



(43) International Publication Date
26 September 2013 (26.09.2013)

(51) International Patent Classification:
C23C 30/00 (2006.01) *C04B 35/50* (2006.01)
C23C 14/34 (2006.01)

(21) International Application Number:
PCT/US2012/030370

(22) International Filing Date:
23 March 2012 (23.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): **MAS-SACHUSETTS INSTITUTE OF TECHNOLOGY** [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139-4307 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **AZIMI, Gisele** [CA/US]; 34 Black Bear Drive, Waltham, MA 02451 (US). **VARANASI, Kripa, K.** [IN/US]; 31 Fletcher Avenue, Unit 5, Lexington, MA 02420 (US). **DHIMAN, Rajeev** [CA/US]; 8 Island Hill Avenue, No. 213, Malden, MA 02148 (US). **PAXSON, Adam, T.** [US/US]; 48 Pearl Street, Cambridge, MA 02139 (US). **KWON, Hyukmin** [KR/US]; 143 Albany Street, Apt. 235, Cambridge, MA 02139 (US).

(74) Agents: **HAULBROOK, William R.** et al.; Choate, Hall & Stewart LLP, Two International Place, Boston, Massachusetts 02110 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: HYDROPHOBIC MATERIALS INCORPORATING RARE EARTH ELEMENTS AND METHODS OF MANUFACTURE

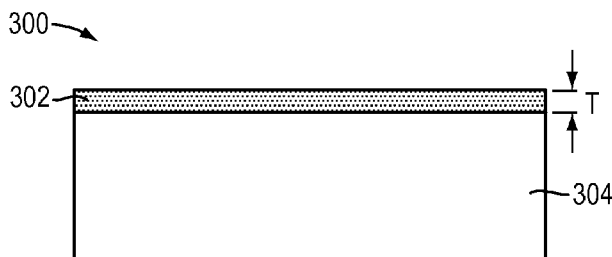


FIG. 3

(57) Abstract: This invention relates generally to an article that includes a base substrate and a hydrophobic coating on the base substrate, wherein the hydrophobic coating includes a rare earth element material (e.g., a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and/or a rare earth boride). An exposed surface of the hydrophobic coating has a dynamic contact angle with water of at least about 90 degrees. A method of manufacturing the article includes providing the base substrate and forming a coating on the base substrate (e.g., through sintering or sputtering).



- 1 -

HYDROPHOBIC MATERIALS INCORPORATING RARE EARTH ELEMENTS AND METHODS OF MANUFACTURE

Field of the Invention

[0001] This invention relates generally to nonwetting materials and, more particularly, to hydrophobic materials that include rare earth elements.

Background of the Invention

[0002] Developing robust hydrophobic surfaces has been a subject of intense research over the past decades. Taking inspiration from natural nonwetting structures, such as lotus leaves, butterfly wings, duck feathers, and water striders, many researchers over the past decades have aimed to decipher some of these peculiar designs to develop novel surfaces that, similar to their natural counterparts, are water repellent. Conventional approaches to designing hydrophobic/superhydrophobic surfaces include creating a rough or textured surface and then modifying the surface by materials with low surface energies, such as polymers or fluoroalkylsilane. These surfaces, although generally nonwetting, face major material-related drawbacks and operational challenges that limit their use in industrial applications. For example, material incompatibility, physical instability, failure under harsh environments, and high cost of fabrication are drawbacks that hinder widespread, large-scale utilization of conventional hydrophobic and superhydrophobic surfaces. Certain hydrophobic and superhydrophobic surfaces are described in Kesong Liu & Lei Jiang, *Metallic Surfaces with Special Wettability*, Nanoscale, 2011, 3, 825–838.

[0003] Recent developments of water-repellent surfaces have pervasively stressed one aspect of hydrophobicity, i.e., designing more complex structures or textures, while overlooking the other aspect, i.e., choosing appropriate materials or chemical compositions, which is equally, if not more, important. For example, the materials used for most hydrophobic surfaces have insufficient mechanical resistance, chemical resistance, and thermal stability for many applications. On the other hand, metals and ceramics are materials of choice for harsh environments, but these materials are generally hydrophilic and may require conformal polymeric hydrophobic coatings or modifiers to render them hydrophobic or superhydrophobic.

- 2 -

These modifiers, however, break down or deteriorate in harsh environments. Robust superhydrophobic surfaces have therefore been difficult to realize.

[0004] What is needed, then, is a robust, hydrophobic material for use in harsh environments where conventional hydrophobic materials have failed. A particular need exists for
5 hydrophobic materials that are resistant to high temperatures, harsh chemicals, and mechanical wear and tear (e.g., abrasion and impact).

Summary of the Invention

[0005] The articles, devices, and methods presented herein provide robust hydrophobic surfaces with applications across a broad range of industries and technologies. In certain embodiments, novel hydrophobic ceramics comprising rare earth oxides are described that
10 demonstrate superior water repellency and promote dropwise water condensation. These ceramics surpass the state-of-the-art in the field of water repellency in their capability to repel water droplets even from smooth surfaces and their ability to promote dropwise condensation, with remarkably improved heat transfer coefficients. Because these novel ceramic surfaces are robust (i.e., capable of withstanding harsh environments), their deployment may enhance
15 process efficiency, while reducing overall costs and energy consumption in a wide variety of applications that are negatively affected by droplet impingement and filmwise condensation. Examples include steam turbine blades, heat exchangers, condensers, and waterproof consumer products.

[0006] The articles, devices, and methods described herein offer several advantages over
20 previous approaches in the field of water repellency and superhydrophobic surfaces. For example, no previous coating materials have been reported that are both robust and hydrophobic. The materials and coatings described herein are uniquely capable of repelling water droplets and offering mechanical resistance, chemical inactivity, thermal stability, ease of cleaning, and other advantages. Further, hydrophobic surfaces based on the materials described
25 herein have the advantage of being more scalable and practical for industrial applications, compared to previous low surface energy organic materials that are physically and thermally unstable and fail under harsh environments.

[0007] The articles and materials described herein may be used in a wide variety of industrial applications where hydrophobicity, droplet repellency, and/or dropwise condensation are
30 desirable. These materials may also offer other industrial implications in development of anti-fouling and anti-icing surfaces. For example, these materials may be used in steam turbines,

- 3 -

condensers, heat exchangers, aircraft, wind turbines, pipelines, evaporators, boilers, medical devices and implants, and separators.

[0008] In one aspect, the invention relates to an article that includes a base substrate and a hydrophobic coating on the base substrate. The hydrophobic coating includes a rare earth
5 element material. An exposed surface of the hydrophobic coating has a dynamic contact angle with water of at least about 90 degrees.

[0009] In another aspect, the invention relates to an article containing a rare earth element material. An exposed surface of the article has a dynamic contact angle with water of at least about 90 degrees.

10 **[0010]** In certain embodiments, the rare earth element material includes a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and/or a rare earth boride. In some embodiments, the rare earth element material includes a combination of one or more species within one or more of the following categories of compounds: a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and a rare earth boride. For example, the rare
15 earth element material may include a combination of at least two members selected from the group consisting of a first rare earth oxide, a second rare earth oxide, a first rare earth carbide, a second rare earth carbide, a first rare earth nitride, a second rare earth nitride, a first rare earth fluoride, a second rare earth fluoride, a first rare earth boride, and a second rare earth boride. For example, the rare earth element material may include a rare earth oxide. In one
20 embodiment, the article includes a metal and/or a ceramic. A thickness of the coating is preferably from about 100 nm to about 300 nm. In various embodiments, the coating includes a ceramic, a metal, and/or a polymer. The coating may be doped with the rare earth element material. In one embodiment, the exposed surface includes (or is) a textured surface (e.g., multiple-scale surface roughness).

25 **[0011]** In certain embodiments, the rare earth element material includes a first rare earth oxide doped with a second rare earth oxide. For example, the first rare earth oxide may be a light rare earth oxide, and the second rare earth oxide may be a heavy rare earth oxide. The heavy rare earth oxide may include, for example, gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide (Ho_2O_3), erbium oxide (Er_2O_3), thulium
30 oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and/or lutetium oxide (Lu_2O_3). In one embodiment, the light rare earth oxide is cerium oxide (CeO_2) and the heavy rare earth oxide is gadolinium oxide (Gd_2O_3).

- 4 -

[0012] In various embodiments, the rare earth element material includes scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and/or lutetium (Lu). In one embodiment, the rare earth element material includes scandium oxide (Sc_2O_3), yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), cerium oxide (CeO_2), praseodymium oxide (Pr_6O_{11}), neodymium oxide (Nd_2O_3), samarium oxide (Sm_2O_3), europium oxide (Eu_2O_3), gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide (Ho_2O_3), erbium oxide (Er_2O_3), thulium oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and/or lutetium oxide (Lu_2O_3). In some

embodiments, the rare earth element material includes cerium carbide (CeC_2), praseodymium carbide (PrC_2), neodymium carbide (NdC_2), samarium carbide (SmC_2), europium carbide (EuC_2), gadolinium carbide (GdC_2), terbium carbide (TbC_2), dysprosium carbide (DyC_2), holmium carbide (HoC_2), erbium carbide (ErC_2), thulium carbide (TmC_2), ytterbium carbide (YbC_2), and/or lutetium carbide (LuC_2). In various embodiments, the rare earth element

material includes cerium nitride (CeN), praseodymium nitride (PrN), neodymium nitride (NdN), samarium nitride (SmN), europium nitride (EuN), gadolinium nitride (GdN), terbium nitride (TbN), dysprosium nitride (DyN), holmium nitride (HoN), erbium nitride (ErN), thulium nitride (TmN), ytterbium nitride (YbN), and/or lutetium nitride (LuN). In one embodiment, the rare earth element material includes cerium fluoride (CeF_3), praseodymium

fluoride (PrF_3), neodymium fluoride (NdF_3), samarium fluoride (SmF_3), europium fluoride (EuF_3), gadolinium fluoride (GdF_3), terbium fluoride (TbF_3), dysprosium fluoride (DyF_3), holmium fluoride (HoF_3), erbium fluoride (ErF_3), thulium fluoride (TmF_3), ytterbium fluoride (YbF_3), and/or lutetium fluoride (LuF_3).

[0013] In certain embodiments, the article is a steam turbine, a condenser, a heat exchanger, an aircraft, a wind turbine, a pipeline, an evaporator, a boiler, a medical device, a medical implant, and/or a separator.

[0014] In another aspect, the invention relates to an article having a bulk material doped with a rare earth element material. An exposed surface of the bulk material or the article has a dynamic contact angle with water of at least about 90 degrees.

[0015] In certain embodiments, the rare earth element material includes a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and/or a rare earth boride. The bulk material may include a ceramic (e.g., a metal oxide, a metal carbide, and/or a metal nitride).

- 5 -

For example, the ceramic may include aluminum oxide, aluminum nitride, boron oxide, boron nitride, boron carbide, titanium oxide, titanium nitride, and/or titanium carbide. In one embodiment, the bulk material is a light rare earth oxide doped with a heavy rare earth oxide. In some embodiments, the bulk material is cerium oxide (CeO_2) and the rare earth element material includes gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide (Ho_2O_3), erbium oxide (Er_2O_3), thulium oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and/or lutetium oxide (Lu_2O_3).

[0016] In various embodiments, the rare earth element material includes scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and/or lutetium (Lu). For example, the rare earth element material may include scandium oxide (Sc_2O_3), yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), cerium oxide (CeO_2), praseodymium oxide (Pr_6O_{11}), neodymium oxide (Nd_2O_3), samarium oxide (Sm_2O_3), europium oxide (Eu_2O_3), gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide (Ho_2O_3), erbium oxide (Er_2O_3), thulium oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and/or lutetium oxide (Lu_2O_3). In some embodiments, the rare earth element material includes cerium carbide (CeC_2), praseodymium carbide (PrC_2), neodymium carbide (NdC_2), samarium carbide (SmC_2), europium carbide (EuC_2), gadolinium carbide (GdC_2), terbium carbide (TbC_2), dysprosium carbide (DyC_2), holmium carbide (HoC_2), erbium carbide (ErC_2), thulium carbide (TmC_2), ytterbium carbide (YbC_2), and/or lutetium carbide (LuC_2). The rare earth element material may include, for example, cerium nitride (CeN), praseodymium nitride (PrN), neodymium nitride (NdN), samarium nitride (SmN), europium nitride (EuN), gadolinium nitride (GdN), terbium nitride (TbN), dysprosium nitride (DyN), holmium nitride (HoN), erbium nitride (ErN), thulium nitride (TmN), ytterbium nitride (YbN), and/or lutetium nitride (LuN). In one embodiment, the rare earth element material includes cerium fluoride (CeF_3), praseodymium fluoride (PrF_3), neodymium fluoride (NdF_3), samarium fluoride (SmF_3), europium fluoride (EuF_3), gadolinium fluoride (GdF_3), terbium fluoride (TbF_3), dysprosium fluoride (DyF_3), holmium fluoride (HoF_3), erbium fluoride (ErF_3), thulium fluoride (TmF_3), ytterbium fluoride (YbF_3), and/or lutetium fluoride (LuF_3).

[0017] In certain embodiments, the article is a steam turbine, a condenser, a heat exchanger, an aircraft, a wind turbine, a pipeline, an evaporator, a boiler, a medical device, a medical implant, and/or a separator. In some embodiments, the bulk material contains at least about 10

- 6 -

weight percent rare earth element material, or at least about 25 weight percent rare earth element material.

[0018] In another aspect, the invention relates to an article having carbon nanotubes and a hydrophobic coating on the carbon nanotubes. The hydrophobic coating includes a rare earth
5 element material. An exposed surface of the hydrophobic coating has a dynamic contact angle with water of at least about 90 degrees.

[0019] In certain embodiments, the rare earth element material includes a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and/or a rare earth boride. The coating may be doped with the rare earth element material. The article may be, for example, a
10 steam turbine, a condenser, a heat exchanger, an aircraft, a wind turbine, a pipeline, an evaporator, a boiler, a medical device, a medical implant, and/or a separator.

[0020] In another aspect, the invention relates to a method of manufacturing a hydrophobic article. The method includes providing a ceramic material and a rare earth element material, and heating the ceramic material and the rare earth element material to a temperature of at
15 least about 1600 °C. The method forms a hydrophobic coating having a dynamic contact angle with water of at least about 90 degrees.

[0021] In certain embodiments, the rare earth element material includes a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and a rare earth boride. The method may include adding a binder and/or a promoter to the ceramic material and the rare earth
20 element material.

[0022] In another aspect, the invention relates to a method of manufacturing a hydrophobic article. The method includes: providing a powder having a rare earth element material; pressing the powder at a pressure greater than 30,000 tsi (tons per square inch) to form a pressed rare earth element material; and sintering the pressed rare earth element material in an
25 argon environment. In certain embodiments, the rare earth element material includes a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and/or a rare earth boride.

[0023] In another aspect, the invention relates to a method of manufacturing a hydrophobic article. The method includes providing a base substrate and forming a coating on the base
30 substrate. The coating includes a rare earth element material.

- 7 -

[0024] In certain embodiments, the rare earth element material includes a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and/or a rare earth boride. The forming step may include, for example, sputtering and/or sintering.

[0025] Elements of embodiments described with respect to a given aspect of the invention may be used in various embodiments of another aspect of the invention. For example, it is contemplated that features of dependent claims depending from one independent claim can be used in apparatus and/or methods of any of the other independent claims.

Brief Description of the Drawings

[0026] The objects and features of the invention can be better understood with reference to the drawings described below, and the claims. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the drawings, like numerals are used to indicate like parts throughout the various views.

[0027] While the invention is particularly shown and described herein with reference to specific examples and specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention.

[0028] FIG. 1 is a schematic side view of a droplet resting on a surface during a static contact angle measurement, according to an illustrative embodiment of the invention.

[0029] FIG. 2 is a schematic side view of a droplet on a sloped surface during a dynamic contact angle measurement, according to an illustrative embodiment of the invention.

[0030] FIG. 3 is a schematic cross-sectional view of a hydrophobic material having a base substrate and a hydrophobic coating, according to an illustrative embodiment of the invention.

[0031] FIG. 4 is a schematic cross-sectional view of a hydrophobic material having a base substrate and a hydrophobic coating, according to an illustrative embodiment of the invention.

[0032] FIG. 5 is a schematic cross-sectional view of a hydrophobic material having a bulk material doped with a rare earth oxide, according to an illustrative embodiment of the invention.

[0033] FIG. 6 is a schematic illustration of a method of forming a hydrophobic coating on carbon nanotubes, wherein the hydrophobic coating includes a rare earth oxide, according to an illustrative embodiment of the invention.

[0034] FIG. 7 is a schematic side view of water molecules on a hydrophilic aluminum oxide surface, according to an illustrative embodiment of the invention.

- 8 -

[0035] FIG. 8 is a schematic side view of water molecules on a hydrophobic rare earth oxide surface, according to an illustrative embodiment of the invention.

[0036] FIG. 9 is a photograph of a water droplet on a hydrophilic alumina surface, according to an illustrative embodiment of the invention.

5 [0037] FIG. 10 is a photograph of a water droplet on a hydrophilic silica surface, according to an illustrative embodiment of the invention.

[0038] FIG. 11 is a photograph of a water droplet on smooth silicon modified with cerium oxide, according to an illustrative embodiment of the invention.

10 [0039] FIG. 12 is a photograph of a water droplet on nanoglass silicon posts modified with cerium oxide, according to an illustrative embodiment of the invention.

[0040] FIG. 13 is a collection of photographs of sintered rare earth oxide ceramics, according to an illustrative embodiment of the invention.

[0041] FIG. 14 is a plot of measured advancing contact angles of water on sintered ceramics and on hydrophilic alumina and silica, according to an illustrative embodiment of the invention.

15 [0042] FIG. 15 is a plot of calculated total surface free energy and the polar and apolar components of surface free energy, for sintered rare earth oxide ceramics, according to an illustrative embodiment of the invention.

[0043] FIG. 16 is a scanning electron microscope image of nanoglass silicon post arrays, modified for superhydrophobicity with a thin layer of sputtered ceria, according to an illustrative embodiment of the invention.

[0044] FIG. 17 is a photograph of sessile water droplets in a Cassie state ($\theta=160^\circ$) on nanoglass silicon posts modified with ceria, according to an illustrative embodiment of the invention.

25 [0045] FIG. 18 includes sequential high-speed photographs of a droplet impinging a smooth hydrophobic silicon wafer modified with a thin film of a rare earth oxide, according to an illustrative embodiment of the invention.

[0046] FIG. 19 includes sequential high-speed photographs of a droplet impinging a nanoglass silicon posts modified with a thin layer of ceria, according to an illustrative embodiment of the invention.

30 [0047] FIG. 20 is a photograph of filmwise water condensation on a smooth, hydrophilic silicon surface, according to an illustrative embodiment of the invention.

- 9 -

[0048] FIG. 21 is a photograph of dropwise water condensation on a smooth, hydrophobic fluorosilanized silicon wafer, according to an illustrative embodiment of the invention.

[0049] FIG. 22 is a photograph of dropwise water condensation on a smooth, hydrophobic film of cerium oxide on a silicon wafer, according to an illustrative embodiment of the invention.

[0050] FIG. 23 is a photograph of dropwise water condensation on a smooth, hydrophobic film of erbium oxide on a silicon wafer, according to an illustrative embodiment of the invention.

[0051] FIG. 24 is a plot of measured condensation heat flux values for a cerium oxide surface, an erbium oxide surface, a fluorosilanized silicon surface, and a silicon surface, according to an illustrative embodiment of the invention.

[0052] FIG. 25 is a photograph of water droplets resting on a hydrophobic cerium oxide surface and a hydrophobic silicon surface, according to an illustrative embodiment of the invention.

[0053] FIG. 26 is a photograph of a water droplet on a fluorosilanized surface after the surface had been exposed to 400 °C for two hours, according to an illustrative embodiment of the invention.

[0054] FIG. 27 is a photograph of a water droplet on a cerium oxide surface after the surface had been exposed to 400 °C for two hours, according to an illustrative embodiment of the invention.

Detailed Description

[0055] It is contemplated that compositions, mixtures, systems, devices, articles, methods, and processes of the claimed invention encompass variations and adaptations developed using information from the embodiments described herein. Adaptation and/or modification of the compositions, mixtures, systems, devices, methods, and processes described herein may be performed by those of ordinary skill in the relevant art.

[0056] Throughout the description, where devices and systems are described as having, including, or comprising specific components, or where processes and methods are described as having, including, or comprising specific steps, it is contemplated that, additionally, there are devices and systems of the present invention that consist essentially of, or consist of, the recited components, and that there are processes and methods according to the present invention that consist essentially of, or consist of, the recited processing steps.

[0057] Similarly, where devices, articles, mixtures, and compositions are described as having, including, or comprising specific compounds and/or materials, it is contemplated that, additionally, there are devices, articles, mixtures, and compositions of the present invention that consist essentially of, or consist of, the recited compounds and/or materials.

5 [0058] It should be understood that the order of steps or order for performing certain actions is immaterial so long as the invention remains operable. Moreover, two or more steps or actions may be conducted simultaneously.

[0059] The mention herein of any publication, for example, in the Background section, is not an admission that the publication serves as prior art with respect to any of the claims presented
10 herein. The Background section is presented for purposes of clarity and is not meant as a description of prior art with respect to any claim.

[0060] Referring to FIG. 1, in certain embodiments, a static contact angle θ between a liquid and solid is defined as the angle formed by a liquid drop 12 on a solid surface 14 as measured between a tangent at the contact line, where the three phases – solid, liquid, and vapor – meet,
15 and the horizontal. The term “contact angle” usually implies the *static* contact angle θ since the liquid is merely resting on the solid without any movement.

[0061] As used herein, dynamic contact angle θ_d is a contact angle made by a *moving* liquid 16 on a solid surface 18. The dynamic contact angle θ_d may exist during either advancing or receding movement, as shown in FIG. 2.

20 [0062] In certain embodiments, an intrinsically hydrophobic material (i.e., a material having an intrinsic contact angle with water of at least 90 degrees) exhibits superhydrophobic properties (e.g., a static contact angle with water of at least 120 degrees and a contact angle hysteresis of less than 30 degrees) when it includes a surface texture (e.g., micro-scale or nano-scale). For superhydrophobicity, typically nano-scale surface textures (e.g., pores and/or posts)
25 are preferred.

[0063] As used herein, an intrinsic contact angle is a static contact angle formed between a liquid and a perfectly flat, ideal surface. This angle is typically measured with a goniometer. The following publications, which are hereby incorporated by reference herein in their entireties, describe additional methods for measuring the intrinsic contact angle: C. Allain, D. Aussere, and F. Rondelez, *J. Colloid Interface Sci.*, 107, 5 (1985); R. Fondecave, and F. Brochard-Wyart, *Macromolecules*, 31, 9305 (1998); and A. W. Adamson, *Physical Chemistry of Surfaces* (New York: John Wiley & Sons, 1976).

30

[0064] As used herein, “multiple-scale surface roughness” is understood to mean physical surface features with two or more characteristic lengths that differ by at least a factor of ten. For example, a surface having multiple-scale surface roughness may include nanoscale and microscale pores and/or protrusions. In certain embodiments, the multiple-scale surface roughness features are produced using mechanical abrasion, self-assembly (e.g., layer by layer assembly or electric field assisted assembly) of nanoparticles, growth or deposition of nanostructures (e.g., carbon nanotubes), and/or lithography.

[0065] As used herein, “rare earth element material” is understood to mean a material with at least one component that contains (or is) a rare earth element material. For example, a rare earth element material may contain or be a compound with a rare earth element chemical symbol in its chemical formula.

[0066] In certain embodiments, hydrophobic or superhydrophobic materials are achieved through the use of a rare earth element material. In one embodiment, the rare earth element material includes any material having at least one rare earth element. The rare earth element may include, for example, scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and/or lutetium (Lu). In some embodiments, the rare earth element material comprises an elemental form of one or more rare earth elements. In certain embodiments, the rare earth element material includes one or more rare earth compounds.

[0067] In various embodiments, the rare earth element material includes or consists of a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and/or a rare earth boride. For example, in one embodiment, the rare earth oxide includes scandium oxide (Sc_2O_3), yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), cerium oxide (CeO_2), praseodymium oxide (Pr_6O_{11}), neodymium oxide (Nd_2O_3), samarium oxide (Sm_2O_3), europium oxide (Eu_2O_3), gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide (Ho_2O_3), erbium oxide (Er_2O_3), thulium oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and/or lutetium oxide (Lu_2O_3). Likewise, the rare earth carbide may include cerium carbide (CeC_2), praseodymium carbide (PrC_2), neodymium carbide (NdC_2), samarium carbide (SmC_2), europium carbide (EuC_2), gadolinium carbide (GdC_2), terbium carbide (TbC_2), dysprosium carbide (DyC_2), holmium carbide (HoC_2), erbium carbide (ErC_2), thulium carbide (TmC_2), ytterbium carbide (YbC_2), and/or lutetium carbide (LuC_2). Possible rare earth nitrides include

cerium nitride (CeN), praseodymium nitride (PrN), neodymium nitride (NdN), samarium nitride (SmN), europium nitride (EuN), gadolinium nitride (GdN), terbium nitride (TbN), dysprosium nitride (DyN), holmium nitride (HoN), erbium nitride (ErN), thulium nitride (TmN), ytterbium nitride (YbN), and/or lutetium nitride (LuN). Examples of rare earth

fluorides include cerium fluoride (CeF₃), praseodymium fluoride (PrF₃), neodymium fluoride (NdF₃), samarium fluoride (SmF₃), europium fluoride (EuF₃), gadolinium fluoride (GdF₃), terbium fluoride (TbF₃), dysprosium fluoride (DyF₃), holmium fluoride (HoF₃), erbium fluoride (ErF₃), thulium fluoride (TmF₃), ytterbium fluoride (YbF₃), and/or lutetium fluoride (LuF₃).

[0068] In certain embodiments, the rare earth element material includes a light rare earth element having an atomic number less than or equal to 63 and/or a heavy rare earth element having an atomic number greater than 63. With respect to rare earth oxides, for example, a light rare earth oxide may include scandium oxide (Sc₂O₃), yttrium oxide (Y₂O₃), lanthanum oxide (La₂O₃), cerium oxide (CeO₂), praseodymium oxide (Pr₆O₁₁), neodymium oxide (Nd₂O₃), samarium oxide (Sm₂O₃), and/or europium oxide (Eu₂O₃). Likewise, in certain embodiments, a heavy rare earth oxide includes gadolinium oxide (Gd₂O₃), terbium oxide (Tb₄O₇), dysprosium oxide (Dy₂O₃), holmium oxide (Ho₂O₃), erbium oxide (Er₂O₃), thulium oxide (Tm₂O₃), ytterbium oxide (Yb₂O₃), and/or lutetium oxide (Lu₂O₃).

[0069] In certain embodiments, the rare earth element material includes any possible combination of two or more rare earth element materials. For example, the rare earth element material may include a first rare earth oxide, a first rare earth carbide, a first rare earth nitride, a first rare earth fluoride, and/or a first rare earth boride combined with a second rare earth oxide, a second rare earth carbide, a second rare earth nitride, a second rare earth fluoride, and/or a second rare earth boride. As another example, the rare earth element material may include two or more rare earth oxides, two or more rare earth carbides, two or more rare earth nitrides, two or more rare earth fluorides, and/or two or more rare earth borides.

[0070] In certain embodiments, a chemical formula for the rare earth element material is RΦ_x, where R represents one or more rare earth elements in any molar ratio, Φ represents oxygen, carbon, nitrogen, fluorine, boron, or combinations thereof, in any molar ratio, and x is a number of atoms in the material or compound. Depending on the composition of the rare earth element material, x may or may not be an integer.

[0071] In various embodiments, the hydrophobic material includes a rare earth element material combined with a non-rare earth element material (i.e., a material that does not include

a rare earth element). For example, the rare earth element material (e.g., a rare earth oxide) may be combined with one or more metals or ceramics, including a metal oxide, a metal nitride, a metal carbide, a metal fluoride, and/or a metal boride.

[0072] Referring to FIG. 3, in certain embodiments, a hydrophobic material 300 includes a coating 302 and a base substrate 304. The coating 302 includes or consists of one or more rare earth element materials, such as one or more rare earth oxides. A thickness T of the coating may be, for example, from about 100 nm to about 300 nm. The base substrate 304 includes a metal, a ceramic, and/or a polymer. For example, the base substrate 304 may include a metal and/or a transition metal and/or their alloys, e.g., aluminum, copper, titanium, and/or steel. The base substrate 304 may include, for example, a ceramic such as a metal oxide, a metal carbide, and/or a metal nitride. Examples of ceramic materials include aluminum oxide, aluminum nitride, boron oxide, boron nitride, boron carbide, titanium oxide, titanium nitride, and/or titanium carbide. A method of producing the hydrophobic material includes providing the base substrate 304 and applying the coating onto the base substrate 304 using, for example, sputtering, sintering, and/or spraying. In some embodiments, an adhesion or bonding layer is disposed between the coating 302 and the base substrate 304. The bonding layer may provide improved adhesion between the coating 302 and the base substrate 304. The bonding or adhesion layer may include, for example, a metal, an intermetallic, an alloy, and/or a ceramic. Specific examples include indium (In), titanium (Ti), titanium nitride (TiN), chromium nitride (CrN), nickel aluminide (e.g., NiAl), MCrAlY, platinum, nickel, and/or aluminum.

[0073] Referring to FIG. 4, in certain embodiments, a hydrophobic material 400 includes a coating 402 and a base substrate 404 that each contain a rare earth element material (e.g., a rare earth oxide), although the concentration of rare earth element material is higher in the coating 402 than in the base substrate 404. For example, the coating 402 may include a weight percent of the rare earth element material that is about an order of magnitude greater than the weight percent of the rare earth element material in the base substrate 404. In various embodiments, the weight percent of rare earth element material in the coating 402 is at least about 10 percent, at least about 25 percent, or at least about 50 percent. A thickness of the coating 402 may be, for example, from about 100 nm to about 500 nm.

[0074] The base substrate 404 may include, for example, a ceramic, such as a metal oxide, a metal carbide, and/or a metal nitride. Specific examples of ceramics include aluminum oxide, aluminum nitride, boron oxide, boron nitride, boron carbide, titanium oxide, titanium nitride,

- 14 -

and titanium carbide. In various embodiments, a weight percentage of rare earth element material (e.g., rare earth oxide) in the base substrate 404 is less than about 1 percent, less than about 10 percent, or less than about 25 percent. A weight percentage of the rare earth element material in the base substrate 404 may be substantially uniform, or the weight percentage may
5 be higher near the coating 402 than away from the coating 402.

[0075] A method of forming the base substrate 404 and the coating 402 includes exposing the material components (e.g., the rare earth element material and a ceramic) to high temperatures (e.g., from about 1200 °C to about 1600 °C) in a furnace, under atmospheric pressures. Under these conditions, the molecules of the rare earth element material (e.g., a rare earth oxide)
10 migrate toward the surface of the material and accumulate to form the coating 402. At the same time, the ceramic material moves away from the surface to form the base substrate 404. To facilitate the desired migration of rare earth element material and ceramic, a binder or promoter (e.g., polyvinyl alcohol and/or polystyrene) may be added to the material components before they are placed in the furnace.

[0076] Referring to FIG. 5, in certain embodiments, a hydrophobic material 500 includes a bulk material 502 that is impregnated or doped with a rare earth element material, such as a rare earth oxide 504. In one embodiment, the hydrophobic material 500 includes at least about 10 percent, at least about 25 percent, or at least about 50 percent rare earth element material, by weight. For example, the weight percentage of rare earth element material in the hydrophobic
20 material 500 may be from about 10 percent to about 25 percent, from about 25 percent to about 50 percent, from about 50 percent to about 75 percent, or from about 75 percent to about 99 percent.

[0077] The bulk material 502 includes a metal, a ceramic, and/or a polymer. For example, the bulk material 502 may include a metal and/or a transition metal and/or their alloys, e.g.,
25 aluminum, copper, titanium, and/or steel. The bulk material 502 may include, for example, a ceramic such as a metal oxide, a metal carbide, and/or a metal nitride. Examples of ceramic materials include aluminum oxide, aluminum nitride, boron oxide, boron nitride, boron carbide, titanium oxide, titanium nitride, and/or titanium carbide. In certain embodiments, the bulk material 502 is a coating. For example, the bulk material 502 with the doped rare earth element
30 material may be coated onto a ceramic, metallic, or polymeric substrate, such as a tube, a block, or a turbine blade.

[0078] Typically, in its impregnated or doped form, the rare earth element material (e.g., a rare earth oxide) is distributed within the bulk material 502 as individual molecules.

Alternatively, the rare earth element material may be dispersed within the bulk material 502 as small micro or nano-sized particles. In certain embodiments, the rare earth element material
5 reacts with another compound (e.g., a ceramic compound) in the bulk material 502 to form a new compound. For example, lanthanum oxide (La_2O_3) may react with boron oxide (B_2O_3) to form LaBO_4 .

[0079] Referring to FIG. 6, in certain embodiments, a hydrophobic material 600 includes carbon nanotubes 602 and a coating 604 having a rare earth element material (e.g., a rare earth
10 oxide). A method 606 of producing the hydrophobic material 600 includes disposing a rare earth element material 608 (or a material doped with the rare earth element material) over the carbon nanotubes 602 and sintering the rare earth element material 608 onto the carbon nanotubes 602. The sintering may be performed in an alumina crucible and/or take place at a temperature from about 1200 °C to about 1600 °C. In alternative embodiments, the coating 604
15 is produced by spraying or sputtering. Due to surface textures in the resulting hydrophobic material 600, the hydrophobic material 600 with the carbon nanotubes 602 may exhibit superhydrophobic qualities.

[0080] In certain embodiments, a rare earth element material is formed by dry pressing a powder of the rare earth element material to form a pressed rare earth element material (e.g., a
20 pressed rare earth oxide). The pressing may occur, for example, at a pressure between 30,000 and 50,000 tsi (tons/in²) (e.g., in a cylindrical steel press mold), without use of any binding agents or additives. The pressed rare earth element material may then be sintered (e.g., inside a tube furnace under argon environment). The sintering temperature may be based on the melting point of the rare earth element material. For example, the sintering temperature may be
25 from about 60 percent to about 80 percent of the melting point of the rare earth element material. In one embodiment, the sintering temperature is from about 1400 °C to about 1650 °C.

[0081] In certain embodiments, an article is provided that includes one or more of the hydrophobic materials described herein. The article may have any shape or size and may be
30 used for any purpose. For example, the article may be substantially flat (e.g., a block or a plate), curved (e.g., a sphere, a cylinder, or a tube), small (e.g., a medical device), or large (e.g., an airplane wing or a wind turbine blade). In a typical embodiment, the article is used in an

- 16 -

application where a robust hydrophobic surface is desired. The article may be, for example, a steam turbine, a condenser, a heat exchanger, an aircraft, a wind turbine, a pipeline (e.g., an oil or gas pipeline), an evaporator, a boiler, a medical device or implant, and/or a separator.

[0082] The hydrophobic materials described herein offer vast industrial implications for improving efficiency and reducing overall cost and energy consumption in various industrial applications where hydrophobicity, droplet repellency, and/or dropwise condensation are desirable. The hydrophobic materials also have applications as anti-fouling and anti-icing surfaces.

[0083] For example, the hydrophobic materials described herein may be used by steam turbine manufacturers to achieve higher power outputs by reducing efficiency losses caused by water droplets, entrained in steam, impinging on turbine blades and forming liquid films. Moreover, industries that rely on condensation heat transfer may attain remarkable economic improvements by utilizing the hydrophobic materials in condensers and heat exchangers. Specific industries include power generation and water desalination. In certain applications, such industries may achieve higher heat transfer coefficients (up to one order of magnitude) by promoting dropwise condensation over filmwise condensation.

[0084] In various embodiments, the hydrophobic materials described herein are used in aircraft and/or wind turbines. For example, surface designs made using the hydrophobic materials may prevent liquid water film formation on aircraft wings and wind turbine blades, due to the superior water repellency attribute of these materials. In aircraft applications, the materials may prevent aircraft surfaces from freezing, thereby enhancing safety and improving aerodynamic performance.

[0085] The hydrophobic surfaces also have applications in industries where scaling problems are encountered. Scaling is a persistent problem in various industrial processes, including oil and gas flow through pipelines, desalination, steam generation, and hydrometallurgy. Considering the low surface free energy of the hydrophobic materials, articles that include these materials may be engineered to provide anti-fouling. Such designs not only reduce costs of chemical and thermal treatment for scale inhibition and removal, they also have implications for efficiency, lifetime enhancement, and process reliability improvement in the respective processes.

[0086] In certain embodiments, the hydrophobic materials are used in deep sea oil and gas industries. For example, the hydrophobic materials may be utilized to provide hydrate-phobic

- 17 -

surfaces that prevent hydrate-formation. Such applications may enhance flow assurance and prevent catastrophic failures in deep-sea oil and gas operations.

[0087] The hydrophobic materials may also be used in evaporators and/or boilers.

Evaporators and boilers are heat transfer devices that convert a fluid from a liquid phase to a

5 vapor phase. Similar to condensers, large inefficiencies may occur at the fluid-surface interfaces, due to the formation of vapor films and associated heat transfer resistance. In one embodiment, the hydrophobic materials are used to overcome the fundamental limitations of boiling. For example, these materials may be used in applications in which rare earth oxides act as boiling nucleation sites, thereby resulting in increased rewetting of the surface during
10 boiling and prevention of vapor film formation.

[0088] The hydrophobic materials described herein also have applications in medical devices and/or implants. For example, these materials may be used in joint replacement surgery or other types of surgery, tubing (e.g., catheters), dialysis, and any other medical application in which robust hydrophobic materials are desired.

15 **[0089]** The hydrophobic materials described herein also have applications in separation devices. In one embodiment, these materials are used to separate oil-water mixtures.

[0090] Rare earth elements have a peculiar electronic configuration, characterized by the successive addition of electrons to the inner $4f$ orbitals across the lanthanides row. Because the deep-lying $4f$ electrons are well shielded from the chemical surrounding by eight electrons of
20 the ($5s^2p^6$) outer shell, they do not take part in chemical bonding. This unique electronic structure accounts for relatively low standard atomization enthalpy and ionization potential of the rare earths, a property which makes them highly active reducing elements with comparatively low electronegativities, ranging from 1.01 (Eu) to 1.14 (Lu), similar to that of some alkali earth metals, e.g., calcium (1.04). This implies rare earths react readily with the
25 oxygen in the natural environment to form ceramic oxides (mostly sesquioxide, R_2O_3). Similar peculiarities may explain other unique properties of the rare earths and their compounds, including outstanding paramagnetic and luminescent attributes, that make them superior to other transition elements in the Periodic Table, even the actinides with a comparable $5f$ configuration.

30 **[0091]** Despite the exceptional properties and potential advantages of the rare earth oxides, the wetting properties of these materials, however, have been left unexplored due to the belief that most metal oxides are hydrophilic. The reason for such belief arises from the fact that

- 18 -

common metal oxides demonstrate significant polar component of surface free energy due to the large number of acid and base sites at their surfaces. These polar (i.e., acid and base) sites originate from unsaturated metal atoms that could accept a pair of electrons, acting as Lewis acid sites, and oxygen atoms, capable of donating a pair of electrons and acting as Lewis base sites, when in contact with wetting liquids.

[0092] It has been shown through molecular dynamics (MD) simulations that the surface chemistry and surface polarity are likely in direct correspondence with the orientation of water molecules at the interface, and therefore each defines the hydrophobicity or hydrophilicity of the surface. In the case of common metal oxides such as Al_2O_3 , polar component of surface free energy becomes significant due to the large number of acid and base sites at their surfaces. These polar sites may accept a pair of electrons, acting as Lewis acid sites, or donate a pair of electrons and acting as Lewis base sites, when in contact with wetting liquids.

[0093] A schematic demonstration of the orientation of a water molecule 700 next to an alumina hydrophilic surface 702 is presented in FIG. 7. Aluminum atoms 704 at the surface 702 are electron deficient, with six electrons in their three " sp^2 hybrid" orbitals. Therefore, to achieve a full octet of electrons, the aluminum atoms 704 strive to accept a pair of electrons from the water molecules 700 next to the surface. Such a tendency forces the water molecules 700 at the surface 702 to be oriented in such a way that they have three hydrogen bond (HB) vectors pointing towards the surface. Two of these vectors are associated with electron pairs and the other is associated with one of the OH bonds. The fourth HB vector, which is associated with the other OH bond, is pointing preferentially outward from the surface 702 to the bulk. The depicted water molecule orientation is consistent with results of MD simulations for hydrophilic surfaces.

[0094] In the case of rare earth element materials (e.g., rare earth oxides), however, metal atoms have a different chemistry than that of aluminum atoms. In rare earth elements, electrons are being added into the inner $4f$ orbitals, which are shielded by eight electrons of the $(5s^2p^6)$ outer shell. Therefore, contrary to aluminum atoms, the valence band of rare earth elements has a full octet of electrons, and the empty orbitals, if any, are not accessible to the surrounding environment. Accordingly, it is presently believed rare earth elements have no tendency to either accept or donate electron pairs when in contact with wetting liquids. As a result, unlike other oxide ceramics, rare earth oxides are herein found to be hydrophobic.

- 19 -

[0095] Referring to FIG. 8, and without wishing to be bound by any particular theory, it is thought that water molecules 800 in contact with a surface 802 of a rare earth element material (e.g., a rare earth oxide) orientate themselves in such a way that they have one HB vector, associated with an OH bond, preferentially pointing toward the surface. The remaining three
5 HB vectors preferentially point outward from the surface, thus forming hydrogen bonds with other water molecules in the bulk. Since the $4f$ orbitals 804 of rare earths are completely shielded by the octet electrons of the outer ($5s^2p^6$) orbitals 806, they have no tendency to accept or donate pairs of electrons when in contact with water molecules. In various embodiments, additional atoms 808 in the rare earth element material may include oxygen, carbon, nitrogen,
10 fluorine, and/or boron, depending on whether the rare earth element material includes a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and/or a rare earth boride, respectively.

EXAMPLES

[0096] Hydrophobic surfaces were produced by forming a thin coating (between about 200
15 nm and 350 nm) of a ceramic material containing a rare earth oxide onto both smooth and textured substrates. Wetting measurements indicated that advancing water contact angles of these surfaces ranged from 115° for smooth to 160° for textured substrates. These contact angles are well beyond the water contact angles obtained with common metal oxides, such as alumina (Al_2O_3) and silica (SiO_2), which have water contact angles of about $25-30^\circ$ and about
20 $15-20^\circ$, respectively. FIGS. 9 through 12 depict water droplets 900 resting on the alumina surface 902, the silica surface 1000, the smooth hydrophobic surface 1100, and the textured hydrophobic surface 1200.

[0097] As discussed in more detail below, systematic water droplet impingement, water condensation, and thermal stability experiments were performed to characterize the
25 performance of the hydrophobic materials containing a rare earth oxide, described herein. Results from these experiments show the following: (1) the hydrophobic materials are capable of repelling water droplets even when they are deposited on smooth substrates; (2) the hydrophobic materials promote dropwise water condensation with remarkably improved heat transfer coefficients, when tested inside a condensation chamber under simulated industrial
30 conditions; and (3) the nonwetting properties of the hydrophobic materials remained unchanged when the hydrophobic materials were heated to $400^\circ C$ for two hours and then cooled down to room temperature. By comparison, other hydrophobic surfaces, such as a surface coated with

- 20 -

flourosilane (FOS), a common hydrophobic surface modifier, did not retain the hydrophobic properties under these conditions.

[0098] To assess the hydrophobic properties of the rare earth oxide materials described herein, ceramics of oxide powders were synthesized for all the rare earth elements across the lanthanides row, except for promethium oxide because of its radioactive properties. To produce the rare earth oxide ceramics, rare earth oxide powders were dry pressed at a pressure between 30,000 and 50,000 tsi (tons per square inch) in a cylindrical steel press mold, without use of any binding agents or additives. After pressing, the materials were sintered inside a tube furnace under an argon environment. The sintering temperature for each rare earth ceramic was different and estimated based on its melting point (i.e., between 60% and 80% of the melting point of each rare earth oxide). Accordingly, sintering temperatures were from about 1400 °C to about 1650°C in this work. Photographs of sintered ceramics 1300 are depicted in FIG. 13.

[0099] After synthesizing the rare earth oxide ceramic materials, the wetting properties and total surface free energies were quantified through systematic contact angle measurements on the materials using the following three liquids: diiodomethane (DIM), ethylene glycol (EG), and water. These three well-characterized liquids formed the basis of surface free energy calculations utilizing the van Oss-Good-Chaudhury approach. To determine the relationship between the surface polarity and the nonwetting properties of the rare earth oxides, the apolar and polar components of total surface free energy were assessed. The magnitude of the apolar surface free energy was calculated based on measured contact angle data of the apolar liquid, diiodomethane (DIM), and Lifshitz-van der Waals analysis. The polar component, however, was calculated using the contact angle data of polar liquids, i.e., water and ethylene glycol (EG), and simultaneously solving the modified Young equation. Calculation results revealed that the polar component of surface free energy for all the rare earth oxide materials was negligible. This suggests that the surface of these ceramic oxides, contrary to common hydrophilic oxides, have fewer Lewis acid and base sites. Furthermore, results showed no significant variations in the calculated surface free energy of the ceramics across the lanthanides row, which suggests that these ceramics have comparable wetting properties.

While not wishing to be bound by any particular theory, the reason for such observation may be attributed to the unique electronic configuration of these materials. For example, the chemical significance of electron addition into inner $4f$ orbitals that are shielded by overlying $5s^2p^6$

electrons may be so slight that it results in remarkable similarities between the rare earth oxide wetting materials.

[0100] Measured contact angles and surface energies (i.e., calculated total surface free energy and calculated apolar and polar components) for the rare earth oxide materials are illustrated in FIGS. 14 and 15, respectively. As is clear, the intrinsic water contact angle of all test substrates lies between 105° and 115° , which is well beyond the water contact angle of common metal oxides. For example, alumina and silica have water contact angles of about 30° and 20° , respectively. The results in these figures show that the rare earth oxide materials are hydrophobic.

[0101] To illustrate potential advantages of the new hydrophobic rare earth oxide materials, described herein, systematic water impingement and water condensation experiments were conducted on surfaces having a thin layer (e.g., layer thickness from about 200 nm to about 350 nm) of a representative rare earth oxide (for example cerium oxide) sputtered on smooth silicon wafers as well as silicon nanoglass posts.

[0102] Referring to FIG. 16, silicon nanoglass posts 1600 were arranged in square arrays with a width a of about $10\text{ }\mu\text{m}$, a height h of about $10\text{ }\mu\text{m}$, and a spacing b from about $5\text{ }\mu\text{m}$ to about $30\text{ }\mu\text{m}$. To grow the nanoglass, posts were placed inside an inductively coupled plasma chamber with a controlled flow of etching gases (i.e., SF_6/O_2). The average width of the grass wires was about 100 nm with spacing of about 100 nm to about 200 nm. The nanoglass posts 1600 were then modified for superhydrophobicity with a thin layer of a rare earth oxide through sputtering.

[0103] Referring to FIG. 17, wetting measurements of the nanoglass posts coated with about 300 nm of cerium oxide (ceria) indicated that water droplets 1700 are in a Cassie state. Advancing and receding water contact angles were measured to be 160° and 155° , respectively.

[0104] The dynamics of the impingement of water droplets 1800 on the ceria-coated smooth and nanoglass post surfaces is depicted in the images of FIGS. 18 and 19, respectively. Water droplet impingement velocity was about 1.2 m/s for the ceria-coated smooth surface (FIG. 18) and about 1.6 m/s for the ceria-coated nanoglass post surface (FIG. 19). The results show that both surfaces repelled the water droplets 1800 after impingement. The results were impressive in the sense that water repellency was observed even on smooth ceria-coated surfaces, indicating that this ceramic is intrinsically hydrophobic. Moreover, ceria-coated nanoglass

- 22 -

silicon posts were capable of repulsing water droplets with relatively high impact velocities (e.g., about 3.7 m/s).

[0105] To further demonstrate the industrial implications of the ceramic materials developed herein, systematic water condensation experiments were conducted inside a controlled vacuum condensation chamber, which replicated the condition of a typical industrial condenser. The condensation chamber enabled direct measurement of the heat flux over a wide range of experimental conditions that were analogous to those of real industrial condensers.

[0106] For the condensation experiments, hydrophobic test surfaces were fabricated by depositing a thin layer of a representative rare earth oxide on smooth silicon wafers. The rare earth oxides used for the experiment were cerium oxide and erbium oxide. To establish a benchmark, water condensation experiments were also performed on a hydrophilic silicon wafer as well as a hydrophobic silicon wafer that was modified with a thin coating of (1H,1H,2H,2H-fluorooctyl triethoxysilane) fluorosilane (FOS) through vapor phase deposition.

[0107] In these experiments, after clamping the wafer to an instrumented copper cooling block within the condensation chamber, saturated steam at a pressure of 75 kPa and a temperature of 92 °C was generated by a 20 kW electric boiler. A water-cooled heat exchanger provided 20 kW of cooling power to the test surface. The heat flux was measured by calculating the temperature gradient along the copper cooling block, and the departing drop sizes were measured from images obtained with a high-resolution video camera. Heat flux was measured for each substrate during the experiment.

[0108] Snapshot images of the dynamics of condensate formation and shedding from test substrates are shown in FIGS. 20 through 23. Referring to FIG. 20, in the case of a bare silicon substrate 2000, which is analogous to other hydrophilic surfaces, filmwise condensation was observed. Specifically, a continuous liquid film formed on the silicon substrate 2000, which led to a significant heat transfer resistance between the steam and the surface, and a subsequent decrease in the measured heat flux, as depicted in the plot of FIG. 24.

[0109] Referring to FIGS. 21 through 23, contrary to the filmwise condensation properties of bare silicon, dropwise condensation was observed on a hydrophobic FOS-coated silicon surface 2100 (FIG. 21), a cerium oxide surface 2200 (FIG. 22), and an erbium oxide surface 2300 (FIG. 23). In terms of measured heat flux, however, the rare earth oxide coatings outperformed the state-of-the-art fluorosilane (FOS), which is a common material for surface

- 23 -

modifications. As depicted in FIG. 24, the higher heat flux obtained with the rare earth oxide coatings could result in considerably enhanced heat transfer rates in condensation applications. **[0110]** To further demonstrate the robustness of the rare earth oxide materials described herein, the thermal stability of these materials was examined by placing the sintered materials inside a box furnace and heating to 400 °C for 2 hours and then cooling to room temperature. To establish a baseline, a hydrophobic surface consisting of silicon substrates modified with a layer of (1H,1H,2H,2H-fluorooctyl triethoxysilane) fluorosilane (FOS) polymers was also tested under similar conditions. FIG. 25 includes a photograph of water droplets 2500 on a sintered cerium oxide surface 2502 and a fluorosilanized silicon surface 2504 before heating to 400 °C for 2 hours. FIGS. 26 and 27 include photographs of water droplets 2500 on these surfaces 2502, 2504 after heating to 400 °C for 2 hours. As indicated by the water droplets 2500 on these surfaces 2502, 2504 in these figures, although both surfaces 2502, 2504 demonstrated hydrophobic attributes before the test, the sintered rare earth oxide tablet was the only material to possess hydrophobic attributes after the test (i.e., after heating in the furnace). Because FOS is not thermally stable at such high temperature, the FOS sample showed hydrophilic behavior after the test. This experiment further demonstrates that rare earth oxide materials are not only intrinsically hydrophobic, but they are capable of withstanding harsh industrial environments.

[0111] The results of the contact angle, water impingement, thermal stability, and condensation experiments, described above, show that the rare earth oxide materials are intrinsically hydrophobic and robust. In addition to conformal coating, in certain embodiments, the rare earth oxides (or other rare earth element materials) are incorporated into other engineered materials and structures to achieve enhanced attributes. Examples include ceramics doped with rare earth oxides, metals doped with rare earths oxides, and polymer composites having rare earth oxides. Moreover, doping a rare earth oxide with another rare earth oxide may result in improved properties. For example, in one embodiment, a light rare earth oxide (e.g., ceria) is doped with a heavy rare earth oxide (e.g., gadolinium oxide).

- 24 -

Equivalents

[0112] While the invention has been particularly shown and described with reference to specific preferred embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

[0113] What is claimed is :

1 1. An article comprising:

2 a base substrate; and

3 a hydrophobic coating on the base substrate, the hydrophobic coating comprising a rare
4 earth element material, wherein an exposed surface of the hydrophobic coating has a dynamic
5 contact angle with water of at least about 90 degrees.

1 2. An article comprising a rare earth element material, wherein an exposed surface of the
2 article has a dynamic contact angle with water of at least about 90 degrees.

1 3. The article of claim 1 or 2, wherein the rare earth element material comprises at least
2 one member selected from the group consisting of a rare earth oxide, a rare earth carbide, a rare
3 earth nitride, a rare earth fluoride, and a rare earth boride.

1 4. The article of any one of the preceding claims, wherein the rare earth element material
2 comprises a combination of one or more species within one or more of the following categories
3 of compounds: a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride,
4 and a rare earth boride.

1 5. The article of any one of the preceding claims, wherein the rare earth element material
2 comprises a rare earth oxide.

1 6. The article of any one of the preceding claims, further comprising at least one of a metal
2 and a ceramic.

1 7. The article of claim 1, wherein a thickness of the coating is from about 100 nm to about
2 300 nm.

1 8. The article of any one of the preceding claims, wherein the exposed surface comprises a
2 textured surface.

1 9. The article of claim 8, wherein the textured surface comprises multiple-scale surface
2 roughness.

1 10. The article of claim 1, wherein the coating comprises at least one of a ceramic, a metal,
2 and a polymer.

1 11. The article of claim 1 or claim 10, wherein the coating is doped with the rare earth
2 element material.

1 12. The article of any one of the preceding claims, wherein the rare earth element material
2 comprises a first rare earth oxide doped with a second rare earth oxide.

1 13. The article of claim 12, wherein the first rare earth oxide is a light rare earth oxide and
2 the second rare earth oxide is a heavy rare earth oxide.

1 14. The article of claim 13, wherein the heavy rare earth oxide comprises at least one
2 member selected from the group consisting of gadolinium oxide (Gd_2O_3), terbium oxide
3 (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide (Ho_2O_3), erbium oxide (Er_2O_3), thulium
4 oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and lutetium oxide (Lu_2O_3).

1 15. The article of claim 13, wherein the light rare earth oxide is cerium oxide (CeO_2) and
2 the heavy rare earth oxide is gadolinium oxide (Gd_2O_3).

1 16. The article of any one of the preceding claims, wherein the rare earth element material
2 comprises at least one member selected from the group consisting of scandium (Sc), yttrium
3 (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm),
4 europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er),
5 thulium (Tm), ytterbium (Yb), and lutetium (Lu).

1 17. The article of any one of the preceding claims, wherein the rare earth element material
2 comprises at least one member selected from the group consisting of scandium oxide (Sc_2O_3),
3 yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), cerium oxide (CeO_2), praseodymium oxide
4 (Pr_6O_{11}), neodymium oxide (Nd_2O_3), samarium oxide (Sm_2O_3), europium oxide (Eu_2O_3),
5 gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide
6 (Ho_2O_3), erbium oxide (Er_2O_3), thulium oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and lutetium
7 oxide (Lu_2O_3).

1 18. The article of any one of the preceding claims, wherein the rare earth element material
2 comprises at least one member selected from the group consisting of cerium carbide (CeC_2),
3 praseodymium carbide (PrC_2), neodymium carbide (NdC_2), samarium carbide (SmC_2),
4 europium carbide (EuC_2), gadolinium carbide (GdC_2), terbium carbide (TbC_2), dysprosium
5 carbide (DyC_2), holmium carbide (HoC_2), erbium carbide (ErC_2), thulium carbide (TmC_2),
6 ytterbium carbide (YbC_2), and lutetium carbide (LuC_2).

1 19. The article of any one of the preceding claims, wherein the rare earth element material
2 comprises at least one member selected from the group consisting of cerium nitride (CeN),
3 praseodymium nitride (PrN), neodymium nitride (NdN), samarium nitride (SmN), europium
4 nitride (EuN), gadolinium nitride (GdN), terbium nitride (TbN), dysprosium nitride (DyN),
5 holmium nitride (HoN), erbium nitride (ErN), thulium nitride (TmN), ytterbium nitride (YbN),
6 and lutetium nitride (LuN).

20. The article of any one of the preceding claims, wherein the rare earth element material comprises at least one member selected from the group consisting of cerium fluoride (CeF_3), praseodymium fluoride (PrF_3), neodymium fluoride (NdF_3), samarium fluoride (SmF_3), europium fluoride (EuF_3), gadolinium fluoride (GdF_3), terbium fluoride (TbF_3), dysprosium fluoride (DyF_3), holmium fluoride (HoF_3), erbium fluoride (ErF_3), thulium fluoride (TmF_3), ytterbium fluoride (YbF_3), and lutetium fluoride (LuF_3).

21. The article of any one of the preceding claims, wherein the article is at least one member selected from the group consisting of a steam turbine, a condenser, a heat exchanger, an aircraft, a wind turbine, a pipeline, an evaporator, a boiler, a medical device, a medical implant, and a separator.

22. An article comprising a bulk material doped with a rare earth element material, wherein an exposed surface of the bulk material has a dynamic contact angle with water of at least about 90 degrees.

23. The article of claim 22, wherein the rare earth element material comprises at least one member selected from the group consisting of a rare earth oxide, a rare earth carbide, a rare earth nitride, a rare earth fluoride, and a rare earth boride.

24. The article of claim 22 or 23, wherein the bulk material comprises a ceramic.

25. The article of claim 24, wherein the ceramic comprises at least one of a metal oxide, a metal carbide, and a metal nitride.

26. The article of claim 24 or 25, wherein the ceramic comprises at least one of aluminum oxide, aluminum nitride, boron oxide, boron nitride, boron carbide, titanium oxide, titanium nitride, and titanium carbide.

27. The article of any one of claims 22 to 26, wherein the bulk material is a light rare earth oxide doped with a heavy rare earth oxide.

28. The article of any one of claims 22 to 27, wherein the bulk material is cerium oxide (CeO_2) and the rare earth element material comprises at least one member selected from the group consisting of gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide (Ho_2O_3), erbium oxide (Er_2O_3), thulium oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and lutetium oxide (Lu_2O_3).

29. The article of any one of claims 22 to 28, wherein the rare earth element material comprises at least one member selected from the group consisting of scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm),

europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu).

30. The article of any one of claims 22 to 29, wherein the rare earth element material comprises at least one member selected from the group consisting of scandium oxide (Sc_2O_3), yttrium oxide (Y_2O_3), lanthanum oxide (La_2O_3), cerium oxide (CeO_2), praseodymium oxide (Pr_6O_{11}), neodymium oxide (Nd_2O_3), samarium oxide (Sm_2O_3), europium oxide (Eu_2O_3), gadolinium oxide (Gd_2O_3), terbium oxide (Tb_4O_7), dysprosium oxide (Dy_2O_3), holmium oxide (Ho_2O_3), erbium oxide (Er_2O_3), thulium oxide (Tm_2O_3), ytterbium oxide (Yb_2O_3), and lutetium oxide (Lu_2O_3).

31. The article of any one of claims 22 to 30, wherein the rare earth element material comprises at least one member selected from the group consisting of cerium carbide (CeC_2), praseodymium carbide (PrC_2), neodymium carbide (NdC_2), samarium carbide (SmC_2), europium carbide (EuC_2), gadolinium carbide (GdC_2), terbium carbide (TbC_2), dysprosium carbide (DyC_2), holmium carbide (HoC_2), erbium carbide (ErC_2), thulium carbide (TmC_2), ytterbium carbide (YbC_2), and lutetium carbide (LuC_2).

32. The article of any one of claims 22 to 31, wherein the rare earth element material comprises at least one member selected from the group consisting of cerium nitride (CeN), praseodymium nitride (PrN), neodymium nitride (NdN), samarium nitride (SmN), europium nitride (EuN), gadolinium nitride (GdN), terbium nitride (TbN), dysprosium nitride (DyN), holmium nitride (HoN), erbium nitride (ErN), thulium nitride (TmN), ytterbium nitride (YbN), and lutetium nitride (LuN).

33. The article of any one of claims 22 to 32, wherein the rare earth element material comprises at least one member selected from the group consisting of cerium fluoride (CeF_3), praseodymium fluoride (PrF_3), neodymium fluoride (NdF_3), samarium fluoride (SmF_3), europium fluoride (EuF_3), gadolinium fluoride (GdF_3), terbium fluoride (TbF_3), dysprosium fluoride (DyF_3), holmium fluoride (HoF_3), erbium fluoride (ErF_3), thulium fluoride (TmF_3), ytterbium fluoride (YbF_3), and lutetium fluoride (LuF_3).

34. The article of any one of claims 22 to 33, wherein the article is at least one member selected from the group consisting of a steam turbine, a condenser, a heat exchanger, an aircraft, a wind turbine, a pipeline, an evaporator, a boiler, a medical device, a medical implant, and a separator.

1 35. The article of any one of claims 22 to 34, wherein the bulk material contains at least
2 about 10 weight percent rare earth element material.

1 36. The article of any one of claims 22 to 34, wherein the bulk material contains at least
2 about 25 weight percent rare earth element material.

1 37. An article comprising:

2 a textured surface; and

3 a hydrophobic coating on the textured surface, the hydrophobic coating comprising a
4 rare earth element material, wherein an exposed surface of the hydrophobic coating has a
5 dynamic contact angle with water of at least about 90 degrees.

1 38. The article of claim 37, wherein the rare earth element material comprises at least one
2 member selected from the group consisting of a rare earth oxide, a rare earth carbide, a rare
3 earth nitride, a rare earth fluoride, and a rare earth boride.

1 39. The article of claim 37 or 38, wherein the coating is doped with the rare earth element
2 material.

1 40. The article of any one of claims 37 to 39, wherein the article is at least one member
2 selected from the group consisting of a steam turbine, a condenser, a heat exchanger, an
3 aircraft, a wind turbine, a pipeline, an evaporator, a boiler, a medical device, a medical implant,
4 and a separator.

1 41. A method of manufacturing a hydrophobic article, the method comprising:

2 providing a ceramic material and a rare earth element material; and

3 heating the ceramic material and the rare earth element material to a temperature of at
4 least about 1600 °C, thereby forming a hydrophobic coating having a dynamic contact angle
5 with water of at least about 90 degrees.

1 42. The method of claim 41, wherein the rare earth element material comprises at least one
2 member selected from the group consisting of a rare earth oxide, a rare earth carbide, a rare
3 earth nitride, a rare earth fluoride, and a rare earth boride.

1 43. The method of claim 41 or 42, comprising the step of adding at least one of a binder and
2 a promoter to the ceramic material and the rare earth element material.

- 30 -

- 1 44. A method of manufacturing a hydrophobic article, the method comprising:
2 providing a powder comprising a rare earth element material;
3 pressing the powder at a pressure greater than 30,000 tsi (tons per square inch) to form a
4 pressed rare earth element material; and
5 sintering the pressed rare earth element material in an argon environment.
- 1 45. The article of claim 44, wherein the rare earth element material comprises at least one
2 member selected from the group consisting of a rare earth oxide, a rare earth carbide, a rare
3 earth nitride, a rare earth fluoride, and a rare earth boride.
- 1 46. A method of manufacturing a hydrophobic article, the method comprising:
2 providing a base substrate; and
3 forming a coating on the base substrate, the coating comprising a rare earth element
4 material.
- 1 47. The article of claim 46, wherein the rare earth element material comprises at least one
2 member selected from the group consisting of a rare earth oxide, a rare earth carbide, a rare
3 earth nitride, a rare earth fluoride, and a rare earth boride.
- 4 48. The method of claim 46 or 47, wherein the forming step comprises sputtering.
- 5 49. The method of claim 46 or 47, wherein the forming step comprises sintering.

1/13

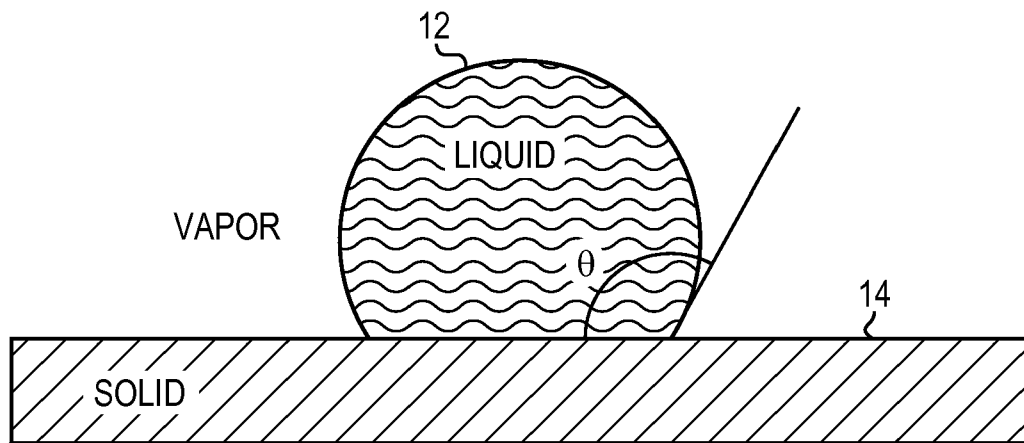


FIG. 1

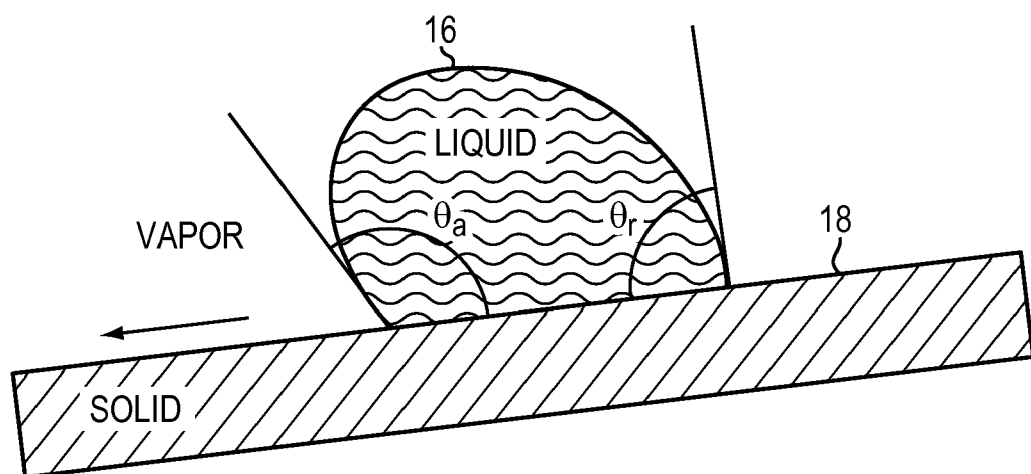


FIG. 2

2/13

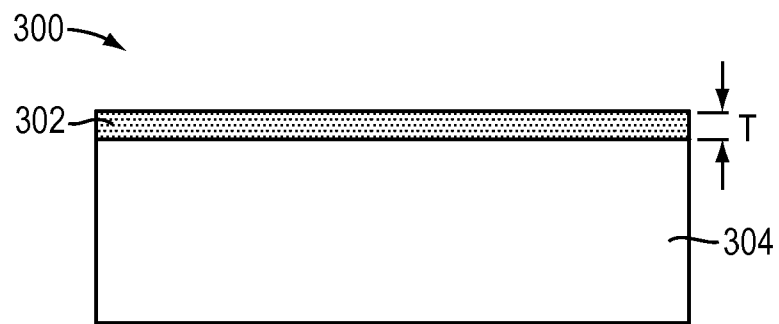


FIG. 3

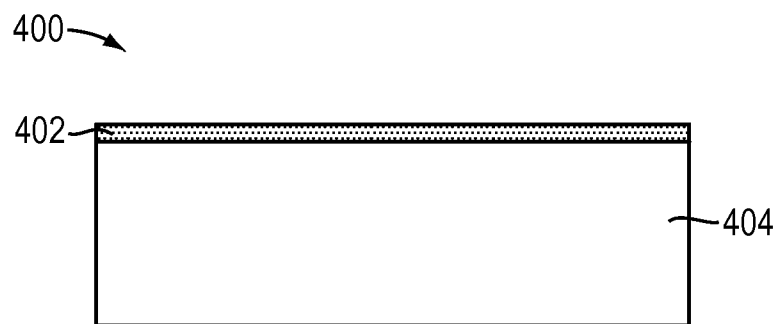


FIG. 4

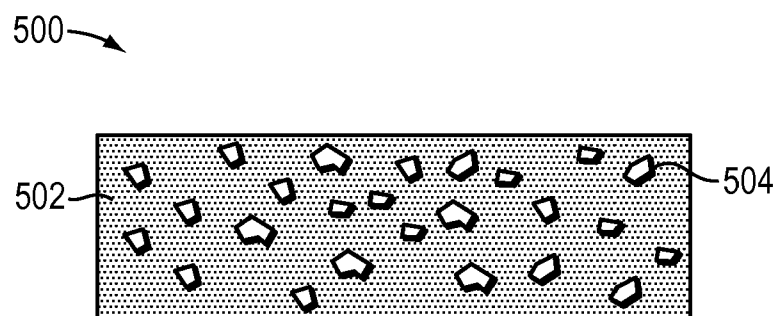
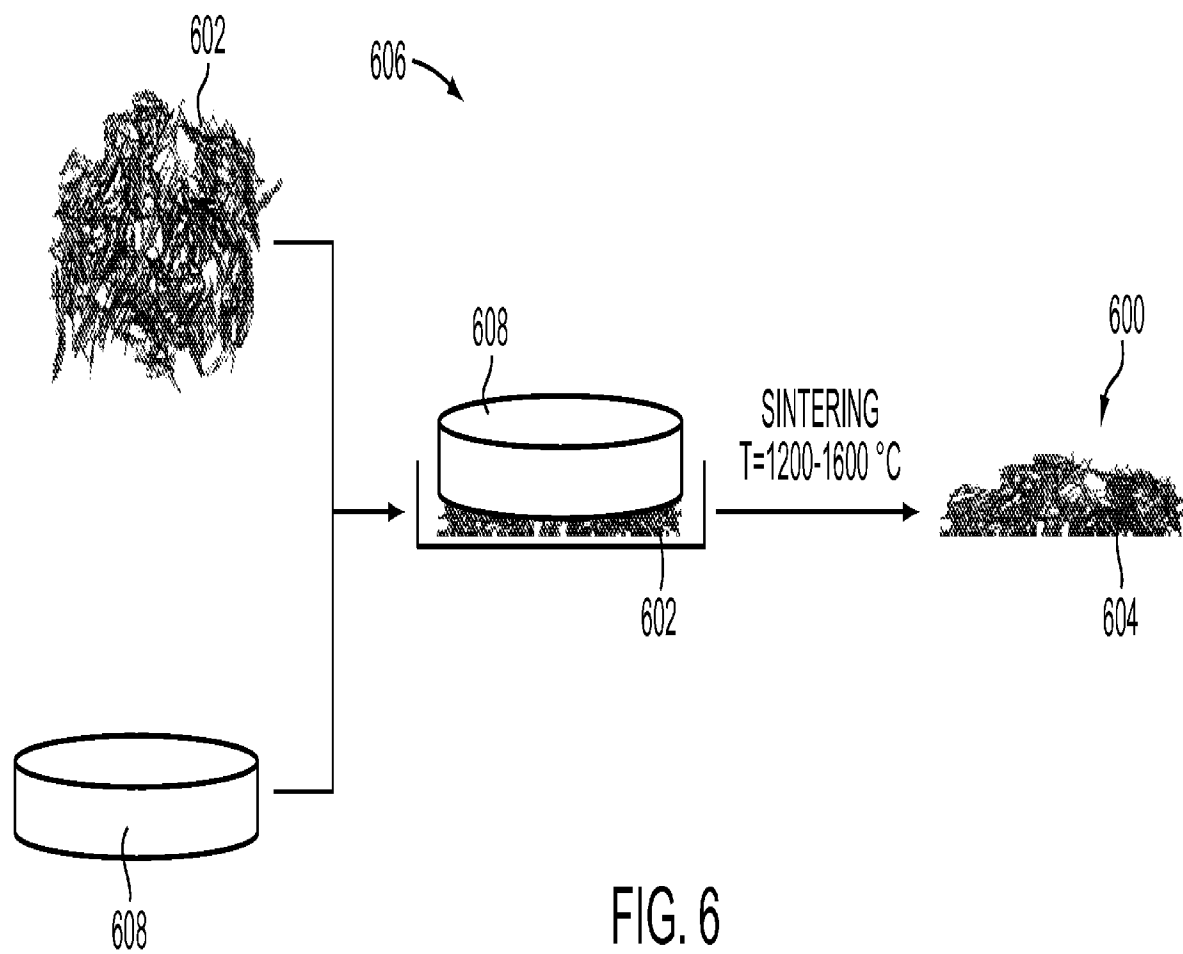


FIG. 5



4/13

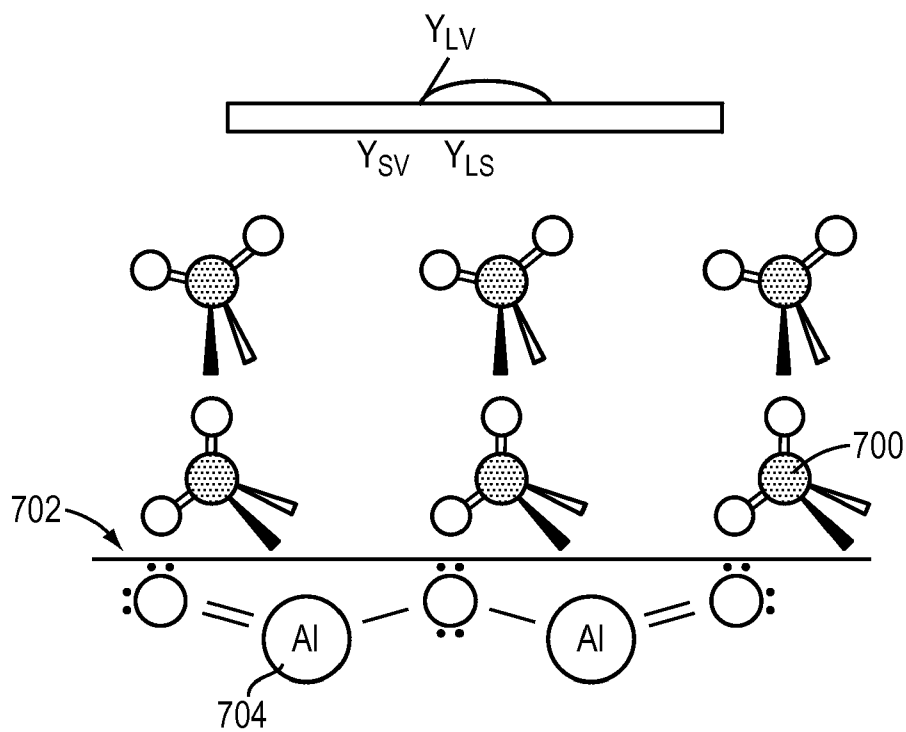


FIG. 7

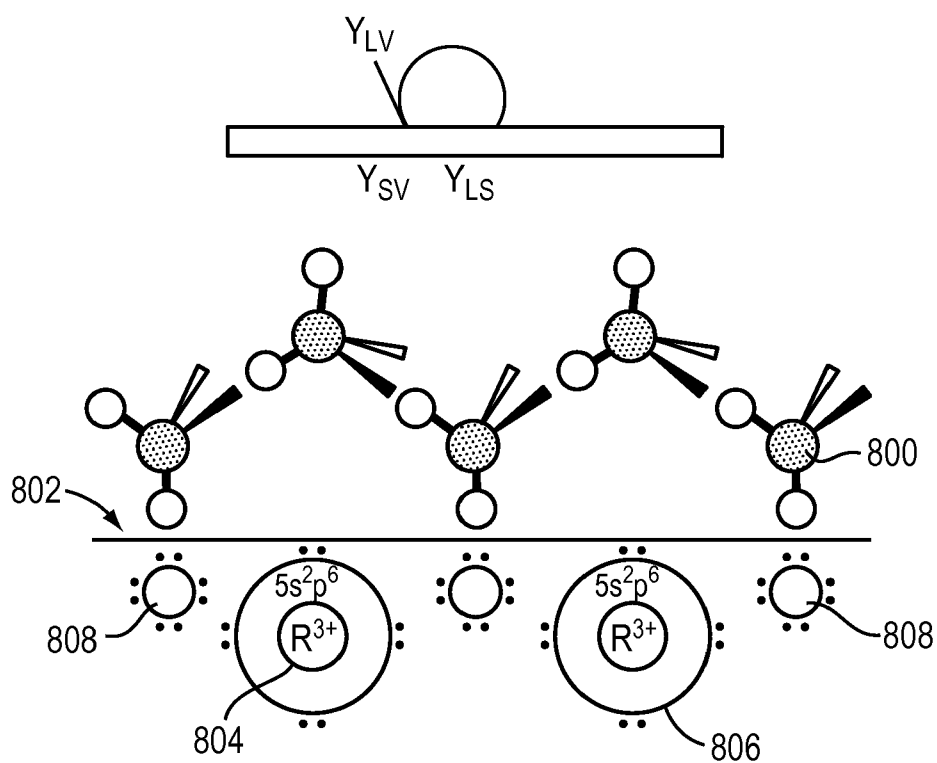


FIG. 8

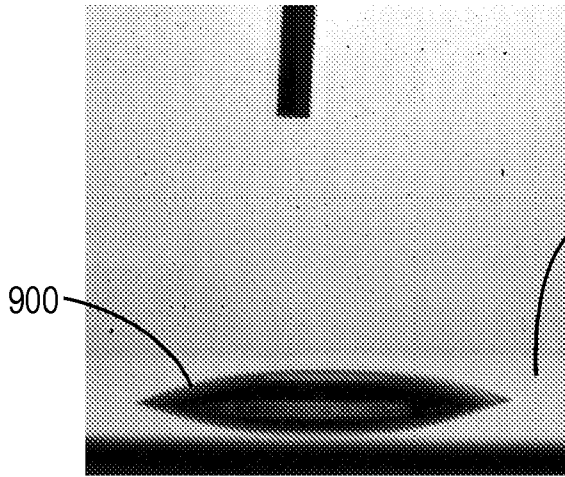


FIG. 9

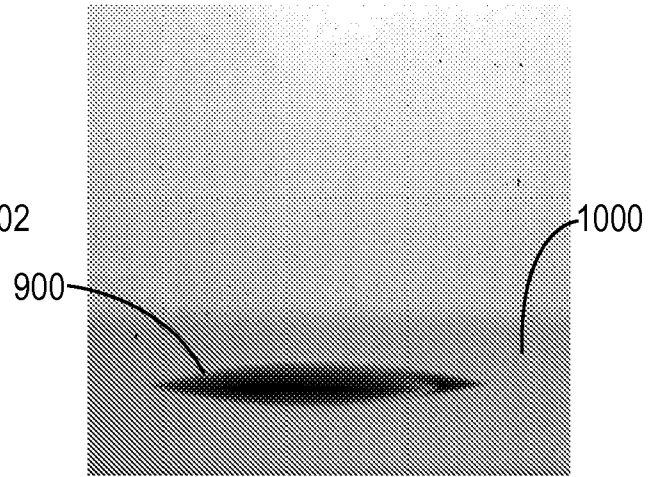


FIG. 10

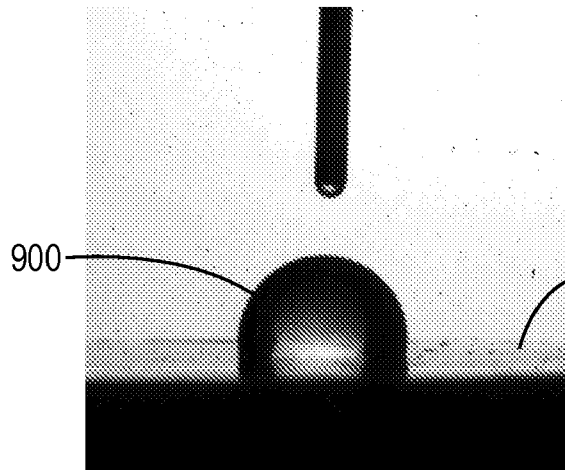


FIG. 11

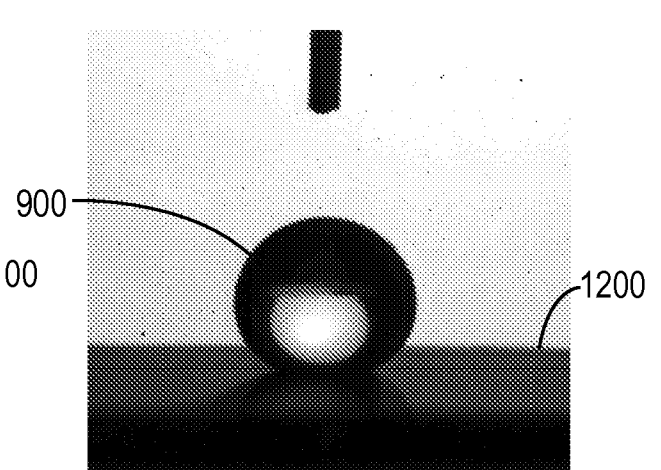


FIG. 12

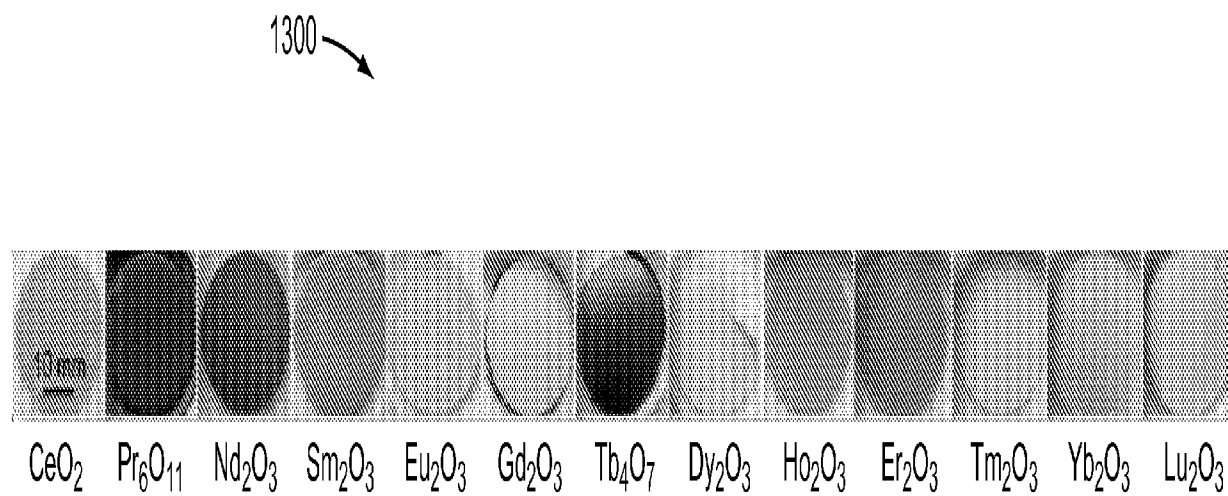


FIG. 13

7/13

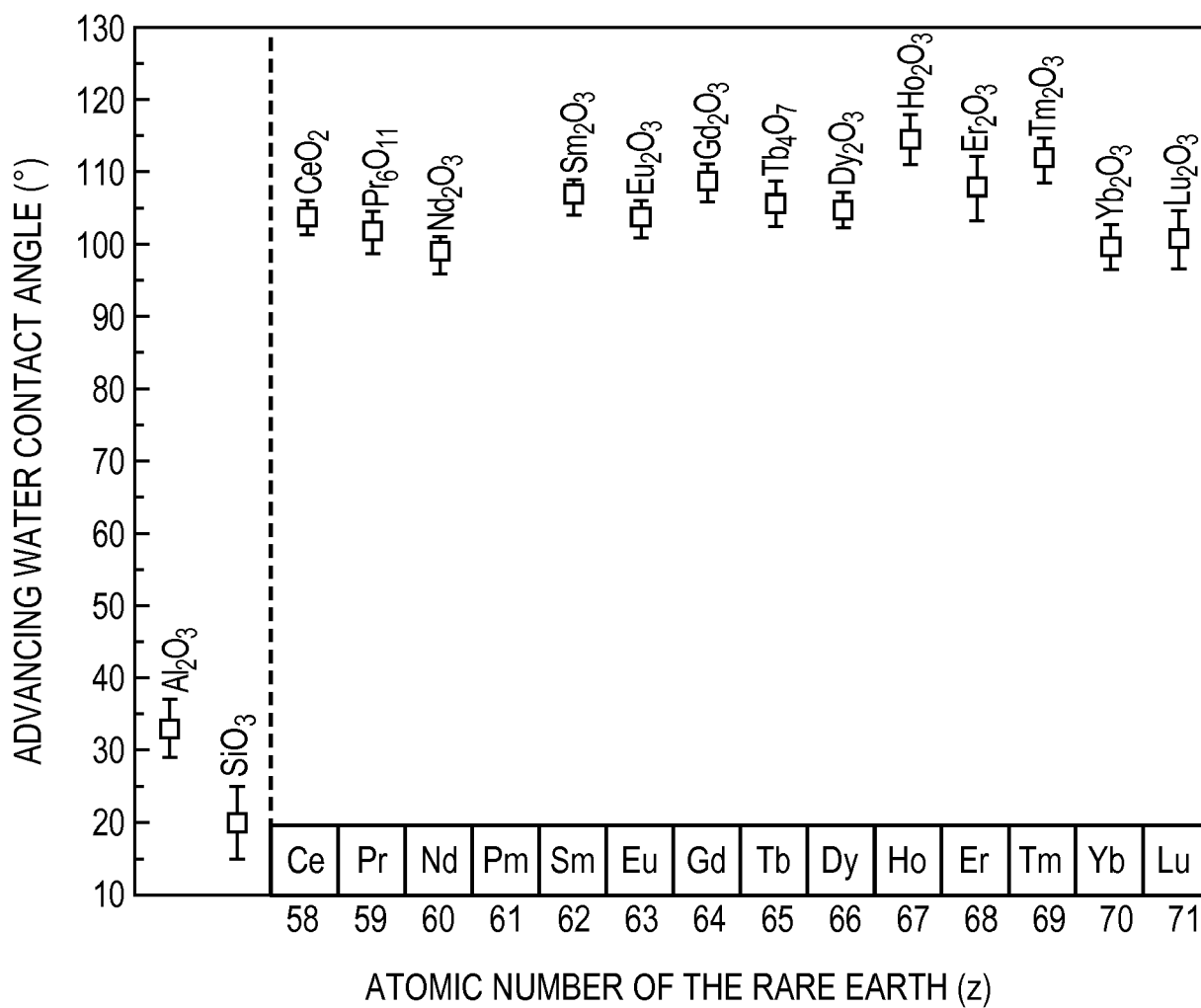


FIG. 14

8/13

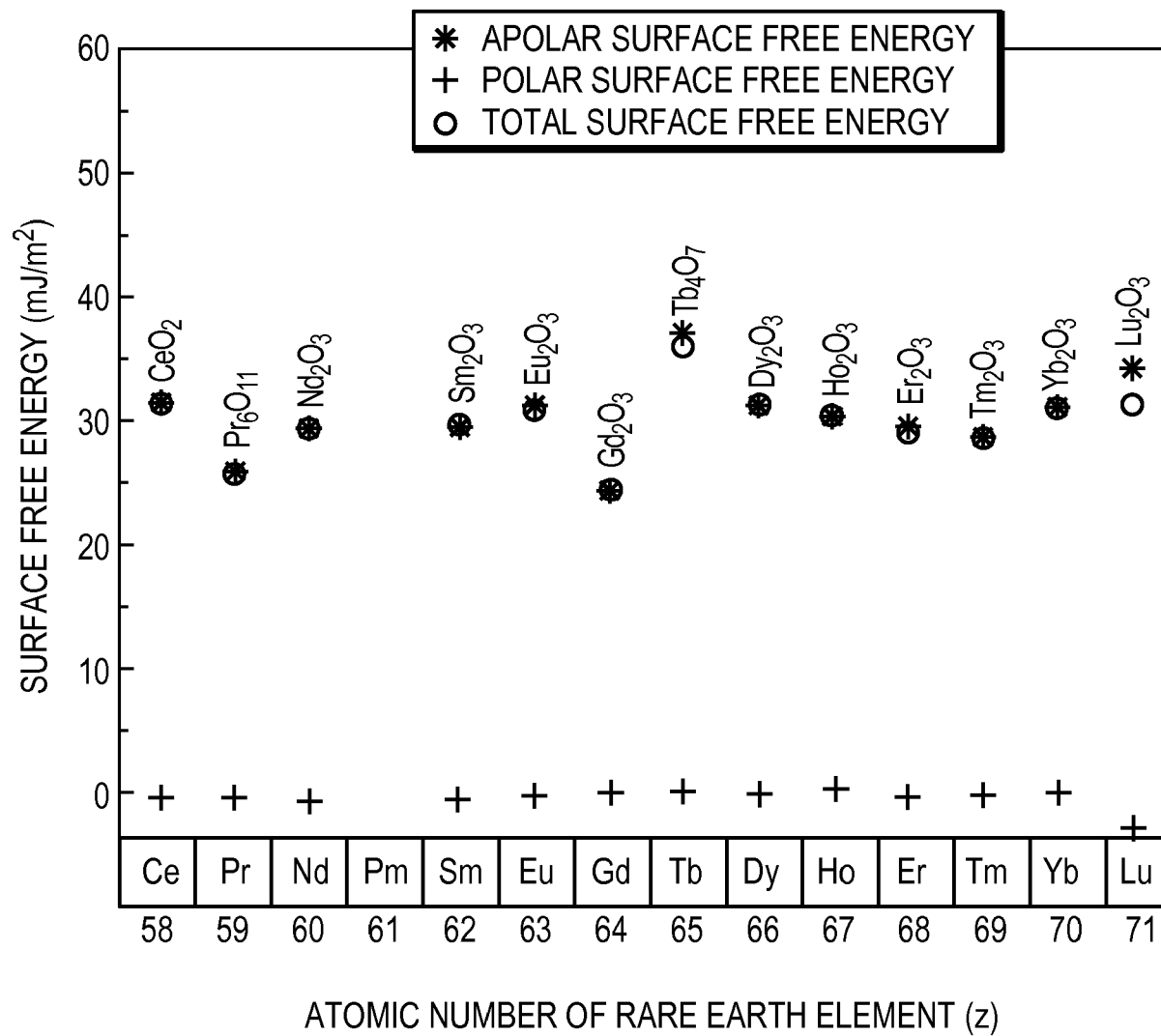


FIG. 15

9/13

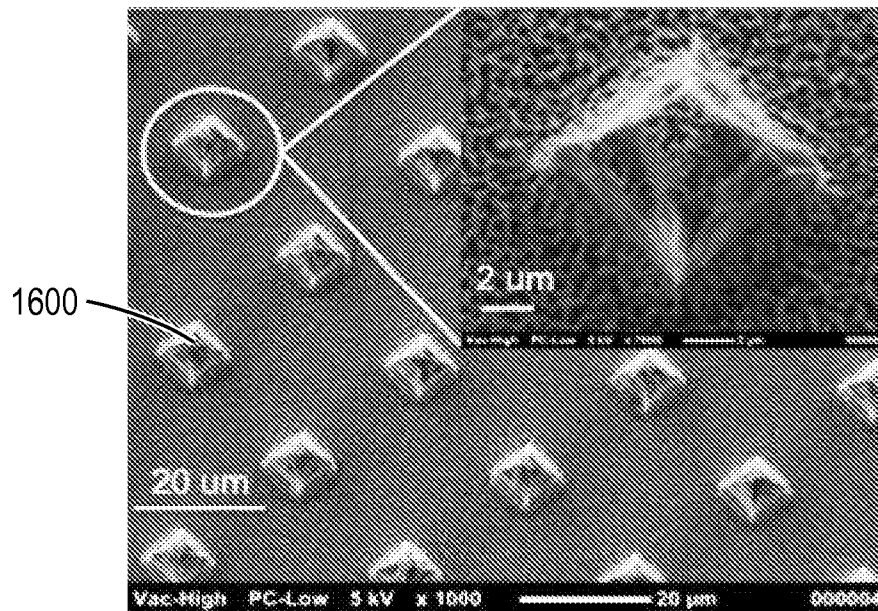


FIG. 16

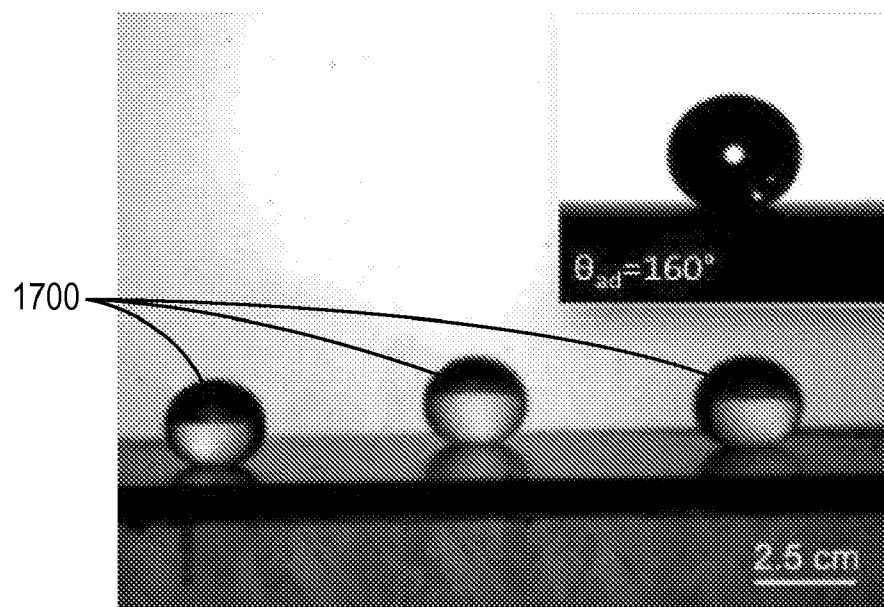


FIG. 17

10/13

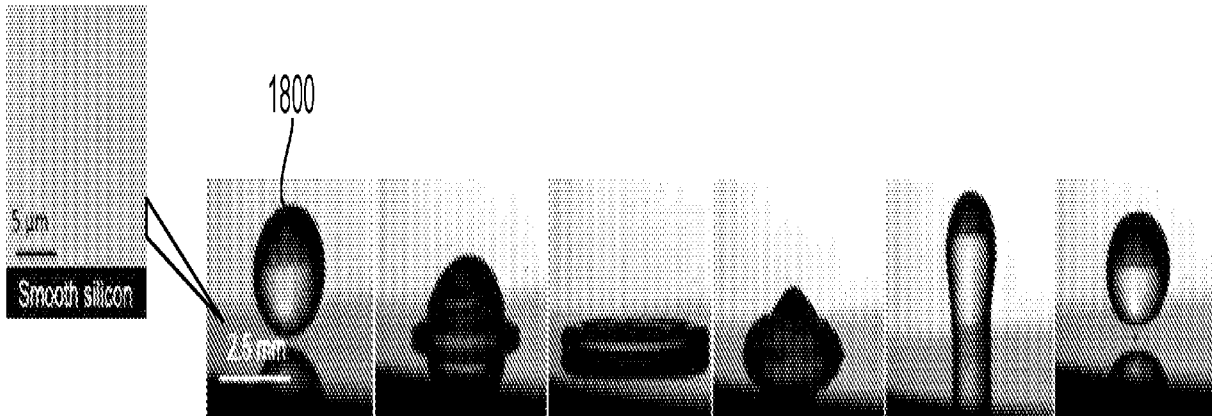


FIG. 18

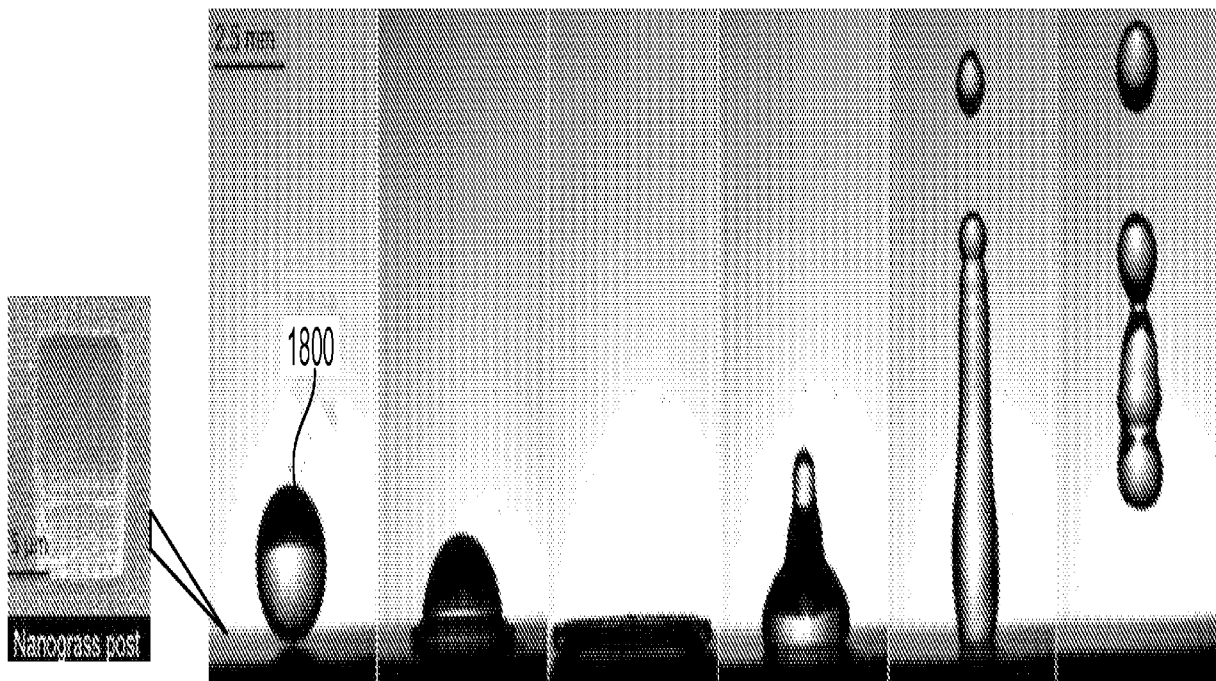


FIG. 19

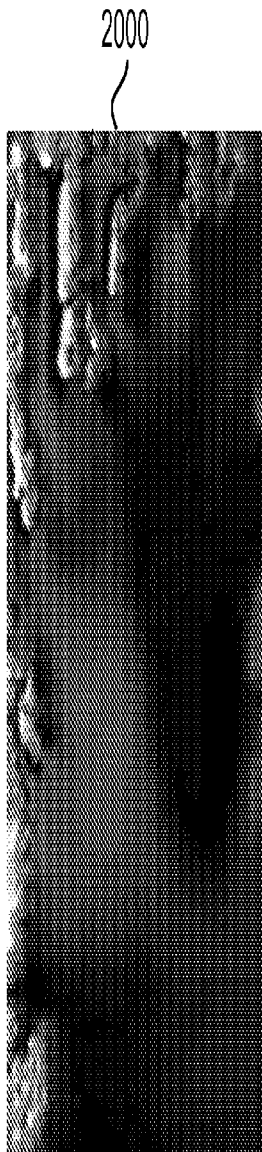


FIG. 20

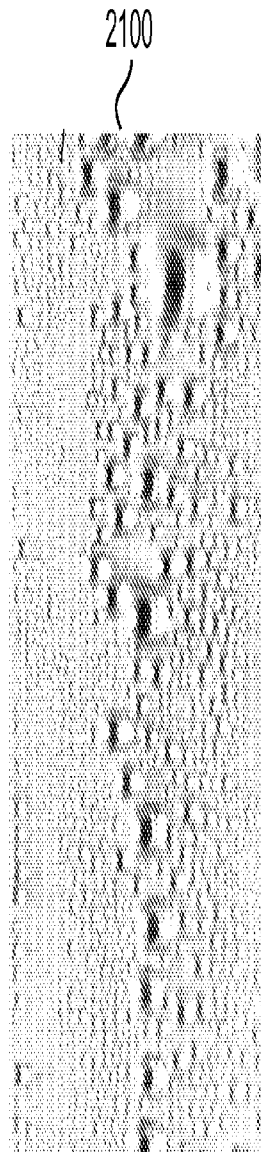


FIG. 21

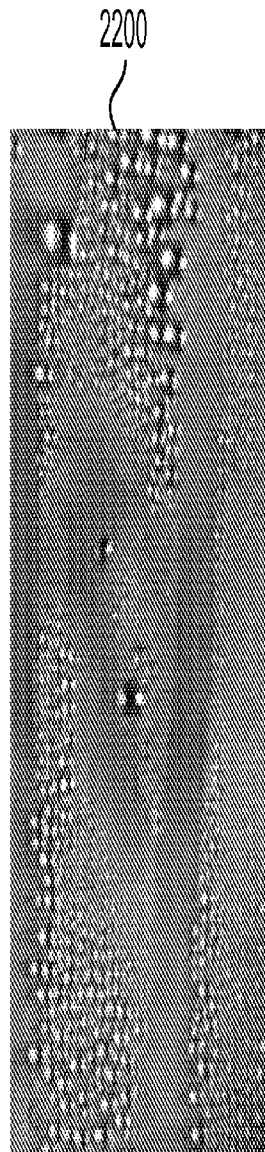


FIG. 22

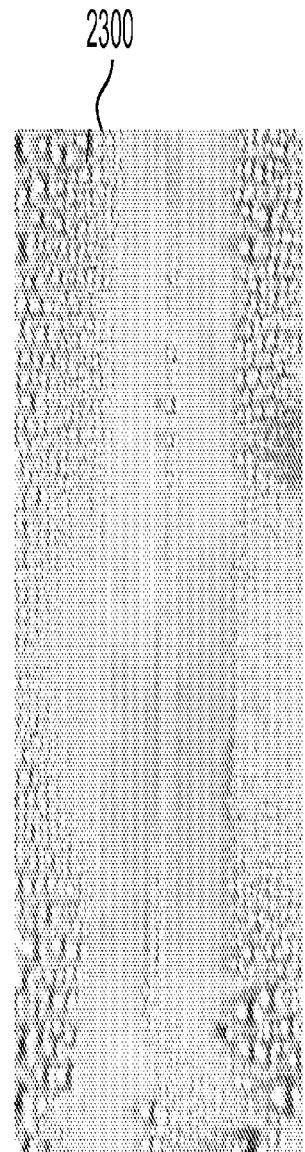


FIG. 23

12/13

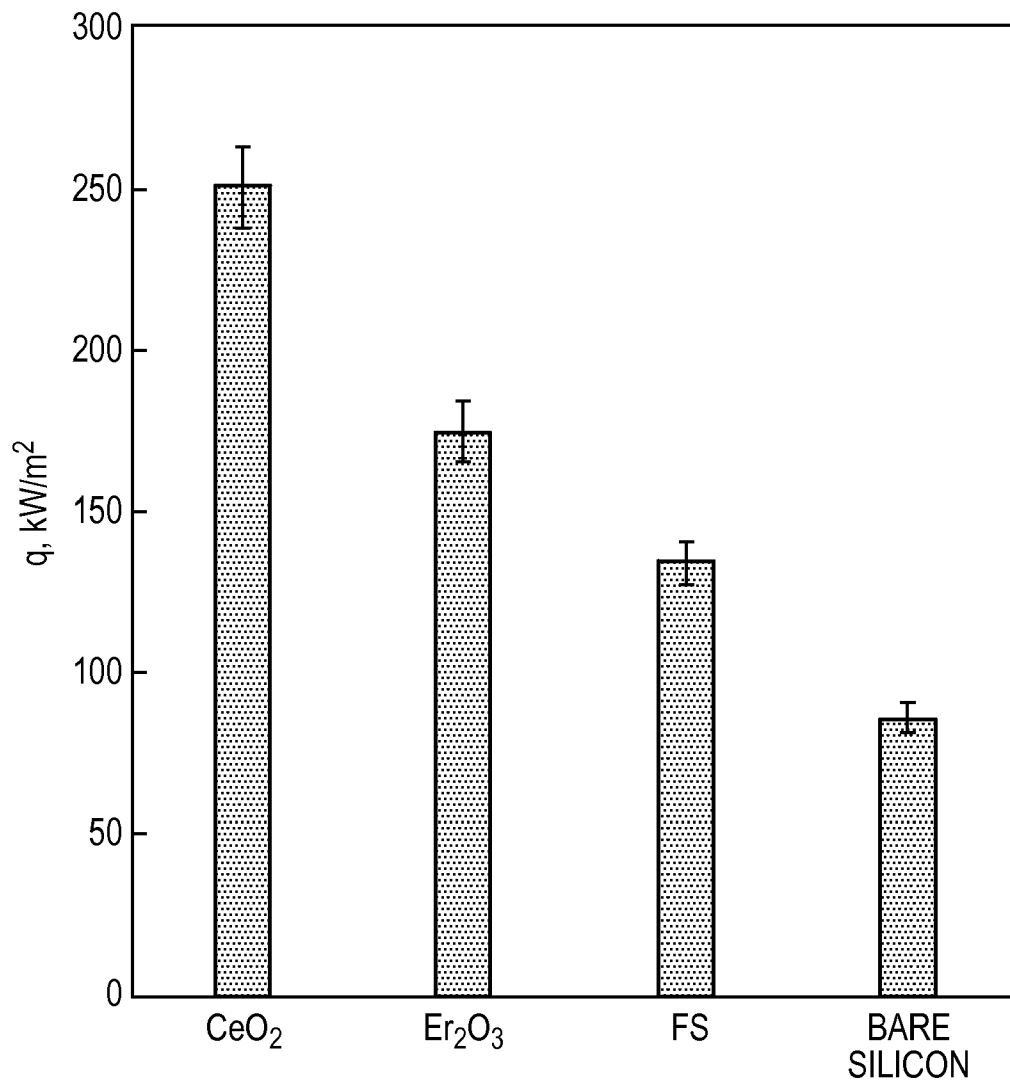


FIG. 24

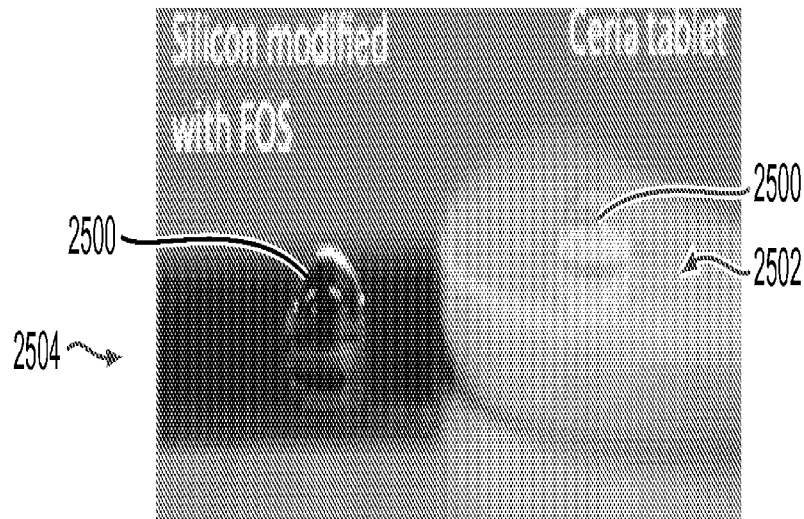


FIG. 25

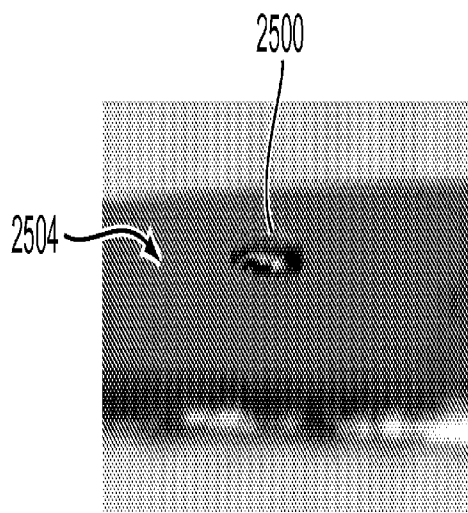


FIG. 26

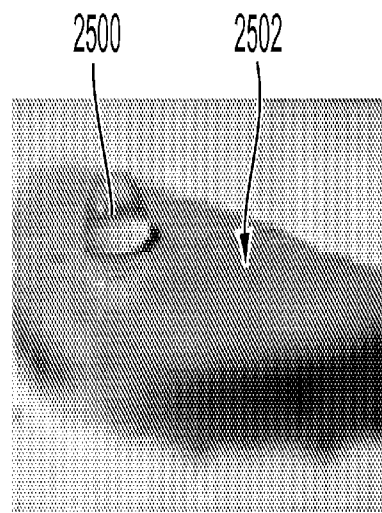


FIG. 27

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/030370

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C30/00 C23C14/34 C04B35/50
ADD.

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)

C23C C04B

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/155609 A1 (GENTLEMAN MOLLY MAUREEN [US] ET AL) 18 June 2009 (2009-06-18)	1-17,21, 46-48
Y	abstract paragraphs [0002] - [0004], [0007], [0009], [0031], [0032], [0045]; claims 1,9,11,13,14	37-40
X	----- CN 101 269 960 A (HARBIN INST OF TECHNOLOGY [CN] HARBIN INST OF TECHNOLOGY) 24 September 2008 (2008-09-24) abstract; claims 1-8	1-6, 10-17, 46,47,49
Y	----- WO 2007/019362 A1 (GEN ELECTRIC [US]; VARANASI KRIPA KIRAN [US]; BHATE NITIN [US]; O'NEIL) 15 February 2007 (2007-02-15) page 15	37-40



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

15 May 2012

Date of mailing of the international search report

15/10/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Oliveras, Mariana

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/030370

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.:
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:

see additional sheet

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 an 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.:

5, 9, 12-17(completely); 1-4, 6-8, 10, 11, 37-40, 46-49(partially)

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 5, 9, 12-17(completely); 1-4, 6-8, 10, 11, 37-40, 46-49(partially)

An article comprising: a base substrate; and a hydrophobic coating comprising a rare earth element oxide and its manufacturing method.

2. claims: 18(completely); 1-4, 6-8, 10, 11, 37-40, 46-49(partially)

An article comprising: a base substrate; and a hydrophobic coating comprising a rare earth element carbide and its manufacturing method.

3. claims: 19(completely); 1-4, 6-8, 10, 11, 37-40, 46-49(partially)

An article comprising: a base substrate; and a hydrophobic coating comprising a rare earth element nitride and its manufacturing method.

4. claims: 20(completely); 1-4, 6-8, 10, 11, 37-40, 46-49(partially)

An article comprising: a base substrate; and a hydrophobic coating comprising a rare earth element fluoride and its manufacturing method.

5. claims: 27, 28, 30(completely); 22-26, 29, 34-36, 44, 45(partially)

An article comprising a bulk material doped with a rare earth oxide and its manufacturing method.

6. claims: 31(completely); 22-26, 29, 34-36, 44, 45(partially)

An article comprising a bulk material doped with a rare earth carbide and its manufacturing method.

7. claims: 32(completely); 22-26, 29, 34-36, 44, 45(partially)

An article comprising a bulk material doped with a rare earth nitride and its manufacturing method.

8. claims: 33(completely); 22-26, 29, 34-36, 44, 45(partially)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

An article comprising a bulk material doped with a rare earth fluoride and its manufacturing method.

9. claims: 41-43

A method of manufacturing a hydrophobic article, the method comprising: providing a ceramic material and a rare earth element material; and heating the ceramic material and the rare earth element material to a temperature of at least about 1600 °C. It is pinpointed that the method of claims 41 to 43 refers to a coating, but it is not clear where and how said coating is formed (Rule 6 PCT).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/030370

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2009155609	A1	18-06-2009	DE 102008055500 A1	25-06-2009
			FR 2925063 A1	19-06-2009
			JP 2009149982 A	09-07-2009
			RU 2008149990 A	27-06-2010
			US 2009155609 A1	18-06-2009
			US 2011083583 A1	14-04-2011

CN 101269960	A	24-09-2008	NONE	

WO 2007019362	A1	15-02-2007	EP 1913325 A1	23-04-2008
			JP 2009503432 A	29-01-2009
			US 2007028588 A1	08-02-2007
			WO 2007019362 A1	15-02-2007
