capping methods (*e.g.*, using less permeable polymers than PDMS) and optimization of the ZIF-8 membrane growth conditions, the small C_3H_8 permeance can be further reduced and the separation factor further increased, leading to a highly attractive membrane platform for hydrocarbon separations. Given the overall importance of tunable ZIF materials for a range of hydrocarbon separations, the membrane processing approach reported here overcomes many of the limitations of current processes and moves significantly towards realizing scalable molecular sieving MOF membranes.

The embodiments and examples set forth herein are presented to best explain the present invention and its practical application and to thereby enable those skilled in the art to make and utilize the invention. However, those skilled in the art will recognize that the foregoing description and examples have been presented for the purpose of illustration and example only. The description as set forth is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many modifications and variations are possible in light of the above teaching without departing from the spirit and scope of the following claims.

Definitions

As used herein, the terms “a,” “an,” “the,” and “said” when used in conjunction with the term “comprising” means one or more, unless the context dictates otherwise.

As used herein, the term “about” means the stated value plus or minus a margin of error or plus or minus 10% if no method of measurement is indicated.

As used herein, the term “or” means “and/or” unless explicitly indicated to refer to alternatives only or if the alternatives are mutually exclusive.

As used herein, the terms “comprising,” “comprises,” and “comprise” are open-ended transition terms used to transition from a subject recited before the term to one or more elements recited after the term, where the element or elements listed after the transition term are not necessarily the only elements that make up the subject.

As used herein, the terms “containing,” “contains,” and “contain” have the same open-ended meaning as “comprising,” “comprises,” and “comprise,” provided above.

As used herein, the terms “having,” “has,” and “have” have the same open-ended meaning as “comprising,” “comprises,” and “comprise,” provided above.

5 As used herein, the terms “including,” “includes,” and “include” have the same open-ended meaning as “comprising,” “comprises,” and “comprise,” provided above.

As used herein, the phrase “consisting of” is a closed transition term used to transition from a subject recited before the term to one or more material elements recited after the term, where the material element or elements listed after the transition term are the only material
10 elements that make up the subject.

As used herein, the phrase “consisting essentially of” occupies a middle ground, allowing the addition non-material elements that do not substantially change the nature of the invention, such as various buffers, differing salts, extra wash or precipitation steps, pH modifiers, and the like.

15 As used herein, the phrase “growth solvent” means a liquid in which the MOF seed crystals can be increased in size, either by crystal deposition or synthesis, but without harming the polymer.

As used herein, the phrase “nanocrystals” means the seed crystals have an average size of less than one micron, preferably about 400-600 nm, and a size distribution of +/- 10%.
20 For polymers with very small pores, a smaller seed crystal may be needed, and therefore the seed crystal size can be reduced as needed.

As used herein, the phrase “non-solvent” means a liquid in which the MOF precursors have a low solubility, such that on introducing the non-solvent to the mixture, the precursors are unable to stay in solution and condense quickly to form a large number of
25 nuclei, which are the seeds for growing a large number of very small crystals.

As used herein, the phrase “seed solvent” means a liquid in which the MOF nanocrystals can be carried into the pores of the polymer. Thus, the seed crystals should have low solubility in the solvent and the solvent should penetrate or wet the pores of the polymer, but without harming the polymer.

30 As used herein, the term “simultaneously” means occurring at the same time or about the same time, including concurrently.

As used herein, “starting material” means that the recited chemical is made or purchased for use as an early reactant in the synthetic pathway. However, if made, rather than purchased, there may be other ingredients that pre-date same.

Abbreviations

5 The following abbreviations are used herein:

DI	Deionized water
DLS	Dynamic light scattering
EDS	Energy dispersive X-ray spectroscopy
H ₂	Hydrogen
IMMP	Interfacial Microfluidic Membrane Processing
mIm	2-methyl imidazole
MOF	Metal organic framework
PDMS	Poly(dimethylsiloxane)
C ₃ H ₈	Propane
C ₃ H ₆	Propylene
SEM	Scanning electron microscope
XRD	X-ray diffraction
ZIF	Zeolitic imidazolate framework
ZIF-8	Zeolitic imidazolate framework 8
ZIF-90	Zeolitic imidazolate framework 90

Incorporation By Reference

All patents and patent applications, articles, reports, and other documents cited herein are fully incorporated by reference to the extent they are not inconsistent with this invention, as follows:

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- 2) K. Varoon, *et al.*, SCIENCE **334** (2011) 72-75.
- 3) M. Shah, *et al.*, IND. ENG. CHEM. RES. **51** (2012) 2179-2199.
- 4) M. G. Buonomenna, RSC ADVANCES **3** (2013) 5694-5740.
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- 15 6) T. Cao, *et al.*, SCIENCE **334** (2011) 1533-1538.
- 7) J. Choi, *et al.*, SCIENCE **334** (2009) 590-593.
- 8) Y. Pan, *et al.*, J. MEMBR. SCI. **421** (2012) 292-298.

- 9) J. A. Thompson, *et al.*, CHEM. MATER. **24** (2012) 1930-1936.
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- 12) A. J. Brown, *et al.*, ANGEW. CHEM. INT. ED. **51** (2012) 10615-10618.
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- 17) Y. Pan, *et al.*, J. MEMBR. SCI. **390** (2012) 93-98.
- 10 18) H. Bux, *et al.*, CHEM. MATER. **23** (2011) 2262-2269.
- 19) Y. Pan, Z. Lai, CHEM. COMM'N. **47** (2011) 10275-10277.
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CLAIMS

What is claimed is:

- 1) A reactor cell for flow processing molecular sieving membranes, comprising:
 - a) A reactor module having a base shape and a first height, wherein the base
5 shape is selected from the group consisting of square, rectangular, circular and ellipse; wherein a reactor chamber extends into the reactor module from an upper surface; wherein a first hole extends into the reactor chamber from a first surface, a second hole opposing the first hole extends into the reactor chamber from a second surface, a third hole extends into the reactor chamber
10 from a third surface and a fourth hole opposing the third hole extends into the reactor chamber from a fourth surface; wherein the first hole is fluidically connected to a first inlet, the second hole is fluidically connected to a first outlet, the third hole is fluidically connected to a second inlet and the fourth hole is fluidically connected to a second outlet;
 - b) a reactor module cover having the same base shape as the reactor module and
15 a second height, wherein the reactor module cover is fastened to the reactor module to seal the reactor chamber; and
 - c) a hollow fiber having a first end and a second end, wherein a length of the first end is supported by and sealed into the first hole and a length of the second end is supported by and sealed into the second hole; wherein the first and
20 second ends of the hollow fiber are capped with a capping solution.
- 2) The device of claim 1, wherein the first hole extends into the reactor chamber
25 from the first surface, the second hole opposing the first hole extends into the reactor chamber from the second surface, the third hole extends into the reactor chamber from the first surface and the fourth hole opposing the third hole extends into the reactor chamber from the second surface.
- 3) The device of claim 1, wherein the first hole extends into the reactor chamber
30 from the first surface, the second hole opposing the first hole extends into the reactor chamber from the second surface, the third hole extends into the reactor chamber from an upper surface of a reactor module cover and the fourth hole opposing the third hole extends into the reactor chamber from a bottom surface of the reactor chamber.

- 4) The device of claim 1, wherein the reactor module and cover are constructed of a metal or a plastic.
- 5) The device of claim 1, wherein the reactor module and cover are constructed from a metal selected from the group consisting of stainless steel and stainless steel alloys.
- 6) The device of claim 1, where the plastic is selected from the group consisting of polyether ketone (PEEK), polymethylene, polytetrafluorethylene (PTFE).
- 7) The device of claim 1, wherein the reactor module and cover are constructed from stainless steel 304.
- 8) The device of claim 1, wherein the first and second holes are offset vertically from the third and fourth holes.
- 9) The device of claim 1, wherein the lengths of the first and second ends of the hollow fiber are sealed into the first and second holes with an adhesive.
- 10) The device of claim 1, wherein the capping solution is about 8 wt% to about 10 wt% poly(dimethylsiloxane) (PDMS) in heptane.
- 11) A method of making the device of claim 1, comprising the steps of:
- a) fabricating a reactor chamber extending into the reactor module from the upper surface of the reactor module;
 - b) fabricating an O-ring groove with an inner dimension slightly larger than and offset from the outer dimension of the reactor chamber;
 - c) fabricating the first hole extending into the reactor chamber from the first surface and the second hole opposing the first hole and extending into the reactor chamber from the second surface;
 - d) fabricating a third hole extending into the reactor chamber from a third surface and a fourth hole opposing the third hole and extending into the reactor chamber from a fourth surface;
 - e) supporting and sealing the length of the first end of the hollow fiber in the first hole and the length of the second end of the hollow fiber into the second hole;
 - f) capping the first and second ends of the hollow fiber with a capping solution; and
 - g) fabricating the reactor module cover to fit on the upper surface of the reactor module and fastening the reactor module cover to seal the reactor chamber.

- 12) The method of claim 11 further comprising the steps of:
- a) fluidically connecting a bore solution to the first inlet;
 - b) fluidically connecting a shell solution to the second inlet; and
 - c) growing a molecular sieving membrane on the inner bore surface of the hollow fiber.
- 13) The method of claim 12, wherein the bore solution contains a limited Zn^{+2} concentration ranging from about 0.005 to about 0.1 mol/L Zn^{+2} in 1-octanol.
- 14) The method of claim 12, wherein the bore solution contains a limited Zn^{+2} concentration ranging from about 0.01 to about 0.03 mol/L Zn^{+2} in 1-octanol.
- 15) The method of claim 12, wherein the bore solution is about 0.018 mol/L Zn^{+2} in 1-octanol.
- 16) The method of claim 12, wherein the shell solution contains an excess mIm ligand concentration ranging from about 0.5 to about 10 mol/L 2-methyl imidazole (mIm) in deionized water.
- 17) The method of claim 12, wherein the shell solution contains an excess mIm ligand concentration ranging from about 1.2 to about 1.6 mol/L 2-methyl imidazole (mIm) in deionized water.
- 18) The method of claim 12, wherein the shell solution is about 1.37 mol/L mIm in deionized water.
- 19) The method of claim 12, further comprising the step of gently stirring the shell solution to prevent formation of local concentration gradients.
- 20) The method of claim 19, wherein the shell solution is stirred at about 40 rpm to about 80 rpm.
- 21) The method of claim 12, further comprising the steps of
- a) flowing the bore solution at a first flow rate for a first period;
 - b) stopping the first flow rate of the bore solution for a second period;
 - c) flowing the bore solution at a second flow rate for a third period; and
 - d) stopping the second flow rate of the bore solution for a fourth period.
- 22) The method of claim 21, wherein the first and second flow rates are about 1 $\mu\text{L}/\text{hour}$ to about 1000 $\mu\text{L}/\text{hour}$ per individual hollow fiber.
- 23) The method of claim 21, wherein the first and second flow rates are about 10 $\mu\text{L}/\text{hour}$ to about 100 $\mu\text{L}/\text{hour}$ per individual hollow fiber.

- 24) The method of claim 21, wherein the first period is about 1 hour to about 3 hours, the second period is about 3 hours to about 4 hours, the third period is about 10 minutes to about 30 minutes, and the fourth period is about 3 hours to about 4 hours.
- 5 25) The method of claim 12, further comprising the step of rinsing the membrane in solvents selected from the group consisting of 1-octanol, heptanes, hexane, methanol and deionized water.
- 26) A method of using the device of claim 12, comprising the steps of:
- 10 a) fluidically connecting a feed mixture to the first inlet;
b) fluidically connecting a sweep gas to the second inlet;
c) collecting a separated mixture from the first outlet; and
d) collecting permeate from the second outlet.
- 27) The method of claim 26, wherein the feed mixture is selected from the group consisting of hydrogen/hydrocarbons, hydrogen/propane, propylene/propane and butenes/butanes.
- 15 28) The method of claim 27, wherein the feed mixture is selected from the group consisting of hydrogen/propane, propylene/propane and butenes/butanes.

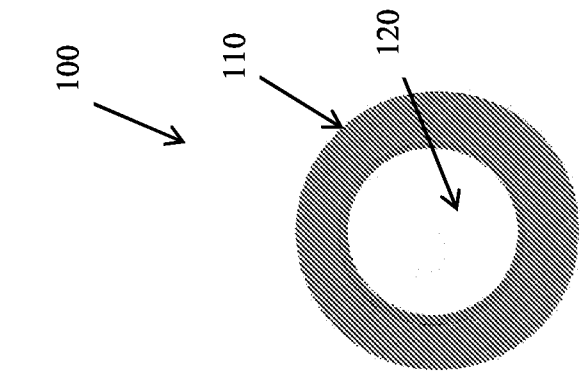


FIG. 1B

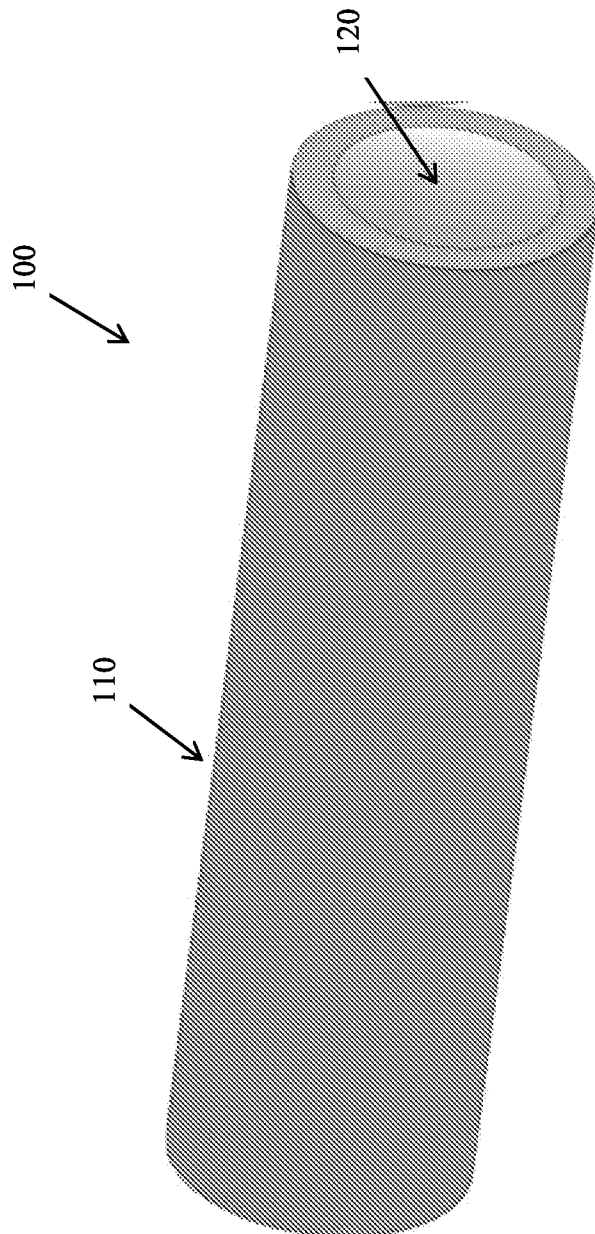


FIG. 1A

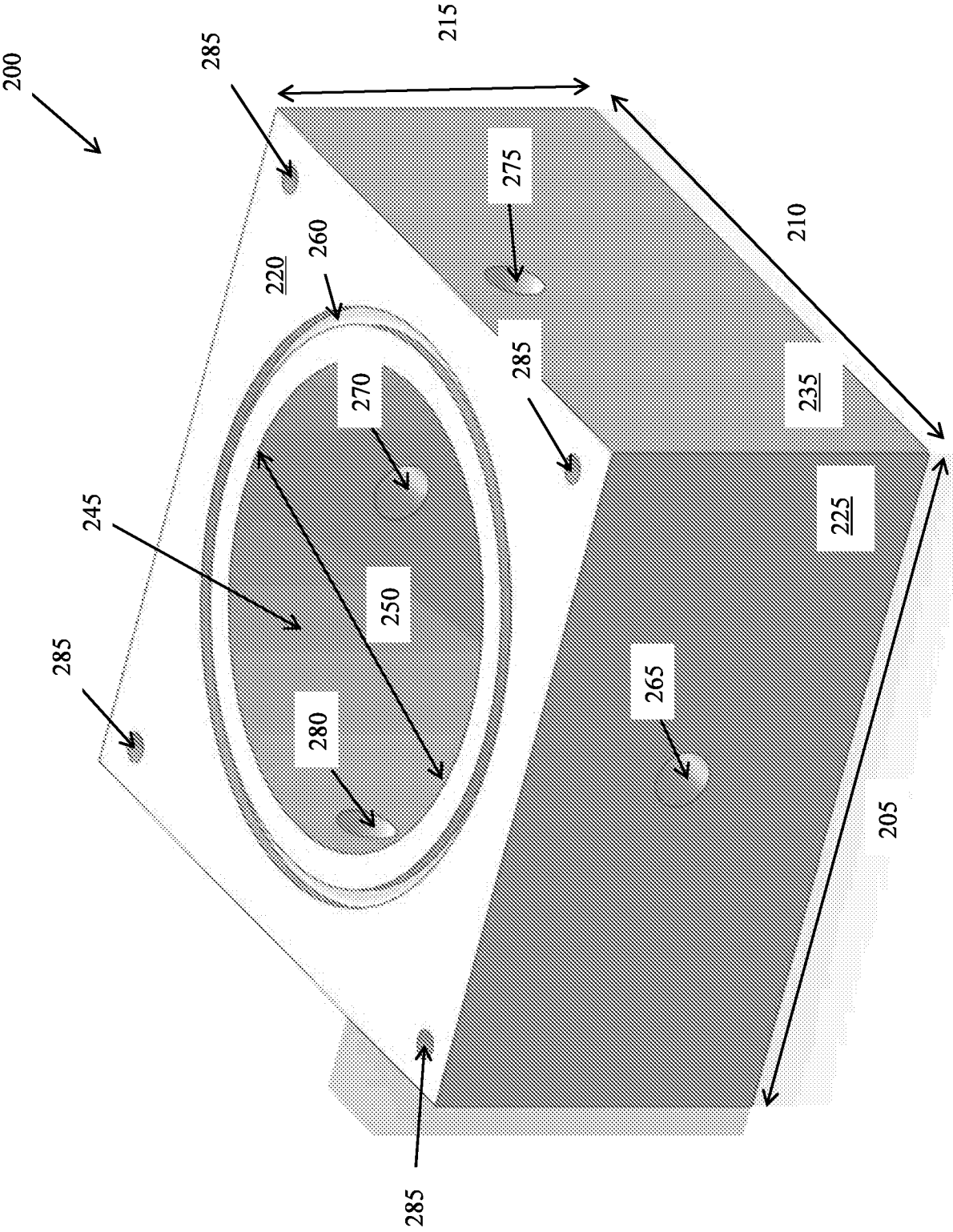


FIG. 2

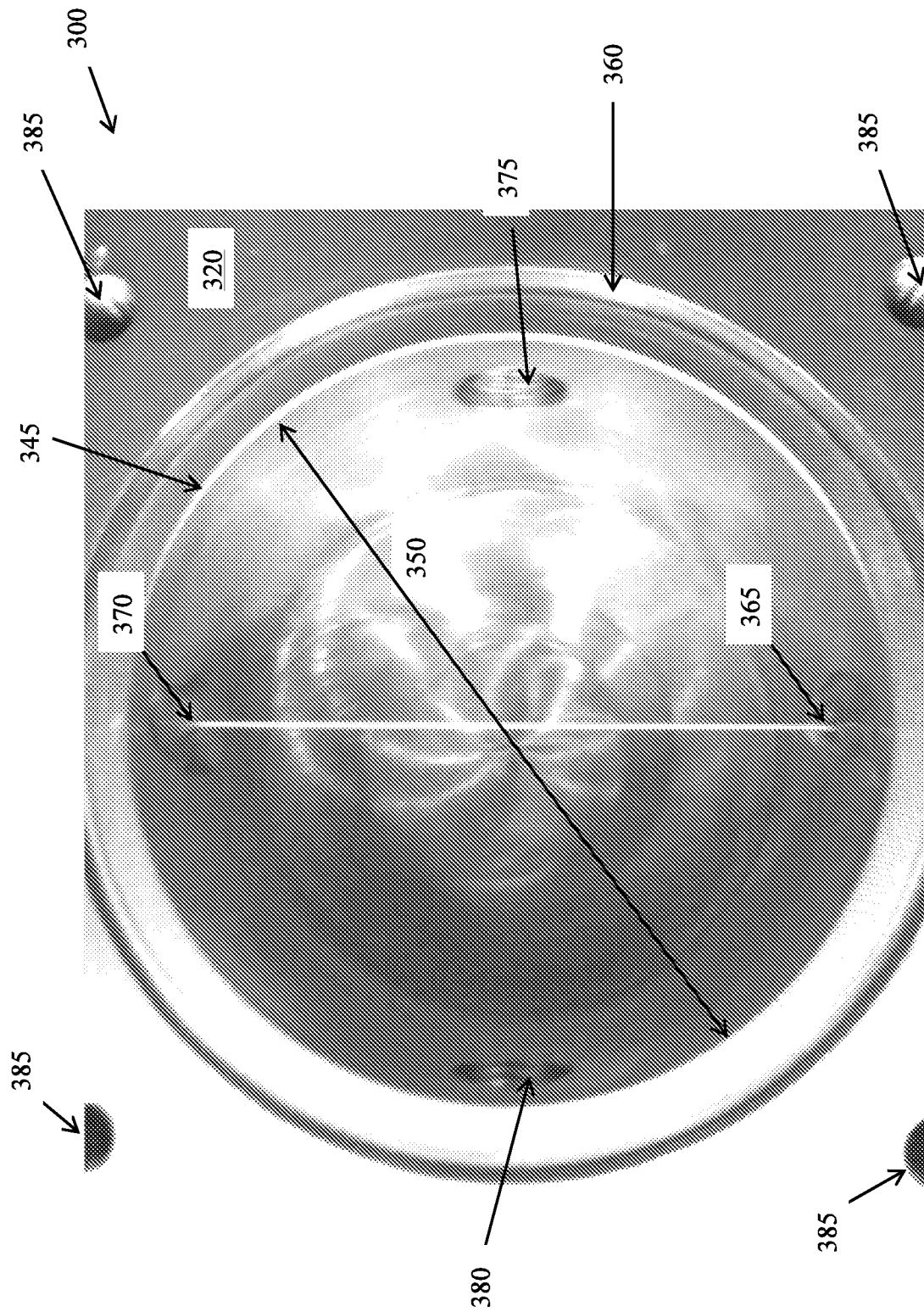


FIG. 3

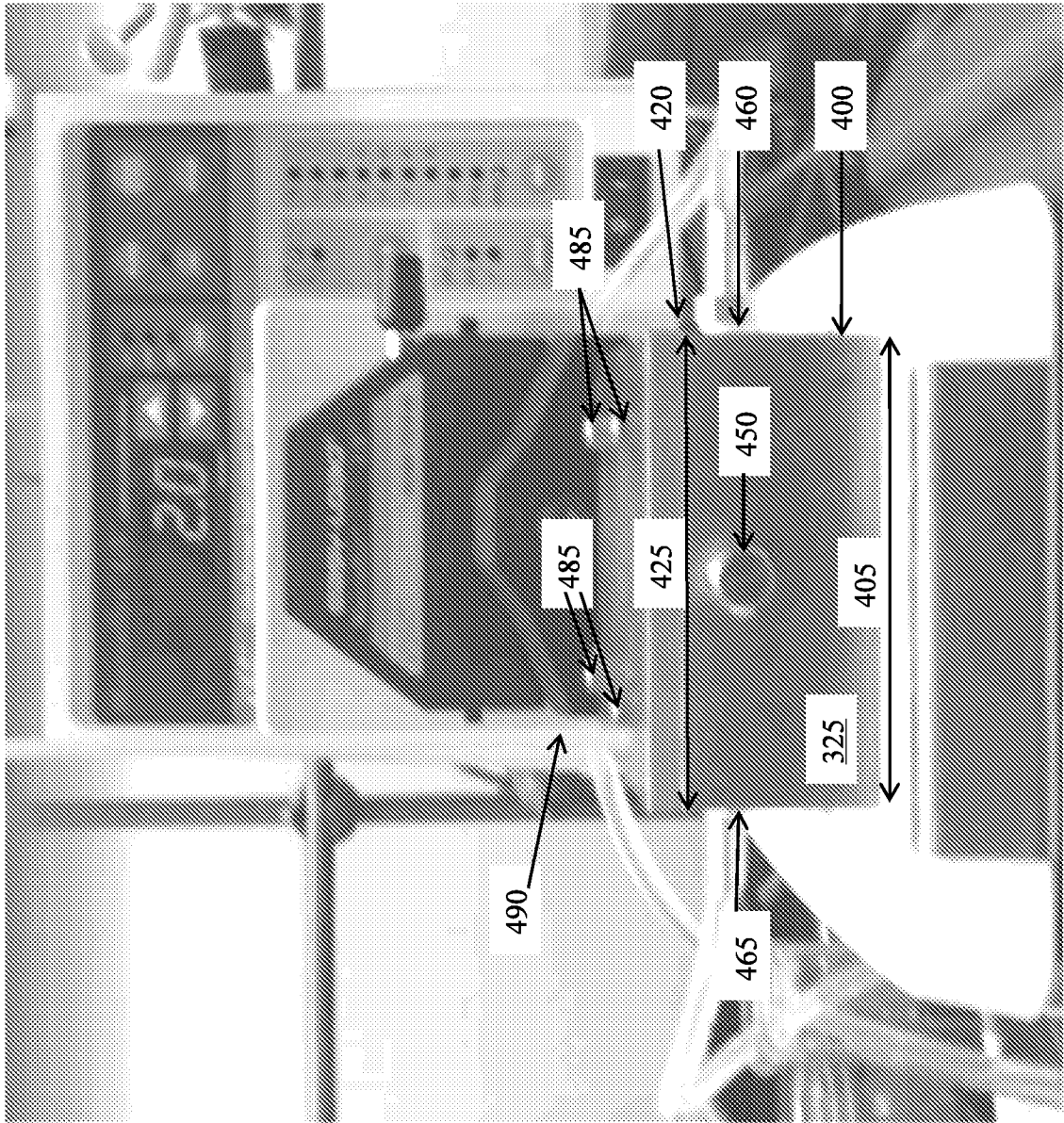


FIG. 4

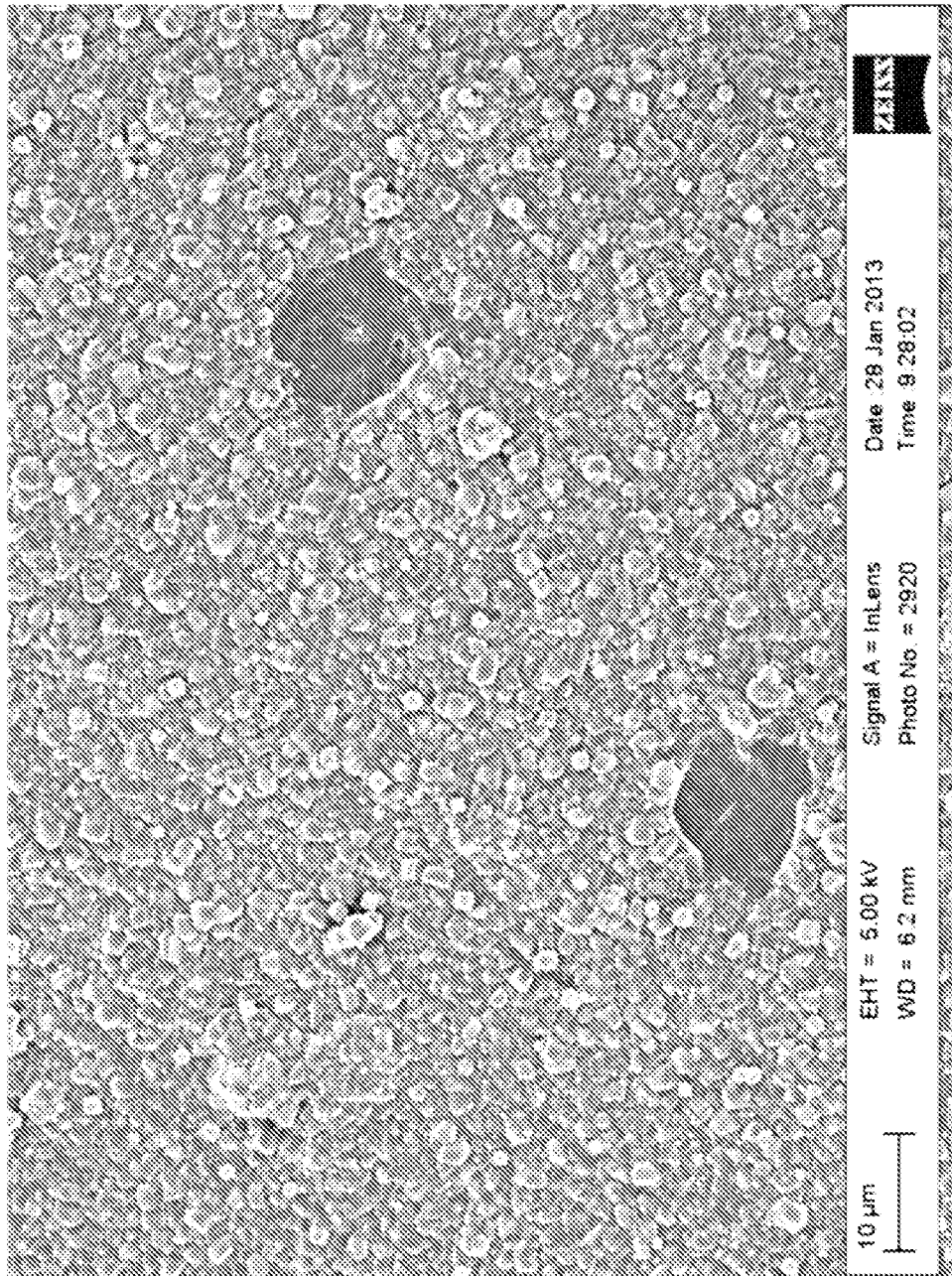


FIG. 5A

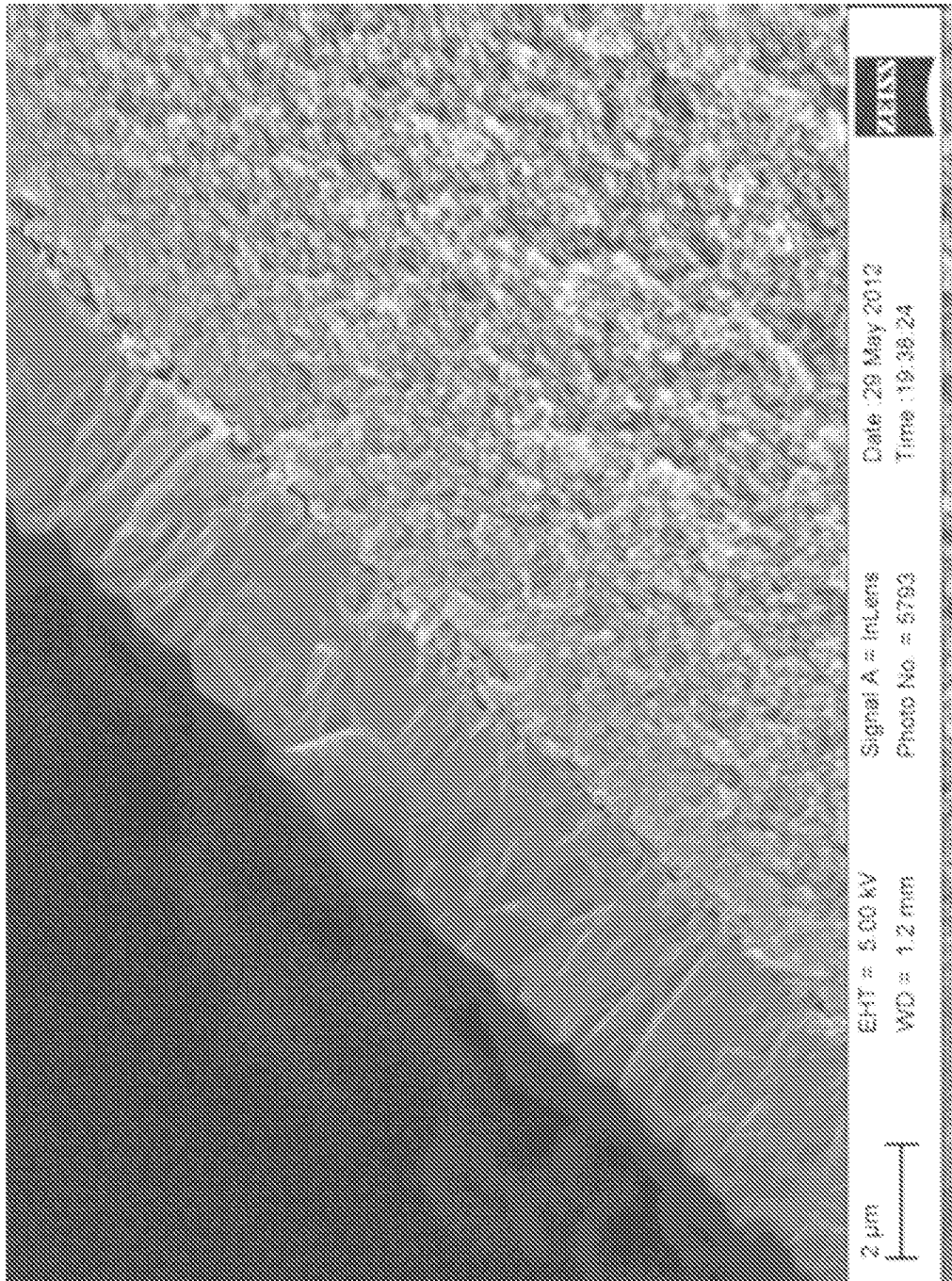


FIG. 5B

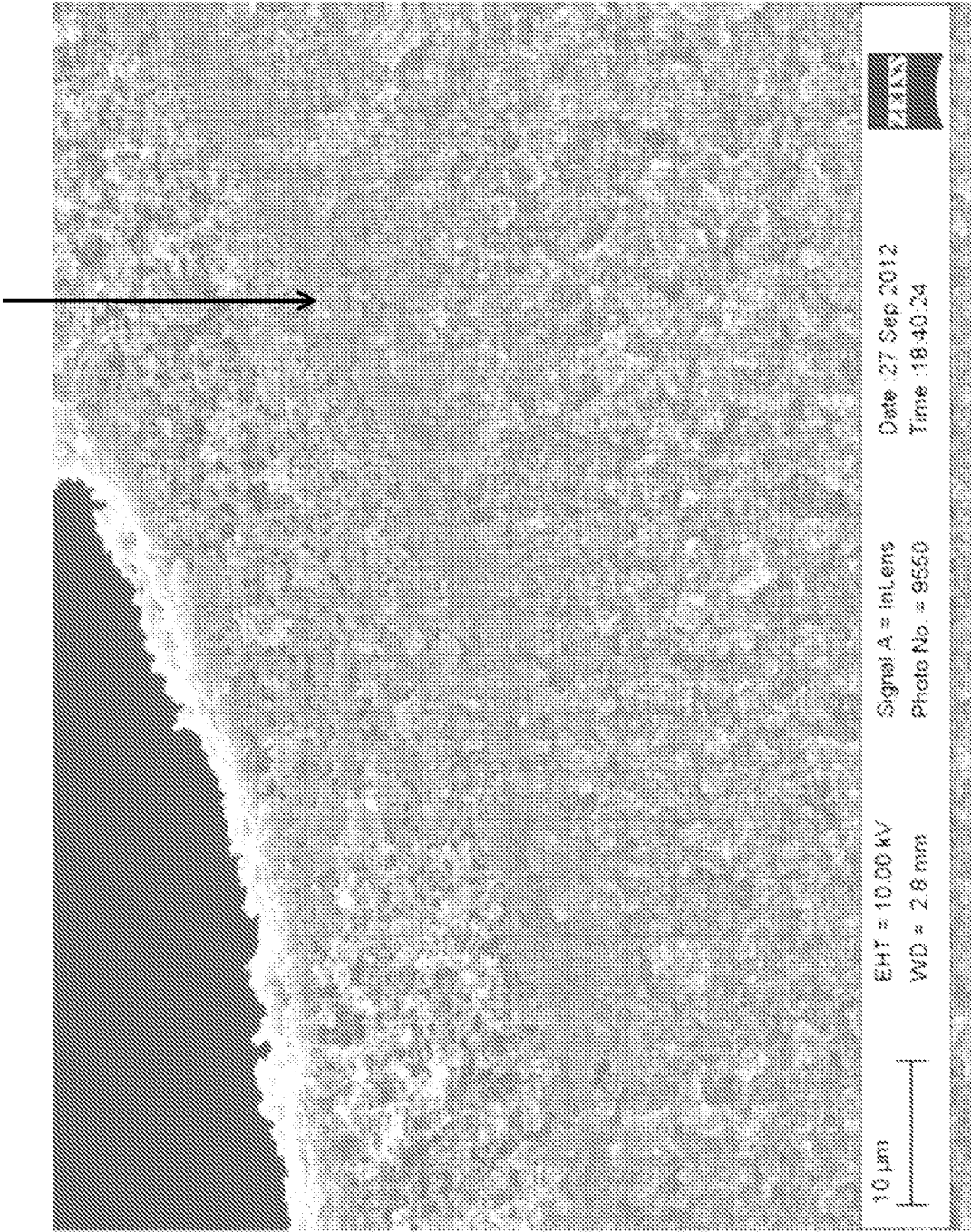


FIG. 6A

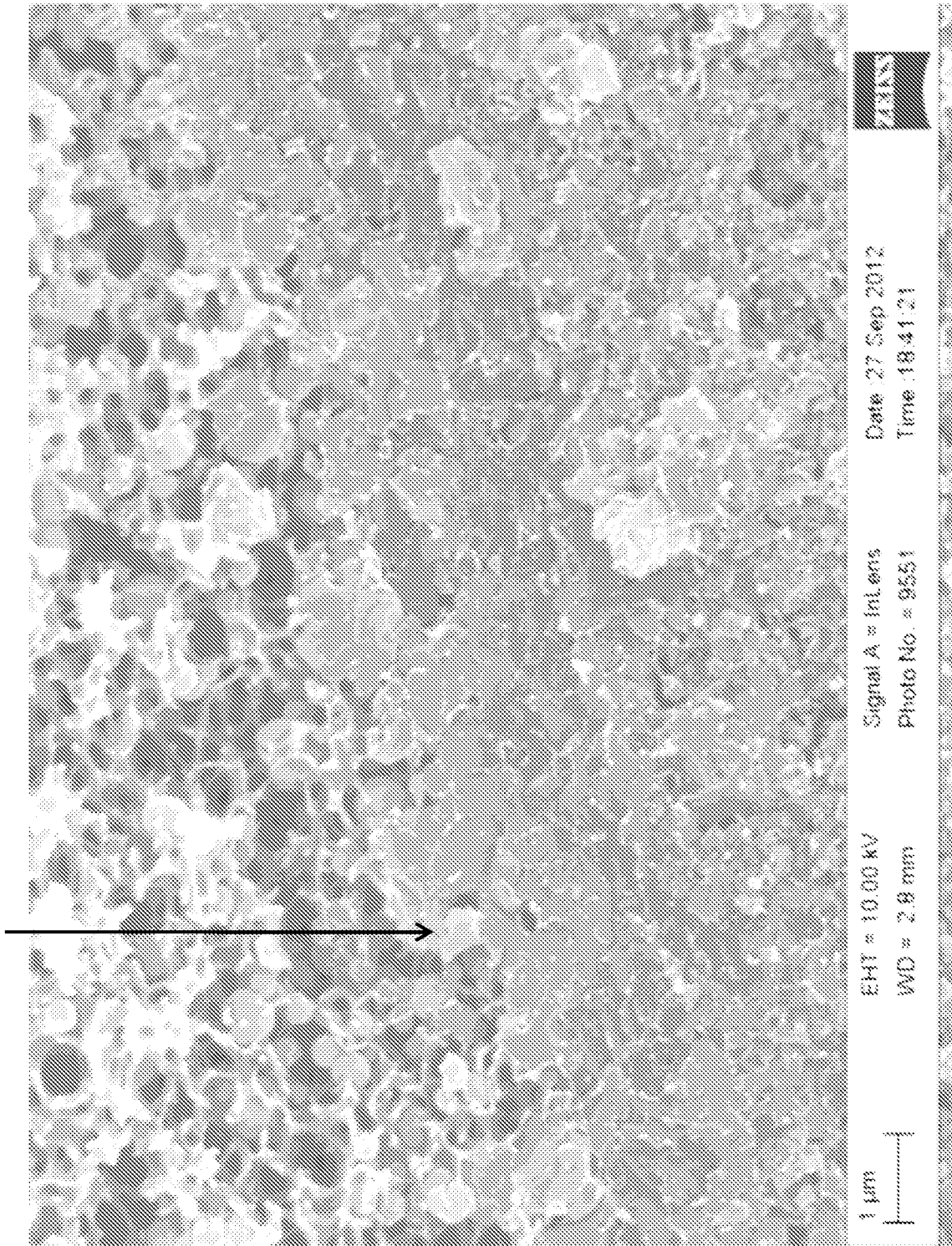


FIG. 6B

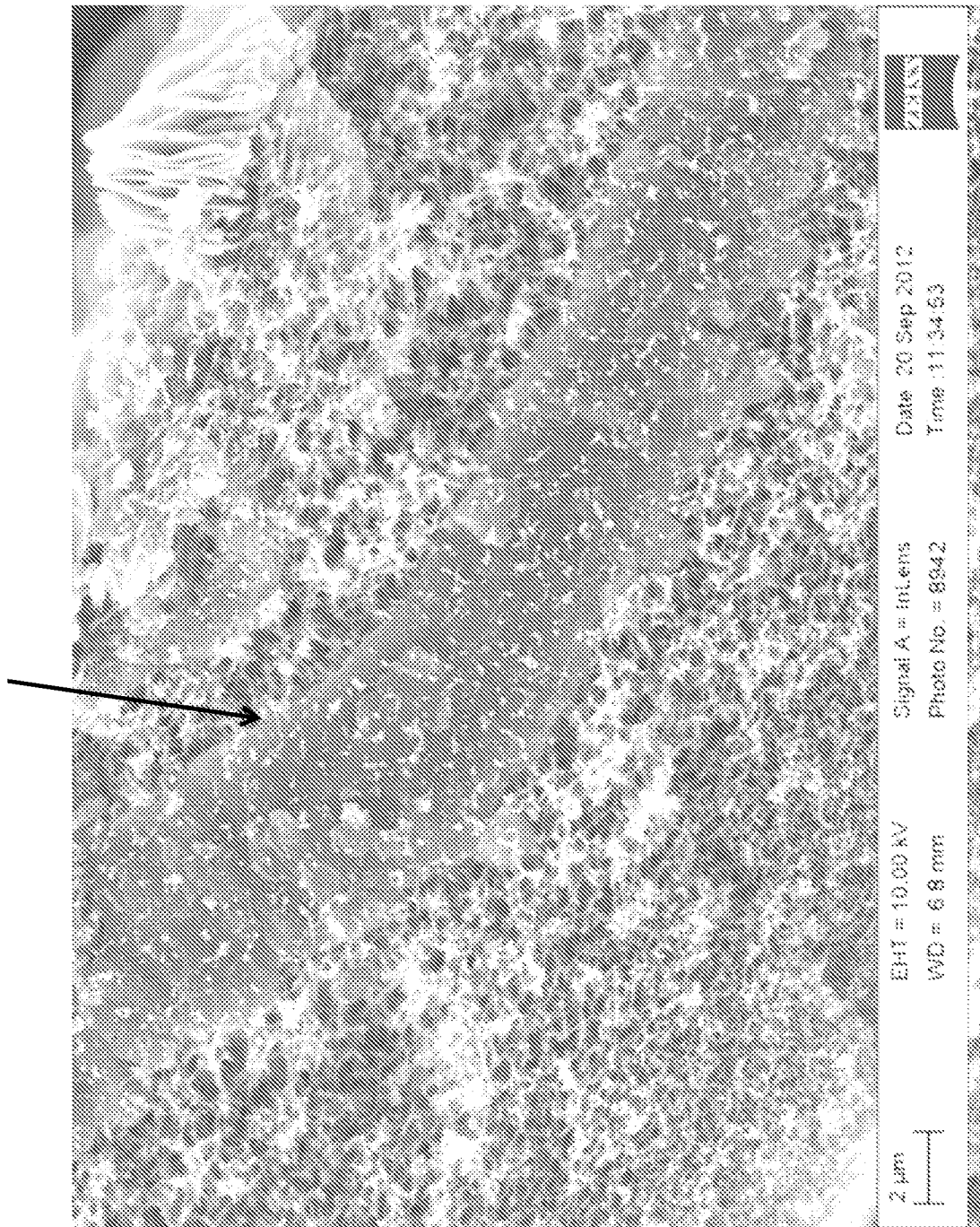


FIG. 7A

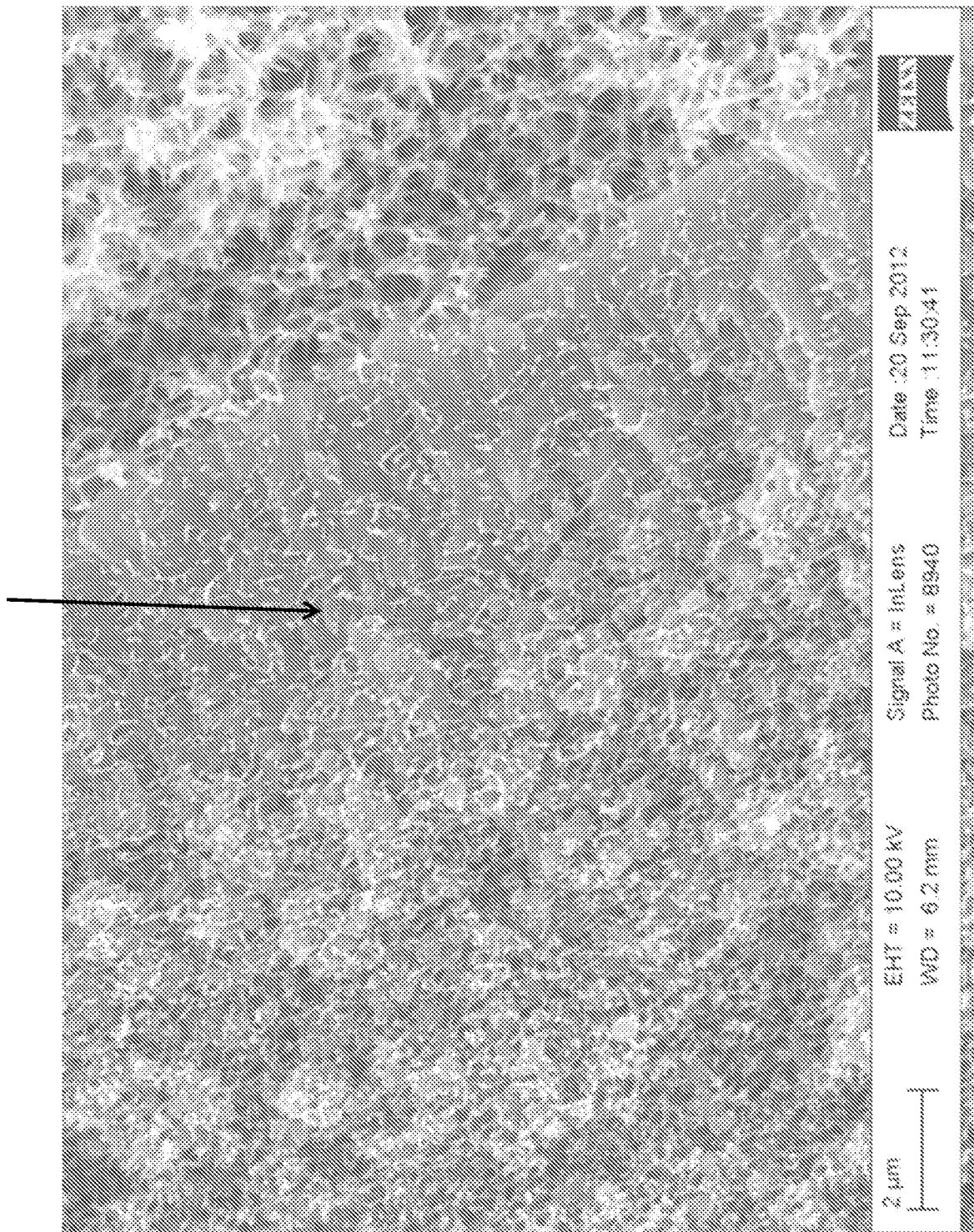


FIG. 7B

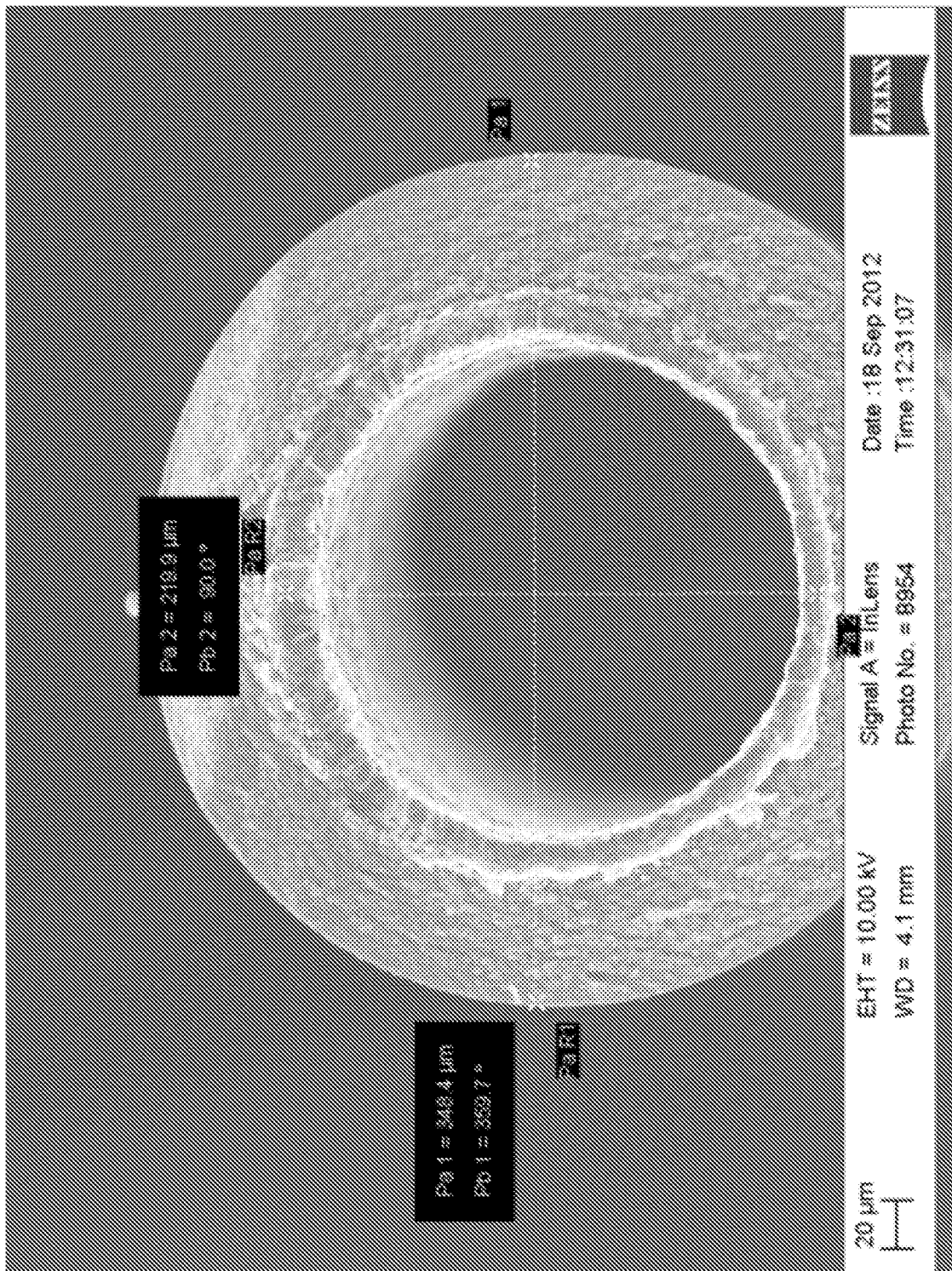


FIG. 8A

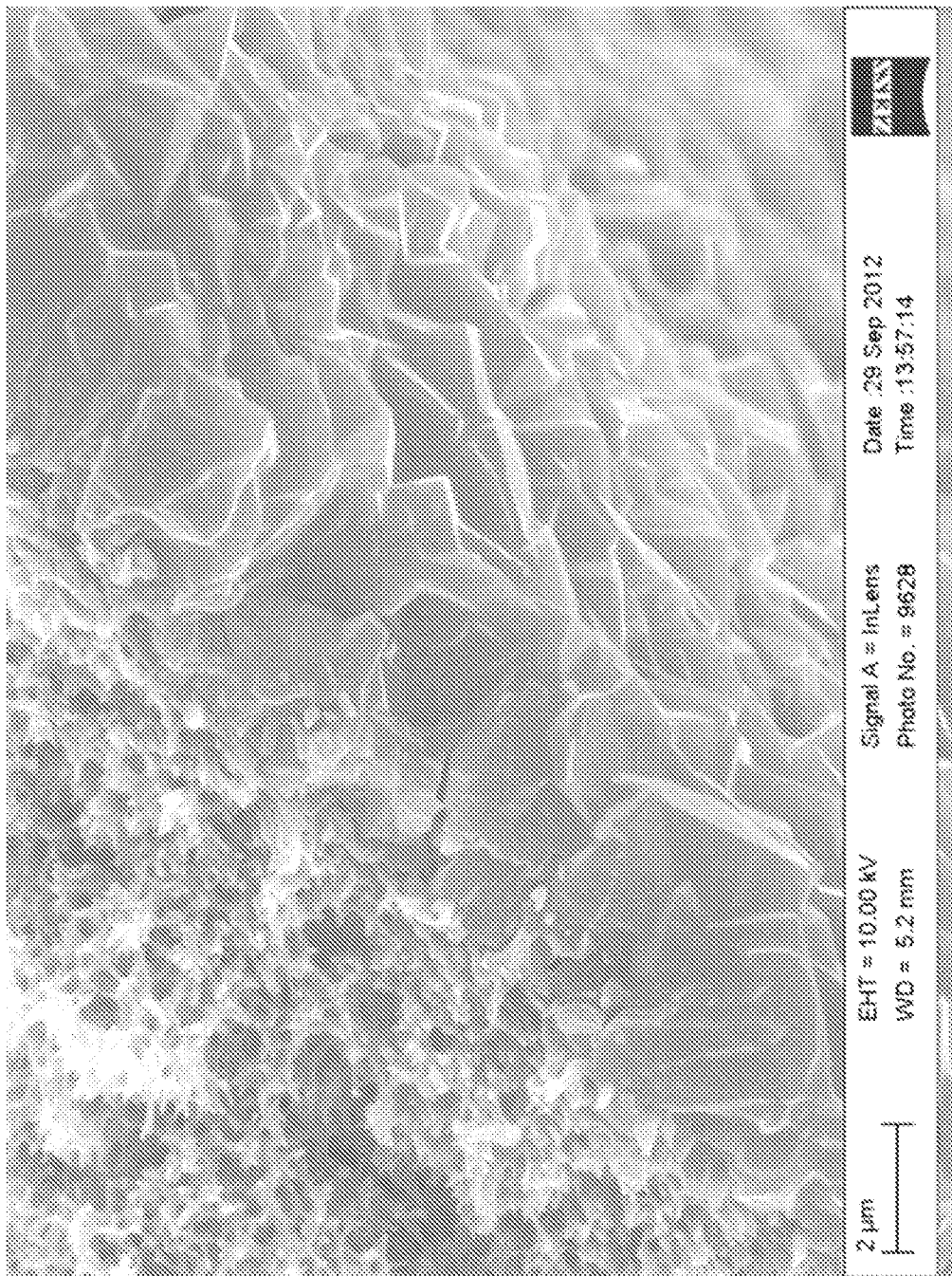


FIG. 8B

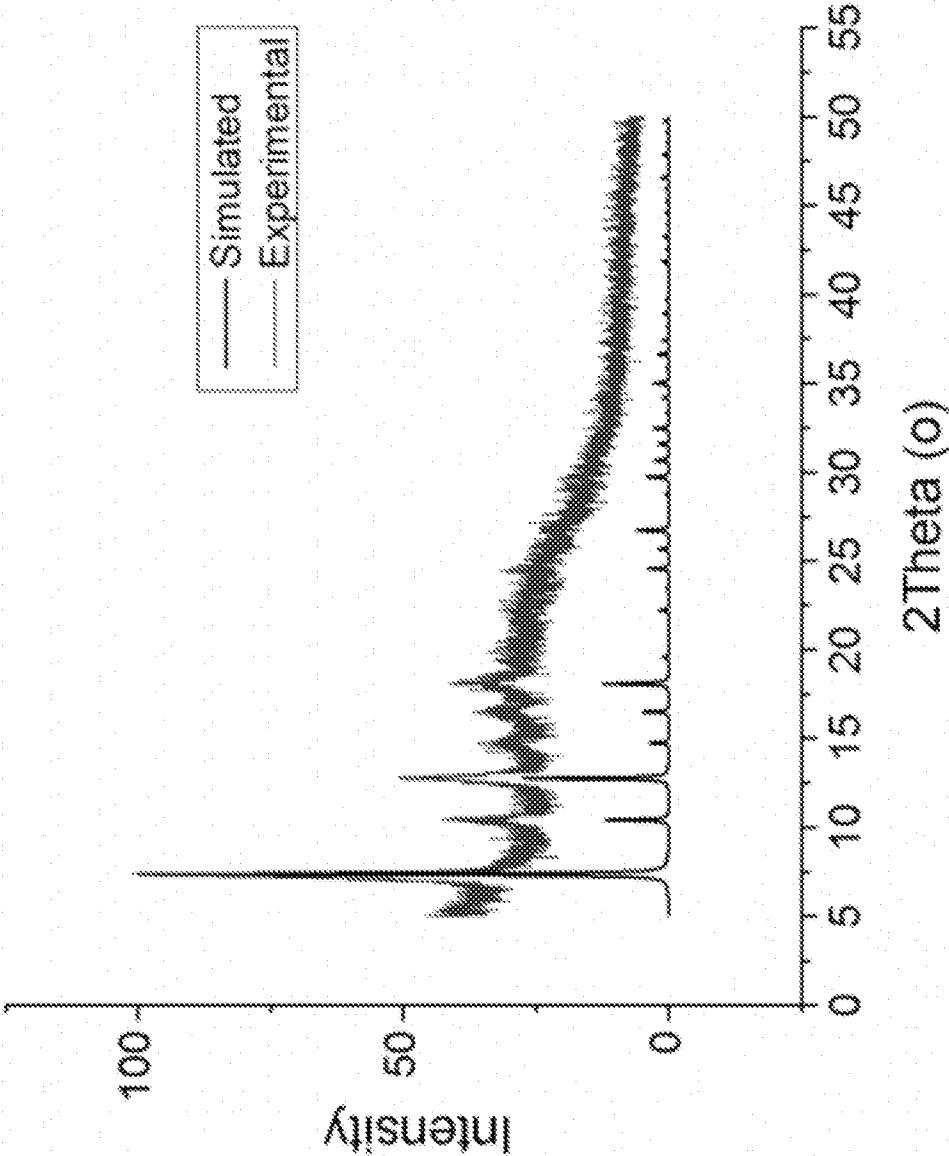


FIG. 9

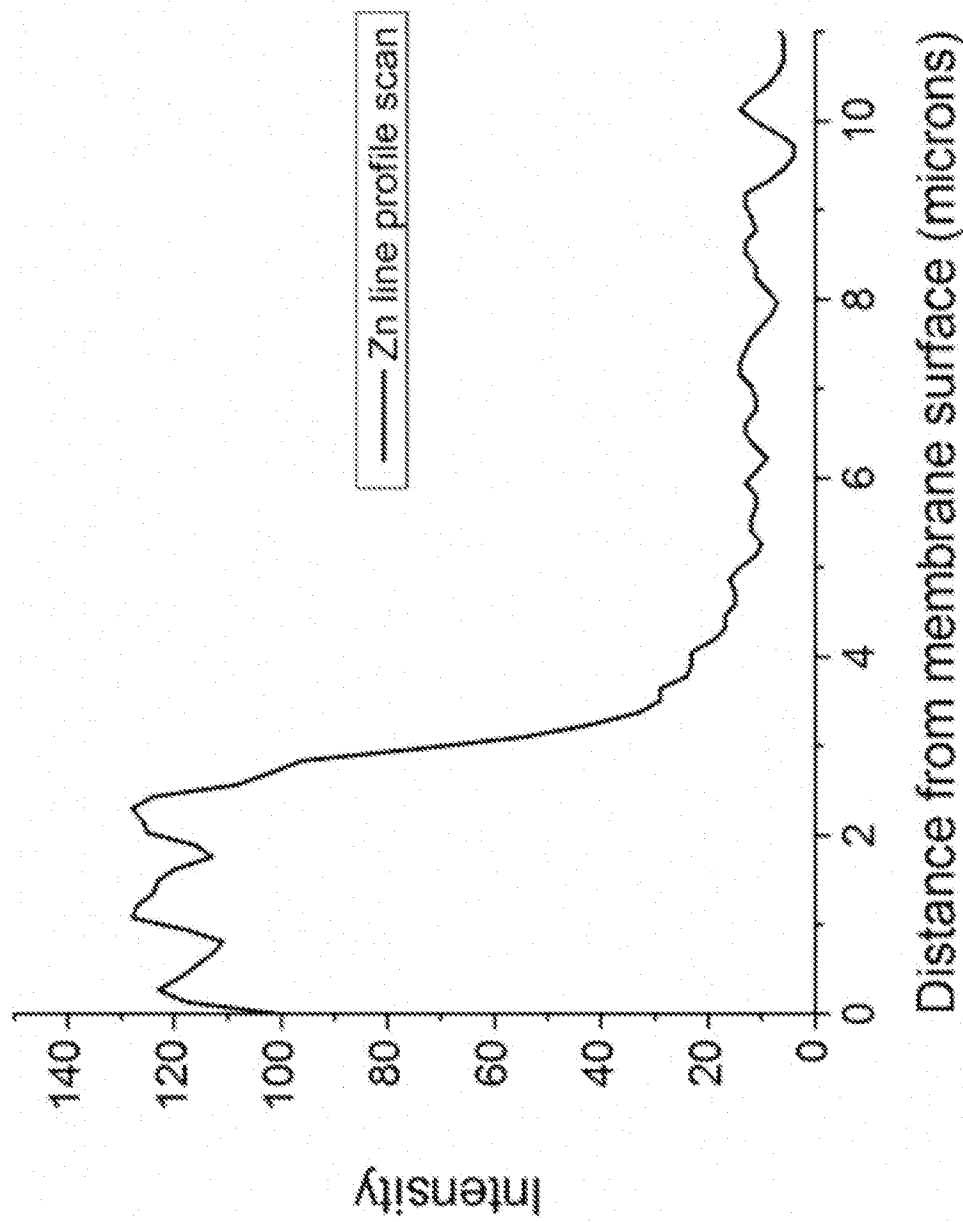


FIG. 10

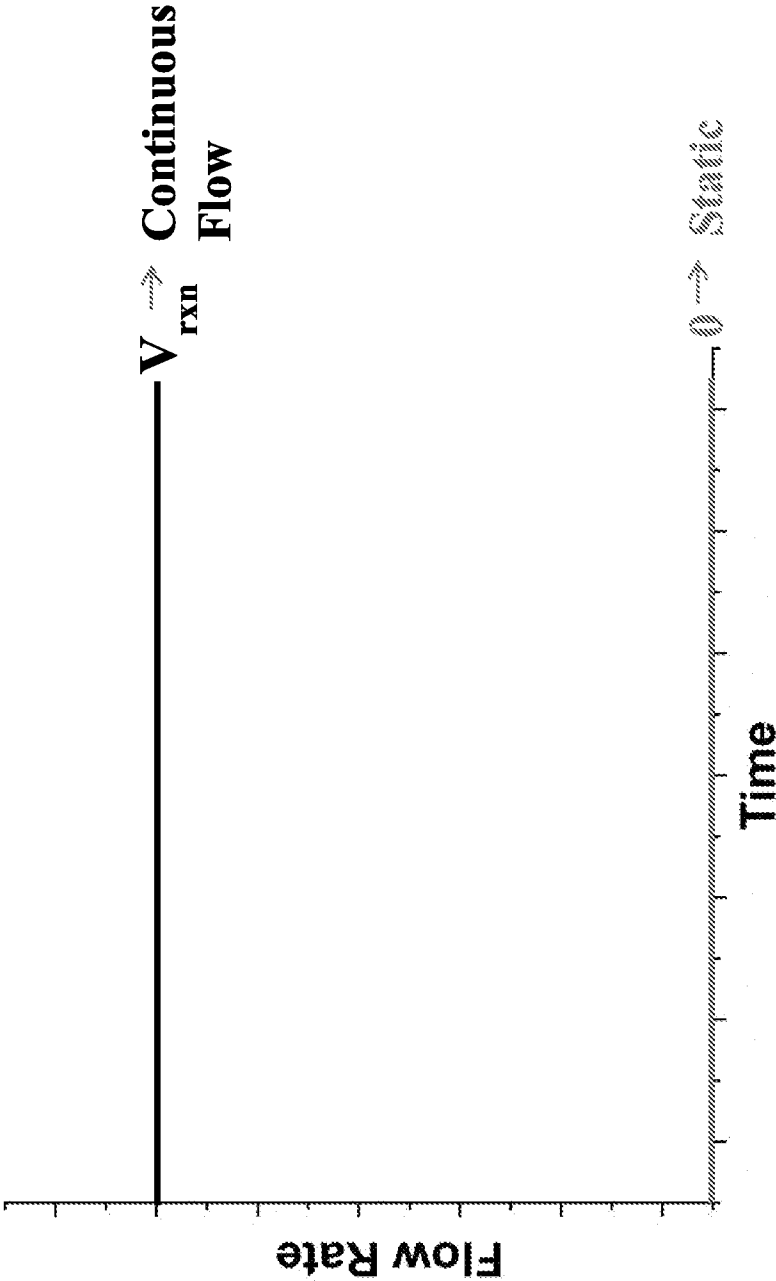


FIG. 11

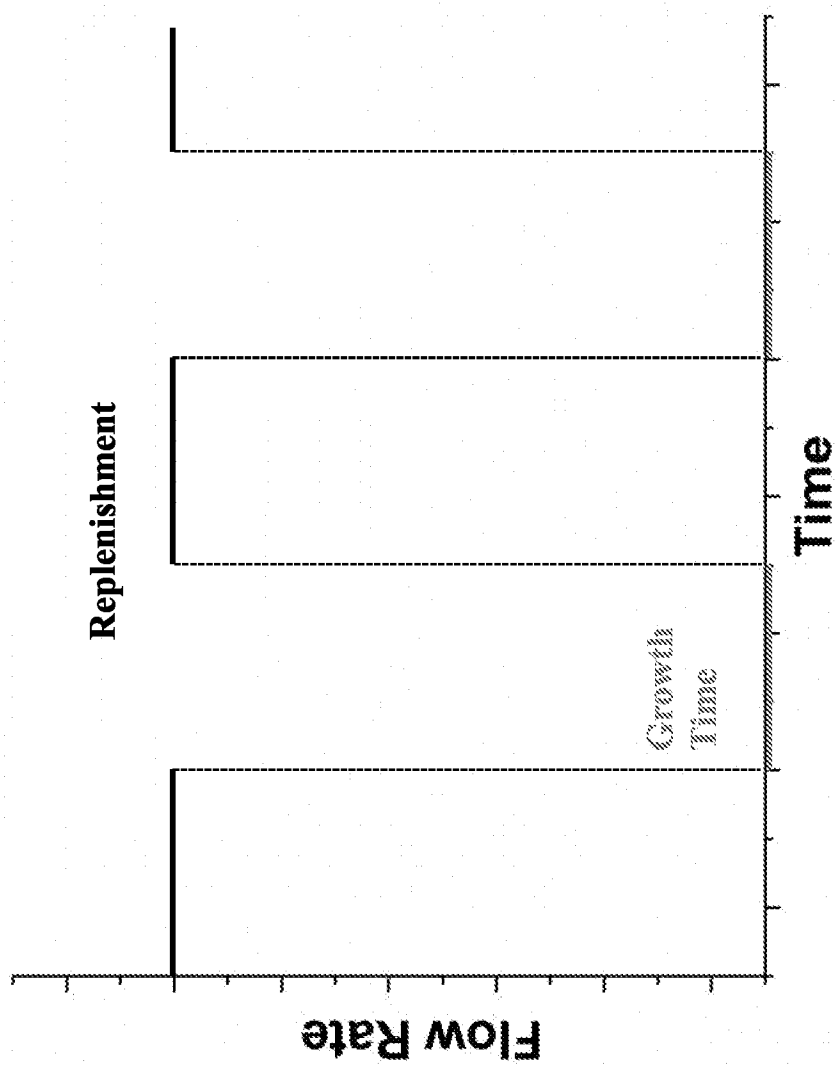


FIG. 12

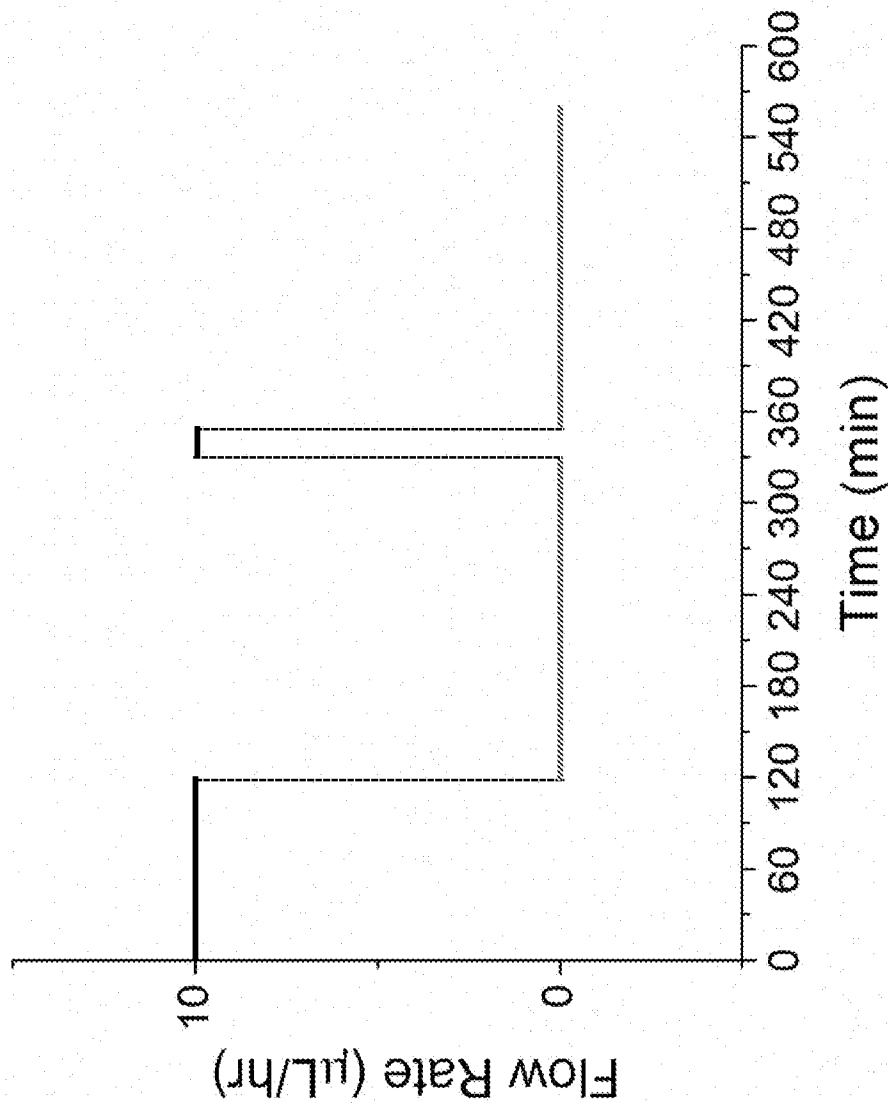


FIG. 13

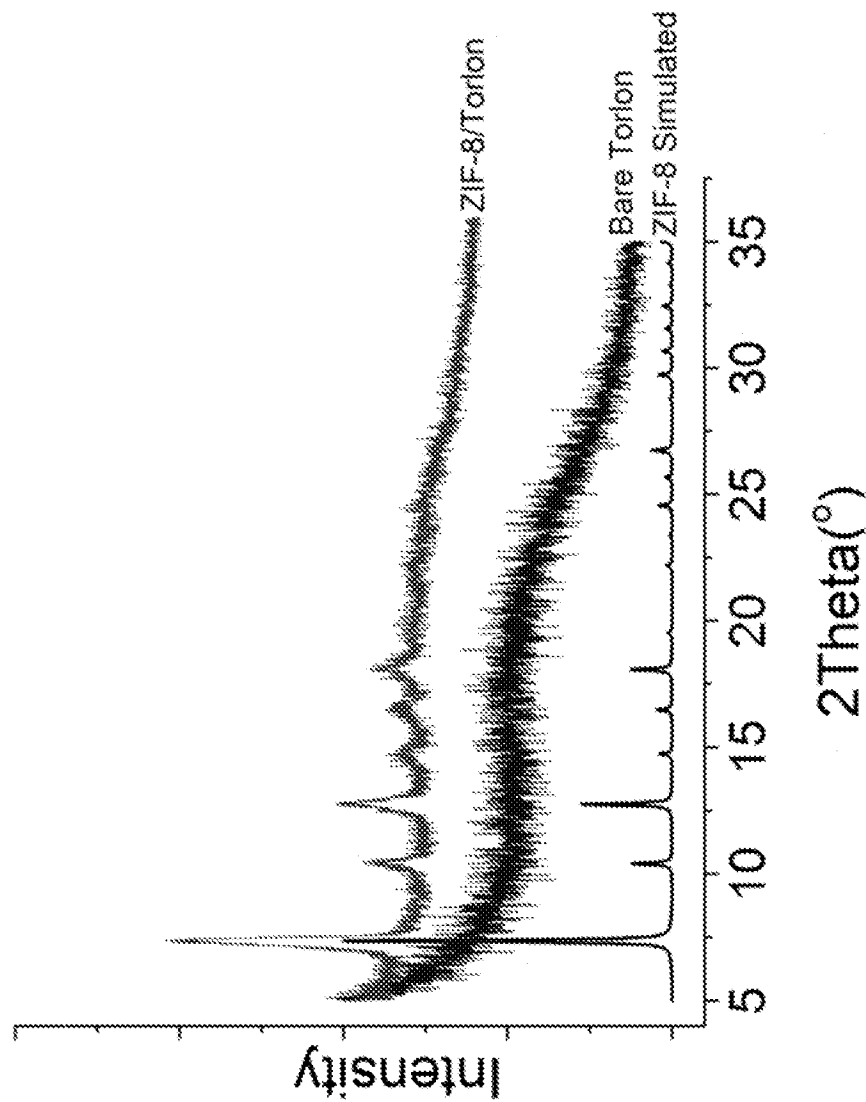


FIG. 14

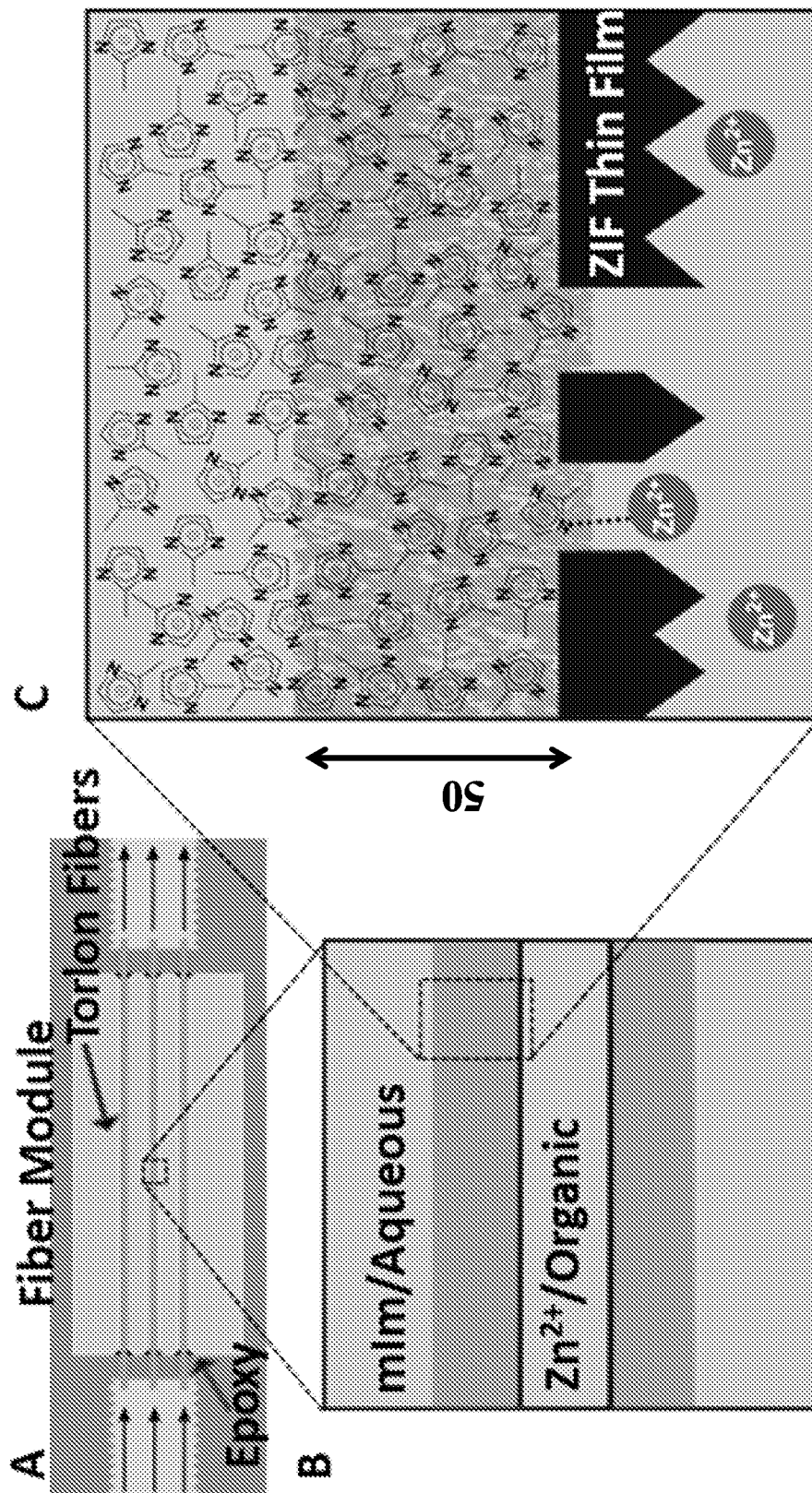


FIG. 15

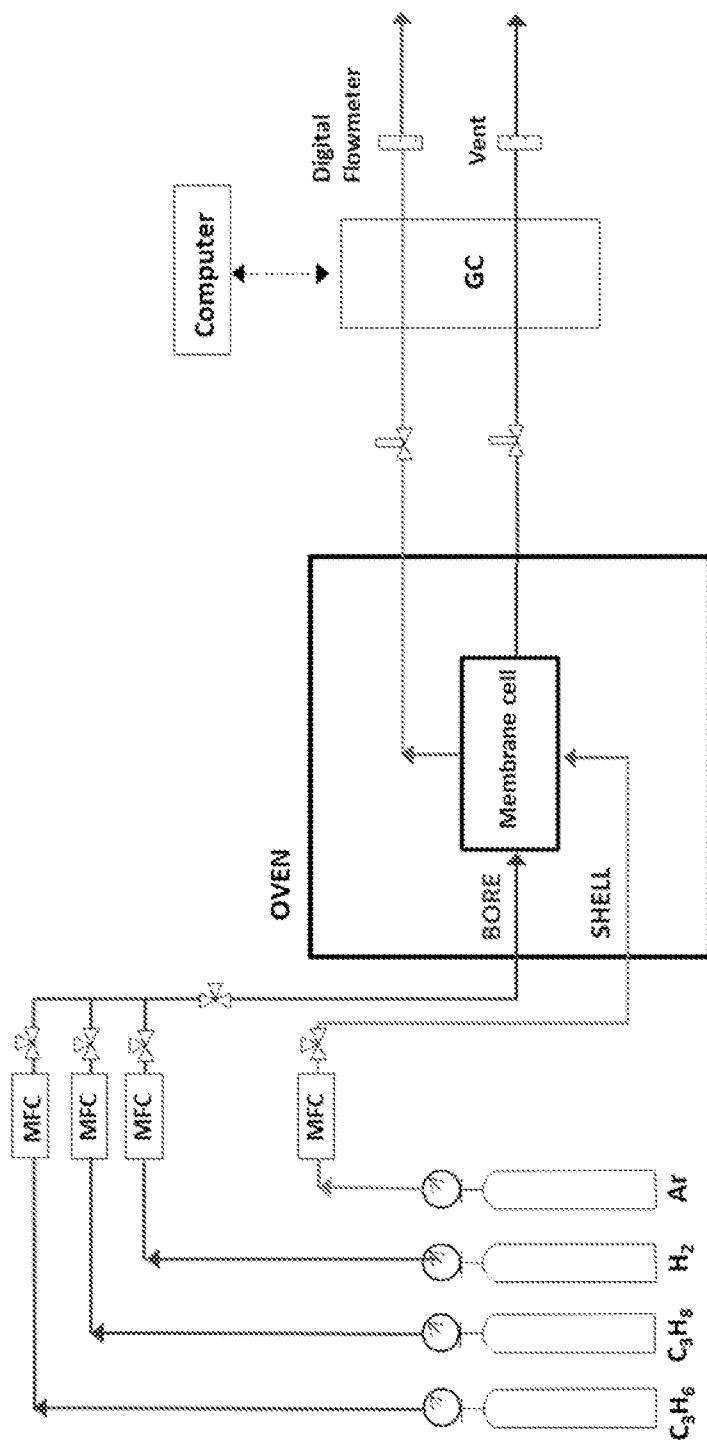


FIG. 16

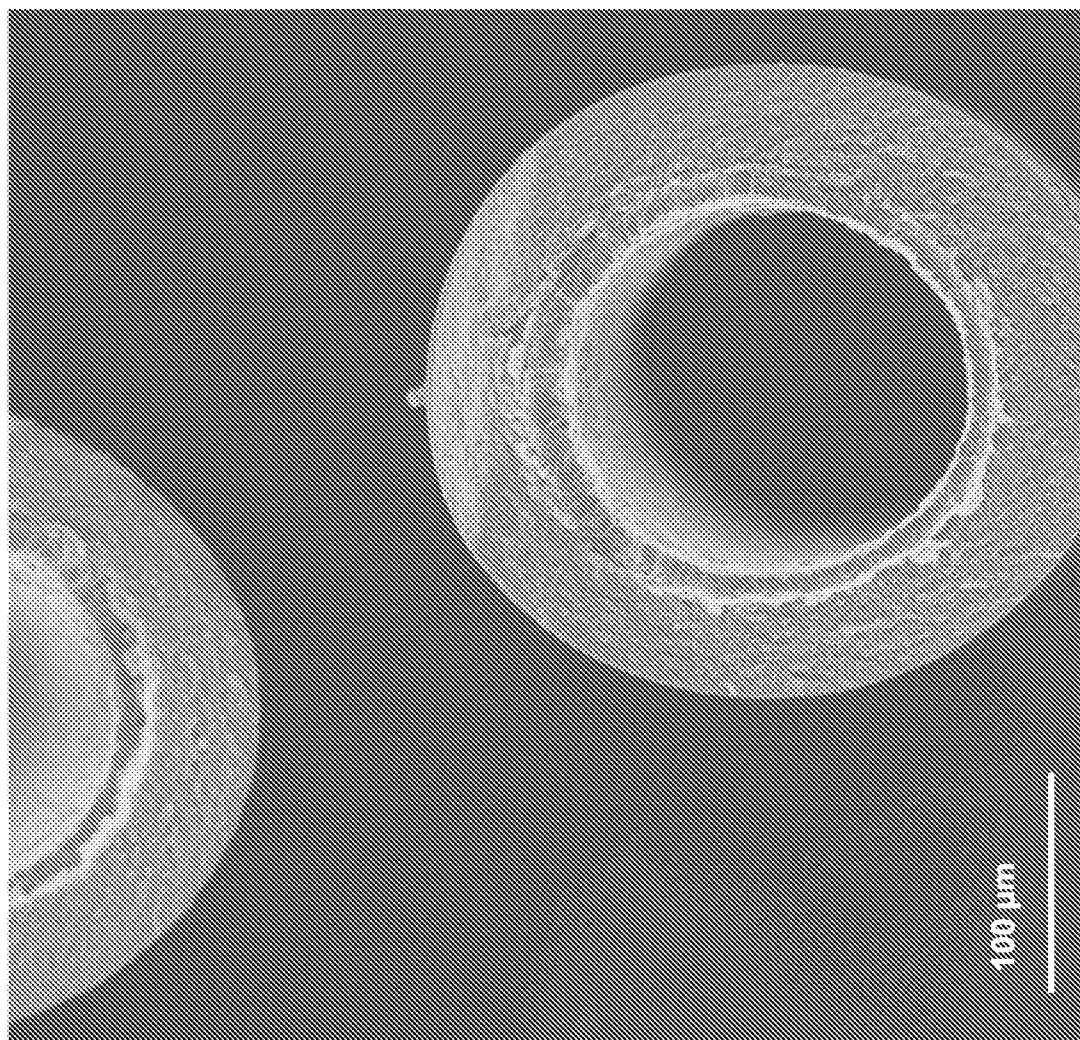


FIG. 17A

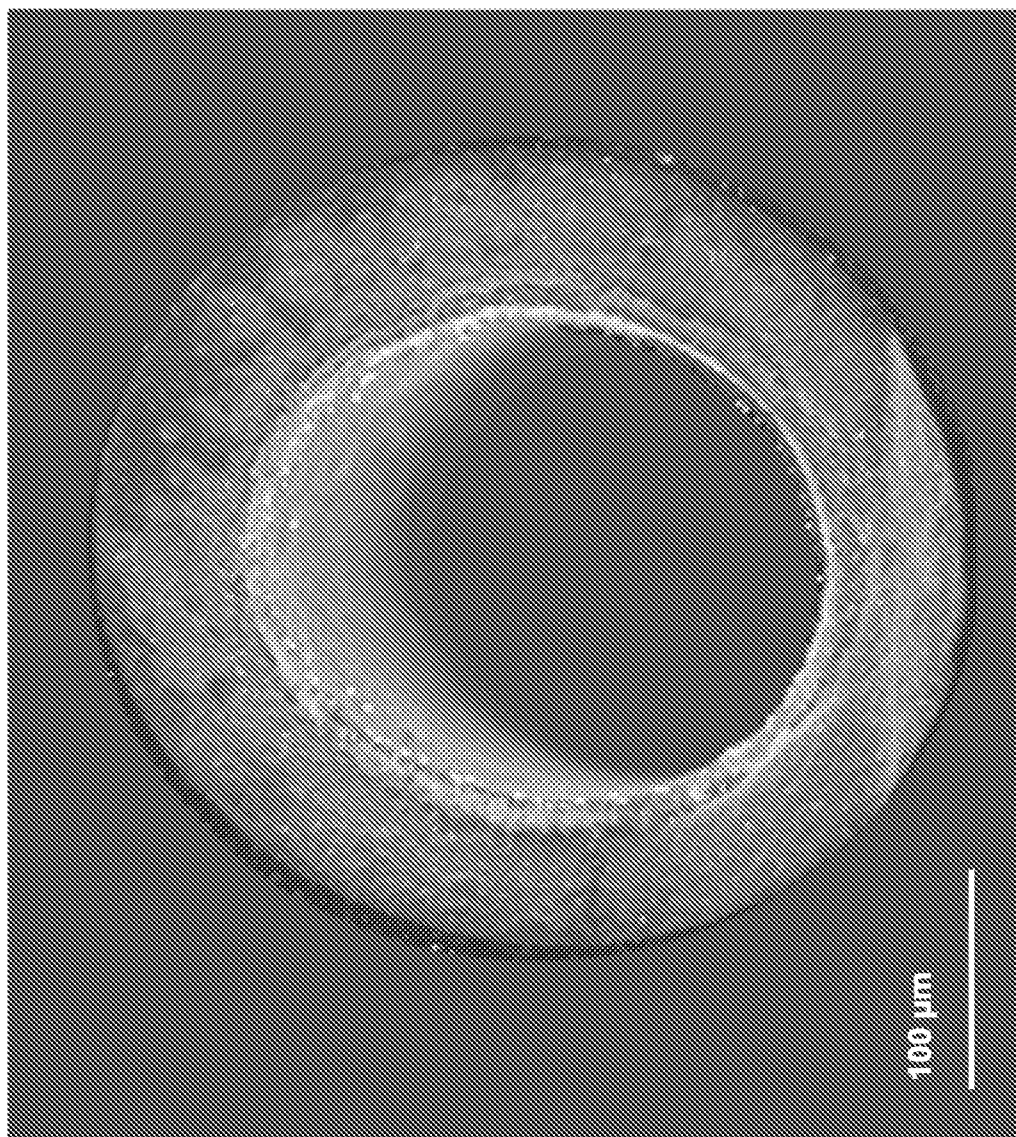


FIG. 17B

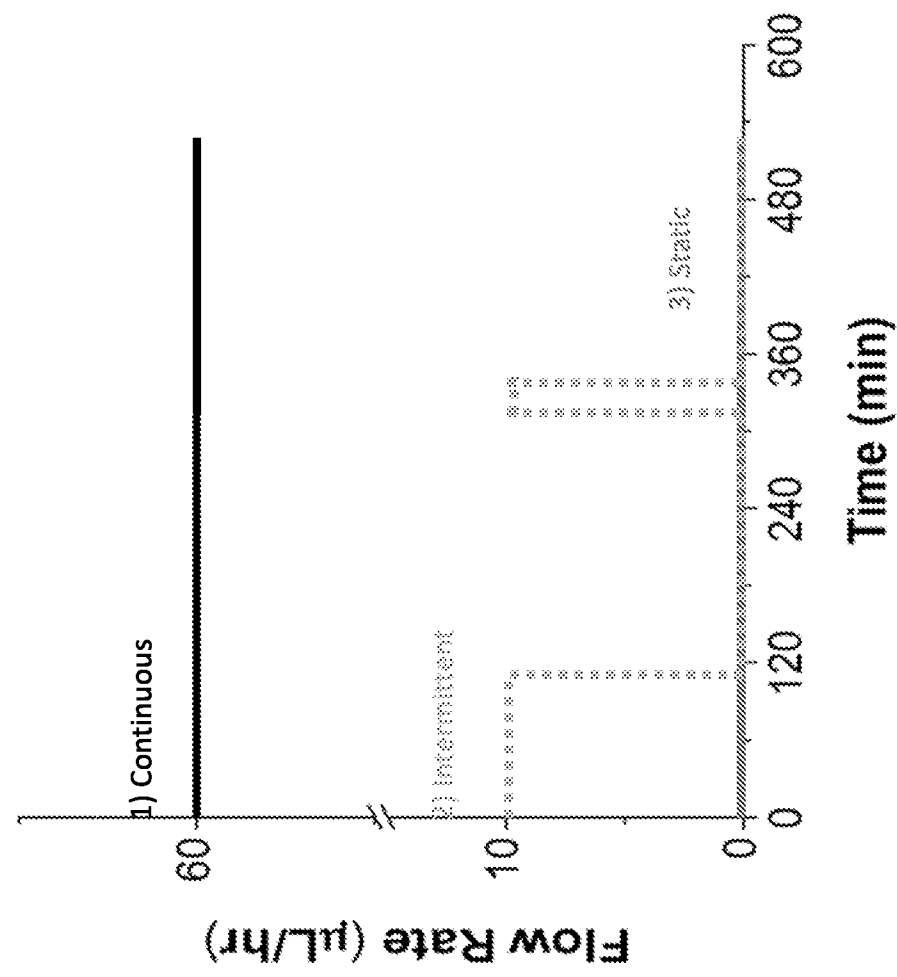


FIG. 18A

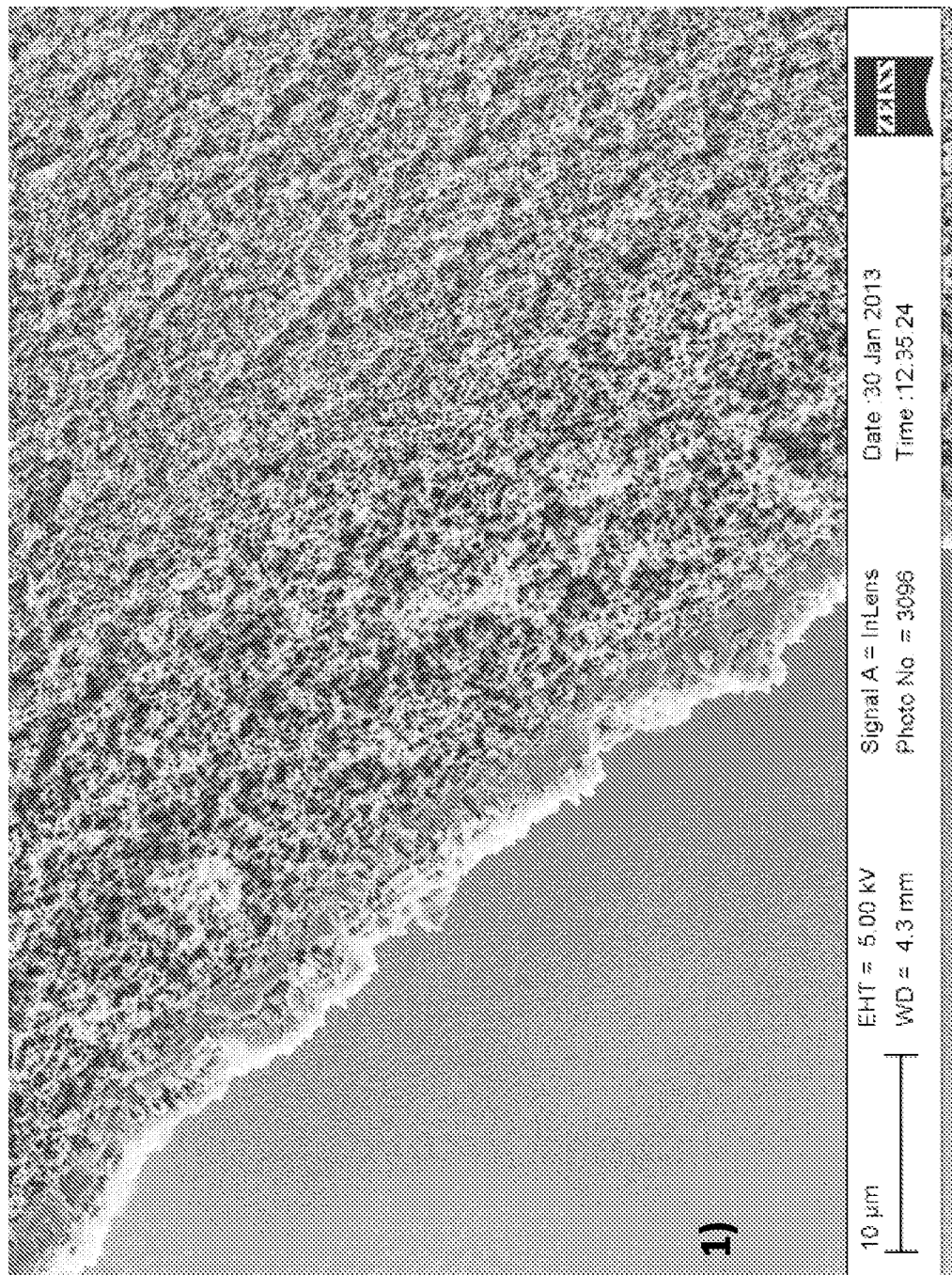


FIG. 18B

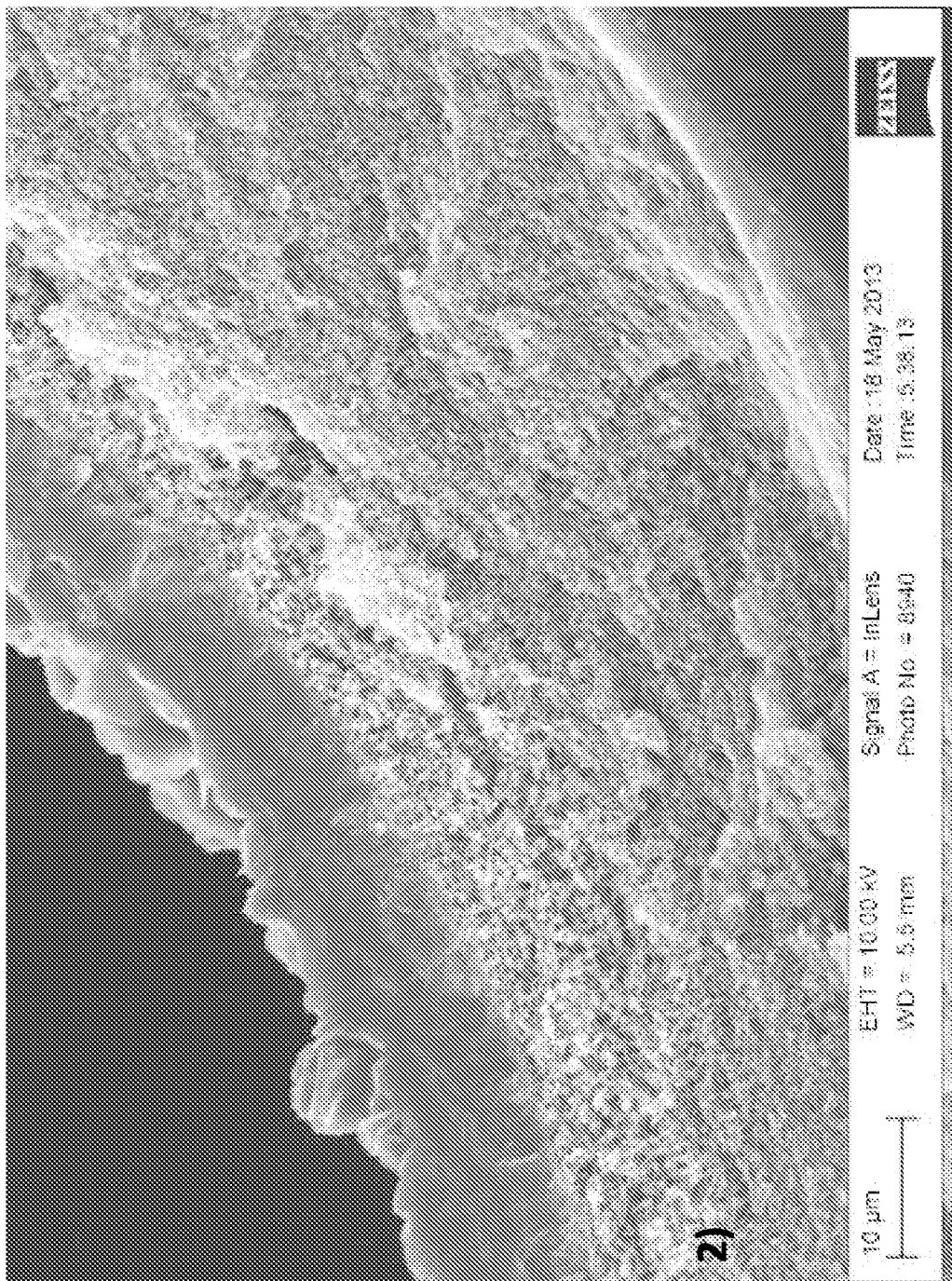


FIG. 18C

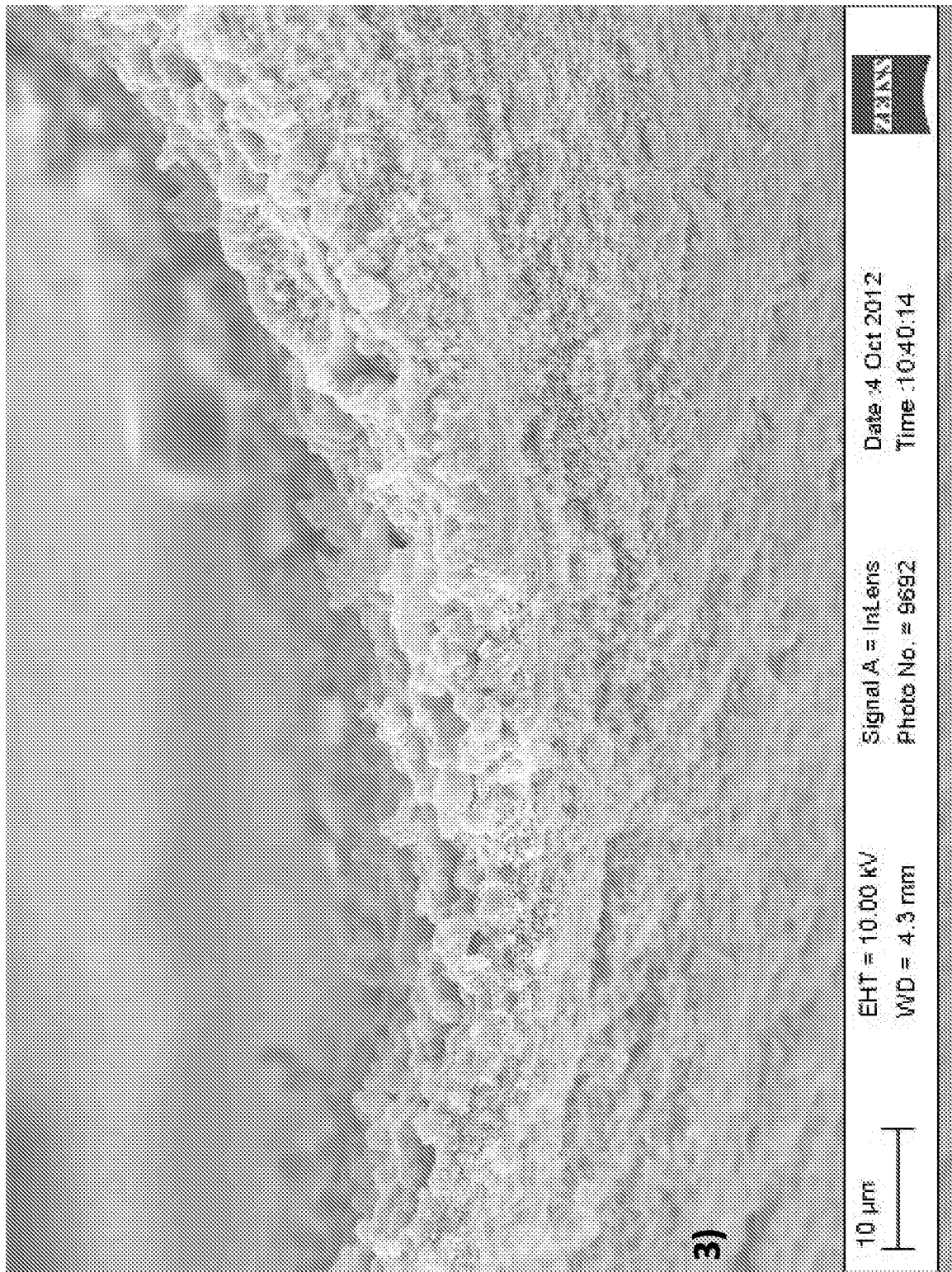


FIG. 18D

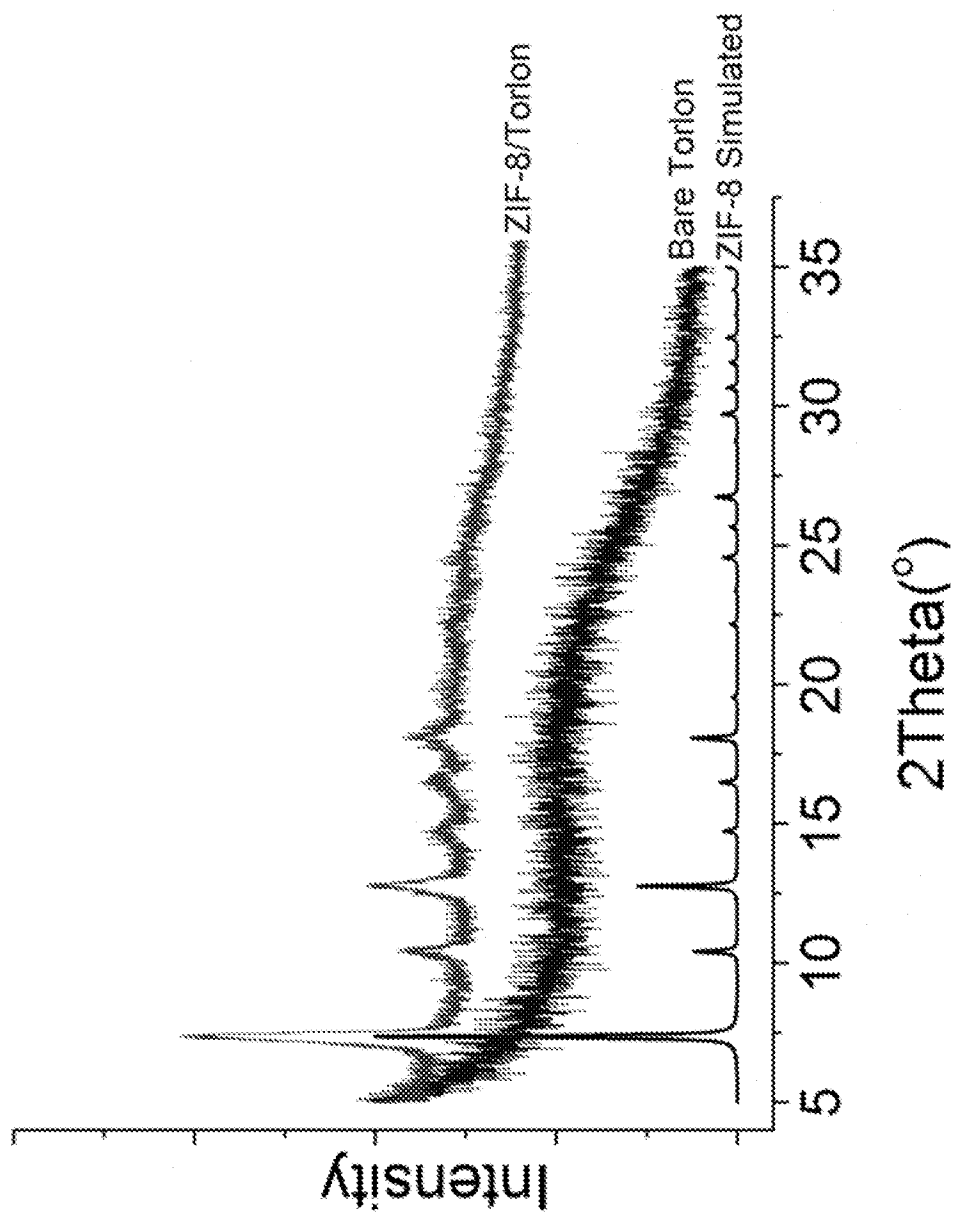


FIG. 19

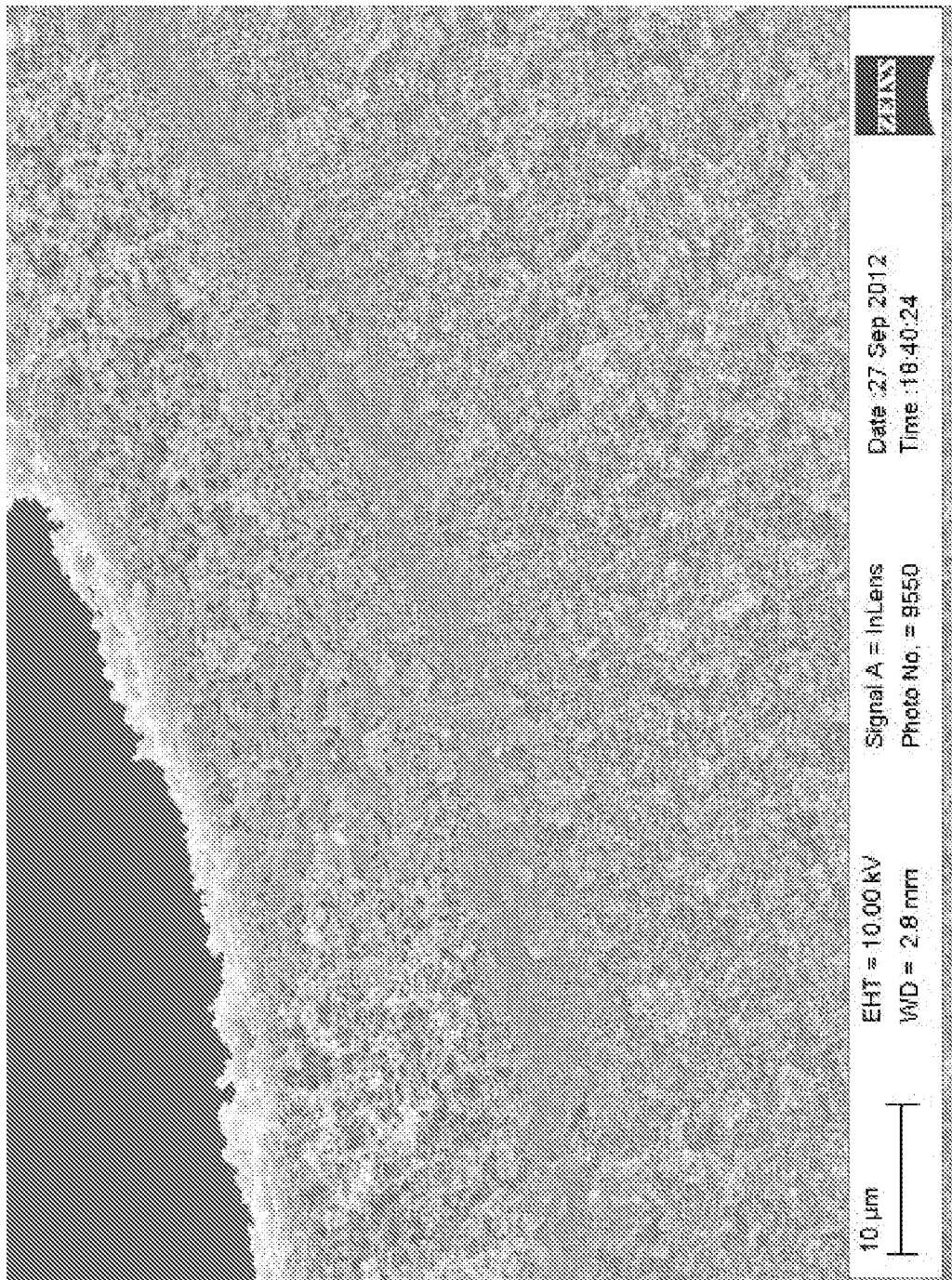


FIG. 20A

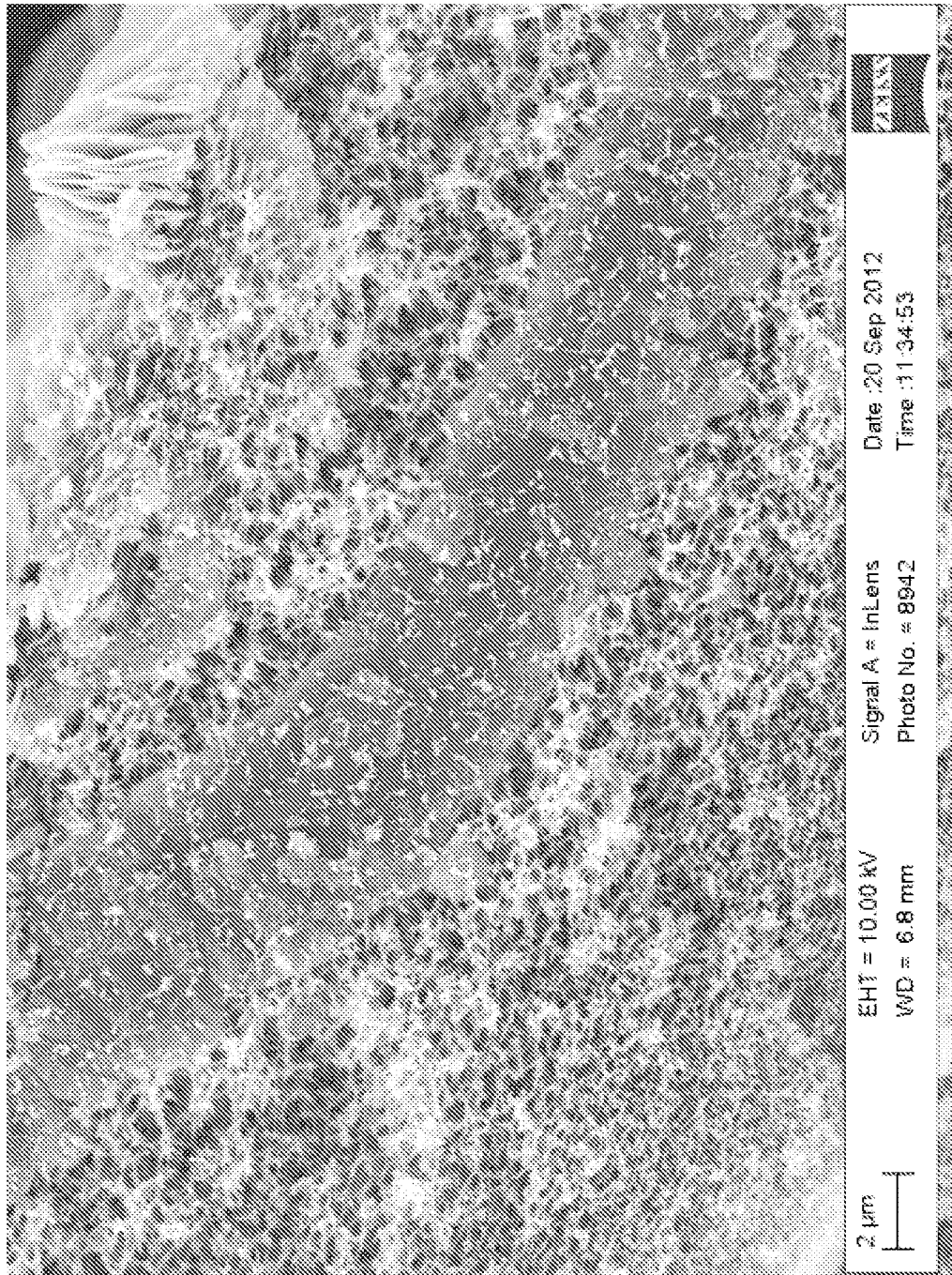


FIG. 20B

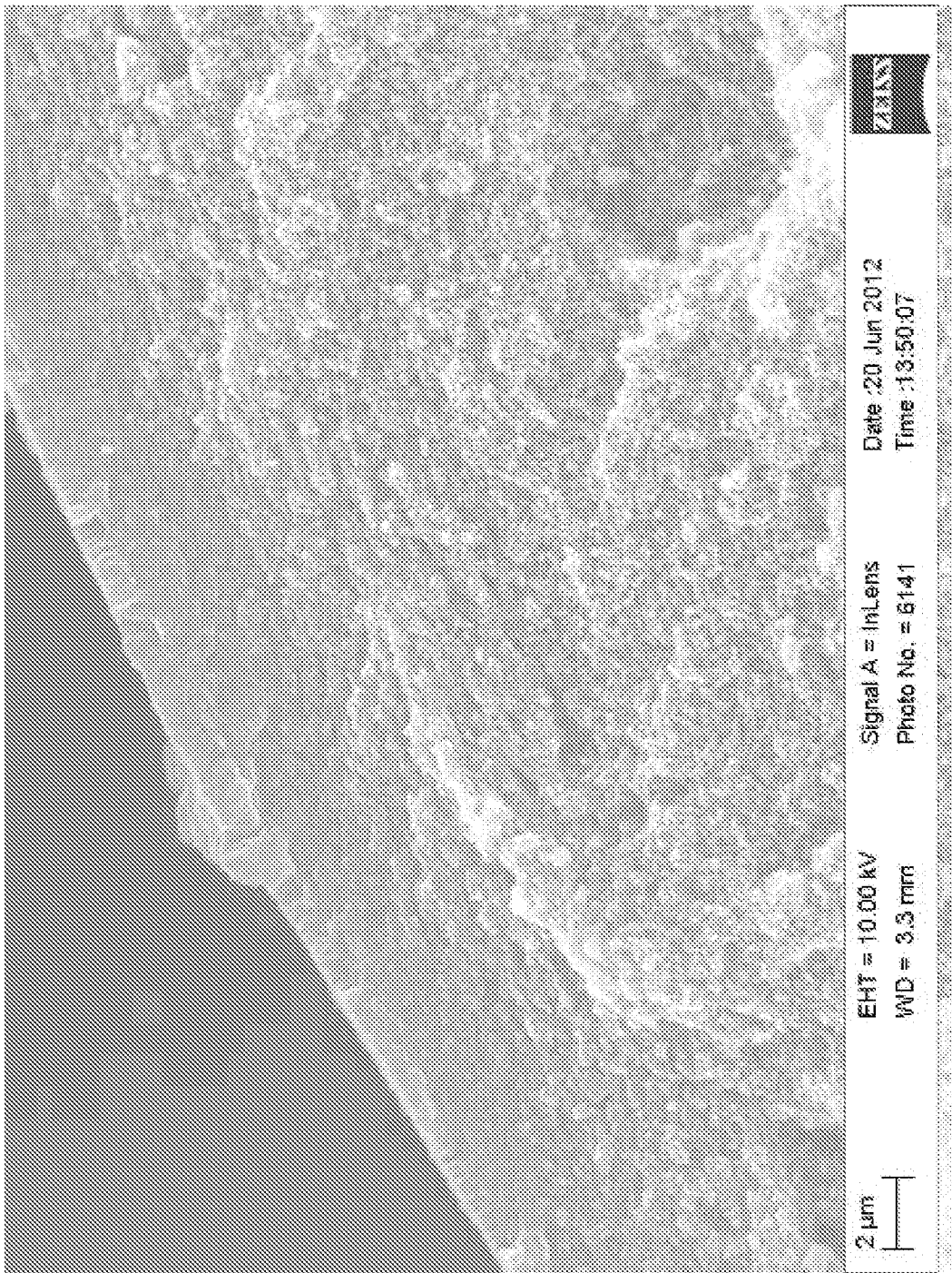


FIG. 20C

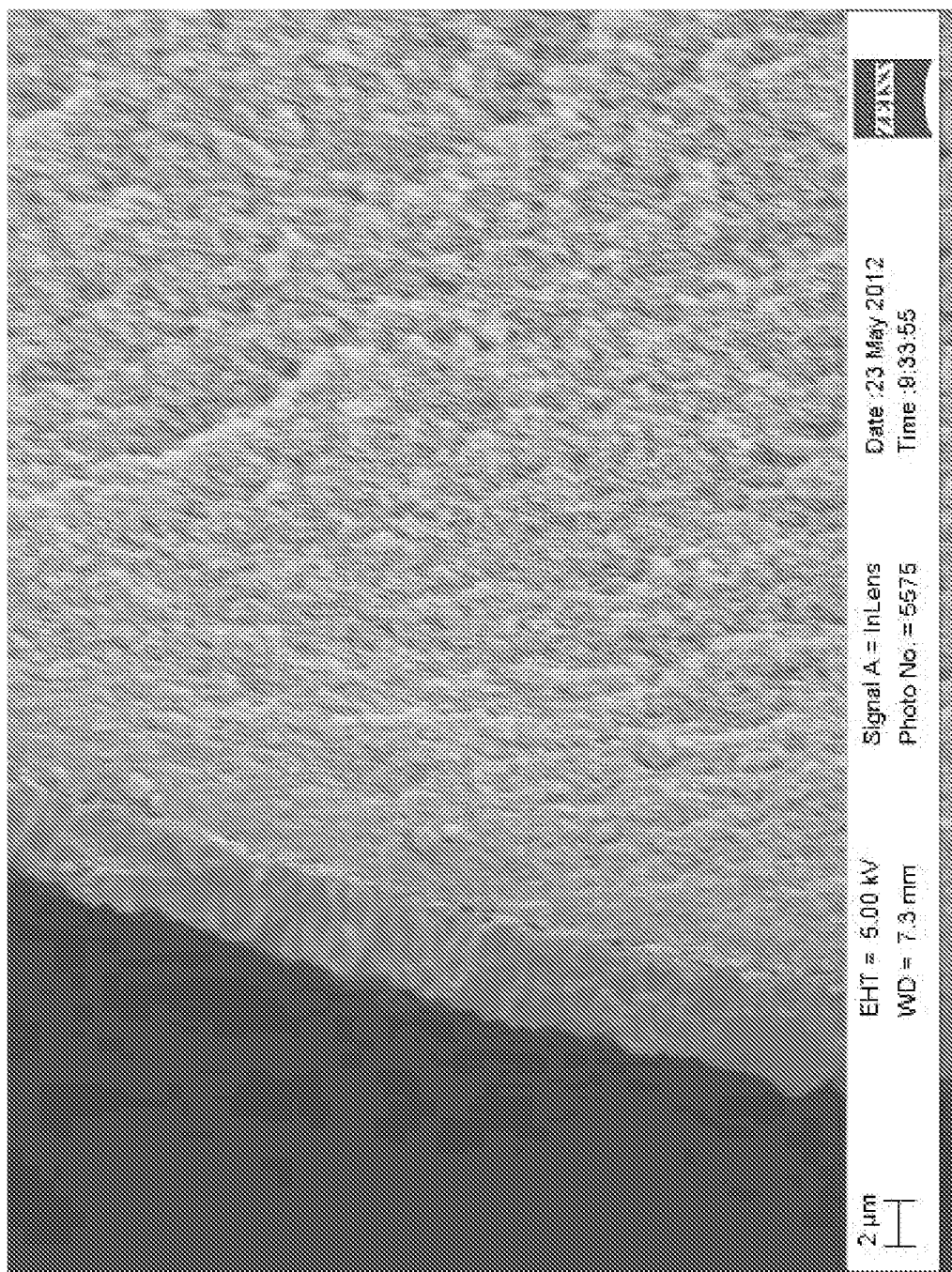


FIG. 20D

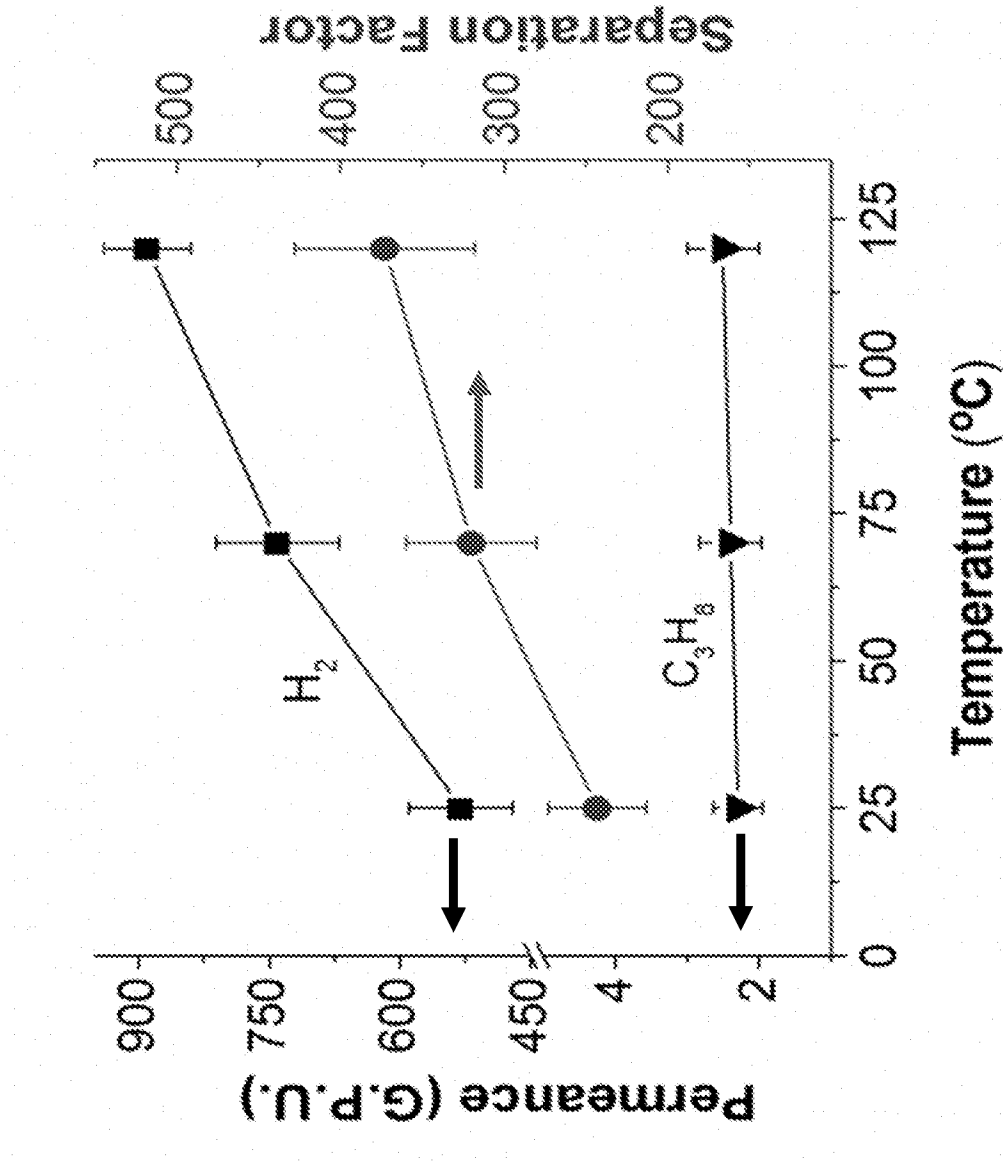


FIG. 21A

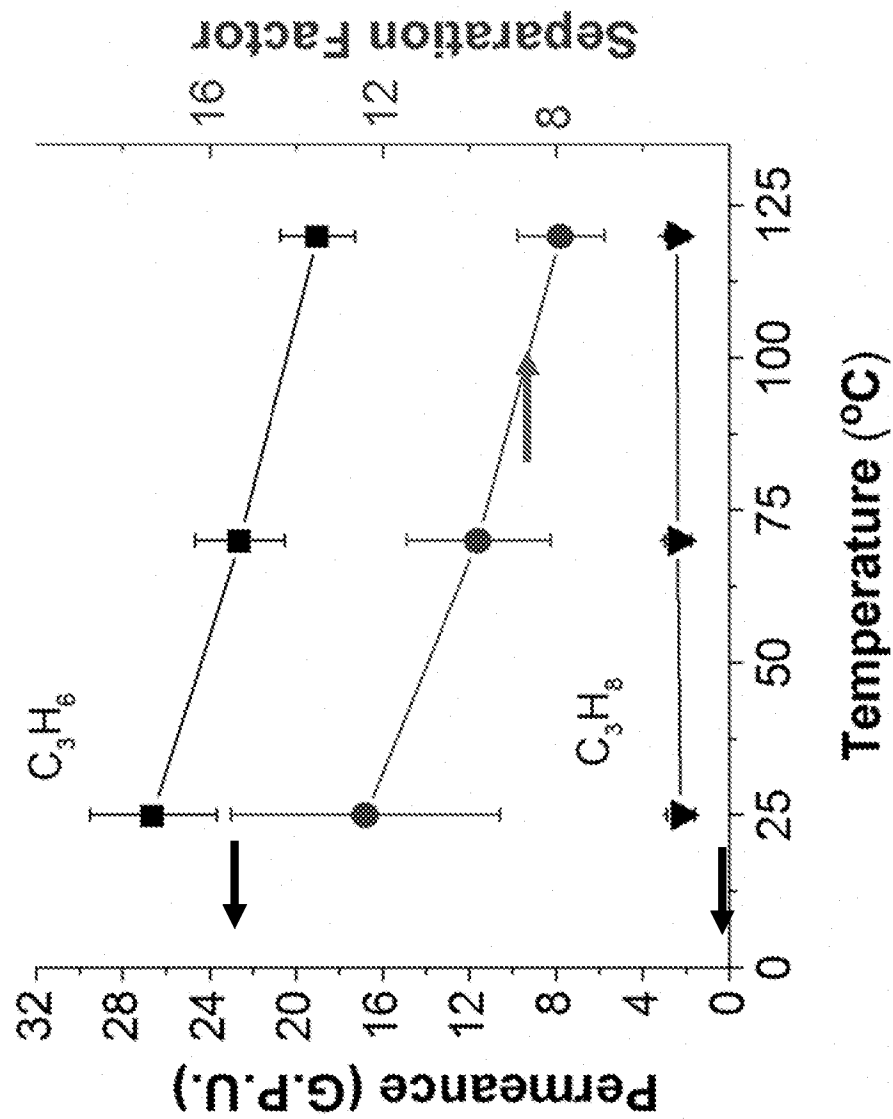


FIG. 21B

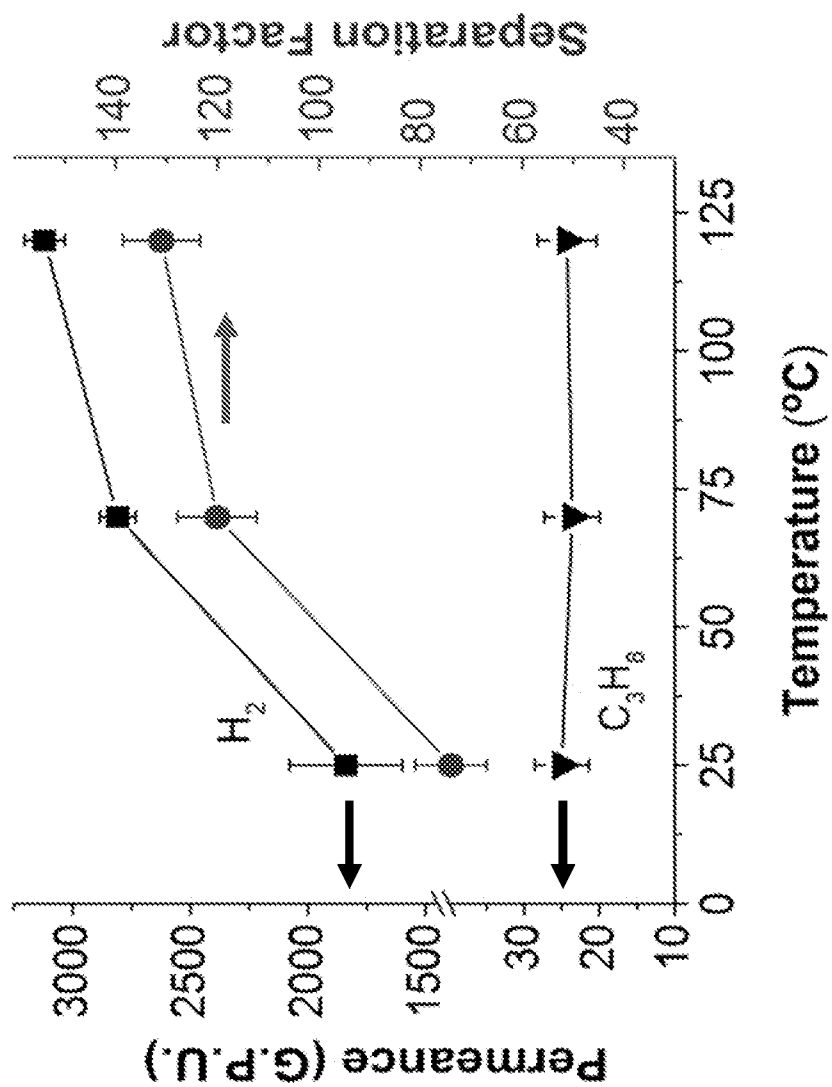


FIG. 22A

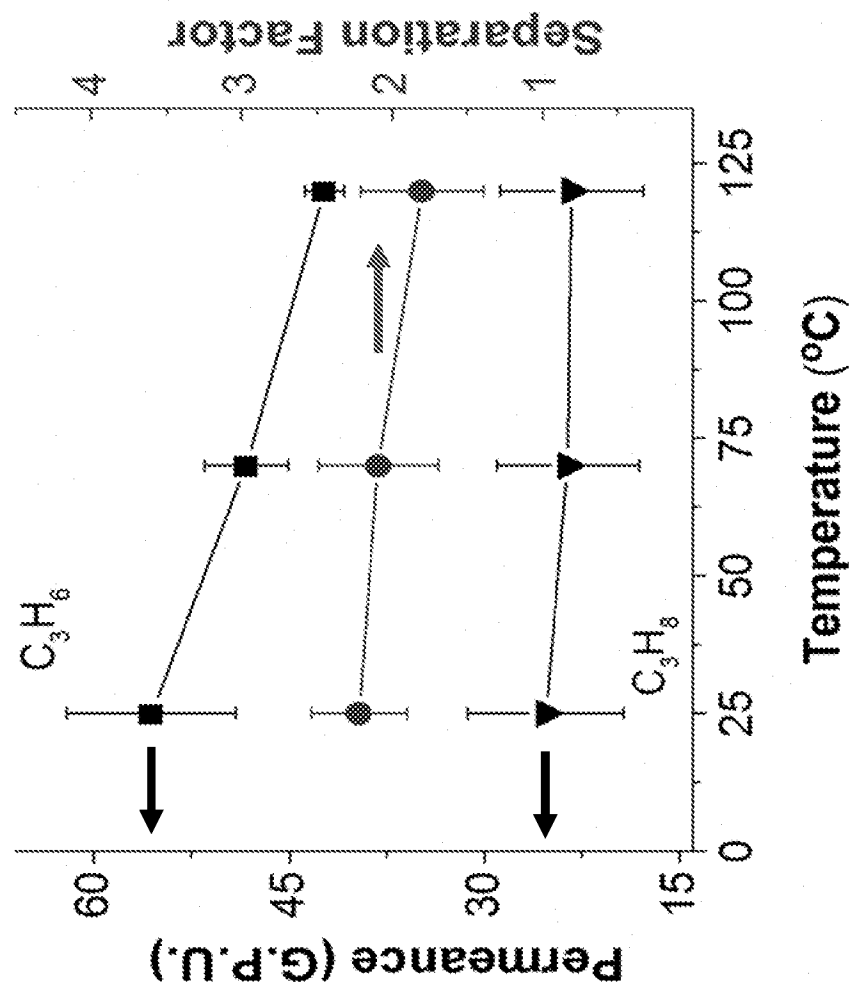


FIG. 22B

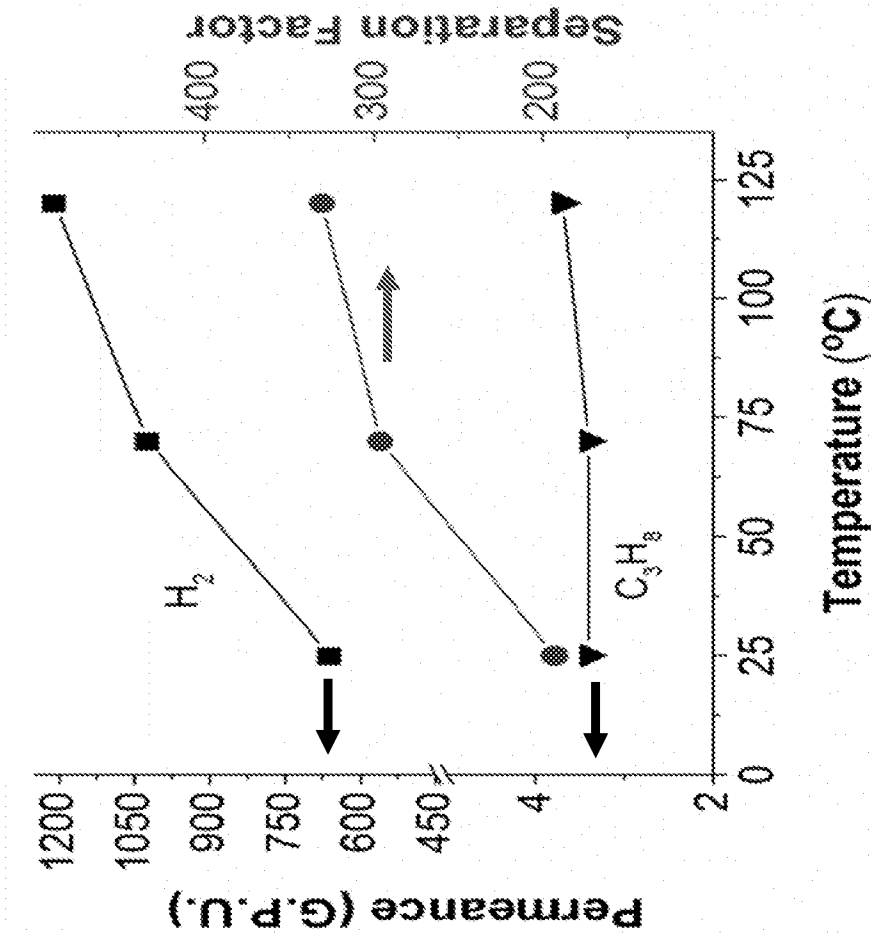


FIG. 23A

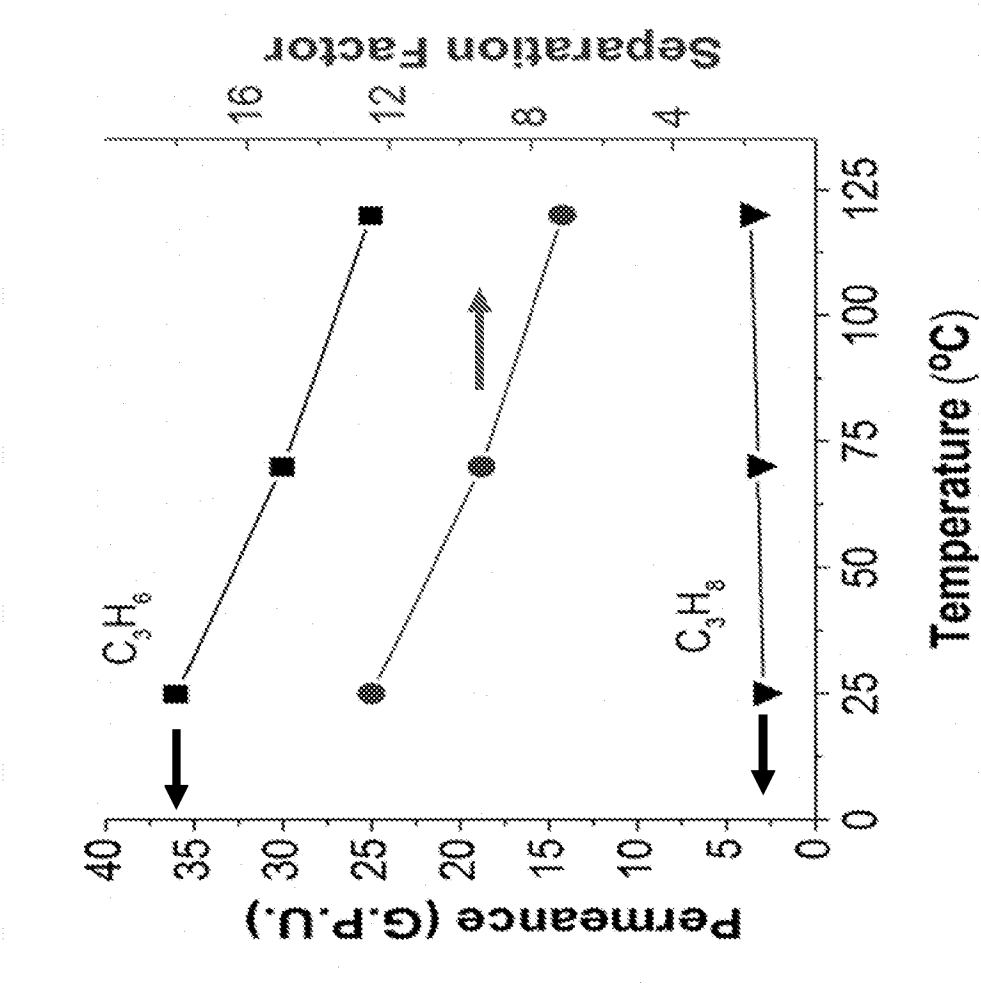


FIG. 23B

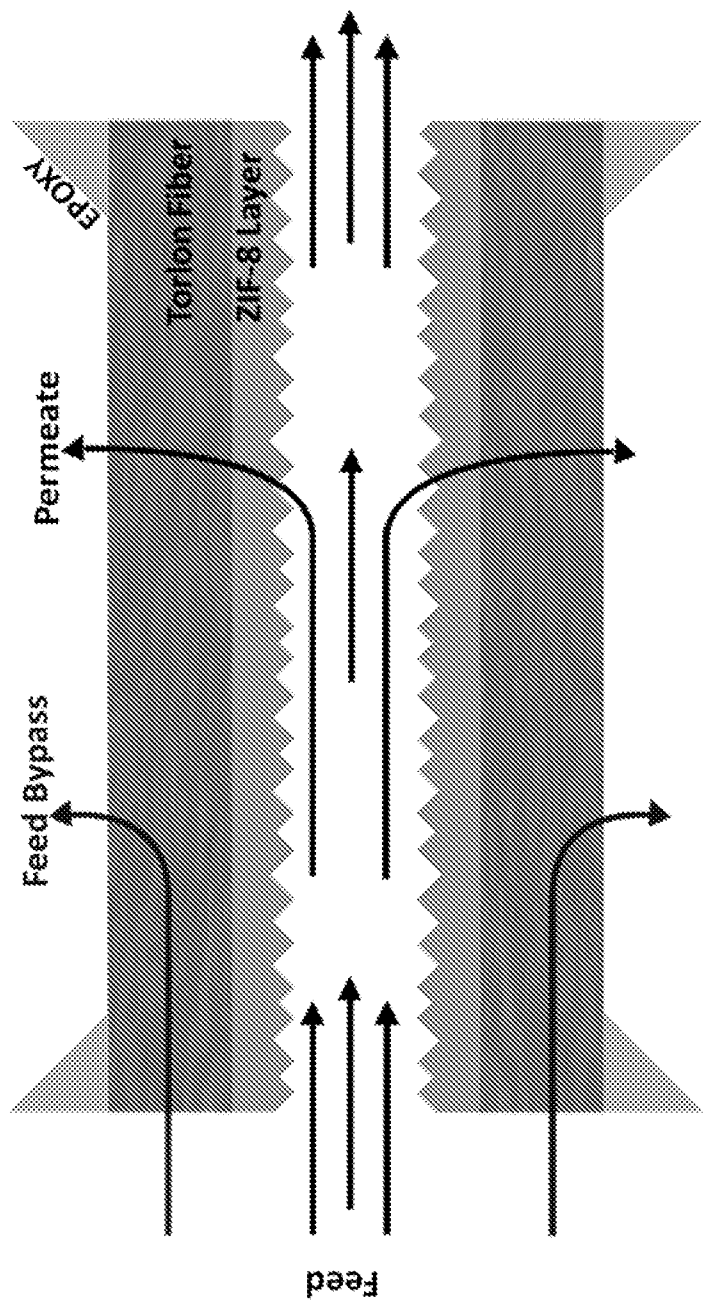


FIG. 24A

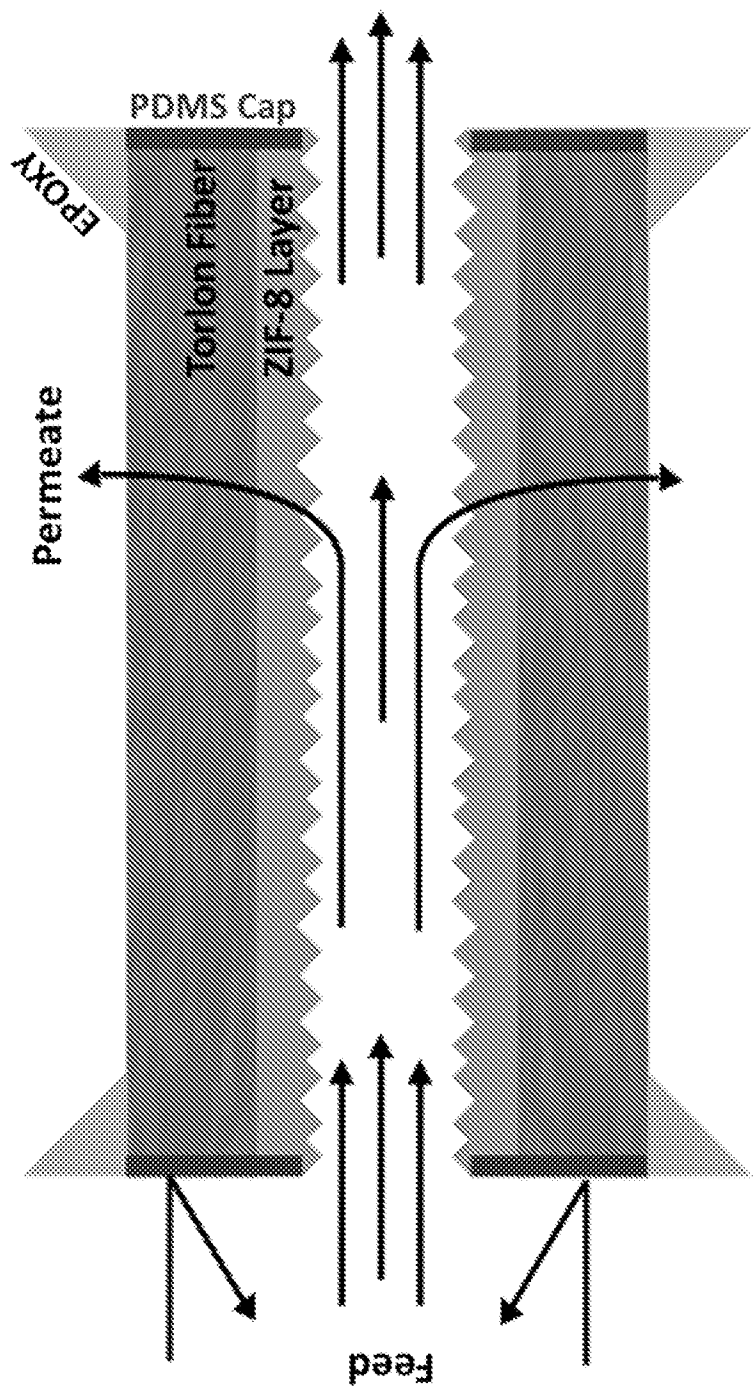


FIG. 24B

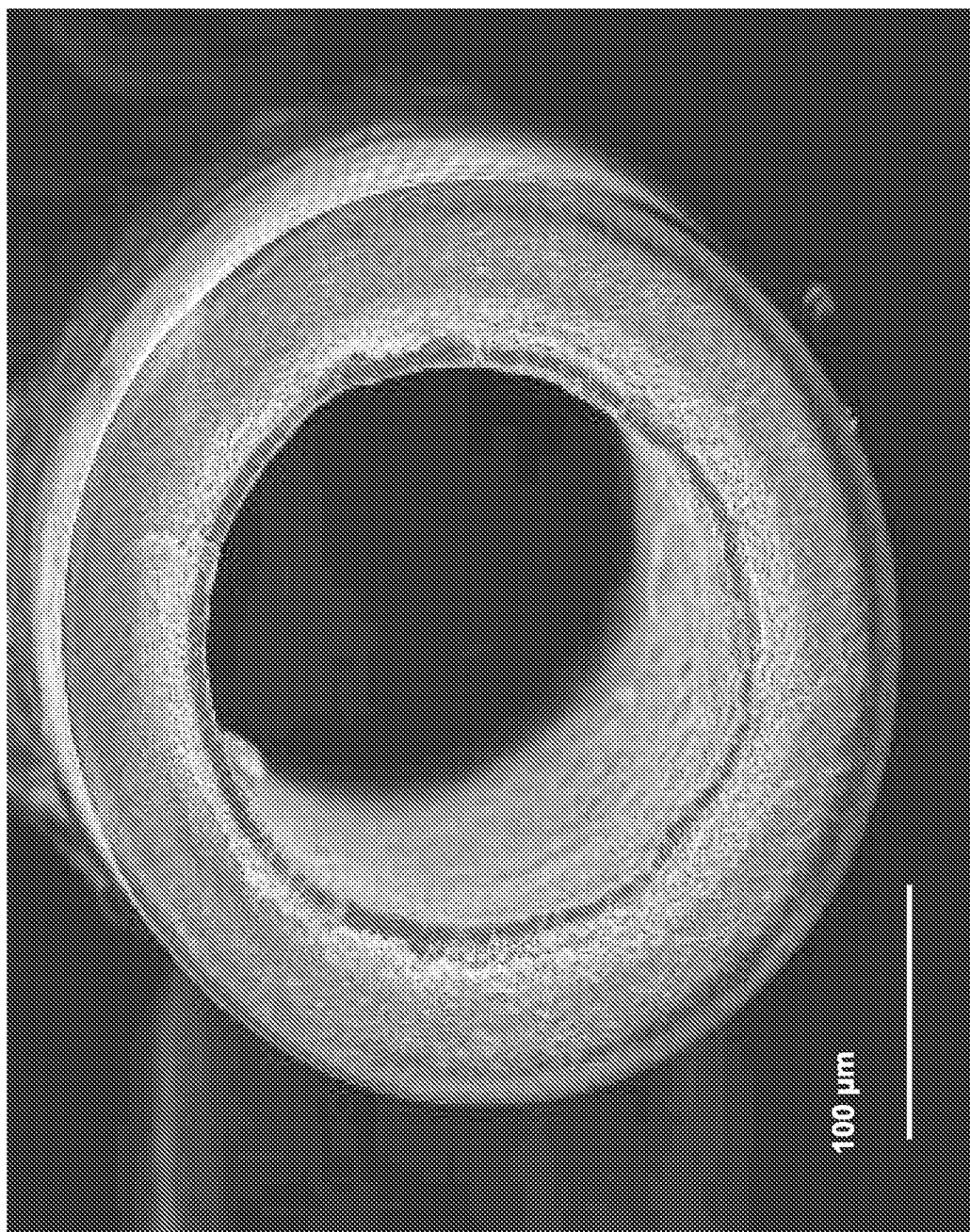


FIG. 25A

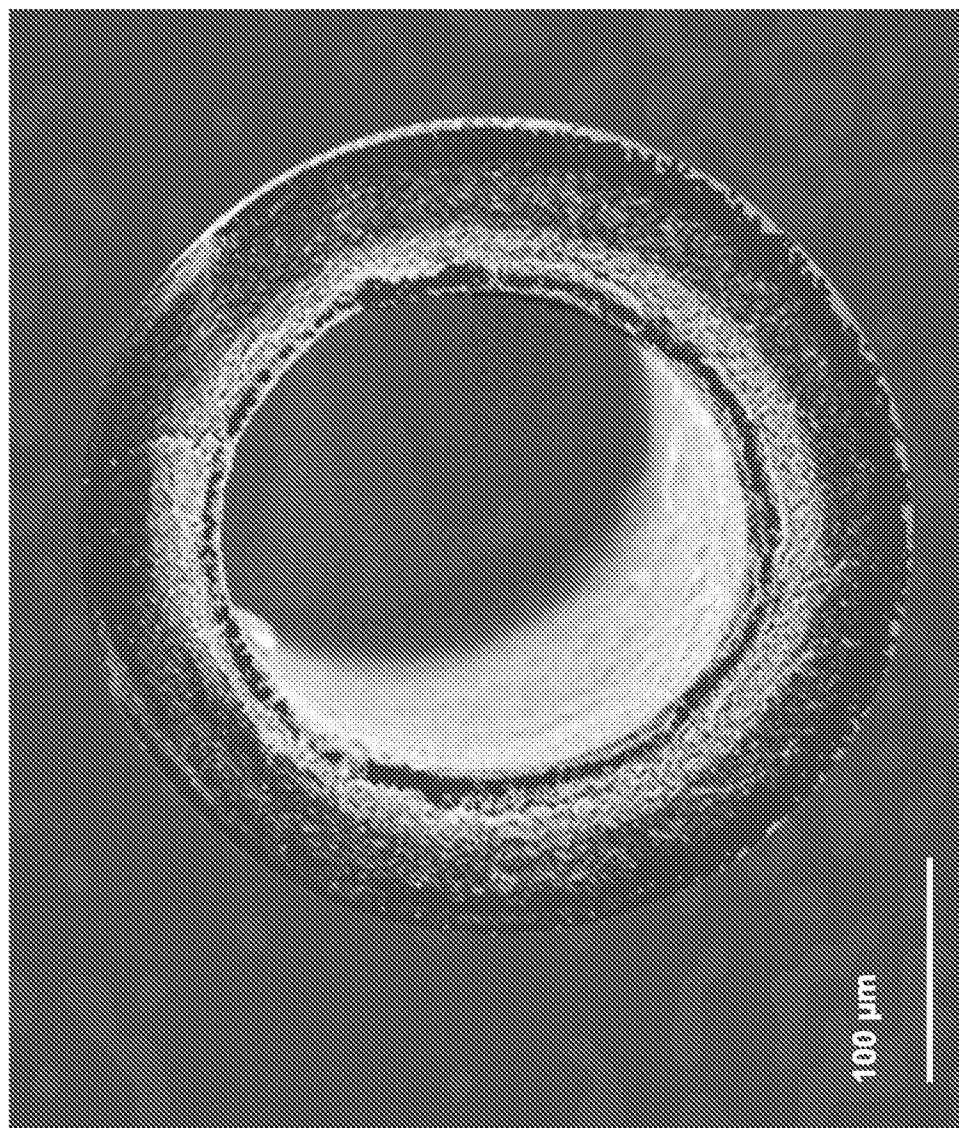


FIG. 25B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/33169

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 61/00, 63/02; B01J 19/24 (2014.01)

USPC - 435/297.4, 299.1; 210/638

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): B01D 61/00, 63/02; B01J 19/24 (2014.01)

USPC: 435/297.4, 299.1; 210/638

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

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

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); ProQuest; Google/Google Scholar; IP.com; KEYWORDS: reactor*, react*, chamber*, vessel*, molecu*, siev*, filt*, separat*, MOF, membrane*, hollow*, fiber*, fibr*, capping, capped, *dimethylsiloxane, PDMS, heptane*, C7H16, zinc, Zn, octanol, methylimidazole, methyl-imidazole, methyl ADJ imidazole, ZIF

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 8,042,695 B2 (ISHIBASHI, Y) 25 October 2011; figures 1, 6; column 2, lines 56-62; column 5, line 65 to column 6, line 25; column 9, lines 36-61; column 11, line 42 to column 12, line 32	1-12, 19, 25-28
Y	US 2002/0003105 A1 (MCEVOY, TJ) 10 January 2002; abstract; figures 1-4; paragraphs [0006]-[0016], [0029]-[0033], [0041]	1-12, 19, 25-28
Y	WO 2005/099885 A1 (CHELLAPPA, A) 27 October 2005; abstract; paragraphs [0076]-[0077]; figures 2-3	5, 7
Y	US 7,494,610 B2 (YEUNG, KL et al.) 24 February 2009; column 6, lines 11-27	6
Y	US 2013/0064747 A1 (ZHOU, Z et al.) 14 March 2013; paragraphs [0036], [0089]	10, 25
Y	WO 2013/020968 A2 (AGARWAL, A et al.) 14 February 2013; paragraphs [0025], [0029], [0037], [0053], [0063]-[0064], [0066]; figures 3, 8	12, 19, 25-28
Y	GASCON, J et al. "Accelerated synthesis of all-silica DD3R and its performance in the separation of propylene/propane mixtures" Microporous and Mesoporous Materials 2008, Volume 115; pages 585-593; abstract	27-28
A	WO 2012/074487 A1 (WANG, R et al.) 07 June 2012; entire document	1-28
A	US 2004/0058224 A1 (ESHRAGHI, RR et al.) 25 March 2004; entire document	1-28
A	AMELOOT, R et al. "Interfacial synthesis of hollow metal-organic framework capsules demonstrating selective permeability" Nature Chemistry 10 April 2011, Volume 3; pages 382-387; entire document	1-28

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

23 July 2014 (23.07.2014)

Date of mailing of the international search report

22 AUG 2014

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
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Authorized officer:

Shane Thomas

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

014/033169-22.06.2014
International application No.

PCT/US14/33169

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/0158923 A1 (GALEONE, FS et al.) 30 June 2011; entire document	1-28