

PHOTOCATALYTIC REACTOR HAVING MULTIPLE PHOTOCATALYTIC REACTOR CELLS

BACKGROUND OF THE DISCLOSURE

1. Related Applications

[01] The present application claims priority to and hereby incorporates by reference the entireties of the following U.S. patent applications: U.S. Provisional Patent Application No. 62/525,301, filed on June 27, 2017, U.S. Provisional Patent Application No. 62/525,305, filed on June 27, 2017, U.S. Provisional Patent Application No. 62/525,380, filed on June 27, 2017, and U.S. Provisional Patent Application No. 62/586,675, filed on November 15, 2017.

[02] In addition, the entireties of the following patent applications are incorporated by reference herein: International Patent Application No. PCT/US18/32375, filed on May 11, 2018, U.S. Patent Application No. 15,977,843, filed on May 11, 2018, and International Patent Application No. (to be assigned), titled "Reactor Cell with a Transparent Enclosure," filed concurrently herewith.

2. Field of the Disclosure

[03] The present disclosure relates generally to reactor systems having at least one light source and reactor cells, each including an optically transparent enclosure and one or more plasmonic photocatalysts on a catalyst support disposed within the enclosure.

3. Technical Background

[04] Industrial processes depend extensively on heterogeneous catalysts for chemical production and mitigation of environmental pollutants. These processes often rely on metal nanoparticles dispersed into high surface area support materials to both maximize catalytically active surface area and for the most cost-effective use of the catalysts (such as palladium, platinum, ruthenium, or rhodium). The catalytic processes utilizing transition metal nanoparticles are often energy intensive, relying on high temperatures and pressures to maximize catalytic activity. Thus, there remains a need for an efficient and cost-effective catalytic system.

SUMMARY OF THE DISCLOSURE

[05] The inventors have found efficient reactor systems that utilize an artificial or natural light source. The reactor systems of the disclosure can be designed to maximize absorption of one or more target wavelengths and/or catalyze a desired chemical reaction. As a result, the reactor systems disclosed herein may be cost effective and environmentally sustainable solutions for many current industrial processes.

[05a] Aspects of the invention are defined in the independent claims. Some optional features of the invention are defined in the dependent claims.

[06] Thus, in one exemplary arrangement, the present disclosure provides a reactor system that includes a housing and at least one reactor cell disposed within an interior of the housing. The at least one reactor cell comprising an enclosure and a plasmonic photocatalyst on a catalyst support disposed within the at least one enclosure, wherein the enclosure is optically transparent and comprises at least one input for a reactant to enter the at least one cell and at least one output for a reformat to exit the at least one cell;. When at least one light source is applied, the reactor cell is configured to transform the reactant into the reformat.

[07] In another exemplary arrangement, the present disclosure provides a solar concentrator and a photocatalytic reactor cell positioned relative to the solar concentrator to increase an incidence of electromagnetic radiation on the photocatalytic reactor cell.

[08] In yet another exemplary arrangement, the present disclosure provides a method for transforming at least one reactant into at least one reformat. The method includes (a) distributing at least one reactant into a plurality of reactor cells disposed within a housing, where each reactor cell comprises an optically transparent enclosure and a plasmonic photocatalyst on a catalyst support disposed within the optically transparent enclosure, (b) illuminating, via at least one light source, an interior of the housing to cause the plurality of reactor cells to transform at least one reactant into at least one reformat, and (c) accumulating the at least one reformat from the plurality of reactor cells.

BRIEF DESCRIPTION OF THE DRAWINGS

[09] The accompanying drawings are included to provide a further understanding of the methods and devices of the disclosure, and are incorporated in and constitute a part of this specification. The drawings are not necessarily to scale, and sizes of various elements may be distorted for clarity and/or illustrated as simplistic representations in order to promote comprehension. The drawings illustrate one or more embodiment(s) of the disclosure, and together with the description, serve to explain the principles and operation of the disclosure.

[010] **Figure 1A** is a cross-sectional side view of a reactor cell according to one embodiment of the disclosure.

[011] **Figure 1B** is an exploded perspective side view of a reactor cell according to one embodiment of the disclosure.

[012] **Figure 2A** is a perspective side view of a configuration of a reactor system according to one embodiment of the disclosure.

[013] **Figure 2B** is an exploded perspective side view of a configuration of a reactor system according to the embodiment of Figure 2A.

[014] **Figures 3A** is cross-sectional side view of an example configuration of the reactor cell according to one embodiment of the disclosure.

[015] Figure 3B is a cross-sectional end view of an example configuration of the reactor cell according to the embodiment of Figure 3A.

[016] Figure 4A is a cross-sectional side view of an example configuration of the reactor cell according to one embodiment of the disclosure.

[017] Figure 4B is a cross-sectional end view of an example configuration of the reactor cell according to the embodiment of Figure 4A.

[018] Figure 5A is a cross-sectional side view of an example configuration of the reactor cell according to one embodiment of the disclosure.

[019] Figure 5B is a cross-sectional end view of an example configuration of the reactor cell according to the embodiment of Figure 5A.

[020] Figure 6 is a cross-sectional detail view of an example configuration of the reactor cell having a catalyst support in bead form.

[021] Figure 7A is a cross-sectional end view of an example configuration of a reactor cell system according to one embodiment of the disclosure.

[022] Figure 7B is a cross-sectional end view of an example configuration of a reactor cell system according to one embodiment of the disclosure.

[023] Figure 7C is a cross-sectional end view of an example configuration of a reactor cell system according to one embodiment of the disclosure.

[024] Figure 7D is a cross-sectional end view of an example configuration of a reactor cell system according to one embodiment of the disclosure.

[025] Figure 8 is a perspective view of an example configuration of a reactor system having a solar concentrator according to one embodiment of the disclosure.

DETAILED DESCRIPTION

[026] Before the disclosed systems and methods are described, it is to be understood that the aspects described herein are not limited to specific embodiments, apparatus, or configurations, and as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and, unless specifically defined herein, is not intended to be limiting.

[027] Throughout this specification, unless the context requires otherwise, the word "comprise" and "include" and variations (e.g., "comprises," "comprising," "includes," "including") will be understood to imply the inclusion of a stated component, feature, element, or step or group of components, features, elements or steps but not the exclusion of any other component, feature, element, or step or group of components, features, elements or steps.

[028] As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise.

[029] As used herein, the term “coupling” includes physical, electronic, thermal, or optical coupling of one element to another element.

[030] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[031] All percentages, ratios and proportions herein are by weight, unless otherwise specified. A weight percent (weight %, also as wt %) of a component, unless specifically stated to the contrary, is based on the total weight of the composition in which the component is included (e.g., on the total amount of the catalyst material).

[032] In view of the present disclosure, the processes and active materials described herein can be configured by the person of ordinary skill in the art to meet the desired need. In general, the disclosed systems, methods, and apparatus provide improvements in photocatalysis processes and materials. In general, the present disclosure provides a reactor system that includes a housing having an interior surface that may be at least partially reflective. The reactor system also includes at least one reactor cell disposed within an interior of the housing. The at least one reactor cell includes an enclosure and a plasmonic photocatalyst on a catalyst support disposed within the at least one enclosure. The enclosure of the cell is optically transparent and includes at least one input for a reactant to enter the at least one cell and at least one output for a reformat to exit the at least one cell. The reactor system further includes at least one light source, which may be disposed within the interior of the housing and/or external to the housing.

[033] In general, the reactor system is designed to allow for illumination of the reactor cells with a light source, which itself may be comprised of one or more individual light sources. One embodiment of the reactor system of the disclosure is shown in cross-sectional view in Figure 2A. The same reactor system **200** elements are also shown in exploded view in Figure 2B. In this embodiment, at least one reactor cell **100** and at least one light source **220** are disposed within reactor housing **230**. The reactor system **200** further comprises reactor fittings **240** that may be further coupled to another system (e.g., another system used for reforming reactions). Several other embodiments of the reactor system of the disclosure are shown in Figures 3A-3B, 4A-4B, and 5A-5B. In some embodiments, as shown in Figures 7A-7D, the reactor system may have several light sources **220** and/or thermal management features **250**.

[034] In one embodiment, the reactor fittings **240** may comprise a reactor fluid distributor (for input) and a reactor fluid accumulator (for output). Any reactor fluid distributor or accumulator known in the art might be used. For example, the reactor fluid distributor or accumulator may be similar to those disclosed in U.S. Patent No. 4,788,040 (incorporated by reference herein), where the orifices of the reactor fluid distributor and accumulator will match to the arrangement of the reactor cells. In some embodiments, the interior surfaces (i.e. facing the reactor cells) of the reactor fluid distributor and/or accumulator may be reflective.

[035] In one embodiment, the at least one light source may be elongated and arranged coaxially along a central long axis of the housing. In further embodiments, the at least one light source may include at least one LED, metal halide bulb, high pressure sodium bulb, xenon lamp, incandescent bulb, fluorescent bulb, halogen bulb, HID, laser or combination thereof. In a further embodiment, the at least one light source may include at least one corn cob LED bulb having a plurality of LEDs arranged along its length.

[036] In another embodiment, the at least one reactor cell may be elongated and may have a circular cross-section. In this embodiment, the at least one reactor cell may be arranged parallel to or even coaxial with the at least one light source. For example, in a further embodiment, the at least one light source may be arranged coaxially in the housing and the at least one reactor cell includes a plurality of reactor cells arranged surrounding the at least one light source.

[037] In one embodiment, the housing has a circular or a polygonal cross-section. In one embodiment, the housing may have an inner diameter ranging from about 12 cm to about 128 cm. The housing may further have an inner diameter ranging from about 24 cm to about 72 cm. Each of the plurality of reactor cells has a diameter ranging from about 2 cm to about 4 cm, according to one embodiment. The plurality of reactor cells ranges in number from 12 cells to 24 cells, for example.

[038] In another embodiment, the housing may have an inner diameter ranging from about 12 cm to about 18 cm. As shown in Figures 4A-4B, each of the plurality of reactor cells may have a diameter of about 2 cm, and the plurality of reactor cells may range in number from 50 cells to 100 cells, for example. In a further embodiment, shown in Figures 5A-5B, the plurality of reactor cells may each have a diameter of about 1 cm, and the plurality of reactor cells includes at least 100 reactor cells, for example.

[039] In one embodiment, shown in Figure 7B, the reactor system includes at least one shaft **255** that is arranged coaxially within the housing. The at least one shaft may have a reflective exterior surface. In this embodiment, a plurality of reactor cells and a plurality of light sources are arranged parallel to and surrounding the at least one shaft, such as in an alternating arrangement. In a further embodiment, the at least one shaft **255** may have a

cavity having an input at a first end and an output at a second end such that the at least one shaft 255 is configured to permit fluid to flow there through for thermal management of the reactor system, in which case the fluid would constitute at least part of the thermal management feature 250. In an alternative embodiment, the at least one shaft comprises a metal rod and or metal wires configured for heat conduction.

[040] In another embodiment, the reactor system has a housing with an interior surface coupled to at least one light source. The reactor system further has at least one reactor cell disposed within an interior of the housing. The at least one reactor cell includes an enclosure and a plasmonic photocatalyst on a catalyst support disposed within the at least one enclosure. The enclosure is optically transparent and includes at least one input for a reactant to enter the at least one reactor cell and at least one output for a reformat to exit the at least one reactor cell. The reactor system may include at least one shaft having a reflective exterior surface that is disposed within the housing. In one embodiment, the at least one shaft is arranged coaxially within the housing.

[041] In some embodiments, the light source is a solar light source. For example, the light source may include electromagnetic radiation from the sun, another star, or any other light-emitting celestial body. In such a case, the reactor system may comprise a solar concentrator to provide light energy to a photocatalytic reactor cell, which may be part of a reactor system comprising many such photocatalytic reactor cells.

[042] A reactor system utilizing a solar light source may comprise a solar concentrator, such as a reflector or refractor, and a photocatalytic reactor cell positioned relative to the solar concentrator to increase an incidence of electromagnetic radiation on the photocatalytic reactor cell. According to one example, the solar concentrator comprises a reflector, such as a parabolic mirror trough, a parabolic dish, a Fresnel reflector, a Compact Linear Fresnel Reflector (CLFR), a solar power tower, a flat plate collector, an evacuated tube collector, or another type of reflector. According to another example, the solar concentrator comprises a refractor, such as a lens (e.g. a Fresnel lens).

[043] Figure 8 illustrates one example embodiment, in which the solar concentrator is a parabolic mirror trough 800. As shown, the parabolic mirror trough 800 comprises a parabolically-shaped mirrored surface 800, curved to mathematically define a focal line to which incoming electromagnetic radiation from the sun (or other light source) reflects. The parabolic mirror trough 800 also comprises an attachment mechanism 804, such as a stand, frame, base, or other means for attaching the parabolic mirror trough 800 to an object, such as the Earth (including an object on the Earth), a vehicle, a celestial body, or a satellite, for example. The photocatalytic reactor cell is positioned to be substantially aligned along its central axis (i.e. its long axis, for an elongated cylindrical cell) to the focal line of the parabolic mirror trough.

[044] While Figure 8 illustrates only a single parabolic mirror trough **800** with a single photocatalytic reactor cell **100**, in some embodiments, there may be more than one parabolic mirror trough with a single photocatalytic reactor cell (positioned to be substantially aligned along its central axis to a focal line of at least one of the plurality of parabolic mirror troughs), a single parabolic mirror trough with more than one photocatalytic reactor cell (positioned to be substantially parallel along their central axes to a focal line of the parabolic mirror trough), or multiple parabolic mirror troughs with multiple photocatalytic reactor cells (each positioned to be substantially parallel along its central axis to a focal line of at least one of the plurality of parabolic mirror troughs).

[045] As an alternative to the parabolic mirror trough **800** illustrated in Figure 8, the solar concentrator may comprise a parabolic dish, with the photocatalytic reactor cell positioned substantially at a focal point of the parabolic dish. The parabolic dish may, for example, comprise a plurality of reflective dish portions disposed adjacent to other respective reflective dish portions to form an array.

[046] As another alternative, the solar concentrator may comprise a Fresnel reflector, where the photocatalytic reactor cell is positioned to be substantially aligned along its central axis to a focal line of the Fresnel reflector. The Fresnel reflector may comprise a Compact Linear Fresnel Reflector (CLFR), for example.

[047] As yet another example, the solar concentrator may comprise a solar power tower configured to receive focused electromagnetic radiation from an array of movable reflectors. In such a configuration, the photocatalytic reactor cell is positioned in the solar power tower at a focal point of the array of movable reflectors, according to one embodiment.

[048] Other solar concentrator embodiments utilizing reflectors may also be used. A flat plate collector and/or an evacuated tube collector may possibly be used in some implementations.

[049] As an alternative to a reflector implementation for the solar concentrator, a refractor may be used. For example, the solar concentrator may comprise a refractive lens, with the photocatalytic reactor cell positioned at a focal point of the refractive lens. For example, the solar concentrator may comprise a Fresnel lens, where the photocatalytic reactor cell is positioned at a focal point of the Fresnel lens.

[050] In the above-described embodiments, the particular solar concentrating and/or focusing elements, such as the parabolic mirror trough **800** and others, may constitute a housing or at least a portion of the housing, as otherwise described herein. As an alternative, such solar concentrating and/or focusing elements may reside within a separate housing, such as one that is at least partially optically transparent.

[051] For each of the solar light source embodiments described above, the solar concentrator may be advantageously oriented to substantially maximize an intensity of

electromagnetic radiation incident normal to the solar concentrator. In one embodiment, the length of the solar concentrator is aligned along a north-south orientation, and the reactor system may further comprise a computer-controlled solar tracking system to orient the solar concentrator to maintain an optimized angle of incidence of the electromagnetic radiation to the solar concentrator. In general, any of the solar concentrator alternatives described above may be controlled to track motion of the sun (or other light source) to substantially maximize an intensity of electromagnetic radiation incident normal to the solar concentrator.

[052] For at least some of the solar light source embodiments described above, the photocatalytic reactor cell may advantageously have at least a portion of an interior surface of the enclosure be reflective (e.g. mirrored) in order to reflect received light back into the catalyst support 120 (see, e.g., Fig. 1A). For example, an inner/interior surface of the photocatalytic reactor cell enclosure may be mirrored opposite to the solar concentrator from the photocatalytic reactor cell. The enclosure of the photocatalytic reactor cell should be largely optically transparent, though, at least in a direction toward the solar concentrator.

[053] While several solar light source implementations for a reactor have been described, others are possible and are intended to be within the scope of the appended claims. Moreover, the embodiments described above may have applications with light sources other than the sun, including both natural and artificial (i.e. electric) light sources.

[054] As noted above, the reactor system comprises one or more reactor cells. The reactor cells of the disclosure comprise an optically transparent enclosure comprising at least one input and at least one output; and one or more plasmonic photocatalysts on a catalyst support disposed within the enclosure. Typically, the plasmonic photocatalyst comprises a catalyst coupled to a plasmonic material, such as through a physical, electronic, thermal, or optical coupling. The reactor cells of the disclosure are configured, upon application of a light source, to transform at least one reactant into at least one reformat.

[055] In traditional fixed bed reactors, the catalyst beds are not optically transparent (i.e., the light does not penetrate the catalyst bed). In contrast, according to some embodiments of the disclosure, at least the support is optically transparent. In other embodiments, the reactor cells of the disclosure additionally or alternatively comprise an enclosure that is optically transparent. In some embodiments, the optically transparent enclosure has at least 50% transmittance for a predetermined light wavelength. For example, in some embodiments, the optically transparent enclosure has between about 50% to about 100% transmittance for a predetermined light wavelength; or at least 55%, or at least 60%, or at least 70%, or at least 80%, or at least 90%, or at least 95%, or even at least 98% transmittance for a predetermined light wavelength.

[056] Advantageously, the optically transparent enclosure according to some embodiments of the disclosure may have low thermal expansion. Thus, in one embodiment,

the optically transparent enclosure comprises a material having less than about 1×10^{-4} / °K linear coefficient of thermal expansion (CTE). In another embodiment, the optically transparent enclosure comprises a material having less than about 1×10^{-5} / °K CTE; or less than about 5×10^{-6} / °K CTE; or less than about 3×10^{-6} / °K CTE; or even less than about 1×10^{-6} / °K CTE. For example, some exemplary materials with suitable CTE values include, but are not limited to, borosilicate glass at 3.2×10^{-6} /°K, PYREX® glass at 3.2×10^{-6} /°K, quartz at about 0.59×10^{-6} /°K to about 9×10^{-6} /°K, sapphire at 5.3×10^{-6} /°K, and fused silica at 0.55×10^{-6} /°K.

[057] One of skill in the art will recognize that any material having the desired transmittance for a predetermined light wavelength (or range of wavelengths) and/or coefficient of thermal expansion (CTE) may be used. In some embodiments, the optically transparent enclosure comprises glass, borosilicate glass, quartz, fused quartz, aluminosilicate glass, lithium-aluminosilicate glass, sapphire, or combinations thereof.

[058] In one embodiment, the optically transparent enclosure of the reactor cell is optically transparent on all sides of the enclosure. But one of skill in the art would appreciate that, in one embodiment, the optically transparent enclosure may not be optically transparent on all sides of the enclosure. For example, the outer cavity of the optically transparent enclosure may comprise a reflective surface facing the central cavity (which may be optically transparent).

[059] The reactor cells of the disclosure also require one or more plasmonic photocatalysts comprising a catalyst coupled to a plasmonic material, such as through a physical, electronic, thermal, or optical coupling. Without being bound by theory, the plasmonic material is believed to act as an optical antenna capable of absorbing light due to the unique interaction of light with plasmonic materials and, as a result, generates a strong electric field on and near the plasmonic material (i.e., as a result of collective oscillation of electrons within the plasmonic material). This strong electric field on or near the plasmonic material allows for coupling between the catalyst and the plasmonic material, even when the catalyst and the plasmonic material are separated by distances of up to about 20 nm or more.

[060] In general, the plasmonic material may be any metal, metal alloy, metalloid element, or its alloy. In some embodiments, the plasmonic material of the disclosure is selected from gold, gold alloy, silver, silver alloy, copper, copper alloy, aluminum, or aluminum alloy. In the present disclosure the term "alloys" is intended to cover any possible combination of metals. For example, the alloys may be binary alloys such as AuAg, AuPd, AgPd, AuCu, AgCu, etc., or they may be ternary alloys, or even quaternary alloys.

[061] In some embodiments, the plasmonic material of the disclosure comprises an oxide shell surrounding a non-oxidized core. In one or more embodiments, the oxide shell may be

a natural/native oxide shell that forms upon a metal or alloy's exposure to air or water. For example, a copper plasmonic material may possess a copper oxide (e.g., CuO or Cu₂O) shell surrounding a copper core, or an aluminum plasmonic material may possess an aluminum oxide shell surrounding an aluminum core. In some embodiments, the oxide shell may be at least partially artificially produced, such as by artificially increasing the thickness of a native/natural oxide shell by appropriate chemical methods, or by chemically synthesizing, or otherwise depositing, an oxide material around a pre-formed plasmonic material. In some embodiments, the oxide shell may have a thickness of up to about 30 nm, or up to about 25 nm, or up to about 15 nm. In some embodiments, the oxide shell may have a thickness of at least about 0.5 nm, or at least 1 nm, or at least 1.5 nm. In some embodiments, the oxide shell has a thickness ranging from about 0.1 nm to about 5 nm; or from about 0.1 nm to about 30 nm; or from about 1 nm to about 5 nm; or from about 1 nm to about 30 nm.

[062] One of skill in the art will recognize that the size, shape, and chemical structure of the plasmonic material will affect the absorption of one or more target wavelengths. Thus, the plasmonic material or materials may be designed to maximize absorption of a target wavelength (or a set or range of target wavelengths, such as to recognize the target wavelength but have the material absorb relatively less of other, non-target wavelengths. In another example, the plasmonic material of the disclosure may be designed to catalyze a desired chemical reaction. Thus, in some embodiments, the plasmonic material may have a plasmon resonant frequency, or optical absorption maximum, in the ultraviolet to infrared region of the electromagnetic spectrum. In some embodiments, the plasmonic material has a plasmon resonant frequency in the visible light spectrum (such as at a wavelength ranging from about 380 nm to about 760 nm).

[063] In general, the catalyst material coupled to the plasmonic material may be any compound capable of catalyzing a desired reaction (e.g., even if it were not coupled to a plasmonic material). For example, the catalyst may be capable of oxidation and reduction chemistry, water or air pollution remediation reactions, NO_x and N₂O decompositions, catalyzing hydrogenation reactions such as acetylene hydrogenation, carbon dioxide conversion to carbon monoxide via the reverse water-gas shift reaction (which can be coupled with a hydrogenation to create hydrocarbons using FisherTropsch synthesis), and nitrogen activation chemistry, including the synthesis of ammonia. In some embodiments, the catalyst of the disclosure may be any metal or metalloid element, and any alloy, oxide, phosphide, nitride, or combination thereof of said elements. For example, the catalyst of the disclosure may comprise catalytically active palladium, platinum, ruthenium, rhodium, nickel, iron, copper, cobalt, iridium, osmium, titanium, vanadium, indium, or any combination thereof. The catalyst of the disclosure may comprise any alloy, oxide, phosphide, or nitride

of catalytically active palladium, platinum, ruthenium, rhodium, nickel, iron, copper, cobalt, iridium, osmium, titanium, vanadium, or indium. In some embodiments, the catalyst of the disclosure comprises catalytically active iron or copper. In some embodiments, the catalyst of the disclosure may be intermetallic nanoparticles, core-shell nanoparticles, or semiconductor nanoparticles (e.g., Cu_2O).

[064] In some embodiments, the catalyst may be physically attached to the plasmonic material, while in other embodiments the catalyst may be separated by a small distance from the plasmonic material (but still coupled thereto, such as through a physical, electronic, thermal, or optical coupling). The separation may be either by empty space (i.e., a distinct physical separation) or the separation may be by the thin oxide layer discussed above. For example, the plasmonic material and the catalyst may be separated by a small distance when they are prepared via lithographic methods to have a distinct physical separation. In one or more embodiments, the small separation may be a distance of up to about 30 nm, or up to about 25 nm, or up to about 15 nm. In some embodiments, the separation may be at least about 0.5 nm, or at least 2 nm, or at least 5 nm, or at least 10 nm. In some embodiments, one or more catalysts may be physically attached to the surface of a single plasmonic material, which can increase the surface area available for reactions. In some embodiments, the catalyst may form a shell that surrounds the plasmonic material.

[065] The plasmonic photocatalysts may have a diameter ranging from about 5 nm to about 300 nm. In some embodiments, the plasmonic photocatalyst of the disclosure may have a diameter ranging from about 10 nm to about 300 nm; or about 50 nm to about 300 nm; or about 80 nm to about 300 nm; or about 100 nm to about 300 nm; or about 5 nm to about 250 nm; about 10 nm to about 250 nm; or about 50 nm to about 250 nm; or about 80 nm to about 250 nm; or about 100 nm to about 250 nm; or about 5 nm to about 200 nm; about 10 nm to about 200 nm; or about 50 nm to about 200 nm; or about 80 nm to about 200 nm; or about 100 nm to about 200 nm; or about 80 nm to about 200 nm.

[066] The reactor cells according to at least some embodiments also include one or more plasmonic photocatalysts dispersed onto a catalyst support. As with the enclosure, in some embodiments, the catalyst support has a low absorbance, and in particular, a low enough absorbance (for the particular radiation wavelength or wavelength range) so that the reactants are exposed to a sufficient amount of radiation to result in the desired catalytic effect for the particular reactor cell geometry in use.

[067] One of skill in the art will recognize that any material having the desired absorbance or transmittance for a predetermined light wavelength (or set or range of wavelengths) may be used for the catalyst support. In some embodiments, the catalyst support of the disclosure comprises silica, quartz, fused quartz, glass, borosilicate glass,

aluminosilicate glass, lithium-aluminosilicate glass, sapphire, diamond, or combinations thereof. The catalyst support may be in any form known in the art, such as in the form of beads, microporous beads, fibers, spheres, pellets, cylinders (hollow or otherwise), honeycombs, or symmetrical or asymmetrical tri-quadrulobes (for example, using extrusion or tableting methods). For example, Figure 6 illustrates a cross-sectional view of the catalyst support in the bead form. In some embodiments, the catalyst support of the disclosure may be an aerogel. Suitable aerogels include, but are not limited to, silicon dioxide aerogel, aluminum oxide aerogel, titanium dioxide aerogel, zirconium dioxide aerogel, holmium oxide aerogel, samarium oxide aerogel, erbium oxide aerogel, neodymium(III) oxide aerogel, or a combination thereof. In some embodiments, the catalyst support of the disclosure is a silicon dioxide aerogel. One of skill will recognize that when the support is an aerogel, the plasmonic photocatalyst may be dispersed throughout the aerogel (for example, the plasmonic photocatalyst may be embedded into the aerogel). In some embodiments, the catalyst support of the disclosure may be transparent aluminum oxide (such as α -phase aluminum oxide or γ -phase aluminum oxide).

[068] The plasmonic photocatalyst may be present on the catalyst support in any amount suitable for the desired use. For example, the plasmonic photocatalyst may be present on the catalyst support in an amount between about 0.01 wt % and about 30 wt %; or about 0.01 wt % and about 80 wt %; or about 10 wt % and about 80 wt %; or about 0.01 wt % and about 70 wt %; or about 10 wt % and about 70 wt %. In some embodiments, the plasmonic photocatalyst may be present on the catalyst support in an amount between about 0.01 vol % and about 30 vol %; or about 0.01 vol % and about 20 vol %; or about 10 vol % and about 50 vol %; or about 0.01 vol % and about 70 vol %; or about 10 vol % and about 70 vol %.

[069] In some embodiments, the plasmonic photocatalyst may be present on the catalyst support as a thin coating on the outer surface of the support (e.g., as one or a few layers). In one or more embodiments, the plasmonic photocatalyst layer that is coated onto the support may be up to about 30 nm, or up to about 25 nm, or up to about 15 nm; or at least about 0.5 nm, or at least 2 nm, or at least 5 nm, or at least 10 nm; or between about 5 nm to about 300 nm; or about 10 nm to about 300 nm; or about 50 nm to about 300 nm; or about 80 nm to about 300 nm; or about 100 nm to about 300 nm; or about 5 nm to about 200 nm; about 10 nm to about 200 nm; or about 50 nm to about 200 nm; or about 80 nm to about 200 nm; or about 100 nm to about 200 nm; or about 80 nm to about 200 nm; or about 5 nm to about 100 nm; about 10 nm to about 100 nm; or about 50 nm to about 100 nm; or about 10 nm to about 50 nm; or about 1 nm to about 50 nm.

[070] In some embodiments, the reactor cell comprises one plasmonic photocatalyst on the catalyst support disposed within the enclosure (e.g., one type of supported plasmonic photocatalyst would be disposed within the enclosure). In some embodiments, the reactor

cell comprises two or more plasmonic photocatalysts on the catalystsupport disposed within the enclosure (e.g., two or more different supported plasmonic photocatalysts would be disposed within the enclosure). Two or more plasmonic photocatalysts on the catalystsupport may be provided, either mixed or in distinct layers. For example, each layer would have one type of supported plasmonic photocatalyst having a desired plasmon resonant frequency and/or a desired diameter. In a non-limiting example, one layer would absorb one desired wavelength range relative to other wavelengths, the next layer would absorb another wavelength range, and the final layer (e.g., an intermediate layer) would absorb other wavelengths, such as wavelengths outside the first and second wavelength ranges.

[071] In general, the reactor cell is designed to allow for illumination of the plasmonic photocatalysts with a light source. One embodiment of the reactor cell of the disclosure is shown in cross-sectional view in Figure 1A. The same reactor cell **100** elements are also shown in exploded view in Figure 1B. Here, a reactor cell **100** is shown comprising a plasmonic photocatalyst on a catalystsupport **120** disposed within an optically transparent enclosure **110**. The reactor cell **100** may further comprise fittings **160** configured to attach the cell to at least one delivery channel for at least one reactant input **130** and at least one reformat output **140**. The reactor cell **100** may further comprise one or more packing support elements **150** configured to retain the catalyst within the optically transparent enclosure **110**.

[072] The size and shape of the enclosure of the reactor cell may be adapted to meet the desired need. In some embodiments, the enclosure has an inner diameter ranging from about 0.2 cm to about 10 cm; or about 0.5 cm to about 3 cm. In some embodiments, the enclosure has a length ranging from about 10 cm to about 2 m; or about 50 cm to about 1 m. The enclosure of the reactor cell may have a circular cross-section or a polygonal cross-section, for example.

[073] As noted above, the reactor cell may further comprise one or more fittings (such as fittings **160** in Figures 1A-1B) configured to attach the reactor cell to at least one delivery channel for delivering the at least one reactant to or the at least one reformat from the enclosure. For example, the fittings may comprise a first fitting coupled to the reactant input and a second fitting coupled to the reformat output. The fittings of the disclosure may comprise low alloy steel, high alloy steel, chrome alloys, nickel alloys, plastics, glass, borosilicate glass, quartz, fused quartz, aluminosilicate glass, lithium-aluminosilicate glass, or combinations thereof. Depending on the need, the fittings of the disclosure may further comprise an O-ring or another sealing mechanism. Other fitting materials and/or sealing mechanisms are also possible, and are intended to be within the scope of the present disclosure.

[074] The reactor cell may further comprise one or more packing support elements (such as packing support elements 150 in Figures 1A-1B) configured to retain the catalyst within the enclosure. In some embodiments, the packing support elements are provided at the input end and at the output end of the reactor cell. In some embodiments, the packing support elements are provided at the input end, the output end, and spaced throughout the reactor cell. Conventional materials for use as a packing support may be used, such as metal mesh, glass beads (having a larger diameter than the support), glass wool, monolith, polymer, or elastomer, for example.

[075] In some embodiments, the optically transparent enclosure further comprises an outer cavity and a central cavity arranged coaxially with the outer cavity, wherein the outer cavity contains the plasmonic photocatalyst on the catalyst support and the central cavity is configured to receive a light source or a thermal management feature. In some embodiments, the light source is disposed within the central cavity of the optically transparent enclosure. In some embodiments, the light source extends along or through a length of the enclosure. Any suitable light source may be used such as, but not limited to, LED, metal halide bulb, high pressure sodium bulb, xenon lamp, incandescent bulb, fluorescent bulb, halogen bulb, HID, laser or combination thereof. Natural light, such as solar light, may also be directed into the central cavity to serve as the light source. In some embodiments, the thermal management feature is disposed within the central cavity of the optically transparent enclosure. Any thermal management feature known in the art might be used. For example, the thermal management feature may include a fluid input coupled to a first end of the central cavity and a fluid output coupled to a second end of the central cavity such that fluid may flow through the reactor cell to add or remove heat from the reactor cell; or the thermal management feature may comprise a metal rod or metal wires configured for heat conduction.

[076] In one alternative embodiment, neither the housing of the reactor system nor the enclosure of each reactor cell need be optically transparent. In this alternative embodiment, the reactor system comprises a housing and a plurality of reactor cells each having its own light source. Since, in this embodiment, each reactor cell has its own light source, the enclosure of each reactor cell need not be optically transparent, and may instead be reflective, in order to reflect light from the light source back into the interior of the enclosure. Each reactor cell may also include an input and an output, and each reactor cell includes at least one plasmonic photocatalyst on a catalyst support disposed within the enclosure, where the plasmonic photocatalyst comprises a catalyst coupled to a plasmonic material. The reactor system may further include a distributor for distributing at least one reactant into the plurality of reactor cells via the input of each reactor cell, and an accumulator for

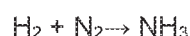
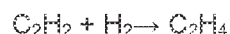
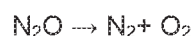
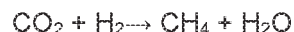
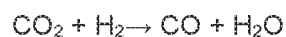
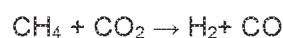
accumulating at least one reformat from the plurality of reactor cells via the output of each reactor cell.

[077] Another aspect provides methods for using the reactor systems to transform reactants. Specifically, the disclosure provides methods for transforming at least one reactant into at least one reformat, the method comprising: adding at least one reactant into a reactor system of the disclosure; and illuminating, via the at least one light source, an interior of the reactor system and/or reactor cell(s).

[078] In an alternative embodiment of the methods of the disclosure, the illuminating is from a light source external to the reactor system.

[079] In some embodiments of the method, no external heating (e.g. from a dedicated heating source) is applied. In some embodiments, the methods further comprise externally heating the reactor cell. The external heating may be accomplished via the thermal management feature as described above, or via some other heating technique.

[080] Representative methods of the disclosure include, but are not limited to, oxidation and reduction, water or air pollution remediation reactions, NO_x and N₂O decompositions, hydrogenation such as acetylene hydrogenation, carbon dioxide conversion, and nitrogen activation, including the synthesis of ammonia. Some of the representative chemical transformations include:



[081] Thus, in some embodiments, the reactants are methane and water; or the reactants are methane and carbon dioxide; or the reactants are carbon monoxide and water; or the reactants are carbon dioxide and hydrogen gas; or the reactant is nitrous oxide; or the reactants are acetylene and hydrogen gas; or the reactants are hydrogen gas and nitrogen gas; or the reactants are carbon dioxide and hydrogen gas.

[082] The methods of the disclosure may be performed at any suitable temperature. For example, in some embodiments, the methods of the disclosure are performed at a temperature ranging from about 100 °C to about 300 °C; or about 100 °C to about 250 °C; or about 100 °C to about 200 °C; or about 150 °C to about 300 °C; or about 150 °C to about

250 °C; or about 150 °C to about 200 °C; or about 200 °C to about 300 °C; or about 200 °C to about 250 °C; or about 180 °C to about 220 °C; or about 190 °C to about 210 °C; or about 20 °C to about 300 °C; or about 20 °C to about 250 °C; or about 20 °C to about 200 °C; or about 20 °C to about 150 °C; or about 20 °C to about 100 °C.

[083] The methods of the disclosure may be performed at any suitable pressure. For example, in some embodiments, the methods of the disclosure are performed at a pressure ranging from about 14 psi to about 300 psi, or about 14 psi to about 200 psi, or about 14 psi to about 100 psi, or about 14 psi to about 50 psi, or about 100 psi to about 300 psi, or about 100 psi to about 200 psi.

[084] In the methods of the disclosure, the reactants might be introduced into the reactor system at any suitable temperature. In some embodiments, the reactant has temperature ranging from about 200 °C to about 300 °C; or about 200 °C to about 270 °C; or about 200 °C to about 250 °C; or about 230 °C to about 270 °C, when introduced into the reactor cell.

[085] It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be incorporated within the spirit and purview of this application and scope of the appended claims. All publications, patents, and patent applications cited herein are hereby incorporated herein by reference for all purposes.

Claims

1. A reactor system comprising:
 - a housing; and
 - a plurality of reactor cells within an interior of the housing and arranged surrounding at least one light source, the at least one light source arranged coaxially in the housing, each of the plurality of reactor cells comprising:
 - an optically transparent enclosure,
 - a catalyst support disposed within the enclosure,
 - a plasmonic photocatalyst on the catalyst support, wherein the plasmonic photocatalyst comprises a catalyst coupled to a plasmonic material having a plasmon resonant frequency to catalyze a desired chemical reaction,
 - at least one input receiving a reactant to enter each of the plurality of reactor cells, and
 - at least one output of a reformat exiting each of the plurality of reactor cells;
 - wherein, the at least one light source is applied to the plurality of enclosures, the plurality of reactor cells transforming the reactant into the reformat.
2. The reactor system of claim 1, wherein the at least one light source is elongated and arranged coaxially along a central long axis of the housing.
3. The reactor system of claim 1, wherein the at least one light source is arranged coaxially with the plurality of reactor cells within the housing.
4. The reactor system of claim 1, wherein the at least one light source comprises at least one light source selected from the group consisting of an LED, a metal halide bulb, a high pressure sodium bulb, a xenon lamp, an incandescent bulb, a fluorescent bulb, a halogen bulb, a HID lamp, and a laser.
5. The reactor system of claim 1, wherein each of the plurality of reactor cells comprises an enclosure having an outer cavity and a central cavity arranged coaxially with the outer cavity, wherein the outer cavity of each reactor cell is arranged to contain the plasmonic photocatalyst on the catalyst support and the central cavity comprises at least one of a light source or a thermal management feature.

6. The reactor system of claim 5, wherein the thermal management feature is at least one of a metal rod, metal wires, or a fluid thermal management system.
7. The reactor system of claim 1, further comprising:
 - a reactor fluid distributor connected to the at least one input of each of the plurality of reactor cells; and
 - a fluid accumulator connected to the at least one output of each reactor cell.
8. The reactor system of claim 1, further comprising one or more fittings coupling each of the plurality of reactor cells to at least one delivery channel and delivering the at least one reactant to or the at least one reformat from the enclosure of each of the plurality of reactor cells.
9. The reactor system of claim 1, wherein the at least one reactant is in fluid form.
10. A reactor system transforming one or more reactant gases comprising:
 - a housing; and
 - a plurality of fixed-bed reactor cells disposed within an interior of the housing to surround a light source, the light source arranged coaxially in the housing, each of the plurality of reactor cells comprising:
 - an optically transparent enclosure;
 - a first fitting attached to the reactor cell at a first end of the enclosure to at least one delivery channel and receiving at least one reactant input gas;
 - a second fitting attached the reactor cell at a second end of the enclosure to at least one delivery channel and outputting at least one output gas;
 - a catalyst support disposed as a fixed bed substantially filling an entirety of the enclosure; and
 - a first plasmonic photocatalyst supported by the catalyst support, wherein the first plasmonic photocatalyst comprises a catalyst coupled to a plasmonic material having a plasmon resonant frequency to catalyze a desired chemical reaction,wherein, the light source is applied to each of the plurality of reactor cells while the at least one reactant input gas is passed through the enclosure, each reactor cell transforms the at least one reactant input gas into the at least one output gas via the at least one reactant input gas reacting with at least the first plasmonic photocatalyst.

11. A method for transforming at least one reactant gas, the method comprising:
distributing at least one reactant input gas into a plurality of fixed-bed reactor cells disposed within a housing, the plurality of reactor cells surrounding at least one light source arranged coaxially in the housing,
supporting a plasmonic photocatalyst on a fixed bed substantially filling an entirety of an optically transparent enclosure within each of the plurality of reactor cells, wherein the plasmonic photocatalyst comprises a catalyst coupled to a plasmonic material having a plasmon resonant frequency to catalyze a desired chemical reaction,
illuminating, via the at least one light source, an interior of the housing while the at least one reactant input gas is distributed into the plurality of reactor cells;
transforming the at least one reactant input gas into at least one output gas via the at least one reactant input gas reacting with at least the plasmonic photocatalyst; and
accumulating the at least one output gas from the plurality of reactor cells.
12. The method of claim 11, further comprising reflecting light from the at least one light source off of a reflective interior surface of the housing and into the plurality of reactor cells.
13. The method of claim 11, wherein the optically transparent enclosure of each of the plurality of reactor cells comprises an outer cavity and a central cavity arranged coaxially with the outer cavity, wherein the outer cavity of each reactor cell contains at least the first plasmonic photocatalyst on the catalyst support and the central cavity of each reactor cell contains a light source, and wherein the illuminating is at least partially from the light source contained in the central cavity of each of the plurality of reactor cells.
14. The method of claim 11, wherein the optically transparent enclosure of each of the plurality of reactor cells comprises an outer cavity and a central cavity arranged coaxially with the outer cavity, wherein the outer cavity of each reactor cell contains at least the first plasmonic photocatalyst on the catalyst support and the central cavity of each reactor cell contains a thermal management feature, and wherein the method further comprises heating, via the thermal management feature in each of the plurality of reactor cells, the plurality of reactor cells to assist in transforming the at least one reactant input gas.
15. The method of claim 14, wherein heating, via the thermal management feature in each of the plurality of reactor cells, comprises supplying fluid from a fluid input coupled to a first end of the central cavity of each of the plurality of reactor cells to a fluid output coupled to a second

end of the central cavity of each of the plurality of reactor cells, such that the fluid heats each of the plurality of reactor cells.

16. The method of claim 11, further comprising heating the plurality of reactor cells via the at least one reactant input gas reacting with at least the first plasmonic photocatalyst in each of the plurality of reactor cells.

17. The method of claim 11, wherein the at least one light source includes a light source external to the housing, wherein the housing is at least partially optically transparent, and wherein illuminating the interior of the housing includes directing electromagnetic radiation from the light source through the housing and into the plurality of photocatalytic reactor cells.

18. A reactor system comprising:
a housing;
a plurality of reactor cells disposed within the housing, each reactor cell comprising:
an enclosure having a reflective interior surface;
an input,
an output, and
a light source; and
at least one plasmonic photocatalyst on a catalyst support disposed within the enclosure, wherein the plasmonic photocatalyst comprises a catalyst coupled to a plasmonic material having a plasmon resonant frequency to catalyze a desired chemical reaction;
a distributor for distributing at least one reactant into the plurality of reactor cells via the input of each reactor cell; and
an accumulator for accumulating at least one reformat from the plurality of reactor cells via the output of each reactor cell.

19. The reactor system of claim 1, wherein the optically transparent enclosure of each of the plurality of reactor cells has at least 50% transmittance for at least one predetermined light wavelength.

20. The reactor system of claim 1, wherein the optically transparent enclosure of each of the plurality of reactor cells comprises glass, borosilicate glass, quartz, fused quartz, aluminosilicate glass, lithium-aluminosilicate glass, sapphire, or combinations thereof.

21. The reactor system of claim 1, wherein the catalyst support of each of the plurality of reactor cells has an absorbance sufficiently low to catalyze the transformation of the at least one reactant input gas into the at least one output gas for at least one predetermined light wavelength.
22. The reactor system of claim 1, wherein the catalyst support of each of the plurality of reactor cells comprises silica, quartz, fused quartz, glass, borosilicate glass, sapphire, diamond, or combination thereof.
23. The reactor system of claim 1, wherein the catalyst support of each of the plurality of reactor cells is an aerogel comprising silicon dioxide, aluminum oxide, titanium dioxide, zirconium dioxide, holmium oxide, samarium oxide, erbium oxide, neodymium(III) oxide, or a combination thereof.
24. The reactor system of claim 5, wherein the thermal management feature includes (a) a fluid input coupled to a first end of the central cavity of each reactor cell and (b) a fluid output coupled to a second end of the central cavity of each reactor cell, and a supplied fluid flows through each of the plurality of reactor cells and modifies a temperature of the reactor system.
25. The reactor system of claim 5, wherein the thermal management feature comprises at least one metal rod or a plurality of metal wires.
26. The reactor system of claim 1, wherein the photocatalyst is a first plasmonic photocatalyst, wherein each of the plurality of reactor cells further comprises a second plasmonic photocatalyst supported by the catalyst support, and wherein the second plasmonic photocatalyst differs from the first plasmonic photocatalyst.
27. The reactor system of claim 26, wherein the second plasmonic photocatalyst has a different plasmon resonant frequency from that of the first plasmonic photocatalyst.
28. The reactor system of claim 26, wherein the second plasmonic photocatalyst has a different diameter from that of the first plasmonic photocatalyst.
29. The reactor system of claim 26, wherein the first plasmonic photocatalyst and second plasmonic photocatalyst are arranged in different layers from one another.

30. The reactor system of claim 26, wherein the first plasmonic photocatalyst absorbs a first wavelength range relative to other wavelengths, while the second plasmonic photocatalyst absorbs a second wavelength range relative to other wavelengths, and wherein the first wavelength range differs from the second wavelength range.

31. A reactor system comprising:

- a housing; and

- a plurality of reactor cells arranged surrounding at least one light source, the least one light source arranged coaxially in the housing, each of the plurality of reactor cells comprising:

 - an optically transparent enclosure,

 - a catalyst support configured to be within the enclosure,

 - a plasmonic photocatalyst configured to be on the catalyst support, wherein the plasmonic photocatalyst comprises a catalyst coupled to a plasmonic material having a plasmon resonant frequency to catalyze a desired chemical reaction,

 - at least one input configured for a reactant to enter each of the plurality of reactor cells, and

 - at least one output configured for a reformat to exit each of the plurality of reactor cells;

- wherein, the at least one light source is configured to illuminate the plurality of enclosures, and the plurality of reactor cells are configured to transform the reactant into the reformat.

32. The reactor system of claim 31, wherein each of the plurality of reactor cells comprises an enclosure having an outer cavity and a central cavity arranged coaxially with the outer cavity, wherein the outer cavity of each reactor cell is configured to contain the plasmonic photocatalyst on the catalyst support and the central cavity is configured to receive at least one of a light source or a thermal management feature.

33. The reactor system of claim 31, wherein the photocatalyst is a first plasmonic photocatalyst, wherein each of the plurality of reactor cells further comprises a second plasmonic photocatalyst supported by the catalyst support, and wherein the second plasmonic photocatalyst differs from the first plasmonic photocatalyst.

34. The reactor system of claim 33, wherein the first plasmonic photocatalyst and second plasmonic photocatalyst are arranged in different layers from one another.

35. The reactor system of claim 33, wherein the first plasmonic photocatalyst absorbs a first wavelength range relative to other wavelengths, while the second plasmonic photocatalyst absorbs a second wavelength range relative to other wavelengths, and wherein the first wavelength range differs from the second wavelength range.

36. A reactor system configured to transform one or more reactant gases comprising:
a housing; and
a plurality of fixed-bed reactor cells disposed within an interior of the housing surrounding a light source disposed within and arranged coaxially in the housing, each of the plurality of reactor cells comprising:
an optically transparent enclosure;
a first end of the enclosure for receiving at least one reactant input gas;
a second end of the enclosure configured for outputting at least one output gas;
a catalyst support configured to be disposed as a fixed bed substantially filling an entirety of the enclosure; and
a first plasmonic photocatalyst configured to be supported by the catalyst support, wherein the first plasmonic photocatalyst comprises a catalyst coupled to a plasmonic material having a plasmon resonant frequency to catalyze a desired chemical reaction,
wherein, the light source is configured to illuminate each of the plurality of reactor cells while the at least one reactant input gas is passed through the enclosure, each reactor cell is configured to transform the at least one reactant input gas into the at least one output gas via the at least one reactant input gas reacting with at least the first plasmonic photocatalyst.

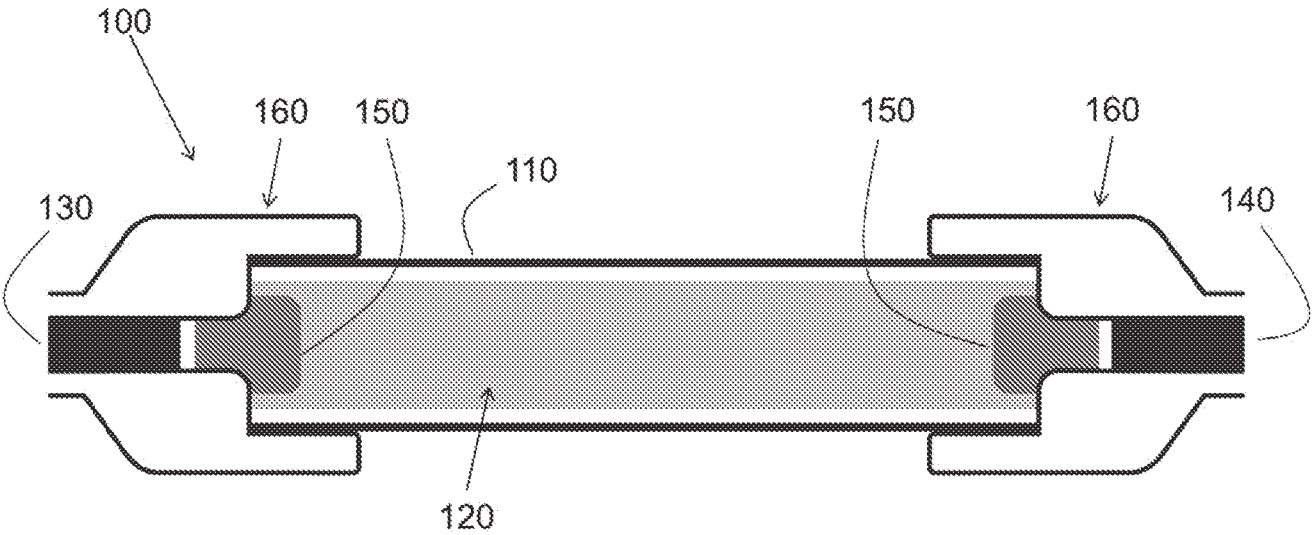


Figure 1A

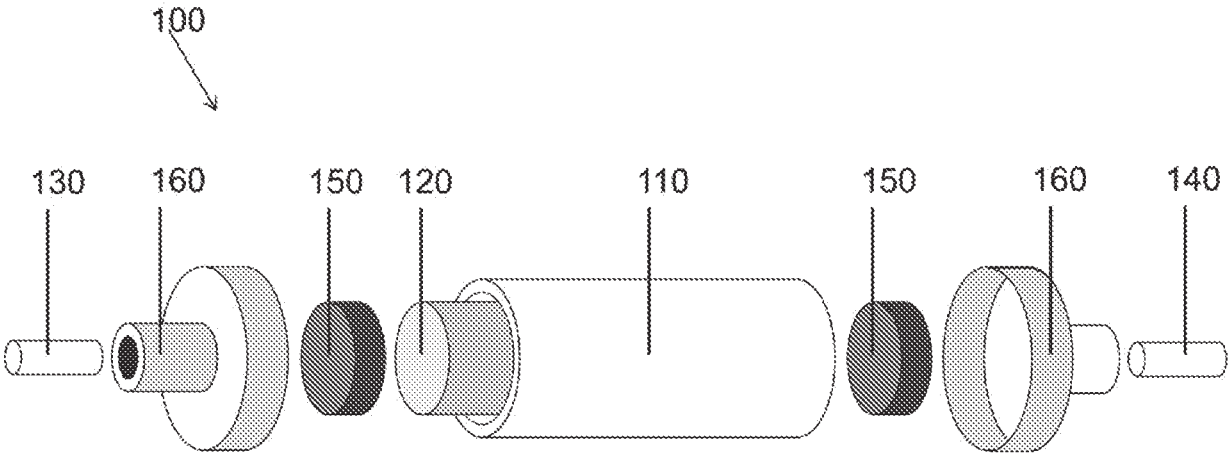


Figure 1B

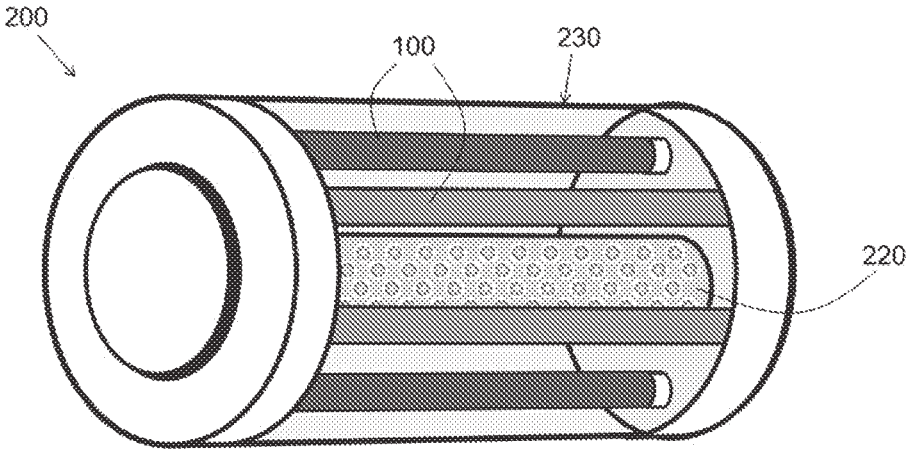


Figure 2A

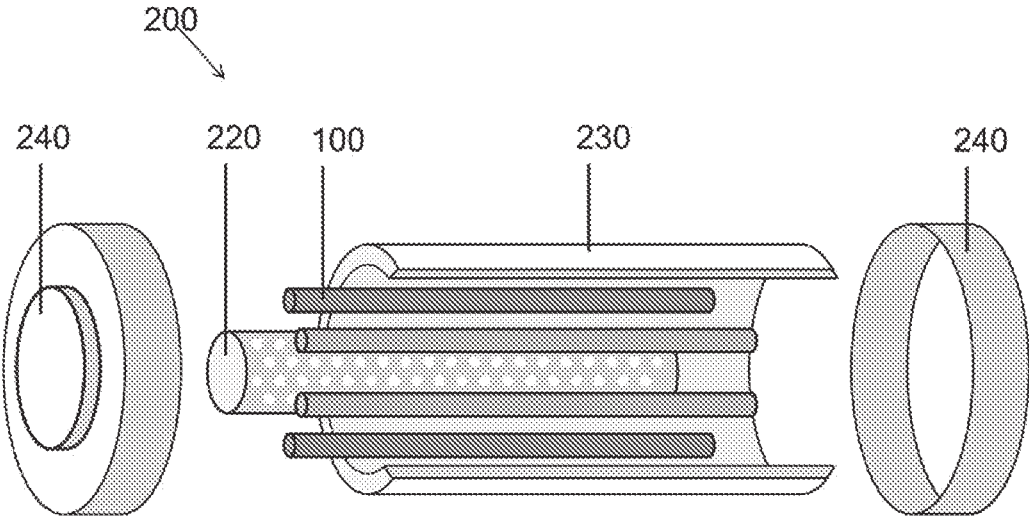


Figure 2B

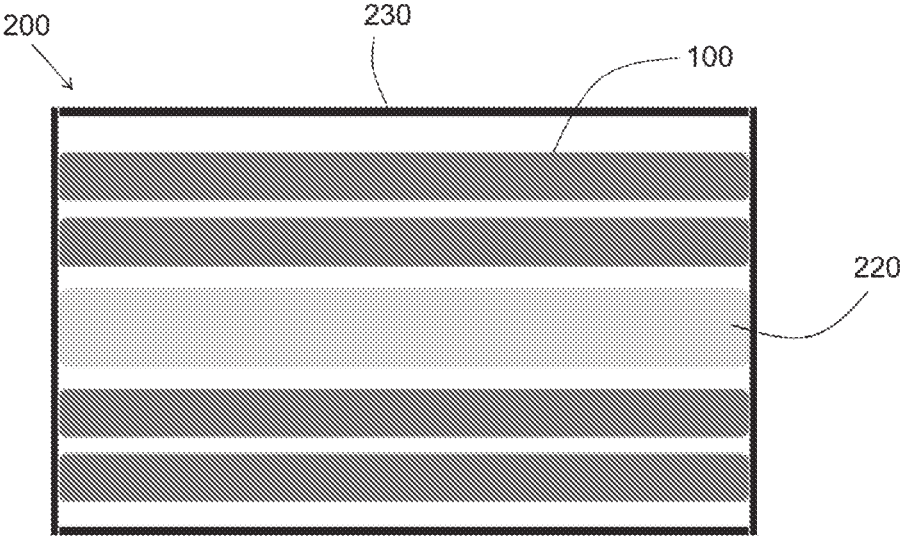


Figure 3A

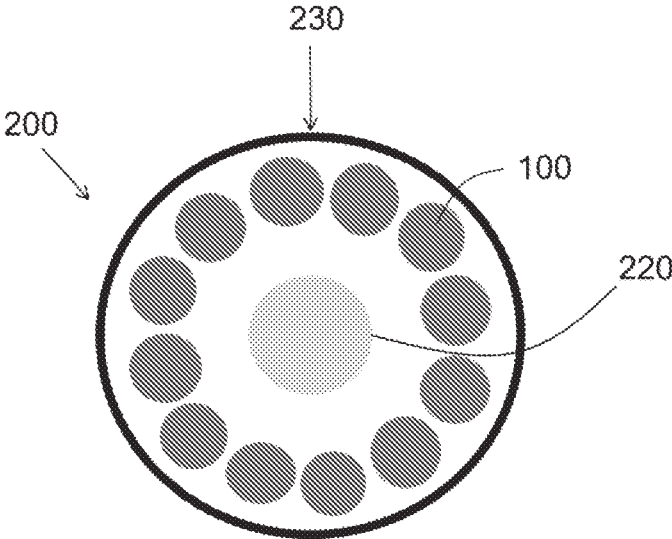


Figure 3B

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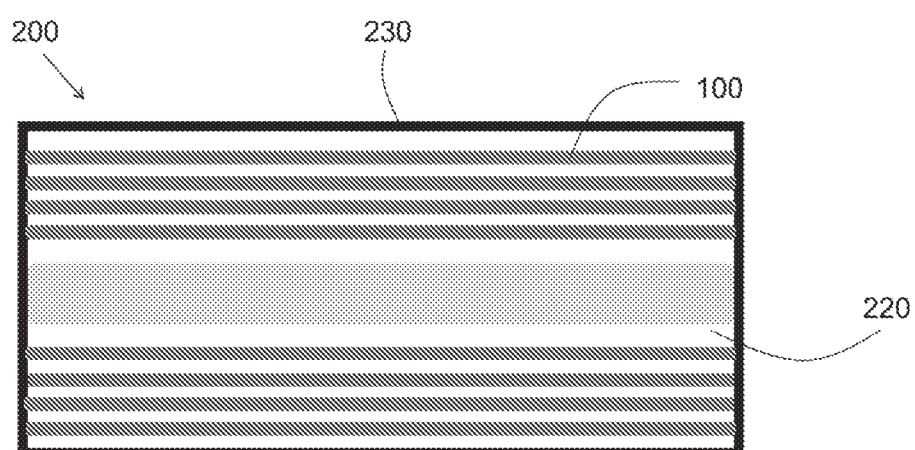


Figure 4A

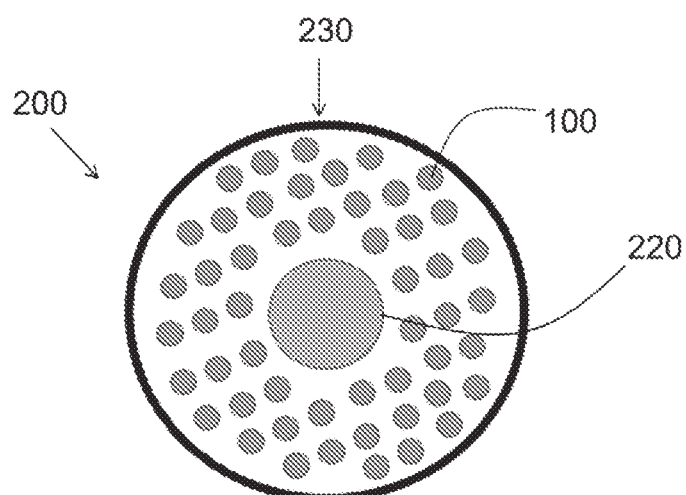


Figure 4B

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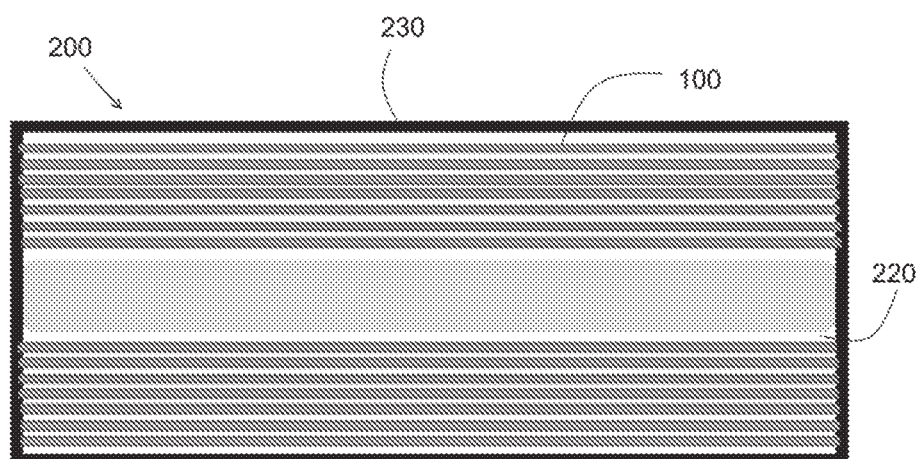


Figure 5A

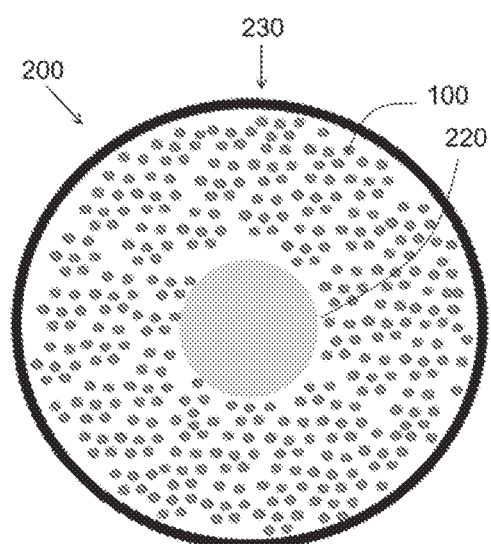


Figure 5B

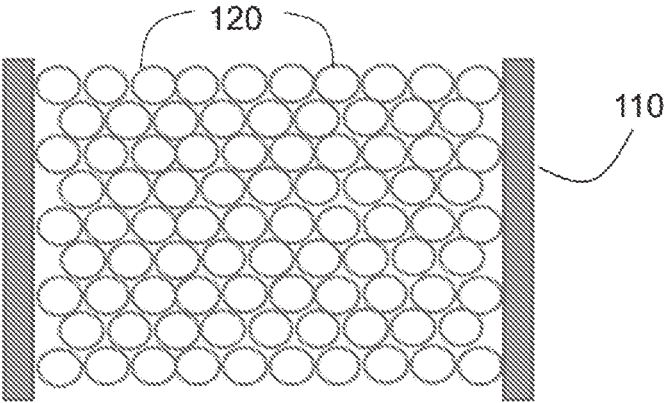


Figure 6

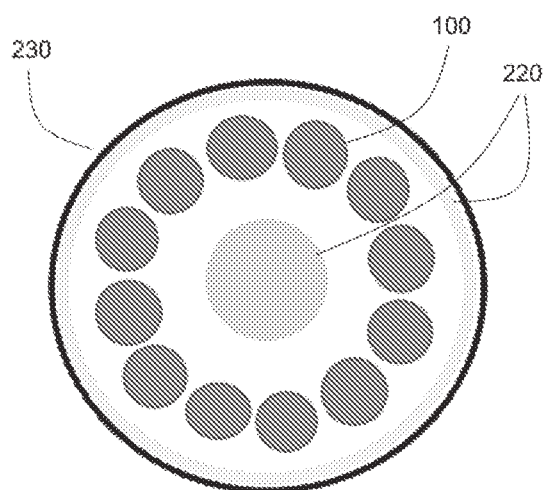


Figure 7A

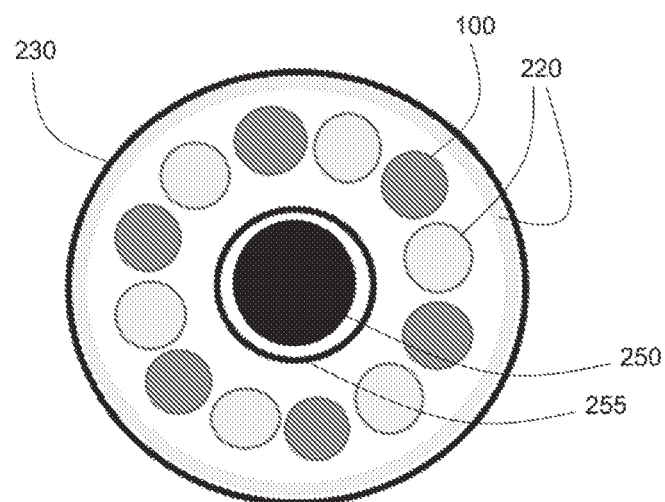


Figure 7B

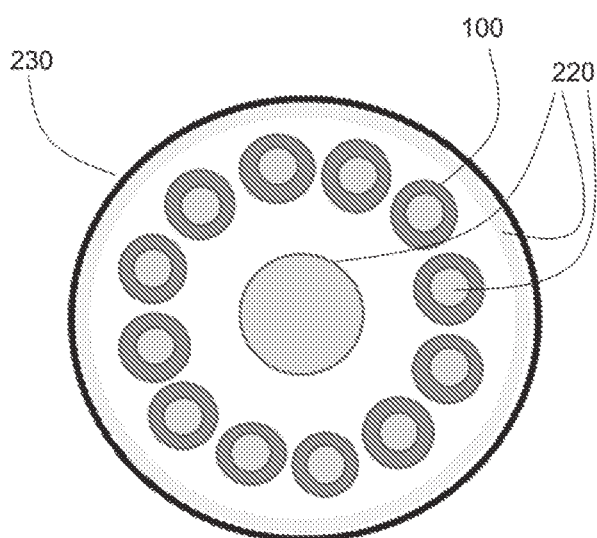


Figure 7C

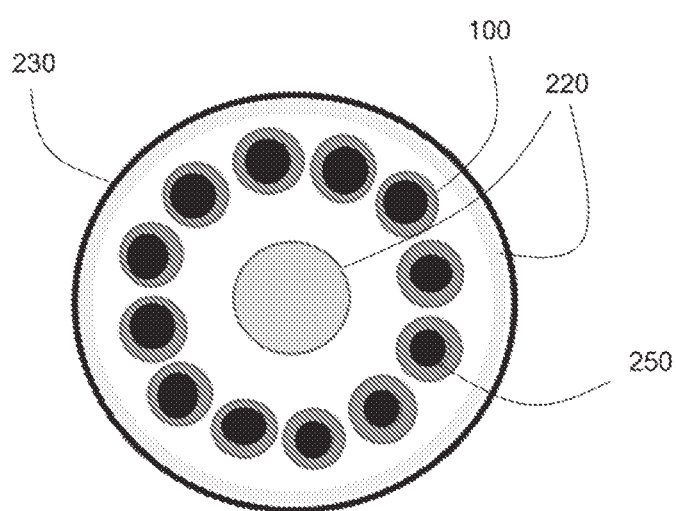


Figure 7D

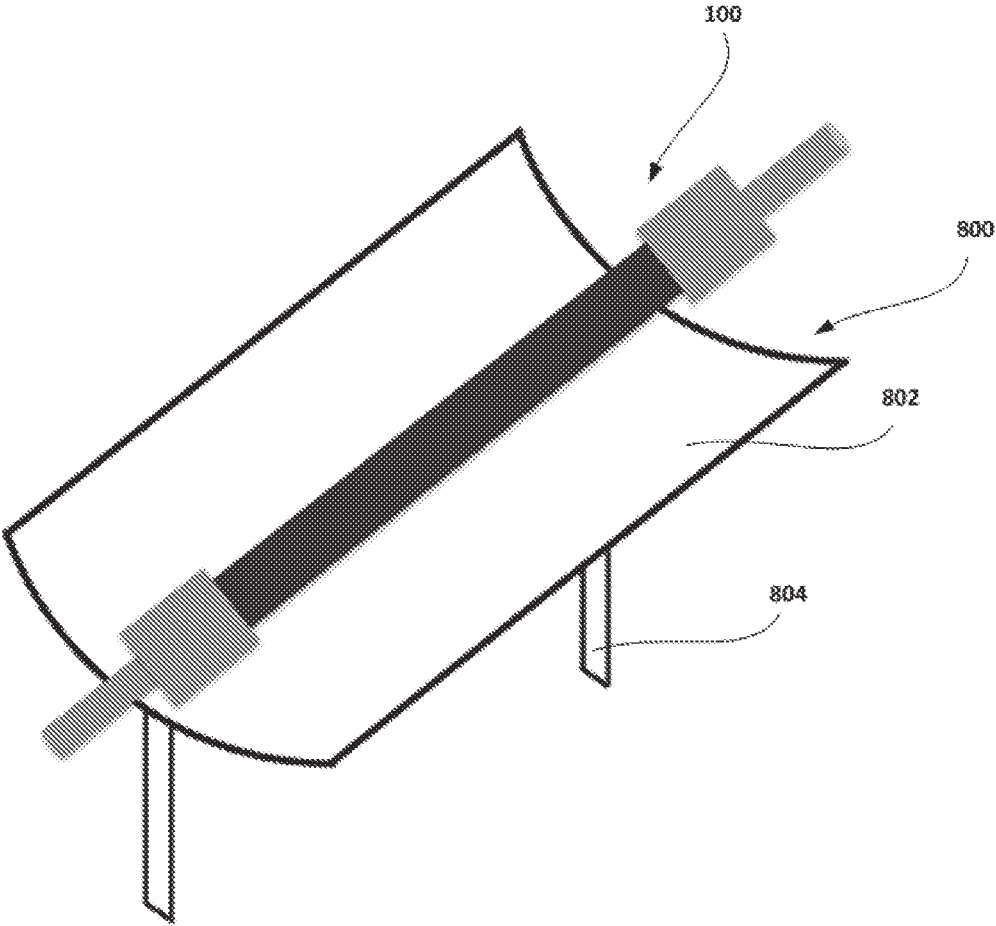


Figure 8