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(54) **SYNTHESIS OF METAL-OXYGEN BASED MATERIALS WITH CONTROLLED POROSITY BY OXIDATIVE DEALLOYING**

(71) Applicant: **Wisconsin Alumni Research Foundation**, Madison, WI (US)

(72) Inventor: **John Harry Perepezko**, Madison, WI (US)

(73) Assignee: **WISCONSIN ALUMNI RESEARCH FOUNDATION**, Madison, WI (US)

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See application file for complete search history.

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*Primary Examiner* — Steven J Bos

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**ABSTRACT**

Functional materials and methods for making the functional materials are provided. Also provided are methods for utilizing the functional materials in a variety of applications, including catalysis, adsorption, energy storage, and biomedical applications. The functional materials are made from metal alloys via an oxidative dealloying process that selectively removes one or more elements from the metal alloy and converts one or more of the remaining elements into a stable metal-oxygen matrix having a controlled porosity.

**22 Claims, 6 Drawing Sheets**

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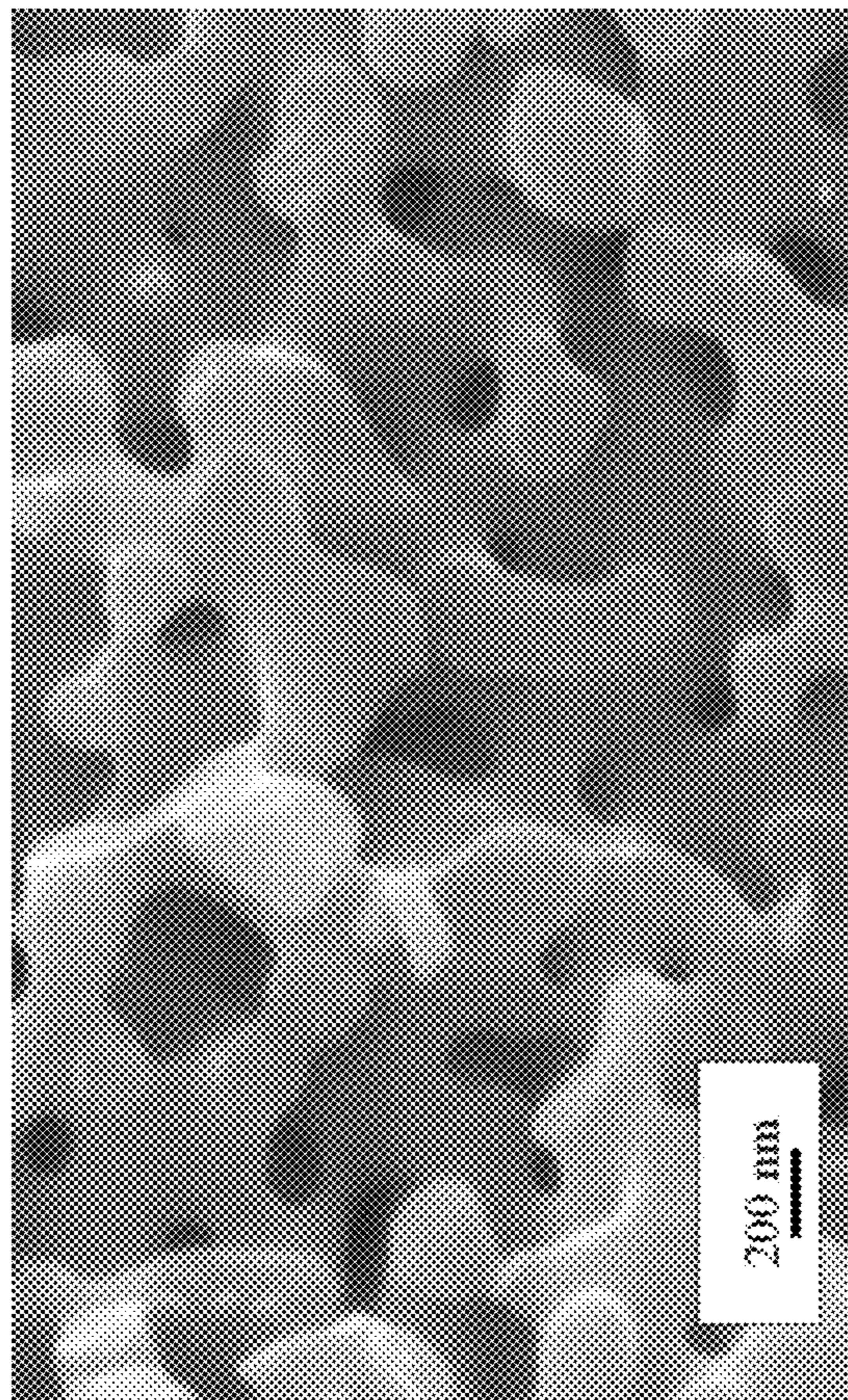


FIG. 1

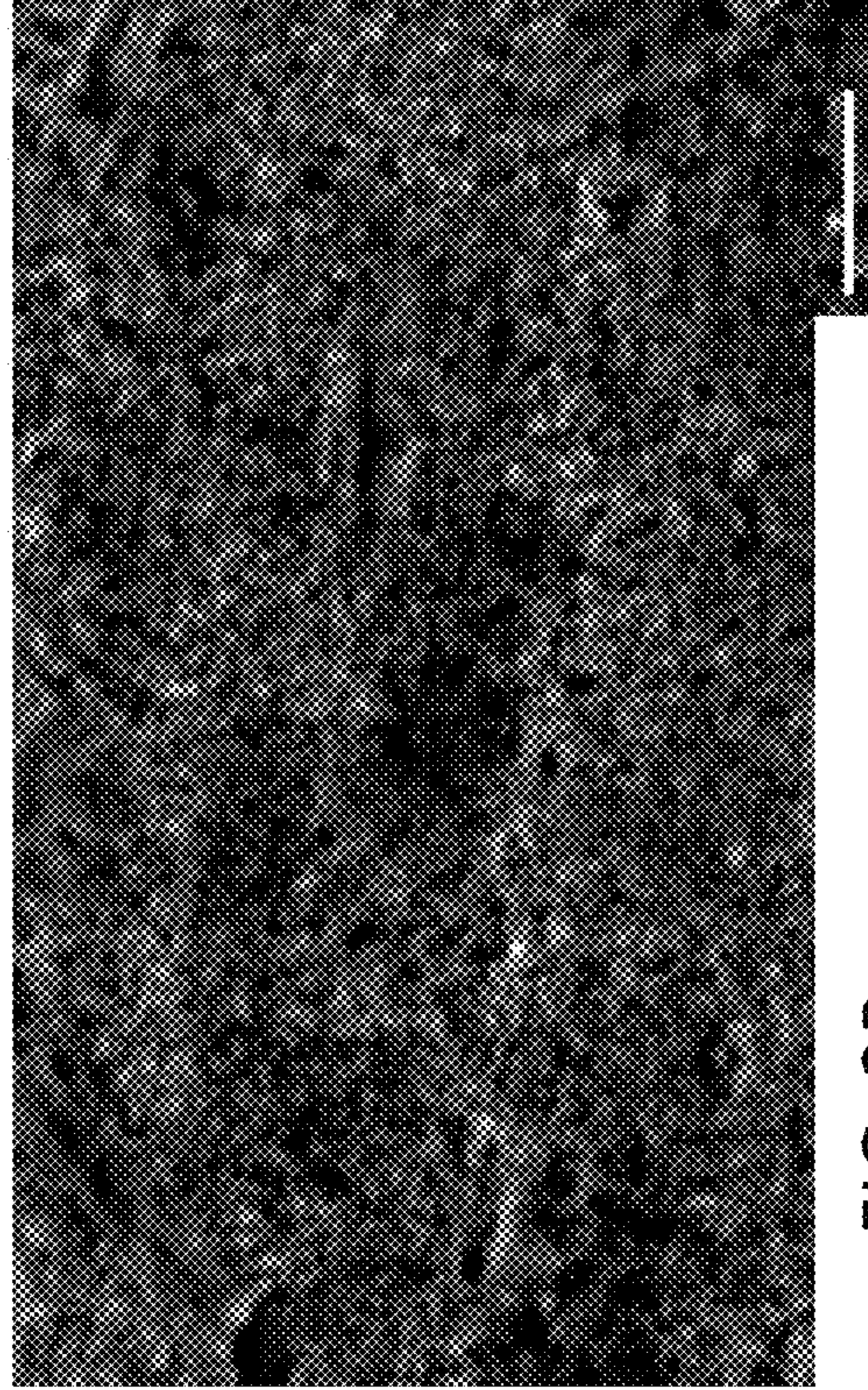


FIG. 2B

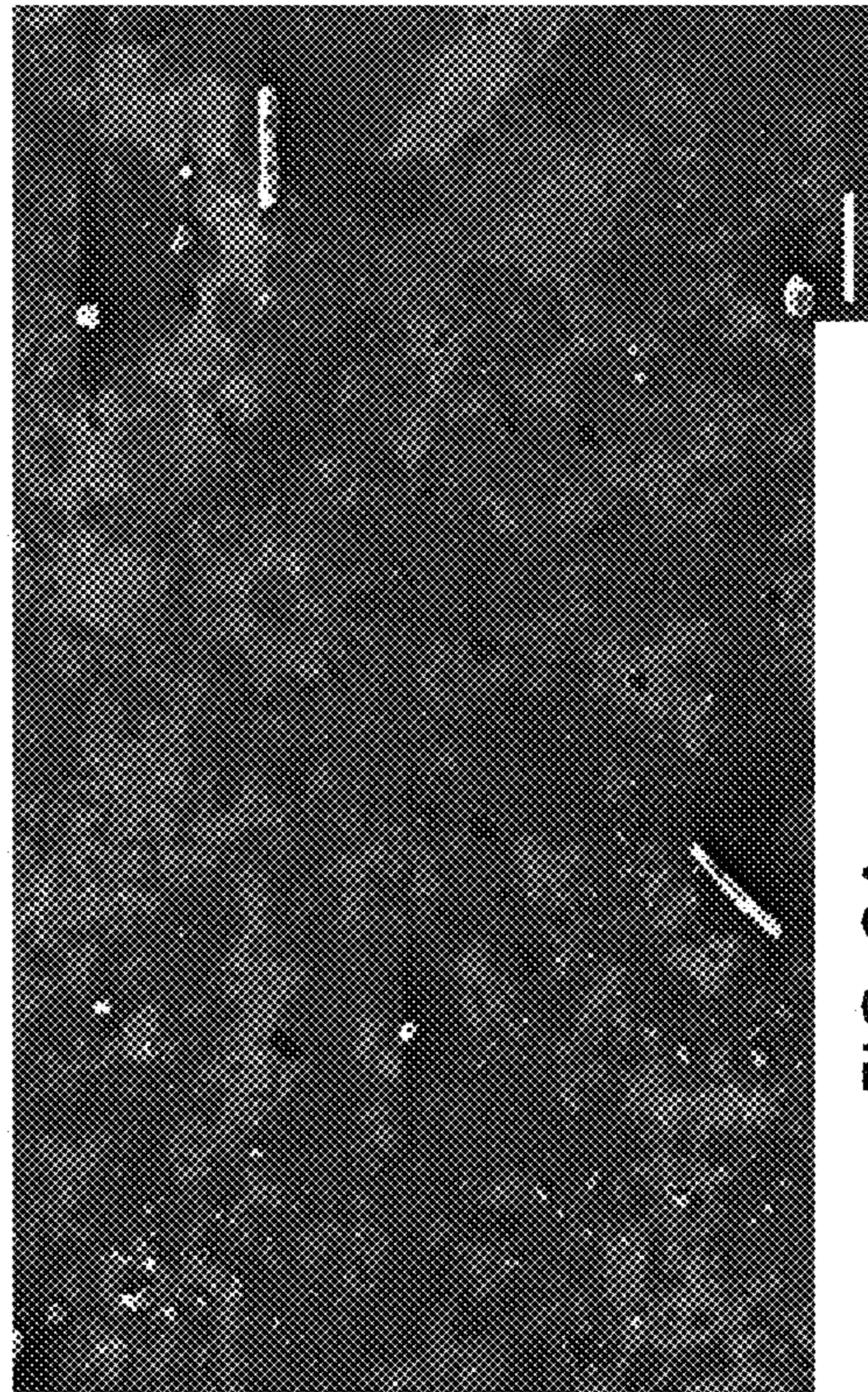


FIG. 2A

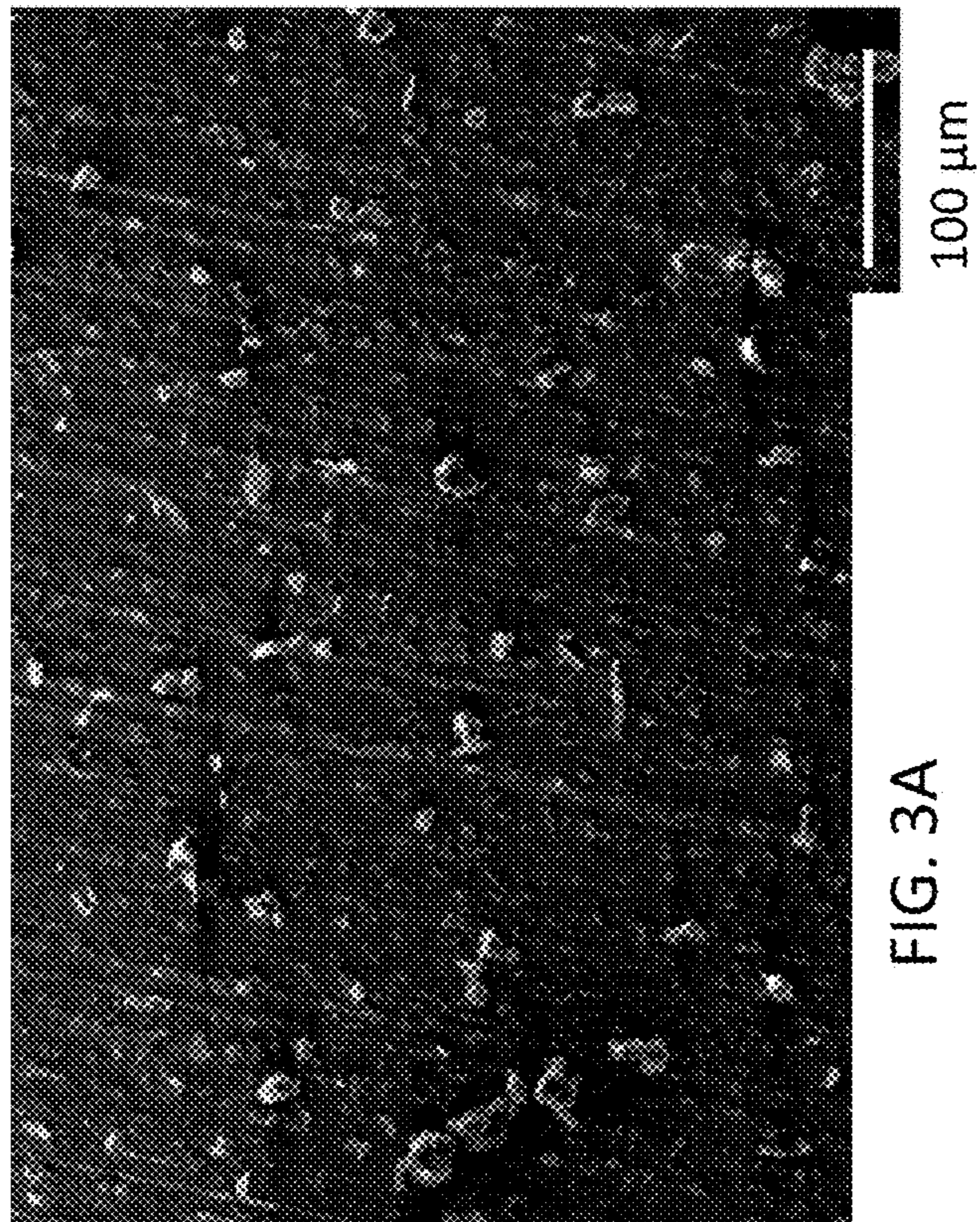
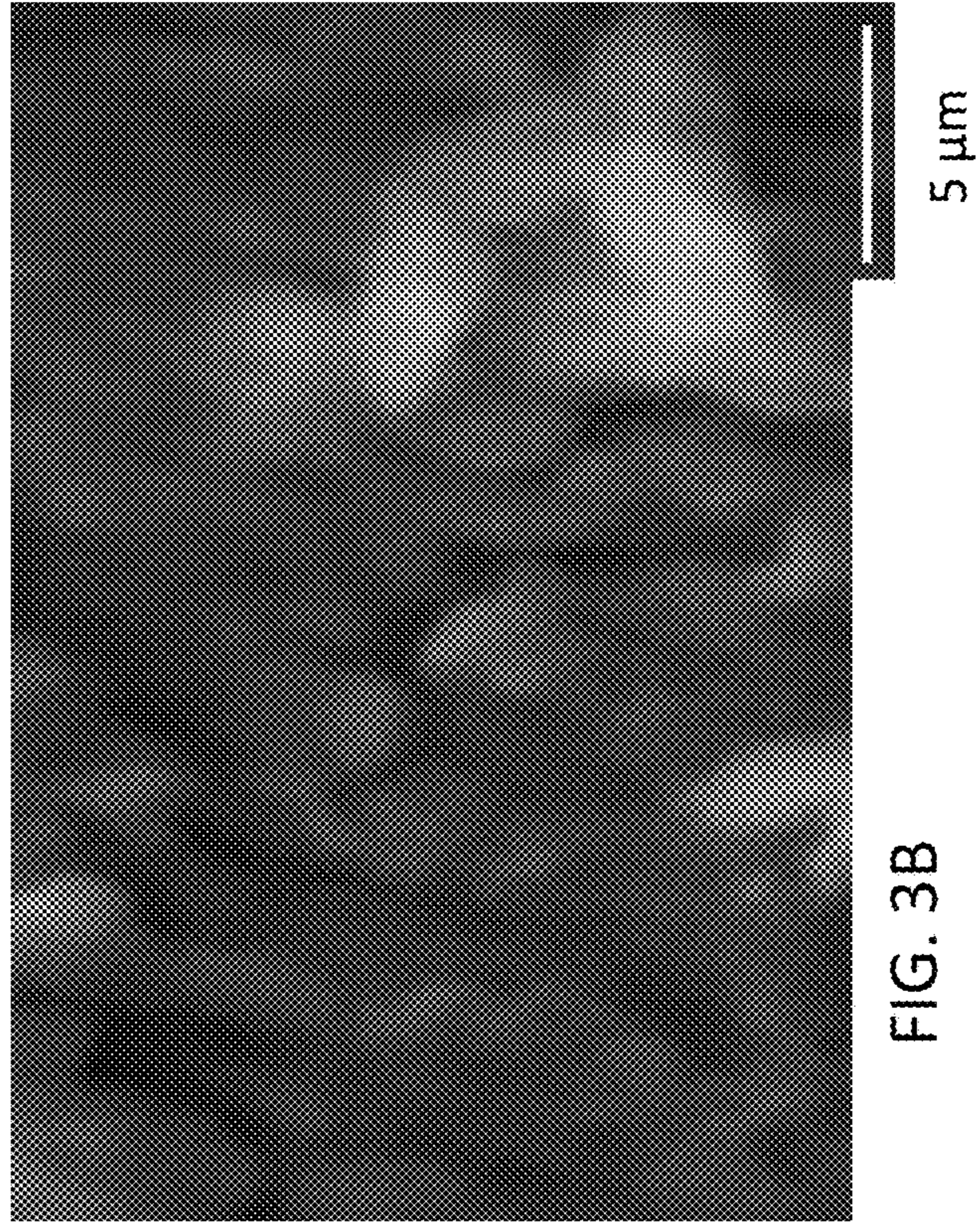




FIG. 4B

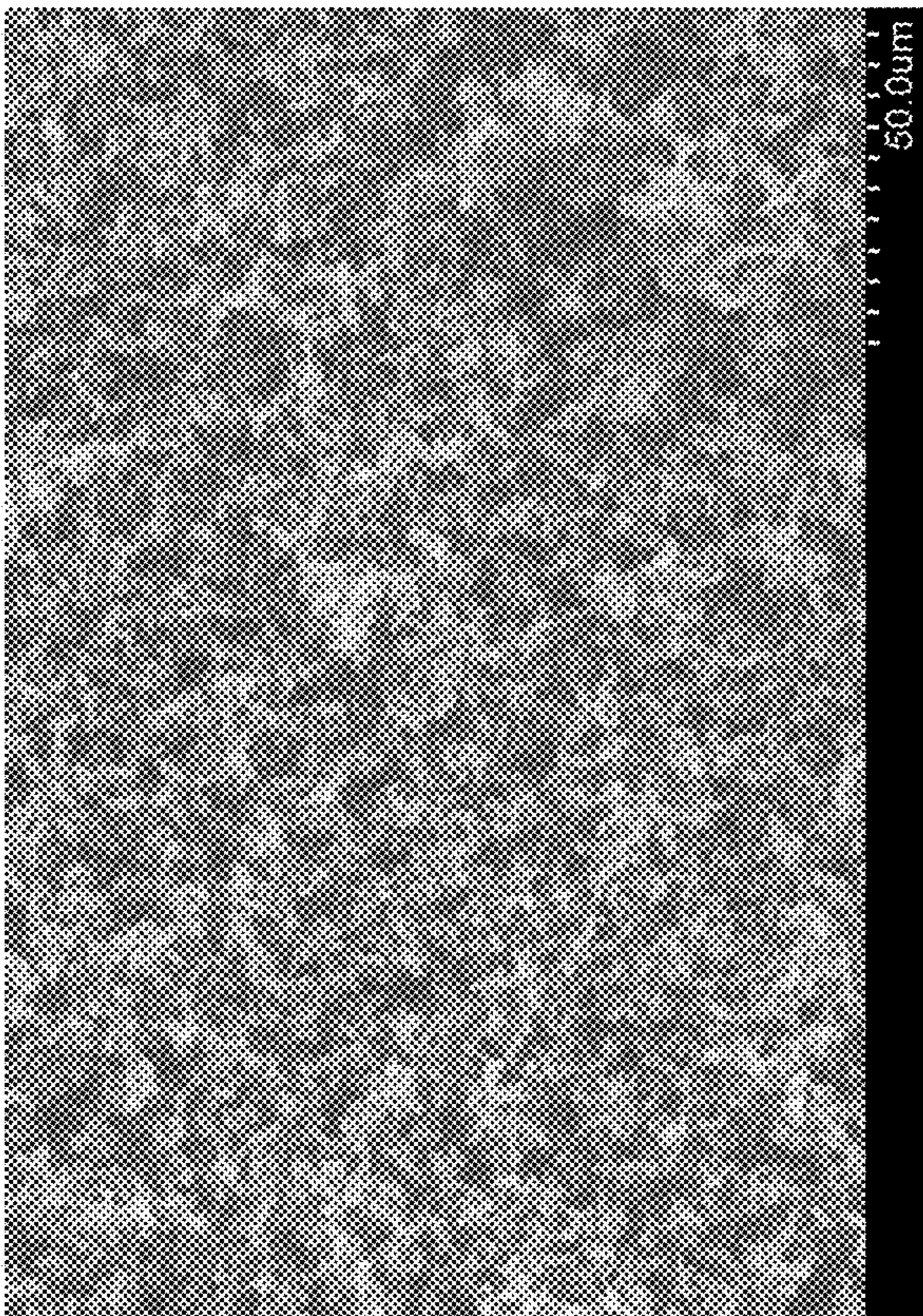


FIG. 4A

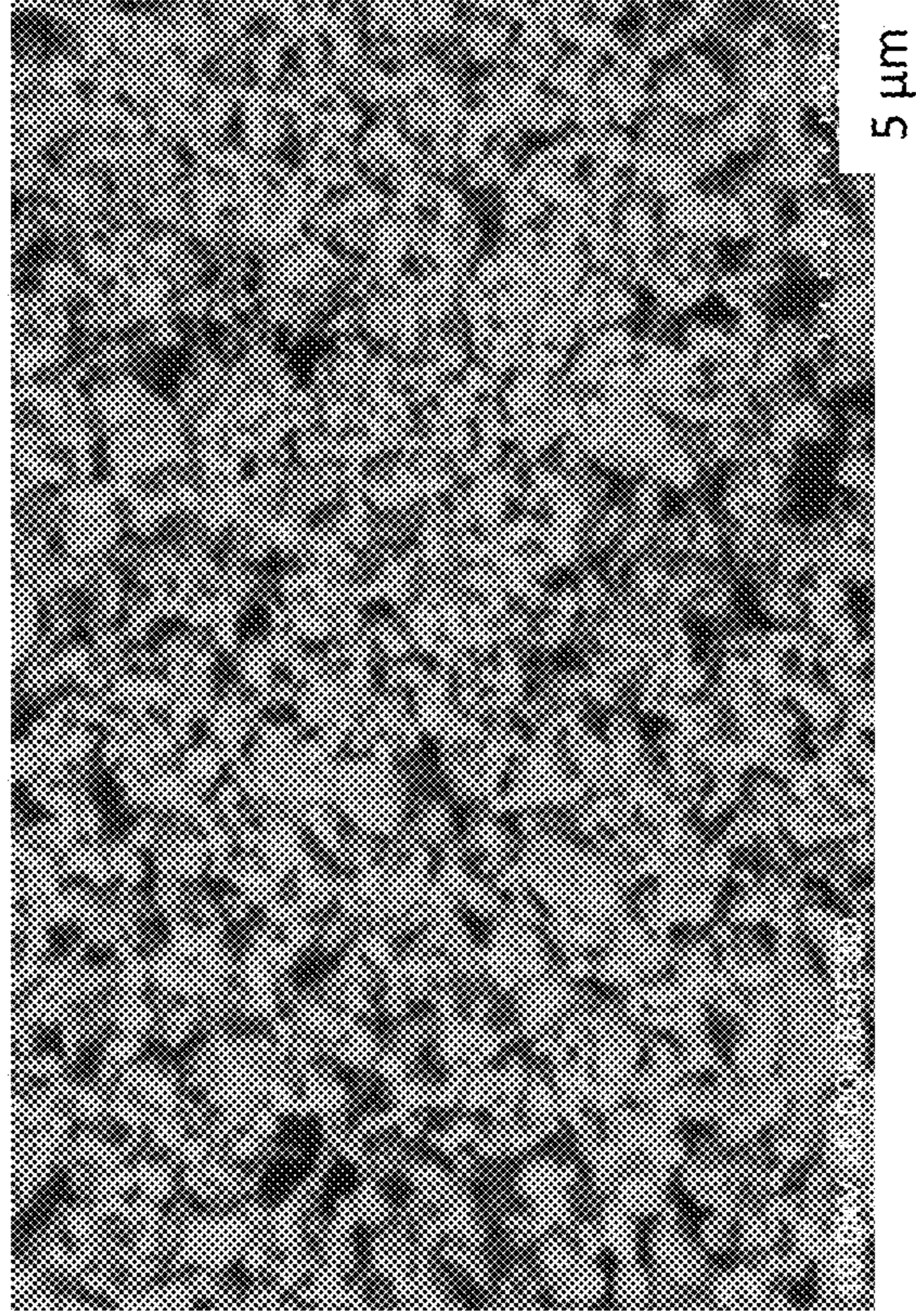


FIG. 5B

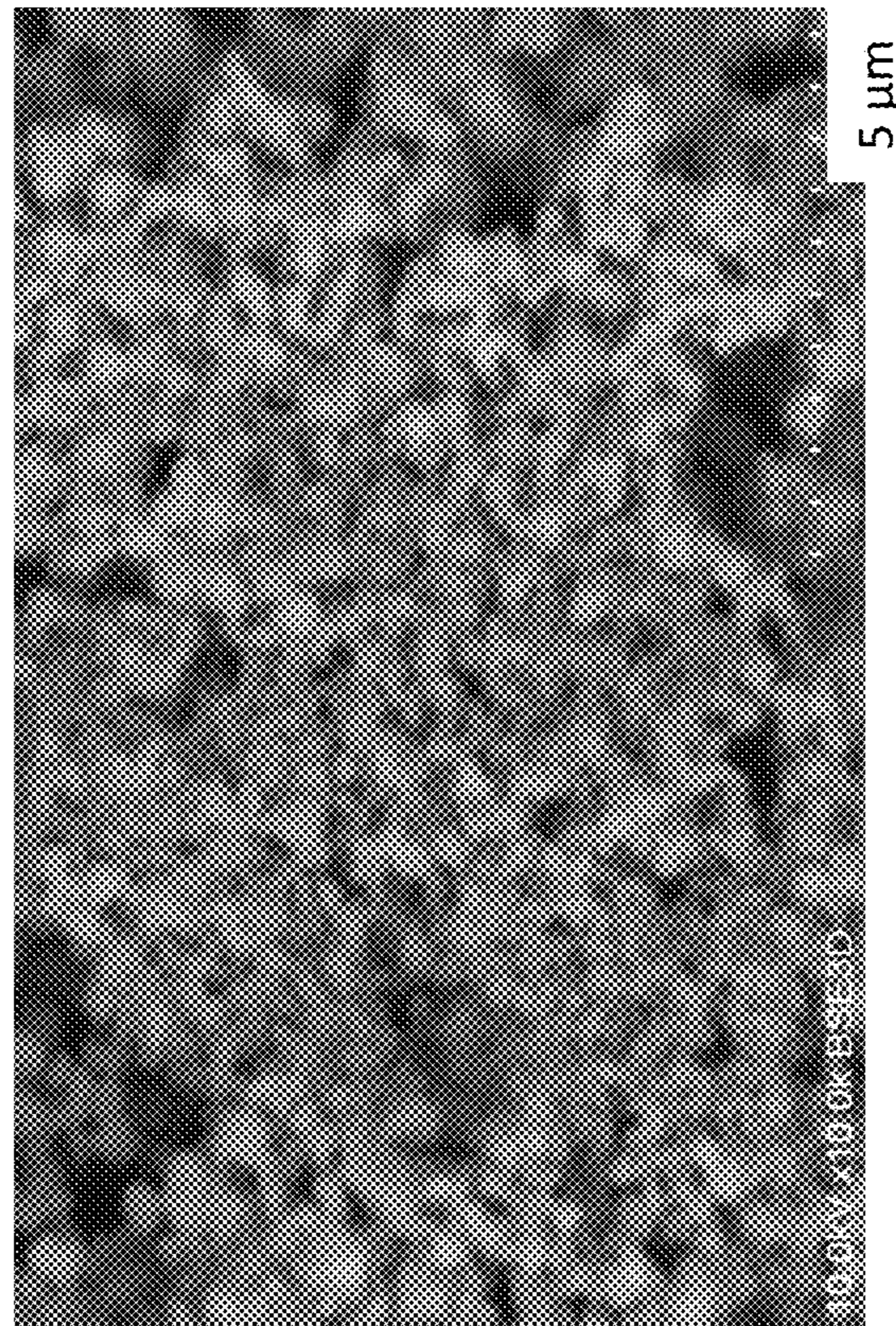


FIG. 5A

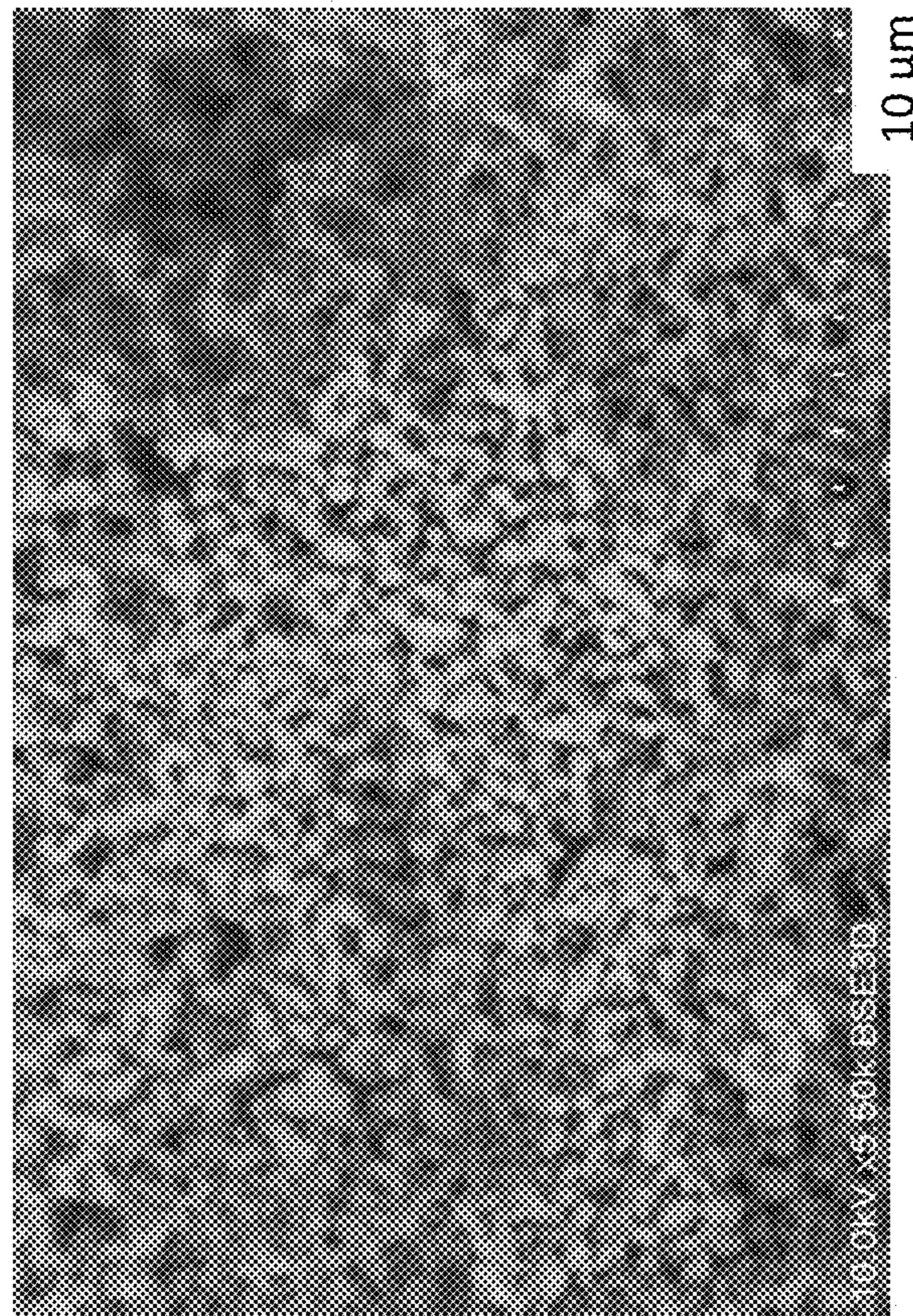


FIG. 5C



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## SYNTHESIS OF METAL-OXYGEN BASED MATERIALS WITH CONTROLLED POROSITY BY OXIDATIVE DEALLOYING

### REFERENCE TO GOVERNMENT RIGHTS

This invention was made with government support under N00014-10-1-0913 and N00014-14-1-0675 awarded by the Office of Naval Research. The government has certain rights in the invention.

### BACKGROUND

Hierarchically porous materials that bridge nano- and macroscopic length scales find use in a wide variety of applications, including catalysis, energy conversion and storage, and membrane filtration, and in emerging technologies for health. Porous zeolites have made the largest contribution to society so far, and that field is still developing. Other porous solids have also entered the scene in the past two decades, such as metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and porous organic polymers. No single class of porous material is ideal for all purposes. For example, crystallinity and long-range order might enhance selectivity for a molecular separation, while reducing mechanical stability or processability with respect to less ordered structures. Well-ordered nanoporous materials derived from small-molecule surfactant and block copolymer (BCP) self-assembly have been explored in the form of amorphous, polycrystalline, and single-crystal solids. Unfortunately, multiple time-consuming processing steps are typically required to generate the final structures. For example, removal of organic components by conventional thermal processing to create porosity typically takes several hours. In addition, nanoporous materials have been fabricated through electrochemical dealloying, powder metallurgy, and bottom-up growth techniques like chemical vapor deposition. To have an impact on real applications, porous materials must be scalable and must satisfy multiple functional criteria, such as long-term stability, selectivity, adsorption kinetics, and processability, all within a viable cost envelope.

### SUMMARY

Methods of making functional materials and the functional materials made using the methods are provided. The materials are made from metal alloys via an oxidative dealloying process that selectively removes one or more elements from the metal alloy and converts one or more of the remaining elements into a stable matrix having a controlled porosity. Once fabricated, the porous matrices are post-treated to render them suitable for various downstream applications.

One embodiment of a method of forming a functional material comprises oxidatively dealloying a metal alloy comprising: a first element that is a transition metal, a post-transition metal, or a metalloid; and a second element that is a transition metal, a post-transition metal, a metalloid, or a non-metal. The oxidative dealloying is carried out by exposing the metal alloy to an oxidizing environment comprising oxygen and/or another oxidizing agent and, optionally, water, wherein the oxygen and/or other oxidizing agent reacts with the first element to form a metal-oxide compound of the first element that is stable in the oxidizing environment and reacts with the second element to form an unstable oxide. The unstable oxide evaporates out of the

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alloy or reacts with water in the oxidizing environment to form volatile hydroxides or oxy-hydroxides that evaporate out of the alloy, leaving a porous matrix comprising the metal-oxygen compound of the first element. Then the resulting porous matrix is subjected to at least one post-dealloying processing step that changes its chemical properties, physical properties, or both.

Other principal features and advantages of the invention will become apparent to those skilled in the art upon review of the following drawings, the detailed description, and the appended claims.

### BRIEF DESCRIPTION OF THE DRAWINGS

Illustrative embodiments of the invention will hereafter be described with reference to the accompanying drawings.

FIG. 1 is an SEM image of a  $\text{SiO}_2$  porous oxide formed by oxidatively dealloying  $\text{Mo}_3\text{Si}$ .

FIG. 2A is an SEM image of a NiO porous oxide formed by oxidatively dealloying  $\text{Ni}_2\text{V}$ .

FIG. 2B is a higher magnification SEM image of the NiO porous oxide.

FIG. 3A is an SEM image of a  $\text{ZrO}_2$  porous oxide formed by oxidatively dealloying  $\text{V}_2\text{Zr}$ .

FIG. 3B is a higher magnification SEM image of the  $\text{ZrO}_2$  porous oxide.

FIG. 4A is an SEM image of a  $\text{ZrO}_2$  porous oxide formed by oxidatively dealloying  $\text{Mo}(2.5 \text{ at. } \%) \text{Zr}$ .

FIG. 4B is a higher magnification SEM image of the  $\text{ZrO}_2$  porous oxide.

FIG. 5A is an SEM image of a  $\text{ZrO}_2$  porous oxide formed by oxidatively dealloying  $\text{Mo}_2\text{Zr}$  at  $900^\circ \text{C}$ .

FIG. 5B is an SEM image of a  $\text{ZrO}_2$  porous oxide formed by oxidatively dealloying  $\text{Mo}_2\text{Zr}$  at  $1000^\circ \text{C}$ .

FIG. 5C is an SEM image of a  $\text{ZrO}_2$  porous oxide formed by oxidatively dealloying  $\text{Mo}_2\text{Zr}$  at  $1100^\circ \text{C}$ .

### DETAILED DESCRIPTION

Functional materials and methods for making the functional materials are provided. Also provided are methods for utilizing the materials in a variety of applications, including catalysis, adsorption, energy storage, and biomedical applications. The materials are made from metal alloys via an oxidative dealloying process that selectively removes one or more elements from the metal alloy and converts one or more of the remaining elements into a stable porous matrix having a controlled porosity. The methods can be carried out on any alloy that oxidizes to produce one or more volatile species, such as volatile oxides, hydroxides, or oxy-hydroxides, along with one or more non-volatile metal-oxygen compounds when exposed to an oxidizing environment.

The metal alloys from which the porous matrices are formed comprise a first element, a second element, and, optionally, one or more additional elements. Within the alloys, the first element, second element, and any additional elements form one or more intermetallic phases and/or alloy solutions. When the metal alloys are exposed to an oxidizing environment, the first element undergoes oxidation (that is—undergoes a reaction in which electrons are lost) by an oxidizing agent in the oxidizing environment to form a metal-oxygen compound that is stable in that environment. In the same oxidizing environment, the second element reacts with an oxidizing agent to form an unstable oxide, or other unstable metal-oxygen compound. The unstable compound may be a volatile oxide that evaporates out of the alloy or it may be an oxide that reacts with water in the

oxidizing environment to form volatile hydroxides or oxyhydroxides that evaporate out of the alloy. The evaporation of the volatile species leaves behind a porous matrix comprising the stable metal-oxygen compound. This process is referred to as oxidative dealloying. Because it is inexpensive and readily available, oxygen is a good candidate for use as the oxidizing agent. However, other oxidizing agents can be used in combination with, or instead of, oxygen. Other examples of oxidizing agents include, but are not limited to, sulfur, chlorine, fluorine, bromine, and ammonium. For example, sulfur could be present in the oxidizing environment to form metal oxysulfides upon reaction with the metal alloy.

In some embodiments of the metal alloys, the first and second elements are independently selected from transition metal elements, post-transition metal elements, and metalloids. Accordingly, as used herein, the term “metal alloy” refers to an alloy in which at least one of the alloy elements is transition metal, a post-transition metal, or a metalloid. In some embodiments of the metal alloys, the first element is a transition metal element, a post-transition metal element, or a metalloid and the second element is a non-metal, such as carbon or nitrogen. The additional elements can be elements that react with an oxidizing agent in the oxidizing environment to form metal-oxygen compounds, such as metal oxides, that are stable in the oxidizing environment. Alternatively, the additional elements can be elements that react with an oxidizing agent to form unstable oxides that react in the oxidizing environment to form volatile species. Thus, the additional elements may be independently selected from transition metal elements, post-transition metal elements, metalloids, and non-metals. If an additional element forms a stable metal-oxygen compound, the porous matrix will comprise mixed metal-oxygen compounds of the first element and the additional element.

As used herein, the term metal-oxygen compound refers to metal oxides—that is, compounds in which oxygen is bonded to one or more transition metal elements, post-transition metal elements, and/or metalloids—and also includes inorganic compounds in which one or more transition metal elements, post-transition metal elements, and/or metalloids are bonded to oxygen and also to carbon, nitrogen, and/or sulfur atoms. Thus, metal-oxygen compounds include metal oxycarbides, metal oxynitrides, metal oxysulfides, and metal oxycarbonitrides, which may be viewed as solid solutions of a metal oxide and a metal carbide, nitride, sulfide, or carbonitride, respectively.

The composition of the metal alloy used to form the porous oxygen-containing matrices can be chosen based on the relative thermodynamic stabilities of the metal-oxygen compounds formed from the alloy elements. Therefore, a wide variety of metal alloys can be used to make porous matrices comprising a wide variety of metal-oxygen compounds. By way of illustration only, elements that can form stable metal-oxygen compounds, including stable metal oxides, in oxidizing environments include silicon (Si), germanium (Ge), aluminum (Al), titanium (Ti), zirconium (Zr), hafnium (Hf), nickel (Ni), and combinations thereof. Examples of elements that can react with oxygen and/or water in an oxidizing environment to form volatile metal- or non-metal-oxygen compounds, such as volatile oxides, hydroxides and/or oxyhydroxides, include nitrogen (N), carbon (C), boron (B), tungsten (W), molybdenum (Mo), chromium (Cr), vanadium (V), and combinations thereof. However, some embodiments of the metal alloys and the porous matrices do not include silicon.

The first element and any additional elements that form stable metal-oxygen compounds in the oxidizing environment can form a continuous porous matrix comprising the metal-oxygen compounds, even if they are present in the metal alloy as minority components. In some embodiments of the metal alloys, the first element and any additional elements that form the stable matrix in the oxidizing environment make up no greater than 20 atomic percent (at. %) of the alloy. This includes metal alloys in which these element make up no greater than 10 at. %, no greater than 5 at. %, and no greater than 3 at. % of the alloy. For applications that require porous structures having a high mechanical strength, it may be desirable to use metal alloys having a higher content of the first element and any additional elements that form the stable matrix compounds in the oxidizing environment.

Typically, at least some of the second element will be retained in the final porous matrix after the termination of the oxidative dealloying. The retained element may be present, for example, as an oxide, as an oxycarbide, as an oxynitride, as an oxysulfide, as an oxycarbonitride, as an intermetallic compound, and/or in an elemental form. The retained element will be a minority component in the porous matrix—making up less than 50 at. % of the matrix. More typically, the retained element will make up a very small, but detectable, component of the matrix. Thus, in some embodiments of the porous matrices, the second element comprises less than 20 at. %, less than 10 at. %, less than 5 at. %, less than 2 at. %, less than 1 at. %, less than 0.1 at. %, or less than 0.01 at. % of the porous matrix.

By way of illustration only, metal alloys that can be used to form porous metal oxides include: (a)  $\text{Mo}_3\text{Si}$ , which can be oxidatively dealloyed to form porous silica via the volatilization of  $\text{MoO}_3(\text{g})$ ; (b)  $\text{Ni}_2\text{V}$ , which can be oxidatively dealloyed to form porous  $\text{NiO}$  via the volatilization of  $\text{V}_2\text{O}_5$ ; (c)  $\text{V}_2\text{Zr}$ , which can be oxidatively dealloyed to form  $\text{ZrO}_2$  via the volatilization of  $\text{V}_2\text{O}_5$ ; (d)  $\text{Mo}(2.5 \text{ at. } \%) \text{Zr}$ , which can be oxidatively dealloyed to form  $\text{ZrO}_2$  via the volatilization of  $\text{MoO}_3$ ; (e)  $\text{Mo}_2\text{Zr}$ , which can be oxidatively dealloyed to form  $\text{ZrO}_2$  via the volatilization of  $\text{MoO}_3$ ; (f)  $\text{MoHf}$ , which can be oxidatively dealloyed to form  $\text{HfO}_2$  via the volatilization of  $\text{MoO}_3$ ; and  $\text{Mo}_3(\text{AlSi})$ , which can be oxidatively dealloyed to form  $[\text{Al}_2\text{O}_3][\text{SiO}_2]_2$  (mullite) via the volatilization of  $\text{MoO}_3$ ; (g)  $\text{ZrB}_2$ , which can be oxidatively dealloyed to form  $\text{ZrO}_2$  via the volatilization of  $\text{BO}$ ,  $\text{BO}_2$ ,  $\text{B}_2\text{O}_2$ , and/or  $\text{B}_2\text{O}_3$ ; (h)  $\text{HfB}_2$ , which can be oxidatively dealloyed to form  $\text{HfO}_2$  via the volatilization of  $\text{BO}$ ,  $\text{BO}_2$ ,  $\text{B}_2\text{O}_2$ , and/or  $\text{B}_2\text{O}_3$ ; (i)  $\text{TiC}$ , which can be oxidatively dealloyed to form  $\text{TiO}_2$  via the volatilization of  $\text{CO}$  and/or  $\text{CO}_2$ ; and (j)  $\text{SiC}$ , which can be oxidatively dealloyed to form  $\text{SiO}_2$  via the volatilization of  $\text{CO}$  and/or  $\text{CO}_2$ .

By way of illustration only, metal oxycarbides, metal oxynitrides, and metal oxysulfides from which the porous matrix can be comprised include transition metal oxycarbides, oxynitrides, and oxysulfides, such as titanium oxycarbides, titanium oxynitrides, and titanium oxysulfides.

The oxidizing environment used for oxidative dealloying will generally be a high temperature, oxygen- (and optionally, water-) containing environment. The working and optimal conditions, including the temperature and partial pressures of the gases present in the environment, can be selected based on the relative thermodynamic stabilities of the metal-oxygen compounds (e.g., oxides) formed from the elements present in the metal alloy. Thus, for a given alloy, one can tailor the oxidizing environment to produce a porous matrix via oxidative dealloying based on the thermodynamics of the system. The enthalpies and entropies of formation

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for many metal and metalloid oxides, oxycarbides, oxynitrides, oxysulfides, and oxycarbonitrides are known. Those that are not known can be calculated or determined experimentally. By way of illustration only, in some embodiments of the methods of forming porous structures, the oxidative dealloying is carried out at temperatures in the range from 700° C. to 1500° C. This includes embodiments of the methods in which oxidative dealloying is carried out at temperatures in the range from 800° C. to 1300° C. and further includes embodiments in which oxidative dealloying is carried out at temperatures in the range from 900° C. to 1100° C. However, since the optimal temperature for oxidative dealloying will depend on the particular metal alloy starting material, temperatures outside of these ranges may be used.

The oxidative dealloying can be carried out in open (ambient) air or under a controlled environment in which the partial pressures of oxygen and/or water vapor are increased. The metal alloys are exposed to the oxidizing environment for a period of time sufficient to achieve the desired degree of porosity in the final structure. For example, for some applications it may be desirable to convert the entire starting metal alloy into a porous matrix having pores running throughout the structure, while other application may require pores extending only partially through the structure, for example, only in the near-surface regions of the structure. Thus, the working and optimal duration will depend, in part, on the thickness and geometry of the starting metal alloy substrate. By way of illustration only, in some embodiments of the methods for making porous matrices, the oxidative dealloying is carried out for time period in the range from five minutes to two hours.

In the oxidizing environment, water can act as a volatilization accelerant to form volatile species (e.g., hydroxides) from the unstable compounds, such as unstable oxides, produced by the reaction of the metal alloy with an oxidizing agent. However, other volatilization accelerants can be included in the oxidizing environment in addition to, or as an alternative to, water vapor. The other volatilization accelerants would also function to form volatile species upon reaction with the unstable compounds.

The pores that are defined in the matrices are tortuous and interconnected and, because oxidative dealloying works from the surface of the metal alloy inward, have a pore diameter gradient, whereby the mean diameters of the pores decrease as the distance into the material increases. The mean pore diameters will depend on the oxidation agents present in the oxidizing environment and the specific reaction conditions used, including the temperature and time of reaction. In some embodiments of the porous matrices, the pores are nanoscale pores, having diameters of less than 1000 nm, including less than about 500 nm (for example, from 10 nm to 500 nm). In other embodiments of the porous matrices, the pores are mesoscale pores, having diameters of 1000 nm or greater, including greater than 2 μm (for example, from 2 to 10 μm). In still other embodiments, the dealloying process produces hierarchical porous matrices that define pores with mean diameters spanning both of these length scales.

By tailoring the temperature, time of exposure, and oxygen pressure in the oxidizing environment, it is possible to tailor the mean pore sizes and pore size gradients in the porous matrices. As discussed above, oxidative dealloying is driven by diffusion of oxygen through the alloy. The oxygen acts to boil off one or more elements of the alloy through the aforementioned oxidation and volatilization reactions, and to form solid metal-oxygen structures with one or more of

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the remaining alloy elements. At the alloy surface, porosity evolution is unstable until a certain amount of the volatile species has been removed. To achieve nanoporosity, the volatilization should occur at a rapid enough rate to prevent coarsening, which acts to smooth the surface. Coarsening (sintering) is driven by Ostwald ripening at high processing temperatures. Sintering is desirable in that it promotes mechanical durability of the stable products of the oxidation and allows for the porosity size scale to be controlled. Higher levels of sintering will provide larger pores and too much sintering can lead to a non-porous material. Thus, it is possible to strike a balance between volatilization and sintering, both of which are highly temperature-dependent, for each material system of interest in order to achieve desired porosity characteristics. Generally, higher temperatures promote oxidation and volatilization, while slowing the kinetics of the reaction through the oxygen pressure will favor smaller pores.

After the porous matrices have been formed they can be subjected to one or more post-dealloying processing steps that change one or more of their physical and/or chemical properties. This converts the porous matrices into functional material that may be porous or non-porous, depending upon the nature of the post-dealloying processing step. For example, the shape of the material (a physical property) can be changed by granulating the porous matrix to form particles of the porous matrix or by molding the porous matrix into a different shape, as by, for example, pelletizing the porous matrix. Bonding the porous matrix, or a portion of the porous matrix, to a substrate other than the metal alloy substrate from which it is formed is another example of a post-dealloying processing step that changes one or more physical and/or chemical properties of the porous matrix. This bonding can be carried out before or after the porous matrix has been separated from any remaining metal alloy starting substrate. Alternatively, the post-dealloying processing step can be the step of applying a solid or liquid coating on at least a portion of a surface of the porous matrix. For example, the porous matrix can be reacted with various chemical species (e.g., atoms, molecules, and/or ions) to chemically functionalize the surface of the porous matrix. However, a chemical reaction between the metal-oxygen compounds of the porous matrix and the chemical species is not required. Rather, a chemical species can simply be deposited on or incorporated into the open pores of the porous matrix. Examples of chemical species that can be reacted with, coated on, or integrated into the porous matrices include metals, metal alloys, ions, including metal ions, ceramics, oxides, including metal oxides, semiconductor compounds, organic molecules (e.g., amines, thiols, carboxylic acids, etc.), polymers—organic or inorganic, and biomolecules. If the chemical species includes a metal, that metal may be different from any metal present in the porous matrix.

The post-dealloying processing steps can be used to render the resulting functional materials suitable for use as substrates in a variety of applications, including catalysis, biomedical, remediation, and energy storage applications. This is significant because, while various oxide scales have been formed on metal alloys as a result of heat treatments in the past, these scales have generally been viewed as protective surface coatings or as unwanted by products of the heat treatments. The present materials, in contrast, are not just surface scales, but can be produced as stand-alone structures that provide starting materials for the fabrication of a variety of useful devices.

For example, catalytic devices can be fabricated from the porous matrices by applying a catalytic material, such as a catalytic metal or catalytic metal alloy, to the surface of the porous matrices to form a catalytic composite. Examples of porous oxides that can be used as supports for catalytic materials include porous SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, or mixtures thereof. The catalytic composite can then be exposed to chemical reactants, wherein the catalytic material catalyzes the reaction of the chemical reactant to form one or more reaction products. The catalytic material can be, for example, an oxidation catalyst, a reduction catalyst, and/or a photocatalyst. Examples of catalytic metals that can be coated onto the surfaces of the porous matrices include gold (Au), nickel (Ni), platinum (Pt), palladium (Pd), rhenium (Rh), ruthenium (Ru), iridium (Ir), and their alloys. These metals can be applied to the porous matrices by, for example, vapor deposition.

For biomedical applications, a coating of a biocompatible material can be formed on the surface of the porous matrices, including porous oxide matrices comprising TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and mixtures thereof. For example, a coating of a material having anti-protein fouling properties can be applied to the surfaces of the porous matrices. Such coatings include fluoropolymers, including sulfonated tetrafluoroethylene (e.g., Nafion). Alternatively, a coating of material that enhances the biocompatibility of the porous matrices can be formed on the surfaces of the porous matrices for medical implant applications. Biomolecules can also be bound to the surface to render the porous matrices suitable for use as biosensors, including sensors that detect analyte biomolecules through the specific binding of those analyte biomolecules with surface-bound biomolecules on the porous matrices. Examples of biomolecules that can be coated onto and/or bound to, including covalently bound to, the porous matrices include proteins, peptides, nucleic acids, oligonucleotides, amino acids, and biopolymers. For tissue engineering applications, such as bone growth engineering, biological cells, cell attachment factors, and/or cell growth factors can be coated onto or incorporated into the porous matrices to provide cell-seeded tissue growth scaffolds. The seeded scaffolds can then be cultured in an appropriate culture medium to grow biological tissues on the porous materials.

The high surface areas of the porous matrices also make them well-suited for use as electrode materials in energy storage applications, such as batteries and supercapacitors. For example, the porous matrices can be impregnated with a liquid electrolyte to provide a battery electrode. For use in lithium ion batteries, lithium can be incorporated into the porous matrices, such as the porous TiO<sub>2</sub>, in a post-dealloying processing step.

The porous matrices, including TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, can be used as adsorbents for removing unwanted chemical species, such as heavy metal ions and organic molecules, from liquid or vapor-phase samples. In these remediation applications, samples are contacted with the porous matrices, whereby targeted chemical species are adsorbed by the porous matrices. The porous matrices and the adsorbates can then be removed from the sample. Chemical species that can be removed include, lead (Pb), cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), alkanes and alkenes.

For remediation and other applications, it may be advantageous to granulate the porous matrices or to mold them into regular shapes. For example, the porous matrices may be subjected to a post-dealloying granulation in which they are crushed, comminuted, and/or sorted by average particle size. Alternatively, the porous matrices can be molded to

form regularly shaped particles (e.g., pellets) or objects from the porous matrices. It is also possible to shape the metal alloy starting material into a desired shape, such that the porous matrix, as formed, has the desired final shape.

The porous matrices can also be bonded to various substrates in a post-dealloying processing step to provide functional substrates for various applications. For example, the porous matrices can be bound to a filtration medium for remediation applications, or to an electrically conductive substrate for biosensor or energy storage applications.

#### EXAMPLE

This example illustrates methods of forming porous oxides from various metal alloys. In each case, the metal alloy was prepared from pure elements weighed to the appropriate proportions and processed by non-consumable arc melting in a titanium gettered argon atmosphere. Following repeated melting (typically five times), the weight change was usually below 1%. The molten alloys were then cast into cylindrical ingots. Disc-shaped samples were cut from the cast cylindrical ingots and cleaned by washing in alcohol. Dealloying of the metal alloys was carried out by oxidation in laboratory air in an open tube furnace at temperatures between 900-1100° C. for times ranging from 10 minutes to one hour. The particular oxidation temperatures and times for some metal alloys are provided in Table 1. Following oxidation, the samples were examined under a scanning electron microscope (SEM).

TABLE 1

Dealloying Conditions			
Metal Alloy	Porous Oxide	Oxidation Temperature (° C.)	Oxidation Time (min)
Mo <sub>3</sub> Si	SiO <sub>2</sub>	1100	10
Ni <sub>2</sub> V	NiO	750	10
V <sub>2</sub> Zr	ZrO <sub>2</sub>	650	10
Mo(2.5 at. %)Zr	ZrO <sub>2</sub>	1100	10
Mo <sub>2</sub> Zr	ZrO <sub>2</sub>	900, 1000, 1100	10
MoHf	HfO <sub>2</sub>	900	10

The porous oxide listed in Table 1 is the primary oxide formed via dealloying. Trace amounts of other metal alloy-derived oxides or metals may also be present. FIG. 1 is an SEM image of a SiO<sub>2</sub> porous oxide formed by oxidatively dealloying Mo<sub>3</sub>Si. FIGS. 2A and 2B are SEM images, at different magnifications, of a NiO porous oxide formed by oxidatively dealloying Ni<sub>2</sub>V. FIGS. 3A and 3B are SEM images, at different magnifications, of a ZrO<sub>2</sub> porous oxide formed by oxidatively dealloying V<sub>2</sub>Zr. FIGS. 4A and 4B are SEM images, at different magnifications, of a ZrO<sub>2</sub> porous oxide formed by oxidatively dealloying Mo(2.5 at. %)Zr. FIGS. 5A, 5B, and 5C are SEM images of a ZrO<sub>2</sub> porous oxide formed by oxidatively dealloying Mo<sub>2</sub>Zr at 900° C., 1000° C., and 1100° C., respectively.

The word “illustrative” is used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as “illustrative” is not necessarily to be construed as preferred or advantageous over other aspects or designs. Further, for the purposes of this disclosure and unless otherwise specified, “a” or “an” means “one or more”.

The foregoing description of illustrative embodiments of the invention has been presented for purposes of illustration and of description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modi-

fications and variations are possible in light of the above teachings or may be acquired from practice of the invention. The embodiments were chosen and described in order to explain the principles of the invention and as practical applications of the invention to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto and their equivalents.

What is claimed is:

1. A method of forming a functional material, the method comprising:

oxidatively dealloying a metal alloy comprising: a first element that is a transition metal, a post-transition metal, or a metalloid; and a second element that is a transition metal, a post-transition metal, a metalloid, or a non-metal, by exposing the metal alloy to an oxidizing environment comprising oxygen and, optionally, water, wherein the oxygen reacts with the first element to form a metal-oxygen compound of the first element that is stable in the oxidizing environment and reacts with the second element to form an unstable oxide of the second element that evaporates out of the metal alloy or that reacts with water in the oxidizing environment to form volatile hydroxides or oxy-hydroxides that evaporate out of the metal alloy, leaving a porous matrix comprising the metal-oxygen compound of the first element; and

subjecting the porous matrix to at least one post-dealloying processing step that changes a chemical property, physical property, or both, of the porous matrix.

2. The method of claim 1, wherein the metal-oxygen compound of the first element comprises a metal oxide of the first element.

3. The method of claim 1, wherein subjecting the porous matrix to at least one post-dealloying processing step that changes the chemical property, physical property, or both, of the porous matrix comprises applying a solid or liquid coating on at least a portion of a surface of the porous matrix.

4. The method of claim 3, wherein applying a solid or liquid coating on at least a portion of the surface of the porous matrix comprises chemically functionalizing at least a portion of the surface of the porous matrix by reacting the porous matrix with a chemical species to form a coating of the chemical species covalently bound to the surface of the porous matrix.

5. The method of claim 3, wherein the chemical species are organic molecules.

6. The method of claim 5, wherein the organic molecules are biomolecules.

7. The method of claim 5, wherein the organic molecules are organic polymer molecules.

8. The method of claim 3, wherein the chemical species comprises an electrolyte.

9. The method of claim 3, wherein applying a solid or liquid coating on at least a portion of the surface of the porous matrix comprises applying a catalytic metal or catalytic metal alloy to at least a portion of the surface of the porous matrix.

10. The method of claim 9, wherein the catalytic metal or catalytic metal alloy comprises gold, nickel, platinum, palladium, rhenium, ruthenium, iridium, or an alloy thereof.

11. The method of claim 1, wherein subjecting the porous matrix to at least one post-dealloying processing step that changes the chemical property, physical property, or both of the porous matrix comprises granulating the porous matrix, molding the porous matrix, or both.

12. The method of claim 1, wherein a portion of the metal alloy remains after the oxidative dealloying and further wherein subjecting the porous matrix to at least one post-dealloying processing step that changes the chemical property, physical property, or both of the porous matrix comprises separating at least a portion of the porous matrix from the remaining metal alloy and bonding the porous matrix to another substrate.

13. The method of claim 12, wherein subjecting the porous matrix to at least one post-dealloying processing step that changes the chemical property, physical property, or both of the porous matrix further comprises applying a solid or liquid coating on at least a portion of a surface of the porous matrix.

14. The method of claim 1, wherein the entire metal alloy is oxidatively dealloyed, such that the metal alloy is completely converted into the porous matrix.

15. The method of claim 1, wherein the porous matrix further comprises the second element in its elemental form, an oxide of the second element, an intermetallic compound of the second element, or a combination thereof.

16. The method of claim 5, wherein the first element and the second element are transition metal elements.

17. The method of claim 1, wherein the second element is a transition metal element.

18. The method of claim 17, wherein the second element is not molybdenum.

19. The method of claim 17, wherein the first element is a transition metal element or a post-transition metal element.

20. The method of claim 19, wherein the first element is a transition metal element.

21. The method of claim 1, wherein the second element is vanadium.

22. The method of claim 1, wherein: the metal alloy comprises a third element; the oxygen reacts with the third element to form a metal-oxygen compound of the third element that is stable in the oxidizing environment; and the porous matrix comprises the metal-oxygen compound of the first element and the metal-oxygen compound of the third element.

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