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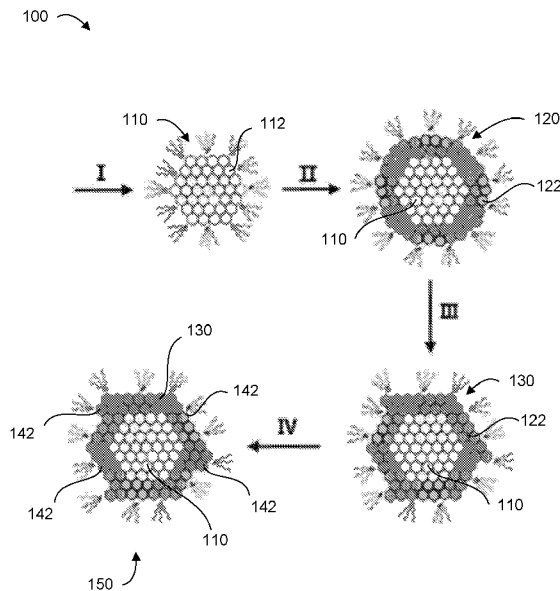


FIG. 1

(57) Abstract: The disclosure relates to a single-atom-based catalyst system with total-length control of single-atom catalytic sites. The single-atom-based catalyst system comprises at least one catalyst structure comprising a first assembly of a plurality of single-atom-catalyst superparticles. The single-atom-catalyst superparticles comprise a second assembly of a plurality of single-atom-catalyst nanoparticles. The single-atom-based catalyst system has controlled porosity and spatial distribution of active single-atom catalysts from the atomic scale to the macroscopic scale. This abstract is intended as a scanning tool for purposes of searching in the particular art and is not intended to be limiting of the present disclosure.



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SINGLE-ATOM-BASED CATALYST SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This Application claims the benefit of U.S. Provisional Application No. 62/719,848, filed on August 20, 2018, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Methane is the most abundant organic compound on earth, and it is the main constituent of natural gas (typically more than 90 %). To date, a few large-scale commercial gas-to-liquid plants have been in operation (Ref. 1) but they are based on an indirect route and complex Fischer-Tropsch technology with high capital costs. To be competitive, these plants rely on low cost natural gas and high crude oil prices (significantly higher than the current crude oil prices of approximately \$40 per barrel).

[0003] Direct conversion of methane to higher value chemicals (e.g., ethylene) would be much more cost-effective. (Refs. 2, 3) Ethylene is a major hydrocarbon building block in industry; (Ref. 4) its worldwide production was over 150 million tonnes in 2016, which exceeds that of any other man-made organic compound. Currently, ethylene is produced from crude oil in a multistep high-temperature (~950 °C) process (Ref. 5), and is the largest contributor to greenhouse gas emissions in the chemical industry. Therefore, the ability to use methane as the raw material in the production of ethylene, fuels and other higher value chemicals would be highly advantageous due to the abundance of low cost, domestic natural gas, (Ref. 6) and the potential for using biogas in the future.

[0004] These needs and other needs are satisfied by the present disclosure.

SUMMARY

[0005] In accordance with the purpose(s) of the disclosure, as embodied and broadly described herein, the disclosure, in one aspect, relates to a single-atom-based catalyst system with single-atom catalytic sites in a controlled hierarchical structure over length scales ranging from macroscopic dimensions down to atomic scales, the single-atom-based catalyst system comprising: at least one catalyst structure comprising a first assembly of a plurality of single-atom-catalyst superparticles, further comprising a second assembly of a plurality of single-atom-catalyst nanoparticles. According to the aspect, each of the single-atom-catalyst nanoparticles comprises a core-shell support structure having a crystalline metal oxide support surface, and one or more single-atom catalysts anchored to the support surface, wherein the density and location of the

single-atom catalysts on the support surface are controlled within a 20% variance to provide a highly uniform spatial distribution of single-atom catalysts. Further, each of the second assemblies is a sub-micron-sized superlattice of a plurality of the single-atom-catalyst nanoparticles, the superlattice having a second density and a second porosity, wherein the second density is controlled within a 20% variance to provide a single-atom-catalyst superparticle having a precise porosity and a highly uniform spatial distribution of the single-atom catalysts. The first assembly of single atom-catalyst superparticles has a first density and a first porosity, wherein the first density of the first assembly is controlled within a 10% variance to provide a catalyst structure having a precise porosity and highly uniform spatial distribution of the single-atom catalysts. Optionally, the single-atom-based catalyst system can comprise one or more catalytically-inactive support materials.

[0006] According to some aspects, a tandem catalyst structure can comprise: a first catalyst layer comprising a first catalyst structure; and a second catalyst layer in fluid communication with the first catalyst layer, said second catalyst layer comprising a second catalyst structure. Optionally, the first catalyst layer, the second catalyst layer, or both can comprise a support layer comprising a catalytically inactive supporter material that supports the respective catalyst structure and/or a spacer layer.

[0007] According to additional aspects, a method for three-dimensional printing a single-atom-based catalyst system, such as those described herein, can comprise: providing a first ink substrate comprising a plurality of positively-charged first single-atom-catalyst superparticles; providing a second ink substrate comprising a plurality of positively-charged second single-atom-catalyst superparticles; providing a support ink substrate comprising a plurality of catalytically inactive supporter particles; providing a binder ink substrate comprising a plurality of negatively-charged polymeric binders; and selectively depositing with a 3D printing apparatus each of the first ink substrate, the second ink substrate, the support substrate, and the binder ink substrate to provide the elements of the single-atom-based catalyst system.

[0008] According to additional aspects, a method of converting methane to ethylene can comprise providing a single-atom-based catalyst system as described herein, wherein the single-atom-based catalyst system has a first catalyst layer comprising a first catalyst for the oxidative coupling of methane (OCM) into ethane and a second catalyst layer comprising a second catalyst for the oxidative dehydration of ethane (ODE) to ethylene; wherein the method comprises: introducing a first fluid comprising methane to the single-atom-based catalyst system; passing the first fluid through the first catalyst layer so that at least a portion of the methane contacts the first

single-atom catalyst structure, providing a first reaction product comprising ethane; passing the first reaction product through the second catalyst layer so that at least a portion of the ethane contacts the second single-atom catalyst structure, providing a second reaction product comprising ethylene; and withdrawing the second reaction product from the single-atom-based catalyst system.

[0009] Other systems, methods, features, and advantages of the present disclosure will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional systems, methods, features, and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims. In addition, all optional and preferred features and modifications of the described embodiments are usable in all aspects of the disclosure taught herein. Furthermore, the individual features of the dependent claims, as well as all optional and preferred features and modifications of the described embodiments are combinable and interchangeable with one another.

BRIEF DESCRIPTION OF THE FIGURES

[0010] Many aspects of the present disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the principles of the present disclosure. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

[0011] FIG. 1 shows a schematic diagram illustrating an exemplary method of synthesizing single-atom-catalyst nanoparticles, including: step I: core synthesis, step II: shell growth, step III: crystallization, and step IV: surface doping.

[0012] FIGS. 2A and 2B show schematic diagrams illustrating an exemplary method of synthesizing superparticles, including: step I(a,b) formation of nanoparticle micelles and step II(a,b): formation of superparticles. Different shades represent different materials/compositions.

[0013] FIG. 3 shows a schematic diagram illustrating an exemplary method of self-Assembly of superparticles into superstructures with controlled structural porosity with precision at the sub-micron scale.

[0014] FIGS. 4A-4C show a schematic diagrams illustrating an exemplary 3-D printed catalyst pellet as part of a reactor assembly. FIG. 4A shows a front elevation view of an exemplary catalyst pellet with a radial structure. FIG. 4B shows a perspective view of an exemplary catalyst pellet

with a radial structure. FIG. 4C shows a partial side view of an exemplary catalyst pellet in a reactor assembly.

[0015] FIG. 5 shows a TEM image of exemplary 6.0-nm Fe_3O_4 Nanocrystals, in accordance with the Examples.

[0016] FIG. 6 shows TEM image of exemplary Sm-doped $\text{Fe}_3\text{O}_4/\text{MgO}$ core/shell Nanocrystals, in accordance with the Examples.

[0017] FIG. 7 shows TEM image of exemplary superparticles showing exemplary assemblies of Sm-doped $\text{Fe}_3\text{O}_4/\text{MgO}$ core/shell Nanocrystals, in accordance with the Examples.

[0018] Additional advantages of the disclosure will be set forth in part in the description which follows, and in part will be obvious from the description, or can be learned by practice of the disclosure. The advantages of the disclosure will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

DETAILED DESCRIPTION

[0019] The disclosure pertains to a total-length-scale control approach to design and construction of heterogeneous catalysts, such as those to be used for direct conversion of natural gas to higher value chemicals. At the atomic scale, a single-atom catalyst nanoparticle can be synthesized with precise control over the location of the catalyst on the nanoparticle. Chemical-composition and lattice-strain engineering principals can be used to control the crystal structure of the nanoparticle and surface habits of catalyst matrices and to stabilize single-atom catalytic sites at high reaction temperatures, which also allows fine-tuning of the selectivity and activity of these single-atom sites. At the nanometer scale, a plurality of the nanoparticles can be assembled to form a sub-micron scale superparticle. For example, a nanoparticle self-assembly method can be used to control catalyst porosity and to increase the volume density of single-atom catalytic sites in sub-micrometer superparticles. At macroscopic scale, the superparticles may be assembled into composite catalyst structures. For example, a 3-D printing technique can be employed to assemble the superparticles into composite catalyst pellets with sub-millimeter scale structures, allowing fine control over reaction kinetics to minimize non-selectively oxidization of methane and to maximize the ethylene production yield.

[0020] This total-length-scale control approach is comprehensive for design of functional materials. It can be readily extended for construct the powerful single-atom catalysts for other

reactions with extraordinarily high selectivity and activity, as well as reaction kinetics control ability. This may open an opportunity to modernize many of conventional catalysts with improved chemoselectivity, allowing the production of daily used chemicals (e.g., food packaging materials, eyeglasses, medical devices, display liquid crystals, lubricants and engine coolants) in a cheaper, greener and energy more efficient manner.

[0021] In addition, the disclosed methods and devices potentially make the direct conversion of methane to ethylene economically viable for industrial operation. This can have a significant economic impact, since abundant domestic natural gas can be utilized rather than foreign oil, and this synthesis route have a higher overall energy efficiency and lower greenhouse-gas emission as compared to current ethylene production route using petroleum-based naphtha.

[0022] Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, and as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

[0023] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

[0024] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

[0025] As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited

method can be carried out in the order of events recited or in any other order that is logically possible.

[0026] Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, materials science, mechanical engineering, and the like, which are within the skill of the art.

[0027] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the probes disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by volume, temperature is in °C, and pressure is at or near atmospheric. Standard temperature and pressure are defined as 20 °C and 1 atmosphere.

[0028] Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequences where this is logically possible.

[0029] It must be noted that, 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. Thus, for example, reference to “a compound” includes a plurality of compounds. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

[0030] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The publications discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided herein can be different from the actual publication dates, which can require independent confirmation.

[0031] In accordance with the purpose(s) of the present disclosure, as embodied and broadly described herein, embodiments of the present disclosure relate to single-atom-catalyst systems

having total-length-scale control of single-atom catalytic sites. In other words, the single-atom-catalyst systems have single-atom catalytic sites in a controlled hierarchical structure over entire length scales ranging from macroscopic dimensions down to atomic scales. The various embodiments disclosed herein provide a method of using a lattice strain in core-shell nanoparticles to stabilize single-atom catalytic sites on their surface. The existence of lattice strain could also affect the selectivity and reactivity of these catalytic sites. The various embodiments also provide a method of using most closely packed supercrystalline superparticles to increase the volume loading density of single-atom catalytic sites, which could, in principle, be more than 10 times higher than that of the current single-atom catalysts reported in literature. Further embodiments relate to a method that employs a 3D printing technique to construct macroscopic catalyst pellets, which can further optimize the proposed tandem catalysts from a materials engineering standpoint, and potentially making direct conversion of methane to ethylene economically viable for industry.

[0032] According to the various embodiments, the single-atom-based catalyst system comprises a catalyst structure comprising a first assembly of a plurality of single-atom-catalyst superparticles, further comprising a second assembly of a plurality of single-atom-catalyst nanoparticles, described further herein.

A. ATOMIC SCALE

[0033] According to some embodiments, preparation of the single-atom-catalyst system can start at the atomic scale. At this level, chemical-composition and lattice-strain engineering can be used to assemble nanoparticles to provide a core-shell support structure having a controlled crystalline support surface. One or more single-atom-based active catalysts can be doped onto the support surface in a highly controlled manner to provide a nanostructure having a highly uniform distribution of single-atom catalyst sites.

[0034] In one aspect, providing single-atom-catalyst nanoparticles comprises synthesizing core-shell nanoparticles having position-controlled dopants comprising the catalytic active material. Exemplary methods and materials for forming the nanoparticles include, but are not limited to, those described in U.S. Patent No. 9,406,759 to Cao, the disclosure of which is incorporated herein by reference, to the extent consistent with the present disclosure. According to the embodiments, the step of providing a single-atom-catalyst nanoparticle comprises synthesizing a metal oxide core-shell structure. Referring to FIG. 1, an exemplary method 100 of forming a single-atom-catalyst nanoparticle includes a first step (step I) that includes selecting a core material 112 and synthesizing a core structure 110. According to various embodiments, the core

material 112 is selected to provide a desirable lattice structure, and desirable chemical affinity for the shell material 122. In certain embodiments, the core material 112 comprises a metal oxide nanoparticle such as nickel oxide (NiO_x) or iron oxide (FeO_x), which have lattice constants that can be tuned to a predetermined value such as by controlling redox reactions through Kirkendall process. In embodiments, the core material 112 comprises a plurality of spherical nanoparticles having size (diameter) of about 10, or about 20, or about 30 nm. In embodiments, the size distribution of the nanoparticles in the core is within about 10% or within about 5% of a target size value.

[0035] According to various embodiments, the disclosed method 100 of providing a single-atom-catalyst nanoparticle further comprises a second step (step II) which includes selecting a shell material 122 and growing a shell 120 on the core structure 110. According to the various embodiments, the shell material 122 is selected to provide, for example, a suitable support structure for the nanoparticle, a desired chemical affinity to the core material 112, and a desired lattice matching to the core material 112. In certain embodiments, the shell material 122 comprises a metal oxide such as magnesium oxide (MgO), calcium oxide (CaO), silicon dioxide (SiO_2), nickel oxide (NiO_x), aluminum oxide (AlO_x), zinc oxide (ZnO), titanium oxide (TiO_x), or Graphene, or a combination thereof. In certain embodiments, the core material comprises NiO_x , and the shell material comprises MgO , CaO , or a combination thereof. In certain embodiments, the core material comprises FeO_x , and the shell material comprises SiO_2 .

[0036] In an embodiment, the shell structures 120 can be introduced and grown on the cores using a solvent such as octadecene solution containing the respective organometallic precursors. For example, according to some embodiments, the shells 120 are grown on the core structure 110 to provide a shell thickness of from about 3 nm to about 8 nm. According to the various embodiments, the disclosed method 100 can include a further step (step III) which includes crystallizing the shell structure 120 to provide a crystallized shell structure 130 having a desired crystalline form. In an embodiment, the shell structure 120 can be annealed in a pure octadecene solution at 320 degrees C to achieve a desired crystalline form. In some embodiments, the shell material 122 is MgO or CaO , and the resulting crystalline shell structure 130 is a cubic rocksalt structure. In some embodiments, the shell material 122 is SiO_2 , and the resulting crystalline shell structure 130 is a tetragonal α -cristobalite crystal structure.

[0037] According to the embodiments, the disclosed method 100 of providing a single-atom-catalyst nanoparticle includes a further step (step IV) which includes position-controlled surface

doping of the shell structure 130 with one or more single-atom-based catalytic active materials 142, forming the single-atom-catalyst nanoparticle 150. According to the embodiments, a catalytic active material is selected, at least in part, for its desired catalytic activity. In various embodiments, at least one of the catalytic active materials is selected from samarium (Sm), iron (Fe), manganese (Mn), sodium (Na), tungsten (W), platinum (Pt), tin (Sn), nickel (Ni) or a combination thereof. In an embodiment, at least one of the single-atom-catalysts will be used as a catalyst for oxidative coupling of methane (OCM) into ethane, and the catalytic active material is Sm, Fe, Mn, Na, W, or a combination thereof. In an embodiment, at least one of the single-atom-catalysts will be used as a catalyst for oxidative dehydration of ethane (ODE) into ethylene, and the catalytic active material is Ni, Pt, Sn, or a combination thereof.

[0038] According to the various embodiments, the precursors of these one or more catalytic active materials are provided in an organometallic form with bulky ligands. The bulky ligands are selected to induce entropy effects to control the location of the dopants, e.g., to prevent growth of two dopants at neighboring lattice sites of the shell. Exemplary bulk ligands include ethyl-hexyl or heptyl-undecyl groups, or the like. In some embodiments, the number of dopants on a nanoparticle can be controlled, at least in part, by controlling the amount of the precursor of the catalytic active materials introduced to the nanoparticle.

[0039] According to some embodiments, the nanoparticles may comprise one or more types of single-atom catalysts. For example, in one embodiment, a single-atom-catalyst nanoparticle comprises a homo system of catalysts, for example only OCM catalysts or only ODE catalysts. In another embodiment, a single-atom-catalyst nanoparticle comprises a heterosystem of catalysts, for example having a combination of OCM catalysts, and ODE catalysts.

[0040] According to the embodiments, the resulting surface-doped nanoparticles can be activated to form single-atom catalysts. For example, the doped nanoparticles can be subject to stepwise pyrolysis of organic binding materials in the presence of oxygen at a temperature of about 600 degrees C to about 1000 degrees C. The pyrolysis may be conducted for a period of time to produce a necessary or desired activation. In some embodiments, the pyrolysis may be performed for a period of from about three to about six hours.

[0041] In embodiments, the density and location of the single-atom-catalytic sites on the support surface are closely-controlled, e.g., within about a 20% variance, or within about 15% variance, or within about 10% variance, or within about 5% variance from a target value. Controlling the variance of the density and location of the single-atom-catalyst sites results in a single-atom-catalyst nanoparticle having a highly uniform spatial distribution of single-atom catalysts.

B. NANOSCALE

[0042] According to some aspects, preparation of the single-atom-catalyst system can continue at the nanometer scale. At this level, a plurality of the single-atom-catalyst nanoparticles described herein are further assembled into sub-micron-sized superlattices. The volume and density of the assembly of nanoparticles within the superlattice assembly can be precisely controlled so that the superlattice has a necessary or desired porosity. In addition the size, structure and configuration of the assembly of nanoparticles can be precisely controlled so that the resulting superparticle has a necessary or desired volume, density, and/or distribution of single-atom-based active catalyst sites.

[0043] According to some embodiments, a plurality of single-atom-catalyst nanoparticles (having a particle size of less than about 100 nm) can be assembled into superparticles having a micron or sub-micron size (e.g., about 0.02 to about 1 micron in diameter). As used herein, “superparticles” refers to nanoparticle assemblies (also referred to herein as “second assemblies”) in the form of colloidal particles. The plurality of nanoparticles are bound together through non-covalent interactions. In some embodiments, the superparticles may be supercrystalline collections of nanoparticles, in other words, a plurality of nanoparticles arranged in a superlattice structure. According to the embodiments, the superparticles comprise an assembly of single-atom-catalyst nanoparticles that can be arranged to provide a predetermined reactivity. The reactivity of a superparticle can be controlled, at least in part, by controlling the volume loading density of single-atom catalytic sites, and the porosity of the superparticle structure. For example, nanoparticles assembled into close-packed superlattices can increase the volume loading density of single-atom-catalytic sites in a structure with controlled porosity. According to the various embodiments, the resulting superparticles can form stable colloids, which can be used as building blocks for constructing the radially-structured tandem catalysts described herein. Exemplary methods and materials for forming superparticles include those described in U.S. Patent Publication No. 2011/0150938 to Cao, et al, the disclosure of which is incorporated herein by reference, to the extent consistent with the present disclosure.

[0044] Referring to FIG. 2A, according to various embodiments, a method 200 of assembling the single-atom-catalyst superparticles comprises a first step (step Ia) of passivating the single-atom-catalyst nanoparticles 150 with hydrophobic ligands 212 to form an aqueous solution of nanoparticle micelles 210. The nanoparticles 150 can be passivated with a passivation agent such as dodecyl trimethylammonium bromide (DTAB). In a second step (step IIa), the solution comprising the nanoparticle-micelles 210 may then be mixed with a solvent to form a solution of

colloidal superparticles 220a. In some embodiments, the solvent is a polar organic solvent (e.g., ethylene glycol, di-ethylene glycol, tri-ethylene glycol, diethanolamine, triethanolamine) an oxygen-containing organic solvent, or a combination thereof. The combination of the nanoparticle-micelle solution with the solvent can cause a controlled decomposition of the micelle structures, and controlled aggregation of the nanoparticles to form the superparticles. According to various embodiments, the size of the superparticles may be controlled, at least in part, by the amount of the passivation agent. According to certain embodiments, the resultant superparticles have a passively-charged surface and a size of about 250 nm.

[0045] According to some embodiments, the superparticles may comprise an assembly of one or more types of nanoparticles. For example, referring to FIG. 2A, in one embodiment, a single-atom-catalyst superparticle 220a comprises an assembly of a homo system of nanoparticles 150, for example only nanoparticles having OCM catalysts or only nanoparticles having ODE catalysts. Referring to FIG. 2B, in another embodiment, a single-atom-catalyst superparticle 220b comprises an assembly of a heterosystem of nanoparticles, for example having a combination of nanoparticles 150a having OCM catalysts 142a, and nanoparticles 150b having ODE catalysts 142b.

[0046] In embodiments, the density of the single-atom-catalyst nanoparticles within the superparticles can be closely-controlled, for example, within about a 20% variance, or within about 15% variance, or within about 10% variance, or within about 5% variance of a target value. Precise control of the density of the nanoparticles can provide a single-atom-catalyst superparticle having a precise porosity and a highly uniform spatial distribution of the single-atom catalysts.

C. MACROSCOPIC SCALE

[0047] According to some aspects, preparation of the single-atom-catalyst system can continue at the macroscopic scale. At this level, a plurality of the single-atom-catalyst superparticles described herein are further assembled into composite catalyst structures. The volume and density of the assembly of nanoparticles (also referred to herein as a “first assembly”) can be precisely controlled so that the catalyst structure has a necessary or desired porosity, e.g., to provide a certain fluid throughput. In addition the size, structure and configuration of assembly of superparticles that make up the catalyst structure can be precisely controlled so that the resulting catalyst structure has a necessary or desired volume, density, and/or distribution of single-atom-based active catalyst sites. For example, in some embodiments, the density of the single-atom-catalyst superparticles within the single-atom-catalyst structure can be closely-controlled, e.g., within about a 10% variance, or within about 5% variance from a target value. Controlling the

density and spatial distribution of the single-atom-based active catalyst sites can enable fine control over reaction kinetics, e.g., to optimize desired reactions and to minimize side reactions.

[0048] According to some embodiments, the single-atom-catalyst systems and/or structures may comprise one or more types of superparticles. For example, in one embodiment, a single-atom-catalyst system or structure comprises an assembly of a homo system of single-atom-catalyst superparticles, for example where all of the superparticles are substantially the same. In another embodiment, a single-atom-catalyst system or structure comprises an assembly of a heterosystem of superparticles, having superparticles with differing properties and/or structures and/or single-atom-catalyst species.

[0049] According to some aspects of the present disclosure, a method for making a single-atom-catalyst system, as described herein, comprises, generally, three-dimensional (3D) printing of one or more catalyst structures using one or more inks comprising a plurality of the single-atom-catalyst superparticles to form a predetermined assembly of the single-atom-catalyst superparticles. Generally speaking, 3D printing can be used to produce complex 3D objects directly from computer-aided digital design. 3D printing technologies include, among others: (1) stereolithography ("SLA"), (2) melt deposition modelling, or fused deposition modelling ("FDM"), (3) powder bed technology involving a laser beam and/or an E-beam, (4) multi jet fusion ("MJF"). SLA selectively solidifies photosensitive (UV curable) polymers by laser (e.g., laser sintering) or other light source, while FDM selectively deposits thermoplastic molten polymer through a heated nozzle. During MJF, an entire layer or several layers of a build material (also referred to as build material particles) is/are exposed to radiation, but a selected region (in some instances less than the entire layer(s)) of the build material is fused and hardened to become a layer or several layers of a 3D object/part. These or other techniques can be employed with the systems described herein.

[0050] Referring to FIG. 3, according to the embodiments, a method 300 of 3D printing the single-atom-catalyst system comprises depositing an ink 310 comprising one or more catalytically-active single-atom-catalyst superparticles (312, 314) to provide an assembly 320 of single-atom-catalyst superparticles (and, optionally, other components such as binders and catalytically-inactive particles) having a predetermined structure. According to the embodiments, an ink substrate 310 comprising the single-atom-catalyst superparticles can comprise a dispersion of the catalytically-active superparticles which are in the form of stable colloids in a dispersion media, such as an aqueous media. In some aspects, these catalytically-active superparticles can be functionalized with a plurality of surface ligands which stabilize the

superparticles in the ink formulation. In some embodiments, the surface ligands can be either positively-charged or negatively-charged.

[0051] According to the embodiments, 3D printing the single-atom-catalyst system and/or structure further comprises depositing one or more catalytically-inactive particles, for example, those which can provide structural support for the assembly of catalytically-active superparticles. The catalytically-inactive particles can be provided as part of the ink substrate comprising the single-atom-catalyst superparticles, or can be provided as a separate ink composition. In some embodiments, the catalytically-inactive particles are provided in the form of stable colloids in a dispersion media, such as an aqueous media. These catalytically inactive particles are functionalized with a plurality of surface ligands which stabilize the superparticles in the ink formulation. In some embodiments, the surface ligands can be either positively charged or negatively charged.

[0052] According to the embodiments, 3D printing the single-atom-catalyst system further comprises depositing one or more binder inks to increase the structural stability of the catalyst system or structures (including assemblies of single-atom-catalyst superparticles and/or catalytically-inactive particles) during 3D printing. Exemplary binder inks comprise adhesive polymer substrates having a charge that is opposite to the charge of the catalytically-active superparticles and/or catalytically-inactive particles with which the binder is intended to interact. In other words, when the binder is intended to interact with catalytically-active superparticles or catalytically-inactive particles that are positively charged, the binder ink should be negatively charged, and vice versa.

[0053] According to the embodiments, the single-atom-catalyst system can comprise two or more single-atom catalyst structures, each structure comprising an assembly of respective single-atom-catalyst superparticles. For example, a single-atom-catalyst system can comprise a first region or first layer having a first single-atom-catalyst structure, and a second region or second layer comprising a second single-atom-catalyst structure. In some embodiments, the first single-atom-catalyst structure and the second single-atom-catalyst structure have the same active catalytic species. In some embodiments, the first single-atom-catalyst structure and the second single-atom-catalyst structure may have different active catalytic species. Structures comprising multiple active single-atom-catalyst species can be useful, for example, for multi-step reactions. These single-atom catalyst systems can comprise one or more additional layers or structures, as necessary or desired, such as to provide support or spacing to the single-atom-catalyst system.

[0054] According to some embodiments, a method for making a single-atom-catalyst system

comprises providing a first ink substrate comprising a plurality of positively-charged first single-atom-catalyst superparticles; providing a second ink substrate comprising a plurality of positively-charged second single-atom catalyst superparticles; providing a first support ink substrate comprising catalytically inactive supporter particles; providing a first negatively-charged adhesive substrate; and using a 3D printing process to deposit the ink substrates in a predetermined configuration to provide a catalyst structure as described herein.

[0055] According to the various embodiments, a single-atom-catalyst system and/or catalyst structure can comprise any necessary or desired shape or geometry. For example, a single-atom-catalyst system or structure can be provided in plate form or cylindrical form, where the plate or cylinder comprises one or more layers comprising the single-atom-catalyst structures or systems described herein.

[0056] According to some embodiments, one or more single-atom-catalyst systems described herein may be combined with a reactor apparatus. According to some embodiments, a reactor apparatus may have a fluid inlet and fluid outlet that are in fluid communication with the single-atom-catalyst system. Generally speaking, in use, a fluid comprising one or more reactants may be provided through the fluid inlet of the single-atom-catalyst system. The fluid comprising the reactants can pass through the at least one single-atom-catalyst structure, so that the reactants contact the single-atom-catalyst, and undergo a catalytic reaction to provide a fluid comprising one or more reaction products. The fluid containing the one or more reaction products then exits the reactor at the fluid outlet. The reactor apparatus may comprise a plurality of single-atom-catalyst systems, e.g., in parallel or series.

[0057] In certain embodiments of the present disclosure, a single-atom-catalyst structure comprises two single-atom-based catalyst layers for tandem catalysis reactions, such as the direct conversion of methane to ethylene. The ability to use methane as the raw material in the production of ethylene, fuels and other higher value chemicals would be highly advantageous due to the abundance of low cost, domestic natural gas (Ref. 6) and the potential for using biogas in the future. However, because methane's extraordinarily high thermodynamic stability, methane activation remains one of the most challenging subjects in heterogeneous catalysis. A reaction of oxidative coupling of methane (OCM) to ethane and ethylene was discovered in the 1980s. (Refs. 7, 8, 9) In this reaction, methane is activated heterogeneously on the catalyst surface, forming methyl free radicals, and coupling in the gas phase to form ethane, which subsequently undergoes dehydrogenation to form ethylene. The economic promise of OCM has attracted significant attention in both industry and academic research areas since then. Hundreds of

catalysts have been synthesized and examined, but none of these catalytic reactions has achieved the required chemo-selectivity for economic operation. Instead of producing ethylene, the majority of methane is non-selectively oxidized to carbon monoxide and carbon dioxide, or decomposed leading to the formation of coke. The other issue is that ethane is often the major product in current OCM reactions, particularly at the lower temperature range, as it forms first in this reaction.

[0058] To overcome the major challenges in the direct conversion of methane to ethylene, the various aspects of the disclosure include new and stable single-atom-based tandem catalysts with unique compositions and structures. Single-atom catalysts possess single-atomically-dispersed catalytic sites on surface of their matrices. Recent research has shown that single-atom catalysts exhibit unique activity and extraordinarily high selectivity as compared to the conventional bulk catalysts. Without being bound by any particular theory, it is believed that single-atom catalysts hold an important key to the improvement of the selectivity and reaction yield in of methane to ethylene conversion. However, single-atom catalysts can often suffer from low thermal stability due to surface diffusion at high temperatures, and low volume loading density associated with their stoichiometry.

[0059] In accordance with various embodiments, a single-atom-catalyst system comprises a tandem catalyst structure, i.e., a catalyst system having two catalyst structures provided in tandem relation, as described further herein. Referring to FIGS. 4A-4C, in accordance with some embodiments, the single-atom-catalyst system comprises a radially-structured tandem catalyst 400 that has a generally cylindrical or tubular structure. While certain embodiments are described with reference to a radially-structured tandem catalyst 400, it will be understood that other geometries, e.g., a plate geometry, can be employed within the scope of the present disclosure. The cylindrical catalyst structure 400 has a longitudinal dimension 401 extending parallel a longitudinal axis from a first end 402 to a second end 403, and a radial dimension or diameter 404 extending radially across a longitudinal centerline 405 of the catalyst to an outer surface 406 of the catalyst. The catalyst structure comprises at least a central fluid conduit 480 that receives a fluid, at least two substantially concentric catalyst layers (430, 460), and an outer annulus 420. Within the catalyst structure, the fluid conduit 480 and concentric catalyst layers 430, 460 and outer annulus 420 are in fluid communication so that a fluid may pass from the central fluid conduit 480 through the concentric catalyst layers 430, 460 to the outer annulus 420. These and other features and aspects of the single-atom-catalyst system and radially-structured tandem catalyst are described in more detail.

[0060] In embodiments, the central portion of the cylindrical catalyst 400 is a central fluid conduit 480. The central fluid conduit 480 may be hollow, or it may comprise one or more support structures. For example, the central fluid conduit 480 may have a lattice or honeycomb support structure. According to some embodiments, the central fluid conduit 480 has a diameter measured in the radial direction of from about 0.10 inches to about 0.40 inches, or about 0.15 inches to about 0.35 inches, or about 0.20 inches to about 0.30 inches, or about 0.25 inches.

[0061] According to the various embodiments, a first catalyst layer 460 extends radially outward from the central fluid conduit 480. The first catalyst layer 460 comprises a first catalyst structure which comprises an assembly of a plurality of first single-atom-catalyst superparticles. In embodiments, the first single-atom-catalyst superparticles comprise a catalyst for oxidative coupling of methane (OCM) into ethane. The first catalyst structure can be configured to optimize the desired reaction kinetics. For example, the reaction kinetics can be controlled, at least in part, by controlling one or more of the thickness, porosity, density, and distribution of the single-atom active catalytic sites. During use, a fluid will pass through the first catalyst structure and in the presence of the catalyst, constituents of the fluid will react to provide an intermediate fluid.

[0062] In some embodiments, the first catalyst layer 460 may further comprise a first support structure 470 intermediate the first catalyst structure and the central fluid conduit 480. The first support structure 470 may support the first catalyst structure. According to some embodiments, the first support structure may comprise a porous layer of SiO₂.

[0063] In some embodiments, the first catalyst layer 460 may further comprise a first spacer or gap layer 440 extending radially outward from the first catalyst layer 460. After the fluid passes through the first catalyst structure, it may be desirable to provide additional residence time within the catalyst to increase the yield of the reaction catalyzed by the first catalyst, before proceeding further. The first spacer or gap layer 440 has a thickness and/or volume to enable a necessary or desired residence time. The first spacer or gap layer 440 may comprise a support structure or material 450.

[0064] According to the various embodiments, a second catalyst layer 430 extends radially outward from the first catalyst layer 460. The second catalyst layer 430 comprises a second catalyst structure comprising an assembly of a plurality of second single-atom-catalyst superparticles. In embodiments, the second single-atom catalyst superparticles comprise a catalyst for oxidative dehydrogenation of ethane (ODE) into ethylene. The second catalyst structure 430 can be configured to optimize the desired reaction kinetics. For example, the reaction kinetics can be controlled, at least in part, by controlling one or more of the thickness,

porosity, density, and distribution of the single-atom active catalytic sites. During use, a fluid will pass through the second catalyst structure and in the presence of the second catalyst, constituents of the fluid will react.

[0065] In some embodiments, the second catalyst layer may further comprise a second support structure intermediate the second catalyst structure and the first catalyst layer. The second support structure may support the second catalyst structure. According to some embodiments, the second support structure may comprise a porous layer of SiO₂.

[0066] In some embodiments, an outer annulus 420 may extend radially outward from the second catalyst layer 430. After the fluid passes through the second catalyst layer, it may be desirable to provide additional residence time within the catalyst structure to increase the yield of the reaction catalyzed by the second catalyst. The outer annulus 420 has a thickness and/or volume to enable a necessary or desired residence time.

[0067] The radially-structured tandem catalyst 400 may further have a housing 410 that at least partially surrounds and contains the elements of the catalyst. The housing 410 may be integrally formed with the radially-structured tandem catalyst, e.g., a structural layer that is deposited adjacent the outer annulus 420. In alternative embodiments, the housing 410 may be separately provided, e.g., a pre-formed tube that receives the radially-structured tandem catalyst 400. In some embodiments, the housing 410 is configured to be impermeable, e.g., to contain the reactants and reaction products.

[0068] According to the embodiments, the radially-structured tandem catalyst 400 has an overall longitudinal dimension 401 of from about 2 inches to about 6 inches, or about 3 inches to about 5 inches, or about 4 inches. According to certain embodiments, the radially-structured tandem catalyst has an overall diameter, measured in the radial direction, from about 1 inch to about 20 inches, from about 1.25 inches to about 1.75 inches, or about 1.50 inches.

[0069] One or more radially-structured tandem catalysts described herein may be combined with a reactor apparatus. For example, referring to FIG. 4C, according to some embodiments, a reactor apparatus 500 may have a fluid inlet 580 that is in fluid communication with the central fluid conduit 480 of the radially-structured tandem catalyst, and a fluid outlet 520 that is in fluid communication with the outer annulus 420. Generally speaking, in use, a fluid comprising one or more reactants may be provided through the fluid inlet 580 to the central fluid conduit 480 of the radially-structured tandem catalyst 400. The fluid comprising the reactants can pass through the first catalyst layer 460, undergoing a first catalytic reaction to provide a fluid

comprising one or more first reaction products. The intermediate reaction products then can pass through the second catalyst layer 430, undergoing a second catalytic reaction to provide a fluid containing one or more second reaction products. The fluid containing the one or more second reaction products then exits the reactor at the fluid outlet 520. The reactor apparatus may comprise a plurality of radially-structured tandem catalysts 400 arranged in parallel or series.

[0070] According to certain embodiments, the radially-structured tandem catalysts can be 3D printed from one longitudinal end to another, by depositing layers of pre-determined arrays of the first single-atom-catalyst inks and the second single-atom-catalyst inks to form the first catalyst layer and second catalyst layer, respectively, of the radially-structured tandem catalyst, as described herein. By 3D printing with inks comprising the first and second single-atom-catalyst superparticles, respectively, self-assembly of the superparticles further can form superstructures with controlled porosity with sub-micron precision.

D. REFERENCES

[0071] References are cited herein throughout using the format of reference number(s) enclosed by parentheses corresponding to one or more of the following numbered references. For example, citation of references numbers 1 and 2 immediately herein below would be indicated in the disclosure as (Refs. 1 and 2).

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[0089] Before proceeding to the Examples, it is to be understood that this disclosure is not limited to particular aspects described, and as such may, of course, vary. Other systems, methods, features, and advantages of foam compositions and components thereof will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional systems, methods, features, and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only, and is not intended to be limiting. The skilled artisan will recognize many variants and adaptations of the aspects described herein. These variants and adaptations are intended to be included in the teachings of this disclosure and to be encompassed by the claims herein.

E. EXAMPLES

[0090] Now having described the embodiments of the present disclosure, in general, the Examples describe some additional embodiments of the present disclosure. While embodiments of the present disclosure are described in connection with the Examples and the corresponding text and figures, there is no intent to limit embodiments of the present disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

1. EXAMPLE 1

[0091] This Example demonstrates through the use of combined fields of chemistry, chemical engineering, materials science and physics, the state of the art synthesis of specifically designed complex nanoparticle systems using colloidal synthesis for use as heterogeneous catalysts and the novel reactor design using 3D printing together with reaction engineering measurements,

[0092] Specifically, this example demonstrates a total-length-scale control approach to design and construction of novel heterogeneous catalysts for direct conversion of natural gas to higher value chemicals. *At the atomic scale*, lattice-strain engineering was used to control the crystal structure and surface habits of catalyst matrices and to stabilize single-atom catalytic site at high reaction temperatures, which also allowed fine-tuning of the selectivity and activity of these single-atom sites. *At the nanometer scale*, a nanoparticle self-assembly method was used to control catalyst porosity and to increase the volume density of single-atom catalytic sites in sub-

micrometer superparticles. *At macroscopic scale*, a 3-D printing technique was employed to assemble the superparticles into composite catalyst pellets with sub-millimeter structures, which allowed fine control over reaction kinetics to minimize non-selectively oxidization of methane and to maximize the ethylene production yield.

[0093] This total-length-scale control approach is comprehensive for design of functional materials. It can be readily extended for construct the powerful single-atom catalysts for other reactions with extraordinarily high selectivity and activity, as well as reaction kinetics control ability. This advance may open an opportunity to modernize many of conventional catalysts with improved chemoselectivity, allowing the production of daily used chemicals (e.g., food packaging materials, eyeglasses, medical devices, display liquid crystals, lubricants and engine coolants) in a cheaper, greener and energy more efficient manner.

[0094] In addition, the disclosed methods and devices potentially make the direct conversion of methane to ethylene economically viable for industrial operation. This can have a significant economic impact, since abundant domestic natural gas can be utilized rather than foreign oil, and this synthesis route have a higher overall energy efficiency and lower greenhouse-gas emission as compared to current ethylene production route using petroleum-based naphtha.

[0095] This Example demonstrates synthesis, characterization and optimization of an exemplary single-atom based tandem catalysts at three length scales. The composition of catalytically active component and metal-oxide core-shell nanoparticles were carefully selected. NiO_x and FeO_x were used as nanoparticle cores because their lattice constants can be easily tuned via redox reactions through Kirkendall process. MgO , CaO and SiO_2 were used as a support matrix as nanoparticle shells. (Refs. 10, 11, 12) Sm, Fe, Mn, Na, W, Pt, Sn were chosen as catalytically-active components. Specifically, Sm-doped MgO/CaO , Fe-doped SiO_2 , Mn-doped SiO_2 and Na-W doped SiO_2 were used as the catalysts for oxidative coupling of methane (OCM) into ethane, (Refs. 11, 12, 13) and Ni-doped SiO_2 and Pt-Sn doped SiO_2 for subsequent oxidative dehydrogenation of ethane (ODE) into ethylene. (Refs. 14, 15, 16)

**a. SYNTHESIS AND CHARACTERIZATION OF SINGLE-ATOM CATALYST
NANOPARTICLES THROUGH SURFACE DOPING COLLOIDAL NANOPARTICLES.**

[0096] Lattice-strain induced by lattice mismatching between core and shell have significant effects on the crystal structure and habit of shell because of surface free energy relaxation of shell materials. NiO_x and FeO_x were chosen as core materials for two reasons: (1) their synthesis procedure has been well-established, and (2) they adopt a cubic lattice structure and their lattice

constants can be controlled to about 20% variance, which is ideal for controlling the growth of MgO, CaO and SiO₂ shells through lattice-strain engineering. Single-atom catalyst nanoparticles were synthesized in four steps). Referring to FIG. 1, first, spherical NiO_x and FeO_x nanoparticles of 10, 20, and 30 nm with size distribution of 5% were synthesized using published procedure. (Ref. 17) Second, MgO, CaO and SiO₂, NiO_x, AlO_x, ZnO, TiO_x, Graphene shells with thickness of 3-8 nm were grown onto these cores in octadecene solution using corresponding organometallic precursors. MgO, CaO, FeO_x, AlO_x, ZnO, TiO_x and Graphene shells were grown on NiO_x cores and SiO₂ shell were grown on FeO_x cores because of their chemical affinity and lattice matching level. Third, the resulting shells were annealed in a pure octadecene solution at 320 °C to achieve desired crystalline form, where MgO and CaO shell on NiO_x cores adopted cubic rocksalt structure and SiO₂ shell on FeO_x cores displayed a tetragonal α -cristobalite crystal structure. Fourth, the chosen catalytic active materials (Sm, Fe, Mn, Na, W, Pt, and Sn) were used as dopants to growth onto the surface of core-shell nanoparticles. The precursors of these elements were in an organometallic form with bulk ligands comprising ethyl-hexyl or heptyl-undecyl groups. Such bulky ligands can induce entropy effects to prevent the growth of two dopants at neighboring lattice sites of the shell. The number of dopants were controlled by precursor amount. The resulting surface doped nanoparticles were activated to form single-atom catalysts through stepwise pyrolysis of organic binding materials in the presence of oxygen at a temperature of 600-1000 °C over 3-6 hours. These single-atom catalyst nanoparticles were characterized using XRD, XPS, high-resolution TEM and XPS, and their catalytic activity, selectivity and stability in OCM and ODE reactions were monitored using gas chromatography.

b. SYNTHESIS AND CHARACTERIZATION OF SINGLE-ATOM CATALYST SUPERPARTICLES.

[0097] Superparticles are nanoparticle assemblies in the form of colloidal particles. The choice to make superparticles was for two reasons: (1) nanoparticles are assembled into close packed superlattices can increase the volume loading density of single-atom catalytic sites in a structure with controlled porosity (e.g., superlattices of 25-nm nanoparticles have about 3.8 nm pores), thus leading to an overall high reactivity. (2) The resulting superparticles form stable colloids and they can be used as building blocks in a form of inks to construct structures in a larger scale.

[0098] Superparticles of single-atom catalyst nanoparticles were prepared using a two-step method. Referring to FIG. 2, in the first step (Ia or Ib), the nanoparticles made in Example 1a, with hydrophobic ligands were passivated with dodecyl trimethylammonium bromide (DTAB) forming nano particle micelles in aqueous solution. In the second step (IIa or IIb), under stirring,

the nanoparticle-micelle solution was injected into a flask with ethylene glycol, causing the decomposition of nanoparticle-micelles, and subsequent the aggregation of nanoparticles and the eventual formation of superparticles. Two types of superparticles were synthesized: (a) single-component superparticles with OCM or ODE catalysts (FIG. 2A), and (b) binary superparticles with both OCM and ODE catalysts at a controlled ratio (FIG. 2B). The size of superparticles was controlled by controlling the amount of DTAB. We made superparticles with passively charged surface and size of 250 nm for the use as inks to print final catalyst pellets. The resulting superparticles were characterized using XRD, XPS, high-resolution TEM and XPS, as well as Brunauer–Emmett–Teller (BET) surface area measurements.

c. CONSTRUCTION AND CHARACTERIZATION OF 3-D PRINTED CATALYST PELLETS.

[0099] In this Example, we used a 3D printing technique to form a catalyst pellet structure. The inks used in the 3D-printing included certain functional components, as described. Positively charged SAC superparticles made in Example 1b were used as inks for catalysts. Positively charged catalytically inactive supporter particles (200-nm SiO₂ nanoparticles) were used as inks for gap support structures and OCM catalyst support structures. Negatively charged polymers such as sodium polyacrylate were used as binder inks. Glass micro-capillaries with 20-μm tips were used for injection. Injection of different inks were controlled by three syringe pumps, and linear translational stages were used to control the location of printing objects. During 3D-Printing, self-assembly of superparticles took place, leading to the formation of superstructures with controlled structural porosity with sub-micron precision. This self-assembly process was controllable by controlling the surface nature of superparticles and chemical nature of binders. The density and average distance between SAC superparticles were controlled by controlling the concentration and surface nature of the catalytically inactive supporter particles in the ink.

[00100] Referring to FIG. 4A-4B, catalyst pellet tubes were printed starting from a bottom cap at the first end 402 of the pellet 400, and continuing layer-by-layer in the longitudinal direction of the pellet to the second end 403 of the pellet. The pellets 400 were configured to have a first catalyst layer 460 comprising an OCM catalyst, and a second catalyst layer 430 comprising an ODE catalyst, with a gap layer 440 intermediate the first catalyst layer 460 and second catalyst layer 430. The pellets 400 were printed to have an outer diameter (404) of 1.5 inches, and a longitudinal dimension (401) of 4 inches, with a central fluid conduit (480) having a diameter of about 0.25 inches. The catalyst pellet tubes 400 were used in a reactor, such as the reactor 500 in FIG. 4C. During reaction, gas entered the pellet via the central fluid conduit 480 (see arrows) and flowed radially outward through the catalyst pellet, as shown with the arrows in FIG. 4C. In other words,

the gas (or its reaction product) flowed through sequential layers. A porous SiO₂ layer served as a gas distribution layer as well as a support 470 for the thin OCM catalyst layer 460. A gap layer 440 allowed the methyl radicals generated by the OCM layer 460 further time to react before entering the ODE catalyst layer 430 and reacting with ethylene which flowed out via the annulus 520 formed between the reactor housing 410 and the catalyst pellet tube, and the reaction product comprising ethylene flowed from the reactor at fluid outlet 520. These radial-structured catalysts allowed fine control over reaction kinetics by designer's dynamic feeding procedures, such as, cycles of the following; (1) Continuous flow of O₂ (for catalyst activation); (2) He₂ for purging excess O₂, and (3) CH₄ for conversion reaction, as this operation limited the existence of free O₂ and thus minimized the formation of CO and CO₂ in the conversion reaction.

[00101] The performance of the exemplary catalyst pellet outperformed with the performance of a 3D printed catalyst pellet tube with only a catalyst support structure and gas distribution layer and a catalyst layer composed of mixed OCM and ODE catalysts.

2. EXAMPLE 2. SYNTHESIS OF IRON-OXIDE NANOCRYSTALS AS CORE

[00102] Synthesis of iron-oleate precursor. Iron chloride (10.8 g, 40 mmol) was first dissolved in a mixture of 80 mL ethanol and 60 mL Nanopure® water in a three-neck flask (500 mL). Afterwards, sodium oleate (36.5 g 120 mmol) was quickly added to the iron chloride solution along with 140 mL hexane. The resulting solution was allowed to stir until the sodium oleate was completely dissolved. Next, the reaction solution was heated to reflux for 4 hours. When the reaction was finished and cooled to room temperature, the upper organic layer containing the iron oleate was washed three times with 30 mL of Nanopure® water in a 250 mL separatory funnel. Excess hexane was then evaporated using a rotovap. The resulting iron oleate was transferred into a 100 mL round bottom flask and connected to a Schlenk line where it was placed under a vacuum of about 25 mtorr overnight, and then the iron oleate was well sealed in a glass vial and stored in a desiccator for two days of aging. The reaction yield of iron oleate was about 90%.

[00103] Synthesis of 6-nm Iron Oxide Nanocrystals. Iron oleate (5.0 mmol, 4.5 g) and oleic acid (2.5 mmol, 0.75 g) were added into a three-neck flask (100 mL) with a solvent mixture of ODE (25.0 g). The mixture was heated to 120 °C and was pumped for 1 hour, and the mixture was purged with argon. Under an argon flow, the reaction solution was heated to 320 °C at a heating rate of 3.0 °C/min. Reaction time was counted from the moment when 320 °C was reached. After 30-min reaction, the reaction solution was quickly cooled to room temperature by blowing air across the reaction flask. The resulting nanocrystals were precipitated using acetone, and then were purified using three rounds of precipitation/ redispersion cycles with acetone and

hexane as the solvents. After purification, the product was dispersed in nonpolar solvents such as hexane or toluene. A transmission electron microscope (TEM) image of representative iron-oxide nanocrystals 500 is shown in FIG. 5.

3. EXAMPLE 3. SYNTHESIS OF SM-DOPED $\text{Fe}_3\text{O}_4/\text{MgO}$ CORE/SHELL NANOCRYSTALS.

[00104] Surface-doped iron-oxide/magnesium oxide core/shell nanocrystals were synthesized in two steps. In the first step, a hexane solution of iron-oxide nanocrystals (6.0 nm in diameter, 4.0 g) was mixed with a 15-mL octadecene solution containing 1,2-tetradecanediol (4 mmol), oleic acid (4 mmol) and oleylamine (4 mmol), and hexane was removed via pumping at room temperature. Under an argon flow, the resulting solution was heated to 305 °C, and then an octadecene solution containing magnesium 2-ethylhexanoate (0.05 mM) was added in dropwise, forming iron-oxide/magnesium-oxide core/shell nanocrystals. When a desired shell thickness was achieved, the reaction solution was heated to 320 °C and aged for 30 min. In the second step, an octadecene solution of samarium(III) 2-ethylhexanoate (0.05 micron molar, at amount of a doping level of 10-15 samarium atoms per nanocrystals) was added dropwise into the reaction solution, forming doped $\text{Fe}_3\text{O}_4/\text{MgO}$ core/shell nanocrystals with samarium at their surface. The resulting solution was further aged for 1 hour, and then was cooled to room temperature over a period time of about 20 min. The resulting Sm-doped $\text{Fe}_3\text{O}_4/\text{MgO}$ core/shell nanocrystals were precipitated using ethanol, and then were purified using two rounds of precipitation/redispersion cycles with ethanol and chloroform as the solvents. After purification, the product was dispersed in chloroform for further use. TEM images of representative nanocrystals 600 are shown in FIG. 6.

4. EXAMPLE 4. SYNTHESIS OF SUPERPARTICLES WITH SM-DOPED $\text{Fe}_3\text{O}_4/\text{MgO}$ CORE/SHELL NANOCRYSTALS.

[00105] DTAB (20.0 mg, 65.0 μmol) was dissolved in Nanopure water (1.0 mL) to form a solution. A chloroform solution of Sm-doped $\text{Fe}_3\text{O}_4/\text{MgO}$ nanoparticles (30 μM , 1.0 mL) was thoroughly mixed with the DTAB solution by a vortex mixer. Afterwards, the chloroform was removed from the mixture by bubbling argon at 35 °C, yielding a clear superparticle aqueous solution. Then a 3-mL aqueous of polyvinylpyrrolidone (PVP, 2.0 mM, MW=55,000) was added into the superparticle solution, and the resulting solution was further stirred for 30 min. The resulting colloidal superparticles were separated by centrifuge (500g, 15 min). The black precipitate was re-dispersed into ethanol and the superparticles were further purified twice through centrifugation and dispersed in water for future use. A TEM image of representative superparticles is shown in FIG. 7, which shows exemplary assemblies of nanoparticles 710 into superparticles 720.

[00106] It will be apparent to those skilled in the art that various modifications and variations can be made in the present disclosure without departing from the scope or spirit of the disclosure. Other embodiments of the disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the disclosure disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the disclosure being indicated by the following claims.

CLAIMS

What is claimed is:

1. A single-atom-based catalyst system with single-atom catalytic sites in a controlled hierarchical structure over length scales ranging from macroscopic dimensions down to atomic scales, the single-atom-based catalyst system comprising:

at least one catalyst structure comprising a first assembly of
a plurality of single-atom-catalyst superparticles, further comprising a second assembly
of a plurality of single-atom-catalyst nanoparticles;

wherein each of the single-atom-catalyst nanoparticles comprises a core-shell support structure having a crystalline metal oxide support surface, and one or more single-atom catalysts anchored to the support surface, wherein the density and location of the single-atom catalysts on the support surface are controlled within a 20% variance to provide a highly uniform spatial distribution of single-atom catalysts;

wherein each of the second assembly is a sub-micron-sized superlattice of a plurality of single-atom-catalyst nanoparticles, the superlattice having a second density and a second porosity, wherein the second density is controlled within a 20% variance to provide a single-atom-catalyst superparticle having a precise porosity and a highly uniform spatial distribution of the single-atom catalysts; and

wherein the first assembly of single-atom-catalyst superparticles has a first density and a first porosity, wherein the first density of the first assembly is controlled within a 10% variance to provide a catalyst structure having a precise porosity and highly uniform spatial distribution of the single-atom catalysts.

2. The single-atom-based catalyst system of claim 1, comprising two or more catalyst structures.

3. The single-atom-based catalyst system of claims 1 or 2, further comprising one or more catalytically-inactive support materials.

4. The single-atom-based catalyst system according to any of claims 1 to 3, wherein at least one of the catalyst structures comprises a single-atom-catalyst nanoparticle having one or more of:

- a core structure comprising a NiO_x or FeO_x nanoparticle lattice structure;
- a shell comprising a support matrix comprising MgO , CaO , SiO_2 , FeO_x , NiO_x , AlO_x , ZnO , TiO_x , Graphene, or a combination thereof;
- a single-atom catalyst dopant comprising Sm, Fe, Mn, Na, W, Pt, Sn, or a combination thereof.

5. The single-atom-based catalyst system according to any of claims 1 to 4, wherein at least one of the single-atom-catalyst nanoparticles comprises one or more of: Sm-doped MgO/CaO , Fe-doped SiO_2 , Mn-doped SiO_2 , Na-W doped SiO_2 , Ni-doped SiO_2 , and Pt-Sn-doped SiO_2 .

6. The single-atom-based catalyst system according to any of claims 1 to 5, comprising a tandem catalyst structure comprising:

- a first catalyst layer comprising a first catalyst structure; and
- a second catalyst layer in fluid communication with the first catalyst layer, said second catalyst layer comprising a second catalyst structure.

7. The single-atom-based catalyst system of claim 6, wherein the first catalyst layer further comprises one or more of:

- a first support layer comprising a catalytically inactive supporter material that supports the first catalyst structure; and
- a first spacer layer in fluid communication with the second catalyst layer.

8. The single-atom-based catalyst system of claim 6 or 7, wherein the second catalyst layer further comprises one or more of:

- a second support layer comprising a catalytically inactive supporter material that supports the first catalyst structure; and
- a second spacer layer.

9. The single-atom-based catalyst system according to any of claims 6 to 8, further comprising one or more of:

- a fluid inlet in fluid communication with the first catalyst layer; and
- a fluid outlet in fluid communication with the second catalyst layer.

10. The single-atom-based catalyst system according to any of claims 1 to 5, comprising a radially-structured tandem catalyst, comprising:

- a cylindrical structure having a longitudinal dimension extending parallel a longitudinal axis from a first end to a second end, and a radial dimension extending radially outward from a longitudinal centerline of the catalyst to an outer surface, said cylindrical structure further comprising:

- a central fluid conduit extending along the longitudinal axis from the first end to the second end and comprising a fluid inlet;

- a first catalyst layer disposed radially outward from the central fluid inlet and in fluid communication with the central fluid inlet and comprising a first catalyst structure;

- a second catalyst layer disposed radially outward from the first spacer layer and in fluid communication with the first spacer layer, said second catalyst layer comprising a second catalyst structure; and

- an outer annulus disposed radially outward from the second catalyst layer and in fluid communication with the second catalyst layer.

11. The single-atom-based catalyst system of claim 10, wherein the first catalyst layer further comprises one or more of:

- a first support layer comprising a catalytically inactive supporter material that supports the first catalyst structure; or

- a first spacer layer disposed radially outward from the first catalyst structure and in fluid communication with the second catalyst layer.

12. The single-atom-based catalyst system of claim 10 or 11, wherein the second catalyst layer further comprises one or more of:

- a second support layer comprising a catalytically inactive supporter material that supports the first catalyst structure; and

- a second spacer layer.

13. The single-atom-based catalyst system according to any of claims 10 to 12, further comprising one or more of:

- a fluid inlet in fluid communication with the central fluid conduit; or
- a fluid outlet in fluid communication with the outer annulus.

14. The single-atom-based catalyst system according to any of claims 6 to 13, wherein the first catalyst structure comprises a catalyst for the oxidative coupling of methane (OCM) into ethane.

15. The single-atom-based catalyst system according to any of claims 6 to 14, wherein the second catalyst structure comprises a catalyst for the oxidative dehydrogenation of ethane (ODE) into ethylene.

16. A method for three-dimensional (3D) printing a single-atom-based catalyst system according to any of claims 1-15, comprising:

- providing a first ink substrate comprising a plurality of positively-charged first single-atom-catalyst superparticles;
- providing a second ink substrate comprising a plurality of positively-charged second single-atom-catalyst superparticles;
- providing a support ink substrate comprising a plurality of catalytically inactive supporter particles;
- providing a binder ink substrate comprising a plurality of negatively-charged polymeric binders; and
- selectively depositing with a 3D printing apparatus each of the first ink substrate, the second ink substrate, the support substrate, and the binder ink substrate to provide the elements of the single-atom-based catalyst system.

17. A method of converting methane to ethylene, comprising:
- providing a single-atom-based catalyst system according to any of claims 6-15;
 - introducing a first fluid comprising methane to the single-atom-based catalyst system,
 - passing the first fluid through the first catalyst layer so that at least a portion of the methane contacts the first single-atom catalyst structure, providing a first reaction product comprising ethane,
 - passing the first reaction product through the second catalyst layer so that at least a portion of the ethane contacts the second single-atom catalyst structure, providing a second reaction product comprising ethylene,
 - withdrawing the second reaction product from the single-atom-based catalyst system.
18. The method of claim 17, further comprising:
- introducing oxygen to the catalyst structure to activate the catalyst; and
 - purging substantially all of the oxygen from the catalyst structure.

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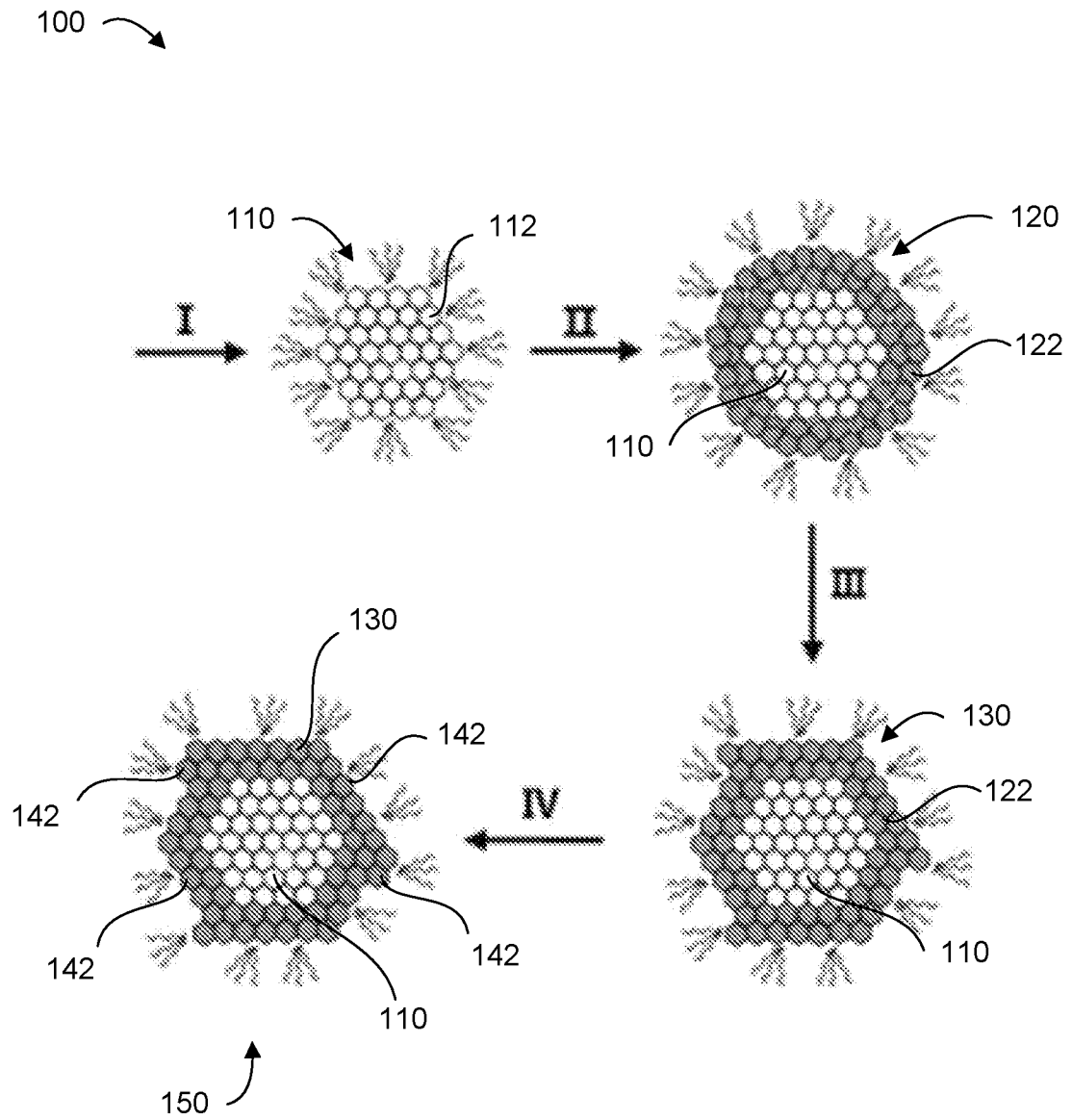
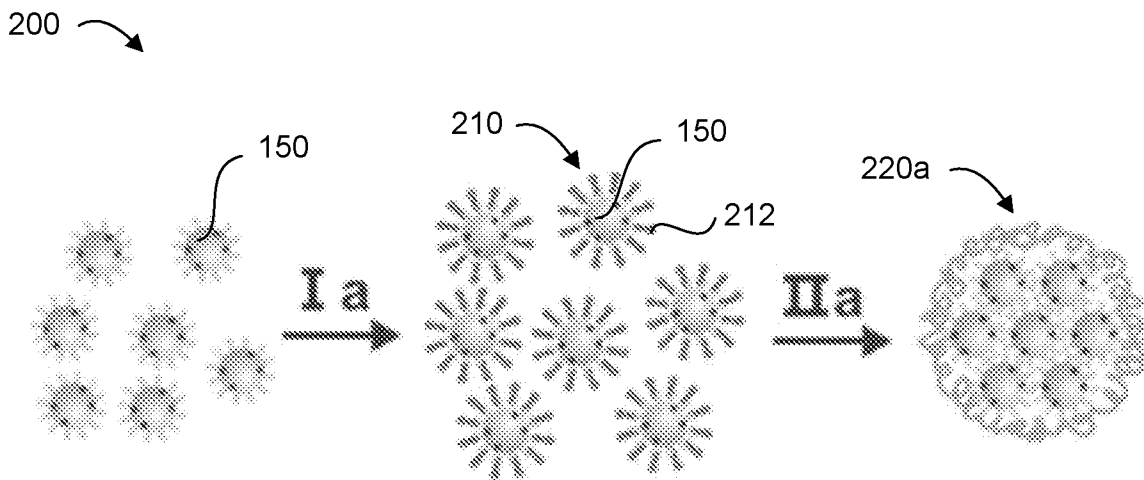
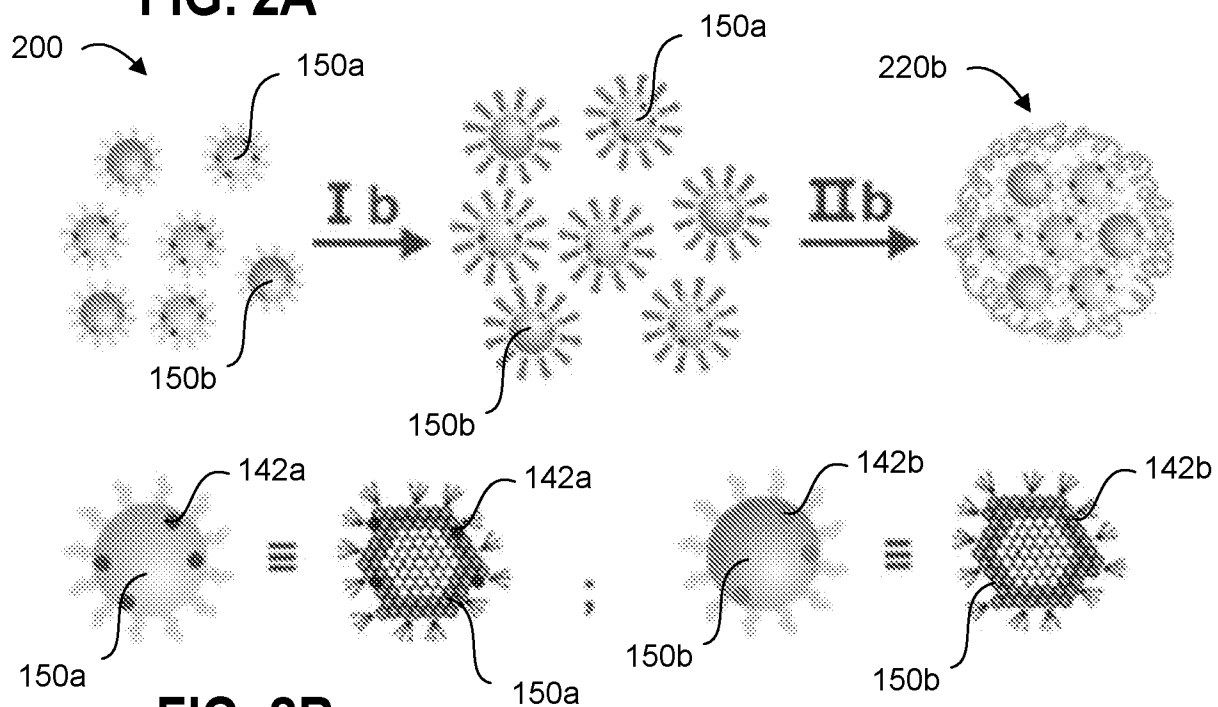


FIG. 1

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**FIG. 2A****FIG. 2B**

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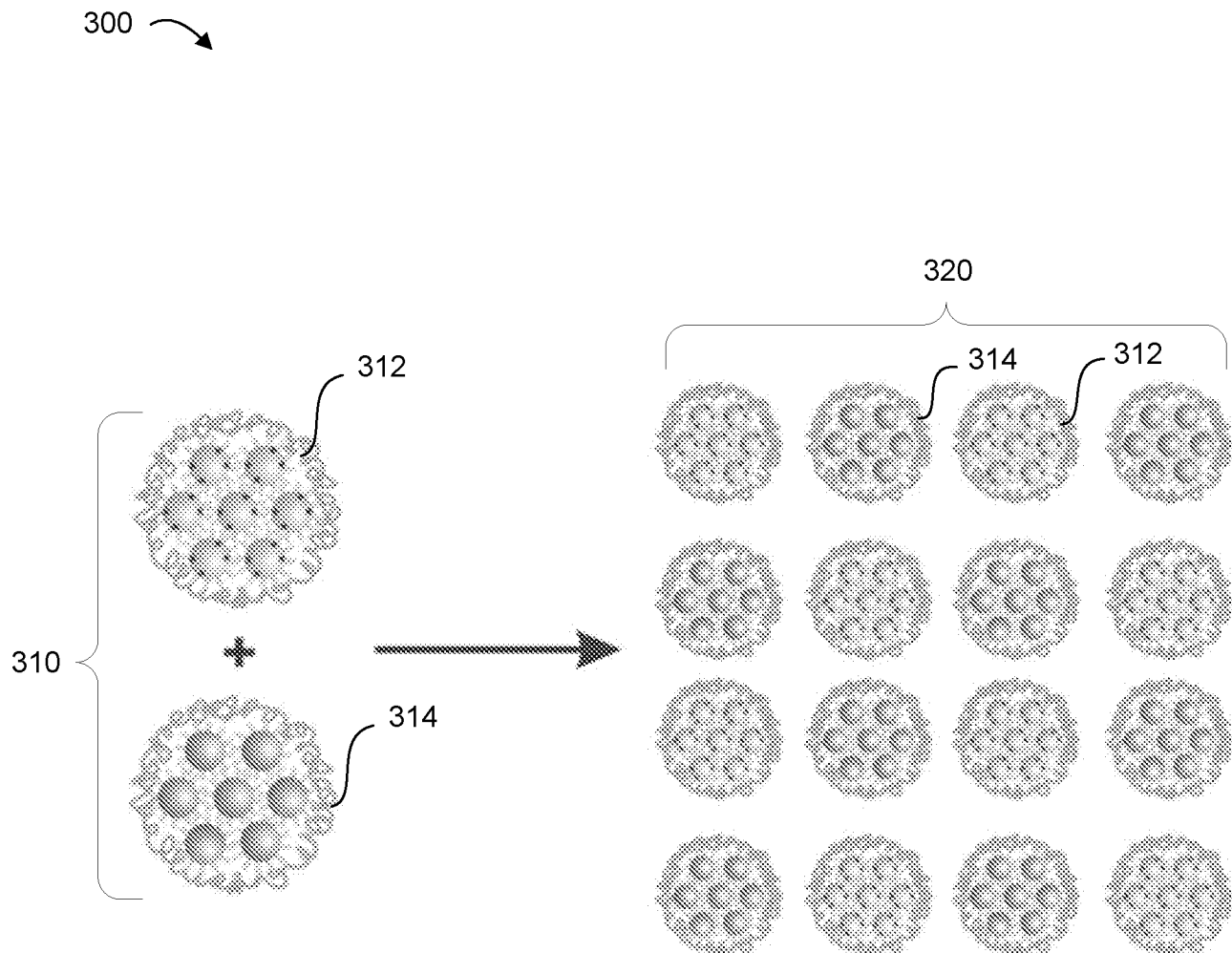
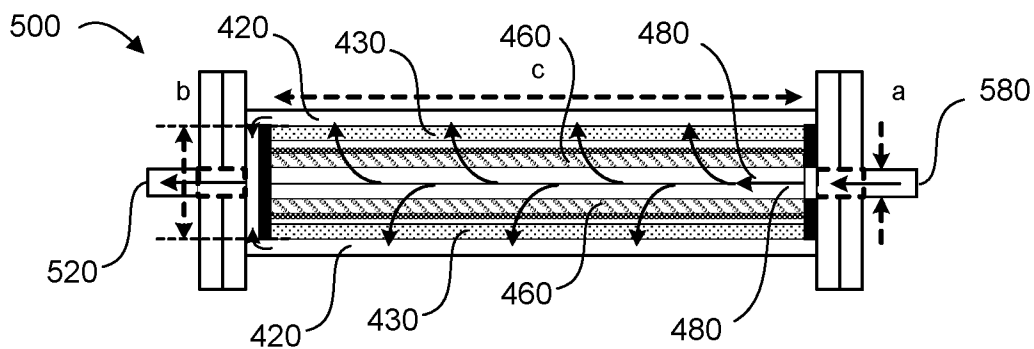
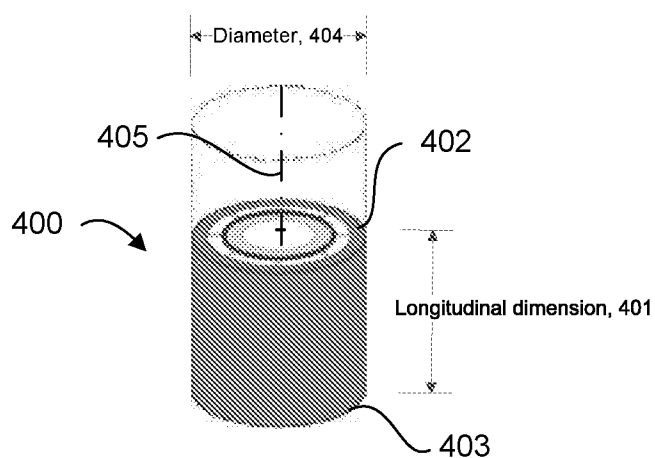
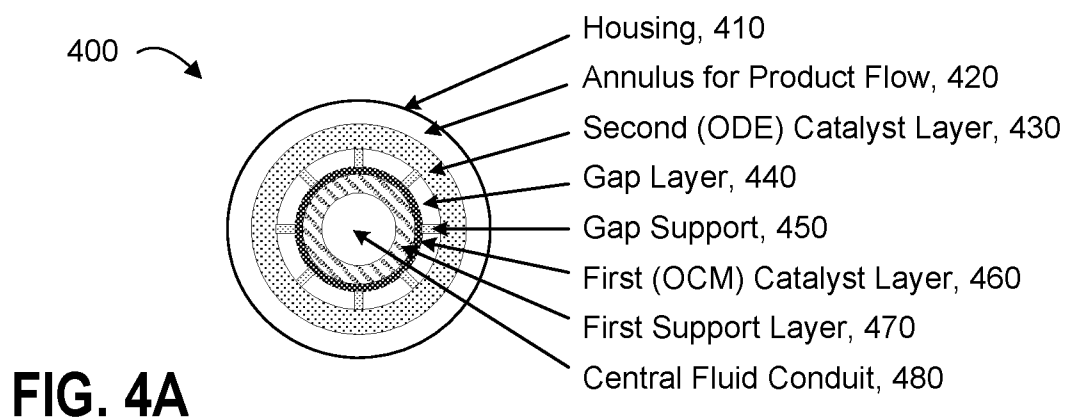


FIG. 3

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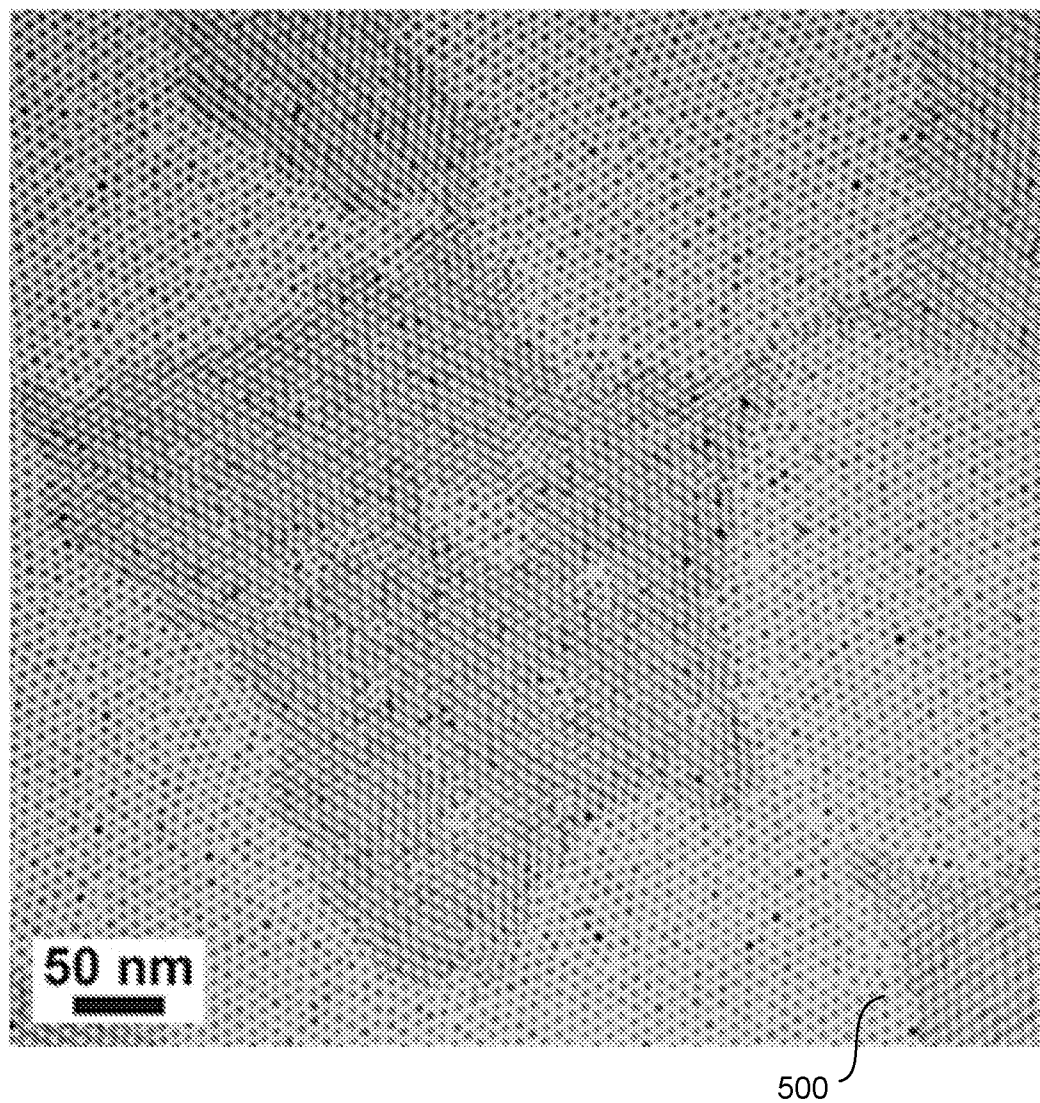


FIG. 5

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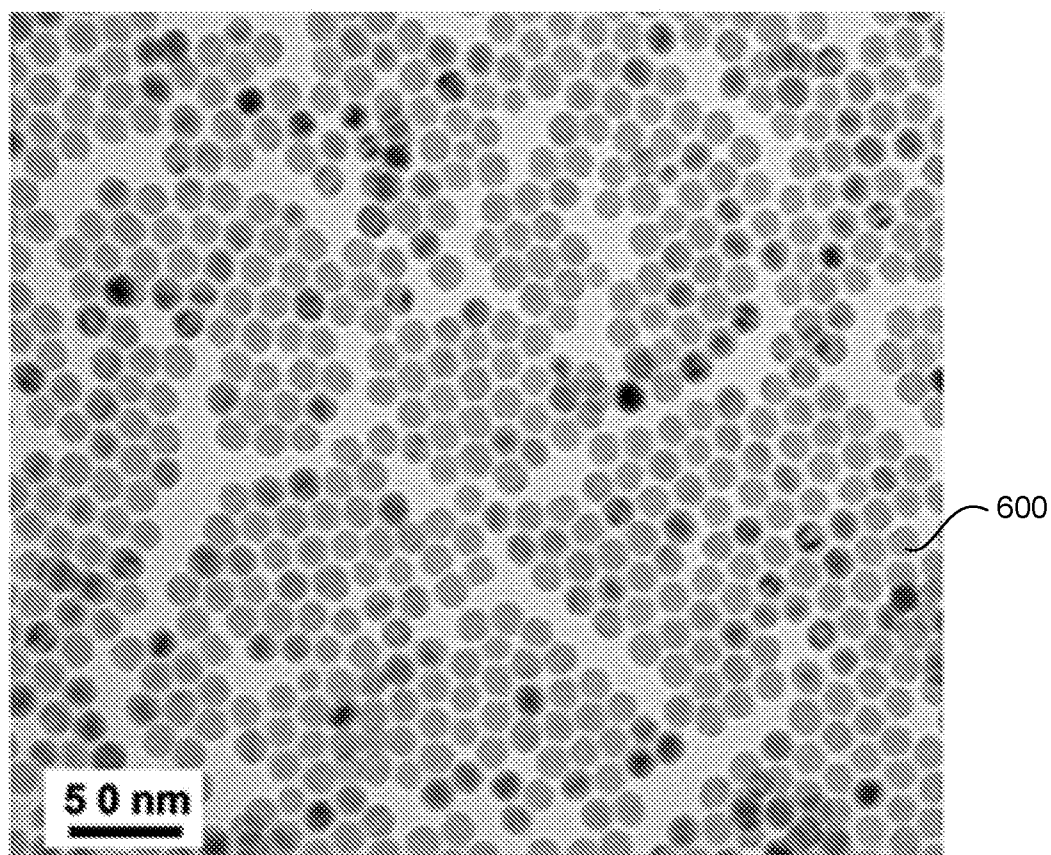


FIG. 6

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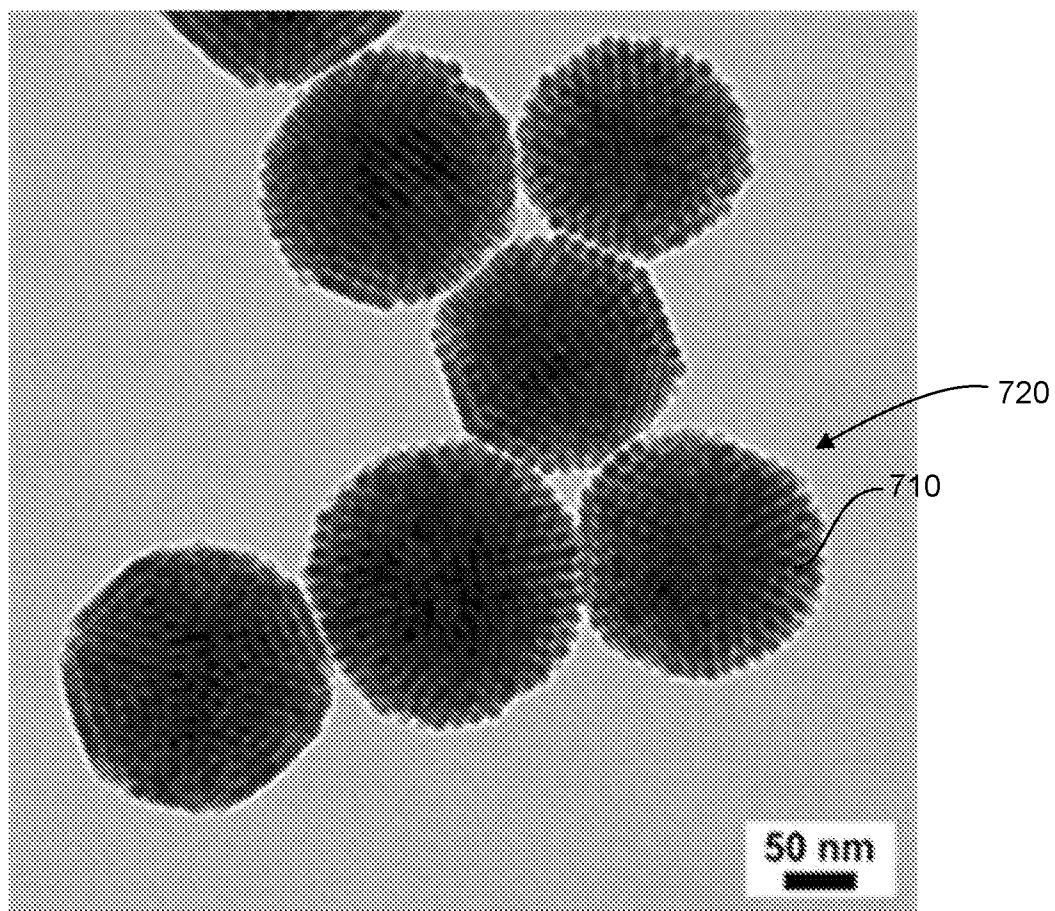


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/47233

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 21/00; B01J 23/74; C07C 2/84; C07C 11/04 (2019.01)

CPC - B01J 21/00; B01J 23/74; C07C 2/84; C07C 11/04; C07C 2521/00; C07C 2523/10

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/0150938 A1 (CAO et al.) 23 June 2011 (23.06.2011); para [0009]-[0012], [0043], [0059], [0134]-[0135]	1-3
A	US 2003/0204111 A1 (CHATURVEDI et al.) 30 October 2003 (30.10.2003); para [0040], [0085], [0092]-[0093]	1-3
A	US 2003/0083194 A1 (SUNG) 01 May 2003 (01.05.2003); para [0026], [0029], [0037]-[0039]	1-3
A	US 2016/0208360 A1 (UCHICAGO ARGONNE, LLC) 12 July 2016 (12.07.2016); see entire document	1-3
A	US 2010/0055462 A1 (CAO) 04 March 2010 (04.03.2010); see entire document	1-3

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

25 September 2019

Date of mailing of the international search report

15 NOV 2019

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PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/47233

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-18
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.