(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 December 2018 (27.12.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/236785 A1

(51) International Patent Classification:
C01B 13/36 (2006.01)

(21) International Application Number:
PCT/US2018/038165

(22) International Filing Date:
19 June 2018 (19.06.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/522,384 20 June 2017 (20.06.2017) US

(71) Applicant: **BOARD OF TRUSTEES OF THE UNIVERSITY OF ARKANSAS** [US/US]; 2404 North University Avenue, Little Rock, Arkansas 72207 (US).

(72) Inventors: **KARABACAK, Tansel**; 2001 Brookford Drive, Little Rock, Arkansas 72211 (US). **SAADI, Nawzat Saeed**; 1701 Westpark Drive, Little Rock, Arkansas 72204 (US). **HASSAN, Laylan Bapper**; 1701 Westpark Drive, Little Rock, Arkansas 72204 (US).

(74) Agent: **XIA, Tim Tingkang**; Locke Lord LLP, P.O. Box 55874, Boston, Massachusetts 02205 (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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

(54) Title: METHOD OF FORMING HIGH SURFACE AREA METAL OXIDE NANOSTRUCTURES AND APPLICATIONS OF SAME

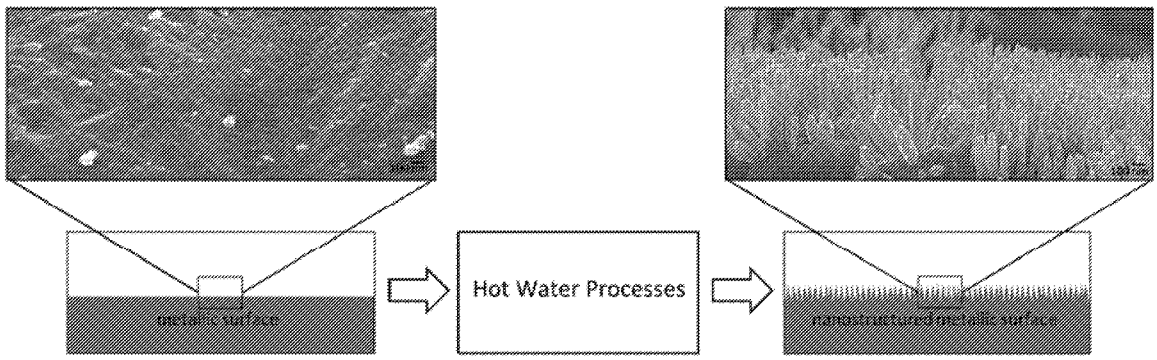


FIG. 1C

(57) Abstract: A method of forming metal oxide nanostructures on a metallic material includes applying a hot water process to the metallic material, which includes treating the metallic material with hot water under a treatment condition for a period of time so as to form metal oxide nanostructures on a surface of the metallic material, where the treated metallic material with metal oxide nanostructures under the hot water process has a high surface area that is higher than its pristine surface area of the metallic material. Also, a method of depositing metal oxide nanostructures on a target material includes applying a hot water process to a source metallic material and the target material, which includes treating the source metallic material and the target material with hot water under a treatment condition for a period of time so as to form metal oxide nanostructures on a surface of the target material.

WO 2018/236785 A1

[Continued on next page]

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, KM, ML, MR, NE, SN, TD, TG).

Published:

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

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

METHOD OF FORMING HIGH SURFACE AREA METAL OXIDE NANOSTRUCTURES AND APPLICATIONS OF SAME

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

This PCT application claims priority to and the benefit of, pursuant to 35 U.S.C. § 119(e), U.S. Provisional Patent Application Serial No. 62/522,384, filed June 20, 2017, which is incorporated herein in its entirety by reference.

This PCT application also relates to U.S. non-provisional application Serial No. 16/011,682. filed June 19, 2018, entitled "METHOD OF FORMING HIGH SURFACE AREA METAL OXIDE NANOSTRUCTURES AND APPLICATIONS OF SAME", the disclosure of which is incorporated herein in its entirety by reference.

Some references, which may include patents, patent applications and various publications, are cited and discussed in the description of this disclosure. The citation and/or discussion of such references is provided merely to clarify the description of the present disclosure and is not an admission that any such reference is "prior art" to the disclosure described herein. All references cited and discussed in this specification are incorporated herein by reference in their entireties and to the same extent as if each reference was individually incorporated by reference. In terms of notation, hereinafter, "[n]" represents the nth reference cited in the reference list. For example, [28] represents the 28th reference cited in the reference list, namely, Hassan, L.B., N.S. Saadi, and T. Karabacak, *Hierarchically Rough Superhydrophobic Copper Sheets Fabricated by a Sandblasting and Hot Water Treatment Process.* The International Journal of Advanced Manufacturing Technology, 2017.

FIELD OF THE INVENTION

The invention relates generally to nanomaterials, and more particularly, to method of forming high surface area metal oxide nanostructures by a hot water process and applications of the same.

BACKGROUND OF THE INVENTION

The background description provided herein is for the purpose of generally presenting the context of the present invention. The subject matter discussed in the background of the invention section should not be assumed to be prior art merely as a result of its mention in the background

of the invention section. Similarly, a problem mentioned in the background of the invention section or associated with the subject matter of the background of the invention section should not be assumed to have been previously recognized in the prior art. The subject matter in the background of the invention section merely represents different approaches, which in and of themselves may also be inventions. Work of the presently named inventors, to the extent it is described in the background of the invention section, as well as aspects of the description that may not otherwise qualify as prior art at the time of filing, are neither expressly nor impliedly admitted as prior art against the present invention.

There are numerous nano-structuring methods that can produce high surface area materials. Some well-known examples of fabrication techniques include chemical vapor deposition (CVD) [7], nano-imprinting [8, 9], solvent thermal synthesis [10-15], nano-lithography [16-18], nano-casting [19], ball milling [20], plasma etching, and wet etching [21]. However, most of these approaches are either un-scalable, complicated, high-cost, environmentally hazardous, or non-robust.

More recently, few researchers (also including one of the inventors of this patent application) has demonstrated that hot water process can be used to form either thin film oxides [22-26] or a nanostructured surface of aluminum oxide [27] copper oxide [28, 29], and zinc oxide [30]. However, none of these prior works reports that the process can be extended to a wide variety of metals.

Therefore, a heretofore unaddressed need exists in the art to address the aforementioned deficiencies and inadequacies.

SUMMARY OF THE INVENTION

One of the objectives of this invention is to develop a hot water process nanostructure growth mechanism for forming a high surface area metal oxide on almost any given metallic substrate. The hot water process can form nanostructured metal oxides on different types of metals and their alloys/compounds.

In one aspect, the invention relates to a method of forming metal oxide nanostructures on a metallic material, comprising applying a hot water process to the metallic material, which includes treating the metallic material with hot water under a treatment condition for a period of time so as to form metal oxide nanostructures on a surface of the metallic material, where the treated metallic material with metal oxide nanostructures under the hot water process has a high

surface area that is higher than its pristine surface area of the metallic material.

In one embodiment, the hot water is a liquid phase of water, a gas phase of water, or a combination thereof.

In one embodiment, the hot water is stirred at various flow patterns, flown at a direction, or in the steam applied at an angle relative to the surface of the metallic material.

In one embodiment, the hot water comprises a type of water with different levels of purity, resistivity, dissolved oxygen, or mineral content.

In one embodiment, the metallic material comprises one or more metallic compositions including elemental metals, alloys, compounds, a combination thereof, or a combination of metallic and non-metallic materials.

In one embodiment, the metallic material comprises a one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) metallic material. In one embodiment, the 1D metallic material has a fiber, wire or rod geometry, the 2D metallic material has a plate, foil or thin film geometry, or the 3D metallic material has a powder, pipe, mesh or foam geometry.

In one embodiment, the metallic material is in a form of substrate being electrically charged or neutral.

In one embodiment, the treatment condition comprises a temperature in a variety of ranges such that the hot water is liquid water at ambient temperatures, warm water below boiling point, boiling water, or steam at much higher temperatures.

In one embodiment, the treatment condition further comprises a variety of environmental pressures including different atmospheric pressures at different altitudes and high or low pressures achieved in a special container, and a variety of dissolved oxygen levels.

In one embodiment, the method further comprises controlling the treatment condition to determine sizes, morphology, stoichiometry, composition, and phase of the metal oxide nanostructures. In one embodiment, the phase of the metal oxides nanostructures comprises thermally stable stoichiometric oxides and hydroxides.

In one embodiment, the step of treating the metallic material with the hot water comprises immersing the metallic material the hot water, or applying a steam of the hot water at the metallic material.

In one embodiment, the step of treating the metallic material with the hot water is assisted by external physical and chemical factors including radiation, applied electric or magnetic fields, mechanical vibrations, and chemical additives. In one embodiment, the radiation includes

microwave, laser, ultraviolet and infrared light, and the chemical additives include metal salt and metal salt solution.

In one embodiment, the method further comprises heating the water, the metallic material, or both of them.

In one embodiment, the method further comprises activating the surface of the metallic material with a pretreatment physical method and/or a pretreatment chemical method so as to enhance formation kinetics of the metal oxide nanostructures during the hot water process. In one embodiment, the pretreatment chemical method includes acid dipping, or plasma exposure, and the pretreatment physical method includes roughening the surface of the metallic material by polishing, abrasive blasting, and/or a mechanical erosion process.

In one embodiment, the method further comprises, prior to the step of treating the metallic material with the hot water, performing surface patterning and/or roughening on the metallic material, so as to form a hierarchically micro-nano-structured metallic material with a surface area that is substantially higher than the high surface area of the treated metallic material.

In one embodiment, the hot water process produces a solution containing metal oxide molecules, useable for other purposes in addition to metal oxide nanostructure growth.

In another aspect, the invention relates to a nanostructured metallic material formed by the above method.

In yet another aspect, the invention relates to a method of depositing metal oxide nanostructures on a target material, comprising applying a hot water process to a source metallic material and the target material, which includes treating the source metallic material and the target material with hot water under a treatment condition for a period of time so as to form metal oxide nanostructures on a surface of the target material.

In one embodiment, the source metallic material comprises one or more metallic compositions including elemental metals, alloys, compounds, a combination thereof, or a combination of metallic and non-metallic materials.

In one embodiment, the target material is a non-metallic material, a metallic material, or a combination thereof.

In one embodiment, the step of treating the source metallic material with the hot water comprises immersing the source metallic material and the target material in the hot water.

In one embodiment, the step of treating the source metallic material with the hot water is assisted by external physical and chemical factors including radiation, applied electric or

magnetic fields, mechanical vibrations, and chemical additives. In one embodiment, the radiation includes microwave, laser, ultraviolet and infrared light, and the chemical additives include metal salt and metal salt solution.

In one embodiment, the method further comprises activating the surface of the target material with a pretreatment physical method and/or a pretreatment chemical method so as to enhance formation kinetics of the metal oxide nanostructures during the hot water process. In one embodiment, the pretreatment chemical method includes acid dipping, or plasma exposure, and the pretreatment physical method includes roughening the surface of the metallic material by polishing, abrasive blasting, and/or a mechanical erosion process.

In one embodiment, the method further comprises, prior to the step of treating the source metallic material with the hot water, performing surface patterning and/or roughening on the target material, so as to form a hierarchically micro-nano-structured metallic material with a surface area that is substantially higher than the high surface area of the treated target material.

In one embodiment, the hot water process produces a solution containing metal oxide molecules, useable for other purposes in addition to metal oxide nanostructure growth.

In one embodiment, the formation of the metal oxide nanostructures on the surface of the target material metal comprises metal oxide formation on a surface of source metallic material, release of metal oxide molecules from the source metallic material, migration of the metal oxide molecules through water, and deposition of the metal oxide molecules on the surface of the target material, and surface diffusion of the metal oxide molecules so as to form the metal oxide nanostructures with smooth crystal facets on the surface of the target material.

These and other aspects of the present invention will become apparent from the following description of the preferred embodiments, taken in conjunction with the following drawings, although variations and modifications therein may be affected without departing from the spirit and scope of the novel concepts of the disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate one or more embodiments of the invention and, together with the written description, serve to explain the principles of the invention. The same reference numbers may be used throughout the drawings to refer to the same or like elements in the embodiments.

FIG. 1A shows schematically a hot water process utilized to produce high surface area

metal oxide nanostructures according to one embodiment of the present invention.

FIG. 1B shows schematically a hot water process utilized to produce high surface area metal oxide nanostructures according to another embodiment of the present invention.

FIG. 1C shows nanostructured morphology by the hot water process according to one embodiment of the present invention, where the SEM image of Zn metal after the hot water process shows the formation of nanostructures.

FIGS. 2A-2D show SEM images of several metals after the hot water process according to embodiments of the present invention, which show the formation of nanostructures.

FIGS. 3A-3B show AFM topography and roughness values for flat-control (FIG. 3A) and hot water processed nano-rough Cu substrate (FIG. 3B) according to embodiments of the present invention.

FIGS. 4A-4B show schematically a hot water process and steps involved in the formation of MONSTRs according to embodiments of the present invention. FIG. 4A shows the hot water process and the metal oxide formation during the hot water process at metal/water interface, while FIG. 4B shows steps involved in the formation of MONSTR during the hot water process. The nanostructure formation mechanism includes “plugging” and surface diffusion.

FIG. 5 shows schematically the steps of ‘plugging’ and surface diffusion in MONSTRs formation by the hot water process as metal oxide nanostructures deposition method according to embodiments of the present invention.

FIG. 6 shows schematically a sandblasting and a hot water process utilized to produce hierarchical micro-nano-structures of high surface areas according to one embodiment of the present invention.

FIGS. 7A-7H show SEM images of several metals after the sandblasting and the hot water process according to embodiments of the present invention, which show the formation of hierarchical micro-nanostructures. These metals have been chosen for demonstration purposes; and hierarchical surface fabrication by the sandblasting and the hot water process can apply to a wide variety of metallic materials.

FIG. 8 shows schematically a sandblasting and a hot water process utilized to produce hierarchical micro-nano-structures of high surface areas according to another embodiment of the present invention.

FIGS. 9A-9D show SEM images of several metals after the sandblasting and the hot water process according to embodiments of the present invention, which show the formation of

hierarchical micro-nanostructures. These metals have been chosen for demonstration purposes; and hierarchical surface fabrication by the sandblasting and the hot water process can apply to a wide variety of metallic materials.

FIGS. 10A-10D show schematically a flowchart of fabricating patterned micro-nanostructures using the sandblasting and the hot water process according to one embodiment of the present invention.

FIGS. 11A-11C show schematically nanostructured morphology of a metal substrate after the hot water process, microstructured morphology of a metal substrate after sandblasting, and hierarchical micro-nano-structured surfaces fabricated by the sandblasting and the hot water process, respectively, according to embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention will now be described more fully hereinafter with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this invention will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like reference numerals refer to like elements throughout.

The terms used in this specification generally have their ordinary meanings in the art, within the context of the invention, and in the specific context where each term is used. Certain terms that are used to describe the invention are discussed below, or elsewhere in the specification, to provide additional guidance to the practitioner regarding the description of the invention. For convenience, certain terms may be highlighted, for example using italics and/or quotation marks. The use of highlighting has no influence on the scope and meaning of a term; the scope and meaning of a term is the same, in the same context, whether or not it is highlighted. It will be appreciated that same thing can be said in more than one way. Consequently, alternative language and synonyms may be used for any one or more of the terms discussed herein, nor is any special significance to be placed upon whether or not a term is elaborated or discussed herein. Synonyms for certain terms are provided. A recital of one or more synonyms does not exclude the use of other synonyms. The use of examples anywhere in this specification including examples of any terms discussed herein is illustrative only, and in no way limits the scope and meaning of the invention or of any exemplified term. Likewise, the

invention is not limited to various embodiments given in this specification.

It will be understood that, as used in the description herein and throughout the claims that follow, the meaning of "a", "an", and "the" includes plural reference unless the context clearly dictates otherwise. Also, it will be understood that when an element is referred to as being "on" another element, it can be directly on the other element or intervening elements may be present therebetween. In contrast, when an element is referred to as being "directly on" another element, there are no intervening elements present. As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

It will be understood that, although the terms first, second, third etc. may be used herein to describe various elements, components, regions, layers and/or sections, these elements, components, regions, layers and/or sections should not be limited by these terms. These terms are only used to distinguish one element, component, region, layer or section from another element, component, region, layer or section. Thus, a first element, component, region, layer or section discussed below could be termed a second element, component, region, layer or section without departing from the teachings of the invention.

Furthermore, relative terms, such as "lower" or "bottom" and "upper" or "top," may be used herein to describe one element's relationship to another element as illustrated in the figures. It will be understood that relative terms are intended to encompass different orientations of the device in addition to the orientation depicted in the figures. For example, if the device in one of the figures is turned over, elements described as being on the "lower" side of other elements would then be oriented on "upper" sides of the other elements. The exemplary term "lower", can therefore, encompasses both an orientation of "lower" and "upper," depending of the particular orientation of the figure. Similarly, if the device in one of the FIGS. is turned over, elements described as "below" or "beneath" other elements would then be oriented "above" the other elements. The exemplary terms "below" or "beneath" can, therefore, encompass both an orientation of above and below.

It will be further understood that the terms "comprises" and/or "comprising," or "includes" and/or "including" or "has" and/or "having", or "carry" and/or "carrying," or "contain" and/or "containing," or "involve" and/or "involving, and the like are to be open-ended, i.e., to mean including but not limited to. When used in this invention, they specify the presence of stated features, regions, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, regions, integers, steps,

operations, elements, components, and/or groups thereof.

Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the present invention, and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

As used herein, "around", "about" or "approximately" shall generally mean within 20 percent, preferably within 10 percent, and more preferably within 5 percent of a given value or range. Numerical quantities given herein are approximate, meaning that the term "around", "about" or "approximately" can be inferred if not expressly stated.

As used herein, the phrase "at least one of A, B, and C" should be construed to mean a logical (A or B or C), using a non-exclusive logical OR.

As used herein, the term “high surface area” material refers to the material after the treatments according to this invention having “higher surface area” compared to its starting (pristine) surface area of the material before the treatments. For example, a nanostructured metal oxide layer formed on the surface of a metal foam will increase the overall surface area of the metal foam and make it even a higher surface area of the metallic materials. Another example can be a metal plate having small nanostructures grown on its surface, which will also have a “higher” surface area compared to the starting flat topography of the metal plate.

As used herein, the term “metallic materials” for the hot water process is not limited to specific chemical compositions such as elemental metals, alloys, compounds or any combination of them, or a combination of metallic and none-metallic materials or any physical dimension such as sheet, foil, plate, mesh and powder. The term also includes an ionic compound that can be formed by the neutralization reaction of an acid and a base, or composed of numbers of cations and anions so that the product is electrically neutral such as metals salt and metal salt solutions. Also, a combination of metal salt or metal salt solution with other elemental metals, alloys, compounds or any combination of them, or a combination of metallic and none-metallic materials is covered by the term “metallic materials”.

As used herein, the term “hot water” refers to water having a temperature higher than the freezing temperature of water. The hot water can be in a liquid phase of water, a gas phase of water, or a combination thereof.

The description below is merely illustrative in nature and is in no way intended to limit the invention, its application, or uses. The broad teachings of the invention can be implemented in a variety of forms. Therefore, while this invention includes particular examples, the true scope of the invention should not be so limited since other modifications will become apparent upon a study of the drawings, the specification, and the following claims. For purposes of clarity, the same reference numbers will be used in the drawings to identify similar elements. It should be understood that one or more steps within a method may be executed in different order (or concurrently) without altering the principles of the invention.

High surface area materials are desired for numerous applications such as catalysis, photonics, optical devices, energy storage, sensors, and biotechnology. Increased surface area can enhance several chemical and physical properties that can improve the functionality, efficiency, and stability of those applications. Nanostructured metallic materials offer the advantage of having high surface-to-volume ratios, which allows the maximum utilization of atoms to be positioned on the surface instead of in the bulk of a metallic material. For example, a nanostructured catalyst can reach superior chemical activity due to the active participation of catalyst atoms available at the high surface provided. In addition, hierarchical micro-nano-structured metallic materials, which are composed of micronized features with nanostructures, possess not only the high surface area and activity of nanomaterials, but also the structural stability and robustness of the bulk material. Thus, they combine the advantages of both nanostructured and bulk metallic materials. Furthermore, with the additional surface are provided by micro-scale features, hierarchical micro-nano-structured metallic materials can achieve even higher surface areas compared to a nanostructured surface alone.

In certain aspects, this invention relates to methods of producing high surface area metal oxide materials by using simple, low-cost, scalable, high-throughput, and eco-friendly hot water process. In certain embodiments, the approach operates in low-temperature and does not require any special environments/steps such as vacuum, acidic, alkaline solutions, or lithographical processing.

According to the invention, the high surface area metal oxide materials produced by the hot water process include a nanostructured metal oxide layer on a base metal. The methods are applicable to a wide variety of metallic materials including elemental, alloy, or compound metals or combination of them with other non-metallic materials. In addition, the methods are applicable to almost any geometry including 1D (e.g., wire, rod), 2D (e.g., plate, foil, thin film),

and 3D (e.g., powder, pipe, mesh, and foam) metallic materials.

The hot water process is a metal oxide nanostructure (MONSTR) growth technique that results in materials with a high surface area by introducing nanoscale surface roughness. The process involving reaction between hot water (deionized (DI), distilled, or purified) and metallic materials surface. This invention utilizes the principle of oxidizing the metallic surface and their respond to hot water to form metal oxides. When a free-oxide metallic surface reacts with hot water, it forms metal oxide nanostructures (MONSTRs) that have different physical and chemical properties from the original surface. The nanoscale dimension of metal oxide features grew on the surface by these processes considered as physical modification which introduce surface roughness after the treatment processes. Because metal oxides formed by these processes have different chemical properties from the surface of the base metal, it undergoes the chemical modification. Thus, these process results in physical and chemical surface modifications on the metal surface that can be utilized in several applications. From the topographical point of view, the growth of MONSTRs on a surface results in the development of rough surface that is in nanoscale (nano roughness), thus increasing the surface area of the treated materials comparing to the starting surface of the materials. In the hot water process, the fabrication of metal oxide can take place at either relatively low water temperature (e.g., between 50-95°C) for liquid water at atmospheric pressure conditions) or at higher temperatures when steam (gas phase of water) is used instead of liquid water. Notwithstanding of the used methods, the treated surface is covered with nanostructures that increase the surface area. Hot water processed-metals form metal oxide surfaces with features in the nanoscale (nanostructured metal oxide) approximately in the range of 25-500 nm on top of the base metal surface. The geometry and size of nanostructures depend on treatment conditions, such as treatment time, water temperature, dissolved oxygen (DO) in water, and the initial surface roughness of the metal. Nanostructures formed by hot water process provide significantly higher surface areas compared to a pristine metal. Previously, the process has mainly been used to fabricate metal oxide thin films, e.g., MgO, ZnO, CuO, and Al_2O_3 [1-6]. Because the process does not involve any chemicals, such as surfactants, reductants, oxidation agents, additives or any byproducts, and takes place at relativity low temperatures, the hot water process is a simple and eco-friendly technique. Since no complicated fabrication processes are involved in the hot water process, such as the need for vacuum environment or plasma, the process is low-cost, scalable, and high-throughput. With almost no restrictions on metal types and their compounds, e.g., alloys or composites, or their geometry, e.g., 1D, 2D or 3D, the

process promises an ideal technique to fabricate metallic materials with high surface areas for several applications.

In certain embodiments, in the hot water process nano-fabrication process, water with high resistivity, low conductivity, and high purity is preferred. However, water of poorer qualities of these properties such as mineral water or even water from lakes, rivers, and sea can be used to practice the invention. When lower quality water is used, it may take longer time to form nanostructured metal oxides by the hot water process, yet it can further lower the fabrication costs.

FIGS. 1A and 1B show the hot water process according to two different embodiments of the invention, respectively.

In one embodiment shown in FIG. 1A, a base metal substrate is disposed in hot water, which involves a reaction between metals and water, such as deionized (DI), distilled, or purified, at temperatures higher than room temperature (usually between 50-95°C). The hot water process results in metal oxide surfaces with features in the nanoscale (nanostructured metal oxide) approximately in the range of 25-500 nm on top of the base metal surface. The geometry and size of nanostructures depend on treatment conditions such as treatment time, water temperature, dissolved oxygen (DO) in water, and also the initial surface roughness of the base metal substrate. Nanostructures formed by the hot water treatment provide significantly higher surface areas compared to a pristine metal. Because the hot water process does not involve any chemicals, such as surfactants, reductants, oxidation agents, additives or any byproducts, and also takes place at relativity low temperatures, the hot water process is a simple and eco-friendly technique. Since no complicated fabrication processes are involved in the hot water process, such as the need for vacuum environment or plasma, the process is low-cost, scalable, and high-throughput.

In another embodiment shown in FIG. 1B, as an even simpler, faster, more scalable and practical alternative to the hot water treatment shown in FIG. 1A, a metal substrate is treated with steam (gas phase) of water. Steam treatment can effectively form high surface area metal oxide nanostructures on a base metal. Different from the hot water treatment shown in FIG. 1A, which is limited to the maximum boiling temperature of water, during the steam treatment, water is delivered to the metal surface in the form of vapor that can acquire almost any temperature. Higher temperatures of the steam can allow much faster nanostructure formation kinetics. Steam also does not require the use high purity or DI water. Regular tap water can be evaporated to

produce a steam that is free from impurities. As explained in more detail in the following sections, mechanisms of the hot water process include the effects of dissolved oxygen, which enhances metal oxide nanostructure formation. During the steam treatment, molecular oxygen from ambient environment can be easily incorporated to the steam that further increases the nanostructure formation kinetics. In addition, the steam treatment can allow spatial control on nanostructuring and easy patterning. For example, using a beam of steam coming out of nozzle, one can do the steam treatment on select regions of a given metal and form a heterogeneous pattern incorporating untreated metal and the steam treated metal oxide nanostructures. Other than these differences, the steam treatment has all the advantages and similar nanostructures formed on the surface of the metal substrate under the hot water treatment shown in FIG. 1A.

As shown in FIG. 1C, during the hot water process, the surface of a given metal substrate reacts with water at temperatures higher than room temperature to form high surface nanostructured metal oxides. In order to introduce a nanostructured layer onto a metal surface, a native oxide layer and potential contamination on the surface are removed, which can enhance the reactions during hot water process. This is followed by a cleaning process such as ultrasonicating the samples first with acetone, isopropanol, and then DI water cleaned metallic materials are then followed by the hot water process. Treatment time may vary depending on the metal. In certain embodiments, it ranges between a couple of minutes up to several hours. The morphology and porosity of the nanostructured layer on a metal can be tuned by varying the process time (from a few minutes up to several hours). FIGS. 2A-2D show scanning electron microscopy (SEM) images of several metals' surface (Cu, Zn, Al, and Pb) after the hot water process. The SEM images show the formation of nanoscale features (nanostructures) in a scale of a few of nanometers. These nanostructures are distributed uniformly on the surface and lead to increasing the surface area and hence enhance its activity. FIGS. 3A-3B show the AFM topography and roughness values for control (pristine Cu) and nanostructured surfaces and a similar morphology of Cu sample (FIG. 2A) can be observed. For the control sample, AFM topography shows the flatness of the control sample (FIG. 3A) with roughness value of about R_a = 7 nm. However, roughness of the Cu sample after the hot water process is significantly higher with R_a = 97 nm (FIG. 3B).

In one aspect of this invention, a hot water process is used to generate high surface area nanostructured metal oxides. As described above, the process is facile, low-cost, scalable, and eco-friendly. The mechanisms of nanostructure formation on metal surfaces to produce high

surface nanostructured materials are the same process involving water-metal reaction.

Formation of planar metal oxide films in water is widely reported in the literature [31-35]. As shown in FIG. 4A, the process starts with the formation of a positively charged metal ion that gets released into the water, leaving electrons behind on the surface. This metal cation still stays close to the water/metal interface due to the negative potential of the solid surface. Then, electrons on the surface can react with adsorbed oxygen and water molecules to produce hydroxyl ions. Finally, metal ions in water can react with hydroxyl ions on the surface to form a metal oxide molecule along with hydrogen [32]. FIG. 4B illustrates the steps of MONSTR formation during the hot water process according to the invention. The first step involves the formation of metal oxide molecules on the surface of a metallic substrate ("1- Metal oxide" shown in FIG. 4B), which follows a reaction similar to the steps of metal oxide film formation described above (FIG. 4A). As a potential next step during MONSTR growth, metal oxide molecules can diffuse on the surface. However, the surface diffusion is not believed to be the dominant mechanism that explains the nanostructure formation at the relatively low temperature conditions. A more likely next step is a dissolution-precipitation process called "plugging" [36] that has been used to describe the corrosion of metals. It involves the release of the metal oxide molecule ("2- Release") from the surface into the liquid followed by transportation through water ("3- Migration") and precipitation ("4- Re-deposition") onto another surface position. Re-deposited molecules can initiate the formation of isolated nanostructures. However, the random nature of plugging might not be sufficient to explain smooth crystalline surfaces observed in hot water process nanostructures. The re-deposited metal oxide molecules can diffuse on the surface, which may help in forming smooth individual nanostructures observed in the SEM images of FIGS. 2A-2D. After the oxidation step, when the adhesion forces between a metal oxide molecule and metal substrate are weak or there is a liquid movement, the release step can become easier and make the plugging process more dominant. Especially in the case of low surface diffusion rates, such plugging process can lead to the formation of fractal-like rough nanostructures. Also, initial substrate surface chemistry can play a critical role in the nucleation of metal oxide nanostructures. It is believed that metal oxide molecules may preferentially stick to defect sites, e.g., voids or grain boundaries with dangling bonds, which can act as nucleation regions. Migration and re-deposition may also depend on external factors such as liquid flow patterns, substrate morphology, mechanical vibrations, or even external magnetic and electric fields.

In certain embodiments, during the hot water process, several factors can enhance the formation of metal oxide nanostructures and speed-up the reaction between water-metal. Such factors can incorporate the kinetics and dynamics of the hot water process. Despite benefits for synthesis of metal oxides nanostructures using solutions based methods, they generally need long time for synthesis. In addition, the factors, such as the concentration of reactants, temperature, pressure, the physical state of reactants and their dispersion, the water, and the presence of a catalyst, may influence the reaction rates of chemical reactions in the hot water process.

In certain embodiments, other physical and chemical factors can also affect the formation of MONSTRs during the hot water process. Such factors can assist the hot water process and offer faster fabrication at lower cost to synthesis metallic materials have a high surface area. In certain embodiments, the hot water process can be enhanced by the assist of thermal effects of radiations, such as microwave, laser, and Infrared (IR) radiation, named as an assisted hot water treatment.

In certain embodiments, the assisted-hot water processes can be achieved by physical factors such as the enhancements generate from radiation, applying electric or magnetic fields, the presence of mechanical factors. Radiation-assisted (such as microwave-assisted) processing attracted a great deal of attention due to its advantages to supply higher synthesis rate, resulting superior to traditional heating. The ability to elevate the temperature of a reaction above the boiling point of the solution increases the speed of reactions by a factor of 10–1000. In certain embodiments, the typical hot water process is performed in temperatures higher room temperature and below the boiling point of water, but cannot reach very high treatment temperatures or pressures. Under such conditions, the hot water process may take several hours for most metals to forms metal oxide nanostructures. In certain embodiments, the steam treatment can speed up the formation of metal oxide nanostructures. Furthermore, the microwave-assisted hot water process can also speed up the synthesis of metal oxide nanostructures. In certain embodiments, when assisted by microwave radiations, the synthesis of metal oxide nanostructures for metals is completed in minutes or even seconds. In certain embodiments, radiations of different wavelengths, such as ultraviolet (UV), laser, and infrared (IR), can be used in the assisted hot water process to speed-up the fabrication of MONSTRs. The radiation reaction with water-metal results in increasing of the thermal conditions of the process, and thus increases the kinetic of metal oxide synthesis. In addition to the radiation effect on the hot water process for metal oxide nanostructures, an electric or magnetic field

voltage (potential difference) may also be applied in speeding up the fabrication process. For example, when a potential difference exits between a base metal surface and water during the hot water process, the rate of oxidation is increased by factors resulting in faster metal oxide formation. Applied electric or magnetic fields in the hot water process also works as driven force in the process and led to a faster deposition of the formed metal oxide as nanostructures and thus speed up the formation of metal oxide nanostructures.

Moreover, the chemical conditions at which the hot water process performs can also enhance the formation MONSTRs. In the hot water process, only water and metallic materials surface are usually involved in the process to synthesize metal oxide nanostructures. On the other hand, several chemical conditions such as the presence of chemical additives in the process can enhance the kinetics and dynamics of the hot water process. Metal salts additive can speed-up the MONSTR formation since the metal salts results in increasing the rate of metal cation in the process, thus higher metal oxide rate formation.

Nanostructure formation kinetics can be enhanced by activating the surface with pretreatment methods such as acid dipping (e.g., HF, HCL, and HNO_3) or plasma exposure. Chemically modified metallic surfaces can incorporate higher number of metal ions that can speed up the fabrication process. Also physical pretreated surface, such as roughened surface mechanically or chemically can enhance the MONSTRs formation in the hot water process.

In certain aspect of the invention, the hot water process can be used to deposit a large variety of MONSTR materials on almost any type of substrate material or geometry. As a deposition method, the hot water process simply involves a source metallic material and a target substrate that are both immersed into hot water. Like the growth of MONSTRs in the hot water process, a growth mechanism that includes the processes of “plugging” and surface diffusion, as shown in FIG. 5. The plugging involves the steps of metal oxide formation on metal-source surface, release of metal oxide molecules from the source, migration through water, and deposition on the target surface. This is followed by surface diffusion of metal oxide molecules that help forming MONSTRs with smooth crystal facets.

In addition, hierarchical topographies that incorporate multi-scale features with different sizes can further increase the surface area beyond one can achieve with single-length-scale structures. Two-tier hierarchical roughness with micro- and nano-scale components is an ideal example of high surface area materials.

In certain embodiments, an abrasive blasting process, such as sandblasting (SB), is used

to fabricate micro-scale features. Sandblasting is used for a wide variety of purposes like smoothing a rough surface, roughening a smooth surface, shaping a surface, and removing surface contaminants. Sandblasting involves a stream of abrasive material propelled against a surface under high pressure. When the target material is impacted by a hard sharp particle, the contact area is plastically deformed due to the high compressive and shear stresses involved. The large tensile stress produced by sandblasting due to the impact results in lateral cracks on material surface causing material removal. Based on material removal rates, surfaces get rougher due to micro-structures being formed. Higher removal rates typically enhance the roughness formation up to a certain limit. Such simple technique can be effectively used to form materials with micro-scale features of surface area higher than that of the starting material. Although, the features are not in very regular shapes or sizes, which can be controlled by masking the surface and blasting time during the sandblasting process, the micro-sized features can effectively serve as the bases of hierarchical micro-nano-structures with a high surface area.

In certain embodiments, a combination of the SB process and the hot water process is used to fabricate metallic materials with hierarchical micro-nano-structures that acquire superior surface areas compared to either of a micro-rough surface by the SB process or a nano-rough by the hot water process alone. Overall, the SB process is a facile, low-cost, environment-friendly, robust, and scalable surface processing method. The combination of the SB process and the hot water process is still a simple and low-cost fabrication process that combine the advantages of both nanostructured and bulk metallic materials, which gives the metallic materials not only the high surface area and activity of nanomaterials, but also the structural stability and robustness of the bulk.

In one embodiment shown in FIG. 6, a clean metal surface is first sandblasted with abrasive particles followed by the hot water treatment to obtain a hierarchical, micro-nano-structured surface. The sandblasting step is used to engrave the metallic materials surface and gain micro-sized features (micro-structures). The size and geometry of micro-structures can be controlled typically in the range of few to tens of micrometers by changing the abrasive particle size and shape. Furthermore, a variety of microstructures of different lateral sizes and depth (that the abrasive digs into the surface) can be generated by utilizing different types, incidence angles, nozzle-substrate distances, flux, and speed of the abrasive particles which drastically affect the formation of micro-structured surface.

After the sandblasting, the micro-rough metal surface is cleaned using conventional

chemical cleaning processes (e.g., with acetone, isopropanol, and then DI water each for 5 min then dried by N_2 gas) to remove the sandblasting residuals and potential contamination on the surface. A clean sandblasted metal surface is then immersed in hot DI water for the hot water treatment, which is described above. The hot water treatment introduces a nanostructured roughness onto the previously imparted micro-structures, which results in a hierarchical micro-nano-roughness of higher surface area than that of the micro-structured surface. SEM images of different metals processed by the sandblasting and the hot water treatment to form surfaces with hierarchical micro-nano-structured structures with high surface areas are shown in FIGS. 7A-7H. Cu, Al, Zn and Pb metal substrates were sandblasted and then exposed to hot water for 24hrs, 10 min, 2 hrs and 15 min, respectively. The SEM images show the surfaces gained hierarchical micro-nano scaled features compare to pristine metal surface. FIGS. 7A, 7C, 7E, and 7H show the micro-structures of the hierarchical surfaces formed by the sandblasting for Cu, Al, Zn and Pb metal substrates, respectively. FIGS. 7B, 7D, 7F, and 7G show that the micro-structured SB metal surfaces have nanostructures formed on the top of micro-structures after the hot water treatment for Cu, Al, Zn and Pb metal substrates, respectively, which also show different shapes and size of metal oxides for different metals formed after the hot water treatment, e.g., nanoplates, nanograss, nanorods, and thick nanoplates for Cu, Al, Zn and Pb, respectively.

In certain embodiments, as a simple and reproducible method of fabricating micro-scale features, the sandblasting can also be combined with the steam treatment to fabricate metallic materials with hierarchical micro-nano-structures of superior surface areas compared to either a micro-rough surface by the sandblasting or a nano-rough by the steam treatment alone. In addition to microstructured surfaces produced by the sandblasting, a sandblasted surface of high surface area can easily gain more surface area and have the activity of nanomaterials when it is combined with the steam treatment. The successful combination of the sandblasting and the steam treatment makes the fabrication of hierarchical surface even simpler and lower cost.

As illustrated in FIG. 8, a clean metal substrate is first sandblasted with abrasive particles to produce a micro-structured surface of the metal substrate. The scale and size of microstructures of the metal substrate can be easily controlled through the abrasive particle size and shape. The sandblasted metal substrate is then exposed to steam of hot water to pair the surface with nanoscale features (nanostructures). Without any need for further fabrication process, the sandblasting and the steam treatment together can easily produce metallic materials of high surface area at very low cost using this ecofriendly route. FIGS. 9A-9D show the

fabrication of hierarchical micro-nano-structured surfaces of high surface areas by the sandblasting and the steam treatment, where FIGS. 9A and 9C show the micro-structures of the hierarchical structured surface by the sandblasting for Mg and Zn, respectively, and FIGS. 9B and 9D show the nano-scaled metal oxide nanostructures (MgO and ZnO) of the high surface areas formed by the steam treatment for Mg and Zn, respectively.

In certain embodiments, the sandblasting and the hot water process can be further extended to generating patterned surfaces incorporating micro-nano-rough regions of different height. For example, FIGS. 10A-10D illustrate the process of using the sandblasting and the hot water process to form plateaus and valleys of hierarchical roughness. In one embodiment, a shadow mask, e.g., a pre-patterned piece of metal with openings that abrasive particles can pass through, is placed on the top of the metallic material before the sandblasting in order to introduce a desired pattern of micro-rough valleys with smooth plateaus (FIGS. 10A-10B). The shadow mask is removed and the whole surface is gently sandblasted for a short amount of time in order to introduce a micro-roughness to the plateaus that were shadowed under the mask (FIG. 10C). Then, the sample can go through the hot water process that results in a hierarchically micro-nano-rough patterned surface (FIG. 10D). One skilled in the art would appreciate that other types of patterning strategies can also be used to fabricate hierarchically rough surfaces of different patterns by the sandblasting and the hot water process.

High surface area materials can serve either as an active material or support for others to attain enhanced chemical and physical properties. Materials with high surface-to-volume ratios can utilize most of the atoms positioned on the surface that can increase a wide range of properties such as catalysis, adhesion, mass transport, electronic conductivity, and optical absorption. According to the invention, the hot water process can be used can be used effectively to fabricate nanostructured materials of high surface-to-volume ratios that can lead to an increase in the surface areas, as schematically shown in FIG. 11A. As described above, the interaction of liquid water or vapor (steam) with a metallic material at high temperatures leads to the formation of metal oxide nano-structures and hence significantly increases the surface area.

In addition, the sandblasting can be successfully used to engrave the material surface and form features in micro-scale, as schematically shown in FIG. 11B, which can further increase the surface area or serve as a template for applications sensitive to micro-features. Therefore, to generate high surface area hierarchical micro-nano-structured materials, a metallic material is first engraved with micro-structures by the sandblasting. Then, the hot water process can be used

to pair the base micro-structures with metal oxide nanostructures that lead to superior high surface area materials, as schematically shown in FIG. 11C. The resultant material of hierarchical micro-nano-structures owns higher surface areas compared to the initial flat surface or a surface with only nanostructures.

Furthermore, the methods described above are applicable to a wide variety of metallic materials including elemental, alloy, or compound metals or combination of them with other non-metallic materials. In addition, the methods are applicable to almost any geometry including 1D (e.g., wire, rod), 2D (e.g., plate, foil, thin film), and 3D (e.g., powder, pipe, mesh, and foam) metallic materials.

High surface area materials are desired for numerous applications such as catalysis, photonics, optical devices, energy storage, sensors, cooling systems, drinking water generation from air, water production for agriculture, self-cleaning surfaces, semiconductor devices, cooling systems, drinking water generation from air, water production for agriculture, self-cleaning surfaces, semiconductor devices and biotechnology. Increased surface area can drastically enhance chemical and physical properties that can improve the functionality, productivity, and permanence of those applications. The following is a few pf examples of such potential applications.

Control on surface wettability of materials: Nanostructured materials can be used to control surface wettability. A surface with hydrophilic (water-attracting) properties can be tuned to become superhydrophilic when nanostructures are imparted on the surface [37]. On the other hand, a nanostructured material can attain superhydrophobicity (highly water-repellant) when coated with low-surface-energy layers. All the models explaining the wetting behavior of liquids on rough surfaces incorporate surface area as a critical parameter. Overall, the higher the surface area is, the more hydrophilic or hydrophobic the material gets [38]. As a potential application, such a control on the surface wettability can be used in anti-fouling surfaces acting as protectors against the adhesion of unwanted biological species to the hull of boats, ships, or to off-shore platforms. Superhydrophobic surfaces can also impart self-cleaning properties, especially useful on everyday products like home appliances, paint, or clothes. Another example of the application of hydrophilic/hydrophobic surfaces is in devices that function based on heat-transfer between a liquid and solid surface such as heat-pipes and heat-sinks. In addition, anti-fogging and anti-freezing properties can also be introduced by generating high surface area hydrophobic materials by the methods described above. Furthermore, it is possible to generate water from atmosphere

based on condensation of water vapor on hierarchical micro-nano-structured superhydrophilic portions of a surface followed by gathering water droplets through superhydrophobic regions. Finally, oil-water separation is another potential application where oil is selectively removed from water through the engineering of hydrophobicity of a filter's surface.

Enhanced photocatalyst activity: Photocatalyst materials can initiate chemical reactions such as the production of hydrogen and oxygen through water splitting or killing harmful biological species for water purification with the absorption of light and corresponding oxidation/reduction reactions. Metal oxide semiconducting materials like titanium oxide and tungsten oxide are few examples of oxide photocatalyst materials. Therefore, introducing nano-roughness or hierarchical micro-nano-roughness to such oxides using the methods described above can increase their surface area and therefore significantly enhance the catalyst activity, which is directly proportional to the exposed surface area to the external environment. In addition, rough surface can increase the optical absorption that can further enhance photocatalyst activity. Overall, high surface area metal oxide photocatalyst materials of this invention can lead to higher reaction rates and functional efficiency.

High-response sensors: Most gas sensors rely on chemical reactions taking place at their surface. Therefore, having high surface area metal oxides can offer opportunities for advanced sensors with enhanced response even to minute amounts of external stimulus. For example, a gas sensor incorporating zinc oxide nanostructures made by HWT or ST can provide enhanced sensitivity over a wide range of dynamic response to gasses like CO_2, CO, SO_2, O_2, O_3, H_2, Ar, N_2, NH_3. For nanostructured semiconductors, most of the conduction electrons are trapped in the surface states. Therefore, due to the high surface to volume ratio of nanostructures, these electrons can be helped to achieve enhanced response for surface reactions. Hierarchical micro-nano-structures of this invention can further increase such sensor activity due to their enhanced surface area.

Advanced storage devices: Batteries and capacitors are few of the most commonly known examples of electrochemical energy storage devices. Several state-of-the-art and advanced battery and capacitor materials utilize metal oxides as active electrodes. Therefore, high surface area metal oxide electrodes of this invention can provide enhanced electrochemical reaction rates that can significantly improve energy storage in such applications. For example, Li-ion batteries involve cathode materials made of metal oxides like cobalt oxide and vanadium oxide, which can be engineered to have nano- or micro-nano-morphologies using the methods of

this invention. Having high surface area can help increase the electrochemical reactions for lithium ions during charging/discharging and therefore improve charge storage. In addition, the porous nature of the nanostructured and micro-nano-structured cathode surface can enhance the mechanical durability of the electrode against volumetric changes in the electrode due to charging/discharging. Also, capacitors made of high surface area materials such as nickel oxide nanostructures or micro-nano-structures using the methods of this invention can significantly enhance double layer formation at the solid/liquid interface and therefore increase the faradaic charge storage.

Efficient optoelectronic devices: Optoelectronic devices include optical-to-electrical or electrical-to-optical response in their operation. For example, this invention can produce high surface area semiconducting metal oxides for energy conversion applications such as solar cells. Modern solar cell devices that are under development can incorporate p- or n-type metal oxides (e.g., copper oxide as p-type or zinc oxide as n-type) that act as critical components in converting solar energy to electricity. Nanostructured semiconducting materials can offer the advantage of smaller dimensions with higher interface that can allow the development of core-shell type nanostructured solar cells. Such geometry can enhance both light trapping and charge carrier collection and significantly improve the solar cell efficiency. Similarly, a photodetector, which is another example of an optoelectronic device, can benefit from the similar nanostructured metal oxide geometry explained for solar cells and produce superior photo-response.

These and other aspects of the present invention are further described below.

In one aspect, the invention relates to a method of forming metal oxide nanostructures on a metallic material, comprising applying a hot water process to the metallic material, which includes treating the metallic material with hot water under a treatment condition for a period of time so as to form metal oxide nanostructures on a surface of the metallic material, where the treated metallic material with metal oxide nanostructures under the hot water process has a high surface area that is higher than its pristine surface area of the metallic material.

In one embodiment, the hot water is a liquid phase of water, a gas phase of water, or a combination thereof.

In one embodiment, the hot water is stirred at various flow patterns, flown at a direction, or in the steam applied at an angle relative to the surface of the metallic material.

In one embodiment, the hot water comprises a type of water with different levels of purity, resistivity, dissolved oxygen, or mineral content.

In one embodiment, the metallic material comprises one or more metallic compositions including elemental metals, alloys, compounds, a combination thereof, or a combination of metallic and non-metallic materials.

In one embodiment, the metallic material comprises a one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) metallic material. In one embodiment, the 1D metallic material has a fiber, wire or rod geometry, the 2D metallic material has a plate, foil or thin film geometry, or the 3D metallic material has a powder, pipe, mesh or foam geometry.

In one embodiment, the metallic material is in a form of substrate being electrically charged or neutral.

In one embodiment, the treatment condition comprises a temperature in a variety of ranges such that the hot water is liquid water at ambient temperatures, warm water below boiling point, boiling water, or steam at much higher temperatures.

In one embodiment, the treatment condition further comprises a variety of environmental pressures including different atmospheric pressures at different altitudes and high or low pressures achieved in a special container, and a variety of dissolved oxygen levels.

In one embodiment, the method further comprises controlling the treatment condition to determine sizes, morphology, stoichiometry, composition, and phase of the metal oxide nanostructures. In one embodiment, the phase of the metal oxides nanostructures comprises thermally stable stoichiometric oxides and hydroxides.

In one embodiment, the step of treating the metallic material with the hot water comprises immersing the metallic material the hot water, or applying a steam of the hot water at the metallic material.

In one embodiment, the step of treating the metallic material with the hot water is assisted by external physical and chemical factors including radiation, applied electric or magnetic fields, mechanical vibrations, and chemical additives. In one embodiment, the radiation includes microwave, laser, ultraviolet and infrared light, and the chemical additives include metal salt and metal salt solution.

In one embodiment, the method further comprises heating the water, the metallic material, or both of them.

In one embodiment, the method further comprises activating the surface of the metallic material with a pretreatment physical method and/or a pretreatment chemical method so as to enhance formation kinetics of the metal oxide nanostructures during the hot water process. In

one embodiment, the pretreatment chemical method includes acid dipping, or plasma exposure, and the pretreatment physical method includes roughening the surface of the metallic material by polishing, abrasive blasting, and/or a mechanical erosion process.

In one embodiment, the method further comprises, prior to the step of treating the metallic material with the hot water, performing surface patterning and/or roughening on the metallic material, so as to form a hierarchically micro-nano-structured metallic material with a surface area that is substantially higher than the high surface area of the treated metallic material.

In one embodiment, the hot water process produces a solution containing metal oxide molecules, useable for other purposes in addition to metal oxide nanostructure growth.

In another aspect, the invention relates to a nanostructured metallic material formed by the above method.

In yet another aspect, the invention relates to a method of depositing metal oxide nanostructures on a target material, comprising applying a hot water process to a source metallic material and the target material, which includes treating the source metallic material and the target material with hot water under a treatment condition for a period of time so as to form metal oxide nanostructures on a surface of the target material.

In one embodiment, the source metallic material comprises one or more metallic compositions including elemental metals, alloys, compounds, a combination thereof, or a combination of metallic and non-metallic materials.

In one embodiment, the target material is a non-metallic material, a metallic material, or a combination thereof.

In one embodiment, the step of treating the source metallic material with the hot water comprises immersing the source metallic material and the target material in the hot water.

In one embodiment, the step of treating the source metallic material with the hot water is assisted by external physical and chemical factors including radiation, applied electric or magnetic fields, mechanical vibrations, and chemical additives. In one embodiment, the radiation includes microwave, laser, ultraviolet and infrared light, and the chemical additives include metal salt and metal salt solution.

In one embodiment, the method further comprises activating the surface of the target material with a pretreatment physical method and/or a pretreatment chemical method so as to enhance formation kinetics of the metal oxide nanostructures during the hot water process. In one embodiment, the pretreatment chemical method includes acid dipping, or plasma exposure,

and the pretreatment physical method includes roughening the surface of the metallic material by polishing, abrasive blasting, and/or a mechanical erosion process.

In one embodiment, the method further comprises, prior to the step of treating the source metallic material with the hot water, performing surface patterning and/or roughening on the target material, so as to form a hierarchically micro-nano-structured metallic material with a surface area that is substantially higher than the high surface area of the treated target material.

In one embodiment, the hot water process produces a solution containing metal oxide molecules, useable for other purposes in addition to metal oxide nanostructure growth.

In one embodiment, the formation of the metal oxide nanostructures on the surface of the target material metal comprises metal oxide formation on a surface of source metallic material, release of metal oxide molecules from the source metallic material, migration of the metal oxide molecules through water, and deposition of the metal oxide molecules on the surface of the target material, and surface diffusion of the metal oxide molecules so as to form the metal oxide nanostructures with smooth crystal facets on the surface of the target material.

The foregoing description of the exemplary embodiments of the invention has been presented only for the purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Many modifications and variations are possible in light of the above teaching.

The embodiments were chosen and described in order to explain the principles of the invention and their practical application so as to enable others skilled in the art to utilize the invention and various embodiments and with various modifications as are suited to the particular use contemplated. Alternative embodiments will become apparent to those skilled in the art to which the invention pertains without departing from its spirit and scope. Accordingly, the scope of the invention is defined by the appended claims rather than the foregoing description and the exemplary embodiments described therein.

LIST OF REFERENCES

1. McCarvill, W.T. and J.P. Bell, *The effect of time and type of water pretreatment on the bond strength of epoxy–aluminum joints.* Journal of Applied Polymer Science, 1974. **18**(2): p. 335-342.

2. Rider, A.N. and D.R. Arnott, *Boiling water and silane pre-treatment of aluminium alloys for durable adhesive bonding.* International Journal of Adhesion and Adhesives, 2000.

20(3): p. 209-220.

3. Shanmugan, S., D. Mutharasu, and I. Kamarulazizi, *Synthesis and Properties of Nano Structured SnO₂ Thin Films Prepared by Hot Water Oxidation of Metallic Sn Thin Film.* Materials Focus, 2014. **3**(1): p. 48-54.
4. Strålin, A. and T. Hjertbergc, *Improved adhesion strength between aluminum and ethylene copolymers by hydration of the aluminum surface.* Journal of Applied Polymer Science, 1993. **49**(3): p. 511-521.
5. Utsunomiya, H., S. Ueno, and S. Fujihara, *Fabrication of Nanostructured Zinc Oxide Films on Plastic Substrates by Pyrolysis Method and their Application to Dye-Sensitized Solar Cells.* Key Engineering Materials, 2013. **582**: p. 206-209.
6. Vedder, W. and D.A. Vermilyea, *Aluminum + water reaction.* Transactions of the Faraday Society, 1969. **65**: p. 561.
7. Zhang, N., et al., *Novel rose-like ZnO nanoflowers synthesized by chemical vapor deposition.* Materials Letters, 2009. **63**(3-4): p. 496-499.
8. Jeon, N.L., et al., *Patterned polymer growth on silicon surfaces using microcontact printing and surface-initiated polymerization.* Appl. Phys. Lett., 1999. **75**(26): p. 4201.
9. Xia, Y., et al., *Unconventional Methods for Fabricating and Patterning Nanostructures.* Chemical Reviews, 1999. **99**(7): p. 1823-1848.
10. Cao, B. and W. Cai, *From ZnO Nanorods to Nanoplates: Chemical Bath Deposition Growth and Surface-Related Emissions.* J. Phys. Chem. C, 2008. **112**(3): p. 680-685.
11. Cao, X., et al., *Large Scale Fabrication of Quasi-Aligned ZnO Stacking Nanoplates.* J. Phys. Chem. C, 2008. **112**(14): p. 5267-5270.
12. Cheng, J.P., et al., *Oriented ZnO nanoplates on Al substrate by solution growth technique.* Journal of Alloys and Compounds, 2009. **480**(2): p. 741-746.
13. Qiu, Y., W. Chen, and S. Yang, *Facile hydrothermal preparation of hierarchically assembled, porous single-crystalline ZnO nanoplates and their application in dye-sensitized solar cells.* J. Mater. Chem., 2010. **20**(5): p. 1001-1006.
14. Shang, T.-M., et al., *Controlled synthesis of various morphologies of nanostructured zinc oxide: flower, nanoplate, and urchin.* Crystal Research and Technology, 2007. **42**(10): p. 1002-1006.
15. Xu, F., et al., *High-yield synthesis of single-crystalline ZnO hexagonal nanoplates and accounts of their optical and photocatalytic properties.* Appl. Phys. A, 2006. **86**(2): p.

181-185.

16. Howard, R.E., et al., *Microfabrication as a Scientific Tool.* Science, 1983. **221**(4606): p. 117-121.

17. Pease, R.F.W., *Nanolithography and its prospects as a manufacturing technology.* J. Vac. Sci. Technol. B, 1992. **10**(1): p. 278.

18. Zwerger, W., *Nanostructures and mesoscopic systems. Edited byW. P. Kirk andM. A. Reed, Academic Press, London 1992, 551 pp., hardcover $69.95, ISBN 0-12-409660-3.* Adv. Mater., 1992. **4**(10): p. 693-693.

19. Wu, J.-J. and S.-C. Liu, *Catalyst-Free Growth and Characterization of ZnO Nanorods.* The Journal of Physical Chemistry B, 2002. **106**(37): p. 9546-9551.

20. Tan, O., *Nanostructured oxides by high-energy ball milling technique: application as gas sensing materials.* Solid State Ionics, 2004. **172**(1-4): p. 309-316.

21. Broers, A.N., *Nanostructure fabrication methods.* Microelectronic Engineering, 1984. **2**(1-3): p. 57.

22. Krengvirat, W., et al., *Low-temperature crystallization of TiO2 nanotube arrays via hot water treatment and their photocatalytic properties under visible-light irradiation.* Materials Chemistry and Physics, 2013. **137**(3): p. 991-998.

23. Matsuda, A., et al., *Preparation of Titania Nanosheet-Precipitated Coatings on Glass Substrates by Treating SiO 2 -TiO 2 Gel Films with Hot Water Under Vibrations.* Journal of Sol-Gel Science and Technology, 2004. **31**(1-3): p. 229-233.

24. Shanmugan, S. and D. Mutharasu, *Synthesis of In2O3 Thin Films from Indium Thin Film by Hot-Water Oxidation Method.* Metall and Mat Trans A, 2011. **43**(1): p. 6-9.

25. Shanmugan, S., D. Mutharasu, and I. Kamarulazizi, *Synthesis and Properties of Nano Structured SnO₂ Thin Films Prepared by Hot Water Oxidation of Metallic Sn Thin Film.* mater focus, 2014. **3**(1): p. 48-54.

26. Tan, W.K., et al., *Formation of highly crystallized ZnO nanostructures by hot-water treatment of etched Zn foils.* Materials Letters, 2013. **91**: p. 111-114.

27. Saifaldeen, Z.S., et al., *Superamphiphobic aluminum alloy surfaces with micro and nanoscale hierarchical roughness produced by a simple and environmentally friendly technique.* Journal of Materials Science, 2013. **49**(4): p. 1839-1853.

28. Hassan, L.B., N.S. Saadi, and T. Karabacak, *Hierarchically Rough Superhydrophobic Copper Sheets Fabricated by a Sandblasting and Hot Water Treatment Process.* The

International Journal of Advanced Manufacturing Technology, 2017.

29. Khedir, K.R., et al., *Robust Superamphiphobic Nanoscale Copper Sheet Surfaces Produced by a Simple and Environmentally Friendly Technique.* Advanced Engineering Materials, 2014. **17**(7): p. 982-989.

30. Khedir R Khedir*, Z.S.S., Taha Demirkan, Rosure B. Abdulrahman, and Tansel Karabacak, *Growth of ZnO Nanorod and Nanoflower Structures by Facile Treatment of Zinc Thin Films in Boiling De-Ionized Water.*

31. Holze, R., *R.C. Alkire and D.M. Kolb (eds): Advances in electrochemical science and engineering, vol. 8, Wiley-VCH, Weinheim, 2003, 378 p., 159€; ISBN 3-527-30211-5.* Journal of Solid State Electrochemistry, 2005. **11**(3): p. 434-436.

32. Marcus, P. and V. Maurice, *Passivity of Metals and Alloys*, in *Materials Science and Technology: A Comprehensive Treatment*. Wiley-Blackwell. p. 131-169.

33. Marcus, P. and V. Maurice, *Oxide Passive Films and Corrosion Protection*, in *Oxide Ultrathin Films*. 2012, Wiley-Blackwell. p. 119-144.

34. Schultze, J.W. and M.M. Lohrengel, *Stability, reactivity and breakdown of passive films. Problems of recent and future research.* Electrochimica Acta, 2000. **45**(15-16): p. 2499-2513.

35. Strehblow, H.-H. and V. Maurice, *Passivity of Metals*, in *Corrosion Mechanisms in Theory and Practice, Third Edition*. 2011, Informa UK Limited. p. 235-326.

36. Svoboda, R. and D.A. Palmer. *Behaviour of copper in generator stator cooling-water systems*. in *15th International Conference for the Properties of Water and Steam, Berlin, Germany*. 2008.

37. Tuteja, A., et al., *Design Parameters for Superhydrophobicity and Superoleophobicity.* MRS Bull., 2008. **33**(08): p. 752-758.

38. Bhushan, B. and M. Nosonovsky, *The rose petal effect and the modes of superhydrophobicity.* Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 2010. **368**(1929): p. 4713-4728.

39. Saifaldeen, Z.S., et al., Superamphiphobic aluminum alloy surfaces with micro and nanoscale hierarchical roughness produced by a simple and environmentally friendly technique. Journal of Materials Science, 2013. 49(4): p. 1839-1853.

40. Khedir, K.R., et al., Robust Superamphiphobic Nanoscale Copper Sheet Surfaces Produced by a Simple and Environmentally Friendly Technique. Advanced Engineering

Materials, 2014. 17(7): p. 982-989.

41. Khedir R Khedir, Z.S.S., TahaDemirkan, Rosure B. Abdulrahman, and TanselKarabacak, Growth of ZnONanorod and Nanoflower Structures by Facile Treatment of Zinc Thin Films in Boiling De-Ionized Water. Nano Communications, in-print.
42. Krengvirat, W., et al., Low-temperature crystallization of TiO2 nanotube arrays via hot water treatment and their photocatalytic properties under visible-light irradiation. Materials Chemistry and Physics, 2013. 137(3): p. 991-998.
43. Matsuda, A., et al., Preparation of TitaniaNanosheet-Precipitated Coatings on Glass Substrates by Treating SiO 2 -TiO 2 Gel Films with Hot Water Under Vibrations. Journal of Sol-Gel Science and Technology, 2004. 31(1-3): p. 229-233.
44. Shanmugan, S. and D. Mutharasu, Synthesis of In2O3 Thin Films from Indium Thin Film by Hot-Water Oxidation Method. Metall and Mat Trans A, 2011. 43(1): p. 6-9.
45. Shanmugan, S., D. Mutharasu, and I. Kamarulazizi, Synthesis and Properties of Nano Structured SnO_2 Thin Films Prepared by Hot Water Oxidation of Metallic Sn Thin Film. mater focus, 2014. 3(1): p. 48-54.
46. Tan, W.K., et al., Formation of highly crystallized ZnO nanostructures by hot-water treatment of etched Zn foils. Materials Letters, 2013. 91: p. 111-114.
47. Saifaldeen, Z.S., K.R. Khedir, M.T. Camci, A. Ucar, S. Suzer, and T. Karabacak, *The effect of polar end of long-chain fluorocarbon oligomers in promoting the superamphiphobic property over multi-scale rough Al alloy surfaces.* Applied Surface Science, 2016. **379**: p. 55-65.

CLAIMS

What is claimed is:

1. A method of forming metal oxide nanostructures on a metallic material, comprising:

applying a hot water process to the metallic material, comprising treating the metallic material with hot water under a treatment condition for a period of time so as to form metal oxide nanostructures on a surface of the metallic material, wherein the treated metallic material with metal oxide nanostructures under the hot water process has a high surface area that is higher than its pristine surface area of the metallic material.

2. The method of claim 1, wherein the hot water is a liquid phase of water, a gas phase of water, or a combination thereof.

3. The method of claim 2, wherein the step of treating the metallic material with the hot water comprises immersing the metallic material the hot water, or applying a steam of the hot water at the metallic material.

4. The method of claim 3, wherein the hot water is stirred at various flow patterns, flown at a direction, or in the steam applied at an angle relative to the surface of the metallic material.

5. The method of claim 1, wherein the hot water comprises a type of water with different levels of purity, resistivity, dissolved oxygen, or mineral content.

6. The method of claim 1, wherein the metallic material comprises one or more metallic compositions including elemental metals, alloys, compounds, a combination thereof, or a combination of metallic and non-metallic materials.

7. The method of claim 1, wherein the metallic material comprises a one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) metallic material.

8. The method of claim 7, wherein the 1D metallic material has a fiber, wire or rod geometry, the 2D metallic material has a plate, foil or thin film geometry, or the 3D

metallic material has a powder, pipe, mesh or foam geometry.

9. The method of claim 7, wherein the metallic material is in a form of substrate being electrically charged or neutral.

10. The method of claim 1, wherein the treatment condition comprises a temperature in a variety of ranges such that the hot water is liquid water at ambient temperatures, warm water below boiling point, boiling water, or steam at much higher temperatures.

11. The method of claim 10, wherein the treatment condition further comprises a variety of environmental pressures including different atmospheric pressures at different altitudes and high or low pressures achieved in a special container, and a variety of dissolved oxygen levels.

12. The method of claim 11, further comprising controlling the treatment condition to determine sizes, morphology, stoichiometry, composition, and phase of the metal oxide nanostructures.

13. The method of claim 12, wherein the phase of the metal oxides nanostructures comprises thermally stable stoichiometric oxides and hydroxides.

14. The method of claim 1, further comprising heating the water, the metallic material, or both of them.

15. The method of claim 1, wherein the step of treating the metallic material with the hot water is assisted by external physical and chemical factors including radiation, applied electric or magnetic fields, mechanical vibrations, and chemical additives.

16. The method of claim 15, wherein the radiation includes microwave, laser, ultraviolet and infrared light, and the chemical additives include metal salt and metal salt solution.

17. The method of claim 1, further comprising activating the surface of the metallic material with a pretreatment physical method and/or a pretreatment chemical method so as to

enhance formation kinetics of the metal oxide nanostructures during the hot water process.

18. The method of claim 17, wherein the pretreatment chemical method includes acid dipping, or plasma exposure, and the pretreatment physical method includes roughening the surface of the metallic material by polishing, abrasive blasting, and/or a mechanical erosion process.

19. The method of claim 1, further comprising, prior to the step of treating the metallic material with the hot water, performing surface patterning and/or roughening on the metallic material, so as to form a hierarchically micro-nano-structured metallic material with a surface area that is substantially higher than the high surface area of the treated metallic material.

20. The method of claim 1, wherein the hot water process produces a solution containing metal oxide molecules, useable for other purposes in addition to metal oxide nanostructure growth.

21. A nanostructured metallic material formed by the method of claim 1.

22. A method of depositing metal oxide nanostructures on a target material, comprising:

applying a hot water process to a source metallic material and the target material, comprising treating the source metallic material and the target material with hot water under a treatment condition for a period of time so as to form metal oxide nanostructures on a surface of the target material.

23. The method of claim 22, wherein the source metallic material comprises one or more metallic compositions including elemental metals, alloys, compounds, a combination thereof, or a combination of metallic and non-metallic materials.

24. The method of claim 22, wherein the target material is a non-metallic material, a metallic material, or a combination thereof.

25. The method of claim 22, wherein the step of treating the source metallic material with the hot water comprises immersing the source metallic material and the target material in the hot water.

26. The method of claim 22, wherein the step of treating the source metallic material with the hot water is assisted by external physical and chemical factors including radiation, applied electric or magnetic fields, mechanical vibrations, and chemical additives.

27. The method of claim 26, wherein the radiation includes microwave, laser, ultraviolet and infrared light, and the chemical additives include metal salt and metal salt solution.

28. The method of claim 22, further comprising activating the surface of the target material with a pretreatment physical method and/or a pretreatment chemical method so as to enhance formation kinetics of the metal oxide nanostructures during the hot water process.

29. The method of claim 28, wherein the pretreatment chemical method includes acid dipping, or plasma exposure, and the pretreatment physical method includes roughening the surface of the metallic material by polishing, abrasive blasting, and/or a mechanical erosion process.

30. The method of claim 22, further comprising, prior to the step of treating the source metallic material with the hot water, performing surface patterning and/or roughening on the target material, so as to form a hierarchically micro-nano-structured metallic material with a surface area that is substantially higher than the high surface area of the treated target material.

31. The method of claim 22, wherein the hot water process produces a solution containing metal oxide molecules, useable for other purposes in addition to metal oxide nanostructure growth.

32. The method of claim 22, wherein the formation of the metal oxide nanostructures on the surface of the target material metal comprises metal oxide formation on a surface of

source metallic material, release of metal oxide molecules from the source metallic material, migration of the metal oxide molecules through water, and deposition of the metal oxide molecules on the surface of the target material, and surface diffusion of the metal oxide molecules so as to form the metal oxide nanostructures with smooth crystal facets on the surface of the target material.

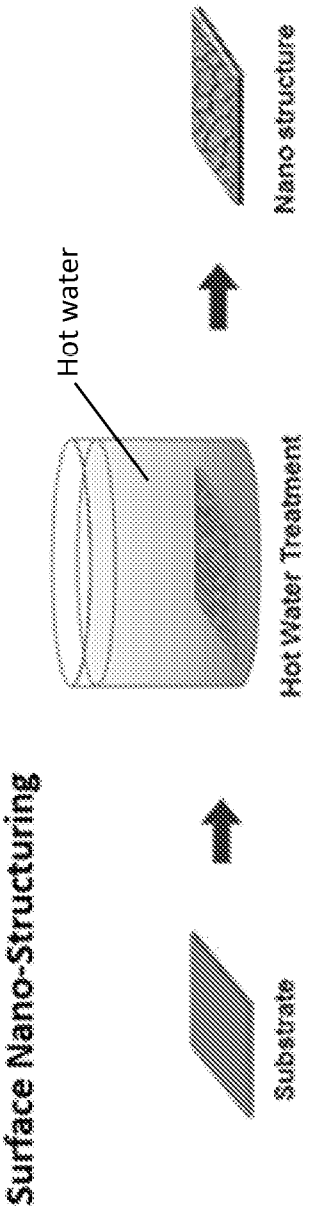

Surface Nano-Structuring
Substrate
Hot water
Hot Water Treatment
Nano structure

FIG. 1A

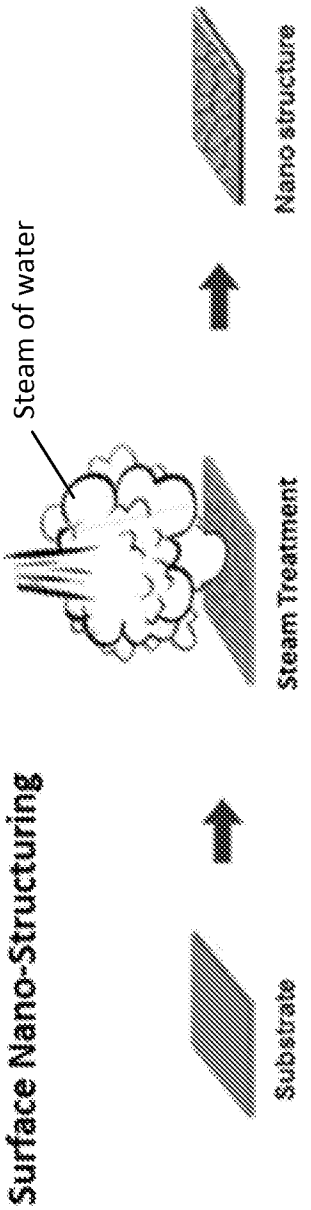

Surface Nano-Structuring
Substrate
Steam of water
Steam Treatment
Nano structure

FIG. 1B

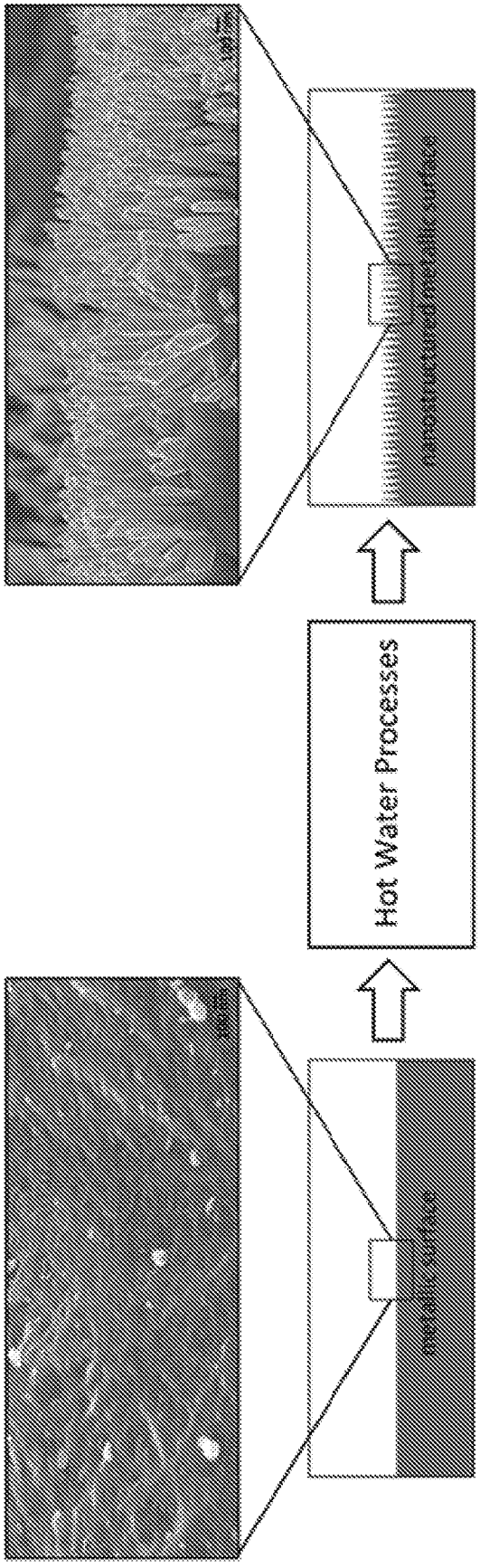


FIG. 1C

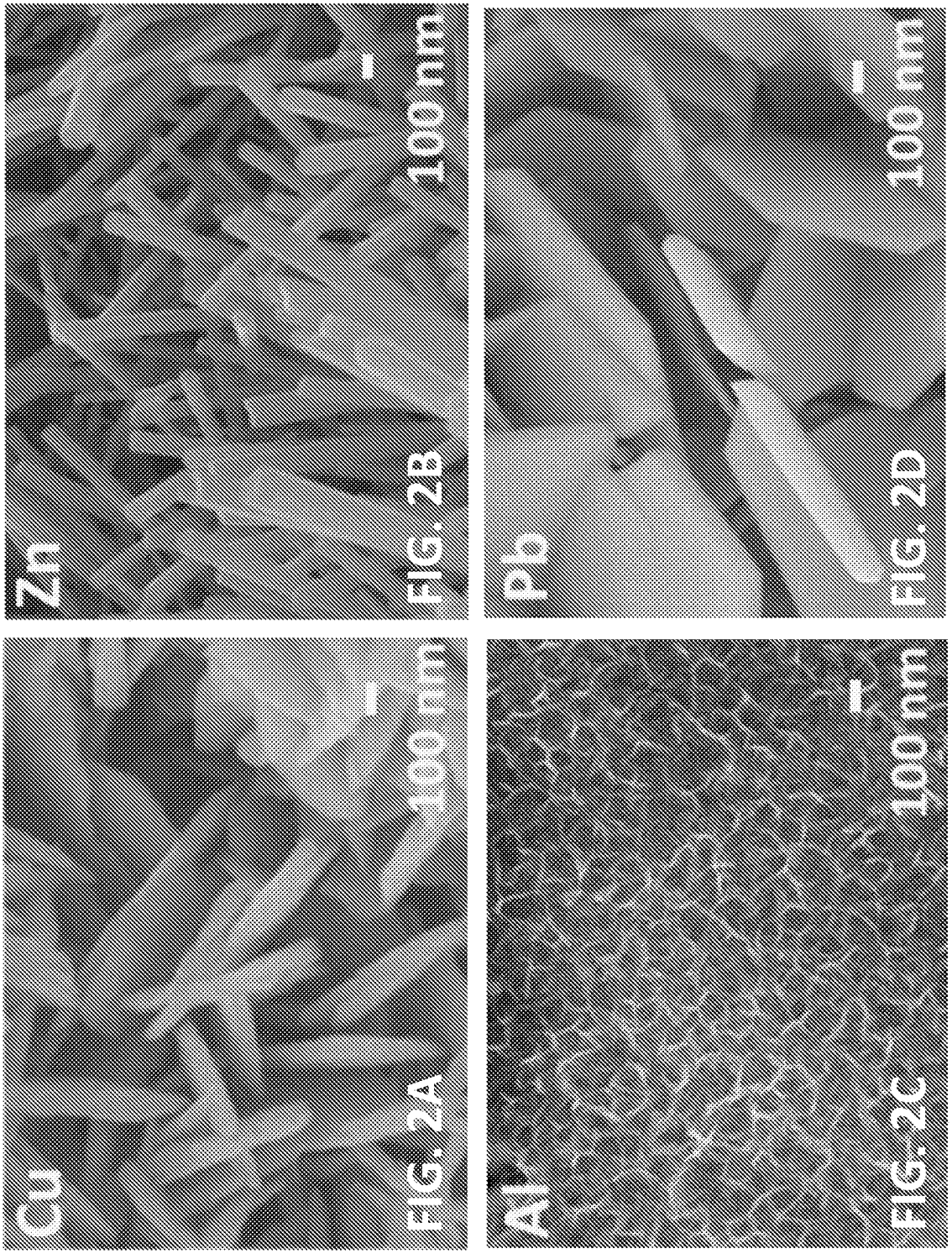


FIG. 2A FIG. 2B

FIG. 2C FIG. 2D

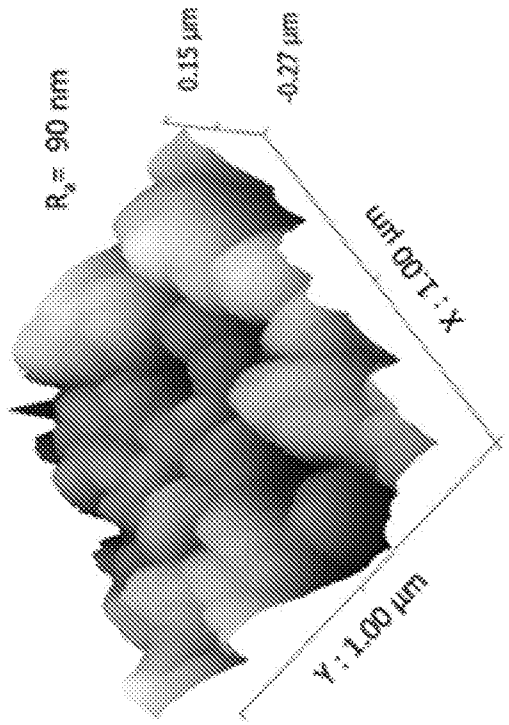

R_a = 90 nm
0.15 µm
-0.27 µm
X : 1.00 µm
Y : 1.00 µm

FIG. 3B

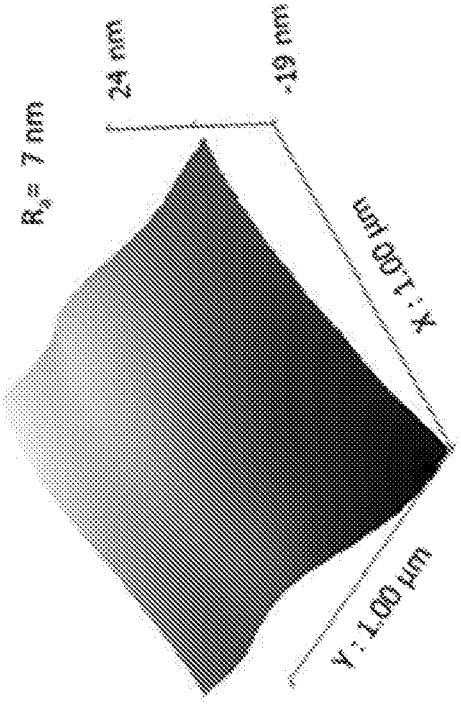

R_a = 7 nm
24 nm
-19 nm
X : 1.00 µm
Y : 1.00 µm

FIG. 3A

FIG. 4A

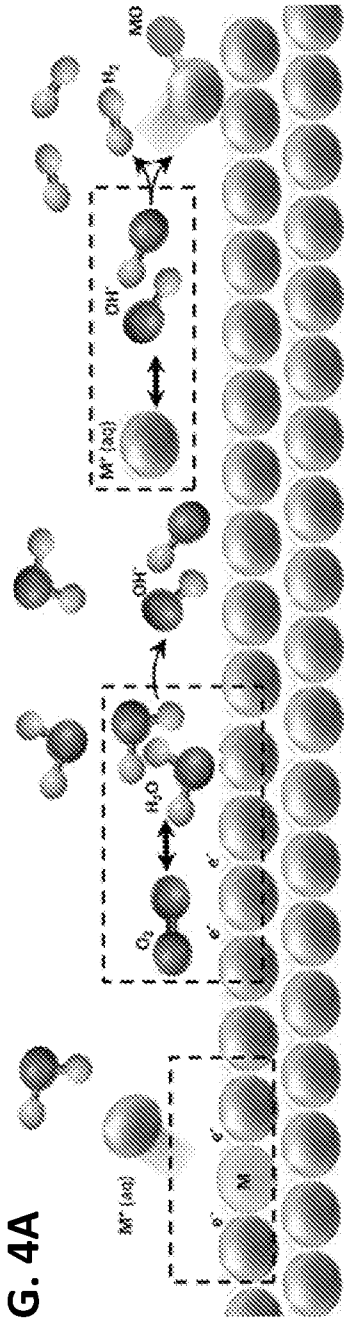
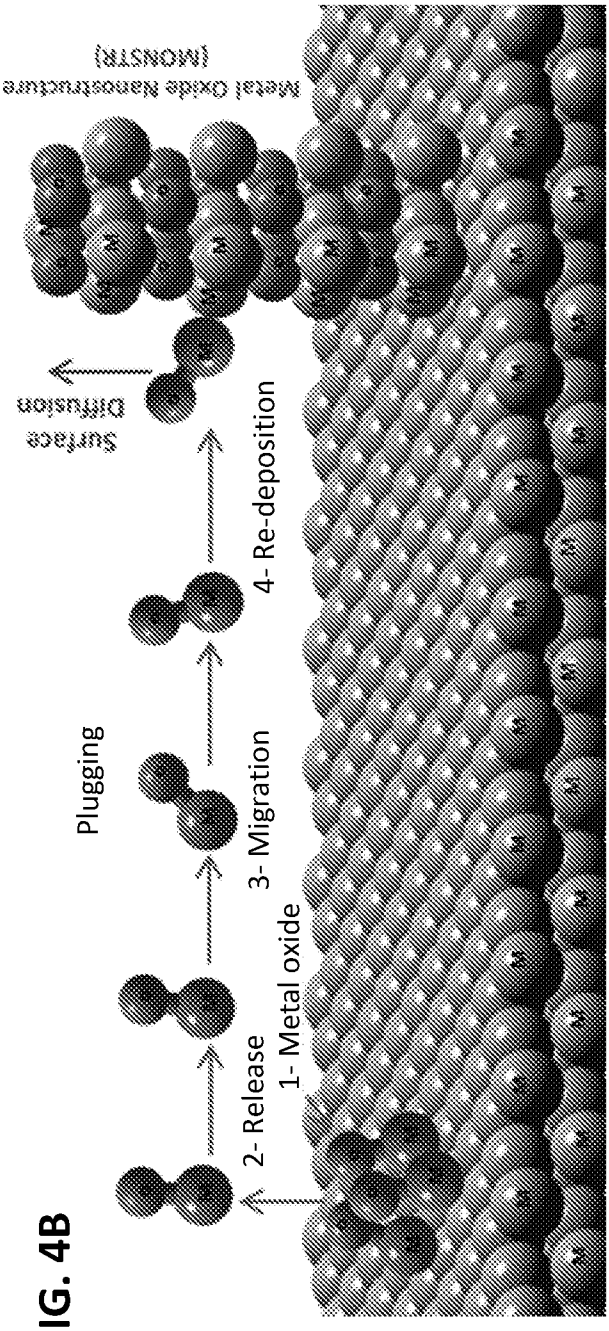


FIG. 4B


Metal Oxide Nanostructure
(MONSTR)
Surface
Diffusion
Plugging
1- Metal oxide
2- Release
3- Migration
4- Re-deposition

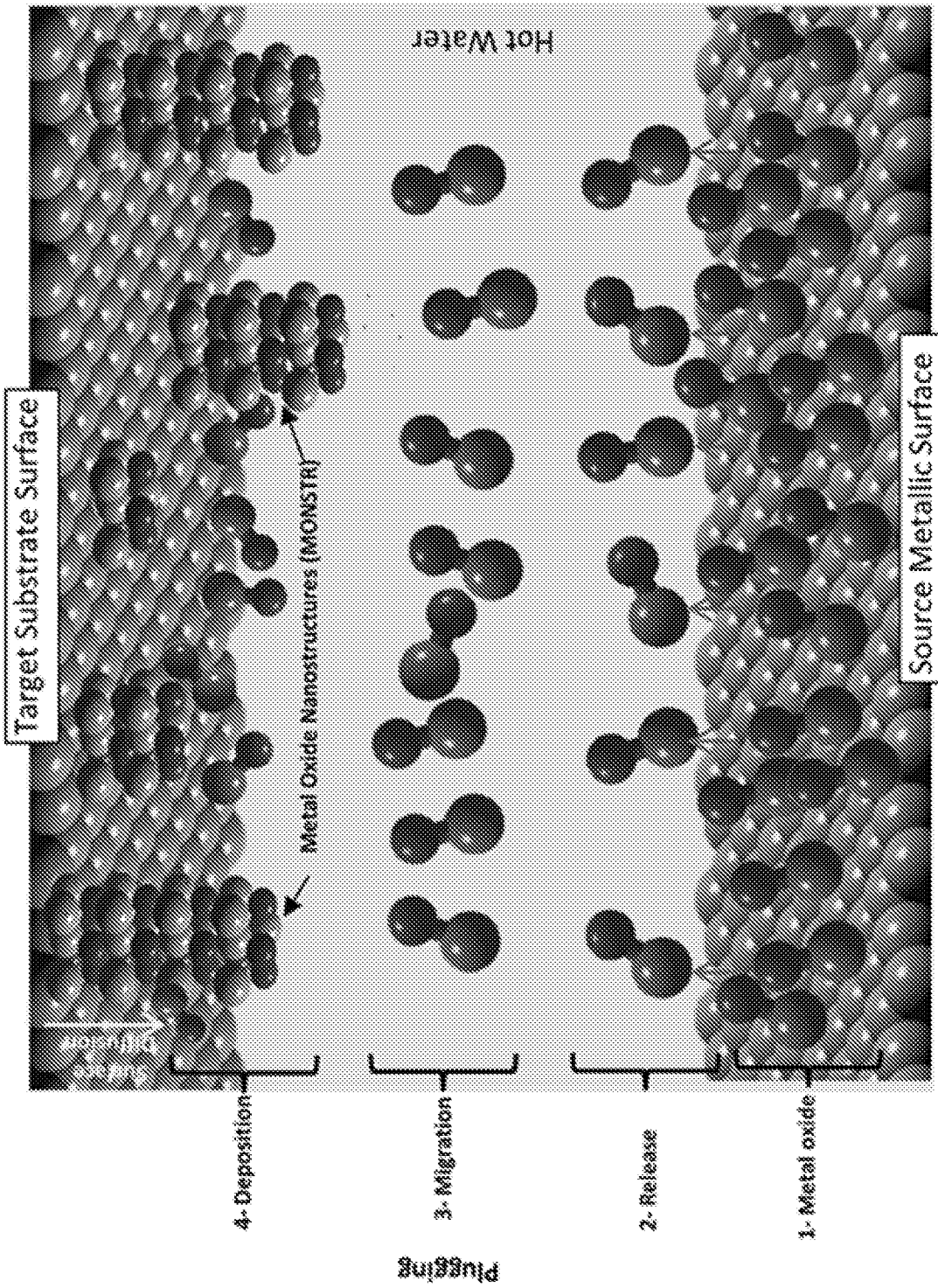

Target Substrate Surface
Metal Oxide Nanostructures (MONSTR)
Hot Water
Source Metallic Surface
4- Deposition
3- Migration
2- Release
1- Metal oxide
Plugging

FIG. 5

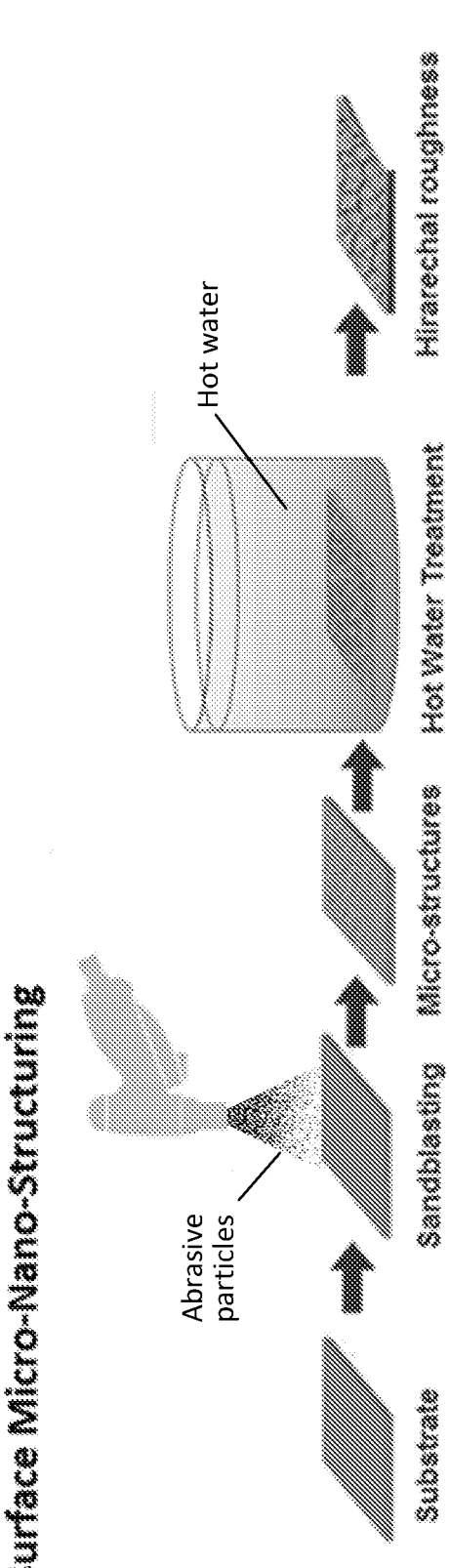


FIG. 6

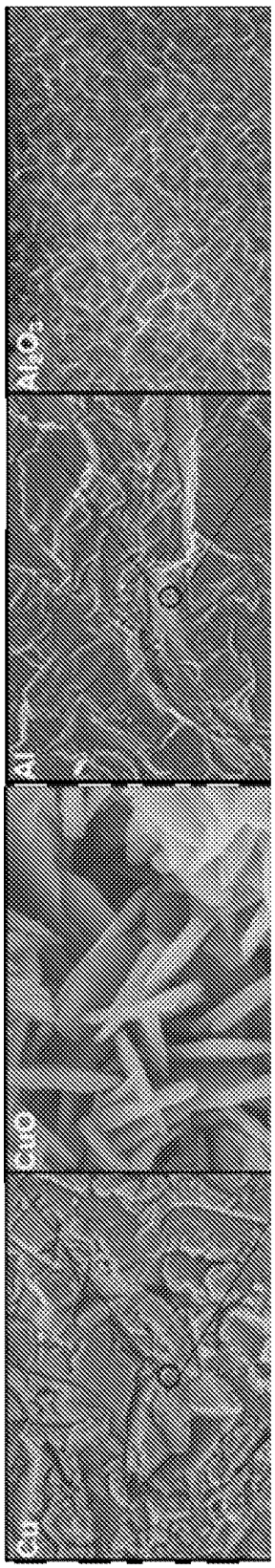


FIG. 7A FIG. 7B FIG. 7C FIG. 7D

FIG. 7E FIG. 7F FIG. 7G FIG. 7H

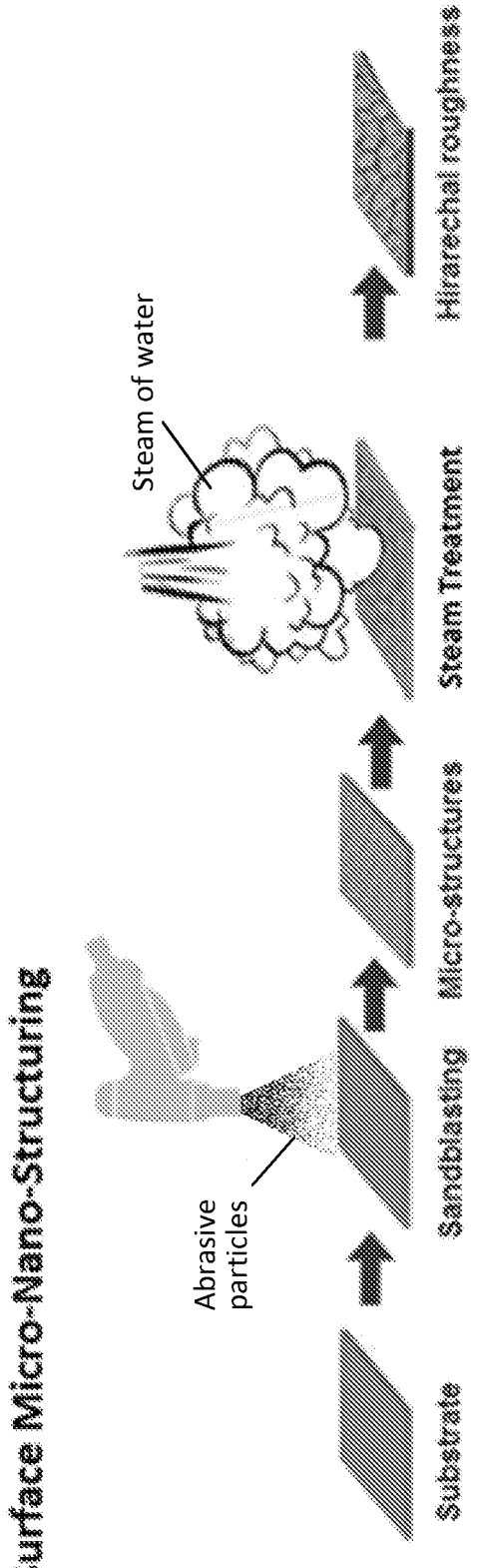


FIG. 8

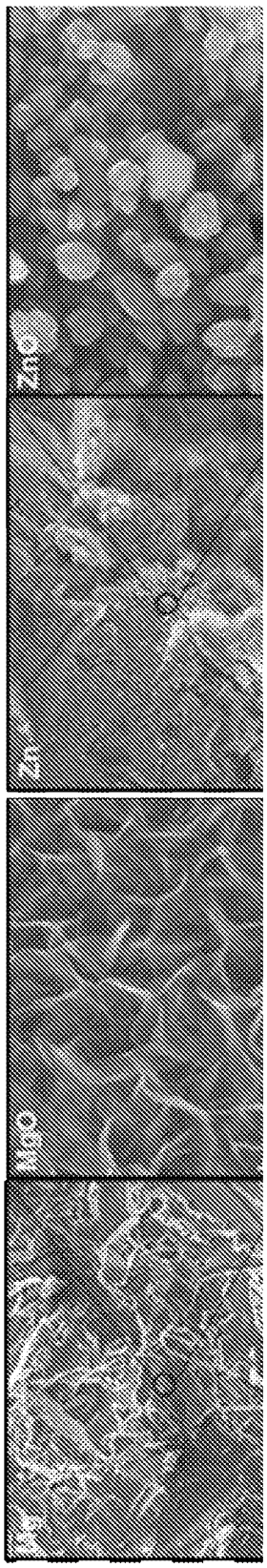


FIG. 9A FIG. 9B FIG. 9C FIG. 9D

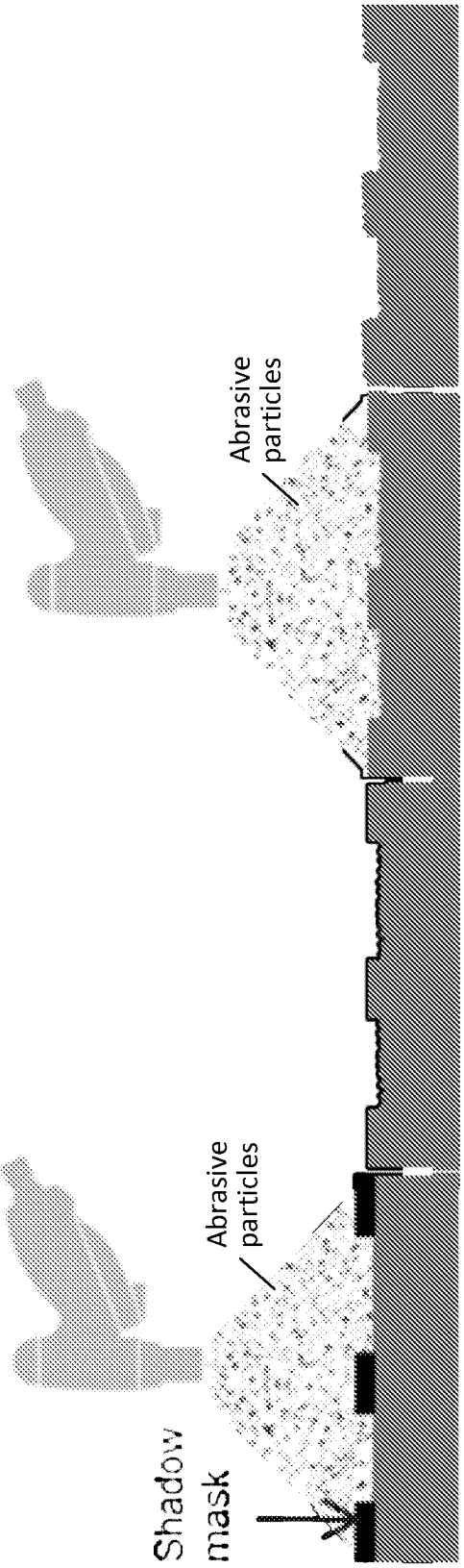


FIG. 10A FIG. 10B FIG. 10C FIG. 10D

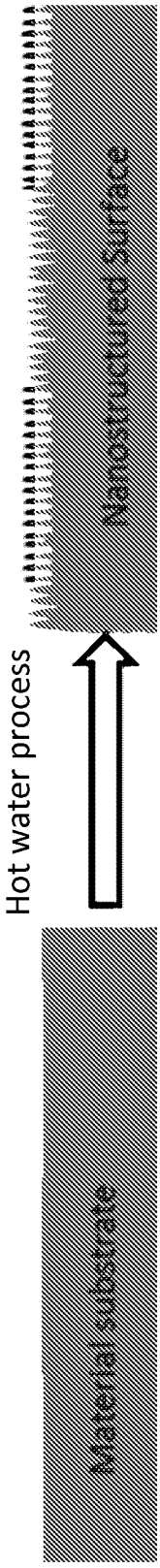


FIG. 11A

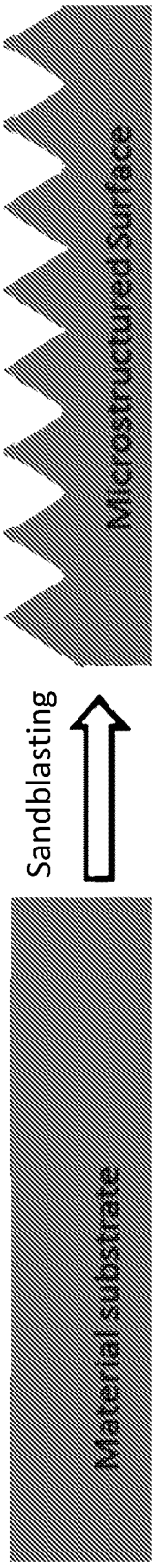


FIG. 11B



FIG. 11C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/038165

A. CLASSIFICATION OF SUBJECT MATTER

C01B 13/36(2006.01)i

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)
C01B 13/36; B05D 3/10; B05D 5/06; B32B 3/00; C09D 5/00; G02B 1/02; G02B 1/11; H01L 21/34; H01L 29/66

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: metal oxide nanostructre, metallic material, hot water, high surface area, target

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HASSAN, LAYLAN B. et al., 'Hierarchically rough superhydrophobic copper sheets fabricated by a sandblasting and hot water treatment process', The International Journal of Advanced Manufacturing Technology, 2017.06.06 (online), vol. 93, issue 1-4, pages 1107-1114 (internal pages 1-7) See abstract; pages 3, 5; and figures 1, 4.	1-32
X	US 2013-0260096 A1 (CANON KABUSHIKI KAISHA) 03 October 2013 See paragraphs [0042], [0044], [0065]-[0076], [0081]; claim 5; and figures 2A, 2B, 3A, 3B.	1-13,21-25
X	US 2010-0247758 A1 (NAKAYAMA, TOMONARI et al.) 30 September 2010 See paragraphs [0068]-[0075]; claim 6; and figures 2C, 2D.	1-13,21-25
X	US 2012-0207973 A1 (SAKAI, AKIRA et al.) 16 August 2012 See paragraphs [0041]-[0043]; claims 4-7; and figure 1.	1-13,21-25
A	US 2011-0049467 A1 (CHO, HYUNG KOUN et al.) 03 March 2011 See the whole document.	1-32

☒ 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	Date of mailing of the international search report
31 October 2018 (31.10.2018)	**01 November 2018 (01.11.2018)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
NAM, EUI HO
Telephone No. +82-42-481-5580

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/038165

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	SAADI, NAWZAT S. et al., 'Metal oxide nanostructures by a simple hot water treatment', Scientific reports, 2017.08.02 (online), vol. 7, no. 7158, pages 1-8 See the whole document.	1-32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2018/038165

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013-0260096 A1	03/10/2013	CN 103364848 A	23/10/2013
		CN 103364848 B	05/08/2015
		EP 2645136 A1	02/10/2013
		EP 2645136 B1	18/01/2017
		JP 2013-228728 A	07/11/2013
		JP 6207199 B2	04/10/2017
US 2010-0247758 A1	30/09/2010	EP 2236462 A2	06/10/2010
		EP 2236462 A3	16/02/2011
		EP 2236462 B1	11/05/2016
		JP 2010-254553 A	11/11/2010
		JP 5645435 B2	24/12/2014
		US 8709144 B2	29/04/2014
US 2012-0207973 A1	16/08/2012	CN 102645681 A	22/08/2012
		CN 102645681 B	06/05/2015
		CN 104765079 A	08/07/2015
		CN 104765079 B	12/04/2017
		EP 2490047 A2	22/08/2012
		EP 2490047 A3	31/10/2012
		EP 2490047 B1	04/07/2018
		EP 2490048 A2	22/08/2012
		EP 2490048 A3	31/10/2012
		EP 2490048 B1	26/07/2017
		JP 2012-185495 A	27/09/2012
		JP 6172889 B2	02/08/2017
		US 2016-0061998 A1	03/03/2016
US 2011-0049467 A1	03/03/2011	KR 10-1137632 B1	20/04/2012
		KR 10-2011-0020963 A	04/03/2011
		US 8202761 B2	19/06/2012